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Magnetic Nanoparticles

A Study by Synchrotron
Radiation and RF Transverse
Susceptibility



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Adriana I. Figueroa

Magnetic Nanoparticles

A Study by Synchrotron Radiation
and RF Transverse Susceptibility

Doctoral Thesis accepted by
the University of Zaragoza, Spain

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*To my dearest family,
in loving memory of my dad...*

Supervisors' Foreword

Magnetic nanoparticles (NPs) are finding their place in many modern technologies such as electronics (memory or spintronic devices) and also in medicine (contrast media, electromagnetic thermal therapy) to name some cases. The application of modern techniques based on synchrotron radiation, X-ray absorption spectroscopy (XAS), extended X-ray absorption fine structure (EXAFS), and X-ray magnetic circular dichroism (XMCD) have allowed Dr. Figueroa to understand the formation of multigranular Co–M alloyed NPs, embedded in an amorphous alumina matrix. The Co–W alloyed NPs constitute a paradigmatic class since the particles show anisotropy in spite of their amorphous character. On the other hand, Co–Pt NPs exhibit perpendicular anisotropy and interesting new magnetic phases. Besides, magnetite NPs coated with oleic acid show excellent human compatibility while preserving the bulk magnetic figures of merit. By means of an RF transverse susceptibility probe, built ad hoc, the intrinsic and extrinsic contributions to the anisotropy could be disentangled. Gold nanoparticles deposited on a biological template, prepared from *Sulfolobus acidocaldarius* S-layer, were shown to possess intrinsic magnetism caused by the electron exchange with the Sulfur atoms provided by the template. Both macroscopic and microscopic properties of several classes of NPs, hitherto unexplained, have been revealed for the first time.

Zaragoza, May 2014

Prof. Juan Bartolomé Sanjoaquín
Dr. Luis Miguel García Vinuesa

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Chapter 1

Introduction

The fundamental understanding of nanoscale materials has been the focus of much scientific and technological interest over the last decades. Nanoparticles (NPs) are widely investigated not only as consequence of the general miniaturization of devices, but also because they constitute ideal systems to study finite-size and surface effects, those yielding new physical phenomena and enhanced properties with respect to their bulk counterpart [1–3]. The scientific and technological importance of magnetic nanostructures lies on the overwhelming variety of structures with interesting physical properties, ranging from naturally occurring nanomagnets and comparatively easy-to-produce bulk nanocomposites to demanding artificial nanostructures [4]. Nanomagnetism has, therefore, opened the door for completely new technologies. From the fundamental science point of view, the involvement of nanoscale effects has allowed further understanding and improvement of the properties of advanced magnetic materials. Let us review the physics behind such fascinating magnetic nanostructures.

1.1 Magnetism in Nanoparticles

Magnetism is a fact of electrons. Being fermions, they bear an intrinsic spin moment and being charged, their circular motion can also create a so-called orbital moment; thus, the total magnetic moment of a single atom comprises a spin moment, m_S , and an atomic orbital moment, m_L . Atoms in solids preserve or not these finite magnetic moments depending on their collective behavior. In some materials, strong correlations between magnetic moments give rise to long range ordering and thermodynamic phases, such as ferromagnetism, ferrimagnetism and antiferromagnetism. These macroscopic magnetic materials reduce their energy by breaking into magnetic domains, or small regions where the spins are aligned. Each domain can have a net magnetization, which is oriented in a different direction from that of its neighbor. The creation of a domain increases the anisotropy energy of the system, defined as the change in the electronic energy, associated to the inversion of its

magnetization; but it reduces the magnetostatic energy, so that the material is in average not magnetized unless an external magnetic field is applied.

The size of a magnetic nanoparticle, however, is comparable to the size of a magnetic domain, which results in a completely novel phenomenology with respect to bulk magnetic materials. In particular, the properties of the valence electrons of atoms (which are mainly responsible of the magnetic character of atoms and solids) change as they become part of a small metallic particle and start to delocalize. Thus, their magnetic properties are very sensitive to size, composition, and local atomic environment, showing a wide variety of intriguing phenomena. This rich variety of behavior can be understood in general terms as arising from the reduced average coordination per atom; the quantum size effect (the wavefunction of electrons changes when they are confined to dimensions comparable with their wavelength, so that the continuous bulk bands split up into discrete levels); and modified collective electron behavior such as screening and charge spill-out from the surface [2].

For a particle of radius R , the energy of a domain wall is expressed as

$$E_p = 4\sqrt{AK}\pi R^2 \quad (1.1)$$

where A is the exchange interaction and K the anisotropy constant. For magnetic particles, there exists a limit of size (critical size) below which it is no longer energetically favorable to create domains in the system. Therefore, it becomes a *single-domain particle* with a net magnetization. As isolated particles they can be considered as single giant moments of ferromagnetically coupled atomic spins that can be aligned by the application of an external magnetic field. When a saturating field is removed, the magnetization decays with a relaxation rate. This behavior is described by the Arrhenius' law

$$\tau = \tau_0 \exp\left(\frac{U}{k_B T}\right) \quad (1.2)$$

with k_B the Boltzmann constant and T the temperature. It describes the time τ for a particle to overcome an energy barrier U , with an attempt frequency τ_0 . The energy barrier is directly related to the anisotropy energy of each particle and is usually expressed as $U = KV$, where V is the particle volume.

The magnetic anisotropy energy of a particle originates from different sources, namely: magnetocrystalline, shape, magnetoelastic and surface anisotropies.

- Magnetocrystalline anisotropy arises from a coupling of the electron spins to the electronic orbit (spin-orbit interaction), which, in turn, is coupled to the crystal lattice. The magnetization of a material with magnetocrystalline anisotropy is energetically favored to align along a specific crystallographic direction called the “easy axis” of the material. The magnetocrystalline anisotropy is usually much larger in small clusters than in the corresponding crystalline solids [5].

- The shape anisotropy is caused by the demagnetizing energy associated to the particle shape. If a particle has elongated shape, for instance, this anisotropy would lead to an energetic saving for keeping the magnetization along its long axis [6].
- Magnetoelastic anisotropies are due to changes in the crystal lattice of the particle by strain. The distances between the magnetic atoms are altered and hence the interaction energies are changed, thus affecting the favorable direction of the magnetization [7].
- Surface anisotropy is of high importance in nanoparticles because of the high surface-to-volume ratio in these low dimensional systems, so that surface effects become more and more pronounced. It arises from the effect of the broken symmetry of the crystal environment of the atoms at the surface (missing neighbors), which affects the magnetic order of the lattice and, therefore, the favorable direction of the magnetization [8, 9].

At high temperatures the thermal energy is much greater than the anisotropy energy of each particle, so that all magnetization directions are almost energetically equal. The magnetization is then described by the classical Langevin function [10] as

$$L(x) = m_{\text{part}} \left(\coth(x) - \frac{1}{x} \right) \quad (1.3)$$

with $x = \frac{m_{\text{part}} H}{k_B T}$, $m_{\text{part}} = M_s V$ the magnetic moment of a single particle, M_s the saturation magnetization, V the particle volume, and H the applied field.

This behavior is known as *superparamagnetism*. The relaxation time in these systems and their magnetization strongly depend on the temperature. If the net moment of the particle can freely flip from one orientation to the other, the particle is said to be unblocked. On the contrary situation, it is said to be blocked. The temperature that separates both regimes is defined as the blocking temperature T_B , which depends on the particle intrinsic properties and size.

The coercivity of a magnetic particle depends heavily on its size. If the particle is large enough to support a multidomain structure, magnetization reversal occurs through a domain walls motion as for bulk ferromagnets [7], which is relatively easy, and hence, the coercivity is low. On the other hand, in a single domain particle that change of magnetization direction can occur only by coherent rotation of spins; this results in a considerably higher coercivity of single domain particles in comparison to multidomain particles. Upon decrease of the particle size, the coercivity falls off due to the progressively increasing role of the thermal fluctuations leading to superparamagnetism.

In reality, free single independent particles are difficult to obtain experimentally. In most systems we deal with a collection of interacting particles, with a distribution of size and shape, and most of the time with crystalline modifications. All these deviations from the ideal system influence the response to temperature and magnetic field, and therefore the values of T_B and K . Interparticle interactions are generally considered to be of dipolar type, where each particle is modeled as a single magnetic

dipole. In fact, the total magnetic energy of each nanoparticle can be expressed as $E = K_0 V - \mu \cdot B_i$, which considers both its intrinsic anisotropy volume density, K_0 , and the influence of the dipolar field B_i created by the surrounding particles at the site of particle i [11]. For an assembly of randomly oriented particles with the same size, properly averaging over all directions of B_i , the energy barrier for magnetization reversal of particle i may be written as

$$\Delta E = K_0 V - \frac{\mu^2 \langle B_i^2 \rangle}{3k_B T} \left(1 - \frac{3k_B T}{4K_0 V} \right) \quad (1.4)$$

where $\langle B_i^2 \rangle$ depends on the interparticle distances, the diameter of the particle, and its magnetization [11].

1.2 Characterization of Magnetic Nanoparticles

The distinct behavior of magnetic NPs constitute an important challenge for technical applications, which include diverse fields such as biomedicine [3, 12], high-density magnetic recording [2, 13, 14], and magnetic resonance imaging (MRI) [15, 16]. Each of these areas require of magnetic particles with specific characteristics, for which it is crucial the comprehension and tailoring of their magnetic properties like anisotropy or dipolar interactions between particles. In the hard drive industry, for example, the main objective is to find ways of increasing the magnetic anisotropy of single domain NPs, so that storage densities can continue to increase without compromising the stability of the media; this may occur since thermal fluctuations can lead to destabilization of the magnetic state of the particles. On the contrary, biomedical applications need magnetic particles with low anisotropy, for their magnetization to be easily reversed inside biological systems.

To study and understand all phenomena arising in magnetic nanoparticles, for both applied and basic science perspectives, we require characterization techniques that allow us to map the magnetization at nanometer length scales and sub-nanosecond time scales, to study buried layers and interfaces, and to access element-sensitive structural, chemical and magnetic characterizations, among other considerations. In terms of structural characterization, standard experimental techniques cover from conventional x-ray diffraction (XRD) to electron microscopies. XRD allows to obtain a general idea of the crystal structure of the particles, but the sensitivity of this technique is usually not enough to characterize these systems where surface effects are relevant since quantitative diffraction studies require theoretical modeling and a priori knowledge of the probed length scale [17, 18]. In this sense, high resolution transmission electron microscopy (TEM) and scanning electron microscopy (SEM) overcome these difficulties providing high quality images of single particles with atomic resolution [19]. High contrast images achieved with these electron microscopies allow to obtain the size distribution of assembled nanoparticle systems [20].

Magnetic characterization can comprise several techniques, from standard vibrating sample magnetometries (VSM), to more sensitive methods such as superconducting quantum interference device (SQUID) sensor based and magneto-optical Kerr effect (MOKE) magnetometers. SQUID magnetometers provide enough sensitivity to measure significantly less than a single cluster layer [21]. MOKE magnetometers using visible light have also become a standard tool for investigating magnetic systems [2]. This instrument is based on the observed effect a ferromagnetic medium has on the polarization or intensity of polarized light when reflected by its surface. The recent advances in this experimental technique has allowed a sensitivity sufficient to detect the magnetic response of a few atomic monolayers and even clusters embedded in non-magnetic matrices [2].

The main parameters for the magnetic characterization of the nanoparticle systems can be extracted from magnetization measurements performed with these magnetometers. The coercive field and saturation magnetization are usually obtained from measurements of magnetization as a function of the external applied field. Magnetization as a function of temperature allows to determine the T_B of the nanoparticle system by measurements in DC zero-field-cooled (ZFC) and field-cooled (FC) conditions. On the former, a sample is cooled under zero applied magnetic field to a temperature well below the suspected T_B . The system is then warmed up and the magnetization is measured as a function of temperature under a relatively low external magnetic field. ZFC conditions allow the particles to be blocked in a aleatory state, and, as the thermal energy increases, the nanoparticles become aligned with the applied field and the magnetization increases. At T_B the magnetization is maximal, since, from that point, the thermal energy effects overcome the anisotropy energy of the particles, yielding to fluctuations of the magnetic moment of the nanoparticles thus decreasing the magnetization of the system. In the FC conditions, a sample is cooled in a small magnetic field thus freezing the nanoparticle moments in the net alignment favored by the magnetic field. The magnetization of the sample is then measured as a function of temperature again. Below T_B the free fluctuations of the magnetic moments are “blocked” by the anisotropy of the particles, but the thermal energy unpins and randomizes them, lowering the sample magnetization. Above T_B the particles are in the superparamagnetic state. At T_B the ZFC and FC curves converge [5, 7].

The conditions given above for superparamagnetism assume that the particles demagnetize due to thermal energy simultaneously with the removal of a field, and on the timescale of most DC measurements this is usually true. However, there is a finite time lag for the particles to demagnetize, and when the magnetic properties are probed with an AC field, the blocking temperature of the system can increase. Thus the study of AC susceptibility measurements under time dependent applied magnetic fields with different frequency yields to valuable information of the dynamic properties of the nanoparticles. The response of the nanoparticle system to the AC field depends on their relaxation time τ , defined by the Arrhenius law (Eq. 1.2). A detailed analysis of the real and imaginary part of the AC susceptibility allows to obtain the distribution of energy barriers of the system, and therefore, to estimate the anisotropy constant of the system [22].

Advanced characterization techniques that make use of large facilities, such as advanced neutron and photon sources, have allowed to obtain even more resolution power to study the structural and magnetic properties of nanoparticle systems. Extensive characterization of magnetic particles has been carried out over the last decades with synchrotron based spectroscopic techniques demonstrating their possibilities [18, 23]. The unique properties of synchrotron radiation such as broad energy spectrum, variable light polarization, and flexible time structure, have made it an enormously powerful tool in the study of magnetic phenomena and structure of materials. This arises from the electronic structure and, particularly, the interaction of electronic states in a material that can be accessed with the use of this radiation. In order to characterize the relation between the electronic structure and magnetism specifically in modern magnetic materials various spectroscopic approaches are involved. By addressing the valence electronic states much can be learned about the electronic bonds and interactions between neighboring atoms. Investigating the more localized core levels with soft X-rays yields information about the magnitude and orientation of the magnetic moments on an element selective basis.

1.3 What We Cover in This Thesis

As described above, research on magnetic nanoparticles involves several aspects to consider, from the preparation procedures to the comprehension, control and optimization of the desired properties. For instance, the possibilities of tuning the magnetic anisotropy of the particles in order to fulfill the requirements for each application seem to be of paramount importance. Different experimental approaches for a complete structural and magnetic characterization of the NPs are fundamental to attain this purpose. Following this scheme, in this dissertation we describe different studies performed on various magnetic nanoparticles systems where a proper combination of structural, electronic and magnetic characterization methods lead to a better understanding of the NPs properties, in particular, of their magnetic anisotropy.

In the first part, we make use of some synchrotron radiation techniques, focussing on X-ray absorption spectroscopies: X-ray Absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and X-ray magnetic Circular Dichroism (XMCD). These techniques constitute very useful methods to directly and selectively examine the electronic state and local structure of the atoms composing the particles. Moreover, the average coordination number, which is also a key parameter that controls the evolution of the magnetic behavior in materials, may be directly determined by EXAFS. On top of that, XMCD arises as an effective method to selectively study the magnetic properties of the particles [2, 24–29], giving access to both contributions to the total average magnetic moment and its components, i.e., orbital moment m_L and spin moment m_S , by application of the magneto-optical sum rules [30, 31].

The possibility of separating both contributions is especially useful in itinerant magnetic materials, which have an orbital magnetic moment induced by spin-orbit

coupling. The general trend in m_L is the same one as for the spin moment: the orbital moment increases with decreasing coordination [2]. However, the orbital moment does not linearly follow the spin moment, the ratio m_L/m_S varies with atomic structure, dimensionality and coordination number. m_L in NPs is very sensitive to neighboring atoms, increasing rapidly with a decrease in the coordination number. This strong dependence with the system dimensionality arises from the fact that the two outer shells of NPs show values significantly different from the bulk values. This enhancement of m_L and its anisotropy at the NPs surface has been demonstrated to contribute significantly to the total magnetocrystalline anisotropy, as proposed by Bruno [32]. Bruno's model states that the orbital moment drives the anisotropic direction at a magnetic metallic surface, and that the difference between the orbital moments along the easy and hard directions is proportional to the magnetocrystalline anisotropy, following the expression

$$\Delta E_{SO} \propto -\xi(m_L^\perp - m_L^\parallel) \propto -K_S$$

with ξ the spin-orbit coupling of the atoms forming the particle surface, $m_L^\parallel$ and $m_L^\perp$ the in-plane and out-of-plane components of the orbital moment, respectively, and K_S the surface anisotropy constant. Therefore, the spin-orbit coupling in systems of nanometric dimensions has been found to be highly relevant. In this sense, this dissertation continues previous studies of spin-orbit enhanced anisotropy observed in different cobalt NPs systems. They consist of self-organized lattices of nanometer-sized Co magnetic clusters (1–4 nm) prepared by sequential deposition of Al_2O_3 and Co layers on a Si substrate. In these granular systems, it is possible to control the clusters size [22], the average number of neighbors to a given cluster [33], and even the surface anisotropy by capping the cobalt nanoparticles with noble metals like Cu, Ag, Au [34]. Those studies allowed quantitative determination of parameters like magnetic anisotropy [35, 36] or dipolar interactions [33]. In the case of Co–metal(M) particles, with $M = Cu, Ag, Au$, the capping metal does not diffuse on Co, so the Co particle retains its integrity as a nearly spherical crystalline particle. A systematic increase in the surface anisotropy of Co–M NPs with capping in the trend Cu, Ag, and Au was then observed, as resulting from the previously described orbital moment anisotropy, caused by hybridization of Co atoms at the particle surface with the capping metal [25].

Beside those surface effects, the magnetic anisotropy of NP systems may be intrinsic, such as that identified in chemically ordered CoPt alloy NPs [19]. The anisotropy of those particles is also correlated with the Co orbital anisotropy, which by hybridization with Pt, and due to the high spin-orbit coupling of the latter, gives rise to an enhanced anisotropy, albeit much smaller than in the bulk CoPt $L1_0$ alloy phase [37, 38]. Therefore, in the Co–M NPs systems that we describe in this thesis, we explore the introduction of high spin-orbit non-magnetic elements and induce their alloying with Co, as a strategy to control their intrinsic anisotropy and magnetic properties. In particular, we study Co NPs capped with Tungsten (W) and Platinum (Pt).

On the one hand, W (electron configuration $[\text{Xe}]4f^{14}5d^46s^2$) is a good candidate as it hybridizes with Co (electron configuration $[\text{Ar}]3d^74s^2$), its affinity to alloy with Co on sputtering grown films at room temperature is known [39], these alloys tend to become amorphous [40–43], and it has a less than half filled $5d$ band. In this way, we end up with a system of amorphous NPs, which constitute a different type with variable anisotropy. Then, the work on Co–W NPs we describe in this dissertation is devoted to investigate the open question whether amorphous alloys may support intrinsic anisotropy, induced by alloying, irrespective of surface effects.

On the other hand, for the Pt case, aside from the previously described hybridization between Pt (electron configuration $[\text{Xe}]4f^{14}5d^96s^1$) and Co, and the high spin-orbit coupling of Pt that gives rise to an enhanced anisotropy, Co–Pt NPs show perpendicular magnetic anisotropy (PMA) [44, 45], which is interesting for applications in spintronic nano-devices implemented to, for example, ultrahigh density magnetic storage, fast memory applications, and nanosensors [46, 47].

Apart from the importance of the orbital moment in nanomaterials, the spin moment still dominates their magnetism, as in the case of transition metals. Reducing the dimension leads to a narrowing of the valence d bands that generate most of the magnetic moment in metallic materials. In some metallic NPs, hybridization of the d -band and the sp -bands at the interface with the surrounding matrices or supports generates a small, albeit non-negligible, number of holes in the metal d -band. This increase in the density of states at the Fermi level E_f has opened the chance to detect magnetic phenomena in materials which are non-magnetic in bulk, for example, in the noble metals of Co–M NPs described above [25], Pt NPs [48] and Au NPs [49], to cite some examples of metallic particles where such phenomena have been observed. Accordingly, in this dissertation we present a review of some of these examples as an attempt towards the comprehension of the d -band magnetism in nanostructured metals via the element-selective XMCD technique.

In addition to synchrotron radiation techniques, the anisotropy may be studied by magnetometry performed in conventional laboratories. One of the rarely used, but effective methods to directly study the magnetic anisotropy of a material is the transverse susceptibility (TS) technique. This measurement system consists in probing the ac magnetic susceptibility of a material in one direction while an external bias magnetic field is applied perpendicular to the measurement direction. Analysis of the TS in magnetic materials have demonstrated its potential and versatility to study singular magnetic properties of bulk [50–52], single crystals [53], thin films [54–57] and nanoparticles (NPs) systems [58–62]. TS measurement techniques developed up to date are based on conventional inductance susceptibility techniques [60, 63, 64], magneto-optical setups [54, 57] and self-resonant circuits in the radio frequency (RF) range [65]. The latter method has demonstrated to be one of the most accurate and versatile developments to measure TS, since it may be implemented on widely used commercial Quantum Design physical properties measurement systems (PPMS). It consists of a self-resonant LC tank coupled to a tunnel diode oscillator (TDO), the latter acting as an active device for losses compensation in the circuit. The magnetic sample is inserted into the inductor (L) core space and its TS is probed by the shift in the resonant RF generated by changes in the sample magnetization.

However, currently operating TS measurement systems for the PPMS are far from being simple and friendly to use. Changing sample usually involves soldering and desoldering the inductance coil, jeopardizing the reproducibility of the system. Moreover, previously published designs of TS susceptometers for PPMS systems [65] introduce a high heat input into the sample space, avoiding the PPMS platform to stabilize the sample temperature below 10 K, and, therefore, impeding the possibility of studying interesting low-temperature phenomena with this technique. On the electronics design, it has been conventionally adopted the use of TDOs, which benefits of a good spectral purity, but limiting the compensation capabilities of the system and hence the range of samples feasible to measure. And finally, the necessity to install extra electronic and computing equipment to acquire data, independent to the control of the PPMS, makes the programming of experiments harder, rendering the previous systems not very efficient.

Then, in the second part of this thesis, we present an implementation of a TS measurement system for the PPMS of the Servicio de Medidas Físicas in the Universidad de Zaragoza. We have improved several aspects of the design, electronics, and data acquisition of previously published transversal susceptometers [65], turning this magnetometric technique a relatively easy one to implement and operate within the widely used PPMS platform. We also describe the use of the developed setup to explore the magnetic anisotropy of two systems of iron oxide nanoparticles, interesting for biomedical applications.

1.4 Outline

This dissertation is aimed to undertake an elaborate study of different magnetic nanoparticles systems, with which we intend to demonstrate the capabilities of two experimental techniques: the X-ray absorption spectroscopies (XANES, EXAFS and XMCD) and the RF transverse susceptibility. By using these techniques for electronic, structural and magnetic characterization of nanoparticles systems, along with other complementary methods, we obtain a better understanding of the origin of their magnetic anisotropy.

The manuscript is organized as follows. In Chap. 2 we describe the main experimental techniques used in the present work to study the structural and magnetic properties of NP systems. In particular, we focus on the X-ray absorption spectroscopies that make use of synchrotron radiation. In the following three chapters we describe the structural, magnetic and electronic properties of two nanoparticles systems, namely: Co–W NPs and Co–Pt NPs, studied with synchrotron radiation techniques. Hence, in Chap. 3 we describe the main properties of the amorphous Co–W alloy NPs. We demonstrate that the magnetic anisotropy of amorphous alloy nanoparticles may be originated in mechanisms other than surface effects, such as structural short range order. A continuation of this study is presented in Chap. 4, where we describe evidences of violation of Hund’s third rule in the W induced magnetic moments of this Co–W system, as consequence of hybridization

effects and local structure in the Co–W alloys. Similarly, in Chap. 5 we describe the properties of the Co–Pt NPs studied, where the presence of Co–Pt alloy in these granular films is determinant in the origin of their perpendicular magnetic anisotropy. Then, a review of noble metals (Ag, Au, Pd, Pt) nanoparticles studied with synchrotron radiation is presented in Chap. 6, where we demonstrate that these techniques are very suitable to study their d -band magnetism.

The last two chapters of this thesis are dedicated to the RF transverse susceptibility (TS) technique. Chap. 7 is devoted to the description of the TS technique and the developed equipment for the PPMS. Then in Chap. 8 we present a couple of examples of magnetic NPs studied with this TS measurement system, namely magnetite and maghemite NPs. Finally, we give some general conclusions and perspectives of this work in Chap. 9.

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Chapter 2

Experimental Techniques

This section is addressed to briefly describe the main experimental techniques used to study the structural and magnetic properties of the nanoparticles included in this thesis. We first explain the transmission electron microscopy techniques used to explore the morphology and structure of the particles. Then, we introduce two techniques to study the magnetic properties of the samples: SQUID based magnetometry and anomalous hall effect (AHE). Finally, we focus on the description of the synchrotron radiation techniques employed, in particular those based on X-ray absorption mechanisms, which allow studying selectively and locally the structural, electronic and magnetic properties of the nanoparticles systems; these are: X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and X-ray magnetic circular dichroism (XMCD).

Later, we will dedicate Chap. 7 to describe the magnetic transverse susceptibility technique, which has been also used to study the magnetic properties of some nanoparticles systems in this dissertation.

2.1 Transmission Electron Microscopy

The transmission electron microscopy (TEM) is a technique whereby an electron beam is transmitted through an ultra thin specimen, forming an image from the interaction between the transmitted electrons and the sample. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small wavelength of electrons. This enables to examine fine details, even as small as a single column of atoms. This technique usually combines the high resolution imaging with elemental microanalysis and electron diffraction, so that a complete characterization of the shape, size, chemical composition and crystalline structure of nanoparticulate materials is achieved.

In a TEM microscope, an electron gun, located at the top of it, emits the electrons by thermionic or field emission. These electrons travel through vacuum in the column of the microscope where electromagnetic lenses focus them into a very thin beam.

The electron beam then travels through the specimen to study. At the bottom of the microscope, the image is formed on the image plane of objective lens from the unscattered electrons. Then, projector lenses form the images on a screen or CCD camera.

One of the main requirements for this technique is that the sample must be thin enough for electrons to pass through; the interaction between electrons and matter is much stronger than that with visible light, so samples for TEM observation must have thickness below 100 nm. There exists a variety of procedures to prepare samples for TEM observation, depending on the kind of materials and their nature. For example, bulk samples must be first cut to an proper size (~ 3 mm in diameter, 300–400 μm thick); after that, they are thinned, first mechanically and then by ionic or electrolytic milling, until reaching the desired thickness.

Some modern TEMs integrate a high angle annular dark field (HAADF) detector that allows to perform scanning transmission electron microscopy (STEM) measurements. In this mode, the electron beam is focused into a narrow spot that is scanned over the sample in a raster. The rastering of the beam across the sample makes these microscopes suitable for analysis techniques such as mapping by X-ray energy disperse spectrometry (EDX) spectroscopy and electron energy loss spectroscopy (EELS). The HAADF detector collects electrons from an annulus around the beam, forming the image only by very high angle incoherently scattered electrons, as opposed to Bragg scattered electrons in the conventional TEM images. By using a STEM and the HAADF detector, it is possible to form atomic resolution images where the contrast is directly related to the atomic number (Z-contrast image).

The microscopy images and analysis of the magnetic nanoparticles in this work were performed with two TEMs, whose technical specifications are described below.

2.1.1 JEOL JEM 3,000 F

A JEOL JEM 3,000 F Field Emission Microscope has been used by Dr. Luisa Ruiz González and Dr. José María González-Calbet of the Departamento de Química Inorgánica in the Universidad Complutense de Madrid¹ to take some of the images of the nanoparticles systems that we show in this thesis. This microscope is shown in Fig. 2.1a. It operates at acceleration voltages between 100 and 300 kV and it is fitted with an Oxford Instruments energy dispersive X-ray spectrometer (EDS). Its high-resolution performance (a point resolution of 0.17 nm) is then complemented by the ability to perform chemical microanalysis from sub-nanometre areas (below 0.4 nm in some cases). This microscope is equipped with a HAADF detector, so that STEM mode and EELS analysis are also possible.

¹ <http://www.cnme.es/>.

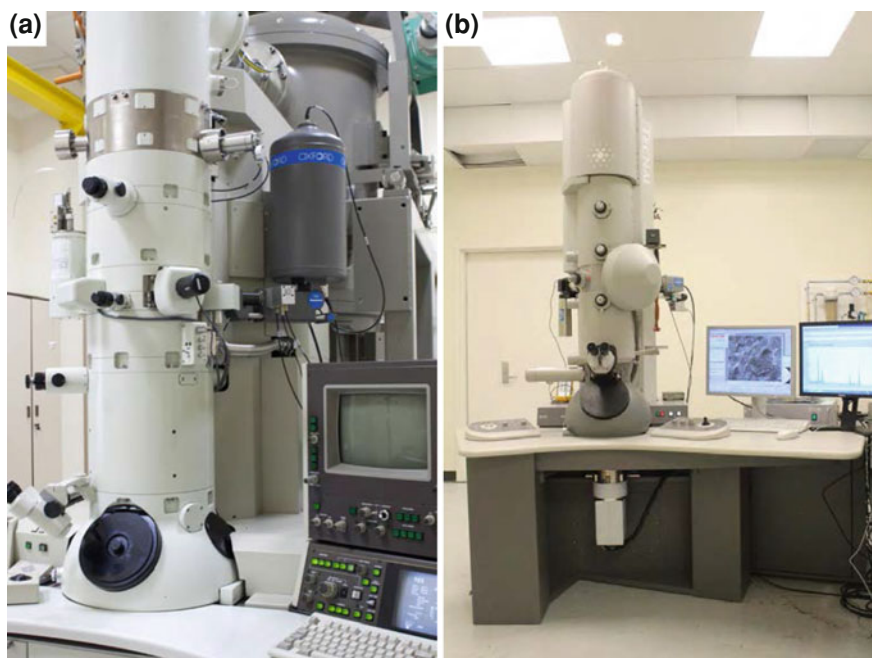


Fig. 2.1 Images of the two models of transmission electron microscopes used to observe the samples. **a** JEOL JEM 3,000 F Field Emission Microscope. **b** FEI Tecnai™ G2 F30 STWIN Field Emission Microscope

2.1.2 FEI Tecnai™ G2 F30 STWIN

Some of the TEM images that we show in this dissertation have taken by Dr. Cesar Magén and Dr. Alfonso Ibarra in a FEI Tecnai™ G2 F30 STWIN Field Emission Microscope of the Laboratorio de Microscopías Avanzadas, Instituto de Nanociencia de Aragón,² Universidad de Zaragoza. A picture of a microscope of this kind is shown in Fig. 2.1b. In this microscope, acceleration voltages as high as 300kV allow reaching a point resolution of 0.2 nm, line resolution of 0.10 nm, and information limit of 0.14 nm. This TEM system is fully loaded including a HAADF detector, EDX, and a Gatan Image Filter (GIF).

2.2 SQUID Based Magnetometry

A magnetometer is an instrument used for the magnetic characterization of a material, by measuring the strength and/or direction of magnetic fields. A superconducting quantum interference device (SQUID) is the most sensitive device available for

² <http://ina.unizar.es/lma/index.html>.

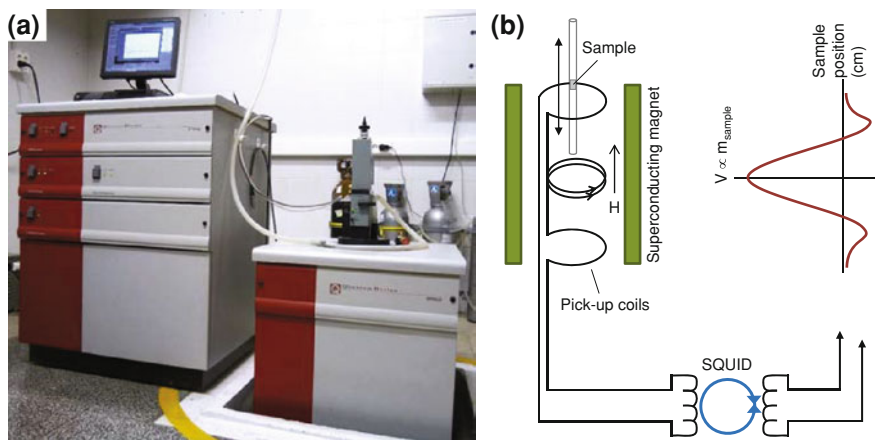


Fig. 2.2 **a** MPMS-XL magnetometer of the Universidad de Zaragoza. **b** Schematics of the SQUID—based measurement system

such purposes. It works as an extremely sensitive current-to-voltage converter, so that, when integrated to a Quantum Design magnetic property measurement system (MPMS), the complete system is a magnetic flux to voltage transducer. The fact of directly measuring magnetic flux is one of the main advantages of SQUID magnetometry, allowing to measure moments on the order of 10^{-7} emu.

A picture of one of the MPMS of the Servicio de Medidas Físicas of the Universidad de Zaragoza,³ which have been used for some of the magnetic characterization described in this manuscript, is shown in Fig. 2.2a. A schematics of the measurement process of a magnetic sample in this equipment is displayed in Fig. 2.2b. In a MPMS, the SQUID does not detect directly the magnetic field from the sample since it may be interfered by any flux from nearby magnetic systems, or even the earth's magnetic field. Instead, a measurement is performed by moving a sample through a system of superconducting pick-up coils, two of them with the same sense very closely spaced, and the other two of the opposite sense, spaced symmetrically outside (see Fig. 2.2b). This system is located outside the sample chamber at the center of the superconducting magnet. As the sample moves through the coils, the magnetic moment of the sample induces an electric current in the detection coils. Because the detection coils, the connecting wires, and the SQUID input coil form a closed superconducting loop, any change of magnetic flux in the detection coils produces a change in the persistent current in the detection circuit, which is proportional to the change in magnetic flux. Since the SQUID is a highly linear current-to-voltage converter, the variation in the current in the detection coils produces corresponding variations in the SQUID output voltage. Based on this profile of voltage (and thus flux) versus position of the sample (see Fig. 2.2b), given the assumption that the signal is from a point dipole, the magnetic moment can be determined.

³ <http://sai.unizar.es/medidas/index.html>.

This MPMS allows measuring magnetization as a function of magnetic fields up to 50kOe, or temperature in a range of 1.9–400 K. AC measurements with a field amplitude of 4Oe and frequencies from 0.01 to 1,000Hz are also possible in this equipment. It integrates a reciprocating sample option (RSO), which consists of a high resolution mode to improve the equipment sensitivity to measure moments as small as 5×10^{-9} emu. Unlike DC measurements where the sample is moved through the coils in discrete steps, the RSO measurements are performed using a servo motor which rapidly oscillates the sample. A digital signal processor (DSP) is incorporated in the RSO, which allows for much more rapid data collection than the standard step scan method. The DSP also decreases the contribution of low frequency noise during data collection, which improves the signal-to-noise ratio resulting in maximum sensitivity.⁴

2.3 Anomalous Hall Effect

The Hall effect [2] (or ordinary Hall effect, OHE) is a well known and studied phenomenon, characterized by the production of a voltage difference (the Hall voltage) across an electrical conductor or semiconductor, transverse to an electric current in the material, and a magnetic field perpendicular to the current. In magnetic materials, there is an additional contribution to the Hall voltage, proportional to the magnetization, called the extraordinary or anomalous Hall effect (AHE). Correlation between the AHE and magnetization enables the use of the Hall voltage measurement for the study of magnetic properties of materials in conditions hardly accessible by other techniques [3].

The Hall voltage in magnetic materials is commonly described by the phenomenological equation [4, 5]

$$V_H = \underbrace{\frac{R_H I}{t} H \cos(\alpha)}_{OHE} + \underbrace{\frac{\mu_0 R_s I}{t} M \cos(\theta)}_{AHE} + \underbrace{\frac{k I}{t} M^2 \sin^2(\theta) \sin(2\phi)}_{PHE} \quad (2.1)$$

where t is the film thickness, R_H , R_s and k are the ordinary, anomalous and planar Hall coefficients, respectively, and the angles α , θ and ϕ are defined in Fig. 2.3. The first term in Eq. 2.1 is the OHE and arises from the Lorentz force acting on conduction electrons. The OHE depends on the z -component of the $\vec{H}$ field, and produces an electric field perpendicular to H_z and the current I . The second term is the AHE and arises due to spin dependent scattering mechanisms. It is associated with a break of the right–left symmetry during the spin–orbit scattering in magnetic materials and its contribution could be much larger than the OHE. The AHE depends

⁴ For further information of SQUID magnetometers see Ref. [1] and/or the Quantum Design website <http://www.qdusa.com/index.html>.

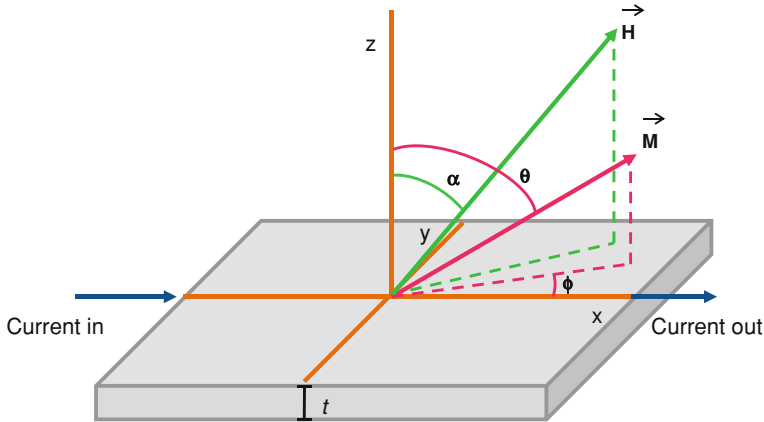


Fig. 2.3 Geometry of the AHE measurement. α is the angle between the applied field and the normal to the sample, θ is the angle between the magnetization and the normal and ϕ is the angle between the current and the in plane component of the magnetization

on the perpendicular component of $\vec{M}$, and produces an electric field perpendicular to M_z and I . The last term in Eq. 2.1 is the planar Hall effect (PHE), or anisotropic magneto-resistance. The PHE is proportional to the square of the planar component of $\vec{M}$, and produces an electric field parallel and perpendicular to the current (the one expressed in Eq. 2.1 is perpendicular to the current). Note that all three terms are inversely proportional to the film thickness t . Given this property, the AHE has been recognized as a useful tool for measuring the magnetic hysteresis $M(H)$ loops of thin films, specially those used in perpendicular magnetic recording media (PMRM), ferromagnetic/semiconductor heterostructures (spintronic devices), and diluted-magnetic-semiconductors [4, 5].

The AHE measurements performed on some of the nanoparticles systems described in this thesis were carried out by Dr. Jolanta Stankiewicz in an electrical transport setup of the Departamento de física de la materia condensada and Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC—Universidad de Zaragoza, and in a Quantum Design Physical Property Measurement System (PPMS) of the Servicio de Medidas Físicas of the Universidad de Zaragoza.⁵

2.4 X-ray Absorption Spectroscopies in Synchrotron Radiation Facilities

Several experimental techniques based on interactions of radiation with matter require of highly intense, bright, continuous and tuneable light sources [6, 7]. These requirements are easily fulfilled with synchrotron radiation sources. These large-scale

⁵ <http://sai.unizar.es/medidas/index.html>.

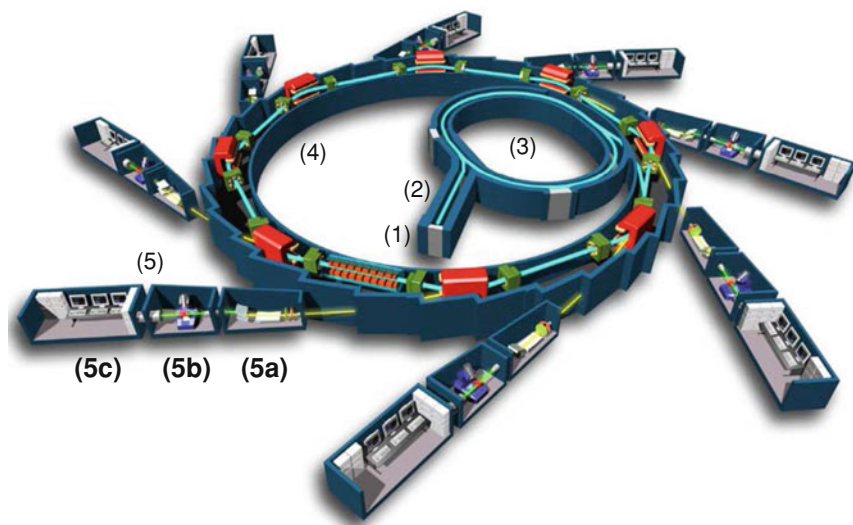


Fig. 2.4 General diagram of a synchrotron facility. 1 Electron or proton gun, 2 LINAC, 3 booster, 4 storage ring, 5 beamline, 5a optics cabin, 5b experimental hutch, and 5c control cabin

facilities consist of particle accelerators that speed up charged particles, such as electrons or protons, into an orbit at almost the speed of light. According to the electromagnetic theory, an electric charge irradiates energy when accelerated. This radiation is emitted tangentially to the circular trajectory of the electric charge when it is deflected. Third generation synchrotron radiation facilities are the most powerful currently operating synchrotron light sources, and have become one of the essential tools for basic and applied scientific research over the world.

The main properties of the synchrotron light may be summarized as follows: it has a broad spectrum from microwaves to hard X-rays, so that it is a tuneable radiation source; its high intensity photon beam of about 10^{18} – 10^{20} photons/s/mm² (compared to the 10^8 photons/s/mm² of a conventional X-ray tube) allows rapid experiments; it is a highly brilliant photon beam generated by a small divergence and small size source (spatial coherence); it is a very stable (submicron source stability) and polarized radiation.

A diagram of a synchrotron radiation facility is shown in Fig. 2.4. The synchrotron light generation starts in an electron (or proton) gun (1), where a cathode produces free electrons released to a linear accelerator or LINAC (2). The LINAC feeds a booster ring (3), where electrons receive a boost in energy from approximately 250 MeV to approximately 1.5–8 GeV from microwaves generated in a radio frequency cavity as they circulate in the ring. The booster increases the speed of the electrons close to the speed of light. When the electrons have enough energy to produce light, an injection system transfers them from the booster ring to the storage ring (4): a tube

with straight and circular sections kept in ultra high vacuum, with quadrupole and sextupole magnets designed to focus the electron beam. Once there, the electrons will circulate for a long period of time producing photons every time the dipole magnets (also called bending magnets) change the direction of the flow of electrons. After each turn there is a photon port to allow the light to travel down the beamlines to the research stations. Aside from the bending magnets, synchrotron light may also be produced by insertion devices, such as wigglers or undulators, located at the straight sections of the storage ring. They consist of periodic magnetic structures that stimulate highly brilliant, forward-directed synchrotron radiation emission by forcing the stored charged particle beam to perform wiggles, or undulations, as they pass through the device. The magnet arrays are designed in such a way that the emitted radiation interferes constructively to produce a very intense and concentrated beam in narrow energy bands in the⁶ spectrum.

Each beamline has an optics cabin (5a), an experimental hutch (5b), and a control cabin (5c). The optics cabin has optical instruments used to tailor the type of radiation to have the characteristics for each experiment. The experimental hutch contains the support mechanism, and the environment for the sample study. Different instruments and detectors record the information produced from the interaction of the synchrotron light and the sample. The control cabin allows the researchers to control the experiments and collect the data.

The synchrotron radiation source used to study the magnetic nanoparticles in this dissertation is the European Synchrotron Radiation Facility (ESRF),⁷ which is a third generation and the most powerful synchrotron in Europe. It is located in Grenoble, France. It operates at a nominal energy of 6 GeV, with a circumference of 844 m, and around 49 operating beamlines.

X-ray absorption spectroscopy (XAS) is one of those techniques that is best performed with the intense and tunable X-ray beams produced in a synchrotron radiation source. This spectroscopy refers to the details of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom. The absorbing process is illustrated in Fig. 2.5a. An X-ray photon reaches the absorbing atom (in blue) and disappears. After the interaction, a photoelectron is emitted. Depending on the energy of the incident X-ray photon, different processes occur. If the binding energy of certain electron in the absorbing atom is equal to the X-ray photon energy, there is a sharp increase in the absorption cross-section, called absorbing edge, corresponding to an emission of the photoelectron to the continuum states, as indicated in 2.5b. The absorption edges are named according to the principle quantum number of the electron that is excited: K for $n = 1$, L for $n = 2$, M for $n = 3$, and so on. The energies at which edges appear are unique for each element, fact that makes this spectroscopy an element-selective technique.

⁶ General diagram of Synchrotron Soleil with Copyright ©EPSIM 3D/JF Santarelli.

⁷ <http://www.esrf.eu/>.

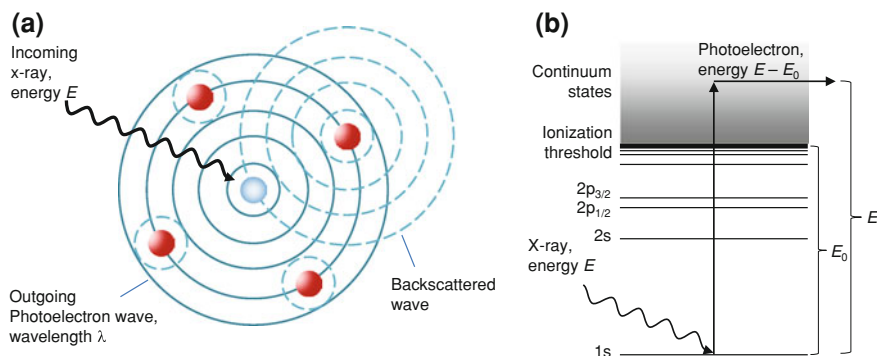
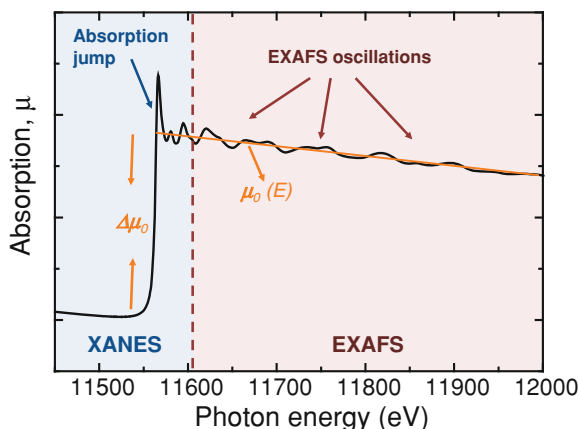


Fig. 2.5 Schematics of the X-ray absorption process. **a** An absorbing atom (blue) is shown here surrounded by several other atoms (red). Whenever the energy of an X-ray is greater than the binding energy of one of the absorbing atom's core electrons, a photoelectron is liberated. **b** Energy-level diagram of an absorbing atom showing the atom's first few core-electron orbitals: $1s$, $2s$, $2p_{1/2}$, and $2p_{3/2}$. The ionization potential energy is denoted by E_0 . With the absorption of a photon of energy E , the electron undergoes a transition to an unbound state in the continuum and, by conservation of energy, acquires a kinetic energy ($E - E_0$) [8]

Fig. 2.6 XAFS spectrum recorded at the Pt L_3 edge for a Pt foil at 300 K. We have divided the spectrum into its two main regions: XANES—X-ray Absorption Near Edge Structure, and EXAFS—Extended X-ray Absorption Fine Structure. The background function μ_0 , and the measured jump at the absorption threshold energy E_0 , $\Delta\mu_0$, are also shown



2.4.1 X-ray Absorption Fine Structure

X-ray absorption fine structure (XAFS) is a specific structure observed in XAS [8, 9]. A usual XAFS spectrum can be seen in Fig. 2.6, where the two spectral regions are identified: the near-edge region XANES, typically within 50 eV of the main absorption edge, and the extended fine-structure (EXAFS) which spans the 50–2,000 eV above the edge. The basic physical description of these two regimes is the same. EXAFS results from the interference in the single scattering process of the photoelectron scattered by surrounding atoms (see Fig. 2.5a), and it provides

information on the local structure such as distances between neighbors, thermal and structural disorder in a material. Information on the geometry of the local structure is provided by the analysis of the multiple scattering peaks in the XANES spectra. However, XANES is harder to be described in a quantitative way since there is not an equation to parameterize this region, while it does exist for EXAFS, as it will be described below.

The X-ray absorption process is a transition between two quantum states: from an initial state with an X-ray, a core-electron, and no photoelectron, to a final state with no X-ray, a core-hole, and a photoelectron. According to the Fermi's golden rule for dipolar transitions (following the dipole selection rules $\Delta l = \pm 1$ and $\Delta s = 0$), the transition probability between two electronic states, per unit time, is defined as

$$W_{if} = \frac{2\pi}{\hbar} \left(\frac{eE_0}{2} \right)^2 |\langle i | \hat{\epsilon} \cdot \vec{r} | f \rangle|^2 \rho(E_f) \quad (2.2)$$

where $\rho(E_f)$ is the density of final states, $\langle i |$ is the initial state of the core-electron, $|f\rangle$ the final state of the photoelectron, and $\hat{\epsilon} \cdot \vec{r}$ the dipole operator. Since the core-level electron is very tightly bound to the absorbing atom, the initial state will not be altered by the presence of the neighboring atom. The final state, on the other hand, will be affected by the neighboring atom because the photoelectron will be able to see it. The absorption coefficient $\mu(E)$ is proportional to the sum of possible final states f of the transition probability in Eq. 2.2. It is calculated according to the first order approximation of the time-dependent perturbation theory, based on the interaction between the electromagnetic field and the atom potential.

In the EXAFS region, the spectrum reflects oscillatory variation of the X-ray absorption coefficient, $\mu(E)$, as a function of photon energy, E , beyond the absorption edge (see Fig. 2.6). We define the EXAFS fine-structure function $\chi(E)$ as

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)} \quad (2.3)$$

where $\mu(E)$ is the measured absorption coefficient, $\mu_0(E)$ is a smooth background function representing the absorption of an isolated atom, and $\Delta\mu_0(E)$ is the measured jump in the absorption $\mu(E)$ at the threshold energy E_0 . These parameters are also represented in Fig. 2.6.

According to the described absorption process, the EXAFS $\chi(E)$ is proportional to the amplitude of the scattered photoelectron at the absorbing atom. Therefore, EXAFS is best understood in terms of the wave-like nature of the photoelectron created in this process. Thus, it is common to convert the X-ray energy to k , the wave number of the photoelectron, being $k^2 = 2m(E - E_0)/\hbar^2$, and m the electron mass. **The primary quantity for EXAFS is then $\chi(k)$, the oscillations as a function of photoelectron wave number.** To emphasize the oscillations, $\chi(k)$ is often weighted by a power of k , typically k^2 or k^3 . The different frequencies composing these oscillations correspond to different near-neighbor coordination shells, described and modeled according to the EXAFS equation

$$\chi(k) = \sum_j \frac{N_j S_0^2 F_j(k) \exp(-2k^2 \sigma_j^2) \exp\left(-\frac{2R_j^2}{\lambda_j(k)}\right)}{k R_j^2} \sin(2k R_j + \delta_j(k)) \quad (2.4)$$

where $F_j(k)$ is the backscattering amplitude from each of the N_j neighboring atoms, $\delta_j(k)$ is the total phase shift experienced by the photoelectron, R_j is the distance to the neighboring atom j , σ_j^2 is the disorder in the neighbor distance, parameter usually known as Debye–Waller factor, and S_0^2 is the amplitude reduction due to many-body effects. The term $\exp(-2R_j^2/\lambda_j(k))$ is due to inelastic losses in the scattering process, with λ_j being the electron mean free path. The EXAFS equation allows us to determine N , R , and σ^2 knowing the scattering amplitude $F(k)$ and phase-shift $\delta(k)$ for each path. Furthermore, since these scattering factors depend on the atomic number, Z , of the neighboring atom, EXAFS is also sensitive to the atomic species of the neighborhood.

The EXAFS $\chi(k)$ is usually Fourier transformed into a radial structure function $\chi(R)$ that represents the data in terms of distances from the absorber. Peak positions in this radial structure function roughly correspond to the radii of the scattering shells.

2.4.1.1 BM29 Beamline at the ESRF

The XAFS experiments on the magnetic nanoparticles system studied here were performed in collaboration with Dr. Sakura Pascarelli at the general purpose X-ray absorption spectroscopy beamline BM29 [10] at the ESRF.⁸ This beamline is devoted to carry out XAFS experiments at a very large operational energy range with reasonable X-ray flux: 4–74 keV, coming from a bending magnet. It has a high energy resolution, typically a factor 3–5 better than the intrinsic spectral broadening at any K or L absorption edge; a high spectral signal to noise ratio, above 7.0×10^4 for well prepared samples; a high beam stability; and a high level of automation.

A schematic diagram of a conventional XAFS beamline, as BM29, is shown in Fig. 2.7. The full spectrum of synchrotron light passes through an entrance slit, which helps collimate the radiation before entering into a double-crystal monochromator. The X-rays diffract off the crystals' lattice planes, which are aligned at an angle θ with respect to the incoming beam. Because of the Bragg scattering condition $n\lambda_j = 2d \sin \theta$, only X-rays of energy $E_n = nhc/\lambda_j$ can reflect off the crystals. Different X-ray energies can be selected by changing the angle θ of the crystals. The monochromatic beam passes through an ion chamber that monitors the beam intensity I_0 by absorbing part of it. The beam then passes through the sample, and the intensity of the transmitted X-ray I is measured by a second ion chamber. Taking the log of the ratio of I/I_0 yields the absorption. We can also determine the sample's absorption by measuring the intensity of its X-ray fluorescence, I_f with a detector

⁸ In a recent upgrade, performed in 2011, the ESRF BM29 beamline has been relocated to the BM23 port, which is the one currently operational. For further information see <http://www.esrf.eu/UsersAndScience/Experiments/ElectStructMagn/BM23/>.

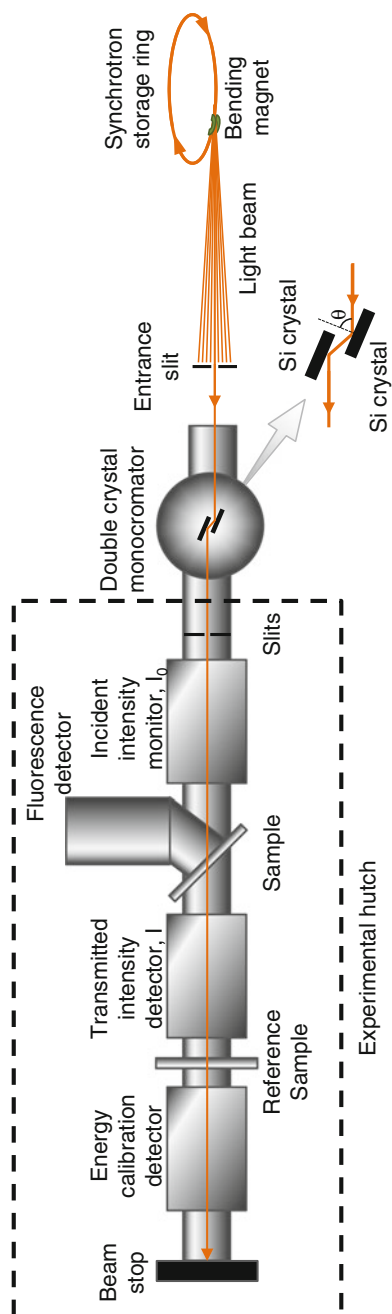


Fig. 2.7 Diagram of the assembly used in a conventional measurement of XAFS

that is out of the beam path, usually oriented at 45° with respect to the sample. Finally, the beam passes through a reference sample whose absorption edge is used to help correct for uncertainties in the beam's energy.

2.4.2 X-ray Magnetic Circular Dichroism

Some synchrotron radiation techniques take advantage of the natural polarization of this light in the plane of the electron orbit in order to perform polarization-dependent measurements. This is the case of the X-ray magnetic circular dichroism (XMCD), where the difference between two X-ray absorption spectra recorded in a magnetic field, one measured with right circularly polarized light (+1 helicity), and one with left circularly polarized light (−1 helicity), is performed. The XMCD is then defined as

$$XMCD(E) = \mu^- - \mu^+ \quad (2.5)$$

where μ^- and μ^+ are the absorption coefficients with left and right circularly polarized light, respectively. The differences in the absorption of light with opposite helicities arise from an additional dipole selection rule for dipolar transitions, $\Delta m_j = \pm 1$ for +1 and −1 helicity, respectively, in Eq. 2.2; the dipole operator, $\hat{\epsilon} \cdot \vec{r}$, must also be expressed as dependent of the light polarization. This way, **XMCD reflects the difference in the density of empty states with different spin moment**, so that by closely analyzing the XMCD signal, information can be obtained on the magnetic properties of the absorbing atom, such as its spin and orbital magnetic moment.

In a simple atomic monoelectronic picture, the XMCD occurrence may be understood in terms of the two-step approach described by Schütz et al. [11]. Let us first consider an X-ray photon with helicity +1 absorbed by an electron from a spin-orbit-split core-level, for example, $2p_{3/2}$ (L_3 edge) and $2p_{1/2}$ (L_2 edge), as illustrated in Fig. 2.8a. When absorbing a circularly polarized photon, some of the orbital moment of the photon can be transferred via the spin-orbit coupling to the electron spin. This results in an effective spin polarization of the excited electrons, process known as Fano-effect [12]. From the $2p_{3/2}$ state, 62.5 % of excited electrons carry a spin of $m_s = +1/2$ and only 37.5 % of $m_s = -1/2$. From the $2p_{1/2}$ state, 75 % of excited electrons carry a spin of $m_s = -1/2$ and only 25 % of $m_s = +1/2$. Note that the sign of spin polarization is different for the different $2p$ states, provided their different spin-orbit coupling: $(l + s)$ at the $p_{3/2}$ -state, and $(l - s)$ at the $p_{1/2}$ -state. If there were no spin-orbit-splitting, that is, no energy gap between $2p_{3/2}$ and $2p_{1/2}$ states, the averaged spin polarization would be zero.

With this spin and orbital polarized excited electrons, the polarization of the unoccupied final states is probed in the second step of this model. Any imbalance in either spin or orbital momentum in the final states will give rise to a dichroic effect. Thus, in a magnetic material, the exchange splitting leads to a splitting of the valence band, lowering the energy for electrons with one spin orientation (majority electrons) and rising it for the other (minority electrons), as illustrated in Fig. 2.8a. The transition

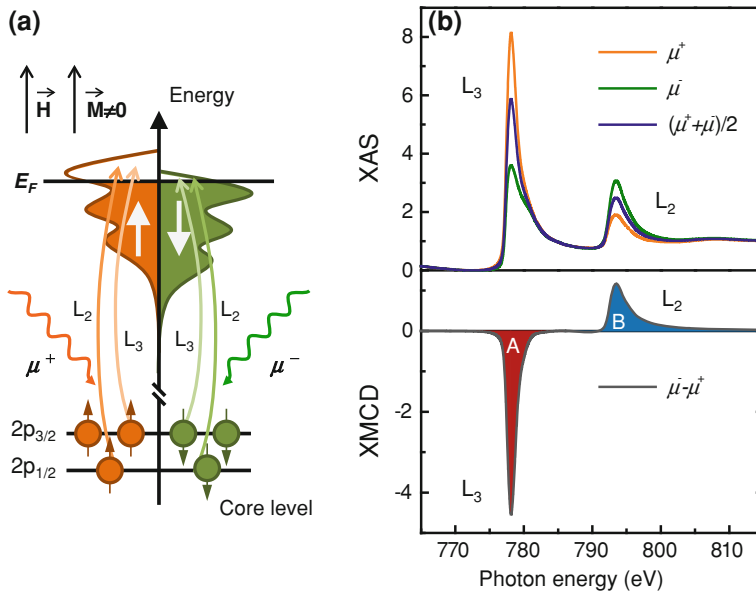


Fig. 2.8 **a** Diagram of the simple mono-electronic two-step picture of the resonant excitation process in a magnetic material, resulting in a XMCD signal. First a circularly polarized photon excites a spin polarized electron (Fano-effect) from a $2p$ level; this spin polarized electron is used in step two to probe the spin polarized occupation levels of the $3d$ states. **b** XAS spectra and XMCD signal at the Co $L_{2,3}$ in a system of Co-Pt NPs. In this case, a scan over the $2p$ absorption edges of Co with circularly polarized light leads to non-statistic absorption lines due to differently spin occupied $3d$ states. This effect is reversed by inverting either the magnetization (change of the magnetic field direction) or the light polarization. In this picture the polarization of the light is reversed between the orange and green absorption curves. The difference of left and right circularly polarized scan is the dichroic signal displayed below

probability of electrons in a dipole transition are proportional to the unoccupied density of states, as expressed in Eq. 2.2. If this density of states is different for different spin orientations and the electrons are spin polarized, the absorption spectra will change when the spin polarization is inverted, as due to the change of the helicity of the incoming light. This results in spectra as the one represented in Fig. 2.8b, where we have plotted the XAS recorded with right and left circularly polarized X-rays at the Co $L_{2,3}$ edges in a Co-Pt NPs sample, along with the resulting XMCD signal.

To see this effect it is required that the magnetization of the sample has at least a component parallel to the incoming light. The inversion of the magnetization has the same effect on the absorption process as the inversion of the photon polarization. Thus, XMCD measurements can be performed in those two equivalent ways: either by changing the helicity while keeping constant the applied magnetic field, or by changing the direction of the magnetic field at a constant helicity of the light.

XMCD became more powerful as a tool for the element-selective characterization of magnetic materials with the derivation of the magneto-optical sum rules by Thole

et al. [13] and Carra et al. [14] for spin-orbit split absorption edges. Via these sum rules it is possible to determine both the spin, $m_S = -2\mu_B \langle S_z \rangle / \hbar$, and orbital, $m_L = -\mu_B \langle L_z \rangle / \hbar$, magnetic moments in the atom being probed with the XMCD measured at its $L_{2,3}$ edges. In order to write the sum rules, let us define the following integrals

$$\begin{aligned} A &= \int_{L_3} (\mu^- - \mu^+) dE \\ B &= \int_{L_2} (\mu^- - \mu^+) dE \\ C &= \int_{L_3+L_2} (\mu^- + \mu^+ + \mu^0) dE \end{aligned} \quad (2.6)$$

which follow the symbols and sign criteria denoted in Ref. [15]. The absorption spectrum μ^0 requires in principle linearly polarized radiation, but is usually approximated by $\mu^0 = 1/2(\mu^+ + \mu^-)$. Before application of the sum rules it is necessary to separate the absorption intensity due to the electron transitions we are interested in. Thus, the C integral must be calculated after removing the unwanted transitions into higher unoccupied states or into the continuum in the absorption spectra. It is usually performed by subtraction of a hyperbolic step function with one step at the L_3 and one at the L_2 edge [16]. If there are less pronounced absorption maxima at the absorption edges, a reference spectrum of a similar element with a well-known number of unoccupied states should be subtracted.

The sum rule for the orbital moment per unoccupied final state n_h is expressed as

$$\frac{m_L}{n_h} = -\frac{2(A+B)}{C} \mu_B \quad (2.7)$$

For the spin sum rule, it is usual to define the *effective* spin moment, $m_{\text{Seff}} = m_S + m_D$, which considers the dipolar term m_D . The latter is expressed as a function of the expectation value of the intra-atomic magnetic dipole operator $\langle T_z \rangle$ [15, 17], as $m_D = -7\langle T_z \rangle \mu_B / \hbar$, which reflects the asphericity of the spin moment distribution around the absorbing atom. In order to determine m_S , one option is to assume that the angle averaged $\langle T_z \rangle$ is much smaller than the spin moment and can be neglected, as in the case where the absorbing atom is in a cubic (undistorted) symmetry. On the contrary, for lower symmetries or distorted systems, $\langle T_z \rangle$ may be obtained from angle dependent experiments or theoretically approximated [17, 18]. For example, for non-cubic structures, $\langle T_z \rangle$ might have a maximum value of $\langle S_z \rangle / 3$, corresponding to the Lorentz local field at the absorbing atom site [19]. However, the angle average of $\langle T_z \rangle$ with this approximation in the whole sample usually cancels out, as well.

If the angle average of $\langle T_z \rangle$ is zero, $m_{\text{Seff}} = m_S$, and the spin moment, also per n_h , is written as

$$\frac{m_S}{n_h} = -\frac{3(A - 2B)}{2C} \mu_B \quad (2.8)$$

Therefore, the orbital to spin moment ratio is defined as

$$\frac{m_L}{m_S} = \frac{4(A + B)}{3(A - 2B)} \quad (2.9)$$

which is independent of n_h and the C integral. For a precise estimation of these moments, one must separate the L_3 and the L_2 contribution of the spectrum, which is fairly easy for the heavier $3d$, and for $4d$ and $5d$ elements since the spin-orbit split increases with the nuclear charge of the atom. Additionally, one needs to know the exact amount of d -holes in the material, for which no straight forward experimental determination procedure exists. This drawback may be solved by either obtaining the number of d -holes from band structure calculations, or by expressing the sum rules results as magnetic moments per d -hole.

2.4.2.1 ID08 and ID12 Beamlines at the ESRF

The XMCD experiments on the magnetic nanoparticles studied here were performed at the ID08 beamline (for soft X-rays ranging between 0.3 and 1.6 keV) in collaboration with Dr. Peter Bencok and Dr. Nick Brookes, and at the ID12 beamline (for hard X-rays ranging between 2 and 20 keV) in collaboration with Dr. Fabrice Wilhelm, Dr. Alevtina Smekhova and Dr. Andrei Rogalev, in the ESRF.⁹ These beamlines are dedicated to polarization-dependent X-ray absorption and excitation spectroscopies. Both beamlines make use of undulators to produce the polarized light for XMCD measurements. By longitudinal phasing of the magnetic arrays, the polarization of the undulator emission can be changed from linear to elliptical and circular. They complement each other to probe magnetism in a diverse range of systems with X-ray magneto-optical techniques and to study the electronic structure of materials X-ray and photoelectron emission techniques.

ID08 is equipped with two APPLE II undulators providing $\sim 100\%$ circular/linear beam polarization, a spherical grating monochromator with an energy resolution close to $\Delta E/E = 5 \times 10^{-4}$ at 850 eV, optics focussing down to 6–40 [60–500] microns (FWHM) vertical [horizontal] beam size, and several different UHV experimental stations and sample preparation facilities. ID12 has three helical undulators installed on the its straight section: HELIOS-II, APPLE-II and the so-called “ElectroMagnet/Permanent magnet Hybrid Undulator” (EMPHU) that have been optimized to complement one another. They give ID12 the advantages of fully control of the polarization state of the incident X-ray beam over a wide

⁹ For further information about ID08 and ID12 beamlines, please visit <http://www.esrf.eu/UsersAndScience/Experiments/ElectStructMagn>.

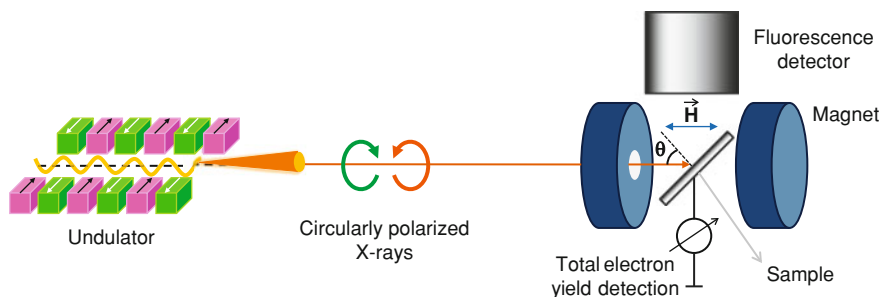


Fig. 2.9 Basic diagram of the XMCD measurement setup at ID08 and ID12

energy range. ID12 uses a double-crystal monochromator with a resolution of $\Delta E/E = \sim 10^{-4}$ to select the energy of the polarized X-rays for experiments.

A schematic of the basic setup for XMCD experiments in these two beamlines is shown in Fig. 2.9. The polarized and monochromatized X-rays are directed through the sample, which is located at the center of a superconducting magnet. The magnetic field is applied on the direction of the incoming beam. The detection of the polarized dependent X-ray absorption spectra may be performed by fluorescence yield (FY) or total electron yield (TEY), the latter regularly used in the soft X-ray regime. The fluorescence detectors are (single- or multi-anode) ion implanted silicon photodiodes, which are characterized by a high efficiency in the X-ray range, fast time response, excellent linearity, and nearly insensitivity to magnetic fields.

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Chapter 3

Structural and Magnetic Properties of Amorphous Co–W Alloyed Nanoparticles

This section is devoted to investigate a system of amorphous Co–W alloy nanoparticles (NPs). The sequential alumina–Co–W deposition technique employed for their preparation allows to obtain self-organized arrays of particles with controlled geometries, i.e., particle sizes and interparticle distances. This potentiality has been expanded to study the magnetic properties of the amorphous Co–W NPs. In particular, we study the open question whether amorphous alloy nanoparticles may support intrinsic magnetic anisotropy, induced by alloying, irrespective of surface effects usually present in NPs systems.

Amorphous NPs constitute a different type with variable anisotropy, but few works on this field have been previously performed. Most of them are focused on Fe-based NPs [1–11] and some on Ni-based NPs [12–14], where surface effects are substantial for the blocking process and magnetic anisotropy, while, to our knowledge, no study on the mechanism of intrinsic anisotropy has been so far performed.

The election of W is based on the known affinity to produce Co–W alloys by sputtering, at room temperature [15–18], on the one hand, and the tendency of these alloys to become amorphous [16, 19–21], on the other hand. Besides, short range structural ordering, observed in films and bulk amorphous alloys [22, 23], has been proposed as the mechanism inducing anisotropy in those systems. So, there was a good chance that Co–W alloying would allow varying the NPs anisotropy as a function of the tungsten concentration.

Thus, we present a systematic study of structural and magnetic properties of the Co–W NPs system. Their size and composition are controlled by varying the amount of Co or W in the samples. The effects of these parameters on the local structure of the particles are described by analysis of high-resolution transmission electron microscopy (HRTEM) and extended X-ray absorption fine structure (EXAFS) measurements; and their magnetic properties are examined by SQUID magnetometry and X-ray magnetic circular dichroism (XMCD).

3.1 Samples Studied

The samples studied here were prepared by Dr. Cyrille Deranlot and Dr. Frederic Petroff at the Unité Mixte de Physique CNRS-Thales¹ in Palaiseau, France, by sequential sputtering deposition of Al₂O₃, Co and W on a Si substrate. The deposition procedure is the same described for the Metal (M)-capped Co–NPs in Ref. [24], and it is illustrated in Fig. 3.1. The cobalt, tungsten and alumina are deposited using Ar plasma, the metals in DC mode and the insulator at a RF power of 2.2 W/cm². The substrate temperature is kept constant at 293 K and the Ar pressure is 2×10^{-3} Torr. The formation of Co aggregates on the amorphous alumina (see Fig. 3.1) is the result of three-dimensional growth because of the different surface energies between alumina and Co [25]. Aggregation occurs below a certain threshold of the nominal thickness of Co, t_{Co} , that the layer would have if it were continuous. Previous studies show that not all the Co deposited on the alumina layer aggregates as forming the particles, but there exists a fraction of Co atoms or small clusters dispersed on the matrix, defined as x_{para} [26]. The values of x_{para} depend on t_{Co} , varying between 0.5 and 0.13 for $t_{\text{Co}} = 0.4$ and 1.0 nm, respectively [26]. The Co clusters are subsequently capped with a W layer, whose nominal thickness is denoted by t_{W} . A new alumina layer of about 3 nm is deposited on top of this Co–W system. At the end of the deposition process, a final thicker alumina layer of 5 nm is deposited for protection purposes. This sequential deposition process is repeated N times in order to get a multilayer system, following the formula Al₂O₃/(Al₂O₃/Co/W) _{N} /Al₂O₃.

The samples measured may be grouped into two series: a , those with t_{Co} fixed at 0.7 nm and varying W capping layer, $t_{\text{W}} = 0.6, 1.5$ and 4.5 nm, and b , with constant capping layer $t_{\text{W}} = 1.5$ nm and varying $t_{\text{Co}} = 0.4, 0.7$ and 1.0 nm. Most of the samples have $N = 25$, except that with $t_{\text{Co}} = 1.0$ nm and $t_{\text{W}} = 1.5$ nm, for which $N = 20$.

A bulk Co₃W alloy has been used in the present study as a reference sample. It has been synthesized by melting the pure metallic precursors in an induction furnace under Ar atmosphere. The encapsulated sample was thermally treated for seven days at a temperature of 1300 K in a muffle furnace. After the annealing, the sample was quenched by immersing the quartz tube in room temperature water.

The chemical composition of the bulk Co₃W alloy was confirmed by means of energy-dispersive X-ray spectroscopy (EDX) performed by an Oxford Instruments INCA 300 X-Sight as part of a JEOL JSM 6400 scanning electron microscope (SEM) in the Servicio de Microscopía Electrónica de Materiales of the Universidad de Zaragoza.² The crystalline structure of the alloy was determined by X-ray powder diffraction (XRD) measurements performed at room temperature using a rotating anode D-Max Rigaku diffractometer. XRD data were collected in a range $20^\circ < 2\theta < 80^\circ$ using Cu K_α radiation, and are shown in Fig. 3.2. The Co₃W alloy is an *hcp* phase with spatial group P6₃*mc*. A profile matching (PM) routine was run on this data using FULLPROF suite code [27]. The position of the diffraction peaks in the XRD profile are well matched with this routine using the Co₃W crystallographic

¹ <http://www.trt.thalesgroup.com/ump-cnrs-thales/>.

² <http://sai.unizar.es/microscop-mat/>.

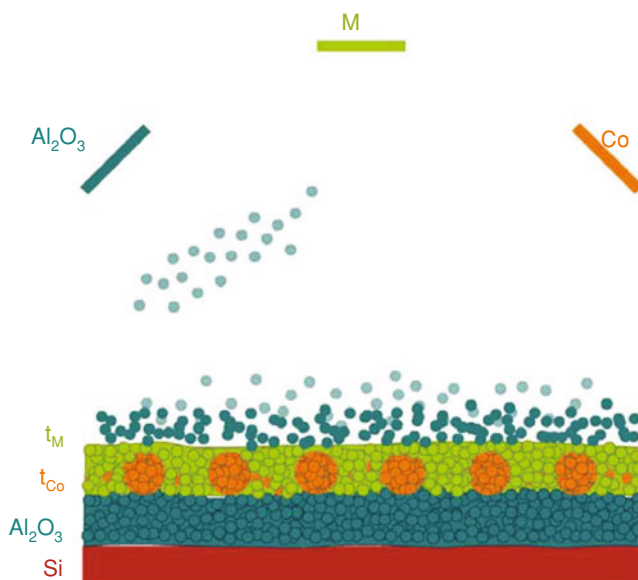


Fig. 3.1 Illustration of the sequential sputtering deposition process of the Co–M NPs

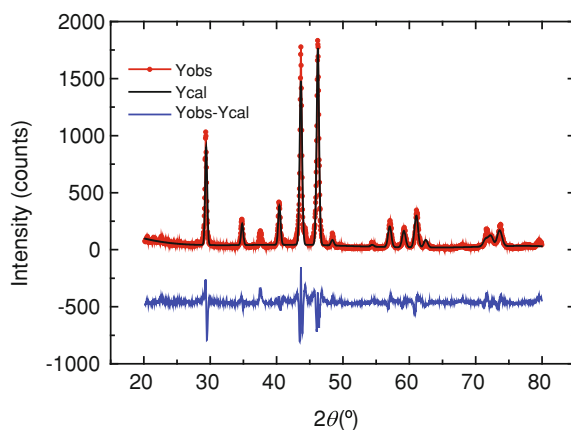


Fig. 3.2 XRD data and PM results of the bulk Co_3W alloy

information taken from the ICSD³ database as initial parameters (see Fig. 3.2). The lattice parameters obtained from the PM for the bulk Co_3W alloy were $a = b = 5.144 \text{ \AA}$ and $c = 4.141 \text{ \AA}$, very close to those of the Co_3W listed in the ICSD. However, the structure in the bulk Co_3W sample is found to be rather disordered, which is evident from the broad and less intense diffraction peaks observed, compared

³ <http://icsd.iqfr.csic.es/icsd/>.

to regular highly crystalline materials, and from the mismatch of the peaks width in the PM results. Thus, a complete Rietveld analysis on this dataset was not possible. There are a very few diffraction peaks not identified by the PM routine that may be assigned to the Co_7W_6 phase; such phase has also been observed in the SEM and EDX study, but it has been estimated to be less than 2 % in the sample.

3.2 Morphological and Structural Study

3.2.1 Microscopy Measurements

HRTEM measurements were performed by Dr. Luisa Ruiz González and Dr. José María González-Calbet of the Departamento de Química Inorgánica in the Universidad Complutense de Madrid.⁴ HRTEM images were taken on both *a* and *b* samples series in cross section configuration, in a JEOL JEM 3,000 F Field Emission Microscope fitted with an Oxford LINK Electron Dispersive Spectrometry (EDS) analyzer. Cross section specimens were prepared by conventional mechanical thinning and ion milling techniques.

HRTEM and high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) measurements were performed on two samples in plan view configuration by Dr. Cesar Magén and Dr. Alfonso Ibarra in a FEI TecnaiTM G2 F30 STWIN Field Emission Microscope of the Laboratorio de Microscopías avanzadas, Instituto de Nanociencia de Aragón, Universidad de Zaragoza.⁵ Samples for plan-view observation were prepared by deposition of a $\text{Al}_2\text{O}_3/\text{Co}/\text{W}/\text{Al}_2\text{O}_3$ sandwich on TEM carbon grids, with $t_{\text{Co}} = 0.7$ nm and $t_{\text{W}} = 0.6$ and 1.5 nm.

Low magnification studies in cross section configuration for all five samples confirmed the presence of 25 layers (20 layers in the case of $t_{\text{Co}} = 1.0$ nm and $t_{\text{W}} = 1.5$ nm) in agreement to the nominal layer preparation. HRTEM images and EDS analysis for both samples series (Figs. 3.3, 3.4) indicate that light gray layers correspond to alumina and darker layers to metal (Co and W). These layers exhibit a washboard cross sectional shape. In stark contrast to Co–nanoparticles systems covered with a noble metal layer, where the crystal structure of the Co particle is not affected by the capping [24], W alloys with Co in those places where the Co NPs were originally formed. By inspection of the particles in Fig. 3.3a, b, there seems to be very short range order within each layer due to the higher Co/W ratio in these two samples, but this is neither detected by SAED (Selected Area Electron Diffraction), nor by Fourier transform. In fact, the SAED images show the typical halo diffraction pattern corresponding to an amorphous structure (see Fig. 3.4d). Regarding this feature, some authors suggest that amorphous Co–W films consist of tetrahedral units composed of one W and three Co atoms, which arrange in a structure that does not exhibit macroscopic crystal symmetry [28]. Others ascribe this short range ordering

⁴ <http://www.cnme.es/>.

⁵ <http://ina.unizar.es/lma/index.html>.

Fig. 3.3 HRTEM images in cross section configuration for samples from the *a* series with $t_{\text{Co}} = 0.7$ nm and **a** $t_{\text{W}} = 0.6$ nm, **b** $t_{\text{W}} = 1.5$ nm and **c** $t_{\text{W}} = 4.5$ nm. Fourier transforms (FFTs) at selected zones of the image in **(c)** are shown in **(d)** and **(e)**. Arrangement of the particles within layers is highlighted in **(a)**. An amorphous zone on one of the layers of sample in **(c)** is demarcated by a *white line*

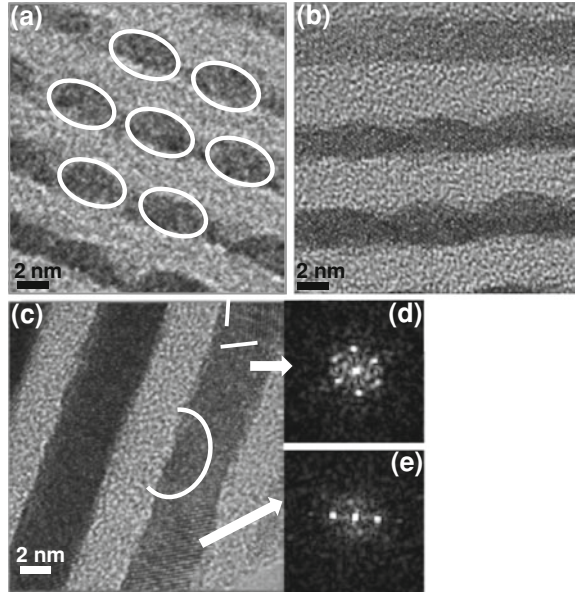
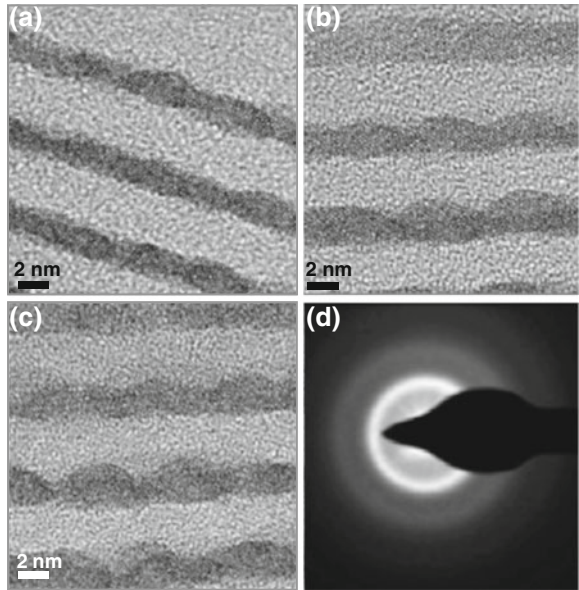


Fig. 3.4 HRTEM images in cross section configuration for samples from the *b* series with $t_{\text{W}} = 1.5$ nm and **a** $t_{\text{Co}} = 0.4$ nm, **b** $t_{\text{Co}} = 0.7$ nm and **c** $t_{\text{Co}} = 1.0$ nm. **d** SAED image of a NP in sample in **(b)**



(SRO) in amorphous alloys to the existence of icosahedral and octahedral clusters [29]. Some of these structures are probably being formed in our Co–W NPs. We will further discuss this topic in Sect. 3.2.2.

The Co–W amorphous particles in series *a* and *b* are more detached in samples with higher Co/W ratio, as in that of $t_{\text{Co}} = 0.7$ nm and $t_{\text{W}} = 0.6$ nm (Fig. 3.3a). In those samples where the Co/W ratio decreases, W tends to join the particles by filling the interparticle spaces (Fig. 3.3b, c). These particles with elongated cross sectional shape arrange within layers in a periodical way, similarly to their assembly with alumina capping [25]. That is, in each layer, particles lay on the depression formed by the previous deposited particles layer so that they form a hexagonal arrangement across the layers, as it is marked in Fig. 3.3a. All this morphology described for samples from the *a* series has also been observed for samples from the *b* series (see Fig. 3.4).

Structural differences are found in the *a* series sample with $t_{\text{W}} = 4.5$ nm. As it is observed in a HRTEM image for this sample (Fig. 3.3c), the interparticle spaces existing in all other four samples have been filled, so that the Co/W film has a nearly constant thickness. Each metallic layer of about 4.2 nm thick, shows ordered zones alternating with amorphous zones. In the ordered regions, periodicity is around 0.2 nm, confirmed by fast Fourier transform (FFT) performed on some of the ordered zones (see bright spots observed in Fig. 3.3d, e). This periodicity and the distances and angles on the FFT are in agreement with the (1 1 0) planes of W bcc structure. There is also evidence of different grains within the crystalline zones on the layer, identified, for example, by the two orientation of the planes observed in the HRTEM image (see Fig. 3.3c), and the splitting of the spots in Fig. 3.3d. EDS analysis show the presence of both Co and W. However, it is not easy to establish differences between ordered and disordered zones by this technique. Given the higher amount of W in this last sample, the Co–W alloy is possibly saturated, so that W starts to generate the crystalline zones identified from the images (Fig. 3.3c). Further discussion about W growing as a crystal in the samples is presented in the EXAFS section (see Sect. 3.2.2).

High contrast obtained in plan view HAADF STEM images for the *a* series samples with $t_{\text{Co}} = 0.7$ nm and $t_{\text{W}} = 0.6$ and 1.5 nm (Fig. 3.5a, b) allows easier identification of the particles than in HRTEM images due to the huge Z contrast between the heavy metal particles and the light oxide matrix. In these images, brighter parts correspond to Co–W nanoparticles, and darker parts to Al_2O_3 . Images obtained are comparable to those of similar systems of metallic nanoparticles embedded in insulator matrices [30], and the shape of the particles is similar to that of Co–nanoparticles embedded in alumina [31]. HAADF STEM images reveal that particles in sample with $t_{\text{W}} = 1.5$ nm (Fig. 3.5b) are bigger and more closely packed than particles in sample with $t_{\text{W}} = 0.6$ nm (Fig. 3.5a).

Size distributions for samples from the *a* series with $t_{\text{Co}} = 0.7$ nm and $t_{\text{W}} = 0.6$ nm (Fig. 3.5c) and 1.5 nm (Fig. 3.5d) were obtained by digital processing of the images taken, for both cross section (Fig. 3.3a, b) and plan view configurations (Fig. 3.5a, b). Results for the diameter distribution on each case were fitted using a Gaussian distribution function. The values obtained from this analysis are listed in Table 3.1. The effective diameters for each configuration, $\langle D_{\text{eff}} \rangle_{\text{CS}}$ for Cross Section and $\langle D_{\text{eff}} \rangle_{\text{PV}}$ for Plan View, were obtained with the assumption that particles have circular in-plane and elliptic out-of-plane projection shape, the latter with short axis *a* and long axis *b* on each projection, so that $D_{\text{eff}} = \sqrt{ab}$. Interparticle distance,

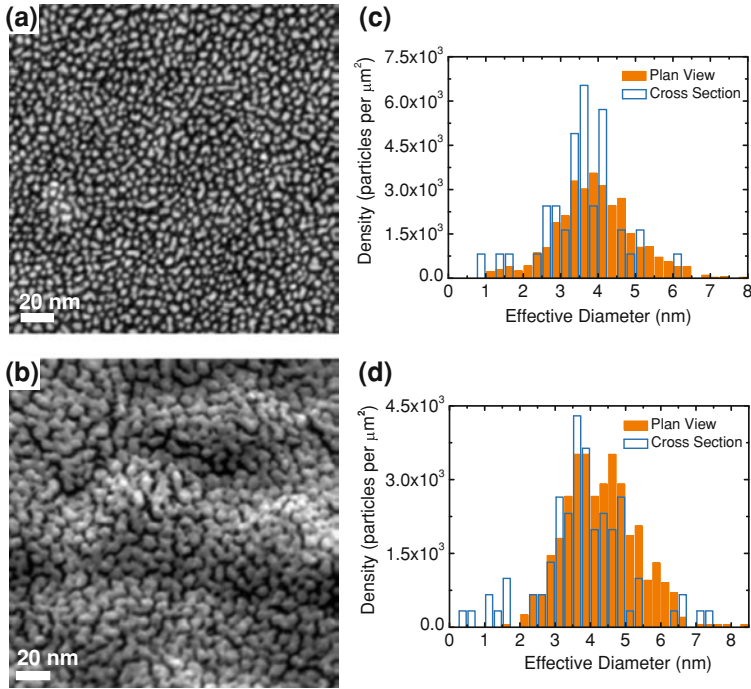


Fig. 3.5 HAADF STEM images in plan view configuration for the *a* series samples with $t_{Co} = 0.7$ nm and **a** $t_W = 0.6$ nm and **b** $t_W = 1.5$ nm. Size distribution of plan view and cross section configurations for the samples in **(a)** and **(b)** are shown in **(c)** and **(d)**, respectively

d , and surface density of particles, N_S , expressed as number of particles per nm^2 for the plan view images, were also obtained (see Table 3.1). These two values are almost equal for both samples analyzed in plan view, which means that particles are spatially distributed on each layer in the same way for those samples from the *a* series. Cross section values have a higher error since they were obtained from poor contrast HRTEM images, so particle identification was less precise than in the HAADF STEM images in the plan view case.

Size distributions for cross section and plan view configurations for the *a* samples series are shown in Fig. 3.5c, for sample with $t_W = 0.6$ nm, and in Fig. 3.5d for sample with $t_W = 1.5$ nm, both with $t_{Co} = 0.7$ nm. These distributions are centered near the same mean $\langle D_{eff} \rangle$; i.e., there is a slight difference between both values. $\langle D_{eff} \rangle$ for the in-plane projection shape obtained from the plan view configuration analysis is larger than the out-of-plane projection from cross section analysis in both samples ($t_W = 0.6$ and 1.5 nm). Thus, Co–W particles have an oblate shape.

Digital analysis of the images obtained in cross section for samples from the *b* series were also performed in order to identify some morphological parameters; however, size distributions in these cases were not obtained, due to the low contrast and less separation between the particles in these two samples (see Fig. 3.4a, c).

Table 3.1 Average particle diameter ($\langle D_{eff} \rangle$), distribution width (σ), interparticle distance (d), and density of particles in the layer (N_S) obtained from digital analysis of TEM images taken in cross section (CS) and plan view (PV) configurations

Samples series	t_{Co} (nm)	t_W (nm)	$\langle D_{eff} \rangle_{CS}$ (nm)	σ_{CS} (nm)	d_{CS} (nm)	$\langle D_{eff} \rangle_{PV}$ (nm)	σ_{PV} (nm)	d_{PV} (nm)	$N_S \cdot 10^2 \text{ nm}^{-2}$
<i>a</i>	0.7	0.6	3.6(1)	0.4(2)	5.8(5)	3.87(4)	0.82(6)	5.3(5)	3.2(1)
	0.7	1.5	3.9(1)	0.9(5)	6.6(7)	4.23(6)	1.0(1)	5.6(9)	3.5(1)
<i>b</i>	0.4	1.5	2.84(2)	—	5.3(5)	—	—	—	—
	0.7	1.5	3.9(1)	0.9(5)	6.6(7)	4.23(6)	1.0(1)	5.6(9)	3.5(1)
	1.0	1.5	4.24(2)	—	6.7(3)	—	—	—	—

A clear tendency in the size of the particles given by the Co/W ratio in the samples is also evident from the values in Table 3.1, so that out-of-plane projection increases from 2.84 to 4.24 nm for samples in the *b* series, as t_{Co} increases from 0.4 to 1.0 nm.

The elemental composition of the nanoparticles has been measured by EDS on the plan view sample with $t_{\text{Co}} = 0.7$ nm, and $t_{\text{W}} = 0.6$ nm. A total of 12 particles were measured yielding to an average composition with tungsten content of 27 ± 6 at.% W; i.e. the particle composition is close to that of Co_3W . Moreover, the composition within one particle was constant within experimental error. The relative variation in the composition of the other particles has been determined by EXAFS analysis at the Co *K*-edge (see Sect. 3.2.2).

From this morphological study we conclude that we have obtained a system of self-organized and uniformly dispersed amorphous Co–W alloy NPs. This occurs since W has alloyed with the preformed Co NPs, instead of growing as a homogeneous crystalline film covering the particles. The size of the amorphous particles depends on the amount of Co and W deposited on each layer. Particles formed within the layers have an oblate shape. When the amount of W increases and the Co–W alloy saturates, W grows as a crystal and fills the interparticle spaces.

Previous works on Co–W thin films have led to similar amorphous structure, when such films are synthesized by sputtering, using composite targets [19, 32]. The amorphous forming ability (AFA) of Co–W has been studied in terms of the Miedema's coordinates model, $Y = |\Delta\phi/\Delta n_{\text{WS}}^{1/3}|$, where $\Delta\phi = \phi_{\text{Co}} - \phi_{\text{W}}$, and $\Delta n_{\text{WS}} = n_{\text{WS}}(\text{Co}) - n_{\text{WS}}(\text{W})$, where ϕ is the chemical potential, and n_{WS} the electron density of the Wigner-Seitz unit cell, and $Z = |(R_{\text{W}} - R_{\text{Co}})/R_{\text{Co}}|$ [32]. The binary alloy phase space is separated by the empirical law $Y = 2.52Z^{-1/4}$ in the amorphous and crystalline areas. It was found that Co–W lies in the amorphous region; the reason for this favorable AFA in this alloy is a negative heat of mixing, large atomic size differences and a low substrate temperature that avoids recrystallization via diffusion. These factors have explained satisfactorily the formation of Co–W amorphous thin films by co-sputtering [19]. In our preparation method Co nanoparticles are formed first, and a subsequent W capping supplies the alloying metal. The sputtering voltage is enough to let W and Co react, while the substrate temperature avoids crystallization. The AFA is high since the W concentration is higher than 17%, a condition needed for the formation enthalpy of the amorphous phase to be lower than the crystalline one [32]. Therefore, amorphization is favorable in the formation of Co–W NPs, just as it is in the thin film case.

3.2.2 XANES and EXAFS Measurements

X-ray absorption near edge structure (XANES) and EXAFS spectra for both *a* and *b* samples series were measured at the Co *K* (7,709 eV) and W *L*₃ (10,207 eV) edges using a double-crystal Si(111) monochromator in the BM29 beamline at the European Synchrotron Radiation Facility (ESRF). Measurements were performed at 300 K in

fluorescence detection mode with a 13-element Ge solid state detector with digital signal processing for fluorescence X-ray absorption spectroscopy (XAS), high energy resolution and high count rate. Reference samples were also measured at different edges: Co particles embedded in alumina matrix (referred in the following as “bare Co NPs”) ($\text{Al}_2\text{O}_3/\text{Co}$)₂₀ with $t_{\text{W}} = 0.7$ nm measured at the Co K edge, Co_3W alloy measured at the Co K and W L_3 edges, Au capped particles with formula ($\text{Al}_2\text{O}_3/\text{Co}/\text{Au}$)₂₅, $t_{\text{Au}} = 1.5$ and 4.5 nm, measured at the Co K and Au L_3 edges. The reference foils: Co metallic foil measured at the Co K edge, W metallic foil measured at the W L_3 edge and Au foil measured at the Au L_3 edge. For each edge measured on each sample, four spectra were taken in order to have enough statistics in data treatment, following a 4 s/point count.

Some of the XANES spectra at the W L_3 edge were recorded at the ESRF ID12 beamline, by a fluorescence detector in backscattering geometry. The APPLE-II undulator and a double —Si-(111)—crystal monochromator were used to collect the spectra.

The X-ray absorption spectra were analyzed following standard procedures. A preliminary reduction of the EXAFS raw data involving background removal of the absorption data $\mu(E)$, conversion of $\mu(E)$ to $\chi(k)$, normalization and weighting scheme were performed with AUTOBK and ATHENA, programs from the simulation package IFEFFIT [33]. EXAFS data analysis and fitting were performed on all reference and samples at their respective edges. All spectra were fitted using the ARTEMIS program from the same IFEFFIT package using models based on the crystallographic information found in the ICSD⁶ database. Atomic clusters used to generate the scattering paths for fitting were generated with ATOMS, a tool from the same simulation package [34].

3.2.2.1 Co K Edge Results

The X-ray absorption near edge structure (XANES) allows to study the electronic structure of Co (electron configuration $[\text{Ar}]3d^74s^2$) and W (electron configuration $[\text{Xe}]4f^{14}5d^46s^2$) atoms of the Co–W systems. Spectra at Co K edge for Co–W NPs from the *a* and *b* series are shown in Fig. 3.6a, b, respectively. In both cases a Co foil XANES is plotted for reference, and a spectrum for bare Co NPs with $t_{\text{Co}} = 0.7$ nm is plotted in Fig. 3.6a for comparison. Changes in the intensity of the pre-edge peak and the white line (denoted as peak I and peak II, respectively, in Fig. 3.6) are noticeable. The variation of the peaks areas ($\Delta A = \int_{E_i}^{E_f} (\mu_{\text{sample}} - \mu_{\text{Co-foil}}) dE$) in series *a* and *b* is shown in the insets of Fig. 3.6a, b, respectively. The integration limits were 7,708.4–7,721.3 eV for peak I, and 7,721.3–7,729 eV for peak II.

The Co K edge white line reflects its 4*p* empty states near the Fermi energy. The origin of peak I is at the density of states (DOS) of *d*–character available at the Fermi energy, projected onto the Co site [35, 36]. This is influenced by intra-atomic Co 4*p*–3*d* hybridization, as it will be further described in Sect. 4.1.1. Moreover, in our samples, this *d*-DOS originates both at the Co 3*d* band and at the W 5*d* states through

⁶ <http://icsd.iqfr.csic.es/icsd/>.

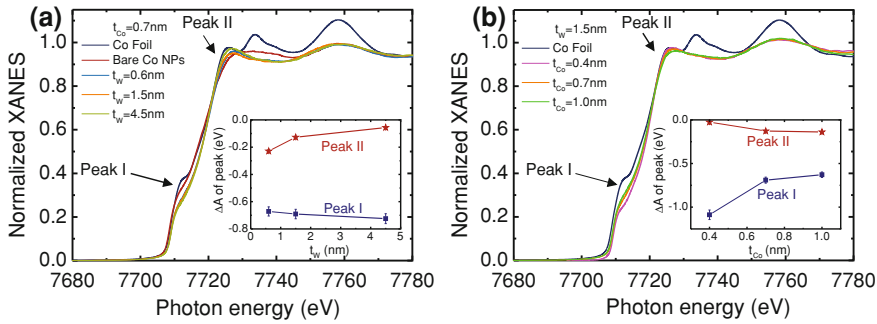


Fig. 3.6 XANES at the Co K edge for the Co-W NPs **a** a samples series, **b** b samples series. A spectrum for the Co foil is plotted for reference in both cases. In **(a)** a curve for bare Co NPs with $t_{Co} = 0.7$ nm has been included for comparison. Insets: Variation of the areas of peak I and peak II in **(a)** and **(b)** as a function of t_W and t_{Co} , respectively

interatomic Co $3d$ –W $5d$ hybridization. The intensity of peak I in Co–W NPs is clearly lower than in metal cobalt, and than bare Co NPs for the a samples series. The same reduction at peak I with respect to Co foil is observed for the b series. Although alloying with W introduces a higher number of d holes in the system, hybridization strongly delocalizes the d empty states, depleting the intensity of peak I by reducing the d -DOS projected at the Co site. Therefore, the strong reduction of peak I at the Co K edge of Co–W NPs is a proof of Co $4p$ – $3d$ –W $5d$ hybridization.

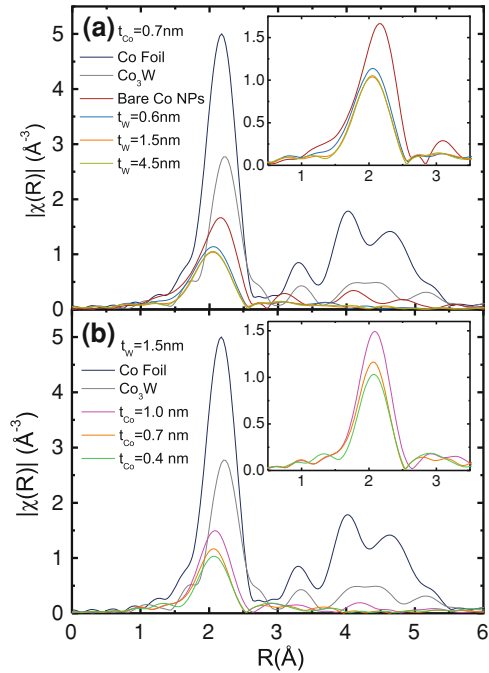
In series a , peak I is practically constant along the series (see inset of Fig. 3.6a), reflecting that Co $3d$ –W $5d$ hybridization is not affected by small variations in the amount of W for a fixed Co content. This, in principle, surprising fact strongly suggests that the alloy composition is similar for the three samples along this series, a result that will be confirmed by EXAFS (later in this section) and by magnetic analysis (Sect. 3.3.1). In contrast, b samples series show a clear increase of the ΔA of peak I upon increasing Co content in the NPs, as shown in the inset of Fig. 3.6b. This trend is the expected one, as a decrease in the proportion of W (or increase of Co/W ratio) in the sample lowers the number of $5d$ holes available for hybridization, increasing the localization of the d -character states at the Co site.

The intensity of peak II depends on both the number of available $4p$ states, and the structure of the system, in a non-trivial way. The comparison of the Co metal and Co–W NPs has to be taken with care, as their structures are different (hcp and amorphous, respectively). However, the trend of ΔA of peak II in samples from the a series indicates that the number of $4p$ holes is enhanced as the W content increases, suggesting an electronic transfer from Co $4p$ towards W $5d$ states. Accordingly, ΔA of peak II in samples from the b series slightly decreases with Co content, suggesting that, for the range of t_{Co} and t_W studied, the number of $4p$ holes is reduced as the ratio Co/W increases. In short, along the a and b series, as the Co/W ratio increases, both the $4p$ number of empty states and the delocalization of $3d$ empty states decrease.

Structural analysis that can be extracted from the $\chi(k)$ EXAFS signal is better studied by its Fourier transform, shown in Fig. 3.7, performed on a k -range from 2.0 to $11.9 \text{ \AA}^{-1}$ using a k^2 weight and a hanning window function. This R -space data show peaks which correspond to different atomic shells surrounding the absorbing atom, Co in this case. In Fig. 3.7a, it can be seen that the position and shape of the peaks in the bare Co nanoparticles and Co foil are very similar, not only for the first coordination shell, but also for outer shells, showing that Cobalt in $\text{Co}/\text{Al}_2\text{O}_3$ aggregates in a similar structure as metallic Co, as it has been reported in the literature [31]. However, the peaks for outer coordination shells are different in the W-capped Co nanoparticles. This is caused by a change in the Co coordination due to alloying between Co–W, which is also evident in Fig. 3.7b for the b sample series. Indeed, intensities of all peaks in Fig. 3.7a, b is larger in the Co foil than in the particulate systems, as it is expected from the reduction in the mean Co coordination due to the size reduction.

In the present study, EXAFS signal for the bare Co nanoparticles with $t_W = 0.7 \text{ nm}$ was fitted using a Co-*fcc* metal model, where the coordination number N was used as a fitting parameter. A reduction from $N = 12$ in the metallic Co to $N = 6.1$ in the first coordination shell of the bare Co nanoparticles was obtained from this fit. However, recent works have demonstrated that such a strong reduction in the number of first neighbors could be an artifact of EXAFS analysis [37], due to effects

Fig. 3.7 Fourier transform of EXAFS signal at the Co K edge on the Co–W samples. **a** a samples series. **b** b samples series. Measurements for Co foil and bulk Co_3W in both cases, and bare Co nanoparticles with $t_{\text{Co}} = 0.7 \text{ nm}$ in (a) are shown for comparison. Inset: zoom of the first coordination shell in the particulate systems



of surface distortions on the nanoparticles, producing an underestimation of the average coordination number.

A reduction in the EXAFS signal as a result of lower Co coordination due to alloying is also observed when the signal for the Co foil is compared with the one for bulk Co_3W in Fig. 3.7a, b. This behaviour supports the scheme of Co–W alloy presence in the Co–W nanoparticles. There is a further reduction in the amplitude of all peaks and lack of structure beyond the first two coordination shells in the Co–W nanoparticles systems, which is characteristic of amorphicity, thus supporting the observation of amorphous structure in the HRTEM measurements. In general, amorphous compounds are characterized by damping of their EXAFS signal compared to a reference foil, consistent with static disorder and reduction of average coordination number [38].

In the HRTEM section we have mentioned that capping the Co nanoparticles with noble metals does not affect the structure of the NPs [24]. This has also been observed with EXAFS, so that bare and Au-capped Co nanoparticles have equivalent *fcc* crystal structure when comparing their Fourier transformed EXAFS signal.⁷ However, capping the Co NPs with W completely modifies the structure of the original particles by forming an amorphous alloy.

Different models were tested in order to fit the Co *K* edge *R*-space data for the W-capped Co nanoparticles. Some of the fitting tests were performed by using a model of pure Co - *fcc* metal, such as the one typically used in the bare Co nanoparticles case, and by using a W - doped metal Co model. However, the best fitting model was obtained by using the Co-scattering paths of the most stable Co–W alloy,⁸ i.e., Co_3W , and determining the deviation in the average coordination (*N*) and interatomic distance (*R*) for each Co–W NPs sample.

Given the high affinity of Co and W to form Co–W alloys [15–18] we have assumed that all Co in the Co–W NPs samples is uniformly alloyed with W. Then, we have estimated the change of the Co environment when increasing the amount of W or Co in the sample, and the different trends the structural parameters follow when varying them.

Due to the amorphous nature of the Co–W NPs, it is very difficult to fit the EXAFS signal beyond the first coordination shell. Moreover, as it was mentioned above, strong structural disorder in the NPs systems can lead to erroneous interpretation of the EXAFS analysis [37, 38]. Then, fitting of the Co–W NPs EXAFS signal was performed on the *R*-space in a range from 1.0 to 3.0 Å using a hanning window function, so that it covered the Co first coordination shell in the alloy

⁷ EXAFS spectra for the Au-capped Co NPs were recorded during the same experiment and compared to those for the uncapped Co–NPs, both with the same $t_{\text{Co}} = 0.7\text{ nm}$. We found that both systems have *fcc* structure and very close first near neighbor distances. Their Fourier Transformed EXAFS profiles are almost identical, even for outer coordination shells. The first coordination shell peak in the Co–Au NPs is higher in amplitude than the uncapped ones and it increases with the content of Au in the sample due to the high crystallinity in these noble-metal capped particles. Then, contrary to the case of W deposit, noble metals-capping do not modify the crystal structure of the Co NPs.

⁸ <http://www.sgte.org/>.

Fig. 3.8 FT EXAFS signal at the Co K edge for the bulk Co_3W alloy and comparison with that of a Co–W alloy NPs sample. *Dashed lines* best fit of the first Co coordination shell for each sample. Inset: an illustration of the structure of a Co first coordination shell

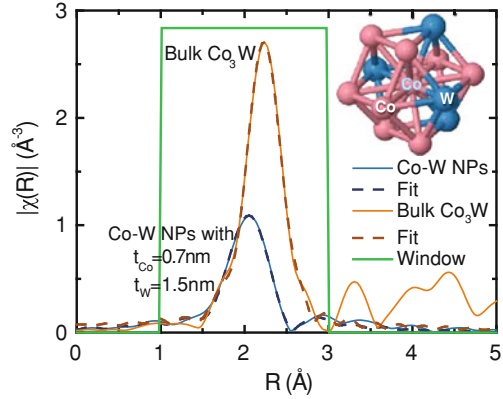
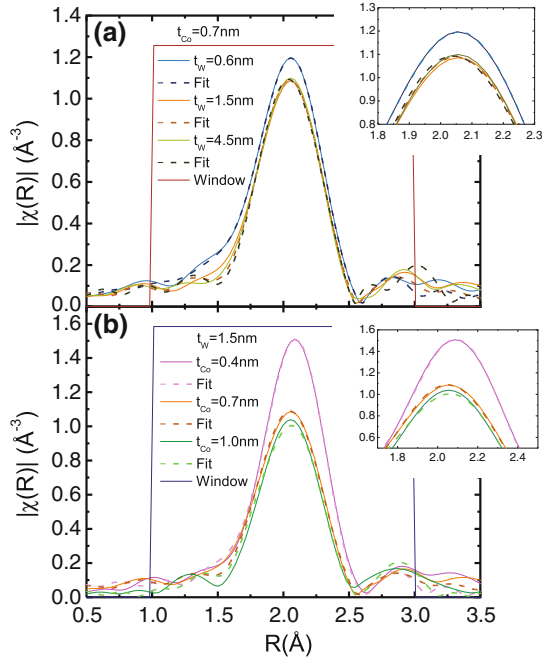


Fig. 3.9 Best fits to the first coordination shell on the Co K edge R -space EXAFS signal for all five Co–W nanoparticles samples studied. **a** a samples series. **b** b samples series. Inset: zoom of the fitted peak



(see Figs. 3.8, 3.9). For comparison, the EXAFS signal of the bulk Co_3W alloy has been fitted in the same R range. An illustration of this Co first coordination shell in the crystal structure of the Co_3W alloy is shown in the inset of Fig. 3.8. In this structure, the central Co is surrounded by a total of twelve atoms ($N_T = 12$, typical in *hcp* structures), from which eight are other Co atoms ($N_{\text{Co-Co}} = 8$) and the remaining four are W atoms ($N_{\text{Co-W}} = 4$). The amplitude reduction factor S_0^2 and the shift in the threshold energy ΔE_0 were set to those obtained for the Co foil fit. A total of 10

fitting parameters were used for an iterative procedure, which consistently included the fitting of both Co K and W L_3 edges (see following section). Results for the Co–W NPs and the bulk Co_3W fits are shown in Fig. 3.9 and the values obtained in each case are listed in Table 3.2. A comparison of the bulk Co_3W and one of the Co–W NPs fits is plotted in Fig. 3.8.

A high accordance between the original EXAFS data and their fits is observed for all samples. Fitting results show that the interatomic distance, R , and the disorder level quantified by the Debye-Waller factor, σ^2 , in the Co–W NPs are strongly affected by the presence of W in the structure, showing the distortion of the Co–Co and Co–W bonds in the amorphous Co–W alloy. These values found for σ^2 are typical of disordered Co environments, e.g., in Co-rich amorphous alloys [39]. It is also observed that the highest σ^2 is obtained in the Co–W bonds, confirming the high amorphicity created by W in the Co nanoparticles.

The average total coordination of the central Co atom, N_T , which includes both Co–Co and Co–W coordination, is reduced from $N = 12$ in the Co_3W alloy to values as low as $N = 9.4$, which corresponds to a decrease of about 22 %. This reduction is observed as the amount of W in the sample increases in the a series and the amount of Co decreases in the b series. However, N_T in most samples still resembles that of the crystal. This is an indication of short range ordering (SRO) in our samples, of chemical or structural origin, or both. Such SRO has been detected in similar $T_{1-x} - M_x$ alloys (T a transition metal and M a metal that favors amorphicity) via EXAFS and Electron Diffraction [29, 40]. In these alloys, it was found that SRO increases with increasing T content. Indeed, we identify a similar trend of N_T approaching the $N = 12$ value in our Co–W NPs as the amount of Co increases in the sample, suggesting a higher SRO in the sample with $t_{\text{Co}} = 1.0\text{ nm}$.

Variation of the coordination of Co atoms in the Co–W NPs samples with t_{Co} and t_{W} is plotted in Fig. 3.10. When analyzing only the coordination between the central Co and their first Co neighbors, $N_{\text{Co-Co}}$ (left y-axis in Fig. 3.10a, b), a clear decrease from $N_{\text{Co-Co}} = 8$ in Co_3W to values as low as $N_{\text{Co-Co}} = 4.6$ for the smallest particles, is observed. This is a reduction of about 42 % in the Co–Co coordination. In general, it is found that the $N_{\text{Co-Co}}$ decreases as the amount of Co in the sample decreases in the b samples series, and the as the W content increases in the a samples series. Similarly, the average coordination of W atoms surrounding the central Co, $N_{\text{Co-W}}$, increases as the amount of W in the sample increases, and as the amount of Co decreases, following an almost linear dependence with t_{Co} and t_{W} (see right y-axis in Fig. 3.10a, b).

A slightly higher coordination has been observed for the sample with the lowest amount of Co ($t_{\text{Co}} = 0.4\text{ nm}$ and $t_{\text{W}} = 1.5\text{ nm}$), which seems to deviate from the trend given the small size of the particles in this sample. This behavior is probably due to the high x_{para} present in this case ($x_{\text{para}} = 0.5$) so that the system is less particulate than the others, forming an almost uniformly distributed Co–W amorphous alloy on each layer.

Table 3.2 Structural parameters obtained from the fits for the Co-W nanoparticles shown in Fig. 3.9 and comparison with the values obtained for the bulk Co₃W alloy

Co ₃ W Alloy		<i>a</i> samples series (<i>t</i> _{Co} = 0.7 nm)									
		<i>t</i> _W = 0.6 nm					<i>t</i> _W = 1.5 nm				
		<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	<i>N</i>	<i>R</i> (Å)	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	<i>N</i>	<i>R</i> (Å)
Bond											
Co-Co	2.0	2.02(2)	0.023(7)	0.004(2)	2.0(2)	2.33(2)	2.0(8)	2.37(4)	0.0040(4)	2.0(8)	2.36(1)
Co-Co	4.0	2.52(2)	0.003(1)	0.002(2)	1.8(3)	2.46(2)	1.8(5)	2.51(5)	0.0044(7)	1.8(1)	2.52(1)
Co-W	2.0	1.90(5)	0.025(8)	0.024(6)	1.7(2)	2.19(2)	1.5(6)	2.14(9)	0.07(1)	2.7(5)	2.22(1)
Co-W	2.0	2.57(5)	0.003(1)	0.009(2)	2.5(2)	2.61(2)	3.0(8)	2.63(9)	0.015(2)	3.0(3)	2.45(1)
Co-Co	2.0	3.19(2)	0.02(1)	0.018(4)	3.6(2)	2.61(2)	1.1(7)	2.71(8)	0.012(3)	0.8(5)	3.36(1)
<i>N</i> _T	12				11.5(3)		9.4(8)			10.3(8)	
<i>N</i> _{Co-Co}	8				7.4(3)		4.9(8)			4.6(8)	
<i>N</i> _{Co-W}	4				4.1(3)		4.5(8)			5.7(8)	
Co ₃ W Alloy		<i>b</i> samples series (<i>t</i> _W = 1.5 nm)									
		<i>t</i> _{Co} = 0.4 nm					<i>t</i> _{Co} = 0.7 nm				
		<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	<i>N</i>	<i>R</i> (Å)	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	<i>N</i>	<i>R</i> (Å)
Bond											
Co-Co	2.0	2.02(2)	0.023(7)	0.0046(8)	1.8(3)	2.27(2)	2.0(8)	2.37(4)	0.0040(4)	2.0(4)	2.32(1)
Co-Co	4.0	2.52(2)	0.003(1)	0.0033(6)	1.8(1)	2.41(2)	1.8(5)	2.51(5)	0.0044(7)	4.0(6)	2.48(1)
Co-W	2.0	1.90(5)	0.025(8)	0.014(2)	3.5(6)	2.21(3)	1.5(6)	2.14(9)	0.07(1)	2.0(4)	2.21(2)
Co-W	2.0	2.57(5)	0.003(1)	0.021(4)	3.0(8)	3.02(8)	3.0(8)	2.63(9)	0.015(2)	2.0(6)	2.40(2)
Co-Co	2.0	3.19(2)	0.02(1)	0.011(3)	1.0(8)	3.23(7)	1.1(7)	2.71(8)	0.012(3)	2.0(6)	2.82(2)
<i>N</i> _T	12				11.1(8)		9.4(8)			12.0(6)	
<i>N</i> _{Co-Co}	8				4.6(8)		4.9(8)			8.0(6)	
<i>N</i> _{Co-W}	4				6.5(8)		4.5(8)			4.0(6)	

Coordination numbers, *N*, interatomic distance, *R*, and Debye-Waller factor, σ^2 for each path used in the fitting model

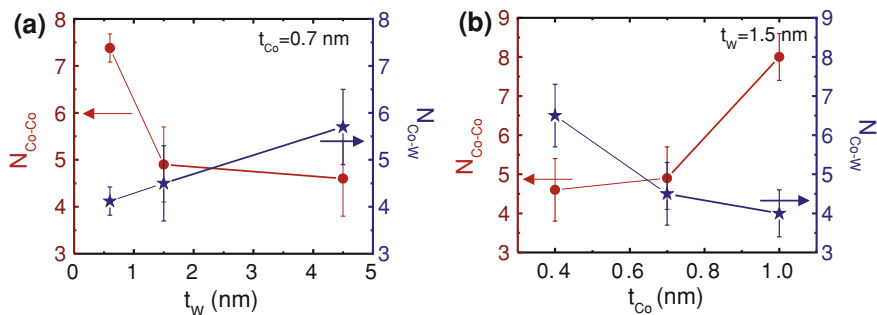


Fig. 3.10 Variation of $N_{\text{Co-Co}}$ and $N_{\text{Co-W}}$ obtained from EXAFS fits. **a** *a* samples series. **b** *b* samples series

3.2.2.2 W L_3 Edge Results

Normalized XANES spectra at the W L_3 edge for Co–W NPs are shown in Fig. 3.11a, b, for *a* and *b* sample series, respectively. XANES of W foil at the same edge is plotted in both cases for comparison. In the case of W, being a 5d metal, L_3 absorption edge appears for transitions from 2p to both $5d_{3/2}$ and $5d_{5/2}$ bands. Then, an increase in W L_3 edge intensity from one sample to the other show an increase in the number of W 5d available empty states. In the *a* series samples (Fig. 3.11a), intensity decreases as t_{W} increases. For the *b* series (Fig. 3.11b), the white-line is systematically enhanced as the amount of Co increases from zero, in the case of W foil, to $t_{\text{Co}} = 1.0$ nm. In both cases, an increase in the Co/W ratio gives rise to an increase in the number of W 5d empty states. We may conclude that as this Co/W ratio increases there is an electron transfer from W towards Co.

Fourier transform of the EXAFS data taken at the W L_3 edge for the Co–NPs is shown in Fig. 3.12. Fourier transformation was performed on the $\chi(k)$ EXAFS signal on a k-range from 2.3 to 9.8 Å⁻¹ using a k^2 weight and a sine window function. Fig. 3.12a shows results for samples from the *a* series and Fig. 3.12b for the *b* series, as well as for a W foil used as a reference and for Co₃W alloy for comparison. In both cases it is evident that the W neighborhood has changed in the Co–W nanoparticles compared to that of metallic W by the presence of Co–W alloying. The first peak in the Co–W samples is very close to that of Co–W in the Co₃W alloy. For the sample with $t_{\text{W}} = 0.6$ nm and $t_{\text{Co}} = 0.7$ nm this peak amplitude is higher showing a higher amount of Co neighbors in the W environment.

EXAFS spectra at the W L_3 edge were fitted following a similar procedure to the one for Co K edge, which included an iterative fitting process of both edges. Fitting was performed on the R -space in a range that covered the W first coordination shell (1.5–3.0 Å), using a hanning window function (see Fig. 3.13). S_0^2 , and ΔE_0 were set to those values obtained for the W foil signal fit. Different models for fitting were

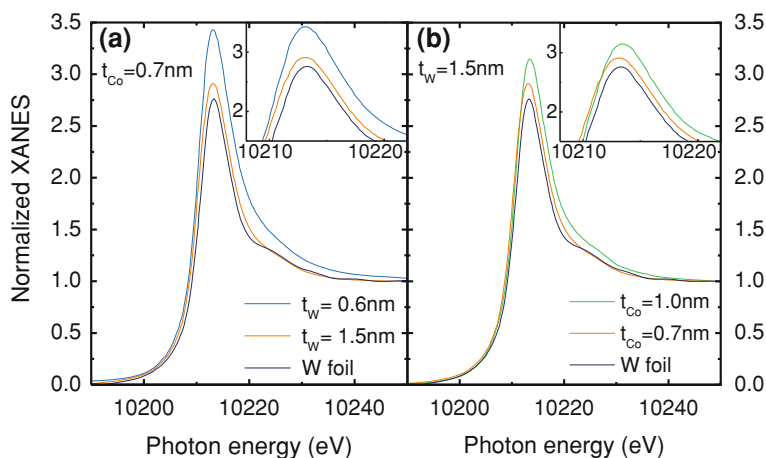
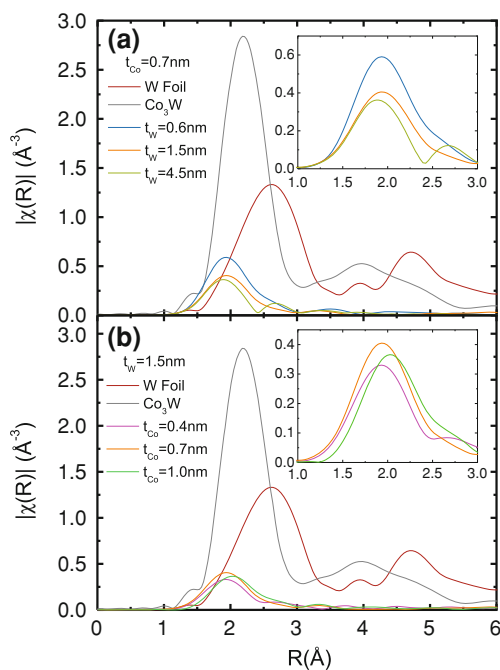


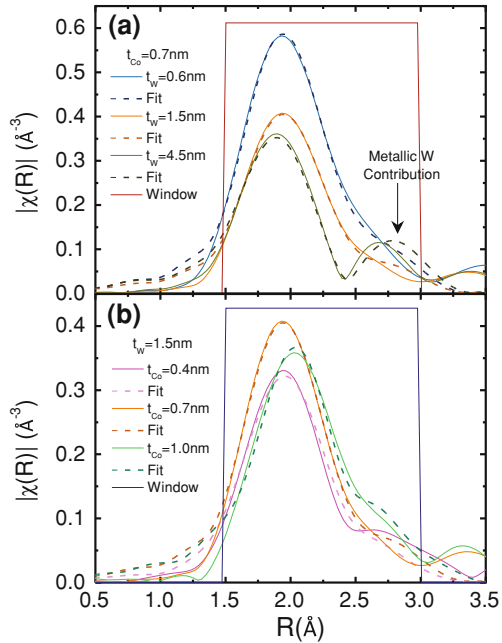
Fig. 3.11 XANES spectra at the W L_3 edge for samples from the **a** samples series and **b** samples series. In both cases, the absorption of the W foil is shown for reference. Insets show details of the white line intensity

Fig. 3.12 Fourier transform of EXAFS signal at the W L_3 edge on the Co–W NPs studied. **a** *a* samples series. **b** *b* samples series. Measurements for W foil and Co_3W are shown for comparison in both graphs. Insets: zoom of the first coordination shell in the particulate systems



tested: a pure metallic W model, a pure Co–W alloy (Co_3W) and a linear combination of these two phases. The latter was the procedure leading to the best fitting results, shown in Fig. 3.13.

Fig. 3.13 Best fits to the first coordination shell on R -space EXAFS signal measured at the W L_3 edge for the Co–W nanoparticles samples. **a** a samples series. **b** b samples series



W environment was found to be consistent with the results of Co–W alloy obtained for the Co K edge, showing evidence of an additional W metal phase in all samples. However, a quantitative determination of this W metal fraction was prevented given the intrinsic difficulties of fitting EXAFS signals for amorphous systems, as mentioned above [37, 38]. In spite of it, W L_3 EXAFS results show interesting trends as shown in Fig. 3.13a, where it is noticeable that the shoulder corresponding to the metallic W contribution increases as the amount of W increases in the sample (a series). A similar trend was also observed in their fitting results and is well in agreement to what was observed by HRTEM. The fraction of W metal was found to be around an almost constant value when fitting the samples from the b series (Fig. 3.13b).

3.3 Magnetic Study

3.3.1 SQUID-Based Magnetometry

The magnetic study of both a and b samples series was performed by $\chi_{dc}(T)$, $\chi_{ac}(T)$ and $M(H)$ measurements in a commercial SQUID magnetometer at the Servicio de Medidas Físicas of the Universidad de Zaragoza. $\chi_{dc}(T)$ was measured after zero-field cooling (ZFC) and field cooling (FC) the sample. Temperature was varied

between 5 and 150 K, and a 200 Oe field was applied. $M(H)$ measurements were performed at $T \approx 3T_B$ (T_B , blocking temperature of the superparamagnetic particles) under applied fields up to 50 kOe. $\chi_{ac}(T)$ was measured by applying an ac field of 4 Oe in amplitude to the sample with frequency $\omega/2\pi$ in between 1 and 480 Hz.

SQUID based magnetic measurements reveal the superparamagnetic behavior of the amorphous Co–W NPs. ZFC and FC curves for both sample series (Fig. 3.14) are similar to those for bare and Cu, Ag and Au–capped Co nanoparticles [24, 26, 41]. At lower temperatures, FC and ZFC for each sample separate and the ZFC curve shows a maximum at a blocking temperature, T_B . The values of T_B for the Co–W NPs are given in Table 3.3. T_B values in all samples are lower than those found for the bare Co–NPs [26]. T_B is also reduced for the *a* series as the amount of W in the sample increases for a constant t_{Co} (Fig. 3.14a) and for samples from the *b* series when the amount of Co decreases at a fixed t_W (Fig. 3.14b). At high temperatures, all curves follow the Curie–Weiss law $\chi_{eq} = C/(T - \theta)$. The values of the Curie–Weiss temperature θ obtained from the curves are shown in Table 3.3.

Although θ values are not negligible, some trends are identified in order to describe the magnetic interactions between Co–W NPs. For the *a* series samples, θ remains approximately constant as the amount of W increases, suggesting that interparticle interactions are quite similar in the series and decrease on a small scale when adding W. This is understandable since particles are similarly and uniformly distributed on the layers of these three samples, as demonstrated by HRTEM (see analysis of N_5

Fig. 3.14 DC susceptibility curves for samples from the *a* series in (a) and from the *b* series in (b)

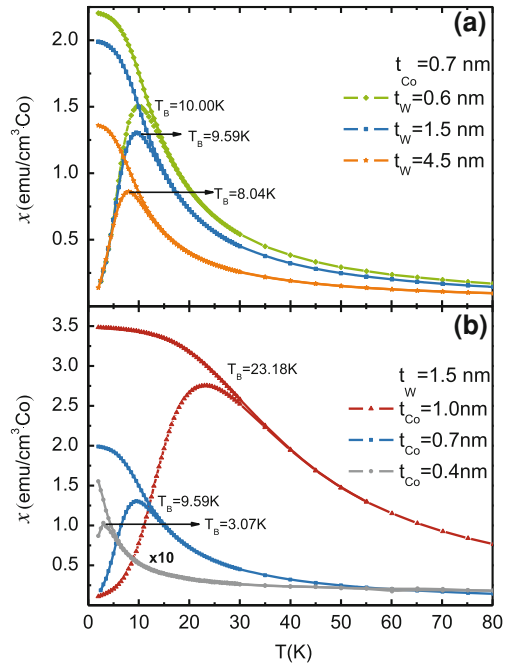


Table 3.3 Summary of the parameters deduced from the magnetic measurements on Co-W Nanoparticles

Samples series	t_{Co} (nm)	t_W (nm)	T_B (K)	θ (K)	m_{tot} (μ_B/Co)	m_{part} ($10^3 \mu_B$)	x in Co-W alloy (%)	M_{sb} (10^{-3} emu/cm ³)	$\langle D_{mag} \rangle$ (nm)	σ_{mag} (nm)	$\langle U \rangle$ (K)	K_{eff} (10^6 erg/cm ³)
<i>a</i>	0.7	0.6	10.00(6)	7.3(2)	0.52(2)	1.03(1)	18.2(4)	0.413(2)	3.4(2)	0.25(5)	270(10)	1.4(3)
	0.7	1.5	9.59(6)	8.0(3)	0.46(1)	0.84(1)	18.8(4)	0.367(2)	3.2(2)	0.32(5)	220(4)	1.2(2)
	0.7	4.5	8.04(3)	5.9(2)	0.30(1)	0.57(1)	20.3(4)	0.235(2)	3.4(6)	0.38(5)	200(10)	1.0(5)
<i>b</i>	0.4	1.5	3.07(6)	1.7(9)	0.088(2)	–	22.3(4)	0.062(2)	2.6(5)	0.25(5)	–	–
	0.7	1.5	9.59(6)	8.0(3)	0.46(1)	0.84(1)	18.8(4)	0.367(2)	3.2(2)	0.32(5)	220(4)	1.2(2)
	1.0	1.5	23.18(7)	13.3(9)	0.93(3)	–	14.1(4)	0.725(2)	4.4(2)	0.38(5)	890(30)	2.4(3)

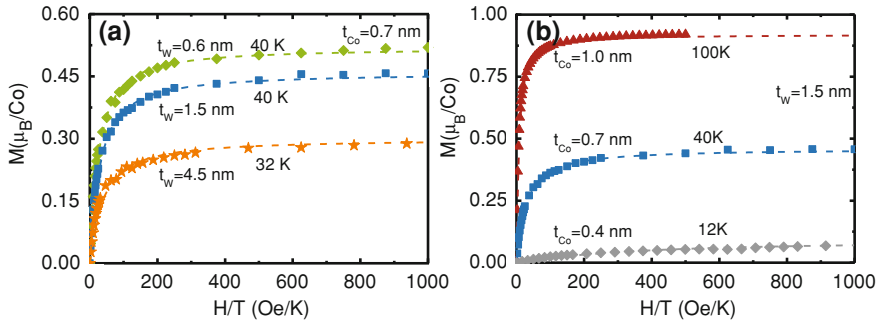


Fig. 3.15 Magnetization curves for samples from the *a* series in (a) and from the *b* series in (b). The dashed lines are fitted Langevin curves with $\langle D_{mag} \rangle$ and σ parameters given in Table 3.3

in Sect. 3.2.1). Instead, for the *b* series, θ values have a drastic change, increasing in one order of magnitude from sample with $t_{Co} = 0.4$ nm to the one with $t_{Co} = 1.0$ nm. Thus, the magnetic interactions in the Co–W NPs increase as the amount of Co increases because particles are bigger and closer. These results of the magnetic interactions in the Co–W NPs are well supported by analysis of the variation of the FC/ZFC—curves height ratios [42], which show the same trend. This is, FC/ZFC—curves height ratios for the *a* series are almost equal and they decrease as t_{Co} increases for the *b* series samples.

Magnetization as a function of field in the paramagnetic region ($M(H)$ at $T \approx 3T_B$) for both sample series are plotted in Fig. 3.15. These $M(H)$ curves were identical when measured with the field parallel and perpendicular to the sample plate, therefore the particle anisotropy axes are randomly distributed in all samples and the demagnetization factor plays no role in the present case.

Values of the magnetization per Co atom deposited in the samples, m_{tot} , obtained from saturation are listed in Table 3.3 and plotted in Fig. 3.16. It was found that m_{tot} decreases for samples from *a* series as the W capping layer thickness increases for a constant t_{Co} (Figs. 3.15a, 3.16a) and in samples from the *b* series as the amount of Co decreases for a fixed t_W (Figs. 3.15b, 3.16b). The magnetization is supported by the Co atoms since W has a negligible induced moment.⁹ Then, there is a strong reduction on the magnetic moment of the Co atoms due to the formation of Co–W amorphous alloy. This reduction may be due to combined effect of charge transfer, hybridization and environmental effects, as it is described in Ref. [16]. According to this author, when the number of Co first neighbors is higher than 3, Co atoms carry their full magnetic moment of $1.7 \mu_B/\text{Co}$ [16]. This is the case of previously studied bare Co nanoparticles [41]. However, if the Co atom has less Co atoms as first neighbors, e.g. 2 or 3 Co atoms, its magnetic moment decreases to about $0.5 \mu_B/\text{Co}$. The latter value is well in agreement with the moments found for Co atoms in the samples studied in this work. The strong reduction of the Co moment in our samples

⁹ See details of the induced magnetic moments in the W atoms of these samples in Chap. 4.

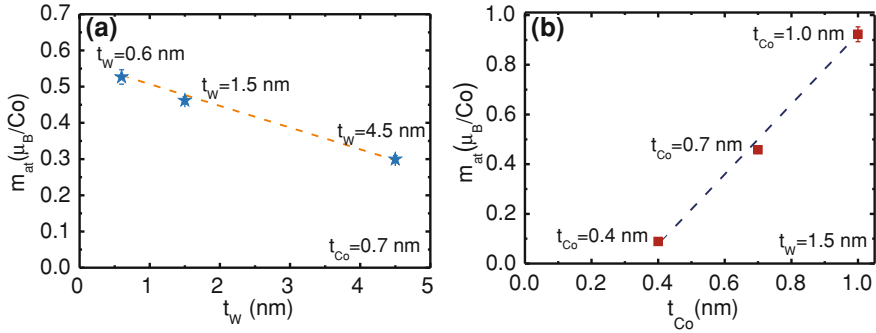


Fig. 3.16 Total Co magnetic moment per Co atom in the Co–W NPs as deduced from the $M(H)$ measurements. *dashed lines* Guide to the eye. **a** a samples series. **b** b samples series

is due to a decrease in the Co coordination of the Co atoms because of the presence of W, demonstrated via EXAFS analysis in the previous section. Such decrease in $T_{1-x} - M_x$ alloys (T being a transition metal and M usually a non-magnetic metal) has been reported in previous works [43] and will be further discussed in Sect. 3.4.

For those samples where the number of particles per unit surface, N_S , was identified from the STEM images in the morphology characterization, we can easily determine the magnetic moment per particle, m_{part} . This is obtained by dividing the saturation magnetization by N_S , both, per unit surface. m_{part} values are listed in Table 3.3. The average amount of Co atoms per particle is also easily determined by the ratio of deposited Co and number of particles, per unit surface. The resulting moment per Co atom (Table 3.3) decreases with increasing the amount of W in the a series samples from 0.52 to 0.30 μ_B/Co , for $t_W = 0.6$ and 4.5 nm, respectively. Also, it strongly decreases with reduction of the amount of Co in the b series samples from 0.93 to 0.08 μ_B/Co for $t_{Co} = 1.0$ and 0.4 nm, respectively. Thus, the reduction in Co moment expected for Co–W alloying [15, 16] is properly verified.

An average $\text{Co}_{1-x}\text{W}_x$ alloy composition in the Co–W NPs may be proposed by comparing the m_{tot} values to those measured for Co–W films deposited by RF sputtering in Ref. [19]. Values of %W in the alloy are shown in Table 3.3. The W concentration that explains the reduction in magnetic moment ranges from 18.2 to 20.3 at % in the a samples series, and from 14.1 to 22.3 at % in the b samples series.

From the equilibrium magnetic properties of each sample we can determine the particle size distribution and compare it with the results obtained by HRTEM and STEM. This is obtained by fitting the $M(H)$ curves at high T to a Langevin function, averaged over the appropriate particle size distribution. We define $g(D_{mag})$ as the gaussian distribution of a number of particles having a diameter equal to D_{mag} . For spherical particles, the particle magnetization is written as $m_{part} = \pi M_{sb} D_{mag}^3 / 6$, where M_{sb} is defined as the particle magnetic density, calculated from the saturation magnetization values and the density of the Co–W alloy formed on each sample as

$$M_{sb}(x) = \frac{m_{tot}(\mu_B/Co)\rho(x)}{M_w(x)} N_a \mu_B \quad (3.1)$$

where x gives the $Co_{1-x}W_x$ alloy composition, $\rho(x)$ is the density and $M_w(x)$ the molecular weight of the alloy, N_a is the Avogadro number and μ_B the Bohr magneton. Since there are no direct values in the literature for the densities of the Co–W alloys found for our samples, we need to calculate them. Knowing that the density for metallic Co is 8.9 g/cm^3 and the one for Co_3W alloy is 12.7 g/cm^3 [44], we can apply linear approximation for $\rho(x)$ versus x . Given the x values found for our Co–W samples (listed in Table 3.3) we can interpolate each composition value and get its respective density.

The experimental data are fitted by the expression:

$$M(H, T) = x_{para} m_{para} + (1 - x_{para}) M_{sb} \frac{\int g(D_{mag}) V [M(H, T, \mu)/m_{tot}] dD}{\int g(D_{mag}) V dD_{mag}} \quad (3.2)$$

Let us recall that x_{para} gives the fraction of non-aggregated Co atoms present in the samples. In the case of bare and noble-metal capped Co NPs they give a paramagnetic contribution as a positive slope of $M(H)$ at high fields [26, 41]. In our Co–W alloy NPs, the non-aggregated Co atoms are also alloyed with W. They do not contribute to the magnetic signal, i.e., at high fields the slope of $M(H)$ is negligible. Then m_{para} in Eq. 3.2 is null and Eq. 3.2 is reduced to the second term.

Results for these fits are the dashed lines in Fig. 3.15. The average magnetic diameter values $\langle D_{mag} \rangle$ and the distribution width for the Gaussian distribution of particle size, σ_{mag} obtained are listed in Table 3.3. These parameters were confirmed by fitting the equilibrium susceptibility $1/\chi_{eq}(T)$ in the superparamagnetic temperature regime, measured for the same samples. This is, for a system of particles of that diameter and size distribution, χ_{eq} can be expressed as

$$\chi_{eq} = \frac{\int g(D_{mag}) V (M_{sb}^2 V / 3k_B T) dD_{mag}}{\int g(D_{mag}) V dD_{mag}} \quad (3.3)$$

Comparing the values of $\langle D_{eff} \rangle$ obtained from the morphological analysis described in Sect. 3.2.1 with the $\langle D_{mag} \rangle$ derived from this magnetic analysis, we note that the latter is smaller. From the above facts we may conclude that our amorphous Co–W NPs are composed by a magnetic Co–W alloy core surrounded by unalloyed metallic W, which tends to fill the interparticle space, as described in Sects. 3.2.1 and 3.2.2.

3.3.2 Magnetic Anisotropy of the Co–W Particles

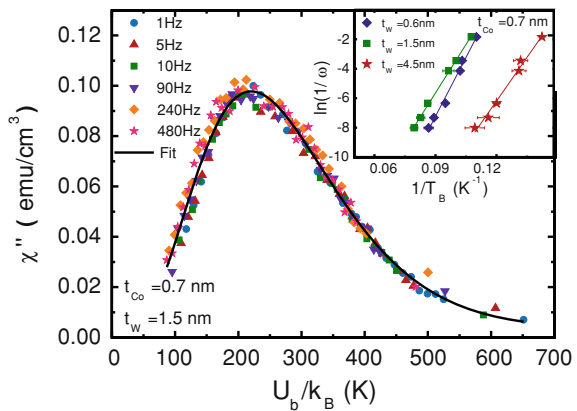
The phenomenon of superparamagnetic blocking described in the FC-ZFC curves analysis is related to the magnetic anisotropy of the particles. The anisotropy favors some particular orientations of the magnetic moment, two opposite to each other in the simplest case of uniaxial anisotropy, which are separated by activation energy barriers U . The rate at which the magnetic moment of the particles flips from one orientation to the other is determined by this anisotropy K_{eff} , so that we write $U = K_{\text{eff}}V$, with V being the particle magnetic volume. The relaxation time, τ , follows an Arrhenius' law ($\tau = \tau_0 \exp(U/k_B T)$), where $\tau_0 \approx 10^{-10}$ – 10^{-13} s is the inverse attempt frequency that depends on the damping of the magnetic moments by the phonons. The superparamagnetic blocking occurs when $\tau = t_e$, where t_e is the measuring time of each experimental point, so $T_B \cong \alpha U/k_B \ln(t_e/\tau_0)$ where α is a constant that depends on the width of the particle size distribution.

An accurate way to obtain U is derived from the full distribution of activation energies $f(U)$ and then to find which value of U corresponds to particles with a diameter equals to D_{mag} . A detailed description of this procedure can be found in Ref. [26]. $f(U)$ can be directly determined from the analysis of the imaginary part of $\chi_{\text{ac}}(T)$, measured near the superparamagnetic blocking temperature T_B . For non-interacting particles we write

$$\chi'' \simeq \frac{\pi}{2} k_B T \chi_{\text{eq}}(T, U) f(U_b) \quad (3.4)$$

where we define $U_b = k_B T \ln(1/\omega \tau_0)$, as a scaling variable, corresponding to the activation energy of those particles having $\tau = t_e = 1/\omega$ at a given T . The frequency dependent χ_{ac} should converge into a single curve when plotting χ'' vs. U_b/k_B . $f(U)$ can be determined from Eq. 3.4 from a $\chi''(U_b)$ fit. In Fig. 3.17 we have plotted the result obtained from this $\chi_{\text{ac}}(T)$ analysis, including the $\chi''(U_b)$ fit, for the sample with $t_{\text{Co}} = 0.7$ nm and $t_{\text{W}} = 1.5$ nm. We also show the Arrhenius plot of $\ln(1/\omega)$ vs.

Fig. 3.17 Imaginary part of the ac susceptibility for the sample with $t_{\text{Co}} = 0.7$ nm and $t_{\text{W}} = 1.5$ nm plotted as a function of the scaling variable U_b . The solid line is the fitting result. Inset: Arrhenius plot of the measuring time ($1/\omega$) as function of T_B , as obtained from χ'' measurements for the *a* series samples



$1/T_B$, from the analysis obtained from χ'' measurements for the *a* series samples. In the case of the sample with the lowest amount of Co ($t_{\text{Co}} = 0.4$ nm and $t_W = 1.5$ nm) this analysis was not performed since the χ_{ac} signal was negligible.

K_{eff} is then obtained from $U(\langle D_{\text{mag}} \rangle) = K_{\text{eff}}(\pi/6)\langle D_{\text{mag}} \rangle^3$, where $\langle D_{\text{mag}} \rangle$ denotes the average magnetic diameter of the spherical particles. All this analysis is performed assuming that the magnetic moment is just supported by the Co–W magnetic alloy core. The values of the average $\langle U \rangle$ and K_{eff} obtained for all samples are shown in Table 3.3.

K_{eff} in our Co–W NPs decreases with increasing t_W for the *a* series samples and with decreasing t_{Co} for the *b* series samples. This gives K_{eff} a trend directly proportional to $\langle D_{\text{mag}} \rangle$, suggesting that surface anisotropy is not playing an important role in the K_{eff} as in other particulate systems [8–11, 24, 41]. Further discussion on these results will be presented in Sect. 3.4.

3.3.3 X-ray Magnetic Circular Dichroism Magnetometry

The XAS and XMCD experiments at the Co L_3 (778.1 eV) and Co L_2 (793.2 eV) edges were performed at the ID08 beamline of the ESRF. An APPLE-II undulator and a spherical grating monochromator were used. The degree of polarization was $\sim 100\%$. The total electron yield (TEY) detection method was employed. The beam direction and parallel magnetic field applied had an incident angle of $10\text{--}15^\circ$ with respect to the normal to the plate sample. The XMCD signal was obtained by a direct difference of the XAS spectra recorded with opposite helicities at each magnetic field value and for both orientations of the field. The applied field was 20 kOe and the temperature was $T = 7$ K in all cases.

XMCD is a very powerful technique that allows to perform an element selective magnetometry on our Co–W NPs. From a XMCD experiment at the $L_{2,3}$ edges of Co one obtains, through the sum rules [45, 46] described in Sect. 2.4.2, the spin and orbital moments averaged over the volume of the particle, and on the number of holes n_h in the empty exchange split nd sub-bands (Co $3d$ in the present case). The sum rules have been applied to the spectra to derive the orbital, spin and total magnetic moments per $3d$ hole of Co, m_L/n_h , m_S/n_h and m_{at}/n_h , respectively, with the symbols and sign criteria defined in Ref. [47]. We define the constant $C = (I_{L2} + I_{L3})$, where I_{L2} and I_{L3} are the white-line integrated intensities after subtraction of the contributions from transitions to the continuum. It is noteworthy that in the present case of amorphous particles, with their individual anisotropy axes oriented at random, the dipolar term m_D in $m_{\text{Seff}} = m_S + m_D$ cancels out, so that the sum rule $(A - 2B) = -Cm_S/(n_h\mu_B)$ yields the spin component m_S/n_h . A and B are the integrated areas of the L_3 and L_2 XMCD peaks, respectively. Besides, from the ratio of the sum rules m_L/m_S is directly derived, which is independent of n_h and of the normalization method used.

XMCD also allows us to study the changes in the orbital magnetic moment in the Co–W NPs samples as a function of t_W and t_{Co} by obtaining the average m_L/n_h per Co atom present in the sample. In the experiments a magnetic field of 20 kOe is

Fig. 3.18 Co- $L_{2,3}$ edges spectra of the $t_{\text{Co}} = 0.7$ nm, $t_{\text{W}} = 1.5$ nm sample measured at $T = 5$ K, $H = 20$ kOe and incident angle 10° . **a** (red) Normalized XAS spectra mean curve. (green) The double-step function used is also indicated. (dark blue) Integrated white line. **b** (light blue) Normalized XMCD spectra, (orange) integrated area

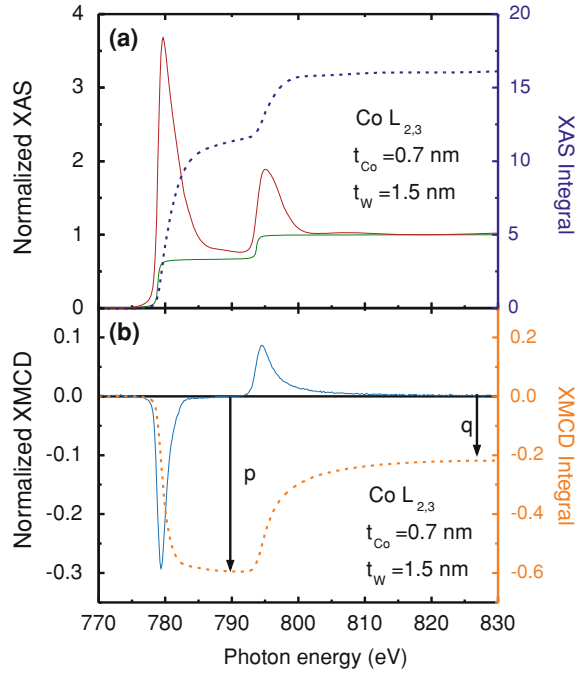


Table 3.4 m_{tot}/n_h , m_L/n_h , m_S/n_h and m_L/m_S per Co atom as determined from XMCD measurements

Samples series	t_{Co} (nm)	t_{W} (nm)	m_L/m_S (μ_B)	m_L/n_h	m_S/n_h (μ_B)	m_{tot}/n_h (μ_B)
<i>a</i>	0.7	0.6	0.082(1)	0.018(1)	0.216(3)	0.234(3)
	0.7	1.5	0.085(1)	0.015(1)	0.172(4)	0.186(4)
	0.7	4.5	0.079(2)	0.010(1)	0.120(5)	0.130(6)
<i>b</i>	0.4	1.5	0.159(7)	0.007(1)	0.042(4)	0.048(4)
	0.7	1.5	0.085(1)	0.015(1)	0.172(4)	0.186(4)
	1.0	1.5	0.071(1)	0.021(1)	0.290(9)	0.310(9)

For the *fcc* bulk Co, $m_L/m_S = 0.078$ [48], $m_L/n_h = 0.134$ and $m_S/n_h = 0.248 \mu_B$ per 3d hole [49] ($3d n_h^{\text{Co}} = 2.49$) [50]

applied, sufficient to saturate the particle spin magnetization. The contribution of the orbital moment to the XMCD signal is the averaged projection of the local orbital magnetic moments in the direction of the applied field (parallel to the photon beam direction in the experiments).

The experimental XMCD spectra at the Co $L_{2,3}$ edges for sample with $t_{\text{Co}} = 0.7$ nm and $t_{\text{W}} = 1.5$ nm is depicted in Fig. 3.18, together with its XAS, for normalization sake. All XMCD results are qualitatively similar, though the actual derived A and B values differ. The derived m_L/m_S , m_L/n_h and m_S/n_h values are given in Table 3.4, along with the values of the total moment m_{tot}/n_h .

Self-saturation effects may affect these TEY measurements in principle. It is customarily corrected in thin films [51], and has been done in the case of rather large Co and Fe nanoparticles [52, 53]. To correct for this effect the electron escape depth parameter λ_e at low kinetic energies of the particular material is needed. The Co–W alloys λ_e at low energies is not known, but at higher energies, of the order of 100 eV, it is very near to that for Co.¹⁰ Under this hypothesis, the correction due to saturation effects would be very similar to that needed for Co particles of the same size. It has been estimated that for Co particles with diameter $D = 3$ nm the m_S and m_L , parameters obtained with the sum rules from uncorrected XAS and XMCD spectra, may be underestimated by 2 and 13 %, respectively [52], which amounts to an underestimation of 3 % in m_{tot} . Such a difference is comparable to the other sources of error in these experiments, like the presence of x_{para} , or the size distribution of the particles. Therefore, to account for this effect, we have added this source of error to the total estimated errors in the Table 3.4 data, and should take conclusions from the trends rather than from the absolute values.

The variation of the m_L/m_S ratio as a function of the amount of Co and W in the samples can be analyzed from the values listed in Table 3.4. In *b* samples series, for $t_{\text{Co}} = 0.4$ nm the ratio is much larger than the value for bulk Co ($m_L/m_S^{\text{Co Bulk}} = 0.078$), and decreases towards that value as the $t_{\text{Co}}/t_{\text{W}}$ ratio increases, being quite close for $t_{\text{Co}} = 1.0$ nm ($m_L/m_S = 0.071$) (see Table 3.4 and Fig. 3.19b). The reason for this difference at low $t_{\text{Co}}/t_{\text{W}}$ can be found in the unusually low value of m_S/n_h ($0.042 \mu_B$ per $3d$ hole) for $t_{\text{Co}} = 0.4$ nm. Although the m_L/n_h decreases with W alloying, the reduction of m_S/n_h is much stronger (see Fig. 3.19b). Therefore, alloying with W affects essentially the difference between up and down filled states in the Co $3d$ band. In contrast, the m_L/m_S ratio as a function of the W capping thickness is practically constant (see variation of m_L/n_h and m_S/n_h in Fig. 3.19a), i.e., the compositional Co/W ratio in the alloys obtained in *a* samples series is similar (see also alloys composition in Table 3.3). It may be concluded that the crucial factor to reach the different alloys in the Co–W NPs depends more on the amount of Co available for alloying than on the amount of W in the sample.

We may estimate n_h for each Co–W composition by substituting in the m_{tot}/n_h values given in Table 3.4, those m_{tot} determined from $M(H)$ measurements in the previous section (see Table 3.3). Although W may be polarized by Co, its contribution to the net magnetization is orders of magnitude lower,¹¹ so it is considered as negligible in this analysis. Therefore, the magnetization of our samples is mainly due to the Co present in the Co–W particles, so we may assume that both SQUID and XMCD magnetometry techniques yield the average total Co moment at saturation (for the sake of comparison we have used values at $H = 20$ kOe). Thus, from the

¹⁰ Data obtained from the NIST *Electron Effective-Absorption-Length Database*, <http://www.nist.gov/srd/nist82.cfm>.

¹¹ XMCD measurements at the W $L_{2,3}$ edges on these W-capped Co nanoparticles samples have been performed to determine the induced magnetic moment of W. It was found to be on the order of $\sim 10^{-3} \mu_B/\text{W}$ at 10 K, which is two orders of magnitude lower than the Co moment measured in the samples. These results will be described in detail in Chap. 4.

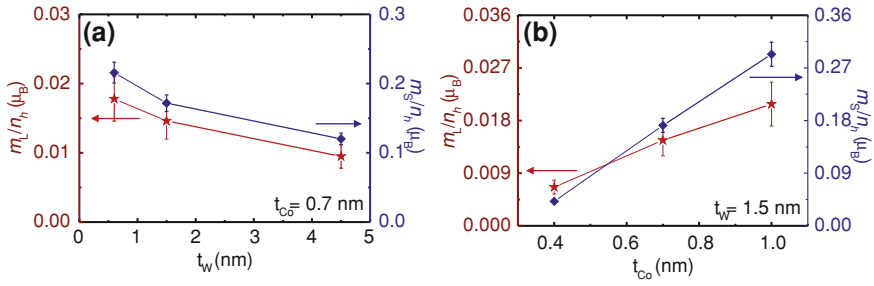


Fig. 3.19 Dependence of Co $m_{\text{L}}/n_{\text{h}}$ and $m_{\text{S}}/n_{\text{h}}$, on the Co and W composition. **a** *a* samples series, **b** *b* samples series

comparison of both values, we can extract the variation of the n_{h} in the Co 3d band in the Co–W NPs. For the *a* series samples, n_{h} was found to be around an almost constant value of $n_{\text{h}} = 2.4(1)$. Within experimental errors, this result is on the order or slightly lower than that for bulk Co ($n_{\text{h}} = 2.49$) [50], and is well in agreement with the insignificant variation observed in the pre-edge peak of Co *K* XAS spectra for the same samples, described in Sect. 3.2.2; i.e., the Co 3d–W 5d hybridization is hardly affected by small variations of the amount of W for a fixed Co, showing once again that the alloy composition the three samples along this series is similar. For the *b* series samples, n_{h} was found to vary within a 20 % of the average value found for the *a* series. The general trend was that of increase as the amount of Co in the sample increases for a fixed t_{W} value. This latter result is also in agreement to what was observed at the Co *K* edge XAS measurements in this samples series since it gives evidence of increasing localization of the 3d states in Co as the Co/W ratio in the sample increases.

3.4 Discussion

We have found that the magnetic moment per Co atom in our alloy decreases with increasing W content. Such dependence has been extensively reported both in crystalline and amorphous alloys following the formula $T_{1-x} - M_x$, with *T* usually being Fe, Co or Ni, and *M* an early transition metal that favors the amorphicity in the alloy [43]. A generalized Slater-Pauling model based on the existence of a gap, or minimum, in the conduction-band density of states has been used to describe this trend [43]. Such gap tends to conserve the number of conduction electrons in an alloy series leading to a linear variation of m_{tot} (the atom-averaged magnetic moment of the alloy) with Z_{M} (the atomic valence of the *M* metal, $Z_{\text{M}} = 6$ for W) [43]. The relation of m_{tot} as a function of *x* is then expressed as

$$m_{\text{tot}}(x) = m_{\text{metal}} - x(10 + Z_{\text{M}} - Z_{\text{T}})\mu_{\text{B}} \quad (3.5)$$

where Z_T and m_{metal} represent the atomic valence and magnetic moment in the pure T metal ($Z_T = 9$ and $m_{\text{metal}} = 1.7\mu_B$ for Co). Strong reduction of m_{tot} is expected when M is a nonmagnetic element. Comparison of this theoretical prediction with the values obtained for our Co–W NPs is shown in Fig. 3.20. Although there is a qualitative agreement in the trends, we find a significant deviation from the predicted slope, which can be attributed to the limitations of the model that takes insufficient account of the atomic structure, nearest-neighbor environments and chemical disorder [43].

In Co amorphous magnetic alloys, which have local anisotropy at the Co sites with randomly oriented local easy axes, the Co–Co exchange interaction is of sufficient intensity to guarantee collective ferromagnetic order if the Co content is above a critical value [43]. In Co–W alloys it is $\sim 76\%$ at. Co, so that those alloys with smaller values have no magnetic moment [19]. In general, for $3d$ -metal based alloys, the orientational correlation length of the local magnetic moments has been estimated to be of the order of a few μm [54]. Therefore, in Co–W nanoparticles, with a diameter of the order of a few nanometers, exchange stiffness can maintain local moment correlation within the whole particle, and thus, yield to a particle net average moment and anisotropy.

Amorphous magnetic alloys are expected to behave magnetically isotropic or to exhibit a low anisotropy (in the case of thin films where a stress-induced anisotropy can be present) given their lack of atomic long range order. In contrast, in our Co–W NPs K_{eff} is all but negligible. Its origin may be traced back to the structural or chemical SRO we have shown to exist in Sect. 3.2.2. Indeed, some amorphous alloys, typically following the formula $T_{1-x} - M_x$, still exhibit remarkable SRO [29, 40] Coordination numbers of about 12 found by structural characterization of these alloys may be visualized as *hcp* or *fcc* like [40]. Such amorphous materials are often simulated by small structural units, which are defined by a reference atom and its nearest neighbors. The structural model should contain sites having *hcp* and *fcc*

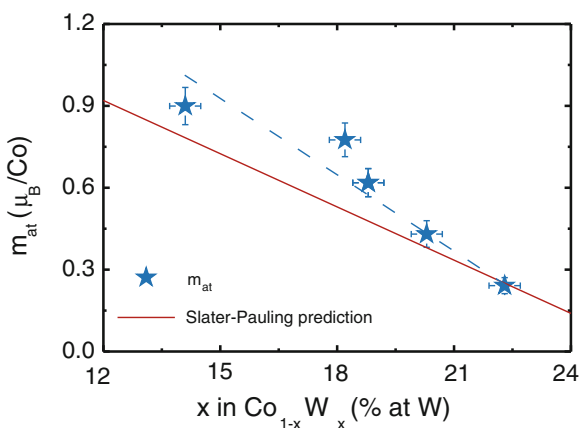


Fig. 3.20 Dependence of m_{tot} with the composition of the Co–W alloy in the NPs. Dashed line Guide to the eye

like symmetries and are modeled as icosahedral, octahedral and trigonal units [29]. Given the presence of SRO, large local magnetic anisotropies, comparable to those of crystalline Co, for example, are expected. Moreover, if the anisotropy is due to chemical SRO, K_{eff} is expected to increase linearly with the W concentration [23], contrary to our observation. The origin of K_{eff} in these materials is then structural. Values of K_{eff} on the order of the 10^5 erg/cm^3 have been reported for amorphous $\text{Co}_{1-x}\text{Ti}_x$ films [22] and on the order of 10^6 erg/cm^3 for amorphous $\text{Co}_{1-x}\text{Zr}_x$ films [23]. The latter is comparable to those obtained for our amorphous Co–W alloy NPs. Such high values of magnetic anisotropy are attributed to the strong local uniaxial anisotropy of the clusters [22, 23]. In $\text{Co}_{1-x}M_x$ amorphous alloys ($M = \text{Ti}$ and Zr), clusters formed of only Co atoms are magnetically isotropic, while those where the Co atom possess a number of M atoms as nearest neighbors present a local anisotropy, so submitted to greater anisotropy energy. The local anisotropy depends on both the local symmetry of the Co atoms and to the saturation magnetization, M_S [23]. If the local disorder increases by increasing the amount of M atoms, the clusters are less defined giving rise to a reduction in K_{eff} . Such dependence of K_{eff} with x has been observed in $\text{Co}_{1-x}\text{Ti}_x$ [22] and $\text{Co}_{1-x}\text{Zr}_x$ films [23], and is also observed in our Co–W NPs (see Fig. 3.21).

In Fig. 3.22, the K_{eff} and m_L/m_S results found for the amorphous Co–W NPs are depicted together with the values found for bulk Co, and NPs of the same average diameter ($D \sim 3 \text{ nm}$); the bare Co NPs [24] and, for completeness, the published values for alloyed Co–Pt particles are included [55]. In all these cases hybridization effects between $3d$ Co and $5d$ metal bands are at the origin of the increase of anisotropy. Thus, alloying Co with W increases the anisotropy with respect to bulk Co where crystalline anisotropy is dominant. The larger K_{eff} values found in the Co–Pt alloyed particles is due to the larger spin-orbit coupling constant in the Pt case with respect to the W one ($\xi_{5d} = 0.66$ and 0.038 eV for Pt [56] and W [57],

Fig. 3.21 Dependence of K_{eff} with m_{tot} for all Co–W NPs samples. Dashed line Guide to the eye

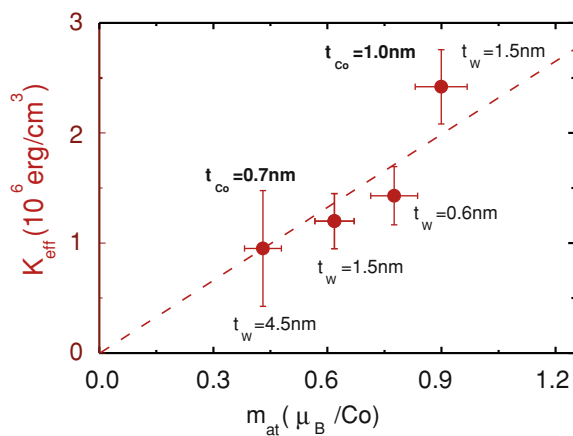


Fig. 3.22 Dependence of K_{eff} with m_L/m_S for the *a* series of Co–W samples and comparison with those for the bulk Co [48], bare Co NPs with $t_{\text{Co}} = 0.7 \text{ nm}$ [24], and Co–Pt NPs with comparable diameters [55]. *Dashed line* Guide to the eye

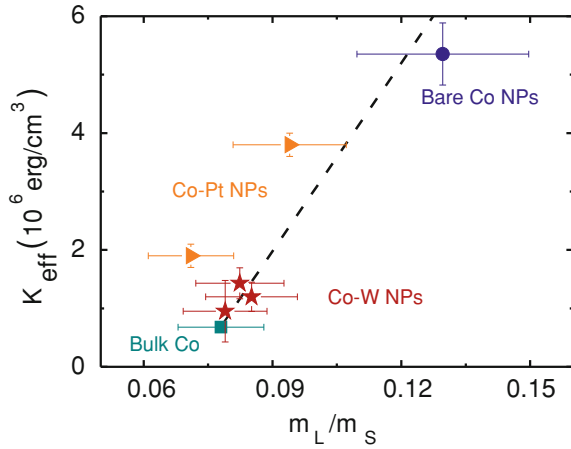
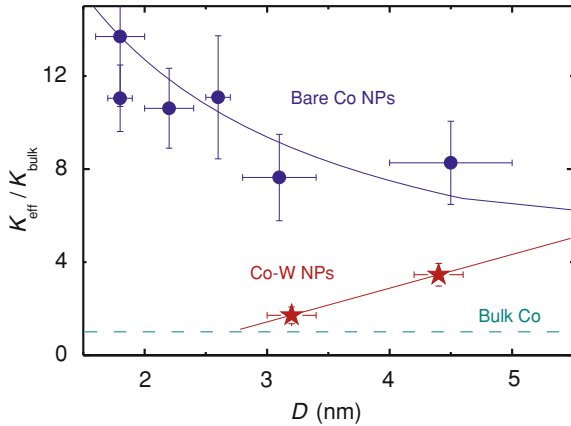


Fig. 3.23 Average magnetic anisotropy normalized to its bulk value ($K_{\text{bulk}} = 7 \times 10^5 \text{ erg/cm}^3$) [58] as a function of the Co–W particle diameter for the *b* samples series along with the values for bare Co NPs [41]



respectively). However, the enhancement driven by surface effects observed in the bare pure Co NPs is significantly larger [24].

Besides, when plotting K_{eff} versus the diameter of the Co–W particles (Fig. 3.23) we find an increase of K_{eff} with increasing the NP diameter, instead of the $1/D$ dependence found for the bare Co NPs [41]. This feature implies that there is an increase in the intrinsic anisotropy of the alloy, while the surface anisotropy is zero, as occurs, for example, in Co–Pt alloy NPs [55].

When comparing the magnetic behavior of our amorphous Co–W NPs with some other amorphous NPs systems studied in the literature, we find a quite different magnetic behavior. Most of the amorphous Fe NPs [1, 2, 4], Fe oxides [3, 5], organic coated Fe NPs [6, 7], amorphous Ni powder [12], Fe–Ni alloys [13], and NiFe_2O_4 [14], are prepared by sonochemical methods which lead to agglomeration of the particles. Thus, in such systems, the magnetic interactions between particles play an

important role. Instead, our Co–W NPs system constitute an ideal example of uniform non-interacting amorphous NPs well dispersed in an insulating matrix. Properties of the amorphous Fe and Ni based NPs systems are also those of superparamagnetic particles, with blocking temperature depending on the particle size [1–7, 12–14]. In the organic coated Fe NPs, the surface dominates their magnetic properties since there is a chemical bonding between the functional groups attached to the particle and the Fe atoms [6, 7]. The chemical bonding modifies their T_B and saturation magnetization, M_S . However, in the case of our Co–W NPs we have demonstrated that surface contribution is not as important as in those particulate systems.

Amorphous boride NPs with formula TM-B (with TM being one or two transition metals) show superparamagnetic behavior, interpreted in the frame of a core-shell model [8–11]. Such particles are prepared by chemical synthesis and dispersed in a polymeric matrix for measurements. Opposite to our Co–W NPs, TM-B have a distinct high temperature blocking temperature T_B , assigned to blocking of the ferromagnetically ordered core spins, and a second one at lower temperature, explained as due to blocking of the disordered shell spins. Besides, the $M(H)$ curves were temperature dependent; i.e., they did not follow a corresponding state law with H/T , on one hand, and had two components, a typical Langevin dependence, contributed by the core, and a linear dependent contribution, contributed by the spin disordered shell, on the other. In contrast, our Co–W NPs do fulfill the corresponding state law and such core-shell model (each with a different magnetic contribution) is not applicable.

In other Co–W multilayer systems the origin of the magnetic anisotropy observed is ascribed to the surface of the Co layers [59, 60] and to volume-type strain anisotropy [59]. However, we have demonstrated that interface effects play no role in the increase of K_{eff} obtained for our Co–W NPs, compared to the bulk Co value.

Our Co–W NPs have an oblate shape with semiaxes $a = \langle D_{\text{eff}} \rangle_{\text{PV}}/2$, and $c = \langle D_{\text{eff}} \rangle_{\text{CS}}/2$, albeit with a small c/a ratio; in the two samples for which the plan view and cross section average diameter could be determined (see Table 3.1), $c/a \approx 0.93(1)$. Then, one may estimate the shape anisotropy constant [61] as:

$$K_{\text{sh}} = \frac{1}{2} (N_a - N_c) M_{\text{sb}}^2 \quad (3.6)$$

where the demagnetization factors for that c/a ratio are $N_a \approx 0.325$ and $N_c \approx 0.350$ [62], for the long and short particle semiaxes, and M_{sb} is the magnetization density of the particle. For the two particles with $t_{\text{Co}} = 0.7$ nm and $t_{\text{W}} = 0.6$ and 1.5 nm, $M_{\text{sb}} = 0.413$ and 0.367×10^3 emu/cm³, respectively (see Table 3.3), which yields $K_{\text{sh}} = -2.0$ and -1.7×10^3 emu/cm³, respectively. These values are nearly three orders of magnitude smaller than the anisotropy constant found from our a.c susceptibility measurements, so, we may consider this contribution as negligible.

Then, shape anisotropy cannot explain the K_{eff} found for our Co–W NPs. Stress anisotropy is also one order of magnitude smaller [43]. Instead, the SRO detected in our amorphous Co–W alloy NPs is probably the main factor in the origin of their magnetic anisotropy.

3.5 Conclusions

We have presented a complete study on a system of self-organized amorphous Co–W alloy nanoparticles, uniformly dispersed in an alumina matrix. The size and composition of the Co–W alloy NPs have been controlled by varying the amount of Co or W in the system. Such parameters strongly affect their structural and magnetic properties. Co–W hybridization and electronic transfer from W $5d$ to Co orbitals have been observed by XANES measurements, so that as the Co/W ratio in the samples increases, there is more electronic transfer from W $5d$ towards Co $4p$ bands and less delocalization of Co $3d$ empty states. The amorphous nature of the Co–W NPs was verified by HRTEM and EXAFS measurements. The particles are superparamagnetic with minimal interactions between them, as demonstrated by the FC-ZFC magnetic measurements. Their magnetism is governed by the Co present in the alloy particles, so we were able to obtain values of the Co magnetic moment in the system via conventional SQUID magnetometry and compare it to results from XMCD measurements. A reduction of the Co moment per Co atom present in the samples was observed, compared to the bulk Co value. We have explained such decrease as due to the reduction of Co coordination in the alloy, which was verified by EXAFS and has been described in the literature. SRO in the amorphous Co–W alloy NPs is evident and is responsible for the magnetic anisotropy detected in the particles, contrary to other amorphous nanoparticles systems where the anisotropy is due to surface effects. With this work, we supply a paradigmatic example in the phenomenological body of magnetic nanoparticle behavior.

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Chapter 4

Breakdown of Hund's Third Rule in Amorphous Co–W Alloy Nanoparticles

In the previous chapter, we have demonstrated that the amorphous Co–W alloy NPs constitute a paradigmatic system among the specific group of magnetic nanoparticles with amorphous structure: contrary to other amorphous nanoparticle systems where the anisotropy is due to surface effects, its origin in the amorphous Co–W alloy NPs lies on the structural short range order (SRO) detected in the particles. We have also described the Co–W hybridization and electronic transfer from W $5d$ to Co orbitals in these Co–W NPs by analysis of X-ray absorption near edge structure (XANES) measurements at the Co K and W L_3 edges (the electron configuration for Co is $[\text{Ar}]3d^74s^2$ and for W is $[\text{Xe}]4f^{14}5d^46s^2$). The electronic transfer from W $5d$ toward Co $4p$ bands, and the delocalization of the Co $3d$ empty states were qualitatively described as a function of the Co/W ratio in these Co–W NPs samples.

The effects of similar $3d$ – $5d$ hybridization, in particular on $5d$ induced magnetic moments, have been previously studied both experimentally and theoretically in Fe/W multilayers [1] and bulk $\text{Co}_{100-x}\text{Ir}_x$ alloys [2], to cite some examples of metallic systems. A remarkable finding in these two systems is the observation of a breakdown of Hund's third rule of the induced orbital and spin magnetic moments in the $5d$ metals. This rule states how spin and orbital total moments in a single atom should be aligned, being parallel for an atom with more than half-filled shell, and antiparallel for a less than half-filled shell [3]. In spite of its phenomenological character and of being defined for single isolated atoms, atoms in solids have been proven to ubiquitously follow this rule, too.

However, the two cases mentioned above are part of the few examples where this rule is not completely fulfilled [1, 2, 4–6]. In the Fe/W multilayers, the total spin and orbital magnetic moments of the $5d$ W shell couple in parallel (notice that W is a less than half-filled $5d$ band metal), and for Ir in bulk Co–Ir alloys they are antiparallel aligned (Ir is a more than half-filled $5d$ band metal), being, in both cases, contrary to the predictions of the Hund's third rule [1, 2]. All these experimental findings have been possible thanks to the highly sensitive X-ray magnetic circular dichroism (XMCD) technique, which, as described in previous chapters, allows to perform element specific magnetometry, as well as to separate the contribution of the

orbital and spin moments to the total magnetic moment and their relative orientation, by applying the magneto-optical sum rules [7, 8].

The structural disorder in transition metal alloys has also been demonstrated to influence their electronic configuration [5]. In fact, for amorphous Fe–Zr and Co–Zr alloy films, the induced spin and orbital moments detected in Zr (a less-than half filled $4d$ element) are found to be parallel aligned, thus breaking down the Hund's third rule. However, for similar crystalline compounds Fe–Zr–Pt and Co–Zr–Pt, the induced orbital and spin moments in Zr are found to fulfill this rule.

Following these results, the amorphous Co–W alloy NPs arise as an attractive system to investigate the hybridization between Co orbitals and the $5d$ band of W, and its consequence on the induced spin and orbital magnetic moments in W. XANES and XMCD are the best techniques to study the electronic transfer between Co and W, and examine the compliance or breakdown of the Hund's third rule in the W atoms in Co–W systems. This chapter is then dedicated to delving into these hybridization effects, both experimentally by XANES and XMCD measurements at the Co K and W $L_{2,3}$ edges, and theoretically by simulations of the XANES and XMCD signals at both edges in the amorphous Co–W alloy NPs system. The polycrystalline bulk Co_3W alloy is also included in the present study, so that, by comparison to the amorphous NPs, the influence of the structural disorder is evaluated.

4.1 XANES and XMCD Measurements

XANES and XMCD measurements at the Co K (7709 eV), W L_3 (10207 eV) and W L_2 (11544 eV) edges on the Co–W NPs samples and the bulk Co_3W alloy were performed at the ESRF ID12 beamline. Spectra for Al_2O_3 —capped Co NPs and on a W metallic foil for reference, were also recorded, at the Co K and W $L_{2,3}$ edges, respectively. The APPLE-II undulator and a double—Si(111)—crystal monochromator were used to collect the spectra at the respective energies. XANES spectra were recorded by a fluorescence detector in backscattering geometry. XMCD signal was obtained by applying a magnetic field of 10 and 50 kOe for the Co–W NPs and the Co_3W alloy, respectively, normal to the sample plane and along the X-ray beam direction. Measurements were performed at 7 and 10 K for the Co–W NPs and the Co_3W alloy, respectively. This field and temperature were chosen according to the magnetic properties of the Co–W NPs, so that the system was reaching its magnetic saturation under these conditions (see Sect. 3.3.1). XMCD was obtained by differences of XANES spectra measured with opposite helicities of the light at a fixed magnetic field value, orienting the field in two inverse directions. Polarization of the circular light was over 90% at the Co K edge and 94% at the W $L_{2,3}$ edges. Due to the low XMCD signal in W, several spectra were taken for each sample, being 16 spectra in average for each direction of the field. Due to experimental difficulties, the Co–W NPs sample with $t_{\text{Co}} = 0.7$ nm and $t_{\text{W}} = 4.5$ nm was not measured at the W $L_{2,3}$ edges.

The absorption spectra and XMCD for the bulk Co_3W alloy were corrected for self-absorption effects after their normalization of the absorption jump to unity. These corrections take into account that the sample is infinitely thick, and uses its chemical composition and density, along with some geometrical parameters of the measurement setup such as the angle of incidence of the X-ray beam and the solid angle of the detector, to estimate the effect of self-absorption from the known energy dependence of the absorption coefficient of the sample. Details of the correction procedure can be found in Ref. [9] and references therein.

4.1.1 Co *K* Edge Results

XANES and XMCD at the Co *K* edge probes the $4p$ empty states of the Co atom in the sample. Analysis of the XANES spectra recorded at this edge on these Co–W alloy NPs samples was described in Sect. 3.2.2. Evidences of Co $4p$ – $3d$ and Co $3d$ –W $5d$ hybridization in the Co–W system and electronic transfer from W $5d$ to Co orbitals were then observed. These findings were obtained not only from the observed changes of the Co *K* edge XANES on the Co–W alloy NPs with respect to that of metallic Co, but also from the reduction of the magnetic moments of the Co atoms obtained in the Co–W alloy NPs by W inclusion in the alloy, as proven by analysis of the XMCD signals at the Co $L_{2,3}$ edges in Sect. 3.3.3.

The detection of a nonzero XMCD signal at the Co *K* edge on all samples, shown in Fig. 4.1, reflects the magnetic polarization of the $4p$ band in Co atoms. In Fig. 4.1 we compare the XMCD spectra for all studied samples, normalized to the energy jump of the absorption edge: the Al_2O_3 capped Co NPs (Fig. 4.1a), the *a* and *b* samples series (Fig. 4.1b, c, respectively), and the bulk Co_3W alloy (Fig. 4.1d). The origin of the energy scale has been chosen at the inflection point of the absorption edge. The XMCD signal in the case of the Al_2O_3 capped Co NPs (Fig. 4.1a) emerges by interatomic exchange interaction between the $4p$ band of the absorbing Co and the $3d$ bands of the neighboring Co atoms. This results from the allowed symmetry operations at the Co site in this cubic structure, so that the $4p$ – $3d$ bands mixing is only possible via the neighboring Co atoms [10]. In the Co–W alloys (Figs. 4.1b–d), with a hexagonal local structure, this signal originates at the intra-atomic exchange interaction between the $4p$ and $3d$ bands in Co. The sign of the XMCD signal in all cases is the same as in Ref. [11], indicating an antiferromagnetic coupling between $4p$ and $3d$ levels in Co.

Visible differences are observed in the Co *K* edge XMCD spectra of the Co–W NPs with respect to that of Al_2O_3 capped (see Fig. 4.1a); however, they are very similar to that of the Co_3W alloy (Fig. 4.1d). The dichroic signal in the Al_2O_3 capped Co NPs consists of a negative one-peak structure between 5 and 10 eV above the edge (marked in Fig. 4.1a as peak A), followed by a positive large bump between 10 and 30 eV (denoted in Fig. 4.1a as peak B), similar to what is observed in metallic Co [10] and other metal capped Co NPs [12]. Instead, in our Co–W NPs (Fig. 4.1b, c) and in the Co_3W alloy (Fig. 4.1d) the broad negative peak A is split, giving rise to a

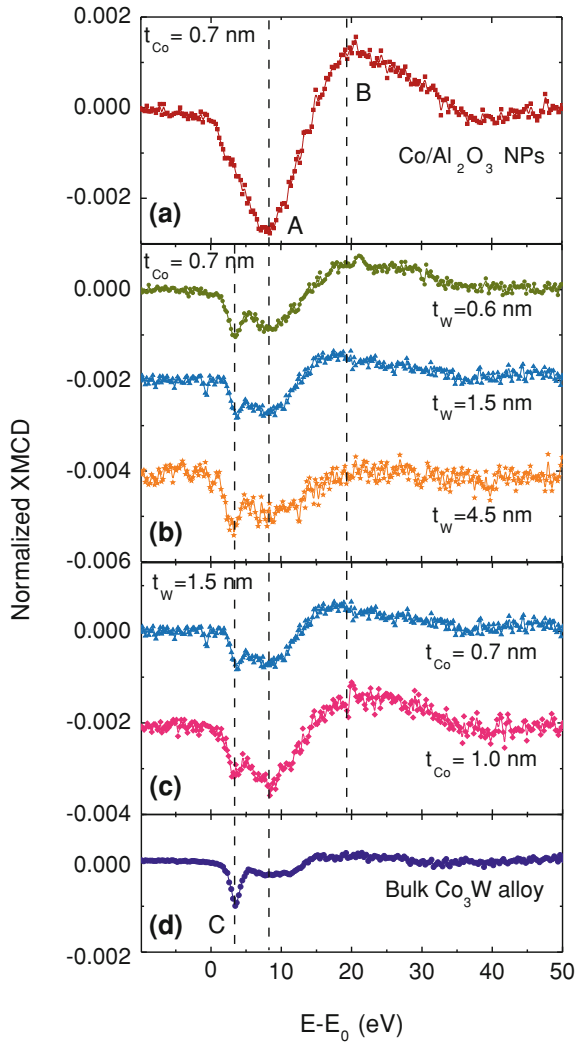


Fig. 4.1 XMCD spectra at the Co K edge for **a** Al_2O_3 capped Co NPs, **b** Co-W NPs *a* sample series, **c** Co-W NPs *b* sample series, and **d** bulk Co_3W alloy

double-peak structure formed by a trace of peak A and an additional negative peak, tagged as C in Fig. 4.1d. This peak C is more pronounced in the XMCD signal of the bulk Co_3W alloy. A similar shape of Co K edge XMCD signal has been observed by Rueff et al. [10] in LaCo_5 alloys, where they discussed the effect of the rare earth on the Co K XMCD signal shape. They ascribe this extra feature in the negative peak to a contribution of the La d empty states. Then, we may conjecture that this splitting in the Co-W systems is due to the W $5d$ states in the Co-W alloy.

4.1.2 W $L_{2,3}$ Edges Results

XANES spectra recorded at the W $L_{2,3}$ were normalized as L_3/L_2 to 2.19/1, according to Ref. [13]. Spectra measured for the Co–W NPs are shown in Fig. 4.2a, along with the one for a metallic W foil. XANES of the bulk Co_3W alloy is plotted in Fig. 4.3a. Changes in the absorption white-line at W $L_{2,3}$ edges for the Co–W NPs are observed and reflect variation of the available states of $5d$ character. Specifically, L_3 absorption edge appears for transitions from $2p$ to both $5d_{3/2}$ and $5d_{5/2}$, while L_2 reveals only transitions from $2p$ to $5d_{3/2}$ band. A qualitative analysis of this variation was described in Sect. 3.2.2. We observed that an increase in the Co/W ratio in the Co–W NPs samples gave rise to an increase in the number of W $5d$ empty states, n_h^W ; i.e., there is an electron transfer from W toward Co. The change in n_h^W for each sample may be quantified by analysis of the W $L_{2,3}$ XANES spectra. The integral of the white line at the $L_{2,3}$ edges of each sample, $r_{\text{Co-W}}$, and that for W foil, r_{Wfoil} , are defined as the sum of the individual L_2 and L_3 integrals, I_{L_2} and I_{L_3} , respectively, calculated by first subtracting the continuum from each XANES. The continuum is artificially represented by a double-step function. This double-step approach is extensively used for the $3d$ FM metals, and its accuracy in the case of W has been previously estimated to be about 94 %, given its relative large white line intensity [1]. Then, assuming that for metallic W $n_h^{\text{W,foil}} = 5.7$ holes [1], we estimate a scaling factor $C^{-1} = n_h^{\text{W,foil}}/r_{\text{Wfoil}} = 0.1936$ holes/eV. Finally, the number of holes for each Co–W sample can be calculated as $n_h^W = C^{-1}r_{\text{Co-W}}$.

Results for these calculations for both the Co–W alloy NPs and the bulk Co_3W alloy are listed in Table 4.1. From these values we observe that the number of holes in W in the Co–W alloy NPs slightly increases with respect to that in metallic W, and to that found for the bulk Co_3W alloy, due to hybridization of the $5d$ band in W with the $3d$ band in Co. Moreover, we notice a further increase in n_h^W when the amount of Co in the sample increases, and when t_W decreases. This means that the electronic transfer from the $5d$ band in W to the $3d$ band in Co depends on the Co/W proportion in the samples. For the Co_3W alloy a slight increase in n_h^W with respect to the value of metallic W is also observed.

The ratio between the unoccupied states in the $5d_{5/2}$ and $5d_{3/2}$ bands in W, $n_h^{5/2}/n_h^{3/2}$, may be evaluated from the branching ratio I_{L_3}/I_{L_2} , following the analysis described in Ref. [14]. The results of $n_h^{5/2}/n_h^{3/2}$ for the Co–W NPs and the bulk Co_3W alloy are given in Table 4.1. Similar to n_h^W , we observe that this ratio varies depending on the Co/W proportion in the sample; i.e., $n_h^{5/2}/n_h^{3/2}$ increases when the Co/W ratio decreases, being highest for the bulk Co_3W alloy.

XMCD signals at the W $L_{2,3}$ on each sample were normalized according to factors obtained from XANES normalization. Figure 4.2b–d show XMCD signals for each Co–W NPs sample, and Fig. 4.3b for the Co_3W alloy. The XMCD integrals at L_3 and $L_{2,3}$ edges, defined as p and q , respectively, are also shown. The existence of a XMCD signal at W $L_{2,3}$ evidences the presence of an induced magnetic moment in the W atoms by the magnetic Co atoms in the Co–W alloy NPs and the Co_3W alloy.

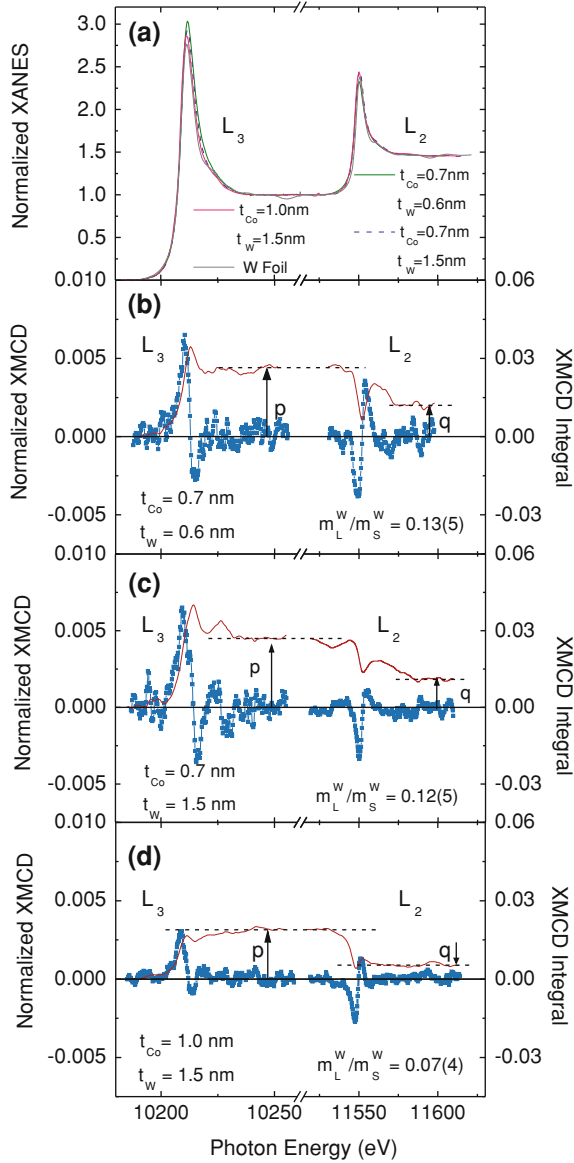


Fig. 4.2 **a** XANES spectra at the W $L_{2,3}$ for the Co-W NPs, and for a W reference foil. **b–d** show normalized XMCD signal and XMCD integral for each Co-W alloy NPs sample at the W $L_{2,3}$ measured at $H = 10\text{ kOe}$. Arrows indicate the energy at which p and q integrals were determined

According to the direction of the applied magnetic field, and considering that the L_3 XMCD signal is mostly positive, while the L_2 XMCD is negative, we can determine that the induced W magnetic moment orients opposite to the direction of the field.

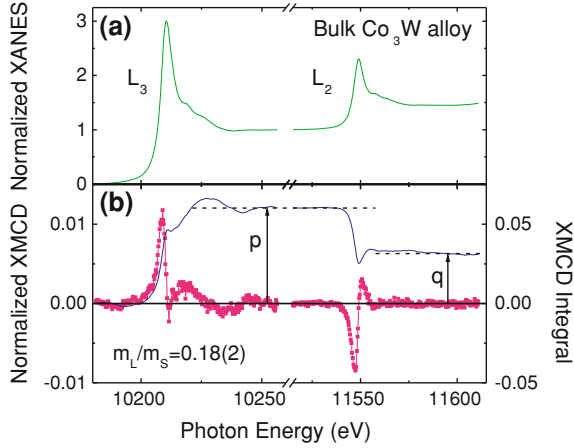


Fig. 4.3 **a** XANES spectra and **b** XMCD signal and XMCD integral at the W $L_{2,3}$ for the Co_3W alloy measured at $H = 50\text{kOe}$ and $T = 10\text{K}$. Arrows indicate the energy at which p and q integrals were determined

Table 4.1 Values of x in the $\text{Co}_{1-x}\text{W}_x$ alloy (values extracted from Table 3.3), n_h^{W} , $n_h^{5/2}/n_h^{3/2}$ ratio, and m_L/m_S ratio as calculated from the XMCD sum rules for the Co–W NPs samples in the present study and the bulk Co_3W alloy

Sample		x	n_h^{W}	$n_h^{5/2}/n_h^{3/2}$	m_L/m_S
Co–W NPs					
t_{Co} (nm)	t_{W} (nm)				
1.0	1.5	14.1(4)	6.09(3)	0.50(1)	0.07(4)
0.7	0.6	18.2(4)	6.06(5)	0.52(1)	0.13(5)
0.7	1.5	18.8(4)	6.00(5)	0.54(1)	0.12(5)
Bulk Co_3W		25(1)	5.85(2)	0.59(1)	0.18(5)
Calc. Co_3W		25	5.96(2)	0.57(2)	0.10(1)

$n_h^{\text{W}} = 5.7$ holes for metallic W [1]

Consequently, W induced moments are antiparallel to the Co magnetic moments deduced for the Co–W NPs in Sect. 3.3.3. This is consistent with the general trend in all transition metal series with the nd band filling: W has a less than half filled $5d$ band, which results in antiparallel coupling of its induced moment with that of the magnetic $3d$ metal [1, 5].

Values of p and q were used to calculate the orbital to spin moment ratio, m_L/m_S , in the induced magnetic moments in W by applying the magneto-optical sum rules [7, 8]. We have followed the symbol and sign criteria used in Ref. [15], so that the effective spin moment obtained from the sum rules is expressed as $m_{\text{Seff}} = m_S + m_D$, where m_D represents the dipolar term, proportional to the expectation value of the magnetic dipole operator $\langle T_z \rangle$. Thus, in order to determine m_S , one has to consider the $\langle T_z \rangle$ value. For alloys with a non-cubic structure, like the *hcp* Co_3W alloy, $\langle T_z \rangle$

might have a maximum value of $\langle S_z \rangle / 3$, corresponding to the Lorentz local field at the W site, as described for Ir in Co–Ir alloys [2]. Following this approximation, $m_{\text{Seff}} \leq 13/6 m_S$.

Notwithstanding, in the case of our amorphous Co–W alloy particles or in the polycrystalline Co_3W sample, where their individual anisotropy axes are randomly oriented, the angle averaged $\langle T_z \rangle$ becomes negligible, thus we consider below that $m_S = m_{\text{Seff}}$. Moreover, we refrain from calculating absolute values of m_S , m_L and m_{tot} in the Co–W NPs because of the uncertainty of the actual amount of W in their Co–W alloy, taking into account that not all of the W in the samples is alloyed with Co, as described in Chap. 3.

m_L/m_S results are listed in Table 4.1. In all the Co–W systems in the present study m_L/m_S in W is positive, which indicates that the orbital and spin moments in W are parallel aligned. Those values in the Co–W NPs samples are found to be nearly constant for a fixed amount of Co, and to decrease as the amount of Co in the sample increases. The latter may be understood as a reduction of the contribution of the orbital magnetism as the Co/W ratio in the sample increases. Comparing m_L/m_S values for the Co–W NPs with that of the Co_3W alloy we observe that the latter is higher. This may also be related to the Co/W ratio on each alloy, as will be discussed in Sect. 4.3.

For the Co_3W alloy, application of the sum rules yields to values of $m_S = -0.023(2)$, $m_L = -0.004(1)$ and $m_{\text{tot}} = -0.027(2) \mu_B/\text{W}$, for $n_h = 5.85$ holes in W atoms. The total magnetic moment in W for this alloy is one order of magnitude lower than the $-0.2 \mu_B/\text{W}$ moment measured for Fe/W multilayers in Ref. [1]. However, the m_L/m_S ratio found in the Co_3W alloy is higher than in the experimental value reported for Fe/W multilayers [1], but comparable to that estimated by first principles calculations for the latter system [16].

4.2 Calculations of DOS, XANES and XMCD

Calculations of the electronic density of states (DOS) projected at the Co $3d$ and W $5d$ orbitals, as well as XANES and XMCD spectra at the Co K and the W $L_{2,3}$ edges in the Co_3W system have been performed in collaboration with Dr. Fernando Bartolomé in the Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, by using the *ab initio* code FDMNES [17, 18]. This program gives the absorption cross section of photons around the ionization edge using fully relativistic monoelectronic calculations (DFT-LSDA). We have used the two different approaches for monoelectronic calculations that this code provides in order to simulate the X-ray absorption spectra: (i) a finite difference method to solve the Schrödinger equation, where the shape of the potential is free, thus a muffin-tin (MT) approximation can be avoided, and (ii) a Green formalism (multiple scattering) with a MT potential.

The structural and crystallographic information of the Co_3W system used to define the position of the absorbing and scattering atoms in the calculations is the one previously described in Sect. 3.1. A cluster of $6 \text{ \AA}$ radius was used and a Fermi

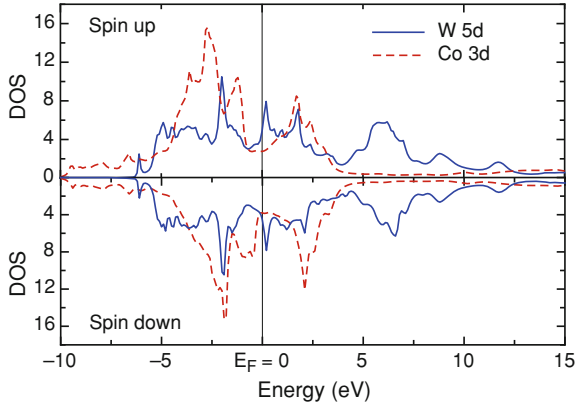


Fig. 4.4 Calculated density of states (DOS) for the Co_3W system. DOS projected at the Co 3d (–) and W 5d (–) orbitals. *Spin-up* DOS are shown as positive and *spin-down* as negative

level of about 7701, 10199, and 11536 eV for the Co K , W L_3 and W L_2 edges, respectively. The initial parameters of the atomic electronic configurations of Co and W have been fixed as those obtained from the analysis of experimental XMCD (see W 5d n_h in Table 4.1). However, slightly modified electronic configurations were tested during the simulations in order to evaluate the dependence of the calculated XMCD signal with the initial moment in the Co and W nd bands, as will be described below.

4.2.1 DOS Calculations

The spin polarized DOS projection at the Co 3d and W 5d orbitals for the Co_3W system were performed as described in Refs. [17, 18], and are shown in Fig. 4.4. The traditional sign of hybridization [19] is observed on the curves; i.e., W 5d states follow the main features of the Co 3d DOS, specially in the energy region where the latter have their dominating weight.

The number of electrons in the W 5d band were calculated by integration of the DOS in Fig. 4.4, up to the Fermi energy, E_f , resulting in 4.04(2) electrons, or equivalently, 5.96(2) holes. This result is very close to the 5.85(2) holes calculated for the W 5d band from the W $L_{2,3}$ XANES analysis in Sect. 4.1.2. The difference between the number of electrons with spin up and down in the W 5d band amounts to 0.014(1) electrons, which results in an estimated spin magnetic moment of 0.014(1) μ_B . This value is on the same order of the m_S derived for the W atoms from the sum rules applied to the W $L_{2,3}$ XMCD results in the Co_3W alloy in Sect. 4.1.2. The difference between the two values may be an artifact of the calculation, due to the MT approximation on the form of the potential [17].

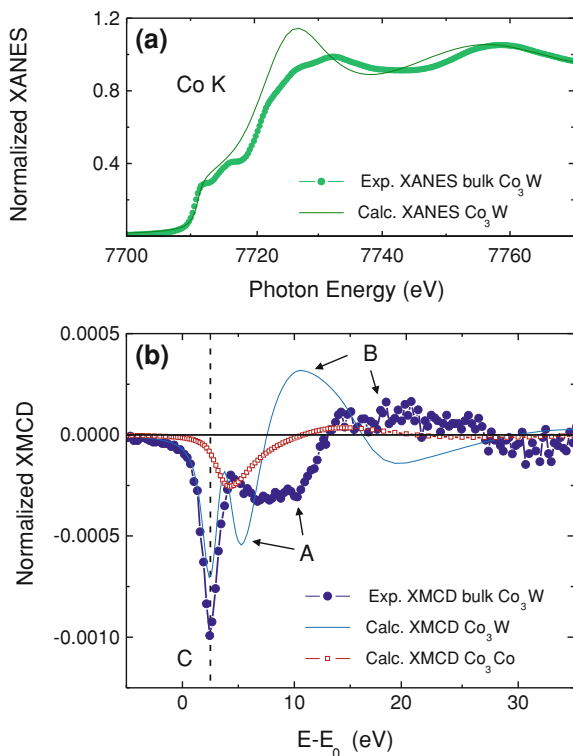


Fig. 4.5 **a** Co K edge XANES spectra for the Co_3W system calculated with FDMNES (—) and comparison with the experimental one for the alloy (●). **b** Calculated Co K edge XMCD signal for a Co_3Co (□) and a Co_3W (—) system, and comparison with the experimental one for the Co_3W alloy (●)

4.2.2 Co K Edge

The calculated XMCD signal at the Co K edge for the Co_3W system is plotted in Fig. 4.5. A qualitative agreement between the simulated and the experimental curves for the Co_3W alloy is found both for XANES and XMCD.

The splitting of the negative peak observed in these Co–W systems at about 5 eV above the edge (marked as peak C in Figs. 4.1, 4.5b) is reproduced in the calculations although the relative intensities and energy positions may vary. In particular, the energy positions of the calculated features above the edge are affected by an overestimation of the interaction with the core-hole in the finite-difference method calculation (peaks A and B in Fig. 4.5b are shifted to lower energies), and, therefore, the agreement with the experiment can only be expected to be qualitative. In order to take insight of the origin of the different peaks of the spectrum, we have calculated XAS and XMCD of a fictitious “ Co_3Co ” system with the Co_3W structure by substituting the W by Co in the definition of the cluster, and therefore, eliminating the presence of $5d$ states in the calculation. The Co_3Co XMCD result is shown in

Fig. 4.5b for comparison. Although the Co K edge XAS calculated in Co_3Co is only slightly different than Co_3W at the pre-edge feature, the Co_3Co XMCD is not split into two negative peaks, but closely resembles the bulk Co XMCD, which is similar to the measurement recorded in bare Co NPs. The calculations confirm our conjecture (Sect. 4.1.1) on the origin of the splitting of the Co K XMCD edge, and therefore, we positively ascribe the first negative XMCD peak experimentally observed in Co_3W to the hybridization of W $5d$ band states with the Co empty states probed in K edge absorption. Nominally, those are the Co $4p$ states through dipolar E1 transitions and the Co $3d$ states through quadrupolar E2 ones. However, the calculated Co K edge XMCD on Co_3W is split also when calculated in dipolar approximation only, showing that the hybridized W $5d$ band is probed also at the Co $4p$ states. Moreover, the correct sign of the calculated split XMCD feature (Fig. 4.5b) is only achieved for the (experimentally observed) antiparallel configuration between the Co magnetic moment and the W induced one, as is the general case for intermetallics with *less-than-half* and *more-than-half* filled bands [20].

4.2.3 W $L_{2,3}$ Edges

Calculations of the XANES and XMCD at the W $L_{2,3}$ edges were performed with the same FDMNES code. The intensity and spectral shape of the XMCD calculated signal is very sensitive to the Co magnetic moment introduced in the calculation. In contrast with the Co K edge, the spectral shape of the W XMCD is very sensitive to the approach used within the FDMNES code. In general, a rather satisfactory qualitative agreement is always found, achieving the best with the non muffin-tin approximation, as shown in Fig. 4.6a. The calculation confirms the antiparallel configuration between

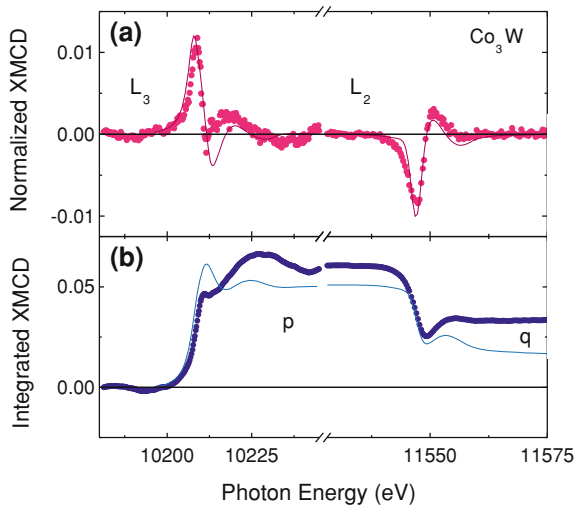


Fig. 4.6 **a** Experimental (●) and calculated (—) XMCD signal at the $L_{2,3}$ edges of W in Co_3W . **b** Integrals of the experimental (●) and calculated (—) signals in (a)

the Co magnetic moment and the W induced one, as described above. It is particularly interesting that the breakdown of Hund's third rule for the W $5d$ magnetic moments in Co_3W ($m_L/m_S > 0$) is also described in the calculation, as shown in Fig. 4.6b, where the experimental integrals are compared to the calculated ones. The signs of p and q are both positive, as in the experiments, leading to the same quantitative result (see values in Table 4.1). Calculations with the multiple scattering formalism with a muffin-tin potential generate extra features which are not observed in the W $L_{2,3}$ XMCD.

4.3 Discussion

The existence of a strong hybridization between the Co $4p$ – $3d$ and W $5d$ orbitals in all the Co–W systems studied has been demonstrated both experimentally and theoretically. Our study of the W $5d$ band by XANES at the W $L_{2,3}$ edges and DOS calculations evidence electronic transfer from Co $4p$ – $3d$ through W $5d$ bands, and its dependence on the Co/W ratio in the samples. The main consequence of this hybridization is the existence of an induced magnetic moment in the W atoms in all the Co–W alloy systems. Moreover, the induced spin and orbital moments in W are found to be parallel aligned ($m_L/m_S > 0$), which is contrary to the prediction of Hund's third rule for W atoms since it is a less-than half filled $5d$ band metal.

How hybridization may influence the breakdown of Hund's third rule in metallic compounds was originally proven by Galanakis et al. in a theoretical study on metallic VAu_4 [19]. They nicely described how the spin-orbit (SO) in Au may influence the orbit in V atoms through hybridization, provoking the reversal of its orbital moment and, therefore, the breakdown of the mentioned rule. Subsequent works on metallic compounds make use of this interpretation to demonstrate that the strong hybridization between the different atoms in the magnetic compounds is the key factor of such a breakdown [1, 2, 5]. Similarly, in our Co–W alloy NPs and in the bulk Co_3W alloy, Co spin-orbit coupling can influence the induced W orbital moment causing its reversal.

The effect of the SO coupling in the reversal of the induced orbital moment in W in Fe/W multilayers is described by Wilhelm et al. [1] using a simple atomic picture based on the competition of interactions between the spin and orbital angular momentum projections in the $3d$ metal and W. Similarly, in our Co–W alloy systems, the interaction mechanisms may be examined as those then observed on Fe/W. The dominant interaction in all cases is the spin-spin interatomic exchange coupling between Co and W, $J_{\text{inter}} \cdot S_z^{\text{Co}} \cdot S_z^{\text{W}}$ which compels the spin in W to align antiparallel to Co. Then, there is a competition between the intra-atomic SO coupling in W, $\lambda_{\text{intra}} \cdot S_z^{\text{W}} \cdot L_z^{\text{W}}$, and the interatomic Co–W SO interaction $\lambda_{\text{inter}} \cdot S_z^{\text{Co}} \cdot L_z^{\text{W}}$. The breakdown of Hund's third rule occurs since the interatomic Co–W interaction overcomes the intra-atomic SO interaction in W, so that Co spin turns m_L^{W} to align antiparallel to m_S^{Co} , but parallel to m_S^{W} , resulting in $m_L/m_S > 0$ in W.

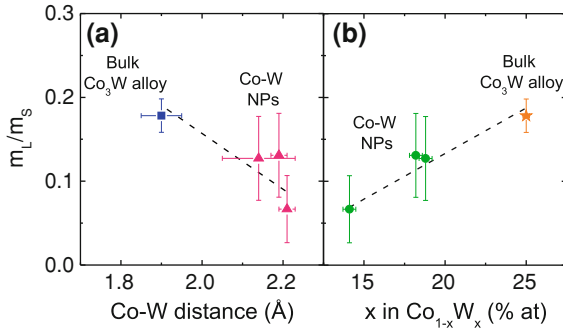


Fig. 4.7 m_L/m_S ratio as calculated from the W $L_{2,3}$ XMCD signal for the Co-W alloy NPs and for the bulk Co_3W alloy, as a function of **a** the first Co-W interatomic distance obtained from EXAFS, and **b** the composition of the Co-W alloy in the samples. Dashed lines guide to the eye

Further theoretical studies for the layered Fe/W system illustrate the influence of a large crystal field splitting in W, and the hybridization between Fe and W taking into account the band-filling and geometrical effects [21–23]. The latter are rather determinant, since the interatomic interactions between Fe and W are mediated by the crystal symmetry and interlayer distances; i.e., an increase of the interatomic Fe-W interaction is observed as the Fe and W interlayer distance decreases, which may be strongly related to the reversal of the orbital moment in W atoms [21].

In fact, recent works on Fe-Zr and Co-Zr amorphous magnetic alloys discuss the strong relationship between the structural properties with the breakdown of Hund's third rule observed in these systems [5]. The dependence of Co(Fe) spin-orbit coupling with the reduction of the Co(Fe)-Zr interatomic distance and the coordination number is determined from first-principles calculations of the m_L/m_S ratio in Zr in the Co(Fe)-Zr alloys, as a function of the lattice parameter, α , for various crystallographic structures. A change in sign of m_L/m_S from negative to positive is observed as α decreases. Following an analogous analysis, we may correlate the structural results obtained on the Co-W alloy NPs and on the bulk Co_3W alloy from extended X-ray absorption fine structure (EXAFS) in Sect. 3.2.2 with the results of induced moments obtained by XMCD in this chapter. In Fig. 4.7a, the obtained m_L/m_S in W in all Co-W systems are plotted as a function of the first Co-W interatomic distance resulting from EXAFS analysis on the same samples. m_L/m_S is found to increase as the Co-W distance shortens. This trend agrees well with the one observed for calculated m_L/m_S versus α in Zr in the Co(Fe)-Zr alloys in Ref. [5]. In the same study, Kapaklis et al. claim that the crystallinity of the materials is determinant in the breakdown of Hund's third rule since Zr induced moments in crystalline FeZrPt and CoZrPt alloys are found to fulfill the rule. In contrast, our observations of the breakdown of the rule on the polycrystalline bulk Co_3W , both experimentally and theoretically, demonstrate that the disorder level in the sample is not its main cause; instead, the reduction of the interatomic distances between dissimilar atoms seems to be the crucial point on this very controversial topic.

The Co influence on the orbital moment of W atoms in the samples may also be examined as a function of the Co/W in the alloy. In fact, m_L/m_S is found to scale with the W concentration in the Co–W alloy, as observed in Fig. 4.7b. As it was described in Sect. 4.1.2, this may be understood as an increase of the induced orbital component of the W magnetic moment as the Co/W proportion on the alloy decreases. A similar trend was observed for the m_L/m_S induced in Ir in Co–Ir disordered alloys, where Hund's third rule is also not fulfilled [2].

4.4 Conclusion

In all the Co–W alloy samples studied, i.e., Co–W alloy NPs and polycrystalline bulk Co_3W alloy, the induced W orbital moment orients parallel to its spin moment, contrary to the prediction of Hund's third rule for W. This breakdown has been proven by experimental and simulated XANES spectra and XMCD signals at the Co K and W $L_{2,3}$ edges. Consequently, we demonstrate that W not only affects the local structure of Co NPs, but also their electronic structure. The Co $3d$ –W $5d$ hybridization is evidenced and becomes a key factor in the breakdown of this rule in the case of induced moments. Our comparison between XMCD and EXAFS results demonstrate that the influence of the Co–W spin-orbit coupling depends on the average Co–W interatomic distance, as consequence of the dependence of the strength of the hybridization. Contrary to the differences found for crystalline and amorphous Co(Fe)–Zr alloys in Ref. [5], we observe the breakdown of Hund's third rule in both amorphous and polycrystalline Co–W systems, which suggests that this behavior is not a general behavior, but depends on the studied material and its local structure. It is worth noting that this is the pioneer observation of the breakdown of this rule on a nanoparticulated system.

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Chapter 5

Structural and Magnetic Properties of Co–Pt Nanoparticles

In this section, we describe the structural and magnetic characterization performed on the Pt-capped Co-nanoparticles system. We examine the role of Co–Pt alloying in the origin and enhancement of the magnetic anisotropy in these NPs. In fact, the production of Co–Pt alloys, given the large affinity of Pt to alloy with Co, is one of the preferred routes currently used in nanoparticles and thin films to increase their magnetic anisotropy [1, 2]. For example, CoPt NPs embedded in different matrices show enhanced magnetic anisotropy with respect to the Co particles [1–4]. This results from the crystallization of Co–Pt alloys in the chemically ordered $L1_0$ phase, which, in bulk form, has a very high magnetocrystalline anisotropy [5].

In addition, many Co–Pt multilayer systems [6–9], $\text{Co}_x\text{Pt}_{1-x}$ alloy films [10–13], and nanopatterned Co–Pt systems [14] show perpendicular magnetic anisotropy (PMA): a property that favors the easy axis of magnetization along the film normal direction. This PMA property is interesting for applications in spintronic nanodevices, for example in ultrahigh density magnetic storage, fast memory applications, and nanosensors [15, 16]. The origin of PMA is also correlated with the Co orbital anisotropy, which by hybridization with Pt, and due to the high spin-orbit coupling of the latter, gives rise to an enhanced out of plane anisotropy [2, 5, 17]. Most of the Co–Pt systems reported in the literature are either produced at high temperatures or annealed in order to favor the crystallization of the Co–Pt alloy in this anisotropic $L1_0$ phase. However, the origin of PMA in Co–Pt alloy systems deposited at room temperature (RT) remains controversial [13].

In order to deepen the understanding of the PMA properties in Co–Pt particulate systems prepared by RT deposition, we have performed a systematic study of the morphological, structural and magnetic properties of Co–Pt granular multilayers prepared by RT sequential sputtering deposition of Al_2O_3 , Co and Pt on a Si substrate. Previous studies of Co–Pt alloy nanostructured systems have demonstrated the importance of a complete investigation of both the local atomic environment and their long range order to clarify the correlation between crystallographic structure and magnetic anisotropy [13]. Thus, we examine the role of Co–Pt alloying in the origin of the magnetic anisotropy in these Co–Pt granular films. Their morphology and local structure are studied by high-resolution transmission electron microscopy

(HRTEM) and extended X-ray absorption fine structure (EXAFS). The magnetic characterization includes macroscopic measurements performed by SQUID and anomalous Hall effect (AHE) magnetometries, and microscopic measurements by X-ray magnetic circular dichroism (XMCD). In addition, we include angle dependent XMCD measurements, which constitute an effective method to explore the anisotropy of the orbital moment in the magnetism of Co–Pt systems with PMA [12, 18].

5.1 Samples Studied

The samples studied in this chapter consist in Pt-capped Co-nanoparticles prepared by Dr. Cyrile Deranlot and Dr. Frederic Petroff at the Unité Mixte de Physique CNRS-Thales¹ in Palaiseau, France, by sequential sputtering deposition of Al_2O_3 , Co and Pt on a Si substrate. The preparation procedure is the same as that previously described for the Co–W NPs in Sect. 3.1, and illustrated in Fig. 3.1, using Pt instead of W in this case. We end up with a multilayer system, following the formula $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3/\text{Co}/\text{Pt})_N/\text{Al}_2\text{O}_3$, with N being the number of repetitions of the Al_2O_3 , Co and Pt trilayer deposition. The characterization of the Co–Pt NPs that we describe in this chapter has been performed on samples with a fixed $t_{\text{Co}} = 0.7 \text{ nm}$, varying $t_{\text{Pt}} = 0.6, 1.5, 4.5 \text{ and } 6.0 \text{ nm}$, and $N = 25$ in all cases. Let us recall that the Al_2O_3 layer thickness is 3 nm in each trilayer, and 5 nm in the one deposited at the end of the process for protection purposes.

5.2 Morphological and Structural Study

5.2.1 Microscopy Measurements

The morphology of the Co–Pt NPs samples has been studied by HRTEM and high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) measurements, performed by Dr. Luisa Ruiz González and Dr. José María González-Calbet of the Departamento de Química Inorgánica in the Universidad Complutense de Madrid.² HRTEM images were taken in both cross section and plan view configurations, in a JEOL JEM 3000 F Field Emission Microscope fitted with an Oxford LINK Electron Dispersive Spectrometry (EDS) analyzer.

Low magnification studies in cross section configuration for all four samples confirmed the presence of 25 layers in agreement to the nominal layer preparation. HRTEM images, shown in Fig. 5.1, and EDS analysis indicate that light gray layers

¹ <http://www.trt.thalesgroup.com/ump-cnrs-thales/>.

² <http://www.cnme.es/>.

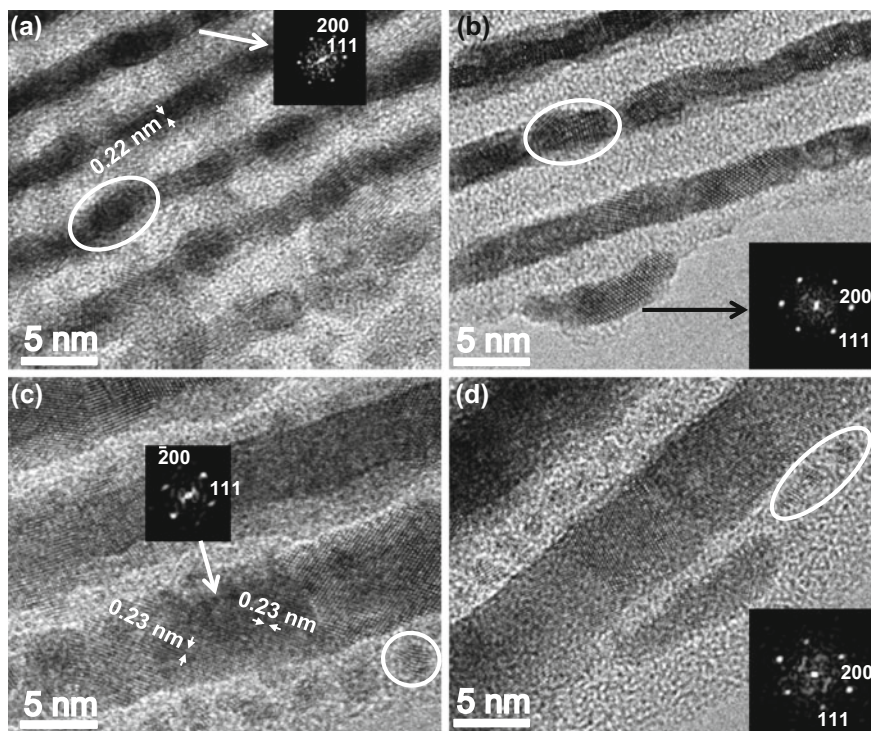


Fig. 5.1 HRTEM images in cross section configuration for samples from with $t_{Co} = 0.7$ nm and **a** $t_{Pt} = 0.6$ nm, **b** $t_{Pt} = 1.5$ nm, **c** $t_{Pt} = 4.5$ nm and **d** $t_{Pt} = 6.0$ nm. Fourier transforms (FFTs) at selected zones of the images are shown. A Co–Pt particle is highlighted in (a) and (b). Pt NPs are marked in (c) and (d)

correspond to the amorphous alumina and darker layers to the Co and Pt metals, similarly to the case of Co–W NPs described in Sect. 3.2. In contrast to the Co–W NPs case, crystallinity in the Co–Pt NPs is observed in all four samples studied by HRTEM. Each metallic layer is about 2.3, 2.5, 5.5 and 6.7 nm thick, for the samples with $t_{Pt} = 0.6$, 1.5, 4.5 and 6.0 nm, respectively.

In the samples with the lowest amount of Pt ($t_{Pt} = 0.6$ and 1.5 nm) there are some signs of particulated morphology, as in the region surrounded by a white ellipse in Fig. 5.1a, b. Some darker shadows inside the layers indicate the presence of Co, located at the center of the layer, suggesting that the capping Pt tends to surround the Co particle. For the other two samples ($t_{Pt} = 4.5$ and 6.0 nm), however, the Co–Pt nanoparticles are not easy to be identified from the images obtained in cross section configuration.

Fast Fourier transform (FFT) performed on selected areas of the images shows spots that are well indexed with the interplanar distances of a *fcc* cell in all cases (see insets in Fig. 5.1). In Fig. 5.1a, c the periodicity found in the selected zone of the image is 0.22–0.23 nm, which is characteristic of the (1 1 1) planes of a *fcc* Pt

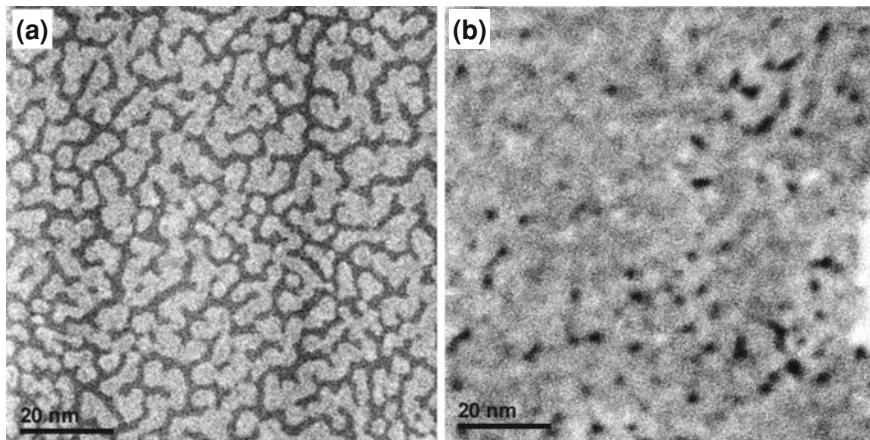


Fig. 5.2 STEM images in plan view configuration for the samples with $t_{\text{Co}} = 0.7$ nm, and **a** $t_{\text{Pt}} = 0.6$ nm and **b** $t_{\text{Pt}} = 1.5$ nm

structure. In Fig. 5.1c, d some small crystalline clusters in the alumina region of the samples are observed (see circled particles in the figures), which have been identified as Pt clusters with *fcc* structure, ranging between 2 and 3 nm in diameter.

Improved contrast to better identify the Co–Pt particles is obtained by plan view STEM images, such as the one shown for the sample with $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 0.6$ nm in Fig. 5.2a. In this image, brighter parts correspond to Co–Pt NPs, and darker parts to Al_2O_3 . The image obtained is comparable to those of similar systems of metallic nanoparticles embedded in insulator matrices [19], and the shape of the particles is similar to that of Co-nanoparticles embedded in alumina [20], and to the one found for the Co–W NPs (see Sect. 3.2.1).

The average diameter of the Co–Pt NPs from the image in Fig. 5.2a was 4.1(2) nm. STEM images for the other three samples (those with $t_{\text{Pt}} = 1.5$, 4.5 and 6.0 nm) did not allowed identification of the Co–Pt particles since they revealed an almost uniform Pt capping, as shown in Fig. 5.2b for the sample with $t_{\text{Pt}} = 1.5$ nm.

5.2.2 XANES and EXAFS Measurements

X-ray absorption (XAS) and EXAFS spectra for the Co–Pt NPs samples with $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 0.6$, 1.5, 4.5 and 6.0 nm were measured at the Co *K* (7709 eV) and Pt *L*₃ (11564 eV) edges using a double-crystal Si(111) monochromator in the BM29 beamline at the European Synchrotron Radiation Facility (ESRF). Measurements were performed at 300 K in fluorescence detection mode with a 13-element Ge solid state detector with digital signal processing for fluorescence XAS, high energy resolution and high count rate. Reference samples were also measured at different

edges: Co particles embedded in alumina matrix (referred in the following as “bare Co NPs”) and the Co metallic foil measured at the Co K edge; and Pt metallic foil measured at the Pt L_3 edge. For each edge measured on each sample, four spectra were taken in order to have enough statistics in data treatment, following a 4 s/point count.

The X-ray absorption spectra were analyzed following standard procedures. A preliminary reduction of the EXAFS raw data involving background removal of the absorption data $\mu(E)$, conversion of $\mu(E)$ to $\chi(k)$, normalization and weighting scheme were performed with AUTOBK and ATHENA, programs from the simulation package IFEFFIT [21]. EXAFS data analysis and fitting were performed on all reference and samples at their respective edges. All spectra were fitted using the ARTEMIS program from the same IFEFFIT package using models based on crystallographic information found in the ICSD³ database. Atomic clusters used to generate the scattering paths for fitting were generated with ATOMS, a tool from the same simulation package [22].

5.2.2.1 Co K Edge

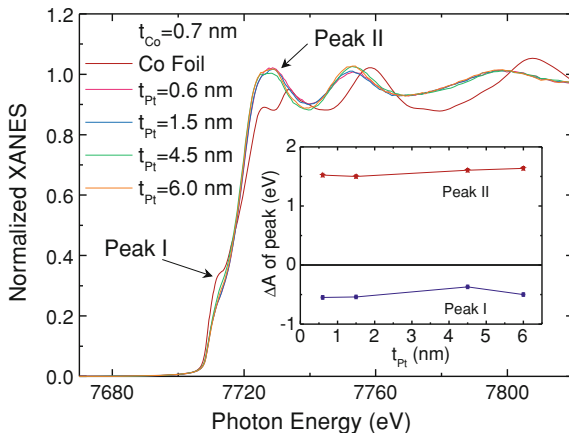
Normalized X-ray absorption near edge structure (XANES) spectra at the Co K edge for Co–Pt NPs with $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 0.6, 1.5, 4.5$ and 6.0 nm are shown in Fig. 5.3, along with the Co foil XANES, plotted for reference. Changes in the intensity and shape of the pre-edge peak and the white line (denoted as peak I and peak II, respectively, in Fig. 5.3) are appreciable and reflect changes in the electronic structure of the Co (electron configuration $[\text{Ar}]3d^7 4s^2$) and Pt (electron configuration $[\text{Xe}]4f^{14} 5d^9 6s^1$) atoms. Analogous to the analysis of such variation described for the Co K edge XANES in the Co–W NPs, we calculate the difference of the peaks areas ($\Delta A = \int_{E_i}^{E_f} (\mu_{\text{sample}} - \mu_{\text{Co-foil}}) dE$). The inset of Fig. 5.3 represents the ΔA as a function of the Pt content in the samples. The integration limits were 7706.1–7717.6 eV for peak I, and 7717.6–7735.1 eV for peak II.

Let us recall that the Co K edge white line reflects the $4p$ empty states of Co near the Fermi energy. Variation of peak I mainly determines changes of the $3d$ character of unoccupied states, which is influenced by Co $4p - 3d$ hybridization. The reduction of the intensity of peak I in the Co–Pt NPs with respect to that of the Co foil, also observed for the in Co–W NPs case, reveals a delocalization of the Co $3d$ empty states, and is a proof of Co $4p - 3d - \text{Pt } 5d$ hybridization.

The intensity of peak II depends on both the number of available $4p$ states, and the structure of the system. It is evident that the intensity of this peak II is higher and its shape different from that of the Co foil. Indeed, it looks closer to those recorded for Co–Pt alloys in Ref. [23], which may be an indication of presence of such kind of alloys in our Co–Pt particles. In any case, it is clear that the $4p$ empty states in the Co–Pt NPs samples increase, compared to those of the bulk Co.

³ <http://icsd.iqfr.csic.es/icsd/>.

Fig. 5.3 XANES at the Co K edge for the Co–Pt NPs and comparison with that of a Co foil for reference. Inset: Variation of the areas of *peak I* and *peak II* in the figure as a function of t_{Pt}



Both peak I and peak II are practically constant along the Co–Pt samples series (see inset of Fig. 5.3a), reflecting that Co $3d$ –Pt $5d$ hybridization is not affected by such variations in the amount of Pt for a fixed Co content. Similarly to the Co–W NPs case, this fact strongly suggests that the alloy composition in the Co–Pt NPs samples is similar for these four samples studied, a result that will be confirmed by EXAFS (later in this section).

The structural analysis of the Co–Pt NPs that can be extracted from the $\chi(k)$ EXAFS signal is better studied by its Fourier transform (FT), shown in Fig. 5.4a, performed on a k -range from 2.4 to $10.6 \text{ \AA}^{-1}$ using a k^2 weight and a kaiser-bessel window function. This Co K edge R -space data show peaks which correspond to different atomic shells surrounding the Co atoms in the samples. We have plotted the FT EXAFS of Co–Pt NPs samples along with the Co foil and bare Co NPs for comparison. As described in Sect. 3.2.2, the Co environment of the latter two samples is very similar, which is revealed from the the same position and shape of the peaks, not only for the first coordination shell, but also for outer shells. However, the peaks for outer coordination shells are different in the Pt-capped Co nanoparticles. The appearance of a peak characteristic of a Co–Pt distance is identified in all four samples, and is marked in the inset of Fig. 5.4a. The intensities of all peaks of the FT EXAFS are larger in the Co foil than in the particulate systems, as it is expected from the reduction in the mean Co coordination due to the size reduction.

From a qualitative inspection of the peaks shape and position of the FT EXAFS at the Co K edge for the four Co–Pt NPs, it is noticeable that the Co neighborhood is very similar in all four samples. This was confirmed by the fitting of EXAFS signal, performed on the R -space in a range from 1.2 to $3.2 \text{ \AA}$ using a kaiser-bessel window function, so that it covered the Co first coordination shell (see Fig. 5.4b). Similarly to the fitting procedure performed for the Co–W NPs, different models were tested in order to fit the Co K edge R -space data. The best fits were achieved with combinations of two Co–Co distances used when fitting the bare Co NPs: a short Co–Co path at around $2.0 \text{ \AA}$ and a Co–Co belonging to the *fcc* Co metal at

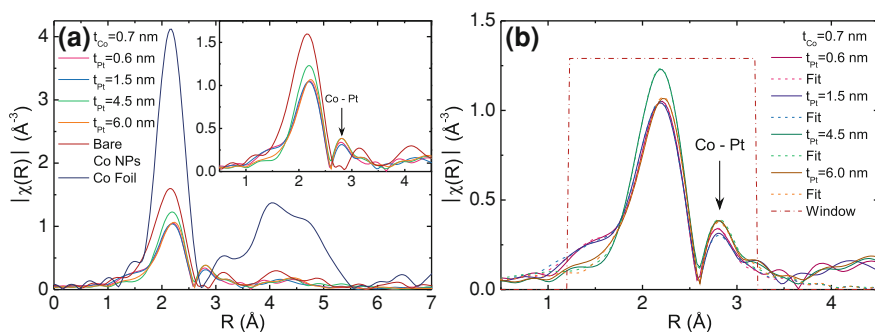


Fig. 5.4 **a** Fourier transform of EXAFS signal at the Co K edge on the Co–Pt samples. The measurements on the Co foil and bare Co nanoparticles with $t_{\text{Co}} = 0.7$ nm in are shown for comparison. Inset: zoom of the first coordination shell in the particulate systems. **b** Best fits to the first coordination shell in **(a)** for the Co–Pt nanoparticles

2.51 Å; and two distances belonging to a CoPt alloy: a Co–Co path at 2.65 Å and a Co–Pt at 2.70 Å.⁴

The structural parameters for fitting the R -space EXAFS at the Co K edge of each Co–Pt NPs sample were the average coordination (N), interatomic distance (R), and the Debye-Waller factor (σ^2) for each path. The amplitude reduction factor S_0^2 was set to that obtained for the Co foil fit, and the shift in the threshold energy ΔE_0 was fit for each sample. A total of 10 fitting parameters were used for an iterative procedure, which consistently included the fitting of both Co K and Pt L_3 edges (see Sect. 5.2.2.2). Results for the Co K edge EXAFS fits for the Co–Pt NPs are shown in Fig. 5.4b and the values obtained for each sample are listed in Table 5.1.

The EXAFS results of distances and coordinations in our Co–Pt NPs differ from those of similar Co-core Pt-shell NPs of comparable sizes [24], demonstrating that the structure of our particles is different from that of a simple Co-core Pt-shell. However, there is a presence of a Co core in the Co–Pt NPs samples since the first two distances Co–Co in Table 5.1 (numbered 1. Co–Co and 2. Co–Co) are in agreement to those found in the EXAFS fitting of the bare Co NPs, though with a smaller Co–Co coordination due to the size reduction of the Co core. For the samples with $t_{\text{Pt}} = 4.5$ and 6.0 nm, the introduction of the 1. Co–Co path had no effect in the fit, therefore it was excluded for the model used for them.

The distances numbered 3. Co–Co and 4. Co–Pt have been identified to belong to a $\text{Co}_x\text{Pt}_{1-x}$ alloy with composition close to that with $x = 0.5$, by comparison to the Co K edge EXAFS results in Co–Pt films with that composition [13]. Such distances, as well as the coordination and Debye-Waller factors for each path, are almost constant along the series, which indicates that the Co–Pt alloy in the samples has the same or very close composition.

⁴ <http://icsd.iqfr.csic.es/icsd/>.

Table 5.1 Structural parameters obtained from the Co *K* edge EXAFS fits for the Co-Pt NPs shown in Fig. 5.4

Sample, <i>t</i> _{Pt}	0.6 nm			1.5 nm			4.5 nm			6.0 nm		
	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)
Bond												
1. Co-Co	1.4(6)	1.96(1)	0.023(2)	1.4(9)	1.93(2)	0.03(1)	–	–	–	–	–	–
2. Co-Co	2.6(9)	2.43(3)	0.028(8)	2.0(6)	2.44(2)	0.011(3)	3.3(8)	2.47(1)	0.022(3)	1.6(4)	2.37(1)	0.007(2)
3. Co-Co	4.6(6)	2.54(1)	0.012(1)	4.7(7)	2.55(2)	0.010(2)	4.4(3)	2.52(1)	0.012(1)	6.3(7)	2.54(1)	0.010(2)
4. Co-Pt	4.6(4)	2.63(1)	0.013(1)	5.0(6)	2.65(2)	0.016(3)	5.0(4)	2.65(1)	0.012(1)	5.7(5)	2.66(2)	0.016(2)
ΔE_0 (eV)	7.0(5)			7.0(5)			6.8(1)			7.2(2)		

Coordination numbers, *N*, interatomic distance, *R*, and Debye-Waller factor, σ^2 for each path used in the fitting model. The energy shift, ΔE_0 , of the fit is also listed

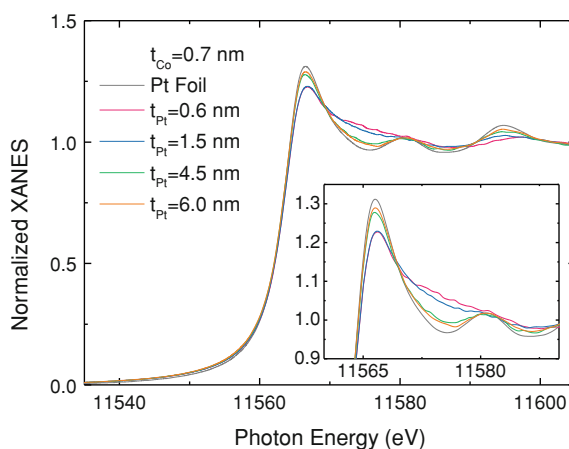
5.2.2.2 Pt L_3 Edge

Normalized XANES spectra at the Pt L_3 edge for the Co–Pt NPs samples are shown in Fig. 5.5, along with that of a Pt foil at the same edge for comparison. Similar to the case of W, being both $5d$ metals, the Pt L_3 absorption edge appears for transitions from $2p$ to both $5d_{3/2}$ and $5d_{5/2}$ bands. In general, the white line feature of the Pt L_3 in the Co–Pt NPs in Fig. 5.5 is reduced with respect to that of the Pt foil as the amount of Pt in the sample decreases. The same trend is also observed for Co–Pt alloys in Ref. [23], as the Co concentration in the alloy increases. A decrease in the Pt L_3 edge intensity from one sample to the other shows a decrease in the number of Pt $5d$ available empty states. Such a decrease may be understood as an electron transfer from Co towards Pt, due to hybridization between the Pt $5d$ and Co $4p - 3d$ electronic states.

It is evident that those samples with high amount of Pt, namely $t_{\text{Pt}} = 4.5$ and 6.0 nm, on one hand, have a spectrum very close in shape and intensity to that of the Pt foil, showing a higher amount of metallic Pt in these two samples. On the other hand, the XANES of those samples with low amount of Pt, that is $t_{\text{Pt}} = 0.6$ and 1.5 nm, differ from that of the Pt foil, showing a broader and less intense white line, which is an indicative of different electronic structure and Pt environment in these last two samples. Later in this section we will demonstrate by EXAFS analysis performed in these samples how the Pt environment differs, being very similar to the metallic Pt in the first two mentioned samples ($t_{\text{Pt}} = 4.5$ and 6.0 nm).

The Fourier transformed EXAFS signals at the Pt L_3 of the Co–Pt NPs samples, along with that of the Pt foil used for reference, are shown in Fig. 5.6a. The k -range for the FT goes from 2.7 to $8.5 \text{ \AA}^{-1}$ using a k^2 weight and a kaiser-bessel window function. A qualitative inspection of the peaks shows, again, that the Pt environment in the samples with $t_{\text{Pt}} = 4.5$ and 6.0 nm is very similar to that of the metallic Pt.

Fig. 5.5 XANES spectra at the Pt L_3 edge for the Co–Pt NPs samples, along with the the absorption of the Pt foil plotted for reference. Inset: details of the variation of the white line intensity



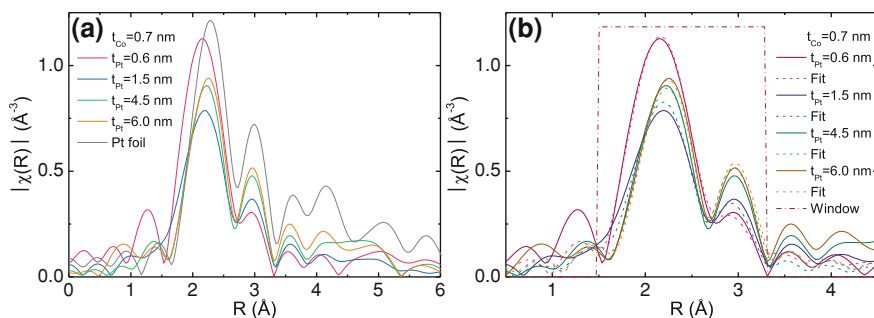


Fig. 5.6 **a** Fourier transform of EXAFS signal at the Pt L_3 edge on the Co–Pt NPs studied and comparison with that of the Pt foil. **b** Best fits to the first coordination shell of the Co–Pt NPs samples in (a)

Table 5.2 Structural parameters obtained from the Pt L_3 edge EXAFS fits for the Co–Pt NPs shown in Fig. 5.6b

Sample, t_{Pt} (nm)	Pt–Co			Pt–Pt			
	N	R (Å)	σ^2 (Å ²)	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)
0.6	4.6(9)	2.62(3)	0.008(3)	4.7(9)	2.65(3)	0.004(4)	3.2(9)
1.5	2.4(5)	2.62(2)	0.012(2)	9.3(5)	2.73(2)	0.008(4)	4.7(8)
4.5	–	–	–	11.8(5)	2.73(1)	0.006(1)	6.7(9)
6.0	–	–	–	11.8(5)	2.74(1)	0.006(1)	7.2(8)

Coordination numbers, N , interatomic distance, R , and Debye–Waller factor, σ^2 for both paths used in the fitting model. The energy shift, ΔE_0 , of the fit is also listed

The Pt L_3 EXAFS fitting was performed on the R -space in a R -range from 1.5 to 3.3 Å, using a kaiser-bessel window function. S_0^2 was set to that value obtained for the Pt foil EXAFS fit, and ΔE_0 was fit for each sample. The Pt L_3 EXAFS fitting model for the Co–Pt NPs included a combination of Co–Pt distances from a Co–Pt alloy, and a Pt–Pt distance from the metallic Pt.⁵ The fitting parameters were seven, in total, in an iterative procedure including the fitting of both Co K and Pt L_3 edges, as it was previously described.

The EXAFS fitting results for the Co–Pt NPs samples are plotted in Fig. 5.6b and the values listed in Table 5.2. The Pt–Co distance of 2.62 Å found for the samples with $t_{\text{Pt}} = 0.6$ and 1.5 nm are well in agreement to the results found for the same samples at the Co K edge EXAFS analysis (see Table 5.1), which confirms the presence of a Co–Pt alloy in the samples.

The sample with the least amount of Pt, $t_{\text{Pt}} = 0.6$ nm, has a Pt environment quite different from the other three samples. The Pt–Pt distance is in this case a bit shorter (2.65 Å) than those found for the others (~ 2.73 Å), which might indicate that Pt is not in its metallic form. Such a short Pt–Pt distance has been detected in electrochemically

⁵ <http://icsd.iqfr.csic.es/icsd/>.

deposited *fcc* Co–Pt alloys [25]. Then, it is very likely that most of the deposited Pt in this sample may be alloyed with the Co atoms.

The EXAFS signals of the samples with the highest amount of Pt, namely, $t_{\text{Pt}} = 4.5$ and 6.0 nm, were fitted only with a Pt–Pt model since introducing a Co–Pt distance had no effect in their fit. From the fitting results in these two samples, we found the same structure around the Pt atoms, as it was observed from the Pt L_3 XANES, being very close to that of the Pt foil. In fact, the Pt–Pt coordination being close to 12, and interatomic distances of 2.73 – 2.74 Å are close to those obtained for the Pt foil used as a reference with *fcc* structure.

Similar Co–Co, Co–Pt and Pt–Pt distances to those found for our Co–Pt NPs have been reported for Co-clusters of similar sizes (~ 3 nm) embedded in a Pt matrix, where diffusion of the atoms at the surface cluster takes place, resulting in a Pt–Co alloyed interface of one or two monolayers [26]. Analogous processes may be present in our Co–Pt NPs. However, the coordination numbers we have obtained for the Co–Pt and Pt–Pt environments are much higher than those listed in Ref. [26], which may indicate that the Co–Pt alloy interface in our Co–Pt NPs extends to more layers at the Co-core surface.

Summarizing, the morphological and structural characterization of the Co–Pt NPs reveal the presence of a Co–Pt alloy with a composition very similar in the four samples studied. Its composition is close to a $\text{Co}_{0.5}\text{Pt}_{0.5}$, according to the Co and Pt coordination and to the Co–Co, Co–Pt and Pt–Pt distances found by EXAFS analysis of the samples. In addition to this alloy, a remnant of the original Co cluster formed on the alumina matrix was identified from the EXAFS fitting at the Co K edge. Thus, the $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy is probably surrounding this Co rich core. In the samples with $t_{\text{Pt}} = 1.5$, 4.5 and 6.0 nm there is an excess of metallic Pt that crystallizes as an *fcc* structure, in agreement to what was observed by HRTEM for these samples. The presence of small Pt clusters in the Al_2O_3 matrix is also observed from the HRTEM images of the latter two samples. The structure of such Pt clusters is that of metallic *fcc* Pt, which contributes to the signal of metallic Pt identified in the Pt L_3 edge EXAFS.

5.3 Magnetic Study

5.3.1 SQUID-Based Magnetometry

Magnetization measurements were performed with a SQUID magnetometer equipped with the high resolution (RSO) option. Both magnetization as a function of the applied field, $M(H)$, and as a function of temperature, $M(T)$, were measured in two configurations: (1) with the field applied parallel, and (2) perpendicular to the substrate plane. The dc susceptibility measurements curves measured with a bias field of $H_{\text{dc}} = 200$ Oe, in both configurations, for the samples series with $t_{\text{Co}} = 0.7$ nm, $t_{\text{Pt}} = 1.5$, 4.5 and 6 nm, and $N = 25$ are plotted in the left panel of Fig. 5.7. The

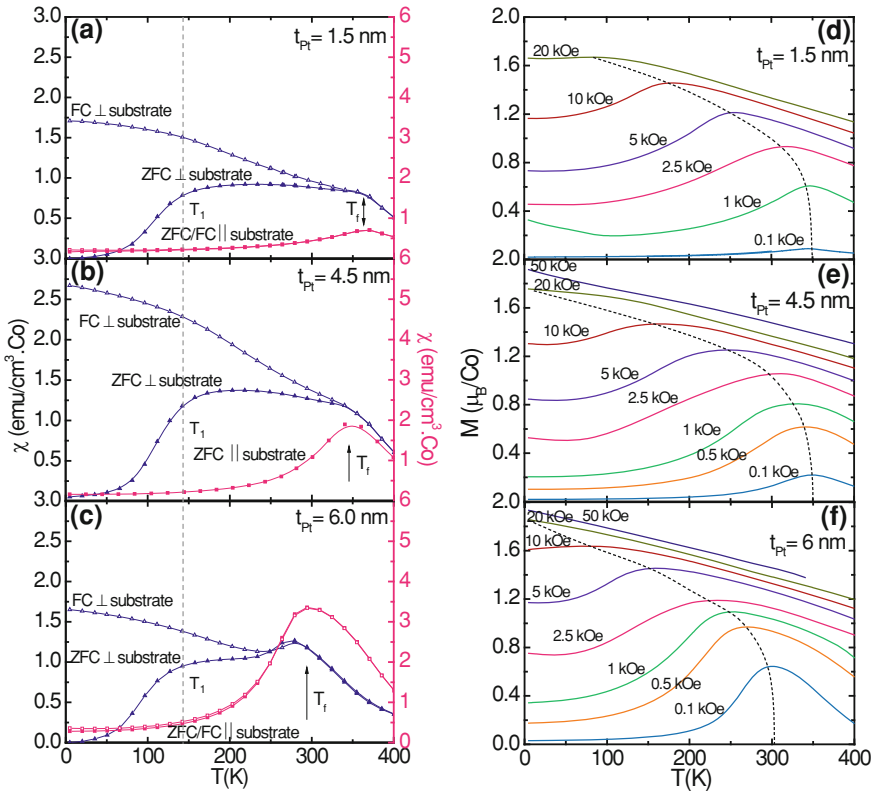


Fig. 5.7 (left panel) DC susceptibility curves measured under an applied field of $H_{\text{dc}} = 200$ Oe perpendicular and parallel to the substrate plane, and (right panel) $M(T)$ at various fields applied in the parallel direction, (H , indicated beside each curve) for samples with $t_{\text{Co}} = 0.7$, $N = 25$, and $t_{\text{Pt}} = 1.5$ nm in (a) and (d), $t_{\text{Pt}} = 4.5$ nm in (b) and (e), and $t_{\text{Pt}} = 6$ nm in (c) and (f). (---) $M(T_f, H)$, superparamagnetic-correlated phase separation line

shape of the curves is very different to that found for the bare Co NPs of the same $t_{\text{Co}} = 0.7$ nm, which show the typical ZFC-FC curve of a superparamagnetic system with a blocking temperature $T_B = 27$ K [27].

In the case of the Co-Pt granular films, the ZFC-FC curves measured in the perpendicular configuration show no overlapping as the temperature increases till it reaches the freezing temperature $T_f = 365, 340$ and 296 K for the samples with $t_{\text{Pt}} = 1.5, 4.5$ and 6 nm, respectively. In fact, three temperature regions are well distinguished from the ZFC curve, namely: (i) an increase of the magnetization with temperature until $T_1 \sim 140$ K for the three samples in the series, which corresponds to the first shoulder observed in the curves in the left panel of Fig. 5.7; (ii) a plateau between T_1 and T_f ; and (iii) a decrease in the magnetization for temperatures above T_f where both ZFC and FC curves merge following a Curie-Weiss law. Values of T_1 and T_f identified for each sample are listed on Table 5.3.

Table 5.3 Summary of the parameters deduced from the magnetic measurements on Co–Pt granular multilayers

t_{Pt} (nm)	T_1 (K)	T_f (K)	T_{He} (K)	$H_{\text{C}\perp}$ (kOe)	$H_{\text{C}\parallel}$ (kOe)	M_{S} (10^{-3} emu/cm 2)	K_{eff} (10^7 erg/cm 3)
1.5	~ 140	350	~ 200	4.0	0.85	2.75	4.80
4.5	~ 140	340	~ 200	3.0	0.46	2.91	2.36
6.0	~ 140	296	~ 200	4.0	0.15	2.64	0.9

Coercive fields saturation magnetization M_{S} and effective anisotropy constant K_{eff} estimated from data measured at $T = 5$ K

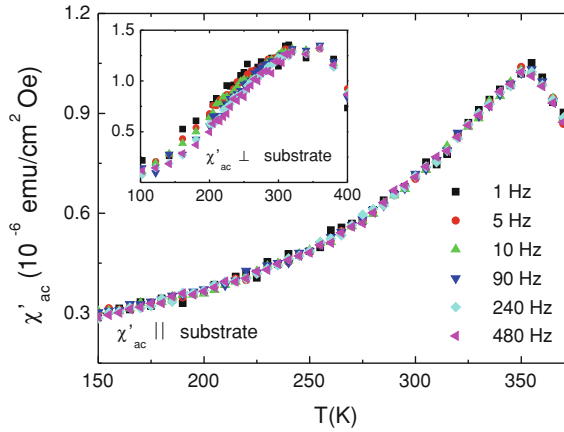


Fig. 5.8 Real part of the ac susceptibility for the sample with $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 1.5$ nm measured with the applied ac field in the parallel configuration as a function of temperature using different excitation frequencies. Inset: analogous ac susceptibility curves measured for the same sample in the perpendicular configuration

In contrast, the ZFC and FC curves measured in the parallel direction overlap even for fields as high as 50 kOe, showing a maximum at T_f , as depicted in the right panel of Fig. 5.7. In all samples, increasing of the external applied field H_{dc} shifts T_f to lower temperatures till the maximum is flattened and all the particles in the film become fully polarized along H_{dc} , as observed in Fig. 5.7. The dependence of T_f with H_{dc} is a monotonously decreasing function $M(T_f, H_{\text{dc}})$, as shown in the right panel of Fig. 5.7. The same cusp at T_f is observed in the real part of the ac susceptibility data, measured with a 4 Oe exciting field, both in the perpendicular and the parallel configuration, as depicted in Fig. 5.8 for the sample with $t_{\text{Pt}} = 1.5$ nm. Between 1 and 480 Hz these data show no dependence on frequency, therefore, the analysis of the magnetic anisotropy performed in Sect. 3.3 from ac susceptibility measurements was not possible for these Co–Pt NPs. In addition, no distinctive features are observed at T_1 from these ac susceptibility measurements.

The field dependence of T_1 and T_f are best observed from the ZFC measured in the perpendicular and parallel configurations, thereby defining the magnetic phase

Fig. 5.9 Magnetic phase diagram of the Co–Pt sample with $t_{\text{Co}} = 0.7$ nm, $t_{\text{Pt}} = 1.5$ nm and $N = 25$, as deduced from $M(T, H_{\text{dc}})$ measurements

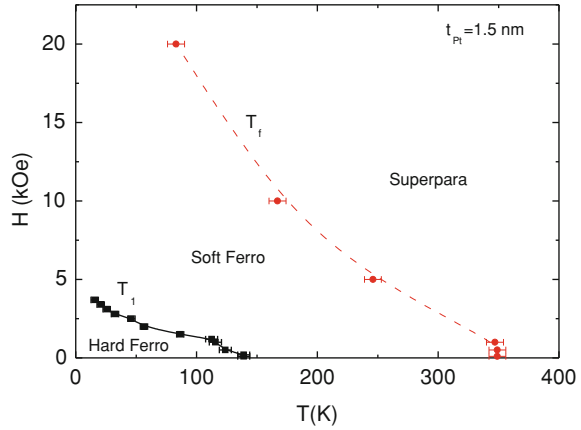


diagram of the multilayer, as illustrated in Fig. 5.9 for a representative sample ($t_{\text{Pt}} = 1.5$ nm). It consists of three magnetic regions, namely: hard ferromagnetic, soft ferromagnetic and superparamagnetic.

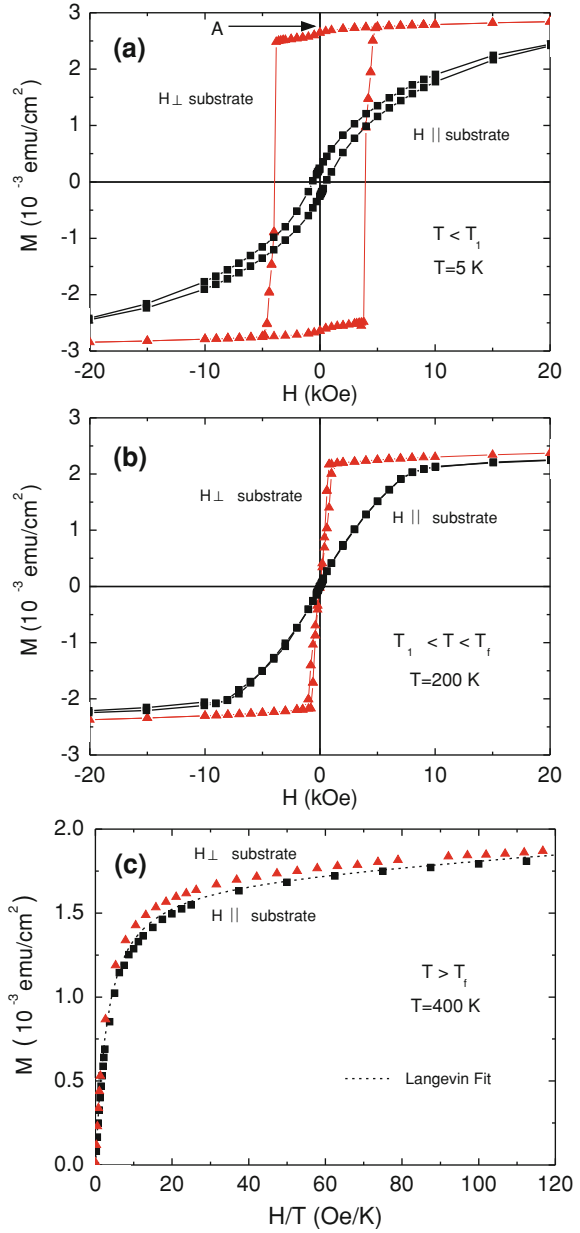
The magnetic behavior of the Co–Pt grains within each region is further understood from the variation of the magnetization with applied field. $M(H)$ curves were measured for all samples with both configurations at several temperatures. Figure 5.10a shows the data recorded at 5 K (i.e., at $T < T_1$) for the sample with $t_{\text{Pt}} = 1.5$ nm. The magnetization is expressed per substrate area, as a usual practice in magnetic recording media and magnetic heterostructures. At low temperatures the hysteresis curves measured in the perpendicular direction are rather square, which indicates the presence of a ferromagnetic hard component, with a quite high coercive field of $H_{\text{C}\perp} = 4, 3$ and 1.9 kOe for the samples with $t_{\text{Pt}} = 1.5, 4.5$ and 6 nm, respectively, at $T = 5$ K. Such a ferromagnetic behavior implies that the Co–Pt particles in the film are strongly coupled.

In addition to the main reversal of the magnetization close to $H_{\text{C}\perp}$, the hysteresis curves measured at low temperatures in the perpendicular direction have a slight step near $H = 0$, which indicates that there is a magnetically soft component present in the sample (see arrow on Fig. 5.10a).

The coercive field measured in the perpendicular direction ($H_{\text{C}\perp}$) decreases with temperature till it disappears at about $T_{\text{Hc}} \sim 200$ K for all samples in the series, as shown in Figs. 5.10b and 5.11. $H_{\text{C}\perp}$ also decreases as t_{Pt} in the sample increases, except for some temperatures near 100 K, where $H_{\text{C}\perp}$ measured for the sample with $t_{\text{Pt}} = 4.5$ nm is higher than that of the sample with $t_{\text{Pt}} = 1.5$ nm. This, in principle, unusual behavior has also been reported for Co/Pt multilayers where an oscillatory dependence of H_{C} with t_{Pt} and N is observed, and has been ascribed to RKKY interactions between the Co layers through Pt [28].

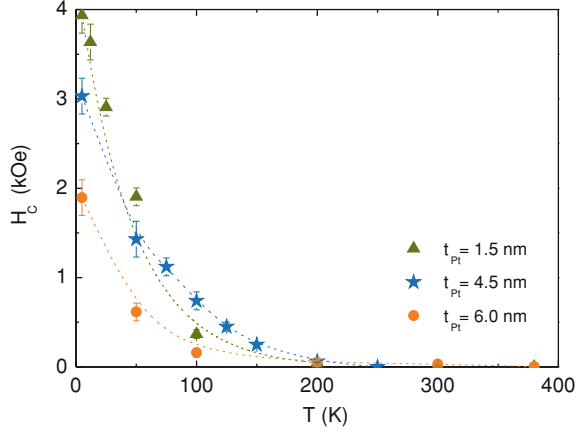
In the direction parallel to the substrate plane the coercive field is much lower, being $0.85, 0.46$ and 0.15 kOe for samples with $t_{\text{Pt}} = 1.5, 4.5$ and 6 nm, respectively, at 5 K (see Fig. 5.10). Such differences between the magnetization curves measured

Fig. 5.10 Magnetization curves measured for the sample with $t_{\text{Co}} = 0.7 \text{ nm}$ and $t_{\text{Pt}} = 1.5 \text{ nm}$, with H_{dc} applied perpendicular ($\blacktriangle$) and parallel ($\blacksquare$) to the substrate: **a** $T = 5 \text{ K}$, **b** $T = 200 \text{ K}$ and **c** $T = 400 \text{ K}$. The dashed line in (c) is the fitted Langevin curve with $\langle D \rangle = 3.5 \text{ nm}$ and $\sigma = 0.4 \text{ nm}$



in orthogonal directions (with the bias field applied parallel and perpendicular to the substrate plane) evidence the presence of perpendicular magnetic anisotropy (PMA) in the Co-Pt samples. The easy magnetization direction has been identified to be the one perpendicular to the substrate.

Fig. 5.11 Temperature dependence of the coercive field measured with H_{dc} applied perpendicular to the substrate plane for the samples with $t_{Co} = 0.7$ nm and **a** ($\blacktriangle$) $t_{Pt} = 1.5$ nm, **b** ($\star$) $t_{Pt} = 4.5$ nm and **c** ($\bullet$) $t_{Pt} = 6$ nm



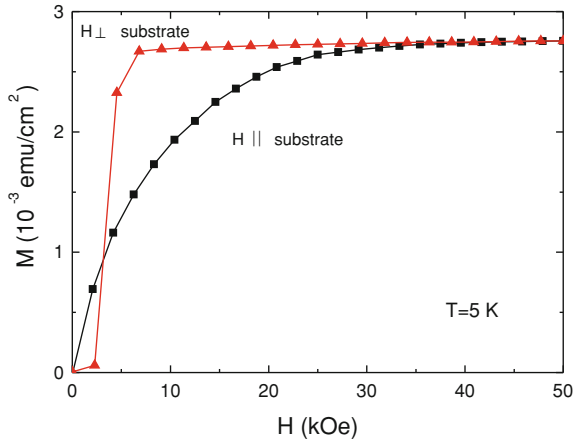
The magnetic anisotropy of the Co–Pt samples can be quantified by analysis of the hysteresis loops measured in the two orthogonal configurations. The magnetic anisotropy energy can be estimated from the area enclosed by the two curves (the parallel and perpendicular configurations), in the first quadrant of the $M(H)$ curve. This area is calculated after averaging the two branches of the hysteresis loop for each configuration [29]. The resulting curves for a representative sample (the one with $t_{Pt} = 1.5$ nm) are plotted in Fig. 5.12. This area yields the quantity $K_{eff}t$, with K_{eff} the effective anisotropy constant and t the film thickness. We have found values of $K_{eff}t = 12(1)$, $13(1)$ and $6(1)$ erg/cm² at $T = 5$ K for the samples with $t_{Pt} = 1.5$, 4.5 and 6 nm, respectively, at 5 K. According to the morphological study described in Sect. 5.2.1, each Co–Pt layer in our films is about 2.5, 5.5 and 6.7 nm thick, for the samples with $t_{Pt} = 1.5$, 4.5 and 6.0 nm, respectively. Then, K_{eff} results in values of 4.8 , 2.36 and 0.9×10^7 erg/cm³ at $T = 5$ K for the samples with $t_{Pt} = 1.5$, 4.5 and 6.0 nm, respectively. K_{eff} decreases with the increase in t_{Pt} , following the same trend as the $H_{C\perp}$ in these samples.

Above T_f the $M(H)$ curves measured in both configurations have the characteristic superparamagnetic behavior, as shown in Fig. 5.10c. These curves can be fitted to a Langevin curve for Co–Pt particle average magnetization, plus a paramagnetic contribution caused by loose Co atoms, following the expression

$$M(H) = \mu \left[\coth \left(\frac{\mu H}{k_B T} \right) - \frac{k_B T}{\mu H} \right] + \chi_o H \quad (5.1)$$

From the fit one obtains the average diameter of the magnetic grain contributing to this magnetization curve. It results in an average diameter of $\langle D \rangle = 3.5$ nm and $\sigma = 0.4$ nm.

Fig. 5.12 Average of the two branches of the hysteresis curves measured for the sample with $t_{\text{Co}} = 0.7 \text{ nm}$ and $t_{\text{Pt}} = 1.5 \text{ nm}$, with H_{dc} applied perpendicular ($\blacktriangle$) and parallel ($\blacksquare$) to the substrate at $T = 5 \text{ K}$



5.3.2 Anomalous Hall Effect Magnetometry

The anomalous Hall effect (AHE) measurement technique is a method frequently used to study the magnetic properties of thin films exhibiting PMA. Measurements of AHE in ferromagnetic granular systems has demonstrated its sensitivity to the local magnetic moments of individual nano-particles [30], so that hysteresis is developed in the Hall voltage versus applied field curve below the blocking temperature of magnetic particles. Thus, by measuring the variation of the hall voltage V_H with the magnetic field applied in the direction perpendicular to the substrate of our Co–Pt NPs samples, hysteresis loops comparable with those of SQUID magnetometry can be obtained.

AHE measurements were performed on two of the Co–Pt NPs samples, those with $t_{\text{Co}} = 0.7 \text{ nm}$, and $t_{\text{Pt}} = 1.5$ and 6.0 nm . These measurements were carried out by Dr. Jolanta Stankiewicz in an electrical transport setup of the Departamento de física de la materia condensada and Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC—Universidad de Zaragoza, and in a Quantum Design Physical Property Measurement System (PPMS) of the Servicio de medidas físicas of the Universidad de Zaragoza.⁶ The measurement configuration is that shown in Fig. 2.3 of Sect. 2.3, with the four contacts placed at the edges of the rectangular samples. The magnetic field was varied within $H = \pm 20 \text{ kOe}$, and applied in the direction perpendicular the substrate. V_H vs. H loops were collected at several temperatures from 2 to 300 K. In Fig. 5.13 we have plotted those $M(H)$ obtained for the two Co–Pt samples at $T = 5 \text{ K}$. These curves show a remarkable squareness and the coercive field coincides well with the one obtained by SQUID magnetometry (see Fig. 5.10). However, the soft component observed in the curves measured in the SQUID magnetometer is not detected by AHE, which instead seems to be very sensitive to the hard

⁶ <http://sai.unizar.es/medidas/index.html>.

Fig. 5.13 AHE hysteresis loops measured at $T = 5$ K and H_{dc} perpendicular to the substrate for the samples with $t_{Co} = 0.7$ nm, $N = 25$, and **a** $t_{Pt} = 1.5$ nm and **b** $t_{Pt} = 6$ nm. Inset in **(b)** details of the first quadrant of the hysteresis loop in **(b)**

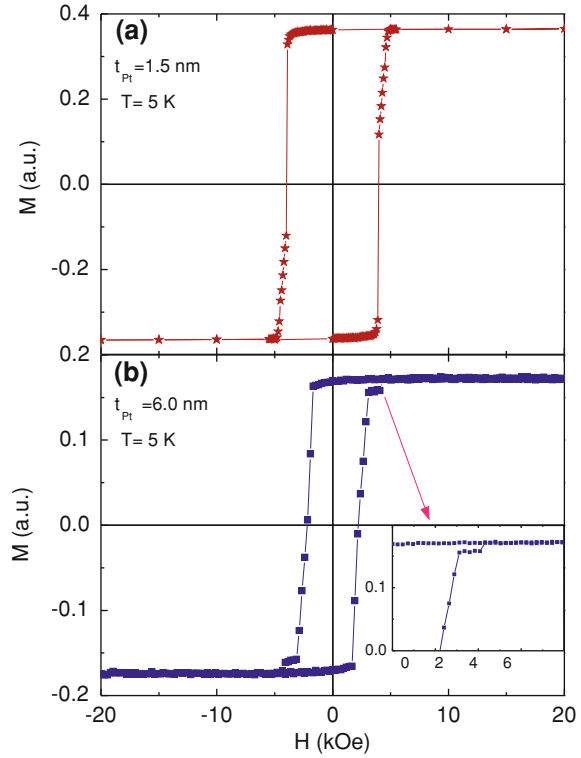
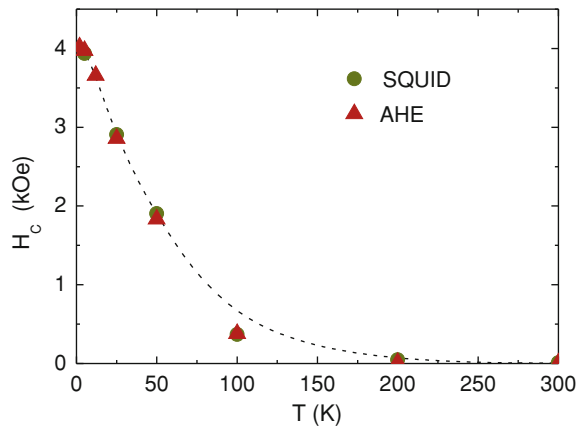


Fig. 5.14 Comparison of the H_C versus T obtained by SQUID (●) and AHE (▲) measurements with H_{dc} applied perpendicular to the substrate plane of the sample with $t_{Co} = 0.7$ nm and $t_{Pt} = 1.5$ nm. Dashed line guide to the eye



component. The H_C values and their temperature dependence obtained by this method perfectly match those observed by SQUID magnetometry in Fig. 5.11, as observed in the direct comparison of H_C versus T for both techniques depicted in Fig. 5.14.

AHE measurements also allow to examine the magnetization reversal mechanisms in our granular films. The inset of Fig. 5.13b reveals details of the switching of magnetization in the sample with $t_{\text{Pt}} = 6.0\text{ nm}$, which was also observed in the hysteresis curve measured in the perpendicular configuration with the SQUID in this sample (data not shown). In the first and third quadrants, the magnetization reversal in this sample apparently proceeds layer by layer. The last layer magnetization reversal involves a variation of $\Delta M_s/M_s = 1/12.1$, where M_s is the saturation moment (measured by SQUID magnetometry). Indeed, if each layer contributes $M_1 = M_s/25$ to the total magnetization, the reversal of the magnetization of one layer will imply a moment difference of twice this quantity.

5.3.3 X-ray Magnetic Circular Dichroism Magnetometry

XANES and XMCD measurements at the Co K (7709 eV), Pt L_3 (11564 eV) and Pt L_2 (13273 eV) edges on the Co–Pt NPs sample with $t_{\text{Co}} = 0.7\text{ nm}$ and $t_{\text{Pt}} = 1.5\text{ nm}$ were performed at the ESRF ID12 beamline. The APPLE-II undulator and a double—Si-(111)—crystal monochromator were used to collect the spectra at the respective energies. XANES spectra were recorded by a fluorescence detector in backscattering geometry. Polarization of the circular light was over 90 % in these cases.

XANES and XMCD experiments at the Co L_3 (778.1 eV) and Co L_2 (793.2 eV) edges on the same Co–Pt NPs sample were performed at the ID08 beamline of the ESRF. An APPLE-II undulator and a spherical grating monochromator were used in this case. The degree of polarization at these Co $L_{2,3}$ edges was $\sim 100\%$ and the total electron yield (TEY) detection method was employed.

The XMCD signal at each edge was obtained by applying a magnetic field of 10 kOe along the X-ray beam direction, at a temperature of 10 K. This field and temperature were chosen according to the magnetic properties of the Co–Pt NPs, so that the system was reaching its magnetic saturation under these conditions (see Sect. 5.3.1). XMCD was obtained by differences of XANES spectra measured with opposite helicities of the light at a fixed magnetic field value, orienting the field in two inverse directions.

5.3.3.1 Co K Edge Results

XANES and XMCD at the Co K edge probes the $4p$ empty states of the Co atom in the sample. Analysis of the XANES spectra recorded at this edge on these Co–Pt samples was described in Sect. 5.2.2. Evidences of Co $4p - 3d$ and Co $3d - \text{Pt } 5d$ hybridization in the Co–Pt granular samples and electronic transfer from Pt $5d$ to Co orbitals were then described. As described for the XMCD at the Co K edge in the Co–W NPs (Sect. 4.1.1), the detection of a nonzero XMCD signal at the Co K edge reflects the magnetic polarization of the Co $4p$ band caused by the intra-atomic exchange interaction with the $3d$ band. The XMCD signal recorded at this edge for

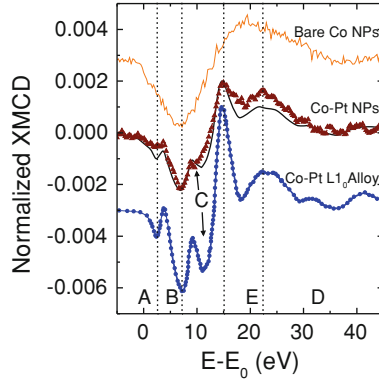


Fig. 5.15 Co K edge XMCD signal measured in the Co-Pt granular film ($\blacktriangle$) with $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 1.5$ nm and comparison to that of a Co-Pt $L1_0$ alloy ($\bullet$) from Ref. [32] and for bare Co NPs ($-$) with the same t_{Co} . Solid line corresponds to a fit of the XMCD for the Co-Pt granular film, as a linear combination of the other two curves. Curves are shifted vertically for the sake of clarity

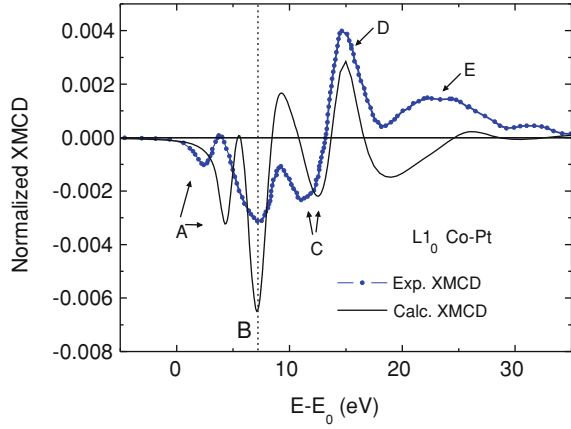
the Co-Pt granular sample is shown in Fig. 5.15, normalized to the absorption jump obtained in the Co K XAS spectrum after background removal. It has the same sign as the Co K XMCD reported in Ref. [31], which results in an antiferromagnetic coupling between $4p$ and $3d$ levels in Co.

The shape of XMCD signal in Fig. 5.15 is very similar to the one reported for ion irradiated Co-Pt films in Ref. [32]. In those Co-Pt films, changes in the electronic structure of Co atoms related to the formation of $\text{Co}_x\text{Pt}_{1-x}$ alloys induced by ion irradiation were observed. Striking similarities between the XMCD spectra of the Co-Pt films and a $\text{Co}_{0.5}\text{Pt}_{0.5}$ $L1_0$ thin-film reference sample were shown, in terms of characteristic peaks at selected energies. This allowed to interpret the XMCD spectrum for the irradiated Co-Pt film as the superposition of pure Co and $L1_0$ $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy contributions.

Similarly, in our Co-Pt samples we may state that the Co K edge XMCD signal that we observe is a combination of these two phases. This is illustrated in Fig. 5.15, where a direct comparison of the XMCD recorded for our Co-Pt granular films with that of a Co-Pt $L1_0$ alloy (from Ref. [32]) and for bare Co NPs with the same t_{Co} is performed. Features of the metallic Co XMCD, such as the peak denoted as B in the figure, are identified in the three curves. Peaks A, C, D and E are common in both the Co-Pt alloy and our Co-Pt granular films, supporting the presence of this alloy in our Co-Pt samples.

Indeed, we have been able to fit the experimental XMCD spectrum obtained at the Co K edge of the Co-Pt granular films (GF) as a linear combination of two empirical reference contributions: the experimental XMCD signal from Co bare NPs (of the same nominal size than those studied in this thesis) and the XMCD $\text{Co}_{0.5}\text{Pt}_{0.5}$ $L1_0$ thin-film reference sample from Ref. [32]. To do so we have fitted both references with a sum of a number of lorentzian curves sufficient to reproduce the spectral features

Fig. 5.16 (●) Experimental and (—) calculated XMCD signal at the Co K edge for a Co–Pt L_{10} alloy. Experimental data from Ref. [32]



in detail. Later on, the experimental data have been fitted to a linear combination of the two analytical reference functions

$$\text{XMCD}_{\text{exp}}^{\text{GF}}(E) = a \text{XMCD}_{L_{10}}(E) + b \text{XMCD}_{\text{Co}}(E) \quad (5.2)$$

The best fit to the Co–Pt data, shown as a solid line in Fig. 5.15, is obtained with $a = 0.58(2)$ and $b = 0.42(3)$, suggesting that approx. 60% of the cobalt initially deposited on the films alloys with Pt upon its deposition.

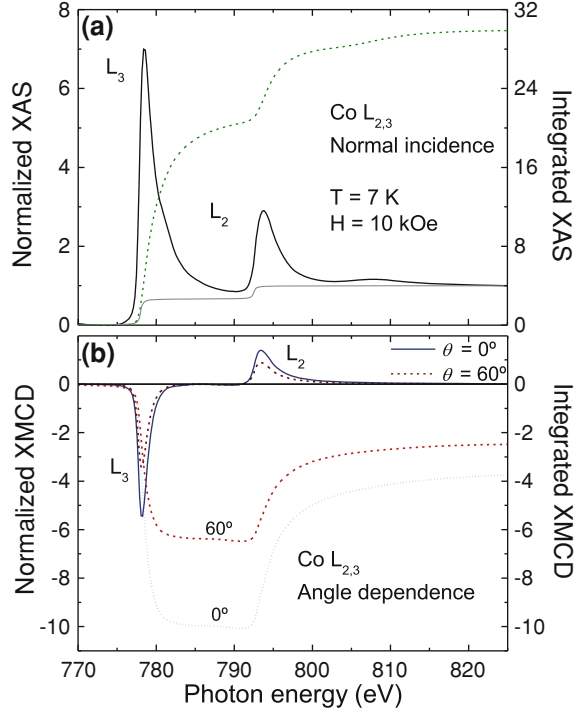
Peaks A–D are characteristic of the L_{10} Co–Pt alloy as it is observed in the direct comparison of both experimental (from Ref. [32]) and calculated L_{10} $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy the Co K edge XMCD signal plotted in Fig. 5.16. The absorption cross section was calculated self-consistently with the fully relativistic FDMNES code [33, 34] in the framework of multiple scattering theory within the muffin tin approximation. The structural and crystallographic information of the L_{10} $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy system used to define the position of the absorbing and scattering atoms in the calculations is the one previously described in Sect. 5.2.2. A cluster of 7 Å radius and a Fermi level of about 7701 eV were used. The calculated absorption cross section were normalized at the same edge jump as in the experiment.

Therefore, XMCD at the Co K edge manifests the existence of both metallic Co and a L_{10} $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy in our Co–Pt granular samples, supporting our EXAFS results (see Sect. 5.2.2).

5.3.3.2 Co $L_{2,3}$ Edges Results

XMCD measurements at the Co $L_{2,3}$ edges as a function of the incident angle ($\theta = 0^\circ$ and 60° , with respect to the sample surface normal) have been performed, looking for anisotropy of the orbital moment. Figure 5.17a shows the Co $L_{2,3}$ XAS recorded at normal incidence, and Fig. 5.17b the XMCD signal obtained for each angle. The

Fig. 5.17 Co– $L_{2,3}$ edges spectra of the $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 1.5$ nm sample. **a** (–) Normalized XAS spectra mean curve measured at normal incidence. (–) The double-step function used is also indicated. (–) Integrated white line. **b** Angle dependent normalized XMCD spectra: (–) normal incidence and (–) 60° . The integrated area of each XMCD signal is also plotted



XMCD signal has been normalized to the XAS spectrum in high energy limit, after background subtraction. We observe a clear angle dependence of the XMCD, which is also reflected in the variation of their integrated intensity (shown in Fig. 5.17b). The angle dependent XMCD reveals the PMA in the film since its intensity, proportional to the magnetization component parallel to the x-ray beam, is larger for the normal incidence than that at $\theta = 60^\circ$. These results are similar to the angle dependent Co $L_{2,3}$ XMCD observed for ion irradiated Co–Pt films with PMA in Ref. [18].

The anisotropy of the orbital moment is analyzed from the estimation of the in-plane and out-of-plane components of the orbital magnetic moment, $m_L^\parallel$ and $m_L^\perp$, respectively, from the angle dependent XMCD data. The orbital moment at each measured angle m_L^θ , as obtained from the magneto-optical sum rule [35], is expressed as

$$m_L^\theta = m_L^\parallel \sin^2 \theta + m_L^\perp \cos^2 \theta \quad (5.3)$$

However, in order to apply the magneto-optical sum rules [35, 36] to the XMCD signal in Fig. 5.17b, the number of unoccupied states in the $3d$ band for Co n_h is required in the calculations, as described in previous chapters. Values of $3d$ n_h reported in the literature are, for example, $n_h = 2.49$ for metallic Co [37] and $n_h = 2.628$ for $\text{Co}_{0.5}\text{Pt}_{0.5}$ $L1_0$ alloy films [12]. Let us recall that the Co atoms

in our Co–Pt granular samples are found to be in these two different environments (metallic Co and $\text{Co}_{0.5}\text{Pt}_{0.5}$ $L1_0$ alloy), but we are not able to quantify each of them. Therefore, the right number of $3d$ holes in Co atoms of our Co–Pt samples is unknown. Thus, we have expressed the orbital moment as per $3d$ hole in the Co atoms. In addition, we have used the integrated $3d$ isotropic absorption cross section R as the one measured in the normal direction (since it is angle independent) following the criteria of Ref. [12]. We obtain $m_L^\parallel/n_h = 0.05(1) \mu_B$ and $m_L^\perp/n_h = 0.08(1) \mu_B$ from the application of the orbital sum rule to the XMCD at the two incident angles ($\theta = 0^\circ$ and 60°).

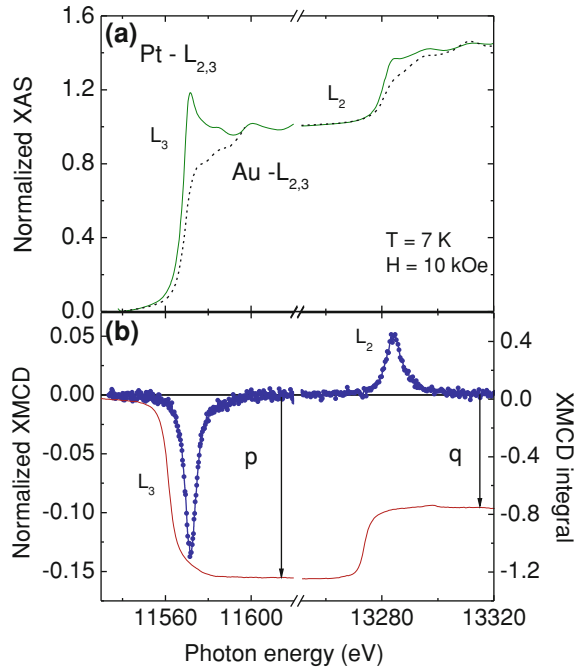
From the spin sum rule, [36] we derive an effective spin magnetic moment per $3d$ hole of $m_{\text{Seff}}/n_h = 0.77(1) \mu_B$, at $\theta = 0^\circ$. This value is comparable to the $m_{\text{Seff}}/n_h = 0.75 \mu_B$ per Co atom obtained for a $\text{Co}_{0.5}\text{Pt}_{0.5}$ $L1_0$ alloy film in Ref. [12]. In order to obtain m_S/n_h , one has to take into account the contribution of the angular dependent magnetic dipole term m_D since the $\text{Co}_{0.5}\text{Pt}_{0.5}$ $L1_0$ structure is highly anisotropic [12]. The angular dependence of m_{Seff} is analogous to that of m_L defined by Eq. 5.3. At the so called “magic angle” (57.3°) m_D vanishes so that $m_{\text{Seff}} = m_S$ [12, 38]. Thus, by applying the spin sum rule to the XMCD signal obtained at the two measured angles ($\theta = 0^\circ$ and 60°) in our Co–Pt granular films, we have derived $m_{\text{Seff}}/n_h(57.3^\circ) = m_S/n_h = 0.51(1) \mu_B$. Finally, at $\theta = 0^\circ$ $m_L/m_{\text{Seff}} = 0.11(1)$ and $m_L/m_S = 0.16(1)$, being of the same order of that for a $\text{Co}_{0.5}\text{Pt}_{0.5}$ $L1_0$ alloy film ($m_L/m_S = 0.15$) [12].

XMCD measurements at the Co $L_{2,3}$ edges on $\text{Co}_x\text{Pt}_{1-x}$ particles prepared by vapor deposition have been recently reported [39, 40]. They find m_L/m_S ranging between 0.10 and 0.14 on particles of comparable size to ours, depending on the composition of the Co–Pt alloy present. Then, the m_L/m_S (for $\theta = 0^\circ$) is higher in our Co–Pt samples. With reference to other XMCD studies in Co–Pt systems, our m_L/m_S in Co is also larger, as compared to CoPt_3 films deposited on a substrate at 800 K ($m_L/m_S = 0.09$) [11], and for annealed $\text{Co}_{0.5}\text{Pt}_{0.5}$ NPs with diameters of about 2.6 nm deposited on amorphous carbon matrices ($m_L/m_S = 0.094$) [2].

5.3.3.3 Pt $L_{2,3}$ Edges Results

The XMCD spectra measured at the Pt $L_{2,3}$ edges are shown in Fig. 5.18. The non-zero values of the XMCD signal reflects the polarization of the Pt by the magnetic Co. From an XMCD experiment at the Pt $L_{2,3}$ edges one obtains, through the sum rules [35, 36], the spin m_S and orbital m_L moments averaged over the whole sample, provided one knows by calculation or estimation the number of holes, n_h , involved in the $2p \rightarrow 5d$ excitations. For Pt we have derived n_h from the white line difference with a Pt foil at the $L_{2,3}$ edges XANES, similarly to the procedure followed for XANES at the W $L_{2,3}$ edges in Sect. 4.1.2. We have obtained $n_h = 1.80(2)$ holes in the $5d$ band, $m_S = 0.14(1) \mu_B$, $m_L = 0.027(2) \mu_B$, and $m_L/m_S = 0.19(1)$ for Pt atoms in the Co–Pt NPs.

Fig. 5.18 (–) Normalized XANES (a) and (•) XMCD (b) at the Pt $L_{2,3}$ edges in the Co–Pt NPs. (–) XMCD integrated area. (– –) The XANES spectrum of Au $L_{2,3}$ edges is shown in (a) for comparison. The higher limit for the p and q integrals, used for the sum rules analysis, is given in (b)



The induced moment on Pt $m_{\text{tot}} = 0.16(1) \mu_B$ is one order of magnitude larger than the moments induced on the Cu, Ag or Au capping cases [41]. Obviously, the reason for this difference is the proximity of Pt, with the $5d^9$ band, to fulfill the Stoner criterion for ferromagnetism [42], instead of the nearly filled noble metal nd^{10} bands ($n = 3, 4$ and 5 for Cu, Ag or Au, respectively).

However, it is important to point out that not all Pt atoms in the Co–Pt NPs of the measured sample ($t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 1.5$ nm) are alloyed or in contact with Co atoms, as described in the HRTEM and EXAFS measurements (see Sect. 5.2) performed in this sample. As a result, it is possible that not all Pt atoms in the sample are polarized by Co. Only those polarized Pt atoms contribute to the Pt $L_{2,3}$ XMCD signal, but all Pt atoms in the sample are reflected in the Pt $L_{2,3}$ XAS. Since the XMCD results are scaled to the Pt $L_{2,3}$ XAS spectra, the m_S and m_L results from Pt XMCD may be lower than the actual ones. The m_L/m_S ratio depends only on the XMCD integral values (see Sect. 2.4.2), so it is not affected by the Pt $L_{2,3}$ XAS scale and we may rely on that value.

Comparing to XMCD measurements at the Pt $L_{2,3}$ edges reported in the literature, the m_L/m_S ratio in the $5d$ band of Pt in our Co–Pt NPs is close to those values obtained for CoPt₃ films in Ref. [11] ($m_L/m_S = 0.18$ – 0.26), but lower than those of Co_{0.5}Pt_{0.5} L1₀ alloy films ($m_L/m_S = 0.27$) [12].

5.3.3.4 Element-Specific Magnetic Hysteresis Measured by XMCD

One important advantage of the selective magnetometry using the XMCD technique is the possibility of performing element-specific magnetic hysteresis measurements. It consists in recording the dichroic signal for a fixed energy while the applied magnetic field is varied, similarly to the magnetization hysteresis measurements with conventional magnetometers. This way it is possible to evaluate the contribution of each atomic species to the magnetic properties of the material. We have performed XMCD(H) at the Co K and Pt $L_{2,3}$ edges on the same sample of Co–Pt NPs with $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 1.5$ nm. Measurements were done at the ESRF ID12 beamline, with the same technical details than in the conventional XMCD experiments described above.

Figure 5.19 shows the XMCD spectra recorded at 12 K in normal incidence at the Co K and Pt $L_{2,3}$ edges, from which XMCD(H) measurements have been performed. The energies at which XMCD(H) were collected were 7723.9 eV and 11571.5 eV for Co K and Pt L_3 edges, respectively (see arrows in Fig. 5.19). The insets in Fig. 5.19 illustrate the curves obtained for each edge. Notice that both hysteresis loops are squared, with a coercive field around 3.6 kOe in both cases, which are consistent with those curves measured by SQUID (Sect. 5.3.1) and AHE (Sect. 5.3.2) techniques. The agreement in the H_C values obtained by XMCD(H) is an indicative that Co and Pt atoms in the Co–Pt NPs are strongly magnetically coupled, as resulting from the Co–Pt alloy in the sample. Both Co and Pt atoms are responsible of the magnetic hard component measured in the sample with the magnetic field in the perpendicular configuration. No clear observation of the soft component has been detected in these measurements.

The decay of the H_C values with increasing temperature has been also examined from the XMCD(H), by measuring the hysteresis loop at the Co K edge at $T = 150$ K. In Fig. 5.20 we have plotted the XMCD(H) curves at 12 K and 150 K to illustrate the

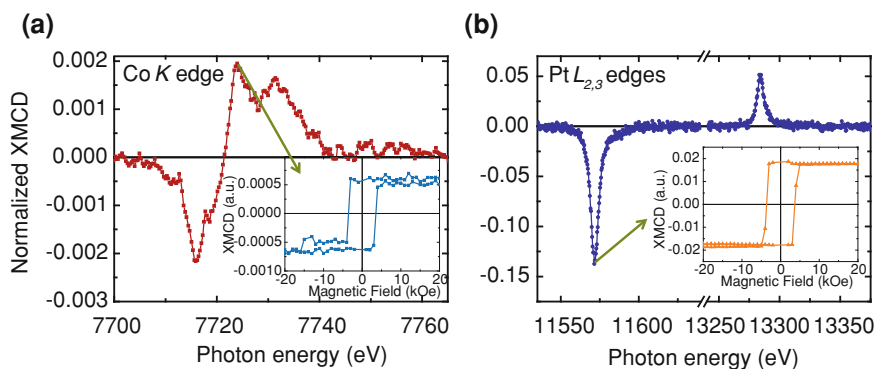
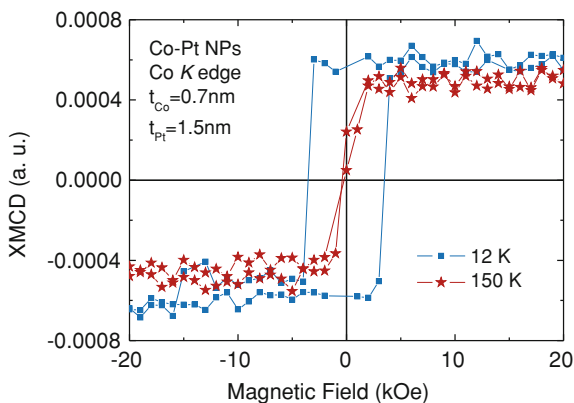


Fig. 5.19 XMCD signal and magnetic hysteresis loops measured at the selected energy in the Co–Pt NPs with $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 1.5$ nm: **a** Co K edge and **b** Pt $L_{2,3}$ edges

Fig. 5.20 Magnetic hysteresis loops measured at $T = 12$ K (■) and 150 K (★) at the selected energy of the XMCD Co K edge in the Co–Pt NPs with $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 1.5$ nm



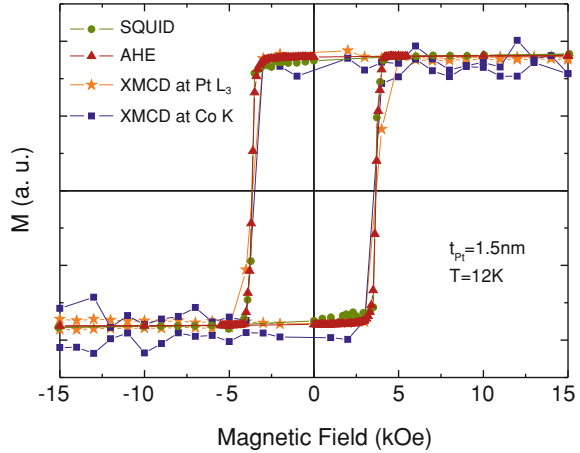
reduction in H_C , from 3.6 kOe down to 0.39 kOe. This behavior is consistent with that observed by SQUID and AHE measurements (see Fig. 5.14).

5.4 Discussion

The formation of a $\text{Co}_x\text{Pt}_{1-x}$ alloy in our Co–Pt granular films has been proven by XANES and EXAFS measurements at the Co K and Pt L_3 edges. It results from the interdiffusion of Co atoms from the previously formed Co clusters towards the Pt matrix, as observed in other Co–Pt systems produced by sputtering [13] and LECBD [43] at room temperature. The composition of the $\text{Co}_x\text{Pt}_{1-x}$ alloy present in all Co–Pt granular samples seems to be close to $\text{Co}_{0.5}\text{Pt}_{0.5}$, according to the EXAFS results. In fact, the morphology of our Co–Pt granular samples may be visualized as that of a $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy surrounding the Co rich core, embedded in metallic Pt, in view of the particulate morphology of the Co–Pt layers observed by TEM and the structure described by EXAFS measurements. Recent calculations of core-shell morphologies in CoPt nanoparticles [44, 45] have demonstrated that the Co core - $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy shell, with some segregation of Pt atoms to the particle surface, is one of the most energetically stable configurations of NPs with diameter close to 3 nm (clusters of ~ 1000 atoms).

The presence of this alloy in our Co–Pt granular films gives rise to a quite different magnetic behavior than the blocked superparamagnetic one observed in Co–M NPs with $M=\text{Cu, Ag, Au}$ and W [41, 46]. The different magnetometry techniques employed to study the Co–Pt granular films reveal the presence of PMA in all the samples in the series (see Fig. 5.21). Similar PMA behavior has been observed in several Co–Pt multilayer systems [6–9], $\text{Co}_x\text{Pt}_{1-x}$ alloy films [10–13], and nanopatterned Co–Pt systems [14], and is correlated to the structure of the alloy present in the sample. For instance, CoPt alloys with composition close to $\text{Co}_{0.5}\text{Pt}_{0.5}$ may have a disordered *fcc* structure or a chemically ordered tetragonal structure $L1_0$. Both

Fig. 5.21 Comparison of the magnetic hysteresis loops measured at $T = 12$ K with different techniques in the Co–Pt NPs with $t_{\text{Co}} = 0.7$ nm and $t_{\text{Pt}} = 1.5$ nm: (●) SQUID magnetometry, (▲) AHE, (★) XMCD at the Pt L_3 edge, and (■) XMCD at the Co K edge



phases are ferromagnetic and the c axis of the $L1_0$ is an easy direction of magnetization. Co–Pt films grown with this $L1_0$ phase show PMA [12]. Therefore, one may identify the PMA appearing on our Co–Pt samples as due to the formation of $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy with short range ordering in the $L1_0$ structure. The XMCD data also point towards the same interpretation, since it allowed to demonstrate that the origin of the PMA in our Co–Pt films is at the anisotropy of the orbital moment, as it has been observed on different Co–Pt systems in the literature [12, 18]. The polarization of the Pt atoms (identified from XMCD measurements) as consequence of the Co $3d$ –Pt $5d$ hybridization in the Co–Pt films also plays an important role in this anisotropic properties. It results from the strong Pt spin-orbit coupling ($\xi_{5d} = 0.66$ eV) [47] that favors a large perpendicular magnetocrystalline anisotropy in Co–Pt systems, as observed in $L1_0$ $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy films [12].

The anisotropy constant of Co–Pt alloy films at $T = 5$ K with such an ordered structure is on the order of $K_{\text{eff}} = 10^7$ erg/cm³ [12, 18]. The K_{eff} values estimated for our Co–Pt granular films (see Sect. 5.3.1) are found to be of this same order (1 – 4.8×10^7 erg/cm³). These values are in contrast to lower K_{eff} obtained for Co–Pt clusters prepared by LECBD with highly ordered $L1_0$ structure, for which $K_{\text{eff}} = 0.19 \times 10^7$ erg/cm³ for as-prepared and $K_{\text{eff}} = 0.38 \times 10^7$ erg/cm³ for annealed particles.

According to the phase diagram showed in Fig. 5.9, the temperature dependence of the magnetic behavior of the granular Co–Pt films can be divided into three magnetic regions, namely:

- Region (i), $0 < T < T_1$: this region has the characteristic behavior of ferromagnetic granular layers, with interlayer ferromagnetic coupling. This statement is supported by the square shape of the hysteresis curves and the high $H_{C\perp}$ values obtained at $T = 5$ K when the field is applied perpendicular to the substrate (see Fig. 5.21). These squared curves also demonstrate that the Co–Pt grains in the samples are strongly magnetically coupled. In all cases studied the samples show

strong PMA anisotropy (see Fig. 5.10). In fact, the inversion of the film magnetization direction upon reduction and switching sign of the applied field perpendicular to the sample plane takes place in steps (see Fig. 5.13b). This is a proof that each layer acts as a ferromagnetic system coupled to the adjacent ones by a weaker inter-action. The difference between the FC and ZFC curves is ascribed to the pinning of the ferromagnetic domain walls. The most probable intra-film interaction between the grains is of long range RKKY type through the connecting Pt metal. We support this statement by the observation of magnetically polarized Pt by means of XMCD measurements at the Pt $L_{2,3}$ edges. Besides, in the hysteresis curves there is some evidence of a soft magnetic Co core (see feature A in Fig. 5.10a). As the temperature increases approaching T_1 , the intra film grain-grain interaction weakens and the coercive field decreases, being zero at a temperature of $T_{Hc} \approx 200$ K in all samples. As the bias field increases this hard ferromagnetic phase tends to be quenched and actually disappears at the $H_{dc} \geq H_C$, as T tends to zero (see Fig. 5.7); i.e., when the applied field orients all ferromagnetic domains parallel to its direction and the magnetization is saturated. This common behavior to all samples suggests that the magnetic hard component is the same along the series.

- Region (ii), $T_1 < T < T_f$: this state is very distinctive in having no coercivity, in contrast to region (i). However, the hysteresis curve measured with the field in the perpendicular configuration, $M_{\perp}(H)$, is also very square, while the one measured with the parallel configuration, $M_{\parallel}(H)$ has a rounded shape, (see Fig. 5.10b). Thus, it behaves as a soft ferromagnet with PMA. The absence of coercivity can be related to the weakening of the inter-grain interactions so that the grains are predominantly magnetically coupled within the layer with short range correlations. Since the coercive field becomes lower than the dc applied field, the ZFC magnetization increases towards the FC curve, as in amorphous asperomagnets [48]. This intermediate behavior is sustained for increasing temperature till a maximum in the $M_{\perp}(H)$ curve indicates the freezing temperature T_f , where the FC-ZFC curves merge. For increasing bias field the intermediate phase range reduces since T_f decreases till actual disappearance for an applied field of about 20 kOe. This phase can be described as an asperomagnetic-like phase in which the spins are oriented in fixed directions, with most nearest-neighbor spins parallel or nearly parallel, so that the spin directions are distributed in one hemisphere below a T_f temperature. As the bias field increases, region (ii) tends to disappear by polarization of all moments along the applied field direction.
- Region (iii), $T > T_f$: intergrain interactions in this region become very weak with respect to the thermal energy and the behavior becomes that of an isotropic superparamagnet as evidenced by the two identical $M(H)$ curves, irrespective of field orientation (see Fig. 5.10c). They are fitted very well for the prediction of $M(H)$ for a collection of independent particles subject to an external field.

Evidently, the intergranular Pt plays an important role in establishing short and long range correlations. At a coverage of $t_{Pt} = 1.5$ nm the interaction is ferromagnetic due to the percolated metallic Pt matrix that supports the CoPt alloyed grains. At

larger cappings, and specially at $t_{Pt} = 6$ nm the excess of Pt filling all intergranular spaces has the effect of decoupling the CoPt correlated grains. Interestingly, the value of T_f decreases and the effective anisotropy K_{eff} decrease with increasing nominal Pt thickness (see Table 5.3). In an interesting paper on the intergranular interactions caused by the interspatial metallic Pt in a monolayer of Co–Pt granular film, similar features, such as the existence of an intermediate region at $T_l < T < T_f$ and the weakening of the interaction when an excess of Pt is present, are found for t_{Pt} comparable to our case [49]. Therefore, and similarly to the Co–Pt granular films described in Ref. [49], the coupling/decoupling between our Co–Pt grains can be tailored by variation of the amount of Pt (t_{Pt}) in the samples.

Finally, we can compare the XMCD results in our Co–Pt granular films with those of recent calculations of the spin magnetic moments of Co and Pt atoms in Co core - Co_{0.5}Pt_{0.5} alloy shell clusters of similar sizes [44, 45]. For the latter, values of $m_S^{Co} = 1.85\text{--}1.96 \mu_B/\text{Co atom}$ and $m_S^{Pt} = 0.26\text{--}0.42 \mu_B/\text{Pt atom}$ are obtained [44, 45]. We have estimated the spin moment in Co in our Co–Pt granular films to range between $m_S^{Co} = 1.27\text{--}1.34 \mu_B/\text{Co}$, assuming the number of unoccupied states in the 3d band for Co to be between the $n_h = 2.49$ holes for metallic Co [37] and $n_h = 2.628$ for Co_{0.5}Pt_{0.5} L1₀ alloy films [12]; thus, the m_S^{Co} in our Co–Pt system is lower than that calculated for clusters of similar morphology. In the case of m_S^{Pt} , the deviation of the $m_S^{Pt} = 0.14(1) \mu_B$ value for our Co–Pt samples from that calculated in Refs. [44, 45] may be related to the difference between the actual amount of Pt in the samples that is polarized by Co and contributes to the XMCD signal, as described in Sect. 5.3.3. Alternatively, for the sake of comparison, we may estimate the total magnetic moment induced in the Pt atoms m_T^{Pt} in our Co–Pt samples from the difference between the total magnetic moment contributing to the saturation magnetization measured in the SQUID and that of the total magnetic moment in Co atoms obtained from XMCD. Following this procedure, we obtain values of $m_T^{Pt} = 0.2\text{--}0.25 \mu_B/\text{Pt atom}$ which are closer to the $m_S^{Pt} = 0.26\text{--}0.42 \mu_B/\text{Pt atom}$ values from the calculations.

5.5 Conclusions

The overall picture describing the Co–Pt granular films obtained by room temperature sequential sputtering deposition is that of a Co-core with a Co–Pt alloy shell particles, embedded in the non-reacted Pt. The alloy between the Co and Pt results from interdiffusion of the atoms, similarly to what is observed in other Co–Pt systems [13]. The short range order within the grains creates the anisotropy in the Co_{0.5}Pt_{0.5} alloy, giving rise to the PMA, as consequence of the anisotropy of the orbital moment of the Co atoms in this alloy. The PMA in our Co–Pt films is on the order of 10^7 erg/cm^3 , comparable to that of highly ordered CoPt L1₀ alloy films [12]. The polarization of the Pt atoms is observed by XMCD measurements and has been demonstrated to have an important role in the magnetic behavior of the Co–Pt granular films, not only in their anisotropic properties, but also in the magnetic coupling between the grains. The collective magnetic behavior of the Co–Pt granular films is temperature depen-

dent, namely: below T_1 the granular sample is ferromagnetic with a high coercive field; for $T_1 < T < T_f$ the granular film behaves as an amorphous asperomagnet, with a coupling between the grains mediated by the Pt; and above T_f the sample has a superparamagnetic behavior. The coupling/decoupling between the grains in our Co–Pt granular films can be tailored by variation of the amount of Pt in the samples. Finally, given that our results differ from those of other Co–Pt NPs systems and Co–Pt granular films prepared by different chemical and physical methods [2, 39, 40, 49], we may conclude that the sample preparation of Co–Pt nanostructures plays an important role in the short range ordering of the Co and Pt atoms, which strongly influence their magnetic properties.

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Chapter 6

d-Band Magnetism of Ag, Au, Pd and Pt Nanostructured Materials

In this chapter we review the interesting magnetic properties of metals (M) that are not magnetic in bulk form, but when shaped in reduced dimensions. In particular, we describe the magnetic behavior of Ag, Au, Pd and Pt nanoparticles. They have in common an incompletely filled $4d$ - (Ag, Pd) or $5d$ -band (Au, Pt), that gives rise partially to this type of magnetism. By means of X-ray magnetic circular dichroism (XMCD) measurements at the Metal- $L_{2,3}$ edges, the orbital and spin contributions to the magnetic moment stemming from the d -band are explored.

6.1 Magnetism in Bulk Metals

The understanding of the magnetism of metals has attracted the attention of physicists for decades, and, as a result, very successful theories and models have been proposed to explain it. The magnetic properties of a metal in the solid state in bulk scale may be rationalized in terms of the spin-split density of states DOS. The Stoner criterion of stability with respect to ferromagnetism in metals states that long range ordering is possible only when the Stoner parameter (repulsion between electrons of opposite spin) I , times the density of states at the Fermi energy $D(\epsilon_F)$ is larger than 1 [1].

As free atoms, the noble metals Ag and Au, and Pd have a full electronic d -band, Ag:[Kr] $4d^{10}5s^1$, Au:[Xe] $4f^{14}5d^{10}6s^1$ and Pd:[Kr] $4d^{10}$, respectively, while Pt has a hole in the $5d$ orbit; Pt:[Xe] $4f^{14}5d^96s^1$. In the solid state, though, Ag and Au metals have a very shallow $D(\epsilon_F)$ and, correspondingly, are non-magnetic, on one hand; Pd and Pt have a maximum in $D(\epsilon_F)$ but do not fulfill the Stoner criterion and remain paramagnetic, on the other hand. This is due to the hybridization between the d -band and the sp -bands, which generates a small, albeit non-negligible number of holes, n_h^d , in the d -band. This parameter varies between $n_h^d = 0.349$ holes for Ag and $n_h^d = 1.635$ holes for Pt, and increases in the trend Ag < Au < Pd < Pt (see Table 6.1). As a result, the four metals have a partially filled d -band.

In non-magnetic metals the magnetic susceptibility response to an applied field can be explained as due to several contributions:

$$\chi_{total} = \chi_{dia} + \chi_{Landau} + \chi_{Pauli}^s + \chi_{orb}^{SO} + \chi_{orb}^{KO} \quad (6.1)$$

χ_{dia} is the diamagnetic susceptibility of the electrons in the core states, χ_{Landau} is the diamagnetic contribution due to the conduction band that splits into discrete Landau transversal orbits upon application of an external field, χ_{Pauli}^s is the Pauli paramagnetism due to the spin density near the Fermi energy, χ_{orb}^{SO} is the paramagnetic orbital component due to spin-orbit (SO) coupling, χ_{orb}^{KO} is the Kubo-Obata paramagnetic contribution due to second order perturbation contribution of the itinerant electrons [2].

Bulk Ag and Au have an overall diamagnetic response to an applied field; i.e., the diamagnetic terms overpower the paramagnetic ones. In contrast, in Pd and Pt, which are paramagnetic, the opposite situation occurs.

The approximation of considering the electron band structure as a *d*-band combined with a conduction band is quite reasonable in these metals, where electrons in the *d*-band play a role of paramount importance. Therefore, the XMCD spectroscopy at the $L_{2,3}$ edges, which excites electrons from a *p* core level to the empty states of *d*-band, is the ideal experimental tool to probe the *d*-band magnetism, since the spin and orbital contributions are discriminated. One must be aware, though, that dipole excitation from $2p$ to $(n + 1)s$ states cannot be ruled out and may give a non-negligible contribution. Besides, the diamagnetic contribution is not observed.

A recent work on Au foil illustrates this approach beautifully [3]. The XMCD at the Au $L_{2,3}$ edges were measured as a function of field up to $H = 100$ kOe, at temperatures ranging between 2.2 and 300 K. The XMCD spectra were clearly non-zero, indicating that an induced moment appears at the $5d$ band and that it aligns parallel to the applied field. Moreover, the magnetic orbital and spin moments were found to depend linearly with the applied field. The orbital to spin moment ratio amounts to $m_L/m_S = 0.28$, thus indicating an important orbital contribution to the susceptibility. The spin Pauli paramagnetism and orbital components to the susceptibility could be deduced, and the resulting susceptibility due to the $5d$ band is compared to the total susceptibility in Table 6.1.

The bulk Pd XMCD spectra, at the Pd $L_{2,3}$ edges, up to $H = 70$ kOe and $4 < T < 300$ K, were also measured [6]. The field dependence is linear, and the susceptibility decreases with increasing temperature. The two components, spin Pauli paramagnetic and orbital susceptibility were deduced and are compared to the rest in Table 6.1. The orbital component could be segregated into the SO and KO terms by comparing the results with a Fe/Pd multilayer. The XMCD at the $L_{2,3}$ edges of bulk Pt were measured likewise [8] (see Table 6.1).

From Table 6.1 several conclusions may be drawn. In Au, diamagnetism is dominant, but the paramagnetic *d*-band susceptibility is nevertheless observable. In Pd and Pt the *d*-band paramagnetism is partially compensated by the diamagnetic terms. Except for Ag where no data exists, the *d*-band magnetism of the bulk metals is paramagnetic and is attributed to the non-zero number of holes induced by hybridization of this band with the *s*-*p* ones. Moreover, the m_L/m_S ratio increases with the number of holes in the *d*-band.

Table 6.1 Collected data for bulk Ag, Au, Pd and Pt metals

Metal	Ag (4d)	Au (5d) ^a	Pd (4d) ^b	Pt (5d) ^b
n_h^d	0.349 ^c	0.617 ^d	1.27 ^e	1.635 ^d
m_L/m_S		0.28 ^a	0.30 ^b	0.38 ^b
χ_{total} (emu/mol) ^f	-1.95×10^{-5}	-2.08×10^{-5}	5.56×10^{-4}	1.89×10^{-4}
χ_d (emu/mol)		7.0×10^{-6}	1.3×10^{-3}	6.1×10^{-4}
χ_{Pauli}^s (emu/mol)		5.4×10^{-6}	9.6×10^{-4}	4.4×10^{-4}
χ_{orb} (emu/mol)		1.5×10^{-6}	3.2×10^{-4}	1.7×10^{-4}

n_h^d , number of holes at the d-band; m_L/m_S ratio obtained from the XMCD $L_{2,3}$ edges analysis; χ_{total} total magnetic susceptibility measured with conventional magnetometry; χ_d , d-band susceptibility, from XMCD magnetometry; χ_{Pauli}^s , Pauli paramagnetic spin component; χ_{orb} orbital component

^a See Ref. [3]

^b See Ref. [6]

^c See Ref. [4]

^d Private communication

^e See Ref. [5]

^f See Ref. [7]

6.2 Induced Magnetism in Nanoparticle Matrix

When any of the four metals is in contact with a strongly magnetic material, the interfacial atoms of $M = \text{Ag, Au, Pd and Pt}$ may also become magnetic in absence of an external applied field. This phenomenon has been extensively studied in T/M thin films, where T is a transition metal as Ni, Fe or Co. The case between the interfacial $T = \text{Ni}$ and $M = \text{Pt}$ is described in [9], where three possible mechanisms for the induction of magnetic moment atoms are discussed: (a) charge transfer by hybridization between T and M d-bands, (b) symmetry breaking at the surface atoms, and (c) spin-orbit couplings between the T and M d-bands.

When the metal M forms part of a magnetic nanoparticle covering it, or intrinsically as an alloy, one or more of the three mechanisms invoked to explain magnetic induction of magnetism in M is also active and magnetism in the M atom is encountered. Such a study on Co nanoparticles capped with $M = \text{Ag, Au, Pd and Pt}$ has been performed, as described for the case of Co–Pt NPs in Chap. 5. In the Ag and Au cases the Co nanoparticle remains in its integrity and M covers, without alloying, the Co nanoparticle. The effect of the metal capping is, thus, embedding the Co particle in an M matrix. The net effect is the increase of surface anisotropy at the Co nanoparticle surface atoms [10, 11]. In contrast, Pt alloys with Co forming particles with high anisotropy (see Chap. 5), and Pd behaves likewise.

In this section, the XMCD results obtained at the $L_{2,3}$ edges of the corresponding capping layer for particles with the same average diameter of $\langle D \rangle \approx 3$ nm are compared. The data have been obtained at the ID12 beamline, at the ESRF, and the detection technique was fluorescence in backscattering geometry. The polarization was over 90 % in the Au and Pt cases, but in the Ag and Pd it was 36 and 22 % at the L_2 edge and 24 and 12.6 %, at the L_3 edge, respectively. The field was applied

with an incident angle of 75° with respect to the normal to the plate. The applied field was $H = 10\text{--}20\text{ kOe}$ and the temperature $T = 5\text{--}10\text{ K}$, thus guarantying the magnetic saturation of the NPs magnetization. The XANES and XMCD results for the four metal-capped Co-NPs, namely, Co-Ag, Co-Au, Co-Pd and Co-Pt NPs are shown in Figs. 6.1 and 6.2. Co-Ag and Co-Au figures are taken from Ref. [11]. The XMCD measurements for Co-Pt NPs are those described in Sect. 5.3.3. Results from the sum rules analysis applied to the XMCD signals in Figs. 6.1 and 6.2 are collected in Table 6.2.

In all cases the non-zero XMCD signal indicates that the ferromagnetic Co has polarized the M atoms with the total moment parallel to the Co magnetization direction. The Pauli paramagnetic contribution, calculated from Table 6.1 data for the applied field, falls within the experimental error bars in the four cases. The m_L/m_S ratio has reduced respect to the bulk metal (compare with Table 6.1), with the exception of the bulk Ag, where there is no data. In the case of Ag and, even more, in Pd, the orbital moment has been practically quenched, while it is at least one order of magnitude larger in the Au and Pt cases. This feature is probably related with the fact that the spin orbit coupling constant ξ_d is larger in the Au and Pt cases (see Table 6.2). The m_{tot} is one order of magnitude smaller in Ag and Au, with respect to Pd and Pt, which is related with the much larger n_h^d in the two latter cases. On the other hand, m_{tot} is thrice as large in Pd with respect to Pt. This trend is similar to that found for the Pauli paramagnetism, and cannot be directly related to the n_h^d variation, but rather to a larger exchange enhancement of the paramagnetism in the Pd case.

6.3 Intrinsic Magnetic Moment in M Nanoparticles

Here, the focus is on NPs formed by clusters of M atoms, and show single particle magnetization. There are two distinct, reported, magnetic behaviors, Langevin superparamagnetism (SP)

$$M(H) = m_{\text{Part}} \left(\coth \left(\frac{m_{\text{Part}} H}{k_B T} \right) - \frac{k_B T}{m_{\text{Part}} H} \right) \quad (6.2)$$

with a single particle moment m_{Part} , and temperature independent magnetism up to room temperature (TI), which may appear simultaneously or independently. Many of the reports deal with conventional magnetometric data, and doubts are cast on the influence of spurious contributions. Our approach to this problem has been to restrict ourselves to the XMCD available data because of its element selectivity that allows to discriminate the magnetization originating from the actual M metal. As in the previous sections, the M $L_{2,3}$ edges inform on the contribution of the nd -band to this NPs magnetism.

It has been reported that Ag NPs of $\langle D \rangle = 2.3\text{ nm}$, capped with dodecanethiol molecules, show a spontaneous, constant moment up to room temperature. However, there are no XMCD experiments yet done on these particles [13, 14].

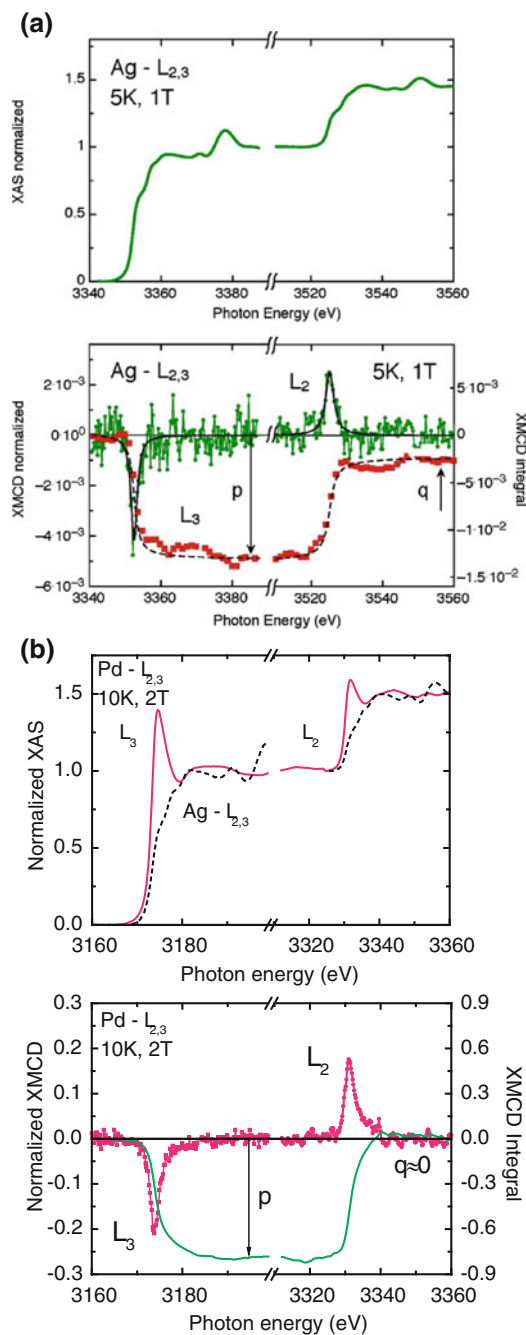


Fig. 6.1 Normalized XANES and XMCD at the M $L_{2,3}$ edges in the Co-M NPs. **a** Co-Ag NPs [11] and **b** Co-Pd NPs. The XANES spectra of Ag $L_{2,3}$ edges are shown in (b) for comparison. The higher limit for the p and q integrals, used for the sum rules analysis, is given

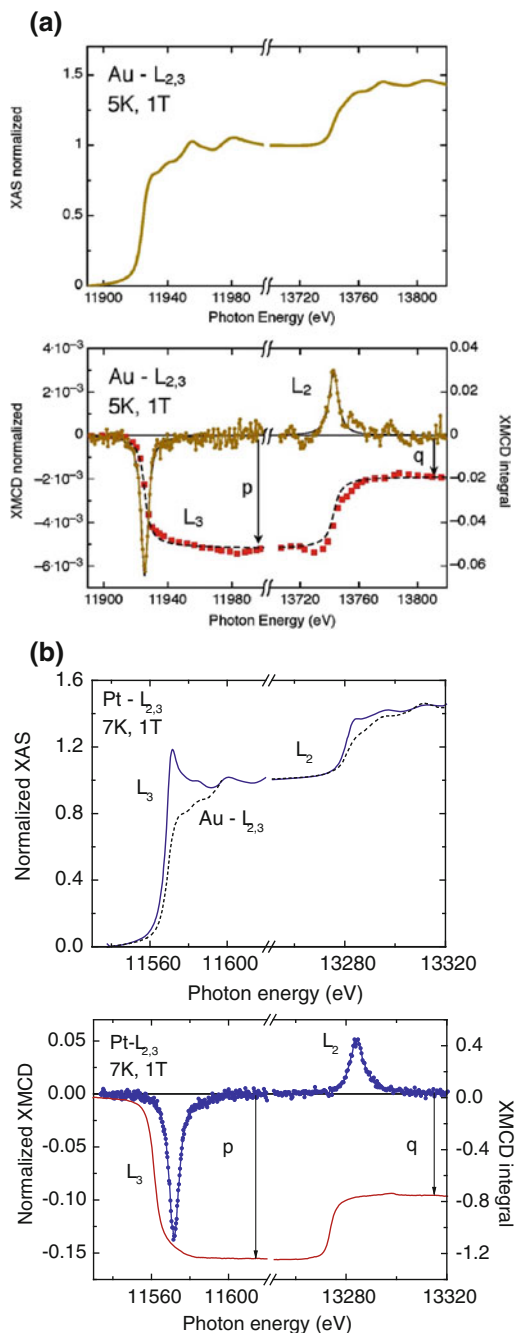


Fig. 6.2 Normalized XANES and XMCD at the M $L_{2,3}$ edges in the Co-M NPs. **a** Co-Au NPs [11] and **b** Co-Pt NPs. The XANES spectra of Au $L_{2,3}$ edges are shown in (b) for comparison. The higher limit for the p and q integrals, used for the sum rules analysis, is given

Table 6.2 Collected data for the M-capped Co NPs with $\langle D \rangle \approx 3$ nm

Capping metal	Ag ^a	Au ^a	Pd	Pt
$\xi_d(\text{meV})^b$	272	608	200	600
n_h^d	0.422	0.688	1.2 ^c	1.80(2)
m_L/m_S	0.045(5)	0.10(5)	-0.006(3)	0.19(1)
$m_L(\mu_B)$	$7(1) \times 10^{-4}$	$1.5(5) \times 10^{-3}$	-0.003(3)	0.027(1)
$m_S(\mu_B)$	0.014(3)	0.015	0.45(9)	0.14(1)
$m_{\text{tot}}(\mu_B)$	0.015(3)	0.016(1)	0.45(9)	0.16(1)

ξ_d , spin-orbit constant at the nd orbital; n_h^d , number of holes at the d -band; m_L/m_S ratio, m_L , orbital moment, m_S , spin moment, $m_{\text{tot}} = m_L + m_S$, obtained from the XMCD $L_{2,3}$ edges analysis

^aSee Ref. [11]

^bSee Ref. [12]

^cSee Ref. [5]

Although Au NPs have been extensively investigated with conventional magnetometry (SQUID), relatively few experiments have been done with XMCD. The first of these experiments detected a Langevin paramagnetism and a small TI contribution in $\langle D \rangle = 1.9$ nm Au NPs capped with polyallyl amine hydrochloride (PAAHC). The NP magnetic moment was determined to be $m_{\text{Part}} = 0.4 \mu_B$. The TI component is quite sizeable and both SQUID and XMCD data coincide below $T = 100$ K. The XMCD signal is very small (10^{-5} XMCD/XAS ratio at the L_3 edge) (see Table 6.3) [15]. The second report concerned Au $\langle D \rangle = 2$ nm NPs capped with dodecanethiol, where the XMCD signal was similar to that of the PAAHC capped Au NP. Again, it yields to a very minute XMCD signal (10^{-5} XMCD/XAS ratio) [14]. However, this small XMCD signal is assigned to the surface atoms only, and the authors propose $m_{\text{at}} = 0.33 \mu_B/\text{magnetic Au atom}$. Finally, Au NPs capped with thiol and embedded in polyethylene were measured with XMCD [16], finding also a very small XMCD signal as compared to the TI component.

Our contribution to this subject has been the detection of a 25 times larger XMCD signal, shown in Fig. 6.3a, in NPs of similar size deposited on a template of the *Sulfolobus acidocaldarius* S-layer [17]. m_{Part} has been estimated to be of several Bohr magnetons. As in the previous cases, the presence of sulfur (S) atoms at the template surface binding the Au particle seems to be of paramount importance to show this type of magnetism, since it does not appear on Au particles deposited on *Bacillus Sphaericus* S-layer, where there is no S present. We demonstrate that on each Au particle the thiols and other groups present in the S-layer supply holes to the $5d$ band. Their spins are ferromagnetically coupled by a spin-spin exchange interactions. In addition, an appreciable orbital moment is generated by spin-orbit couplings. Hund's third rule is complied and the orbital moment is parallel to the spins. The magnetic behavior of the particle is paramagnetic, with very low anisotropy. Thus, the external field sets the common alignment direction of the magnetization of all particles. The very large magnetic moment per Au atom observed in the XMCD measurements originates from the large charge transfer from the S-layer supporting template to the Au surface atoms, and reshuffling of holes to the particle core. Finally,

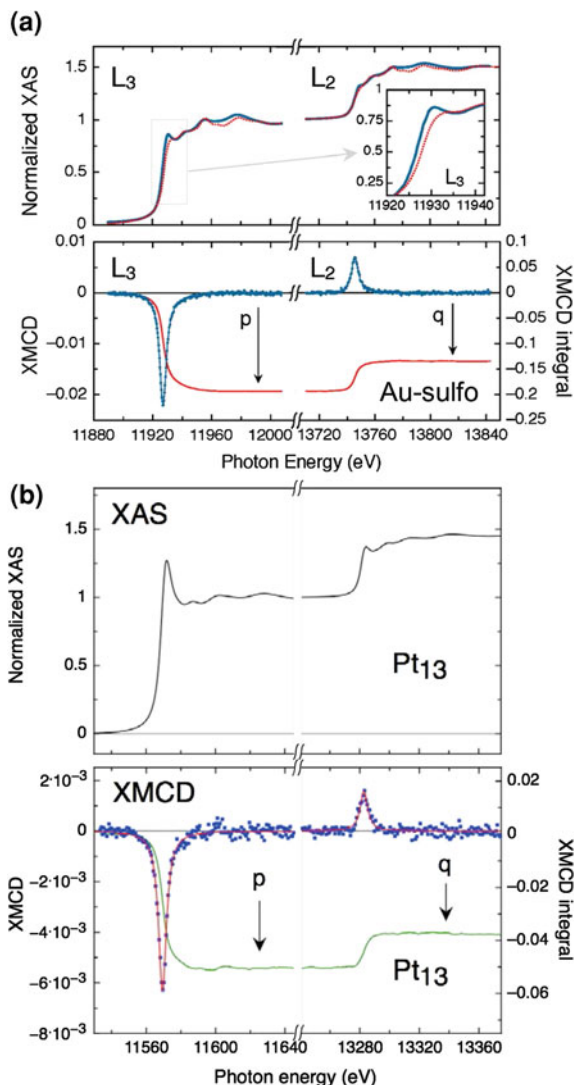


Fig. 6.3 Normalized XANES and XMCD at the M $L_{2,3}$ edges in the **a** Au NPs [18] and **b** Pt NPs [8]. The higher limit for the p and q integrals, used for the sum rules analysis, is given

we may also remark that the striking magnetic properties of these Au NPs are due to the special synthesis on a unique biological matrix containing low number of thiol groups distributed in a highly ordered way [18].

As in the case of the Ag case, Pd NPs have been reported to show a magnetic behavior due to size-effect and, or, surface atoms polarization [19], however, there is no confirmation by XMCD of this feature.

Table 6.3 Collected data for the M NPs studied with XMCD

	Au NPs			Pt NPs ^d
	PAAHC ^a	DT ^b	Sulfolobus ^c	
Type	SP	TI	SP	SP
$\langle D \rangle$ (nm)	1.9	2	2.6(1)	0.7
n_h^d			0.762	1.85
m_L/m_S	0.145	0.10	0.28(1)	0.32(2)
m_L (μ_B/at)			0.0110(1)	0.0055(1)
m_S (μ_B/at)			0.039(1)	0.0171(6)
m_{tot} (μ_B/at)	0.001	0.33	0.050(1)	0.0226(9)
m_{part} (μ_B)	0.4		2.3	3.5–4.9

$\langle D \rangle$, particle diameter; n_h^d , number of holes at the d -band; m_L/m_S ratio, m_L , orbital moment, m_S , spin moment, $m_{\text{at}} = m_L + m_S$, obtained from the XMCD $L_{2,3}$ edges analysis; m_{part} , the NP magnetic moment deduced from the Langevin curve

^aSee Ref. [15]

^bSee Ref. [14]

^cSee Ref. [17]

^dSee Ref. [8]

Finally, Pt₁₃ nanoparticles embedded in a NaY zeolite matrix have also shown superparamagnetic behavior at low temperature and high field, as observed first with SQUID magnetometry [20]. The Pt₁₃ particle crystallizes in icosahedral symmetry and have 12 of its atoms at the surface, thus size and surface effect are maximized. The XMCD measurement performed at the Pt $L_{2,3}$ edges at $T = 7$ K and increasing field up to $H = 60$ kOe gave an unambiguous non-zero signal, as shown in Fig. 6.3b, which proved the existence of intrinsic magnetization in these particles. The m_{part} deduced from the Langevin curve ranges between 3.5 and 4.9 μ_B , and the moment per Pt atom deduced from the experiment is too low to account for all existent particles to be magnetic, actually, only 12 % seem to have this property. It may be due to the different chemical surroundings in the zeolite cavity where the cluster sits [8].

Comparing the results in Table 6.3, the ratio m_L/m_S of Au NPs varies strongly depending on the capping material, but in two out of three cases, it is larger than in the induced magnetic case of Co–Au capping (see Tables 6.2 and 6.3). The value in the case of Pt₁₃ is larger than in the Co–Pt alloyed NPs (see Tables 6.2 and 6.3). In both cases, Au and Pt NPs, there is an increase in the number of holes n_h^d with respect to the corresponding bulk metal. This seems to be a necessary condition for d -band magnetism of intrinsic type.

6.4 Conclusions

XMCD has been able to establish that there is d -band magnetism in the metallic Ag, Au, Pd and Pt at the nanoscale. Besides, it has shown that about 30 % of this magnetism is orbital in its origin. However, this technique gives, inherently, just an

average value of the m_L , m_S components over all M atoms present in the sample. Therefore, it is unable to discriminate whether the magnetism originates at the surface (by chemical bonding, symmetry breaking, or both), or in the core of the particle. In our opinion, at present this is the most intriguing question, there being arguments and theories in both directions [21]. These are, among others, some of the open questions in the fascinating realm of the magnetism of metals.

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Chapter 7

Transverse Susceptibility Measurement System for the PPMS

This chapter is dedicated to describe the magnetic transverse susceptibility (TS) technique: a measurement method, hardly used, but very effective, to directly probe the magnetic anisotropy of interesting materials, especially of nanoparticulate systems. A TS measurement system based on a simple inverter CMOS cell oscillator cross-coupled to a LC tank is presented, which we have implemented to operate at a Quantum Design Physical Properties Measurement System (PPMS) at the Servicio de Medidas Físicas of the Universidad de Zaragoza.¹ This implementation has been performed in collaboration with people from the Servicio de Medidas Físicas and from the Servicio de Instrumentación Electrónica of the Universidad de Zaragoza.² It has also been possible thanks to the advise of Dr. Hariharan Srikanth and members of the Functional Materials Laboratory at the University of South Florida in Tampa, FL, USA.³

We introduce several improvements with respect to similar currently operating TS measurement equipments [1]. The electronics have been redesigned to use CMOS transistors as active devices, which simplifies the circuit design and enlarge the tuning range, thus making the proposed electronic block more feasible, predictable, and precise. Additionally, we propose a newly designed sample holder, which facilitates the procedure to change a sample and improves reproducibility of the circuit. Our design minimizes the thermal leak of the measuring probe *by one order of magnitude*, allowing to measure from 1.8 K in standard PPMS systems, thanks to the use of a low temperature Beryllium-Copper coax cable instead of the conventional RG402 Cu coax cable employed in the insert for the PPMS in similar systems. The data acquisition method is also simplified, so that the measuring sequences are implemented directly in the PPMS controller computer by programming them in the Quantum Design MultiVu software that controls the PPMS. We present the test measurements performed on the system without sample to study the background signal and stability of the circuit. Measurements on a Gd_2O_3 calibrating sample yield to the estimation

¹ <http://sai.unizar.es/medidas/index.html>.

² <http://sai.unizar.es/electronica/index.html>.

³ <http://shell.cas.usf.edu/fml/>.

of the system sensitivity, which is found to be on the order of 10^{-6} emu. Finally, measurements on a TmCo₂ Laves phase sample with a ferrimagnetic transition temperature around 4 K are described, demonstrating that the developed system is well suited to explore interesting magnetic phenomena at this temperature scale.

7.1 Theoretical Model of the Magnetic Transverse Susceptibility

A transverse susceptibility measurement consists in probing the ac magnetic susceptibility of a material in one direction while an external bias magnetic field is applied perpendicular to the measurement direction. Analysis of the TS in magnetic materials have demonstrated its potential and versatility to study singular magnetic properties of bulk [2–4], single crystals [5], thin films [6–9] and nanoparticles (NPs) systems [10–15].

The first coherent theoretical approach for TS was proposed by Aharoni et al. [16], who calculated the reversible susceptibility tensor, χ_{ij} of a Stoner-Wohlfarth (SW) particle [17]. The susceptibility tensor is defined as $\chi_{ij} = dM_i/dH_j$ and its diagonal components comprise the longitudinal susceptibility component, χ_L , measured in the main field bias direction, and the two transverse susceptibility components χ_{T1} and χ_{T2} , measured in directions perpendicular to the bias field.

Lets analyze the case of a SW particle, i.e., an ellipsoid, uniaxial single domain, ferromagnetic particle, with volume V , anisotropy constant K_1 and saturation magnetization, M_S , as the one shown in Fig. 7.1a. The bias field, H_{DC} , is applied along the z axis, and the perturbing radio frequency (RF) magnetic field, H_{RF} , along the x axis. In this case, the longitudinal susceptibility is $\chi_L = \chi_{zz} = dM_z/dH_z$, and the transverse susceptibility components $\chi_{T1} = \chi_{xx} = dM_x/dH_x$ and $\chi_{T2} = \chi_{yy} = dM_y/dH_y$. M_i and H_i are the projections of the vectors saturation magnetization, $\vec{M}_S$, and total magnetic field, $\vec{H}_{DC} = \vec{H}_{DC} + \vec{H}_{RF}$, respectively.

The energy of the SW particle is given by the sum of the anisotropy energy, E_K , and the Zeeman energy, E_H , the latter defining the interaction with the applied field. Based on the coordinate system given in Fig. 7.1a, the total energy may be written as:

$$E = -K_1(\vec{M}_S \cdot \vec{u}_K)^2 - \vec{M}_S \cdot (\vec{H}_{DC} + \vec{H}_{RF}) \quad (7.1)$$

The vector $\vec{u}_K$ is the unit vector in the easy axis direction. The torques caused by the anisotropy and H_{DC} will determine the equilibrium position of the particle magnetic moment (θ_M , ϕ_M) while the small alternating field, H_{RF} , will produce only small perturbations around this equilibrium position. From the point view of the energy of the magnetic system, the stable equilibrium positions of magnetization vector are given by the conditions for minimum of the total energy, this is

$$\frac{\partial E}{\partial \theta_M} = 0; \quad \frac{\partial^2 E}{\partial \theta_M^2} \geq 0 \quad \text{and} \quad \frac{\partial E}{\partial \phi_M} = 0; \quad \frac{\partial^2 E}{\partial \phi_M^2} \geq 0; \quad (7.2)$$

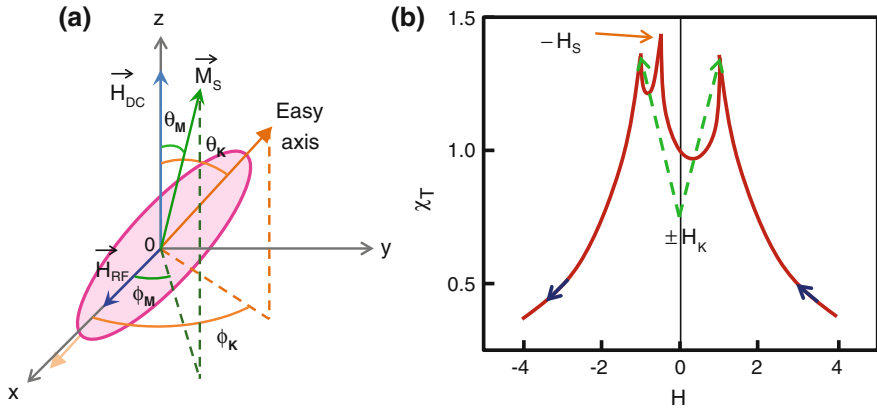


Fig. 7.1 **a** Diagram of a TS measurement geometry of a uniaxial magnetic particle [15]. **b** Typical TS unipolar curve as a function of H_{DC} for a collection of randomly oriented particles

Then, taking into account these conditions, and minimizing Eq. 7.1, one obtains the following expression for the transverse susceptibility, χ_{T1} as an example

$$\chi_{T1} = \frac{3}{2}\chi_0 \left(\cos^2 \phi_K \frac{\cos^2 \theta_M}{h \cos \theta_M + \cos 2(\theta_M + \theta_K)} + \sin^2 \phi_K \frac{\sin(\theta_K - \theta_M)}{h \sin \theta_K} \right) \quad (7.3)$$

where, $\chi_0 = M_S^2/3K_1$, h , the reduced field defined as $h = H_K/H_{DC}$, and $H_K = 2K_1/M_S$ corresponds to the anisotropy field.

For an array of particles with randomly oriented anisotropy axes, assuming the particles are identical and that inter-particle interactions are negligible, the average χ_T becomes

$$\langle \chi_T \rangle = \frac{1}{2\pi} \int_0^{2\pi} \int_0^{\pi/2} \chi_T \sin \theta_K d\theta_K d\phi_K \quad (7.4)$$

after integrating over ϕ_K and substituting back Eq. 7.3, we arrive at the expression

$$\langle \chi_T \rangle = \frac{3}{2}\chi_0 \int_0^{\pi/2} \left[\frac{\cos^2 \theta_M}{h \cos \theta_M + \cos 2(\theta_K - \theta_M)} + \frac{\sin(\theta_K - \theta_M)}{h \sin \theta} \right] \sin \theta_K d\theta_K \quad (7.5)$$

The transverse susceptibility curve for this system, as a function of the bias field, is plotted in Fig. 7.1b. It shows three cusps: two of them located at $\pm H_K$, and the third one at the switching field H_S .

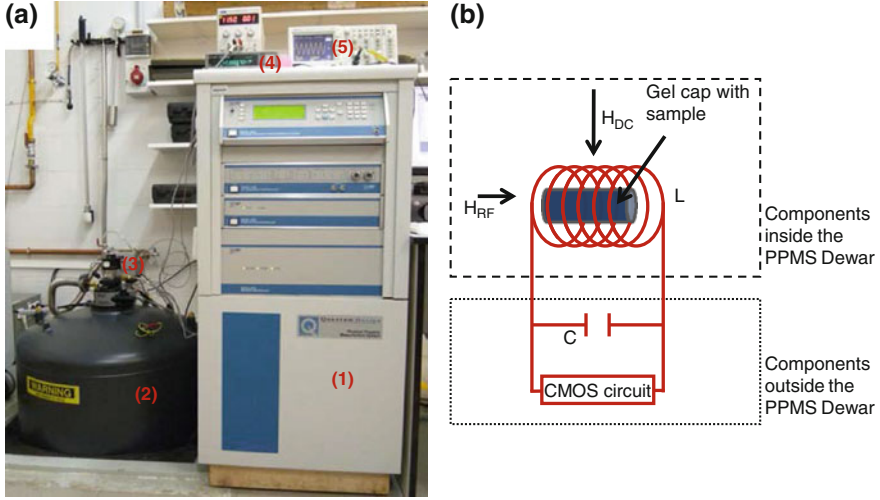


Fig. 7.2 **a** Picture of the PPMS with the TS setup: 1 Model 6000 PPMS control, 2 dewar, 3 multi functional probe's head, 4 frequency counter and 5 oscilloscope. **b** Diagram of the TS measurement system

7.2 Description of the TS Measurement System

The first experimental confirmation of Aharoni's theory for TS was performed in 1987 by Pareti and Turilli [18], who showed the presence of $\pm H_K$ and H_S peaks on barium ferrite particles. Their TS measurement system was based on conventional inductance susceptibility techniques, method also used by other groups [13, 19]. In addition to that system, TS measurement techniques developed up to date are based on magneto-optical setups [6, 9] and self-resonant LC tank circuits in the radio frequency range [1]. The latter technique has demonstrated to be one of the most accurate and versatile developments to measure TS, since it may be implemented on widely used commercial Quantum Design physical properties measurement systems (PPMS), as illustrated in Fig. 7.2. The tank inductance, L , is provided by a pick-up coil located in a controlled temperature and magnetic field environment. The capacitor, C , is usually fixed at room temperature outside the insert. The standard expression to define the resonance frequency of the tank is

$$f = \frac{1}{2\pi\sqrt{LC}} \quad (7.6)$$

In these kind of setups, the magnetic sample is inserted into a gel cap that snugly fits into the inductive coil, and Δf is measured as an external static field (H_{DC}) or temperature are varied. Changes in f are direct consequence of changes in L , described by the expression

$$\frac{\Delta f}{f} \approx -\frac{\Delta L}{2L} \quad (7.7)$$

obtained after differentiating Eq. 7.6.

The total inductance of the coil with the sample inside, L , is defined in terms of the empty coil inductance, L_0 , and the contribution of the sample, L_S . The latter depends on the permeability of the sample, $\mu = \mu_0(1 + \chi)$, where χ is its volume magnetic susceptibility (dimensionless). Then, considering the geometry of the coil, i.e., its volume, V_0 , its length, l , and the number of turns, N , and the volume of the sample inside it, V_S , the total inductance L is expressed as

$$L = \mu_0 \left(\frac{N}{l} \right)^2 (V_0 + \chi V_S) \quad (7.8)$$

The change in inductance ΔL , calculated after differentiating Eq. 7.8, is written as

$$\Delta L = \mu_0 \left(\frac{N}{l} \right)^2 \Delta \chi V_S \quad (7.9)$$

Since we want to express $\Delta L/L$, we divide Eq. 7.9 by L obtaining

$$\frac{\Delta L}{L} = \frac{\Delta \chi V_S}{V_0 + \chi V_S} \quad (7.10)$$

Two approximations may be derived from this expression. On one hand, if $\chi V_S \gg V_0$, Eq. 7.10 is reduced to

$$\frac{\Delta L}{L} \approx \frac{\Delta \chi}{\chi} \quad (7.11)$$

On the other hand, if $\chi V_S \ll V_0$, Eq. 7.10 may be written as

$$\frac{\Delta L}{L} \approx \Delta \chi \eta \quad (7.12)$$

where $\eta = V_S/V_0$ represents the fill factor of the coil core space.

When the geometry of the measurement setup is that illustrated in Fig. 7.2b, where the perturbing RF magnetic field inside the coil ($H_{RF} \sim 10\text{Oe}$) is oriented perpendicular to the bias field, H_{DC} , the magnetic susceptibility of the sample being probed is its transverse component χ_T [1], as described in Sect. 7.1. Therefore, combining Eqs. 7.7 and 7.11, we arrive at the direct relation between Δf and $\Delta \chi_T$, as

$$\frac{\Delta f}{f} \approx -\frac{1}{2} \frac{\Delta \chi_T}{\chi_T} \quad (7.13)$$

and from Eqs. 7.7 and 7.12 we get

$$\frac{\Delta f}{f} \approx -\frac{1}{2} \Delta \chi_T \eta. \quad (7.14)$$

7.3 Design and Implementation of the Oscillator Circuit

TS magnetometry equipments based on self-resonant systems usually employ a tunnel diode oscillator (TDO) as their active device in the radio frequency resonator setup [1]. However, there are several important drawbacks of using TDOs for this application, which may be summarized as: (1) they are complex devices with low market availability and (2) the tuning range for accomplishing the oscillation condition is reduced, thus limiting the nature of the measurable magnetic samples. Instead, the proposed oscillator uses CMOS transistors as active devices, implementing a simple inverter cell in cross-coupled topology, which compensates the energy loss of the LC resonant tank. The choice of these devices and configuration not only solve the above mentioned TDO drawbacks, but also involve some other benefits like: (1) minimum parasitics and noise sources increasing the sensitivity and accuracy of the resonant circuit, (2) higher circuit robustness and predictability, giving a deep understanding about the block properties, and (3) much lower cost in the future case of high-volume manufacturing.

Figure 7.3 shows the electronic schematic of the complete circuit, where the described oscillator is denoted in the (1) zone. The theoretical basis of the oscillator design is detailed in Ref. [20]. The main aspects of the cell modeling are described as follows. The small-signal equivalent model of the proposed oscillator is illustrated in Fig. 7.4a. The LC tank is represented by the impedance Z_L . Applying conventional

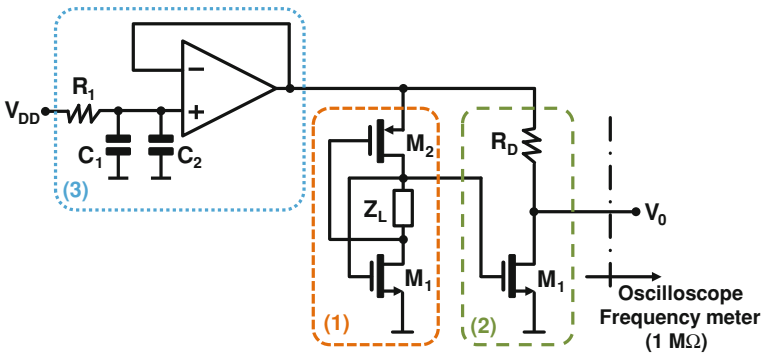
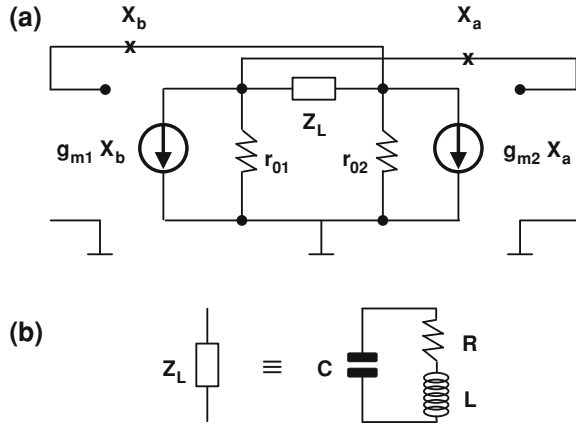


Fig. 7.3 Electronic schematic of the CMOS based LC cross-coupled oscillator circuit used for TS measurements

Fig. 7.4 **a** Small-signal equivalent model of the proposed oscillator. **b** Realistic model of the LC resonant tank



circuit theory, the characteristic equation of this model is obtained as a function of the Z_L transfer function, as

$$A - BZ_L = 0 \quad (7.15)$$

where,

$$A = r_{01} + r_{02} + r_{01}r_{02}(g_{m1} + g_{m2}) \approx r_{01}r_{02}(g_{m1} + g_{m2}) \quad (7.16)$$

$$B = g_{m1}g_{m2}r_{01}r_{02} - 1 \approx g_{m1}g_{m2}r_{01}r_{02} \quad (7.17)$$

Z_L is modeled as a $L - R - C$ circuit given the inherent internal DC resistance of the inductive coil, as drawn in Fig. 7.4b. Given this model, the load transfer function, Z_L , is expressed as:

$$Z_L(s) = \frac{sL + R}{s^2LC + sCR + 1} \quad (7.18)$$

Substituting Eq. 7.18 in 7.15, the final expression of the characteristic equation results in

$$ALCs^2 + s(ARC - BL) + (A - BR) = 0 \quad (7.19)$$

Taking into account solutions $s = \pm j\omega$, and equalling the real and imaginary terms to zero, the oscillation frequency and oscillation condition are functions of L , C , and R , and are expressed as

$$f^2 = \frac{1}{(2\pi)^2 LC} [1 - R\alpha] \quad (7.20)$$

$$1 \leq \frac{L\alpha}{RC} \quad (7.21)$$

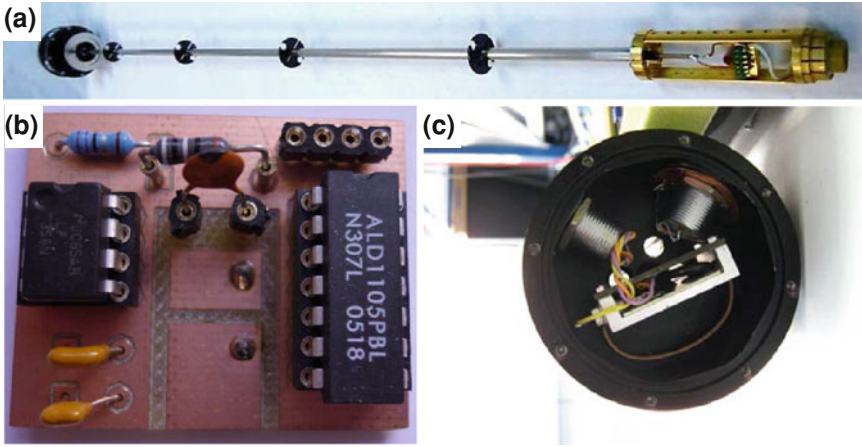


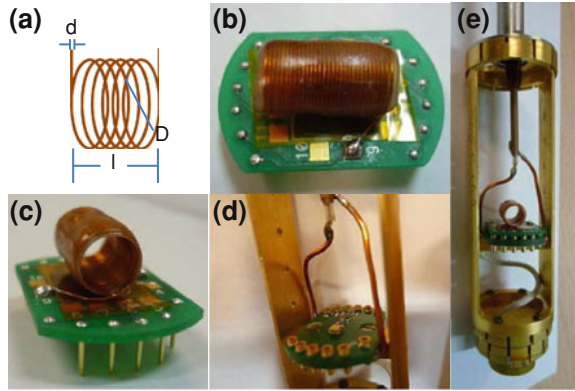
Fig. 7.5 **a** MFP used for the TS setup. **b** Details of the circuit board with the CMOS based circuit. **c** Location of the circuit in the MFP's head

where $\alpha = (g_{m1}g_{m2})/(g_{m1}+g_{m2})$, and $g_{m1,2}$ are the characteristic transconductances of the $M_{1,2}$ transistors shown in Fig. 7.3. These transistors are implemented with a commercial device, ALD1105 IC (two NMOS and two PMOS transistors into a single chip). The use of this standard CMOS chip guarantees high simplicity in modeling the transistors, validating the first order quadratic approximation described in Ref. [21]. This fact is quite important because it minimizes errors when determining the shift in the resonance frequency caused by the change in inductance for the TS calculation.

In addition to the inverter cell and the LC tank, the circuit includes two extra stages. One of them is an output driver working as second oscillator stage. This driver (shown in the (2) marked zone in Fig. 7.3) is made by an NMOS passively loaded common-source stage and isolates the resonator tank from the posterior measurement equipment. This alleviates the load effect, minimizing the electronic impact of the connections to the measurement setup (the oscilloscope and frequency counter that will be described below). The second additional stage (denoted in the (3) area in Fig. 7.3) is a supply isolation block consisting of a voltage amplifier in buffer topology with a RC filtering network. It is crucial to isolate the LC resonant tank since this noise could generate phase noise into the oscillation. Different voltage amplifiers were tested in the design process of this block in order to optimize the stability and working conditions, obtaining the best trade-off with a LF356 OpAmp. Since the designed circuit operates at radio frequencies, the filtering network is based on a $R-2C$ bypassing filter with values of $3\ \Omega$, 2.2 and $220\ \text{nF}$, respectively (see Fig. 7.3, (3) marked area).

The circuit is integrated into the PPMS, using a model P450A—PPMS Multi-Function Probe (MFP) insert, shown in Fig. 7.5a. The components of the circuit were placed as close as possible (thus minimizing parasitic effects) and mounted on a copper double layer board with glass fiber as isolation material, which is located

Fig. 7.6 **a** Diagram of the coil geometry. **b** and **c** views of the coil assembly on the universal sample board. **d** Close up of the plug-in platform. **e** Final assembly of the coil at the bottom of the MFP



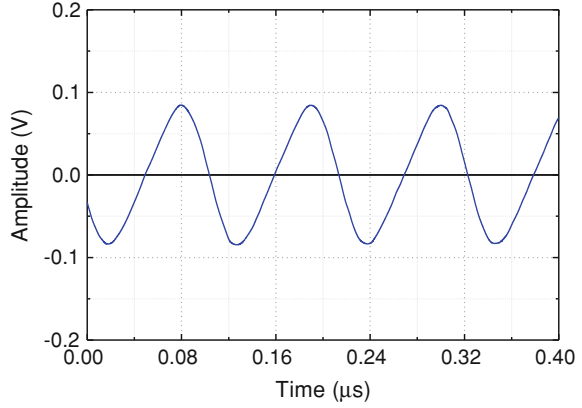
inside the MFP head (see Fig. 7.5b for details of the final board design and Fig. 7.5c for the location of the board circuit into the probe's head). The capacitor of the LC tank, $C = 22$ pF, is located on the circuit board, while the inductor is placed at the end of the MFP, i.e., it is inserted into the PPMS dewar since it holds the sample to be measured (see location of the insert in the PPMS dewar in Fig. 7.2a). Discrete devices have been employed in this prototype in order to check different frequency ranges and bias conditions. Connections between the circuit board and the coil were made by a 0.9 m long non-magnetic beryllium copper-50 Ω semi-rigid coaxial cable, with a 2.19 mm diameter (Coax co. ref. SC-219/50 B-B). The parasitic capacitance of the coaxial is about 86 pF, and the self inductance is around 200 mH, according to the manufacturer specifications; these two contributions must be taken into account when calculating the nominal resonance frequency of the LC tank.

We have chosen this specific coax to minimize the thermal leak in the probe inside the PPMS dewar at low temperatures, as we demonstrate as follows. The thermal leak introduced by the coaxial cable in the low temperature system can be estimated by calculating the heat transfer rate by thermal conductance (Q/t) of the coax, according to the dimensions and thermal conductivity (κ) of the cable.⁴ This thermal leak for the Be-Cu coaxial cable ($\kappa = 65.77$ W m⁻¹ K⁻¹ at 300 K and cross-sectional area = 1.58×10^{-6} m²) is 0.045 W, while the one for a conventional RG402 Cu coaxial used in similar TS setups ($\kappa = 385.95$ W m⁻¹ K⁻¹ at 300 K and cross-sectional area = 3.07×10^{-6} m²) is 1.23 W. The reduction of the thermal transfer rate by a factor of 27 by using a Cu-Be coax in the setup is what allowed us to reach the lowest temperature possible with a conventional probe insert for the PPMS, i.e., $T_{\text{base}} = 1.8$ K.

The circuit specifications were optimized to use an inductive air coil, L , which is a 31—turn solenoid hand—wound using a 0.3 mm in diameter Cu wire, with 10.5 mm in length and 5.5 mm in diameter. According to these dimensions, the calculated inductance of the coil is 2.73 μ H. Figure 7.6a shows a diagram of the coil geometry. The inductance and DC resistance of the coil were measured with a LCR meter,

⁴ A useful tool to calculate the heat transfer by thermal conductance of several materials can be found in the Quantum Design website www.qdusa.com/techsupport/thermalCalculator.html.

Fig. 7.7 Measured output waveform at $V_{DD} = 7\text{ V}$, $C = 22\text{ pF}$ and $L = 2.8\text{ }\mu\text{H}$



obtaining $L = 2.8\text{ }\mu\text{H}$, which results in an error of less than 3 % in the estimated value, and $R = 0.18\text{ }\Omega$. The coil is assembled onto a Quantum Design universal sample board (ref. P103C, shown in Fig. 7.6b, c) that plugs into the platform assembly of the MFP, which includes a calibrated cernoxTM (a zirconium oxynitride film) thermometer (see Fig. 7.6d). This sample board is easy to plug in and take out from the probe, so the coil does not need to be unsoldered and different coils can be used with the same circuit, if needed. A picture of the complete assembly at the bottom of the MFP is shown in Fig. 7.6e. The coil dimensions are designed to hold a conventional gel-cap for PPMS and Magnetic Properties Measurement System (MPMS) measurements, so that it snugly fits into the coil core space.

The resulting oscillator waveform is shown in Fig. 7.7, measured with a Tektronix TDS7104 digital phosphor oscilloscope. The signal is nearly sinusoidal with an oscillation frequency around 9.2 MHz. In order to calculate the frequency and compare both experimental and calculated values, Eq. 7.20 may be approximated to $f \sim 1/(2\pi\sqrt{LC_{\text{total}}})$ (since $\alpha \sim 0.4\text{ mS}$ for the input voltage of 7 V in the measurement of Fig. 7.7, and $R = 0.18\text{ }\Omega$, so that $R\alpha \ll 1$). According to the values of $L = 2.8\text{ }\mu\text{H}$, the circuit capacitor, $C = 22\text{ pF}$, the capacitance and inductance contributions of the coax, $C_{\text{coax}} \sim 86\text{ pF}$ and $L_{\text{coax}} \sim 200\text{ nH}$, the calculated frequency is 9.26 MHz, giving a high accuracy between the calculated and experimental values, with an error of less than 1 %. Following the oscillation condition defined in Eq. 7.21 and the experimental results, the circuit oscillates with an input voltage, V_{DD} , ranging between 6.2 and 13 V, provided by a power supply EL302P programmable PSU.

The oscillation frequency of this designed RF self resonant system may be varied by correctly choosing those values of L and C , so that Eqs. 7.21 and 7.20 are fulfilled. In any case, the upper frequency is limited by the unavoidable parasitic capacitance of the coaxial cable ($C_{\text{coax}} \sim 86\text{ pF}$ for the one used in our design). For example, for $L = 2.8\text{ }\mu\text{H}$ used in this work, the highest frequency is around 10.2 MHz, and the lowest reachable frequency is around 5.4 MHz, the latter obtained with a $C = 220\text{ pF}$.

7.4 Data Acquisition

The output signal of the circuit is read by an Agilent 53131 A frequency counter and a Tektronix TDS2022B oscilloscope (see Fig. 7.2a). Data acquisition is performed by a connection via the IEEE-488 General Purpose Interface Bus (GPIB) between the frequency counter and the Model 6000 PPMS respective port. Then, the resonating frequency acquired is used in the subsequent scripts written for measuring the sample TS. Measuring sequences have been implemented using the Visual Basic interpreter within MultiVu PPMS software.⁵ The executable programs scripted (.BAS files—called macros in MultiVu) allow scanning both H_{DC} field and T (controlled by the PPMS) and measuring the resonance frequency, f . All measuring sequences are programmed directly on the PPMS controller computer and Multivu software, so that no additional equipment is needed for such effect. This fact represents an advantage with respect to similar TS measurement setups.

7.5 Test Measurements

7.5.1 Test Measurements on an Empty Coil

First tests measurements were performed on the empty coil, so that we could study and characterize the response of the system resonance frequency to both H_{DC} and T . Such tests included those of stability of the frequency with time, temperature and field. Results for these tests are shown in Fig. 7.8.

The test of the resonance frequency with time for the CMOS circuit (Fig. 7.8a) reveals the existence of a drift, which is reduced with time from 30Hz/min to 14Hz/min in 150 min (see straight lines in Fig. 7.8a). This drift can be attributed to the time the electronics need to reach a thermal stability after they are turned on. Comparing this result with tests performed on a TDO based circuit,⁶ it is found that both circuits have analogous drifts, but the CMOS based circuit has a smoother and easy to correct curve on each TS scans. How these corrections are performed is described later in this section.

The variation of the frequency of the empty coil with magnetic field is shown in Fig. 7.8b. The total shift in frequency for a complete 9 T unipolar scan (sweeping H_{DC} from 90 kOe to -90 kOe) is 197 Hz.

⁵ For further information see the PPMS Application Note 1070–209 of Quantum Design. www.qdusa.com/techsupport/index.html.

⁶ A TDO based resonant circuit, similar to that described in [1] was also built by us to contrast the frequency stability results of both TDO and CMOS based resonant TS systems. The f_0 versus time curve for the TDO configuration had an average drift of 5 Hz/min, after 120 min. However, the frequency change with time in this case was not monotonic, showing a step-like curve that is not very simple to correct in subsequent TS scans.

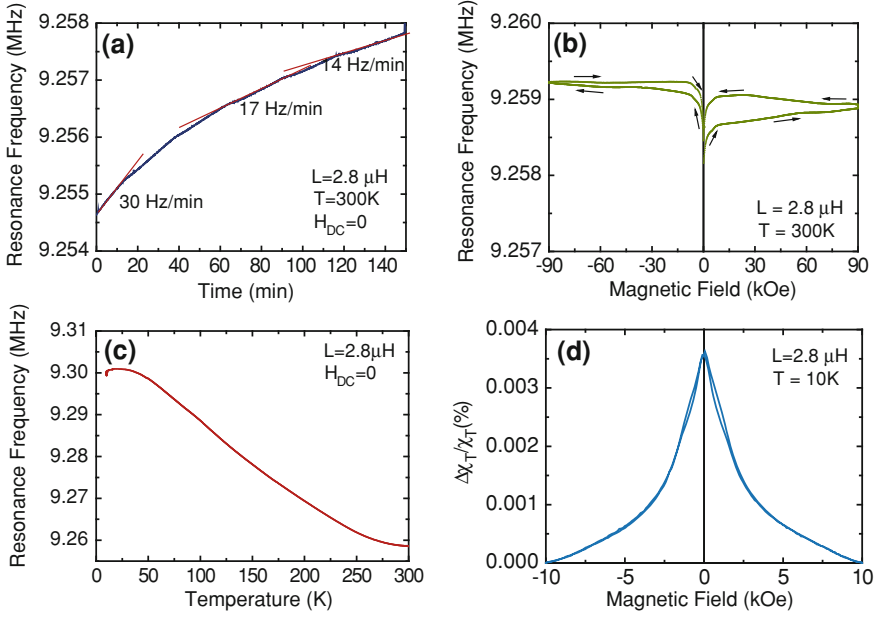


Fig. 7.8 Test measurements of the frequency stability of the empty coil. **a** Drift with time at 300 K. The straight segments indicate the rate of the frequency variation with time at different time intervals. **b** Variation with H_{DC} at 300 K. Arrows show the direction of the field sweeping. **c** Variation with temperature at $H_{\text{DC}} = 0$. **(d)** TS scan at $T = 10\text{K}$ and with $H^{\text{sat}} = 10\text{kOe}$, after corrections from drifts

Temperature dependence of the tank resonator frequency was probed by zero field cooling of the empty coil and it is shown in Fig. 7.8c. This measurement supplies the background signal originated at the empty coil, $f_{\text{bkg}}(T)$. Frequency monotonically increases as temperature is lowered. The total frequency drift with temperature was found to be around 133 Hz/K, showing that the system is very sensitive to thermal changes. This is mostly due to the thermal contraction the inductive coil suffers with decreasing temperature; the estimated rate of the frequency change as consequence of the changes in the dimension of the coil has been estimated as $\sim 100\text{Hz/K}$, calculated with the linear thermal expansion coefficient of copper ($\alpha = 16.6 \times 10^{-6} \text{K}^{-1}$).

A bipolar TS scan of the empty coil at $T = 10\text{K}$ was also performed (see Fig. 7.8d), where the change in resonance frequency was measured as H_{DC} was ramped from negative to positive saturation of 1 T, and vice versa. We considered the quantity

$$\frac{\Delta\chi_T}{\chi_T} \% = \frac{\chi_T^{\text{Sat}} - \chi_T(H_{\text{DC}})}{\chi_T^{\text{Sat}}} \times 100 \propto \frac{\Delta f}{f_0} \% \quad (7.22)$$

where χ_T^{Sat} is the transverse susceptibility at the saturating field $H^{\text{Sat}} = 10\text{kOe}$. This TS scan has been corrected for the previously described time and field linear

drifts, by fitting a straight line between the data at positive and negative saturation and subtracting it from the whole data set. From Fig. 7.8d, the $\Delta\chi_T/\chi_T$ % value at $H_{DC} = 0$ for the empty coil is 0.0036 %, which is very low compared to the $\Delta\chi_T/\chi_T$ % we obtain for a magnetic sample, as we will demonstrate later.

In most cases this technique is applied to obtain intensive parameters, such as transition temperatures and fields, anisotropy, switching or coercivity fields, and, consequently, it is not necessary to determine the absolute χ_T . However, if desired, χ_T may be scaled to absolute values by measuring the absolute ac longitudinal susceptibility, χ_L in a SQUID magnetometer at $H_{DC} = 0$, and compare it with the results obtained in the transverse geometry for $H_{DC} = 0$.

7.5.2 Calibration of the TS Measurement System with Gd_2O_3

The previously described procedure has been used to measure the χ_T of a paramagnetic Gd_2O_3 sample, which is regularly used to calibrate different kinds of magnetometers, and allows us to probe and analyze the sensitivity of our equipment. The ac χ_L was measured in a conventional SQUID magnetometer. Even though the frequency of the ac magnetic field in both measurements is different (1 kHz for χ_L and 9.2 MHz for the χ_T), for this paramagnetic system the results should be identical since in both frequencies the susceptibility of the Gd_2O_3 is in its isothermal limit.

Figure 7.9 shows a plot of the relative change in the resonance frequency of the LC tank in the TS setup with the sample $\Delta f/f_0$ versus $\Delta\chi_L/\chi_0$, at a common temperature range (12–80 K). The references f_0 and χ_0 are taken as those values at $T = 80$ K. A linear fit of the data yields to a slope of $s = 0.607(1)$. This value is used to determine

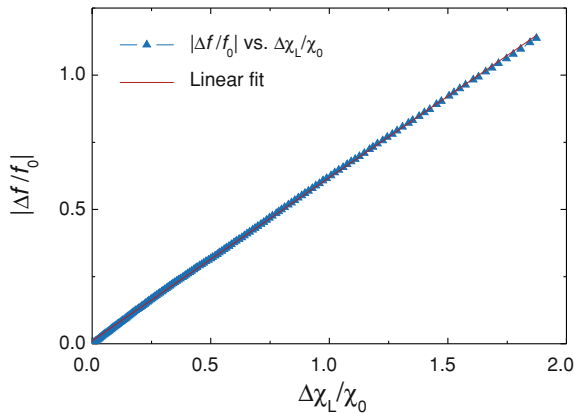


Fig. 7.9 Measurements of the temperature dependence of the magnetic susceptibility of Gd_2O_3 : (solid line) $\Delta\chi_L/\chi_0$ measured in a SQUID magnetometer, and (dashed line) relative change in the resonance frequency of the LC tank in the TS setup with the sample. Inset: $\Delta f/f_0$ versus $\Delta\chi_L/\chi_0$, both at $H_{DC} = 0$ for the equivalent temperatures and fit of two linear regions in the data

the scaling factor to transform frequency readings into absolute susceptibility units. Let us take the references f_0 and χ_0 and define $a = s \frac{f_0}{\chi_0}$, so that $\Delta\chi_L = a\Delta f$. We obtain $a = 1.82 \times 10^8$ emu/Hz.

The sensitivity of the instrument can be evaluated according to the measurement signal to noise ratio (SNR)

$$\text{SNR} = \frac{\Delta f/f_0}{\delta(\Delta f/f_0)} \quad (7.23)$$

SNR is on the order of 10^3 . Let us consider, as sensitivity test, a measurement of $\Delta f/f_0 = 10 \times \delta(\Delta f/f_0)$, so that we ensure that the signal measured is at least 10 times that of the noise. We obtain a sensitivity of $10 \times \delta(\Delta f/f_0) \times f_0/s_1 \approx 2 \times 10^{-6}$ emu.

7.5.3 Test Measurements on a Known and Previously Characterized Sample with a TDO Based TS System

Additional tests of the equipment were performed by measuring a previously studied sample with a similar TDO-based TS system. For this, we have chosen a system of Fe_3O_4 NPs, with a mean diameter of 6 nm, in powder form, synthesized and provided by Dr. Hariharan Srikanth and members of the Functional Materials Laboratory at the University of South Florida in Tampa, FL, USA. Magnetic properties of this and similar NPs systems can be found in [15]. Tests on this sample included bipolar TS scans at fixed temperatures with $H^{\text{Sat}} = 1$ T performed with the two different TS setups: the TDO based and our improved CMOS-based circuit. Figure 7.10a shows a 3D plot of scans measured at different temperatures between 1.8 K and 100 K with the CMOS-based system. A detailed bipolar scan for the sample measured at 1.8 K is shown in Fig. 7.10b. The respective and previously described corrections for the time and field linear drifts have been performed on the scans. Two peaks are identified for each unipolar scan, which correspond to the anisotropy fields, H_K , according to the theoretical model of TS developed by Aharoni et al. (see Sect. 7.1). A clear evolution of the H_K peaks in the sample with temperature is observed in the 3D plot (Fig. 7.10a); i.e., the double peak structure becomes a single peak one as the temperature increases. Such an evolution with temperature is better illustrated in the H_K vs. T plot in Fig. 7.10c. It is observed that the described merging of the double peak structure occurs at the blocking temperature (~ 70 K).

The direct comparison of the results obtained with our CMOS-based TS setup with respect to those with a TDO-based circuit are shown in Fig. 7.11, where we have plotted bipolar scans for the sample measured at 10 K with both setups. Our CMOS-based system reproduces the shape and position of the peaks at H_K of the TS scan measured with a TDO-based circuit setup built by us, and also of those previously reported in [15] performed with a similar TDO-based TS equipment. Moreover, the TS amplitude in our CMOS-based TS setup is enhanced by a factor of

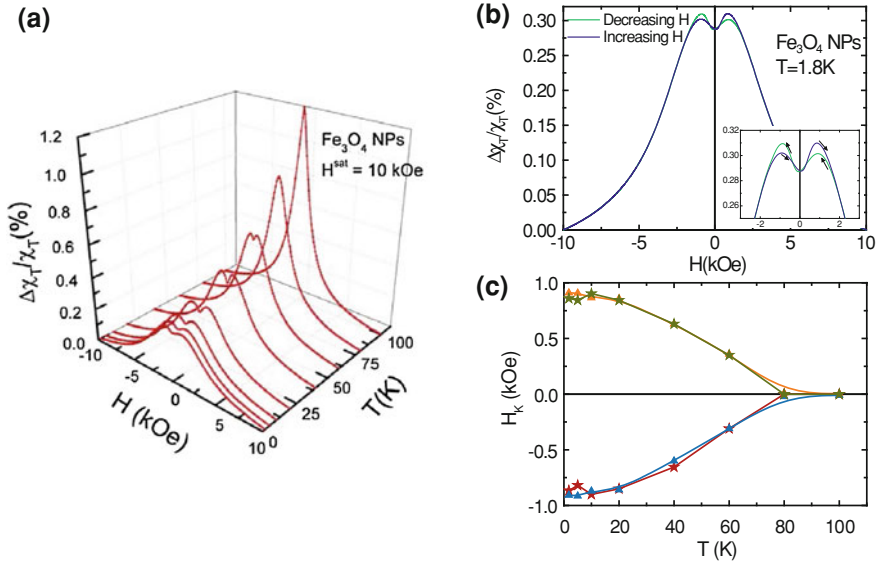
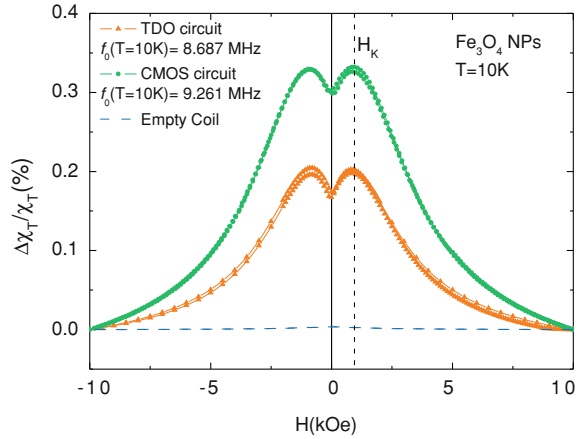


Fig. 7.10 TS test measurements on a Fe_3O_4 nanoparticles samples. **a** 3D plot of unipolar scans. **b** Bipolar scan at 1.8 K. Inset: detail of the anisotropy peaks of this scan. **c** Temperature dependence of H_K

Fig. 7.11 Comparison of bipolar TS scans on a Fe_3O_4 NPs sample at 10 K with $H^{\text{sat}} = 10$ kOe performed with a TDO based ($\blacktriangle$), and with a CMOS based ($\bullet$) TS setup. The measurement on the empty coil (--) is also shown for comparison



almost two at 10 K for the same sample, which demonstrates the high sensitivity of our equipment. The latter is also accentuated by the comparison with the practically flat TS signal for the empty coil, shown in dashes in the same Fig. 7.11 for comparison (notice that this correspond to the same curve shown in Fig. 7.8d), which is negligible compared to that of the sample.

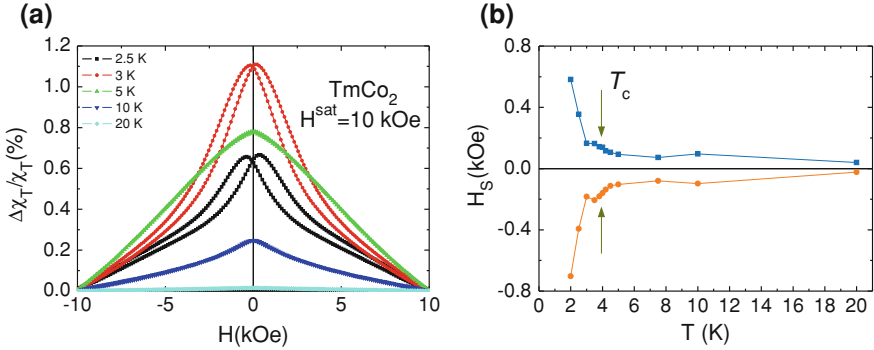


Fig. 7.12 **a** TS bipolar scans of TmCo₂ for selected temperatures between 2–20 K. **b** Switching field values, H_S , identified from the TS profiles

7.5.4 Low Temperature Measurements on TmCo₂

Finally, in order to probe the functionality of the TS system at low temperatures, we have performed measurements on a sample of bulk TmCo₂: a Laves phase with a ferrimagnetic to paramagnetic transition temperature around 4 K [22]. Previous works have demonstrated that this TS technique is well suited to track down and probe interesting magnetic features in similar RCo₂ Laves phases [3, 4]. For the particular case of TmCo₂ we use it to track its magnetic transition at low temperatures (below 10 K). TS measurements on this sample have been performed with a saturating field of 10 kOe from 2 to 20 K.

Figure 7.12a shows selected TS bipolar scans measured for the TmCo₂ sample. Each TS profile in the ferrimagnetic regime (below $T \sim 4$ K) shows pronounced peaks at characteristic fields, which we identified as switching fields, H_S . In Fig. 7.12b we have plotted the values of such H_S as a function of temperature. Close to $T_c \sim 4$ K the peaks are narrower and their values suffer a slight increase (indicated by arrows in Fig. 7.12b), similar to what has been previously observed for similar RCo₂ systems [3, 4]. Above T_c , H_S values rapidly decrease since the sample enters to a magnetic disordered state, but surprisingly they never reach a zero value in this temperature range. The existence of finite H_S in the paramagnetic state of these Laves phases has been ascribed to the occurrence of magnetic clusters, a novel and fascinating phenomenon coined as *parimagnetism* [3, 4, 23].

7.6 Conclusions

A complete TS measurement equipment for the PPMS has been implemented, operating at the MHz frequency range, with a wide temperature and H_{DC} field range of operation. The efficiency, simplicity and versatility of the proposed CMOS

oscillator based on a LC cross-coupled topology guarantee reliability, robustness and portability. Measurement tests demonstrate frequency stability and high performance of the circuit, as well as high sensitivity to probe the transverse susceptibility of interesting magnetic systems. Also, we have demonstrated that our system is well suited to study magnetic phenomena at low temperatures, down to $T = 1.8$ K.

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Chapter 8

Transverse Susceptibility of Iron Oxide Nanoparticles Systems

In this section we introduce two examples of iron oxide nanoparticles systems studied via RF transverse susceptibility (TS). We demonstrate possibilities of the TS technique, extensively described in the previous chapter, to directly probe the magnetic anisotropy of magnetic systems.

In the first example, we present dc SQUID based magnetometry and radio frequency transverse susceptibility measurements on oleic acid- and SiO₂-coated magnetite (Fe_{3-x}O₄) nanoparticles. The effects of the type of coating on the magnetic anisotropy are evaluated as a function of the particle size (5 and 14 nm of average diameter). Coating the samples with SiO₂ reduces the interparticle interactions compared to those oleic acid coated samples, but it seems to be more effective for the particles with 5 nm than for those with 14 nm in diameter. SiO₂ coating also decreases the magnetic anisotropy field measured on the particles, with respect to the oleic acid-coated samples. This is relevant concerning applications in biomedicine, since the SiO₂ coating renders 5 and 14 nm hydrophilic particles with very limited agglomeration, low anisotropy, and superparamagnetic behavior at room temperature.

The second example consists in maghemite (γ -Fe₂O₃) nanoparticles of different sizes, on which the effective anisotropy constant, K_{eff} is estimated from the TS measurements and its variation is examined as a function of the particle size. The resulting values range from 4 to 8×10^4 erg/cm³, being on the order of the magnetocrystalline anisotropy in bulk maghemite. K_{eff} values increase as the particle diameter increases. Evidences of anisotropy field distribution given by the size distribution in the samples, and interparticle interactions that increase as the particle size increases, are also observed in the TS measurements.

8.1 Magnetite Nanoparticles

Magnetite (Fe₃O₄) NPs are one of the most commonly studied nanoparticles systems because of their relatively easy production by chemical routes, low toxicity and fascinating magnetic properties [1–3]. It has been demonstrated that the surrounding

environment of the Fe_3O_4 particles strongly affects their magnetic properties [4–8], in such a way that, for example, bulk-like structural, magnetic and electronic behavior may be recovered in 5 nm particles [1–3]. Such effects are obtained in Fe_3O_4 NPs with oleic acid used as surfactant, covalently bonded to the particle surface. Those particles are good candidates for biomedical applications [9], once the hydrophobic oleic acid-coating is ligand-exchanged to a hydrophilic one, which makes the particles dispersible in aqueous media. Within this framework, magnetic NPs of a few nanometers in size and with the highest possible magnetization are required. They must also show superparamagnetic behavior at room temperature and low interparticle interactions, for which low particle agglomeration is desirable. All these features enable the synthesis of NP dispersions (ferrofluids) which can be injected into biological systems for in vivo applications [10, 11].

Following this scheme, it is crucial to evaluate the effects of the hydrophilic particle coating on the magnetic anisotropy of Fe_3O_4 NPs, in order to get optimum particles for bio-applications. Particle coating also reduces the interparticle interactions, thus shifting the superparamagnetic transition well below room temperature. This allows the use of larger particles with larger magnetic moment, which results in larger signals in the superparamagnetic regime [12].

Then, we use a hydrophilic coating, namely, SiO_2 on 5 and 14 nm Fe_3O_4 NPs, and examine its effects on the magnetic anisotropy of the particles by RF transverse susceptibility measurements. For completeness, we compare the results on these SiO_2 -coated Fe_3O_4 NPs with those obtained for the starting oleic acid-coated particles of the same size.

8.1.1 Experimental

The synthesis of the size controlled oleic acid-coated NPs was carried out by the group of Dr. Amilcar Labarta and Dr. Xavier Batlle from the Departament de Física Fonamental and Institut de Nanociència i Nanotecnologia, Universitat de Barcelona, in Barcelona, Spain. It was performed following conventional thermal decomposition of an iron precursor in an organic medium in the presence of an organic acid as a surfactant, as extensively described elsewhere [6, 13–15]. Samples with 5 and 14 nm particles were prepared. For SiO_2 coating, the hydrolysis of tetra ethoxy silane (TEOS) in water-in-oil (w/o) micro-emulsions has proven to be a reproducible method for the subsequent silica coating of the hydrophobic oleic acid-coated magnetite NPs [16, 17]. The proportion of TEOS and the concentration of magnetite cores of known diameter in the medium allows controlling the shell thickness as well as the number of magnetic cores inside a single shell.

The size and shape of the NPs were examined by transmission electron microscopy (TEM) performed by the group of Dr. Amilcar Labarta and Dr. Xavier Batlle from the Departament de Física Fonamental and Institut de Nanociència i Nanotecnologia, Universitat de Barcelona, in Barcelona, Spain. TEM measurements were carried out on Hitachi H-7500 (low-resolution) and JEOL JEM 2010 (high-resolution)

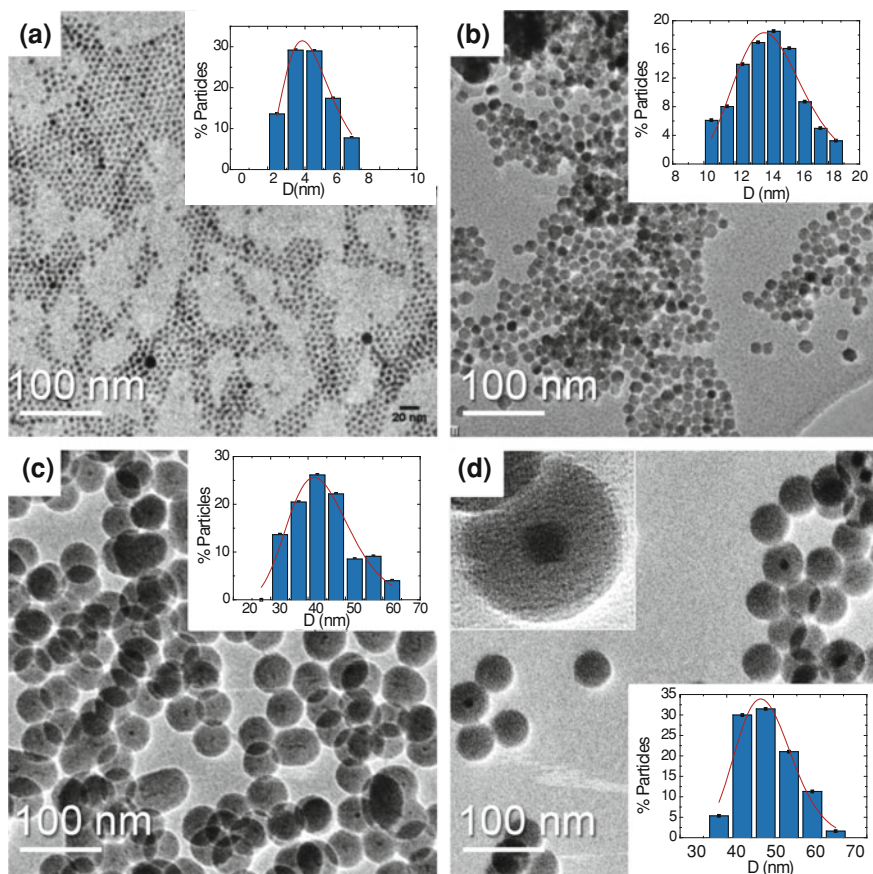


Fig. 8.1 BF TEM images of the oleic acid-coated (a and b) and SiO₂-coated (c and d) Fe_{3-x}O₄ NPs. Insets show the size distributions obtained in each case. Inset in d shows details of a SiO₂ coated particle. The SiO₂ shell thickness in c and d is about 15–20 nm

transmission electron microscopes of the Centres Científics i Tecnològics of the Universitat de Barcelona. Samples for the TEM study were prepared on copper grids coated with carbon. A drop of NP's solution was carefully placed on the copper grid surface and dried. The size distributions of the nanocrystals were determined by analysis of the TEM images.

The bright field (BF) TEM image of each sample is shown in Fig. 8.1 along with the size distributions obtained for each case. The oleic acid-coated particles are very uniform (Fig. 8.1a, b), similarly to those previously reported for this range of sizes. SiO₂-coated particles are shown in Fig. 8.1c, d. Darker and lighter regions correspond to the Fe_{3-x}O₄ core (5 and 14 nm average diameter) and the SiO₂ shell (about 15–20 nm thick in both cases), respectively, as shown in detail in the inset of Fig. 8.1d. These images reveal that the Fe_{3-x}O₄ NPs are well single-coated, with

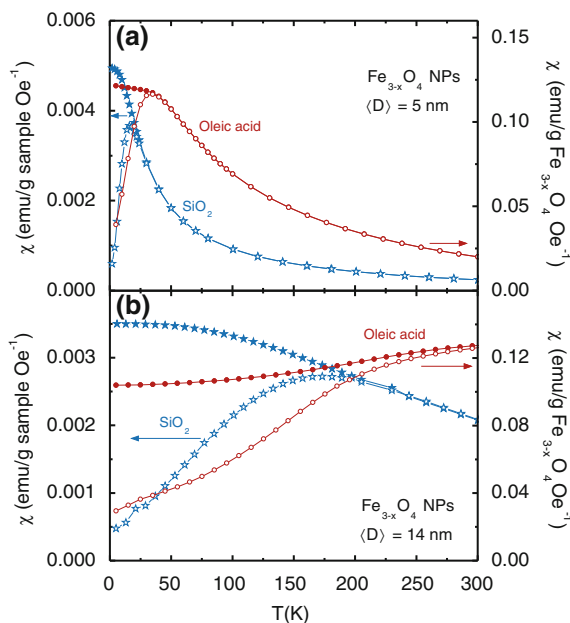


Fig. 8.2 ZFC-FC curves measured for the oleic acid- and SiO_2 -coated $\text{Fe}_{3-x}\text{O}_4$ NPs with average diameters of **a** 5 nm and **b** 10–12 nm

absence of agglomeration, though an excess of SiO_2 is observed from the presence of several SiO_2 beads without $\text{Fe}_{3-x}\text{O}_4$ cores. The average diameter and width obtained from the size distributions for the four samples are listed in Table 8.1.

8.1.2 Magnetic Properties

The magnetic properties of the particles have been determined by dc magnetic susceptibility, $\chi_{\text{dc}}(T)$, and RF transverse susceptibility, performed in the four $\text{Fe}_{3-x}\text{O}_4$ NPs samples. $\chi_{\text{dc}}(T)$ was measured in a SQUID magnetometer at the Servicio de Medidas Físicas of the Universidad de Zaragoza, after zero-field cooling (ZFC) and field cooling (FC) the sample. Temperature was varied between 2 and 300 K, and a 50 Oe field was applied.

The ZFC-FC curves shown in Fig. 8.2 reveal the superparamagnetic behavior of the $\text{Fe}_{3-x}\text{O}_4$ particles. At lower temperatures, FC and ZFC for each sample separate, and the ZFC curve shows a maximum at a blocking temperature, T_B . The blocking temperature of the particles with average sizes of 5 and 14 nm, is 35 and 300 K, respectively, while the SiO_2 -coated samples exhibit a reduced T_B (see Table 8.1) as compared to the oleic acid-coated samples.

Table 8.1 Summary of parameters of the $\text{Fe}_{3-x}\text{O}_4$ NPs

Coating	$\langle D \rangle$ (nm)	σ (nm)	T_B from χ_{dc} (K)	T_M from TS (K)	H_{K0} (kOe)
Oleic	5	3	35(2)	35(2)	0.69(3)
Acid	14	9	~ 300	215(5)	0.90(4)
SiO_2	44	27	16(1)	14(1)	0.65(3)
	49	29	170(1)	140(1)	0.89(4)

Average particle diameter ($\langle D \rangle$) and distribution width (σ) as obtained from TEM, blocking temperature (T_B) obtained from χ_{dc} , blocking temperature (T_M) deduced from TS, and the intrinsic anisotropy field obtained at $T = 2$ K (H_{K0})

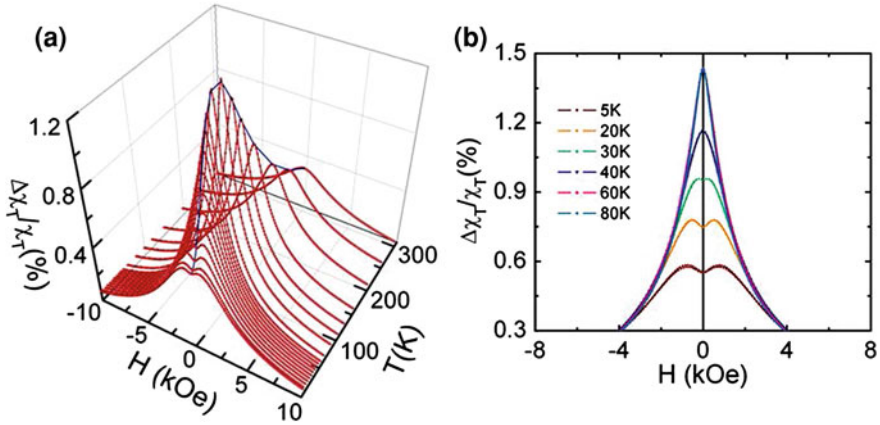


Fig. 8.3 TS results for 5 nm oleic acid-coated $\text{Fe}_{3-x}\text{O}_4$ NPs. **a** 3D plot of TS unipolar scans at several temperatures. **b** TS bipolar scans at selected temperatures

TS measurements were performed using the setup described in Chap. 7. The temperature, T , and static magnetic field, H_{dc} , are varied using the PPMS within 2–300 K and ± 15 kOe, respectively. Figure 8.3a shows the 3D plot of unipolar TS scans for the 5 nm oleic acid $\text{Fe}_{3-x}\text{O}_4$ NPs. At low temperatures the curves show two peaks located symmetrically about the origin of the magnetic field axis, characteristic of the blocked regime. According to the theoretical model of TS developed by Aharoni et al. [18] (see Sect. 7.1), a unipolar scan should reveal the existence of those two symmetric peaks at the anisotropy fields, H_K , and a third one at the switching field, H_S . The absence of the peak at H_S in the TS scans, as well as the rounded characteristic shape of the peaks observed in our case or in similar NP systems [19], are attributed to the presence of a distribution of anisotropy fields, which causes the peak at the switching field to merge indistinguishably with one of the peaks at the anisotropy field [20]. The distribution of anisotropy fields is an unavoidable consequence of the dispersion in particle size.

As temperature increases from 2 K, the double-peak structure of the isothermal unipolar scans becomes less pronounced and merges into a single central peak, as depicted in Fig. 8.3b. This trend is consistent with a gradual transition from a blocked

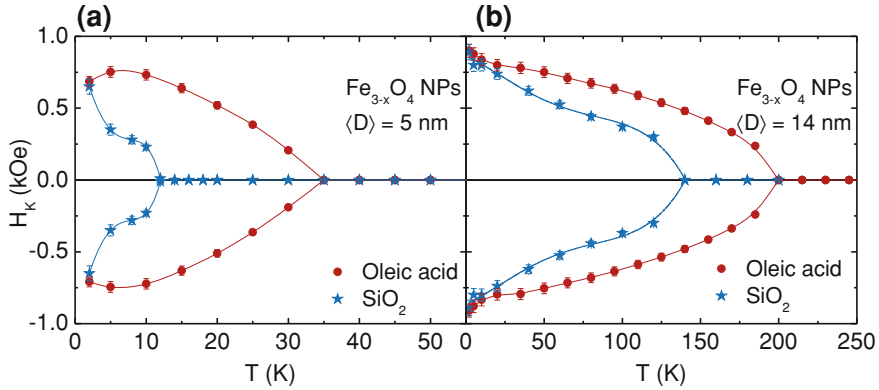


Fig. 8.4 Comparison of the temperature dependence of the values of the anisotropy field (H_K) extracted from the TS scans for the oleic acid- and SiO_2 -coated $\text{Fe}_{3-x}\text{O}_4$ NPs with average diameters of **a** 5 nm and **b** 14 nm

state towards a superparamagnetic one, which will be discussed further in Sect. 8.1.3. Analogous results for the TS measurements have been obtained for the other three samples.

The H_K values obtained from the TS profiles for the four samples are plotted in Fig. 8.4, as a function of temperature. Let us remark that the direct determination of H_K is one of the main assets of the TS technique. We define T_M as the minimum temperature at which $H_K = 0$, corresponding to the blocking temperature where the double peak structure in the TS profiles disappears. T_M values obtained for the four samples are listed in Table 8.1. Note that these values are well in agreement with those of T_B obtained from the ZFC curves measured by conventional SQUID magnetometry (also listed in Table 8.1).

H_K values are found to be lower than 1 kOe in all cases. For most temperatures, H_K are higher for the oleic acid- than for the SiO_2 -coated samples (see Fig. 8.4), for both particle sizes. This is due to a reduction in the T_B value for the SiO_2 -coated particles, fact that will be also discussed in Sect. 8.1.3. At about 2 K, though, H_K values are very close for each group of particles (5 nm with both coatings on one side, and 14 nm with both coatings on the other), which reveals that at very low temperature the strong magnetic behavior of the magnetite core overcomes any effect of the coating.

8.1.3 Discussion

In order to provide a deeper understanding of the TS measurements, we perform a direct comparison between the ZFC curve as obtained from the χ_{dc} SQUID measurements [4, 6] (top panel, left-hand side y-axis) and the TS ratio, $\Delta\chi_T/\chi_T(T)$, at $H_{dc} = 0$ (top panel, right-hand side y-axis), for the 5 nm oleic-coated particles, which

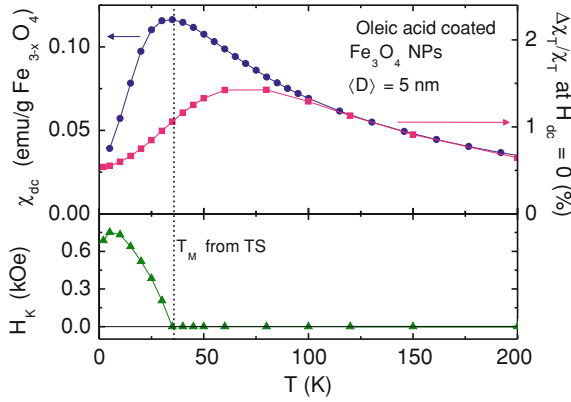


Fig. 8.5 Comparison of the temperature dependence of (i) the ZFC curve (●) obtained from dc susceptibility measurements (χ_{dc}) at 50 Oe; (ii) the curve obtained from the transverse susceptibility values at $H_{dc} = 0$ (■), and (iii) the anisotropy field (H_K), for the oleic acid-coated 5 nm $\text{Fe}_{3-x}\text{O}_4$ particles. Dashed line marks the T_B from the ZFC curve, which matches the blocking temperature, T_M , obtained from TS

is shown in Fig. 8.5 as a function of temperature. As the temperature increases, the TS ratio at $H_{dc} = 0$ increases, similarly to the observed behavior of the ZFC curve, although it has a maximum at a higher temperature (see Fig. 8.5). This is consistent with the well-known increase [21] in the temperature of the ac susceptibility maximum as the exciting frequency increases (with respect to the dc measurements), since TS is measured at a frequency of 12 MHz. Such a feature for TS has been previously described in Ref. [22]. Finally, both χ_{dc} and TS measurements coincide in the paramagnetic region, as it has been proven in Sect. 7.5.2.

For completeness, the temperature dependence of the positive H_K values is plotted on the same graph (bottom panel, left-hand side y-axis). Notice the nice accordance between T_M from TS and T_B from the maximum of the ZFC curve (see dashed line in Fig. 8.5), as mentioned in the previous section, demonstrating that in the blocked state (below T_B) the particles have finite H_K values.

The strong temperature dependence of H_K , observed in Figs. 8.4 and 8.5, accounts for both the thermal variation of the magnetocrystalline anisotropy constant of the material, which is negligible in this case, and for the influence of the thermal energy that overcomes the anisotropy energy of the particles [23, 24]. The decrease of H_K with increasing T is usually described by the relation $H_K = H_{K0}[1 - (T/T_M)^\beta]$, where $\beta \sim 0.5$ [25, 26], for an assembly of aligned particles, and $\beta \sim 0.77$ for an assembly of randomly oriented particles [27–29], and H_{K0} corresponds to the intrinsic anisotropy field of the material. The emerging picture is that, at low temperatures, the magnetite particles are frozen and $H_K \sim H_{K0}$. As T increases, some fraction of the particles become superparamagnetic since the thermal excitations are now capable of reversing the magnetic moment from one orientation to the opposite, and the effective H_K decreases. Thus, well above the blocking temperature, all

the particles are superparamagnetic, which is characterized by the random thermal fluctuations of single-domain particle moments, so that the measured H_K of the collection of magnetite particles is zero. However, the curves of $H_K(T)$ in Figs. 8.4 and 8.5 do not follow the simple $H_K = H_{K0}[1 - (T/T_M)^\beta]$ relation, since additional effects on the magnetic anisotropy of the particles, such as interparticle interactions [30] and anisotropy field distribution [25, 26], should be taken into account.

T_M values, and, correspondingly, T_B , are found to decrease as the particle diameter decreases, from 215 to 35 K for 14 and 5 nm oleic acid-coated NPs, respectively, and from 140 to 14 K for the equivalent SiO_2 -coated particles (see Table 8.1 and Fig. 8.4). This coating also reduces the values of T_M , with respect to those found for the oleic acid-coated case with the same diameter, which is related to the reduction of the dipolar interparticle interactions [19] as consequence of the increased magnetite interparticle core-core distance by the thick SiO_2 shell.

A stronger reduction in T_M by SiO_2 coating is observed for the smaller 5 nm particles than for the larger 14 nm NPs, despite the SiO_2 shell thickness is roughly the same in both cases, since their magnetic moment is reduced with the particle volume, and, correspondingly, their dipole-dipole interactions decrease. Consequently, the smaller the particles the more effective the reduction of the interparticle interactions by SiO_2 coating.

According to these analyzes, with the TS measurements we are observing, on the one hand, a phenomenon related to a dc behavior of the particles, i.e., their superparamagnetic-blocking transition occurring at a characteristic temperature, detectable from the H_K versus T plot and the ZFC from χ_{dc} measurements; and, on the other hand, a dynamic process evidenced in the shift of the ac susceptibility maximum to higher temperatures with increasing frequency. This is possible given that in a TS experiment we are applying both a bias and a dynamic magnetic field at the same time, thus we are able to observe and disentangle both phenomena in the particles.

Figure 8.6 shows the comparison of the ZFC curves and the TS ratio at $H_{dc} = 0$ as a function of temperature for the samples with 14 nm in diameter with both coatings. Since these bigger particles have a wider distribution in size and their interparticle interactions are more evident than the case of the smaller particles in Fig. 8.5, the peak at the ZFC curve is broader. However, T_M obtained from TS seems to coincide with the inflection point of the ZFC curve. At any rate, the value of the blocking temperature is sharper from the TS study (H_K vs. T plot) than from these ZFC measurements, the latter showing a broad maximum.

Finally, an estimation of the effective anisotropy constant, K_{eff} may be directly deduced from the M_S measured from conventional SQUID magnetometry and the values of H_{K0} obtained from the TS measurements at low temperatures (see Table 8.1), as $K_{eff} = 1/2 M_S H_{K0}$ [12]. With M_S for all samples of the sizes studied here being on the order of 80–90 emu/g $\text{Fe}_{3-x}\text{O}_4$ [4, 6], the resulting K_{eff} values are within $1.6\text{--}1.8 \times 10^5$ erg/cm³, which are close to those values reported for both bulk magnetite ($\sim 1\text{--}3 \times 10^5$ erg/cm³) [12, 31, 32], and high quality 5 nm particles ($\sim 4\text{--}5 \times 10^5$ erg/cm³) [4, 32].

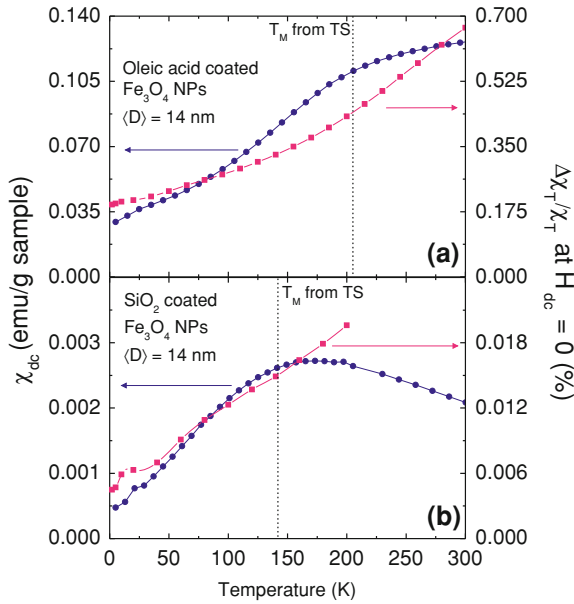


Fig. 8.6 Comparison of the ZFC curve from χ_{dc} (●) with the TS at $H_{dc} = 0$ (■), both as a function of T , for the Fe_{3-x}O₄ NPs with 10–12 nm in diameter: **a** oleic acid coated and **b** SiO₂ coated. Dashed line marks T_M

8.1.4 Conclusions

We have demonstrated that SiO₂ coating of the Fe_{3-x}O₄ particles reduces the interparticle interactions, which is revealed by the reduction of the blocking temperature of the system. This is observed for both particle sizes but it is more efficient in the case of the smaller ones. H_K values of the oleic acid-coated NPs are higher than those of the SiO₂-coated ones because of their higher T_B , and, consequently, larger interparticle interactions. This suggests that the effective anisotropy field increases with interparticle dipole-dipole interactions, which is consistent to what has been described in Refs. [4] and [21]. TS measurements also allow estimating the effective magnetic anisotropy constant, obtaining values in close agreement with others published in literature.

To sum up, let us recall that biomedical applications require hydrophilic particles with high saturation magnetization to manipulate and detect them by application of an external magnetic field, low anisotropy field and superparamagnetic behavior at room temperature so that particle agglomeration, as due to attractive magnetic forces, is avoided [10, 11]. The present work indicates that our 5 and 14 nm SiO₂-coated hydrophilic magnetite nanoparticles fulfill all those requirements (saturation magnetization close to that of the bulk magnetite, H_K below 1 kOe and superparamagnetic behavior at room temperature), which makes them very attractive for such purposes.

8.2 Maghemite Nanoparticles

The chemical stability of the maghemite phase ($\gamma\text{-Fe}_2\text{O}_3$) of iron oxide nanoparticles makes this system very attractive for technological and biomedical applications; this feature is specially important for the latter, since, beside the requirements described in the previous section, particles with low degradability into biological systems for in vivo applications are desired [10, 11]. However, and despite all the research carried out on maghemite NPs, their magnetic behavior is not yet well understood.

Bulk maghemite has a inverse-spinel structure with some vacant sites, exhibiting ferrimagnetic ordering below 918 K. Maghemite nanoparticles show reduced saturation magnetization compared to the bulk, they do not saturate at rather high fields, they show open and shifted hysteresis loops, and irreversibility in ZFC-FC curves [33]. This magnetic behavior has been attributed to finite size and surface effects at the maghemite particles [34]. Accordingly, some theoretical models have been developed to explain such a behavior, in particular the decrease in their magnetization with size reduction; from these models, the most accepted is the one based on a bulk-like ferrimagnetic core and a shell composed of disordered moments [33]. The magnetism of the $\gamma\text{-Fe}_2\text{O}_3$ particles we study here may be understood in the frame of such a core-shell model, which we summarize as follows [33, 35]: the particles consist of a core with structural periodicity exhibiting a superparamagnetic behavior, and a disordered shell without the periodicity. Most of the magnetic contribution of the entire particle usually originates from the bulk-like ferrimagnetic core. The disordered shell at the surface is analyzed as paramagnetic or antiferromagnetic component in the magnetization data at high fields. The magnetic interaction between the core and the shell can appear as an exchange bias effect. The shell has a thickness of about 1 nm, independently of the size of the particle [33, 35].

A previous study on the effects of pressure on these maghemite nanoparticles allowed to disentangle the contribution of the core (K_{core}) and the surface (K_S) to the effective magnetic anisotropy of the system, K_{eff} [36]. The values of K_{core} , on the one hand, were found to be between that from the magnetocrystalline anisotropy for bulk maghemite and that usually found in maghemite nanoparticles ($10^5\text{--}10^6\text{ erg/cm}^3$). On the other hand, K_S is similar to that previously found for maghemite nanoparticles (10^{-2} erg/cm^2). In this section, we study the magnetic anisotropy of maghemite nanoparticles of different sizes, estimated from the direct measurement of the anisotropy field H_K from RF transverse susceptibility measurements.

The series of maghemite nanoparticles samples studied here were synthesized and previously characterized by the group of Dr. Angel Millán and Dr. Fernando Palacio of the Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza. The particles are dispersed in a polymer matrix with low size dispersion and regular distribution of particles. A total of four $\gamma\text{-Fe}_2\text{O}_3$ NPs samples were studied, with average diameters of 5.2, 6, 7 and 13 nm, labeled from S5 to S8 following the nomenclature used in Refs. [33, 35]. The NPs diameter has been determined by transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS),

Table 8.2 Summary of the parameters deduced from the TEM and magnetic measurements on γ -Fe₂O₃ NPs

Sample	$\langle D \rangle$ (nm)	σ (nm)	T_M (K)	M_S (emu/cm ³)	$H_K \times 10^4$	K_{eff} (erg/cm ³)
S5	5.2(9)	0.9	25(5)	217(9)	340(30)	3.7(5)
S6	6(1)	1.1	105(5)	237(9)	460(30)	5.4(8)
S7	7(1)	1.4	140(8)	210(9)	570(40)	6.0(8)
S8	13(3)	3.2	250(10)	356(9)	440(30)	7.8(9)

Average particle diameter ($\langle D \rangle$) and width (σ) of the size distribution obtained from TEM, blocking temperature (T_M) obtained from TS, saturation magnetization (M_S), anisotropy field (H_K) and anisotropy constant (K_{eff}), these last three parameters at $T = 5$ K

as described in the same references [33, 35], measurements carried out by the same group of Dr. Millán and Dr. Palacio. The average diameter and width obtained from the size distributions for the four samples are listed in Table 8.2.

8.2.1 TS Measurements

We have performed TS measurements on the four samples of maghemite nanoparticles using the setup described in Chap. 7. The temperature, T , and static magnetic field, H_{dc} , are varied using the PPMS within 2–300 K and ± 10 kOe, respectively. In Fig. 8.7a we show the 3D plot of unipolar TS scans at several temperatures for particles with $\langle D \rangle = 5.2(9)$ nm. The TS profiles are similar to those described in Sect. 8.1.2 for magnetite NPs. The peak at the switching field merges with one of the anisotropy field peaks due to the presence of a distribution in anisotropy fields in the maghemite NPs system, as described above for the Fe_{3-x}O₄ NPs. However, in the case of γ -Fe₂O₃ NPs, the two peaks observed at the anisotropy field have different heights. As temperature increases from 2 K, the peak heights difference is reduced, and the double-peak structure is less pronounced, evolving into a single central peak, as depicted in the TS bipolar scans plotted for selected temperatures in Fig. 8.7b. This trend, similar to the case of Fe_{3-x}O₄ NPs, is consistent with the gradual transition from a blocked state towards a superparamagnetic one. A better illustration of this evolution is observed in the plot of the H_K values (obtained directly from the TS scans) as a function of T shown in Fig. 8.7c. From these plots, the T_M of each sample is directly obtained as the minimum temperature where $H_K = 0$.

Analogous results for the TS measurements have been obtained for the other three samples. T_M values for the four samples are listed in Table 8.2. They are found to decrease as the NP diameter decreases, from 250 K down to 25 K for particles of 13 and 5.2 nm, respectively. This trend in T_M may be understood as due to the decrease of the particles magnetic moment with their reduced volume, and, correspondingly, the decrease of their dipole-dipole interactions, similarly to the case of Fe_{3-x}O₄ NPs.

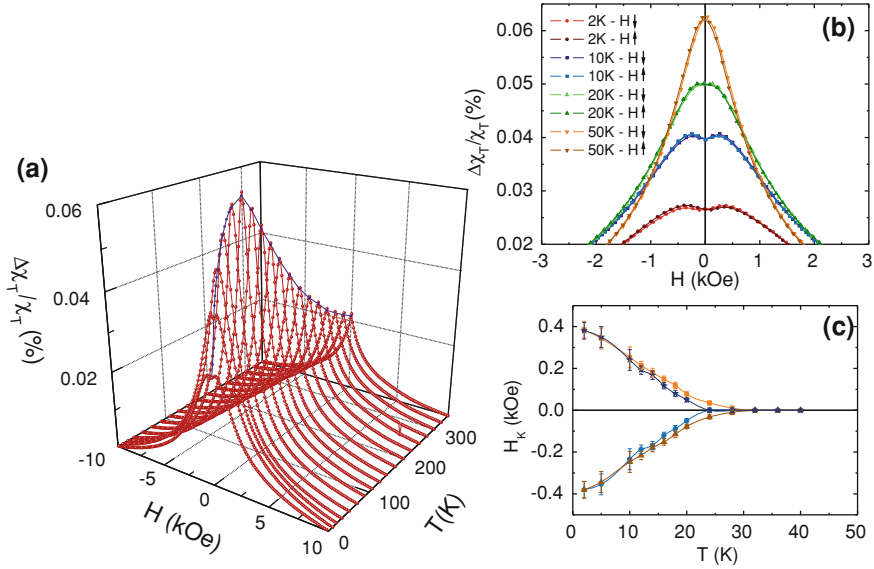


Fig. 8.7 TS results the sample with $\langle D \rangle = 5.2(9) \text{ nm}$. **a** 3D plot of TS unipolar scans at several temperatures. **b** TS bipolar scans at selected temperatures. **c** Values of H_K extracted from the TS scans plotted as a function of T

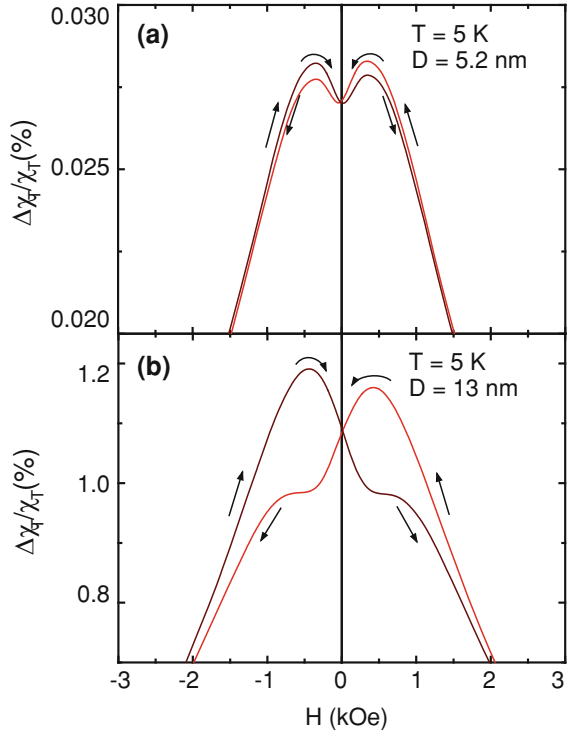
8.2.2 Discussion

As it has been mentioned above, there is a difference in the peaks height of the TS profiles, so that for each unipolar scan from positive to negative field sweep, the peak at the first quadrant is always larger than the peak height in the second one. This feature is better illustrated in Fig. 8.8 where details of a TS bipolar scan of sample S5 (Fig. 8.8a) and S8 (Fig. 8.8a) measured at $T = 5 \text{ K}$ are shown. One way to analyze such an asymmetry is to quantify the peak difference for each unipolar TS scan as

$$\Delta\text{height}(\%) = \frac{[(\text{Peak height})_{\text{first quadrant}} - (\text{Peak height})_{\text{second quadrant}}]}{(\text{Peak height})_{\text{first quadrant}}} \%$$

similar to the procedure described in Ref. [19]. In Fig. 8.10a we have plotted Δheight as a function of the reduced temperature T/T_M for the four samples in the series. It is evident that the asymmetry is found to increase as the particle size increases. This is a fact that has been consistently observed in several TS studies of NPs systems and has been related to the presence of anisotropy field dispersion [20], and also as a consequence of increasing interparticle interactions with the particle size [19]. Both components might be present in our maghemite NPs samples since, on one hand, previous studies of their size have shown a broader size distribution for the

Fig. 8.8 Comparison of the details of the TS bipolar scans measured at $T = 5$ K for the sample with **a** $\langle D \rangle = 5.2$ nm (S5) and that with **b** $\langle D \rangle = 13$ nm (S8). Arrows show the direction of the field sweep



sample with larger diameter than those with smaller ones [33, 35], and, on the other hand, effects of interparticle interactions have been observed in ac susceptibility measurements at different frequencies in these samples (measurements performed by the group of Dr. Millán and Dr. Palacio). The extrapolated values of the microscopic characteristic time, τ_0 , are obtained from a typical Arrhenius plot of $\ln(1/\omega)$ versus $1/T_B$ shown in Fig. 8.9, from frequency dependent ac susceptibility measurements. For non-interacting superparamagnetic maghemite nanoparticles τ_0 values are usually on the order of 10^{-10} s, while in the present case, τ_0 obtained from linear fits of data shown in Fig. 8.9 reaches 10^{-15} s for the particles with $D = 13$ nm. Such a strong reduction in τ_0 is a signature of systems where interparticle interactions are important [37].

The thermal evolution of H_K for the four samples is shown in Fig. 8.10b. H_K are also plotted as a function of the reduced temperature T/T_M in order to have better comparison. H_K values at low temperatures are of the same order for all samples, except for those particles of smallest size. As temperature increases, H_K values seem to follow a general trend of increasing as the particle diameter increases, which is reflected in the effective anisotropy values as it is described below.

The effective anisotropy constant, K_{eff} may be estimated from the M_S obtained from conventional SQUID magnetometry [33] and the values of H_K extracted from

Fig. 8.9 Arrhenius plot of the measuring time ($1/\omega$) as a function of $1/T_B$, as obtained from ac susceptibility measurements in the four maghemite NPs

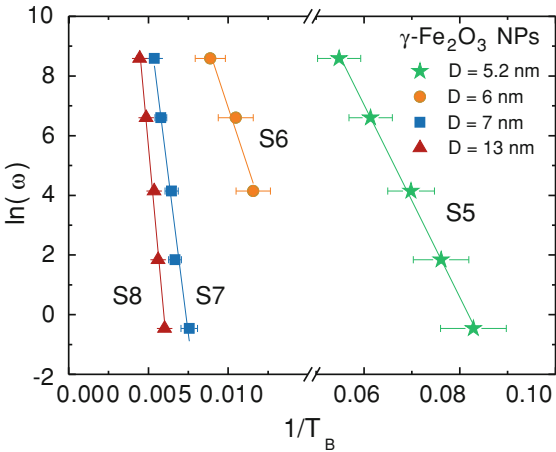
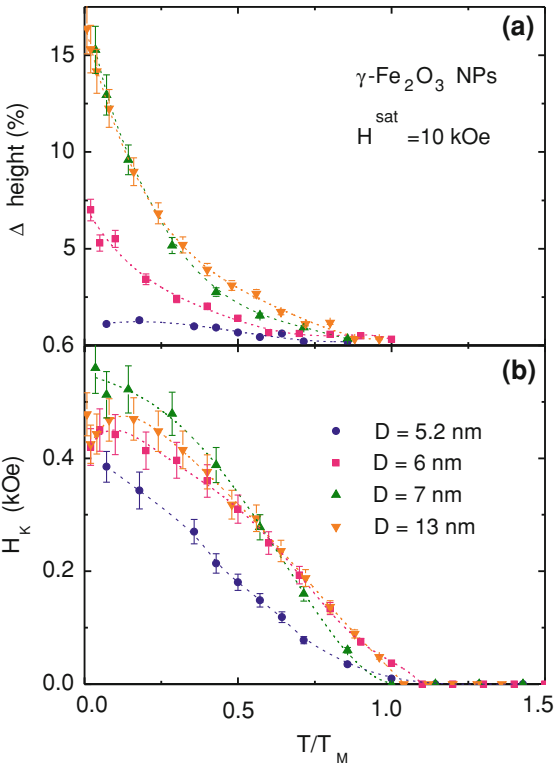


Fig. 8.10 Comparison of **a** the anisotropy peak height difference and **b** H_K values extracted from the TS scans, both plotted as a function of T/T_M in the four maghemite NPs samples. *Dashed lines* are guides to the eye



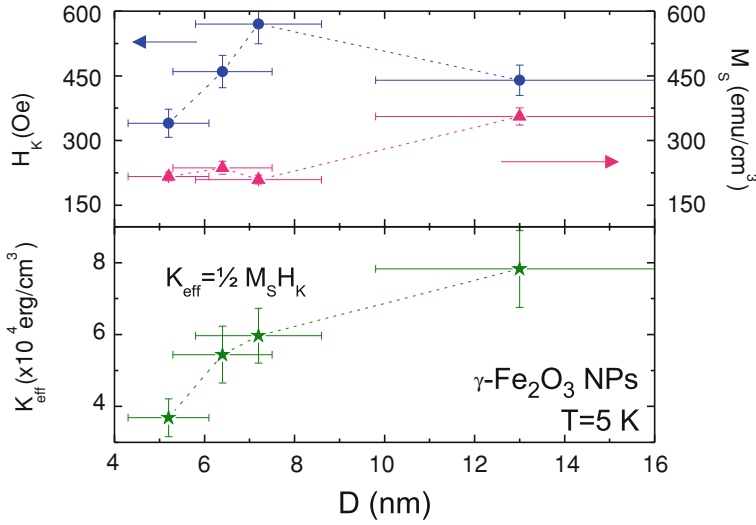


Fig. 8.11 (Top panel) H_K and M_S values as obtained from the TS scans and $M(H)$ measurements, respectively. (bottom panel) K_{eff} estimated from H_K and M_S values. The three parameters are plotted as a function of the particle diameter

the TS measurements, as $K_{eff} = \frac{1}{2} M_S H_K$. The values of H_K and M_S for each sample, both at $T = 5$ K, used to calculate K_{eff} and the resulting values of the latter are given in Table 8.2 and plotted in Fig. 8.11. K_{eff} values are on the same order of those reported for the magnetocrystalline anisotropy in bulk maghemite (2.0×10^4 erg/cm³) [38]. K_{eff} is found to increase as the particle diameter increases, which is consistent with the increase in the anisotropy as the core volume (V_{core}) in the particles increases, as reported in Ref. [36]. Comparing to those values obtained for the same maghemite NPs in Ref. [36] (being of 7.7×10^5 erg/cm³ for the core contribution of particles of 6 nm in diameter) our K_{eff} values are found to be lower in almost one order of magnitude. This difference may stem from the influence of the interparticle interactions in the position of H_K peaks in the TS scans, as it has been observed in similar NPs systems where the anisotropy field is found to increase with increasing interactions [19]. Indeed, we have demonstrated that our TS measurements are strongly influenced by inter-particle interactions, which may be affecting the correct estimation of K_{eff} .

8.2.3 Conclusions

The increasing asymmetry in the peak heights in the TS scans of γ -Fe₂O₃ NPs samples is due to a combination of the anisotropy field distribution given by the size distribution in the samples, and the interparticle interactions that increase as

the particle size increases. K_{eff} values determined from the TS measurements for the particles are found to be close to those of bulk maghemite and increase as the particle diameter increases. These values, however, are lower than those previously determined for the same NPs systems in Ref. [36]. Such a difference may be due to the influence of interparticle interactions and anisotropy field distribution in the determination of H_K from TS measurements.

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Chapter 9

General Conclusions

In this thesis we have performed an extensive study of different magnetic nanoparticles systems, elaborated by combination of diverse experimental techniques. We intended to center the attention in the capabilities of two characterization methods: the X-ray absorption spectroscopies (XANES, EXAFS and XMCD) and the RF transverse susceptibility. By using these techniques for electronic, structural and magnetic studies of nanoparticles systems, along with other complementary methods, it is possible to obtain a better understanding of the origin of their magnetic anisotropy, and many other interesting phenomena. The main findings for the magnetic nanoparticles studied here may be summarized as follows:

- Co–W NPs: we have described a system of self-organized amorphous Co–W alloy nanoparticles, uniformly dispersed in an alumina matrix. They show superparamagnetic behavior and are described as an array of non-interacting particles with random anisotropy axes and an average moment per particle proportional to the particle volume and to the average Co moment for each alloy composition. We prove that, despite their amorphous nature, values of the magnetic anisotropy constant deduced for Co–W alloyed NPs are on the order of 10^6 erg/cm^3 , which is higher than that of bulk Co. Thus, we demonstrate that the magnetic anisotropy of amorphous alloy particles may be originated in mechanisms other than surface effects, such as structural short range order present in the Co–W alloy. Co–W hybridization and short range order identified in these Co–W NPs give rise to breakdown of Hund's third rule in the relative orientation of the induced orbital and spin moments in W atoms. Since such a breakdown is observed both experimentally and theoretically in nanoparticulate and bulk Co–W alloys, as well as in Fe/W films [1], our work suggests that the breakdown of this rule is a rather general trend in the case of W systems, taking place not only in metallic thin films, but also in nano-particulate and bulk materials.
- Co–Pt NPs: these granular films are composed of particles with a pure cobalt core surrounded by an alloyed CoPt interface, embedded in a Pt matrix. The alloy between the Co and Pt in these granular films, prepared by room temperature sputter deposition, results from interdiffusion of the atoms. The presence of this

alloy gives rise to a high perpendicular magnetic anisotropy (PMA) in the granular films, as consequence of the anisotropy of the orbital moment in the Co atoms in the alloy, and comparable to that of highly ordered CoPt $L1_0$ alloy films. Their magnetic properties are those of ferromagnetically coupled particles, whose coupling is strongly temperature dependent: at low temperatures the granular sample is ferromagnetic with a high coercive field; at intermediate temperatures the granular film behaves as an amorphous asperomagnet, with a coupling between the grains mediated by the polarized Pt; and at high temperatures the sample has a superparamagnetic behavior. The coupling/decoupling between the grains in our Co–Pt granular films can be tailored by variation of the amount of Pt in the samples.

- Noble metal (Ag, Au, Pd, Pt) NPs: it is important to recall that without the element selective XMCD technique, this study of the d -band magnetism in noble metals particles would not have been possible, since it rules out any contribution from magnetic impurities other than the metals measured. Then, we have proven that the d -band magnetism in these NPs has an important orbital contribution as resulting of the asymmetry of the noble metal atoms coordination at the surface. This breaking of symmetry narrows the d electron “surface band” and increases the number of d -holes with respect to their bulk counterpart.
- Magnetite ($\text{Fe}_3 - x\text{O}_4$) NPs: radio frequency transverse susceptibility measurements in oleic acid- and SiO_2 -coated $\text{Fe}_3 - x\text{O}_4$ nanoparticles allowed a direct examination of the effects of the type of coating on their magnetic anisotropy, as a function of the particle size. On the one hand, SiO_2 coating reduces the interparticle interactions as compared to oleic acid coating, the reduction being more effective for 5 nm than for 14 nm particles. On the other hand, SiO_2 coating also decreases the magnetic anisotropy field measured on the particles. This is relevant concerning applications in biomedicine, since the SiO_2 coating renders 5 and 14 nm hydrophilic particles with very limited agglomeration, low anisotropy, and superparamagnetic behavior at room temperature.
- Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) NPs: radio frequency magnetic transverse susceptibility measurements on $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles allow to estimate their effective anisotropy constant, K_{eff} . The resulting values range from 4 to $8 \times 10^4 \text{ erg/cm}^3$, being on the order of the magnetocrystalline anisotropy in bulk maghemite. K_{eff} values increase as the particle diameter increases. Evidences of anisotropy field distribution given by the size distribution in the samples, and interparticle interactions that increase as the particle size increases, are also observed in the TS measurements.

9.1 Perspectives

We consider important to mention that there are still some open questions regarding the study of the NPs systems we describe in this dissertation. For example, in the case of Co–Pt nanoparticles, our investigation has to be continued by including the samples series with a fixed amount of Pt and variable Co thickness, in order

to analyze their effects in their magnetic properties and PMA. Angle dependent XMCD measurements both at the Co and Pt $L_{2,3}$ edges have been also performed on these Co–Pt particles in order to explore the evolution of the magnetization as a function of the sample and field orientation, with which we expect to obtain a better understanding of the PMA in these samples. We have also observed that the interactions between Co–Pt NPs play an important role in their magnetic properties, then it would be important to quantify and evaluate them.

Another example is the Co–Pd NPs system introduced in Chap. 6, which shows PMA induced by alloying, just as the Co–Pt NPs case. In this system, the systematic analysis of the structural and magnetic properties is yet to be completed.

The study of noble metal NPs described in Chap. 6 might be complemented with results on assemblies of Pd NPs and Pd₁₃ clusters in a zeolite (a system very similar to the Pt₁₃ described in Chap. 6), which our group are currently working on. We have some projects and proposals in this direction, so that the respective XMCD measurements could be performed.

With respect to the transverse susceptibility measurements on NPs systems, we would like to deepen into the understanding of the anisotropy field dispersion and interparticle interactions observed in both magnetite and maghemite NPs, and their effects on the TS results. This may be achieved by simulations of the TS profiles following previous works, for example, the one by Matarranz et al. in Ref. [2].

Finally, now that we have demonstrated the capabilities of the radio frequency (RF) transverse susceptibility technique (TS) developed for the facilities of the Universidad de Zaragoza, we shall make the most of it by continuing studying other interesting systems. Additionally, let us recall that this TS setup is now part of the Servicio de Medidas Físicas in the Universidad de Zaragoza, which means that many other users may benefit of it for performing their own research on magnetic anisotropy, spin dynamics, and short range correlations, to mention some of the possible topics to study with this equipment.

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