Nanostructured Magnets
Synthesis and Characterization of CoFe$_2$O$_4$ nanoparticles

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Preface

This thesis covers part of the work that I have performed between January 2003 and October 2006. The work has mainly been carried out at the University of Cagliari under the supervision of Prof. Giorgio Piccaluga and with the strong collaboration of Prof. Anna Musinu, Doct. Carla Cannas and Doct. Andrea Falqui. In Cagliari I have carried out the synthesis and the structural characterization and most of the magnetic characterization of the materials.

During my PhD I have spent several weeks in the Magnetism Laboratory of Institute Structure of Matter of the Italian National Research Council under the supervision of Dott. Dino Fiorani, performing part of the magnetic measurements and deepening the interpretation of magnetic data. In addition, I have spent 9 months (October 2004-June 2006) at the Technical University of Denmark, where I performed most of the Mössbauer characterization under the supervision of Prof. Steen Mørup, and with the technical support by Mr. Helge K. Rasmussen. Some Mössbauer measurements were also made in Cagliari by Prof. Giorgio Concas and Prof. Giorgio Spano.

Some of the experimental results summarized in this thesis are discussed in 4 papers already published:


Further results are object of some papers in preparation.

Notes for the reader

The Bibliography in the thesis is independent for each Chapter and the references are indicated with Arabic numeral, bold and underlined in apex (e.g.: [1]). The footnote are indicated with Roman numeral bold and underlined in apex (e.g.: [X]).

Acknowledgements

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Thanks to my parents and my brother for constant support.

Finally thanks to my sweet Nora that always was with me.
List of abbreviations

C: Curie constant

\( \hat{m} \): Magnetic moment

\( m_v \): Magnetic moment for unit of volume

\( \tau_m \): Experimental measuring time

\( \tau \): Superparamagnetic relaxation time

\( \tau_0 \): Relaxation - time constant

\( K \): Anisotropy constant

\( \delta \): Quadrupole splitting

\( \delta \): Isomer shift

\( B_{hf} \): Magnetic hyperfine field

\( T_{max} \): Temp. corresponding to maximum value of magnetization in ZFC curve

\( T_C \): Curie temperature

\( T_N \): Néel temperature

\( T_{irr} \): Irreversibility temperature in ZFC FC curve.

\( T_B \): Blocking temperature

\( T_B^M \): Blocking temperature from Mössbauer Spectroscopy

\( T_{max}^{\prime} \): Temperature corresponding to maximum value of AC susceptibility

\( M_{nr} \): Non relaxing magnetization

\( H_c \): Coercivity field or Coercivity

\( H_e \): Exchange field

\( M_s \): Saturation magnetization

\( M_r \): Remanent magnetization
$M_{nr}$: Non relaxing magnetization

$\vec{H}$: Field strength

$\vec{B}$: Magnetic induction

$\mu$: Permeability of the medium

$\mu_r$: Relative permeability of the medium

$\vec{L}$: Angular momentum

$\gamma_0$: Giromagnetic ratio

$\gamma$: Inversion degree

Value of selected Physical constants

$\mu_0$: Permeability of free space ($4\pi \times 10^{-7}$ H/m)

$h$: Planck’s Constant ($6.626 \times 10^{-34}$ J s)

$h':$ Planck’s Constant divided by $2\pi$ ($1.0546 \times 10^{-34}$ J s)

$k_B$: Boltzmann Constant ($1.381 \times 10^{-23}$ J/K)

$m_e$: electron rest mass ($9.109 \times 10^{-31}$ kg)
CHAPTER 1

Introduction

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1.1 Nanostructured magnets

Magnetic materials have been fascinating human beings for over 4000 years. Since an ancient Greek shepherd noticed in Magnesia that the iron nails in his shoe and the iron tip of his staff stuck to certain rocks (Ladestone),¹ the magnetic phenomena have been object of careful study and it is still common opinion that few subjects in science are more difficult than magnetism.² Ladestone first attracted attention of Greek scholars and philosophers, and the navigational magnetic compass was the first technological product resulting from this study. Later, the magnetic materials have found their way into almost every part of our civilization. In our modern society we use magnetic materials daily, such as computer disk, credit ID cards, loud speakers, refrigerator door seals and a host of other conveniences.

The development of new materials on smaller and smaller length scale has been at the root of progress in material science in the last 40 years. This is particularly true in the development of new magnetic materials.² The discovery of giant magnetoresistance (GMR) in magnetic thin films⁴⁻⁵ and subsequently the observation of GMR in small granular systems of Fe, Co, and Ni and their various alloys in Cu, Ag or Au matrices⁶⁻⁷⁻⁸ are examples of such development.

Broadly speaking, a physical property depends on the size of an object, if its size is comparable to a dimension which is relevant to that property. In magnetism a typical size of magnetic domain is $1 \mu m$ and particles smaller that this will be monodomain. Another scale involves exchange coupling effects, which affect the magnetic polarization of neighbouring ferri- or ferromagnetic particles in non magnetic host and has a range of the order of several nanometers.⁹ Therefore, it is understandable why in recent years great attention has been addressed towards nanostructured magnets, where the term nanostructured describes materials with structure length scale from 1nm to 100 nm.¹⁰

Understanding the magnetic properties of nanometer scale particles is a central issue in nanomagnetism. Indeed, nanoscaled particles have generated remarkable interest among the researchers either for basic curiosity about the properties transformation as the size is decreased¹¹⁻¹³⁻¹⁰ and for their promising applications.¹³⁻¹⁴

1.2 Aim of the work

The research activity of this thesis was carried out in three principal steps: the synthesis, the investigation of structure and the study of the physical properties
of magnetic nanoparticles. Aim of the work is to give a contribution both to understand the properties of the assemblies of fine magnetic particles and to implement new synthetic ways in order to control the properties of the materials.

Figure 1.1 Aim of the work

The understanding of the properties of the superparamagnetic nanoparticles deals with the correlation between structure and magnetic properties. To this end a deep magneto-structural characterization is the key point.

A characterization of the precursors has been performed in order to have a good control of the synthetic procedures. This stage was essential in order to gain control on structure and magnetic properties of the nanoparticles and, so, try to project new magnetic materials. (Figure 1.1.)

Although the exploration of technological potentialities of the prepared materials is not within the scope of this thesis, attention has been also devoted to prepare systems with magnetic and structural features useful for some applications.

1.3 Scientific background
1.3.1 Physical properties of nanoparticles

The energy of a magnetic particle is generally dependent on the magnetization direction, resulting in particular equilibrium directions separated by energy barriers. These energy barriers depend on particle volume and crystalline structure of the materials. Therefore, at any given temperature there is a critical size below which thermal excitations are sufficient to overcome such barrier and to rotate the particle magnetization, thus demagnetizing the assemblies of such particles. Such phenomenon is known as superparamagnetism.
The superparamagnetic behaviour of nanoparticles has been found strongly dependent on particle volume distribution, particle morphology, strength and type of interparticle interactions, disorder and surface effects. Moreover, intraparticle and interparticle effects are so closely related that they can hardly be disentangled. The present thesis has been focused on the understanding of superparamagnetic relaxation, with particular attention to the influence of interparticle interactions, disorder effects, and morpho-structural features of the materials.

The influence of different types of interparticle magnetic interactions on superparamagnetic relaxation has been the subject of numerous studies.\textsuperscript{16,17,18,19} Different models have been proposed in order to explain the experimental results.\textsuperscript{18} In the last years attention has been devoted also to systems with strong interparticle interactions (exchange interactions); indeed exchange interactions are just a potential method in order to determine the position and then the properties of magnetic nanoparticles, opening new application perspectives (e.g. building up nanostructures devices).\textsuperscript{20} In addition, in this connection it is interesting to investigate the possibility that strong magnetic interactions between nanoparticles can lead to spin glass phases or to magnetic collective ordering phenomena.\textsuperscript{21,22}

The magnetic properties of nanoparticles are strongly influenced by disorder and surface effects. It has been found that the degree of order in the structure can be compromised by the reduced particle size, leading to a non collinear spin structure (spin canting).\textsuperscript{21} Such effect can lead to several modifications in magnetic properties of the materials (e.i.: decrease of saturation magnetization\textsuperscript{25} or variation in coercivity\textsuperscript{26}). It has been suggested that the spin canting is a surface phenomenon,\textsuperscript{27,28,29} and therefore it should become increasingly important with the decrease of particle size. However, some studies rather indicate that the non collinear spin structure is a finite size effect which also occurs in the interior of the particles. The real nature of spin canting, that is still object of discussion, has been investigated through this thesis.

As already mentioned above, the magnetic behaviour of an assembly of nanoparticles is related to the crystalline structure. This thesis has been devoted to the study of cobalt ferrite (CoFe$_2$O$_4$) nanoparticles, that have a spinel structure.

The ferrite spinel structure is based on a closed-packed oxygen lattice, in which tetrahedral (called \textit{A} sites) and octahedral (called \textit{B} sites) interstices are occupied by the cations. (\textbf{Figure 1.2})
Spinels with only divalent ions in tetrahedral sites are called *normal*, while compounds with the divalent ions in the octahedral sites are called *inverse*.

In general, the cationic distribution in octahedral and tetrahedral sites may be quantified by the *inversion degree* ($\gamma$), which is defined as the fraction of divalent ions in the octahedral sites. The physical behaviour, and in particular the magnetic properties, depend on the cationic distribution in the $A$ and $B$ sites. Therefore, the control of cationic occupancies of interstices is very important in order to regulate the magnetic properties of the nanoparticles with spinel structure.

1.3.2 Applications of magnetic nanoparticles

The magnetic nanoparticles can be used in high density information storage, ferrofluids technology, magnetocaloric refrigeration, color imaging, catalyst, biomedical applications.

One of the most important problems in the use of the nanopowders is related to the poor mechanical properties and to the instability of the active phases with respect to thermal treatments. Acquiring a good structural and mechanical stability is a primary objective for all the applications.

In magnetic nanoparticles the reduction in dimension can affect the magnetic properties, for instance lowering saturation magnetization. Preventing these effects and, on the contrary, enhancing magnetic properties of the materials

![Figure 1.2 Schematic representation of spinel structure](image-url)
with respect to the bulk is the most important point for application in high density storage and in biomedical field.

1.3.3 Synthesis of nanoparticles

Because the morpho-structural features influence the superparamagnetic behaviour, in the synthesis of nanoparticles the key point is the ability to control the volume, the volume distribution, the morphology and the constituent phases. Tuning the particles size and preparing samples with narrow particles size distribution are fundamental points also in order to interpret magnetic data and, as a consequence, to comply with the theoretical models. The chemical composition of the constituent phases in nanoparticles is also of primary importance. This does not only concerns average composition, but also chemical gradients within the structures. Furthermore, it has to be taken into account that the reduction of particle size can lead to changes in the structure and in the thermodynamic properties of crystalline phases.

Many preparation methods have been proposed for the synthesis of nanoscaled spinel nanoparticles. Because of their advantages (versatility, possible manipulation of matter at the molecular level, better control of the particle size, shape and size distributions), the use of chemical methods has been rapidly growing. \(^{34,36}\) Among the many synthetic methods proposed, good results have been obtained with chemical precipitation, sol-gel processing, microemulsion route, sonochemistry, hydrothermal processing, aerosol-vapour method and high-temperature decomposition of organic precursors. \(^{35,37,38,39}\) Potential difficulties, however, are present in chemical processing, arising from its complexity, possible occurring of impurities, economical drawbacks. In the light of these considerations, great interest arose from a very promising way proposed for the preparation of multicomponent oxide ceramic powders, based on a sol-gel auto-combustion process. \(^{40,41}\) In this method precursor gels are prepared from aqueous solutions of metal nitrates and an organic complexant such as citric acid.

Embedding nanoparticles in a crystalline or amorphous matrix allows reduction of nanoparticles aggregation and good control of structural and morphological features. Therefore, recently growing interest has been addressed to nanocomposite\(^1\) materials, in which nanoparticles are dispersed in matrices as

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\(^1\) The term “nanocomposite” refers to a composite of more than a solid phase where at least one dimension is in the nanometre range. This term was first coined by R. Komarneny and colleagues during the period 1982-1983.
crystalline alumina, polymers and amorphous silica. In particular, amorphous silica has been widely used, because it is easy to prepare and allows improving catalytic, electric, magneto-optic and mechanical properties. The classical sol-gel method, which has been known for more than a century, has been largely used for dispersing small metal and metal oxide particles in silica matrix, producing materials with high purity and high homogeneity. Following this route, the particles nucleate and grow inside a preformed silica network and their morphological and geometrical features are mainly affected by the properties of the host matrix (porosity, surface area) and the control of size and distribution of the particles are fairly complicate.

In the auto combustion method the formation of the nanoparticles can be influenced also by the carboxylate-metal complexes, that form during the gelation stage and from which metal oxides originate during the combustion. For this reason the control of the properties of the nanoparticles should result more effective. Therefore, in order to prepare ferrite silica nanocomposites, the traditional sol-gel method and the complexation - auto combustion method were combined.

An important but rarely investigated point in the study of magnetic silica nanocomposites is concerned with the variation of structural, morphological and physical features of the active phase due to presence of silica matrix. In the literature several works are reported about either unsupported or silica supported nanophases, but there are not many papers devoted to the comparison between analogous systems synthesized by the same procedure. In fact, it is difficult to find a synthesis procedure that allows the preparation of both unsupported and silica supported nanoparticles. The synthetic strategy adopted through this work allowed to perform this kind of comparison.

1.4 Abstract

The thesis is divided in two parts; the first one (chapter 1, 2 and 3) contains the scientific framework within it the research activity was developed and the second contains the experimental results (chapter 4, 5, and 6).

The first part is organized in three Chapter. Chapter 1 is an introduction to the thesis; there, the scientific background and the objectives of the present work are stated. Chapter 2 is devoted to introduce the physics of nanostructured magnets, with particular attention to the behaviour of magnetic nanoparticles. Finally, in chapter 3 the experimental techniques used in this work are discussed. Only few elements about equipments and elaboration data are specified for
techniques devoted to structural and morphological characterization. More prominence is given to magnetic characterization, where for each technique a very short description of physical basic principles is specified. Attention is also devoted to physical meaning of the measurements and to description of the experimental data elaboration.

The second part discusses the experimental results.

In a first stage the sol-gel auto combustion method was settled in order to prepare unsupported cobalt ferrite nanoparticles. To modify the features of the particles according to different requirements, the precursors of the autocombustion process were studied through FT-IR measurements and thermal analysis. The final products obtained with different starting conditions were characterized through X-ray diffraction, Transmission Electron Microscopy and nitrogen physisorption. DC magnetic measurements and Mössbauer spectroscopy were finally carried out and the connection between structural and magnetic properties discussed. These results are described in chapter 4.

In the second stage the traditional sol-gel method and the sol-gel autocombustion method were combined in order to provide ferrite-silica nanocomposites in a wide range of composition (50-5 wt. % of magnetic phase). The work made about the comprehension of the CoFe$_2$O$_4$ formation mechanism in sol-gel autocombustion process was of fundamental importance, in order to set the experimental conditions for the preparation of nanocomposites. Through FT-IR and thermal analysis a complete understanding of the formation mechanism process of the nanocomposite was reached. All the samples underwent thermal treatments between 300°C and 900°C and the evolution of structural properties was studied. The discussion of these results are the subject of chapter 5.

The use of silica matrix allowed to improve the morphology of the particles and, through the variation of magnetic phase content, a good control of particle size and particle size distribution was obtained. Trough the discussion of magnetic properties of some nanocomposites some general questions about magnetic behaviour of nanoparticles are developed.

- The relationship between crystalline structure (i.e: inversion degree), particle size, and magnetic properties

- The problem of non collinear spin structure (spin canting) in relation to particle size
- Effects of strong magnetic interactions and discrimination between superparamagnetism and magnetic ordering phenomena.

All this arguments are discussed in chapter 6 of the thesis
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CHAPTER 2
Physics of nanostructured magnets

2.1 Atomic origin of magnetism

2.2 Magnetism in solids
   2.2.1 Cooperative magnetism
   2.2.2 Magnetic domains

2.3 Single domain particles
   2.3.1 Magnetic anisotropy energy
   2.3.2 Superparamagnetism
   2.3.3 Collective magnetic excitations

2.4 Interparticle interactions
   2.4.1 Curie Weiss analysis

References
2.1 Atomic origin of magnetism

Magnetic phenomena arise from the movement of electrical charges. At atomic level the electrons govern the magnetic properties of the matter in two different ways.

The first is the orbital motion of the electron around the nucleus that can be considered as a current loop. In an atom the magnetic moment ($\vec{m}$) associated with an orbiting electron lies along the same direction as the angular momentum ($\vec{L}$) of that electron and is proportional to it:

$$\vec{m} = \gamma_0 \vec{L}$$  \hspace{1cm} (2.1)

where $\gamma_0$ is a constant called gyromagnetic ratio which, according to electromagnetic theory, is equal to $-e/2m_e$. As the orbital angular momentum is quantized in units of $\hbar$, from the relation (2.1) it is possible to express the magnetic moment in unit:

$$\mu_B = \frac{e\hbar}{2m_e}$$  \hspace{1cm} (2.2)

This quantity, called Bohr Magneton, is a convenient unit to describe the sizes of atomic magnetic moments.

The second is the electron acting as a spinning charged sphere that possesses an intrinsic angular momentum, which is associated to an intrinsic magnetic moment. The intrinsic angular momentum, called spin, is a quantized quantity. Generally both orbital motion and spin contribute with different relative weight. The overall magnetic moment of the atom is the net sum of all the magnetic moments of each individual electron.

2.2 Magnetism in solids

In condensed matter the magnetic moments can mutually act together (cooperative magnetism) and lead to a quite different behaviour from what would be observed if all the magnetic moments were reciprocally isolated (noncooperative magnetism). Coupled to the different types of magnetic interactions that can be found, this leads to a rich variety of magnetic properties in real systems.\(^\dagger\)

\(^\dagger\) The relation between magnetic moment and intrinsic angular momentum is $\gamma_0' = -e/m_e$.\(^\dagger\)
The two basic type of non cooperative magnetism are diamagnetism and paramagnetism.

Paramagnetism arises from identical, uncoupled atomic moments located in isotropic surroundings. Hence, in a paramagnetic material there is no long-range order and in an applied magnetic field the magnetic moments partially align, leading an increase of magnetic flux density. The susceptibility depends form temperature, following the Curie law:

$$\chi = \frac{C}{T}$$

(2.3)

$C$ is called Curie constant and can be defined as:

$$C = \frac{n\mu_0 m_{\text{eff}}^2}{3k_B}$$

(2.4)

where $m_{\text{eff}}$ is know as the effective magnetic moment, $n$ indicate the number of magnetic moments per unit of volume, $k_B$ is the Boltzmann constant and $\mu_0$ is the permeability in the free space. In real systems interactions between the magnetic moments are present, and the susceptibility dependence of the temperature follow the Curie-Weiss law:

$$\chi = \frac{C}{T - \theta}$$

(2.5)

where $\theta$ is called Curie Weiss temperature and it is related to the strength of the interactions between moments. The characteristic plot for Curie behaviour is $1/\chi$ versus $T$ plot, and the same is true for Curie-Weiss behaviour. As shown in figure 2.1 for Curie behaviour it is get a straight line through zero, while for Curie-Weiss behaviour we get an x-axis intercept at a positive or negative $\theta$.

**Figure 2.1** The inverse of $\chi$ as a function of $T$ for systems exhibiting Curie and Curie-Weiss behaviour.
Using the definition in the equation (2.5), for $\theta > 0$ the interactions help to align the moments in the same direction, and for $\theta < 0$ the interactions help to align adjacent moments in opposition.

When a magnetic field is applied, the electronic motions are modified and the magnetic moment changes. The diamagnetism is just due to the effects of applied magnetic field on the motion of the inner electrons of the atoms. In particular, Lenz’s law of electromagnetic induction states that the currents induced by a magnetic field tends to oppose the original field. This explains why the diamagnetic substances have a negative induced magnetization and consequently a negative magnetic susceptibility. All substances have a basic diamagnetism, that is nearly always weak and is very often masked by a much larger paramagnetic susceptibility. Therefore such noncooperative magnetic phenomenon is observed in materials with filled electronic sub-shells where no uncoupled magnetic moments are found.

2.2.1 Cooperative magnetism

A complete discussion of the theory of cooperative magnetism is beyond the scope of this paragraph. Only the basic outlines will be given in order to address the magnetization process in ferrimagnetic nanoparticles.

When atoms are placed close together (e.g. in crystals) the electron wave functions of adjacent atoms may overlap. It is possible to observe that, given a certain direction of magnetization for one atom, the energy of the second atom is higher for one direction of magnetization than the opposite. Such difference in energy between the two states is called exchange energy. Furthermore, when the parallel magnetization is the lower energy state, the exchange is said ferromagnetic, but when the antiparallel magnetization is the lower energy state, the exchange is said antiferromagnetic. The effect of such exchange energy is called exchange coupling and two classes can be distinguished:

Direct exchange that occurs between moments close enough to have significant overlap of their wave functions. In this case, exchange coupling is strong but quickly decreases correspondingly to an increase in interatomic distance.

Indirect exchange, where the atomic magnetic moments are coupled over relatively large distances. It can act through an intermediary nonmagnetic ion (superexchange coupling) or through itinerant electrons (RKKY coupling).

The acronym RKKY is used because of the initial letters of the surnames of the discoverers effect, Ruderman, Kittel, Kasuya and Yosida.
Quantitatively the interaction between magnetic centres in an three dimensional solid can be effectively described by the Heisenberg spin Hamiltonian

$$H_{\text{exch}} = 2 \sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j$$

(2.6)

$J_{ij}$ is the exchange integral describing the magnitude of coupling between the spins $\hat{S}_i$ and $\hat{S}_j$. If the exchange integral has a positive value, below a critical temperature $T_C$ (Curie temperature) the magnetic moments are aligned parallel to each other and the substance is said to be a ferromagnet. A ferromagnetic solid, because of the parallel alignment of the spins, can be spontaneously magnetized even in the absence of magnetic field. The spontaneous magnetization decreases more and more rapidly with rising temperature. Above the Curie temperature, the material in no longer ferromagnetic, but reverts to paramagnetic, and Curie-Weiss law behaviour is usually observed (figure 2.2.a). Instead, if $J_{ij}$ is negative, the spins are aligned antiparallel to each other and below a critical temperature called Néel temperature ($T_N$) the material is said an antiferromagnet (if all the magnetic moments are equal) or a ferrimagnet (if there is no compensation due to the difference between the individual moments).

An antiferromagnet, below the Néel temperature, consists of two identical interpenetrating sublattices, in which the spins of one sublattice are opposed to those of the other. Therefore there is no overall spontaneous magnetization.
**Ferrimagnetism** usually requires two or more chemically different magnetic species that occupy two kinds of lattice sites, producing two sublattices $A$ and $B$. The moments in each sublattice have ferromagnetic coupling, but the coupling between the moments of $A$ and $B$ is antiferromagnetic. Since the net moments of $A$ and $B$ are different, a resultant spontaneous magnetization can be observed. Actually, ferrimagnetic behaviour is also shown in materials in which the same chemical species occupy different kinds of sites in different percentage. The temperature dependence of ferrimagnetism is similar to that of ferromagnetism, except that the spontaneous magnetization decreases more rapidly with increasing temperature (figure 2.2b). Materials with spinel structure show a ferrimagnetic behaviour.

2.2.2 Magnetic domains

Weiss first proposed that a ferromagnet might contain a number of small regions, with different shape and size, called *domains*. Each domain is a uniformly magnetized region, where the local magnetization reaches the saturation value. The directions of magnetization in different domains are different, so that the net magnetization is zero in absence of an external magnetic field. A multidomain structure, observed also in ferri- and antiferromagnetic materials, leads to minimize the total energy of a magnetic body.

![Figure 2.3](image)

**Figure 2.3** (a) 180° domain wall, (b) 90° domain wall

Two adjacent domains are separated by transition regions in which the spins gradually rotate from a domain to the other; such transition region is called *domain wall*. The domain walls can be classified according to the angle between the magnetization in adjacent domains. A 180° domain wall separates domains of opposite magnetization (figure 2.3a). A 90° domain wall separates domains of perpendicular magnetization (figure 2.3b). The most common type of 180° wall is
the Block wall, in which the magnetization rotates in a plane parallel to the plane of the wall (figure 2.4).

The thickness of a domain wall is of the order of $10^2$-$10^3$ Å and depends on the magnetic exchange energy ($J$) and the magnetic anisotropy (i.e. the tendency of the spins to align along a preferred direction) of the compound. These two factors influence the width of the Bloch wall in opposite ways: a larger $J$ requires larger walls, while a larger anisotropy requires smaller walls. Accordingly the width of a Block wall can be written as:  

$$\delta = \pi \sqrt{\frac{A}{K}}$$

(2.7)

Where $A$ is the exchange energy density and $K$ is the anisotropy energy constant.

The hysteretic dependence of the magnetization lies on the base of multi-domain structure. In an unmagnetized ferromagnetic or ferrimagnetic material the collections of parallels spins in a domain are randomly oriented throughout the material and therefore collectively self-cancel, resulting in zero net magnetization. When placed in a sufficiently large external magnetic field, the spins in each domain rotate parallel to the direction of applied field.

Typically, magnetization rises sharply at lower field, as the domains with more favourable alignment expand at the expense of others, and saturates when the maximum domain alignment is reached (figure 2.5). This macroscopically correspond to a plateau region of the magnetization curve (Saturation magnetization, $M_s$). When the applied field is decreased, magnetization decreases.
The magnetization remaining at zero applied field is called Remanent magnetization \( (M_r) \). Very often, for the characterization of a magnetic hysteresis, the reduced remanent magnetization, defined as \( M_r/M_s \), is used. The magnetic field required to demagnetize the material is called coercive field or coercivity \( (H_c) \) (figure 2.6).

The shape of the hysteresis loop is of great interest for magnetic recording applications, which require a large remanent magnetization, moderate coercivity, and (ideally) a square hysteresis loop.

### 2.3 Single domain particles

Below a certain critical size it is non energetically favourable to form magnetic multi domain structures and particles with dimension below this size will therefore consist of a single magnetic domain.\(^{14}\) In fact, when the size of the particle is of the same order than that of the block wall, the energy obtained by the subdivision in a multi domain structure is lower than the energy spent for the formation of domain walls. The critical particle size depends on spontaneous magnetization, magnetic anisotropy energy and exchange energy. For spherical crystals, Kittel\(^{14}\) proposed an expression for the critical diameter:

\[
d_c = 18 \frac{E_o}{m_v M_s^2} \quad (2.8) \quad \text{and} \quad E_o = 2 \sqrt{\frac{K}{A}}
\]

\( E_o \) is the domain wall energy, \( m_v \) is the magnetic moment for unit volume and \( M_s \) is the saturation magnetization. \( K \) and \( A \) have the meaning as in equation (2.7). Typical values of critical diameters of ferromagnetic particles are 15 nm for Iron, 70 nm for Cobalt, 55 nm for Nickel.\(^{15}\) Single domain particles of ferromagnetic materials usually have larger critical size because of the smaller magnetic moment for unit volume (166 nm for \( \gamma \)-Fe\(_2\)O\(_3\) and 128 nm for Fe\(_3\)O\(_4\)).\(^{15}\)

Some authors\(^{16-18}\) have discussed the meaning of term single domain particle. Except where specifically stated otherwise, in this thesis single domain
particle will mean a particle that is in a state of uniform magnetization at any field. In this framework we can define the magnetic moment of a single domain particle, as:

\[ \vec{m} = \vec{M} V \]  

(2.9)

Where \( \vec{M} \) is the saturation magnetization and \( V \) is the volume of the particle. The coercivity depends strongly on the domains size. Figure 2.7 show schematically the variation of coercivity with the domain size.

![Figure 2.7 Dependence of the coercivity on the domain diameter along the easy axis.](image)

In a multidomain system, coercivity is related to motions of domains and the size dependence is experimentally given by:

\[ H_c = a + \frac{b}{D} \]  

(2.10)

Surface disorder leads to a magnetic moment value different from that expected from the saturation magnetization of the bulk material. To highlight this difference the saturation magnetization for fine particles, especially in theoretical discussion, is called non relaxing magnetization and defined as \( M_{sr} = \vec{m}_{sr} / V \), in absence of any relaxation effect, where \( \vec{m}_{sr} \) is nonrelaxing magnetic moment.
where \( a \) and \( b \) are constant and \( D \) is the diameter of the domains. The equation (2.10) indicates that as particle size decreases, the coercivity increases (figure 2.7 curve a). Afterward the particles become a single domain and the coercivity reaches a maximum \( D_c \). Then, \( H_c \) decreases with decreasing particle (figure 2.7 curve b) as described from the equation:

\[
H_c = g - \frac{h}{D^{\frac{3}{2}}}
\]  

(2.11)

where \( g \) and \( h \) are constant. The decrease of \( H_c \) observed in magnetic monodomain system is due to thermal effects.

2.3.1 Magnetic anisotropy energy

In a magnetically ordered material, there are certain preferred orientations of the magnetization. These easy directions are given by the minima in the magnetic anisotropy energy, which is a sum of several contributions.\(^{21,22}\) In bulk materials, magnetocrystalline and magnetostatic energies are the main sources of anisotropy. In monodomain particles, other kinds (e.g., exchange and dipolar anisotropy, surface anisotropy, stress anisotropy) of anisotropy can have the same order of magnitude as the usual anisotropies. A complete description of each anisotropy energy can be found in\(^ {11,23}\). A short qualitative discussion of each anisotropy energy will be given here.\(^ {15}\)

**Magnetocrystalline anisotropy**

The origin of this contribution lies in the spin-orbit coupling, that leads to coupling between the magnetic moment and the crystal structure. Such property is intrinsic to the material, being related to the crystal symmetry and to the arrangement of atoms in the crystal lattice. In fact, the orbital wave function will reflect the symmetry of the lattice and the spins will be affected by anisotropy via the spin-orbit coupling. Magnetocrystalline energy can show various symmetry, but uniaxial and cubic forms cover the majority of cases.

**Magnetostatic anisotropy**

This contribution is due to the presence of free magnetic poles on the surface of a magnetized body. These poles create a magnetic field inside the system, called demagnetizing field, which is responsible for the magnetostatic energy. For a particle with finite magnetization and non-spherical shape, the
magnetostatic energy will be larger for some orientations of the magnetic moments than for others. Thus, the shape determines the magnitude of magnetostatic energy as a function of magnetization orientation. Therefore this kind of anisotropy is often called \textit{Shape anisotropy}.\textsuperscript{13}

\textbf{Surface anisotropy}

The surface atoms have a lower symmetry compared to that of atoms within the particle and their influence on the energy of the particle may depend on the orientation of the magnetization. This gives rise to \textit{surface anisotropy} which may also depend on adsorbed species on the surface. The magnitude of this contribution to the magnetic anisotropy energy increases with the decrease of particle size.\textsuperscript{14} Néel has shown that the surface contribution becomes relevant only for particle smaller than \(~ 10 \text{ nm}\).\textsuperscript{14}

\textbf{Stress anisotropy}

Another contribution to the anisotropy energy comes from magnetostriction, (i.e. coupling between the mechanical properties and the magnetic properties which is again due to spin-orbit coupling). For the first time in 1842 Joule observed this phenomenon: in a specimen magnetized in a given direction he observed a change in length in that direction. Since the strain is related to any stress that may be acting on the considered system, this implies that the anisotropy energy depends on the stress state of the system.

\textbf{Exchange and dipolar anisotropy}

Two particles in close proximity have a magnetic interaction. This interaction, which can be either due to magnetic dipole interaction or to exchange interaction, leads to an additional anisotropy energy. In this case the easy direction is determined by the relative orientation of the two interacting magnetic moments.

In most cases, it is assumed that the sum of all contributions to the magnetic anisotropy energy results in an effective uniaxial anisotropy. This anisotropy in its general form can be expressed as the series expansion:

\begin{equation}
\label{eq:anisotropy}
E_\chi(\theta) = K_1 V \sin^2 \theta + K_2 V \sin^4 \theta + \ldots.
\end{equation}
where $K_1$, $K_2$, … are the effective anisotropy energy constant, $\theta$ is the angle between the direction of the magnetic moment and the easy axis. The terms of higher order than $\sin^2 \theta$ are usually neglected and the magnetic anisotropy energy can be written:

$$E_a(\theta) = KV \sin^2 \theta$$  \hspace{1cm} (2.13)

The magnetic energy for uniaxial anisotropy as a function of $\theta$ is shown in figure 2.8. From the equation (2.13) comes out that there are two minima corresponding to $\theta=0$ and $\theta=\pi$ which are separated by an energy barrier $E_a = KV$.

2.3.2 Superparamagnetism

The atomic spins in the core of a ferromagnetically ordered single domain particle are parallel. As a consequence of either thermal agitation or external magnetic field, a switch of the magnetization between the easy directions of magnetizations is possible.

At a given temperature for which the thermal energy is much lower than the energy barrier ($k_B T < KV$), the probability that the magnetization forms an angle $\theta$ with the easy axis has a finite value only in correspondence of the two minima. In this case the magnetic behaviour of an assembly of independent particles is quasi static, like in the bulk material, being the thermal energy very weak.

As the temperature increases, the probability that $k_B T$ surmounts the barrier separating two easy directions increases. Finally, as $k_B T > KV$, the magnetization can flip freely among the two easy directions and therefore its time average in absence of an external magnetic field is zero. In such condition the assembly of the particles behaves like a paramagnetic system and also the coercivity becomes zero (figure 2.7., curve c). The difference from a paramagnet is the magnetization scale because the magnetic moment per spin in a paramagnet is replaced by the magnetic
moment of the particle, which is much higher.\textsuperscript{ix} For this reason the magnetic behaviour of fine particles is called superparamagnetism.

If an external magnetic field ($H$) is applied parallel to the easy axis, the anisotropy energy of the particle is modified as follow:

$$E = KV \sin^2 \theta - m \cdot H$$  \hspace{1cm} (2.14)

Using (2.9), the equation (2.14) can be rewrite as:

$$E(\theta) = KV \sin^2 \theta - HM \cos(\theta)$$  \hspace{1cm} (2.15)

If $H < 2K/M_s$ there are still two minima but they are no longer equivalent, since the energy barrier from $\theta = 0$ to $\theta = \pi$ is higher than that from $\theta = \pi$ to $\theta = 0$. When $H \geq 2K/M_s$ there is only one minimum and the superparamagnetic relaxation is no longer observed. This effect of the external field is shown in figure 2.9, where $E(\theta)$ for different values of $H$ is reported.

![Figure 2.9](image)

\textbf{Figure 2.9} $E(\theta)$ for $H = 0$, for $H < 2K/M_s$ (A) and for $H > 2K/M_s$ (B)

Also small particles of antiferromagnetic materials may exhibit superparamagnetic behaviour. In antiferromagnetic substances the magnetic moments are exactly compensated. However, this is not true for surface spins, and therefore a small net magnetization arises. Although in a large crystal the effect is negligible, in a small particle an appreciable percentage of the total magnetic moments is uncompensated.\textsuperscript{x}

The flip of magnetization in the superparamagnetic systems may take place via different modes. For large single domain particles, it can be energetically favorable for the atomic moments to perform an incoherent rotation via the \textit{curling mode} to minimize the magnetostatic energy.\textsuperscript{xi} For small single domain particles the atomic moments will be parallel during the magnetization reversal. The value of the critical size below which the spins rotate coherently depends in a given material

\textsuperscript{ix} The magnetic moment in a nanosized monodomain particle is due to the sum of the moments of $10^2$-$10^4$ spins.
on its shape. Anyway, for particles smaller than \( \sim \) 30 nm the relaxation occurs only with coherent rotation.\(^{28}\) Thus, since we are dealing with particles size below this limit, only this reversal mode will be consider from now on.

The average time for the switching of the magnetization direction between the easy directions of magnetization is called the superparamagnetic relaxation time \( (\tau) \). For a mono domain ferromagnetic particle with uniaxial anisotropy, if the reversal of the magnetization occurs only through coherent rotation, it is found that \( \tau \) follows an Arrhenius Law:

\[
\tau = \tau_0 \exp \left( \frac{KV}{k_B T} \right) \tag{2.16}
\]

\( \tau_0 \) is called pre-exponential factor (or relaxation time constant\(^ {28}\)) and it is considered as the average time between attempts to jump over the energy barrier.\(^ {29}\) The exponential factor can be considered as the probability to overcome the energy barrier in an attempt. The first evaluation of the relaxation time is due to Néel in 1949 and therefore the equation (2.16) is often called the “Néel relaxation time”.

He also considered the temperature dependence of the pre-exponential factor. Later the Néel’s calculation was criticized and refined by some authors.\(^ {30,31,32}\) They derived approximations for uniaxial and cubic anisotropy for the limiting cases of low and high energy barriers.\(^ {33,34}\) Recently, Coffey et al re-viewed the theory, and reported an analytic formula valid for all barrier heights.\(^ {35,36}\) They derived formulae very similar to equation (2.16); the most important difference was in the temperature dependence of pre exponential factor.\(^ {37}\) The best approximation for thermal dependence of \( \tau_0 \) is:\(^ {38}\)

\[
\tau_0 = \frac{\sqrt{\pi}}{4} \frac{\left| m_{nr}(0) \right|}{E_n \gamma_0} \times \left| \frac{1}{\eta_r} + \eta_r \left( \frac{M_{nr}(T)}{M_{nr}(0)} \right)^{1/2} \right| \times \sqrt{\frac{E_n}{k_B T}} \times \left( 1 + \frac{k_B T}{E_n} \right) \tag{2.17}
\]

Where \( \left| m_{nr}(0) \right| \) is the modulus of the nonrelaxing magnetic moment of the particle at 0 K and \( M_{nr}(0) \) the corresponding non relaxing magnetization. \( \gamma_0 \) is the electronic gyromagnetic ratio, and \( \eta_r \) is a dimensionless constant, such that \( \eta_r = \eta \gamma_0 M_{nr}(0) \), \( \eta \) being the damping constant.

\(^{28}\) \( \tau_0 \) is of the order of \( 10^{-12} - 10^{-9} \) s for ferromagnetic or ferromagnetic nanoparticles
In real samples it is very difficult, due to size distribution and irregular morphology, to observe experimentally a variation of the pre-exponential factor with temperature. For such a reason, according to Aharoni, for particles with uniaxial anisotropy and with $KV/k_B T >> 1$ a good approximation is to use expression (2.16). For materials with cubic anisotropy there is a considerable deviation between the new expression for the relaxation time and the Néel relaxation time. Through this work will be demonstrated that the magnetic anisotropy of CoFe$_2$O$_4$ has uniaxial symmetry; therefore the equation (2.16) will be used as the expression for the superparamagnetic relaxation time.

The magnetic behaviour of single domain particles is strongly dependent on time, as expressed of equation (2.16). Therefore the magnetic properties of an assemblies of single domain particles depends on the experimental measuring time ($\tau_m$) of the technique employed to observe the relaxation. In fact if $\tau << \tau_m$, the relaxation during the experiment is so fast that only a time average of the magnetization is observed and the particles will be in the superparamagnetic state. In such conditions an assembly of noninteracting single domain particles do not show magnetic hysteretic behaviour (i.e. zero coercivity and remanent magnetization).

On the contrary if $\tau >> \tau_m$ the relaxation is so slow that only static properties are observed, as in a large ordered magnetic crystal (blocked state). In this condition the magnetization curves in function of applied field show hysteresis loop. The Blocking Temperature ($T_b$) is defined as the temperature at which the relaxation time is equal to the experimental measuring time. From the definition of $T_b$ the equation (2.16) can be rewritten as:

$$\tau_m = \tau_b \exp\left(\frac{KV}{k_B T_b}\right) \quad (2.18)$$

Let us consider now in more detail some aspects of the magnetic behaviour at temperature higher and lower than the Blocking Temperature.

Above $T_b$

The dependence of the magnetization from the temperature and magnetic field is similar to that of a classic paramagnet, using instead of the atomic moment the particle moment:
\[ M(T,H) = xM_s(T) \frac{m_s H}{k_B T} \]  (2.19)

where \( M_s \) is the saturation magnetization, \( x \) the volume fraction and \( L(x) \) is the classical Langevin function:

\[ L(\frac{m_s H}{k_B T}) = \coth(\frac{m_s H}{k_B T}) - (\frac{k_B T}{m_s H}) \]  (2.20)

It is shown in figure 2.11.\textsuperscript{10} For \( m_s H/k_B T << 1 \) the Langevin function can be approximated with

\[ L(\frac{m_s H}{k_B T}) = \frac{m_s H}{k_B T} \]  (2.21)

as indicated by the line tangential to the curve near the origin.

As the magnitude of magnetic field is increased \( (m_s H/k_B T >> 1) \), the magnitude of the magnetization increases. In such condition the Langevin function can be approximated with:

\[ L(\frac{m_s H}{k_B T}) = 1 - (\frac{k_B T}{m_s H}) \]  (2.22)

Assuming \( k_B T >> m_s H \) the susceptibility can be obtained by differentiation of the equation (2.21) with respect to the field \( H \).
\[
\chi = \frac{xVM_s^2}{3k_B T}
\]  

(2.23)

The equation (2.19) must be modified in the real samples in which a distribution of sizes occurs.

\[
M(H,T) = xM_s \frac{\int L \frac{\mu, H}{k_B T} VP(V)dV}{\int VP(V)dV}
\]

(2.24)

where \(P(V)\) is the probability to find a particle with volume \(V\).

The more common approach consists in assuming that the size distribution has a certain form. The width and the mean particle diameter can in principle be directly evaluated. O’ Grady and Bradbury\(^{39}\) suggested a Log-Normal particle size distribution and determined the distribution parameter through a \(M(H,T)\) curves fitting.\(^{40}\) A Log–Normal distribution is often in good agreement with the distribution obtained experimentally by TEM observations for many kinds of nanoparticles. Deviation from the Langevin function, even when the particles size distribution is taken into account, can be observed. Such behaviour is often due to the effects of magnetic anisotropy.\(^{41}\)

**Below \(T_b\)**

Below the blocking temperature superparamagnetic ferri- or ferromagnetic nanoparticles show hysteretic behaviour like bulk material.

When a magnetic field is applied, in the expression of the anisotropy energy the additional term \(\cos \theta\) appears (equation 2.15)

The direct consequence is a magnetization different to zero that can be expressed as:

\[
M(H,T) = xM_s <\cos \theta>
\]

(2.25)

where \(<\cos \theta>\) is the average cosine of the angle between the particle moments and the applied field value and \(x\) the volume fraction. By increasing the external field, the magnetization increases reaching the maximum value \(xM_s\) when all the moments are aligned with the applied field.

\(^{31}\) It should be remarked that the equation (2.23) is analogous to the expression of paramagnetic susceptibility.
If the external field is then decreased, the magnetization decreases down to a remanence value (correspondent to $H=0$) that is expected to be one half of the saturation value, $M_r=xM_s/2$. This is because the magnetic moments will be blocked along the easy axes, which are random oriented over the hemisphere defined by the applied field and $<\cos\theta>=1/2$. On increasing temperature a certain fraction of particles will be in the superparamagnetic state, thus lowering the remanence value, $M_r$. Thus $M_r/M_s$ gives the fraction of blocked particles at a certain temperature.

This is true when all the particles at low temperature are in the blocked state. But often, even at the lowest temperature investigated, a fraction of particles (with a volume so small that $KV$ is always lower than $k_BT$) can be still in the superparamagnetic state. The consequence will be that the saturation of the magnetization will be partial, and in this case $M_r$ value will be lower than $M_s/2$, even at high field.

2.3.3 Collective magnetic excitations

In superparamagnetic systems with low thermal energies with respect to energy barrier, the magnetization vector has a finite probability to form a small angle with the easy direction of magnetization. The probability that the magnetization vectors form an angle between $\theta$ and $\theta+d\theta$ with the easy direction of magnetization is given by

$$p(\theta) = \frac{\exp\left(-\frac{E(\theta)}{k_BT}\right) \sin\theta d\theta}{\int_{0}^{\pi} \exp\left(-\frac{E(\theta)}{k_BT}\right) \sin\theta d\theta}$$ (2.26)

where $E(\theta)$ for uniaxial symmetry is expressed from the equation (2.13).

Thus, even for $k_BT<<KV$ the direction of the magnetization vector may fluctuate in direction close to an easy direction of magnetization (Figure 2.11\hspace{1em}). These so called transverse fluctuations (collective magnetic excitations) are fast compared to the time scales of magnetization measurement and Mössbauer Spectroscopy.\hspace{1em} Therefore, in this uses, the observed quantities will be average values.


2.4 Interparticle interactions

In a system of magnetic nanoparticles, coupling between magnetic moments of the particles can occur. One can expect that the laws are similar to those governing spin interactions in bulk sample, but on a different scale. The magnetic moment of the individual spin is replaced by the giant moment of the particle and the actual length is the interparticle distance $d$. If the particles are in close contact, exchange interactions between the surface atoms of neighbouring particles may be significant.

The exchange energy due to the coupling between particle $i$ and particle $j$ can be written as:

$$E_i^{\text{exchange}} = J_{ij} \mathbf{M}_i \cdot \mathbf{M}_j$$

(2.27)
where $j_{ij}$ is the exchange coupling constant and $\vec{M}$ is the saturation magnetization. \textsuperscript{VII}

If the particles are not in direct contact but dispersed in a non-conducting medium, the magnetic moments of the nanoparticles can only interact via magnetic dipole-dipole interactions. With spherical coordinates $(\theta_i, \varphi_i)$ and $(\theta_j, \varphi_j)$ as defined in figure 2.12, for the directions of $\vec{m}_i$ and $\vec{m}_j$, the dipolar interaction energy of particle $i$ due to the presence of particle $j$, can be written as

\[
E_{\text{dipole}}^i = \varepsilon \left[ m_i \cdot m_j \left( m_i \cdot \hat{r}_{ij} \right) \right] (2.28)
\]

\[
\varepsilon = \frac{\mu_0 m_i m_j}{4\pi r_{ij}^3}
\]

where $r_{ij}$ is the distance between the centres of the particle and $\hat{r}_{ij}$ denotes unit vector. \textsuperscript{43}

If the grains are dispersed in an electrically conducting medium, RKKY interactions are also important, varying as $1/r_{ij}^3$, \textsuperscript{VIII} like dipolar interactions.

The effect of the magnetic interparticle interactions on the superparamagnetic relaxation is an extremely complex problem. In fact, different factors, such as particle size distribution, material morphology (e.i. arrangement of grains, which can forms chain or agglomerates) and orientations of easy axes of the magnetization interplay in determining the effects and the strength of the interactions.

Numerous theoretical and experimental studies have been performed to account for the effects of interparticle interactions on the superparamagnetic relaxation. In 1988 Dormann et al \textsuperscript{44} published a model based on a statistical calculation of the dipolar energy, predicting that the energy barrier increases along with growing interaction strength. The total energy of a particle $i$ was found by summing up the contributions from all the neighbouring particles $j$, and adding the anisotropy energy:

\[
\text{VII}
\]

\textsuperscript{VII} For ferromagnetically ordered particles $\vec{M}_i$ and $\vec{M}_j$ are the saturation magnetizations, and for antiferromagnetically and ferrimagnetically ordered particles $\vec{M}_i$ and $\vec{M}_j$ are the sublattice magnetizations.

\textsuperscript{VIII} In the case of RKKY interactions the equation (2.27) is still valid, and the coupling constant is $j_{RKKY} \propto \cos(2\kappa \pi + \theta) \cdot (k \pi r)^{-3}$.
\[ E_i \approx (E_{bi} + KV \cos^2 \theta) \]  
\[ F_{bi} = \sum_j E_{bi,j} \]  

where \( E_{bi,j} \) is considered as the interaction anisotropy energy of particle \( i \) induced by particle \( j \). The relaxation is obtained through equation (2.16), and assuming constant \( \tau_0 \) is:\(^{43,45}\)

\[ \tau = \tau_0 \exp \left( \frac{KV}{k_B T} + \frac{E_{bi}}{k_B T} \right) \]  

\[(2.30)\]

Since \( E_{bi} \) is always positive, this implies that the energy barrier increases with the interactions strength. This model was successfully applied to explain measured data on iron nanoparticles dispersed in an alumina matrix.\(^{44}\) Later, \( \gamma \)-Fe\(_2\)O\(_3\) nanoparticles showed a decrease in the Mössbauer blocking temperature (i.e., decrease of relaxation time) with an increase of interparticle interactions.\(^{46,47,48}\) Dormann et al.\(^{49}\) explained these Mössbauer results by a decrease of \( \tau_0 \); they affirm that the damping parameter, \( \eta \) (equation 2.17), increases in presence of a growing interaction strength.

A different approach to explain the Mössbauer data on \( \gamma \)-Fe\(_2\)O\(_3\) weak interacting particles was proposed by Mørup et al.\(^{47}\); \( \tau_0 \) was assumed independent of interactions and a decrease of the effective energy barrier with increasing interactions was predicted. They considered the superparamagnetic relaxation of a particle, \( i \), in a static dipolar interaction field \( (B_i) \) due to neighbouring particles. In a system of polar coordinates (figure 2.13) the magnetic energy can be written\(^{47}\)

\[ E = KV \sin^2 \theta - mB_i(sin \theta \cos \varphi + \cos \nu \cos \theta) \]  
\[(2.31)\]

Assuming \( mB_i < k_B T \) they derived an expression for the superparamagnetic relaxation time:

![Figure 2.13 Polar coordinate used in the Mørup model](image)
\[ \tau = \tau_0 \exp \left[ \frac{KV}{k_B T} - \frac{\mu_i^2 (B_i^2)}{3k_B T^2} (1 - \frac{3}{4} \frac{k_B T}{K V}) \right] \]  

(2.32)

When \( k_B T < K V \), the interactions lead to a decrease of the relaxation time. This effect is related to a lowering of the energy barrier for some \( \phi \) values.\(^{41}\)

Both Dormann and Mørup models can explain the experimental observation for weakly interacting particles, even if they give conflicting predictions for the effective energy barriers.

### 2.4.1 Curie Weiss analysis

The variation of the initial susceptibility in a superparamagnetic assembly of nanoparticles when \( \tau < \tau_m \) (unblocked state) is often examined on the basis of a Curie-Weiss type law (equation 2.5). By analogy with paramagnetism, the Curie temperature (\( \theta \)) is often related to the interparticle interactions. Gittleman et al.\(^{50}\) have examined the variation of \( \chi' \) with \( T \) for Nickel particles in an alumina matrix. In the superparamagnetic region the data were fitted to a line which gave a zero ordering temperature for a low concentration of nickel particles. At higher concentration a positive Curie temperature was found. Fiorani et al.\(^{51}\) have also found that the variation of \( \chi' \) with \( T \) for a system of iron particles dispersed in Al\(_2\)O\(_3\) matrix followed a Curie-Weiss law with positive \( \theta \). The value of the Curie Temperature was considered as reflecting the strength of the positive inter-particle interactions and implied ferromagnetic ordering of the particles moments. Other authors have utilized the Curie Weiss analysis so as to evaluate the strength of interparticle interactions.\(^{52,53,54}\)

Therefore the Curie Weiss analysis represents an easy method for an overall evaluation of the effect of interparticle interactions in the crossed evaluations of different materials examined in similar conditions. However some considerations should be made. The Curie constant is correlated with the square of magnetic moment, and \( m_0 \) is temperature dependent. Therefore, a thermal correction for the relative thermal variation of \( m^2 \) is necessary in order to obtain a straight line for \( 1/\chi \). In some cases it is possible to make such thermal correction utilizing the Block law, but very often this approach is not satisfactory.
The real meaning of Curie temperature is not clear. Dormann et al. proposed an analytical expression for $\theta$, showing that it depends either on magnetic moment (i.e. from the temperature) and strongly on the sample shape. Consequently $\theta$ should depend on the temperature and also on the geometry of the experiment. Finally El-Hilo et al. pointed out that Curie temperature in systems of fine particles can be examined like a sum of two different contributions, due to blocking and interactions effect.

The conclusion is that any consideration about interparticle interactions through Curie analysis must be down with caution.
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CHAPTER 3
Experimental methods and techniques

3.1 Structural characterization
3.2 Magnetic characterization
3.3 Mössbauer spectroscopy
  3.3.1 Basic principle and equipment
  3.3.2 Mössbauer spectroscopy in magnetic small crystals
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3.1 Structural characterization

Several techniques have been used to obtain structural and morphological information on the materials. In the following a brief description of the equipments and some mentions about elaboration data are given.

X-Ray Diffraction

Powder X-Ray Diffraction (XRD) spectra of the samples were collected using a D500 diffractometer Siemens with a conventional $\theta$-2$\theta$ Bragg-Brentano focalising geometry, $Mo-K\alpha$ wavelength, graphite monochromator on the diffracted beam and scintillation counter.

An estimate of mean particle size (\( <D_{\text{XRD}} > \)) was obtained from XRD patterns. The relation between average crystal size without disorder effects and full width at half maximum (fwhm) is expressed by Scherrer’s equation

\[
< D_{\text{XRD}} > = \frac{K\lambda}{B \cos \theta} \quad (3.1)
\]

where $\lambda$ is the wavelength of X-Ray, $\theta$ is the angle of incident of X-ray beam, $B$ is the width in $2\theta$ units (radian) of the “pure” diffraction profile and $K$ is a constant approximately equal to unity. $B$ is obtained subtracting from the width of the experimental profile the width of the experimental peak given by a sufficiently large perfect crystal at about the same angle.\(^1\)

Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) micrographs were obtained using a JEOL 200CX microscope operating at 200kV. Finely ground samples were dispersed in octane and further submitted to ultrasonic bath. The suspensions were then dropped on conventional copper grids for the observations. Under the experimental conditions adopted, the wavelength of the incident beam is about $2.51 \times 10^{-2}$ nm and the camera length is 82 cm. The particle size distribution was fitted using the log-normal curve:

\[
p(D) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left( -\frac{1}{2\sigma^2} \times (\ln \frac{D}{D_0})^2 \right) \quad (3.2)
\]

where $\sigma$ is the standard deviation and $D_0$ is the mean diameter.

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High Resolution (HR) TEM images were obtained with a JEM 2010 UHR equipped with a Gatan Imaging Filter (GIF) and a 794 slow scan CCD camera.

**Thermogravimetry and Differential thermal Analysis**

Thermogravimetry analysis (TGA) and simultaneous differential thermal analysis (SDTA) of the samples were carried out on a Mettler-Toledo TGA/SDTA 851. Thermal analysis data were collected in the range 25-1000°C with an heating rate of 10°C min⁻¹ under oxygen flow (flow rate =50 ml. min⁻¹)

**Infrared Spectroscopy**

The absorption spectra were collected using an Equinox 55 (Bruker) spectrophotometer. The samples were prepared in pellets obtained by dispersing the finely ground powder in KBr.

**Nitrogen –physisorption measurements**

N₂ –physisorption measurements at 77 K were carried out on a Sorptomatic 1990 System (Fisons Instruments). Before analysis, the samples were outgassed by heating at a rate of 1°C min⁻¹ under vacuum at 200°C for 18 hours.

The value of surface area obtained from the average particle size of unsupported nanoparticles was determined. This was calculated by the formula

\[
< D_{BET} > = \frac{6}{\rho A} \tag{3.3}
\]

where \( \rho \) is the theoretical density of the material and \( A \) is the specific surface area.

**3.2 Magnetic characterization**

The experimental investigation of the superparamagnetic behaviour is strongly dependent on the measuring technique, on the precise measuring procedure and on magnetothermal history of the sample. In this introduction the influence of the experimental measuring time will be discussed shortly, while in the following sections details about the experimental procedures and magnetothermal history of the samples will be considered.

As already discussed in chapter 2, the experimental observation of superparamagnetism depend on the value of the characteristic measuring time of the experiment (\( \tau_m \)) with respect to the superparamagnetic relaxation time (\( \tau \)). When \( \tau_m < < \tau \), the magnetization of the sample seems static and the properties are
similar to those of the bulk (Static Properties). On the other hand, if $\tau_m \gg \tau$ the magnetization fluctuates between the easy directions with a characteristic relaxation time (Dynamic Properties). As $\tau$ varies with temperature, it will be possible to study the static and dynamic properties as a function of the temperature by choosing experiments with different $\tau_m$. The experimental techniques currently used are Neutron diffraction, Mössbauer spectroscopy, Muon spin rotation, Alternate Current (AC) susceptibility and Direct Current (DC) magnetization (Figure 3.1).

![Figure 3.1](image)

**Figure 3.1** Schematic illustration of experimental measuring times accessible by different experimental techniques

Usually, static properties are deduced from measurements performed in the following conditions:

a) At the thermodynamical equilibrium the measurements are usually performed by AC or DC instruments. It should be remarked that in DC measurement $\tau_m$ is not well defined. This uncertainty is however not important, because the experimental time window is much different from superparamagnetic relaxation time.

b) Out of equilibrium, like the zero field cooled (ZFC) field cooled (FC) magnetization, thermoremanent magnetization (TRM) close and below $T_B$. The properties are considered static–like because of the long measuring time.

To get a full understanding of the dynamics properties, the use of various, complementary techniques, with different and well defined experimental

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1 The AC magnetization measurement allow to use a wide range of experimental measuring times: $\tau_m = 10^{-2} - 10^5$ s for experiments at very low frequencies, $\tau_m = 10^{-1} - 10^3$ s for classical experiments and $\tau_m = 10^3 - 10^9$ s for measurements at very high frequencies.
measuring times is required. In particular, it is essential to investigate the magnetic properties around the blocking temperature and for this reason it’s very important to use experimental techniques with a well defined $\tau_m$.

The parameters $K$ and $\tau_0$ in equation (2.18), don’t depend on $\tau_m$, and are key points in the understanding of the superparamagnetic relaxation. They may depend on the temperature and on the interparticle interactions and such effects can easily be misinterpreted if only a single observation time is used.

Through this work Mössbauer spectroscopy, DC Magnetization and AC susceptibility with $\tau_m$ typical of classical experiments will be used.

3.3 Mössbauer spectroscopy

Resonant absorption is the fundamental working mechanism in modern spectroscopic methods. Photons from a radiation source are absorbed by a sample inducing a change in state between two energy levels that matches energy of the incident photons. When the energy transitions are between the energy states of a nucleus, and the photons are in the $\gamma$-ray region, such a resonant absorption is known as Mössbauer Spectroscopy.\(^2\)\(^3\)

3.3.1 Basic principle

The foundation of Mössbauer spectroscopy is, then, nuclear gamma resonance, which was discovered by Rudolph Mössbauer in 1958.\(^4\)

When a nucleus emits an electromagnetic wave (i.e $\gamma$-quantum) during the transitions from an excited state with energy $E_e$ to the ground state $E_g$,\(^\dagger\) another nucleus can absorb this $\gamma$ quantum passing from the ground state $E'_g$ to an excited state $E'_e$.\(^5\) The condition for resonance between the two nucleus will be:

$$E_e - E_g = E'_e - E'_g \quad (3.4)$$

When an high energy $\gamma$-ray photon is emitted, a free nucleus at rest usually recoils with a recoil energy $E_R$. The overall energy is conserved during the transition

$$E_e = (E_e - E_g) + E_R \quad (3.5)$$

The Nobel laureate Mössbauer demonstrated that a significant fraction of $\gamma$-rays can be emitted in solids without recoil. Therefore, $E_R$ is negligible and strong

\(^\dagger\) Where $E_e-E_g = E_\gamma$ is the energy of $\gamma$-quantum.
nuclear gamma resonant absorption occurs in the samples in the solid-state form. Such recoil free emission and resonant absorption of $\gamma$-rays are the essence of Mössbauer effect.

The resonance condition, expressed from the equation (3.4), imposes that only the same type of nucleus, with the same difference between $E_e$ and $E_g$, can show resonant absorption. Therefore each radioactive source is limited only to study samples containing the same nucleus as the source. There are more than 45 elements in which nuclear gamma resonance has been observed. In this work Mössbauer spectroscopy with $^{57}$Fe will used.

In figure 3.2 the principle of a Mössbauer experiment for $^{57}$Fe is illustrated. A source containing $^{57}$Co nuclei provides a ready supply of excited $^{57}$Fe nuclei. $^{57}$Co decays radioactively with a half life of 270 days to an excited state of ($^{57}$Fe) having a nuclear spin quantum number $I=5/2$.

This falls to its ground state ($I=1/2$) either directly (9%) or via intermediate state (91%) which has $I=3/2$. The $I=3/2$ state has an energy of 14.4 eV above the ground state. The energy of the transition between $I=3/2$ and $I=1/2$ can excite a transition in the sample being studied, if it is absorbed resonantly. To do this, its energy must match with the energy gap in the sample. By moving the source at speed $v$, one can very finely adjust the frequency of the gamma ray utilizing the Doppler effect. In fact the energy

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$^I$ is the spin quantum number

$^IV$ Corresponding to a frequency of $3.5\times10^{18}$ Hz
will depend of the velocity of the source:

\[ E(\nu) = E_0(1 + \frac{\nu}{c}) \]  \hspace{1cm} (3.6)

where \( c \) is the velocity of the light. The plot of the intensity as a function of the velocity of the source is called Mössbauer Spectra.

The energy levels can be affected by three different interactions. Here only a short qualitative description of each kind of interaction will be given. For a detailed treatment see references.\textsuperscript{2,7}

The interactions between the nuclear charge and the electronic charge (called \textit{electric monopole interaction}) results in a shift of all the transition energies. This shift, called \textit{isomer shift} (\( \delta \)) and measured in mm/s, is proportional to the density of s-electron at the nucleus. The isomer shift is used to measure the difference in s-electron density at the nucleus between different environmental states of the same kind of atoms.\textsuperscript{8} Then this parameter is highly dependent upon chemical environment (i.e.: oxidation state of the element and its binding with the ligands).\textsuperscript{2}

When the nuclear charge is not spherical (i.e. there is an electric gradient at the nucleus), an \textit{electric quadrupole interaction} is observed. Then, the presence of an electric field gradient can split the energy levels of the excited states in two sub-levels, leading to a doublet in a Mössbauer spectrum. The splitting of the doublet (\( \varepsilon \), called \textit{quadrupole splitting}) is proportional to the electric field gradient; it is measured in mm/s and it is reported as the magnitude of the split between two peaks. \( \varepsilon \) is used in many Mössbauer spectroscopy studies for helping to solve structure, ligand position and even behaviour of unbound electron pairs.\textsuperscript{3}

In a magnetic field both levels (\( I=1/2 \) and \( I=3/2 \)) split by an amount that is proportional to the field. The selection rule for the transition leads in this case to six different transition energies and six lines spectrum (\textit{Zeeman effect}). The Zeeman effect can be induced from a magnetic field at the nucleus \( (B_{hf}) \) that is proportional to the splitting of the lines. This kind of interaction is called \textit{magnetic dipole interaction}.
3.3.2 Mössbauer spectroscopy in magnetic small crystals

Mössbauer spectroscopy has been extensively used for studies of small magnetic crystals. The same expression (equation 2.16) that describe the superparamagnetic relaxation time was developed using Mössbauer Spectroscopy. When an assembly of magnetic monodomain particles is observed through the Mössbauer spectroscopy, it is found that the superparamagnetic relaxation phenomena results in a broadening of the absorption Zeeman lines for relaxation times of the order of $10^{-8}$ s. For $\tau \leq 10^{-9}$ s, the magnetic hyperfine splitting disappear. The total spectrum is thus a superposition of a magnetic and a quadrupolar pattern, the relative weight of the latter increasing with temperature as the number of rapidly fluctuating particles increases. In this framework we can define the blocking temperature in the Mössbauer Spectroscopy ($T_B^M$) as the temperature at which 50% of the spectral area is magnetically split. This corresponds to an average relaxation time of about $5 \times 10^{-9}$ s. As a consequence it will be used as experimental measuring time of Mössbauer spectroscopy just the value $\tau_m = 5 \times 10^{-9}$ s.

The collective magnetic excitations are fast with respect to the time scale of Mössbauer spectroscopy. Therefore, for particles with uniaxial symmetry, the observed magnetic hyperfine field, will be an average hyperfine field and can be given by:

$$\langle B_{hf}\rangle = B_{hf} \langle \cos \theta \rangle$$

(3.7)

and $\langle \cos \theta \rangle$ is given by

$$\langle \cos \theta \rangle = \frac{\int \cos \theta p(\theta) d\theta}{\int p(\theta) d\theta}$$

(3.8)

where $\theta$ is the angle between the magnetization vector and the easy axis, and $p(\theta)$ has the meaning defined in the subsection 2.3.3.

With a good approximation, for $K V \gg k_B T$, it is possible to define the average hyperfine field as:

$$\langle B_{hf}\rangle = B_{hf} \times (1 - \frac{k_B T}{2K V})$$

(3.9)
At low temperatures the field observed in small crystals decreases with temperature faster than in bulk materials, because of the influence of collective magnetic excitations (Figure 3.3).

3.3.3 Mössbauer spectra in high magnetic field

Mössbauer spectra in large applied field give important information about the magnetic microstructure of the nanoparticles. For a thin absorber, for which thickness effects are negligible and where the direction of the hyperfine field is at random with respect to the gamma ray direction of propagation, the relative area Zeeman sextet are in the ratio 3:2:1:1:2:3. In general case where the magnetic field at the nucleus form an arbitrary angle $\theta$ with the $\gamma$-ray the line areas have the following angular dependence:

\[
\begin{align*}
A_{i,b} &= 3(1 + \cos^2 \theta) \\
A_{i,s} &= 4 \sin^2 \theta \\
A_{i,t} &= 1 + \cos^2 \theta
\end{align*}
\]

Where $A_{ij}$ is the area of line $i$ or $j$. In the presence of an external magnetic field ($\vec{B}_{ext}$) parallel to the gamma-ray direction (i.e. $\theta$ is equal the angle between $\vec{B}_{ext}$ and $\vec{B}_{efc}$), the relative areas of the six lines give information about the
degree of alignment of the magnetization with the applied field. In detail, if the external field is sufficiently strong so as to reorient all the spins \( \mathbf{B}_{\text{ext}} \parallel \mathbf{B}_{\text{efc}}, \theta = 0 \), the intensity of lines 2, and 5 (equation 3.10b) vanishes. If, instead, the external magnetic field is not able to make this and some spins are canted, the relative area of six line are in the ratio 3:p:1:1:p:3 with:

\[
p = \frac{2 \sin^2 \theta}{(1 + \cos^2 \theta)} \tag{3.11}
\]

In presence of an external magnetic field, the effective field at the nucleus can be given by the vector sum of the \( \mathbf{B}_{\text{hf}} \) and \( \mathbf{B}_{\text{ext}} \) (Figure 2.4). Thus \( \mathbf{B}_{\text{hf}} \) can be found from the equation:

\[
\langle B_{\text{hf}}^2 \rangle = \langle B_{\text{efc}}^2 \rangle + B_{\text{ext}}^2 - 2 \times \langle B_{\text{efc}} \rangle \langle B_{\text{ext}} \rangle \cos \theta \tag{3.12}
\]

### 3.3.4 Equipment and elaboration data

The \(^{57}\text{Fe}\) Mössbauer spectra in zero magnetic field were obtained with two different equipments, that will be called (a) and (b).

In (a) equipment Mössbauer spectra were obtained using constant acceleration spectrometer with 50mCi source of \(^{57}\text{Co}\) in rhodium. The spectrometer was calibrated with a 12.5 \( \mu \text{m} \alpha \)-foil at room temperature and isomer shifts are given with respect to that of \( \alpha \)-Fe at room temperature. The Mössbauer spectra, measured below 80K, were obtaining using a close cycle helium refrigerator APD Cryogenics Inc., and the spectra obtained between 80 and 295 K were obtained using a liquid nitrogen cryostat. Spectra in a magnetic field of 6T applied parallel to the gamma ray direction were obtained using liquid helium cryostat with a superconducting coil. The fitting of the spectra was performed using the software mfit.\(^{14}\)

In (b) equipment only Mössbauer spectra at room temperature on powder samples contained in a Plexiglas holder were collected by using a source of \(^{57}\text{Co}\) in Rhodium with activity 370 MBq. The spectrometer has a standard transmission
geometry; it was calibrated with a 6 µm α-Fe foil at room temperature and isomer shifts are given with respect to that of α-Fe at room temperature. All the measurements were performed with an amount of Iron in the sample corresponding to an effective thickness τ~ 3 mm, in order to avoid an excessive peak broadening. The analysis of Mössbauer spectra was performed by fitting the data by peaks of Lorentzian shape and applying a least squares method through the Levenberg-Marquardt algorithm. The fitting was performed using the software MOSSFIX.

3.4 Magnetization measurements

The magnetic properties of the nanoparticles are usually studied by observing the response of the material to applied magnetic field and to variations of temperature. As already mentioned in section 3.2, the behaviour of an assembly of superparamagnetic nanoparticles depends on its magnetic and thermal history. For these reasons it is quite important to have the possibility to vary simultaneously and in a wide range of values both the temperature of the sample and, eventually, the external magnetic field. In addition, in order to perform a fine magnetic analysis, it is useful to dispose of equipments with high sensitivity.

Through this work the magnetization measurements were carried out with a Superconducting Quantum Interference Device (S.Q.U.I.D.). The S.Q.U.I.D. magnetometer is, actually, the most sensitive magnetometer. It contains an superconducting magnet able to produce magnetic fields from zero to several positive and negative Tesla. In addition, it allows a precise control of the sample temperature from the liquid Helium temperature (4.2K) to 400K.

3.4.1 Basic principle and equipment

The working mechanisms of the S.Q.U.I.D. are based on two fundamental principles of superconductivity. One is the quantization of the magnetic flux in a superconducting ring. The other one is the superconducting technology called Josephson junction, a device based on a tunnelling effect proposed in theory by Nobel prize winning B.D. Josephson in 1962 and observed experimentally in 1964 by Anderson and Rowell. Josephson hypothesized that superconducting electron pairs (called Cooper pairs) can tunnel from a superconductor through a thin layer of an insulator into another superconductor.

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2 The S.Q.U.I.D. is capable of resolving changes in external magnetic fields that approach to $10^{-15}$ T, yet can be made to operate in fields as large as 5-7 T.
The S.Q.U.I.D. is a superconducting ring with a small insulating layer (Josephson junction). The flux passing through the ring is quantized once the ring has gone superconducting, but the weak link enables the flux trapped in the ring to change by discrete amounts. Changes in the pick-up voltage occur as the flux change and this device can, thereby, be used to measure vary small variation in flux. The S.Q.U.I.D. is coupled to an superconducting pick up coils through induction. The loops of the pickup coils encircles the magnetic samples. The magnetic field from the sample is inductively coupled to the pickup coil when the samples moves through them. The detection coils measure the local changes in magnetic flux density due to the magnetic field from the sample.

**Equipment**

DC Measurements were performed on a Quantum Design SQUID magnetometer, equipped with a superconducting magnet able to produce fields up to 5 T. The samples in form of powder were immobilized in a epoxy resin to prevent any nanoparticles movement.

**3.4.2 ZFC FC magnetization**

The measurements of Magnetization versus temperature, performed with the ZFC and FC protocols, are one of the most classical approaches in order to observe superparamagnetic relaxation in nanoparticles.

The ZFC protocol consists in cooling the sample from high temperature, where all the particles are in superparamagnetic state, to the lowest measuring temperature in zero magnetic field. Then a static magnetic field is applied and magnetization is measured during warming up ($M_{ZFC}$). The resulting curve is called Zero Field Cooled because the sample has been previously cooled in absence of a magnetic field. When the nanoparticles are cooled below the blocking temperature without magnetic field, all the net magnetic moments in each single domain particle point along the easy axis of the nanoparticles. Magnetic anisotropy acts as an energy barrier to prevent the magnetization direction switching away from the easy axis. Due to the high number of particles and the random distribution of the easy axes directions, the average magnetization, as well as the susceptibility, is about zero. (Figure 3.5a).
When the temperature rises, the magnetic anisotropy in some nanoparticles is overcome and the magnetization directions of these thermally activated nanoparticles start to align with the applied field. Therefore, the total magnetization initially increases with increasing temperature. Then, the ZFC curve exhibits a maximum and the corresponding temperature \( T_{\text{max}} \) is, for non-interacting particles, directly proportional to the average blocking temperature:

\[
T_{\text{max}} = \beta T_B
\]

where \( \beta \) is a proportionality constant that depends on the type of size distribution. In the literature, it has been reported that, for a random assembly of not interacting nanoparticles, \( \beta \) is typically within 1.5-2.0. \( T_{\text{max}} \) can be related to the blocking of particles with mean particle size.\(^{21,22}\)

It should be remarked that \( T_{\text{max}} \) depends on magnetic field cooling. In particular the application of a magnetic field reduces the energy barrier for rotation and consequently will cause the associated blocking temperature at which thermal equilibrium occurs to decrease. Several theoretical and experimental studies indicate a linear dependence between \( T_{\text{max}} \) and \( H^{2/3} \) with a crossover to \( H^2 \) behaviour as applied field using in the cooling of the samples tend to zero.\(^{23,24,25,26}\)

When the interactions between nanoparticles are strong (especially in presence of exchange interactions) the maximum temperature in ZFC magnetization can be explained by “spin glass like” ordering of magnetic moments. Also in this case linear dependence between \( T_{\text{max}} \) and \( H^{2/3} \) is observed.\(^{26}\)
conclusion in presence of $T_{mrr}$ versus $H^{2/3}$ dependence it is difficult to distinguish between a spin glass freezing and a superparamagnetic blocking process.

![Image](image.png)

**Figure 3.6** (a) Random packing of nanoparticles after FC process, (b) FC measurement on CoFe$_2$O$_4$ nanoparticles

The FC protocol consist in cooling the sample in a small DC field and measuring the magnetization during warming up without remove the field. When a magnetic field is applied during the cooling process (FC), all the net magnetic moments of the nanoparticles are aligned along the field direction regardless of the easy axis directions of each individual nanoparticles. As the nanoparticles are cooled at low temperature, the magnetization direction of each particle is frozen in the field direction (Figure 3.6a). By increasing the temperature, an increasing number of particles will be in superparamagnetic state and the magnetization monotonically will decrease, giving rise to a typical “paramagnetic behaviour” (Figure 3.6b).

In figure 3.7 the ZFC and FC curves are reported superimposed. Below a given temperature the two curves diverge and an irreversible magnetic behaviour is observed.
The temperature at which the irreversibility is observed is called *irreversibility temperature* \( (T_{irr}) \) and can be related to the blocking temperature of the biggest particles.\(^{27,28}\) The difference between \( T_{\text{max}} \) and \( T_{irr} \) provides a qualitative measure of the width of blocking distribution (i.e. of the size distribution in absence of interparticle interactions).

The time experimental windows of the ZFC and FC measurements is approximately given by the time between the measurements. Through this thesis a value of \( \tau_n = 100 \, \text{s} \) will be used.

**Measurement protocol**

ZFC FC magnetization measurements were carried out by cooling the sample from 325K to 5 K in zero magnetic field. Then a static magnetic field was applied. \( M_{ZFC} \) was measured during warming up from 4.2 to 325K, whereas \( M_{FC} \) was recorded during the subsequent cooling. Stringently both \( M_{ZFC} \) and \( M_{FC} \) should be measured in warming up. Anyway, Dormann et al.\(^{29}\) affirm that there is no appreciable difference if cooling rate and heating rate are not too different.

**Data elaboration**

The temperature corresponding to the maximum in ZFC curve was determined, fitting the experimental data around the maximum with a polynomial function. Through a second derivative of this function the \( T_{\text{max}} \) value was obtained.

In order to determine the irreversibility temperature, \( T_{irr} \) was defined as the temperature at which the difference between \( M_{FC} \) and \( M_{ZFC} \), normalized to its maximum value at the minimum temperature, becomes smaller than 3%.

**3.4.3 TRM magnetization**

The anisotropy energy barrier \( (\Delta E_a=KV) \) is a key point in order to understand the superparamagnetic relaxation. To obtain information about \( \Delta E_a \), measurements of thermoremanent magnetization can be performed.

In the TRM measurement the sample is cooled from high temperature in an external static magnetic field, then the field is turned off and the magnetization is measured on warming up. In figure 3.8a The TRM curve of CoFe\(_2\)O\(_4\) nanoparticles is reported. After field cooling the nanoparticles are frozen as shown in figure 3.6a. Although the magnetic field is turned off at 5 K, the magnetic anisotropy energy barrier blocks any change of the magnetization direction. The anisotropy
energy barriers usually have a broad distribution in random oriented nanopowder samples for many reasons, including the size distribution and the distribution of the angles between the easy axis.\textsuperscript{29} As the temperature rises, some of the nanoparticles, are able to overcome their energy barrier thanks to their thermal activation energy $k_BT$. Consequently, the magnetization direction of each thermally activated nanoparticle starts to flip randomly faster than the measuring time taken by the magnetometer.\textsuperscript{22} Then the overall magnetization of the nanoparticles decreases with increasing temperature. $M_{TRM}$ is related to the distribution of anisotropy energy barriers:

$$M_{TRM} = M_{nr} \int_{\Delta E_c} f(\Delta E) d\Delta E$$

(3.14)

where $M_{nr}$ is the non relaxing component of the magnetization and $\Delta E_c$ is a critical value of energy, below which all the particles are blocked.\textsuperscript{22,30} From the relation (2.11) results that the derivative of $M_{TRM}$ with respect to temperature gives an estimate of the anisotropy energy barrier distribution:\textsuperscript{30,31}

$$f(\Delta E_c) \propto \frac{dM_{TRM}}{dT}$$  \hspace{2cm} (3.15)

In Figure 3.8b report (continuous line) $f(\Delta E_c)$, obtained from the $M_{TRM}$ shown in figure 3.8a. In chapter 2, the blocking temperature was defined as the temperature for which the relaxation time is equal to the experimental measuring time. In practice, the samples of small particles always exhibit particle size
distributions, and often $T_B$ is defined as the temperature at which 50% of the sample is in the superparamagnetic state.\textsuperscript{31,32} We can obtain an estimate of the blocking temperature from the distribution of magnetic anisotropy energy barriers ($T_B^w$), evaluating the temperature at which 50% of the particles overcome their anisotropy energy barriers. Indeed, at a given temperature ($T'$) the nanoparticles can be divided into two subpopulations, $P_b(T')$ and $P_s(T')$, which represent respectively the nanoparticles in the “blocked” state and in the superparamagnetic state. The integration of the areas under the $f(\Delta E_a)$ curve gives the relative ratio of these two subpopulations:

$$R(T) = \frac{P_b(T')}{P_s(T')} = \frac{\int_{T'}^{T_B} f(T')dT'}{\int_{T'}^{T_B} f(T)dT}$$  \hspace{1cm} (3.16)

The temperature at which $R=1$, correspond to the Blocking temperature.\textsuperscript{31}

Practically, in order to determine the value of $T_B^w$ the ratio $R$ is rewrite as:

$$R(T) = \frac{P_s(T) - P_s(T)}{P_s(T)}$$  \hspace{1cm} (3.17)

Where $P_s(T)$ represent the total population of nanoparticles. $P_b(T)$ is determined integrating the function $f(\Delta E_a)$ in the whole range of temperature, and $P_s(T)$ is the maximum value of this integral.\textsuperscript{31} (Figure 3.8b)

It should be remarked that $P_s(T)$ cannot represent the nanoparticles fraction eventually superparamagnetic at 5 K. Therefore, for ultrafine particles, an estimation of the blocking temperature using this approach would produce an incorrect value. For this reason $T_B^w$ is sometimes defined as the temperature at which the magnetic anisotropy distribution has its maximum. This approach assumes that the distribution of particles size is symmetric\textsuperscript{31} and that the interparticle interactions are very weak.

Measurement protocol

In the TRM measurements the sample was cooled from 325 K to 4.2 K in an external magnetic field of 5 mT; then the field was turned off and magnetization was measured by warming up.
3.4.4 Magnetization Vs. field

The response to a variation of external magnetic field is very important in order to evaluate the behaviour of a superparamagnetic assemblies of monodomain particles. Above blocking temperature the coercivity is zero and superparamagnetic particles show a reversible behaviour (Figure 3.9a), while below $T_B$ an irreversible, trend like in ferromagnetic material (Hysteresis loop) is observed (Figure 3.9b).

**Figure 3.9** Hysteresis loops of an weakly interacting assembly of CoFe$_2$O$_4$ nanoparticles above blocking temperature (a) and below blocking temperature(b)

**Measurement protocol**

The measurement of magnetization as a function of magnetic field were carried out at different temperature in fields between -5 and 5 T. The samples in form of powder were immobilized in an epoxy resin to prevent any movement of the nanoparticles during the measurements.

**Data elaboration**

Several Parameters were extracted from Hysteresis loops: Saturation magnetization ($M_s$), Coercive field ($H_c$), and Remanent Magnetization ($M_r$). In addition, for the Hysteresis post field cooling, also the Exchange field is calculated. Practically the value of $M_s$ are is calculated as:

$$M_s = \frac{|M'_s| + |M''_s|}{2}$$  \hspace{1cm} (3.18)
Where $M_r^+$ and $M_r^-$ are indicated in figure 3.9b. When the maximum field is not sufficient to saturate the sample, $M_r$ was obtained by fitting the high field part of hysteresis curve:

$$M = \pm M_r^+ \times \left( 1 - \frac{a}{H} - \frac{b}{H^2} \right)$$  \hspace{1cm} (3.19)

where $H$ is the applied field and the $a$ and $b$ are parameters determined by the fitting procedure.

The remanent magnetization $M_r$ can be defined as the magnetization at zero field, after $H_{\text{max}}$ has applied. It was calculated as:

$$M_r = \frac{|M_r^+| + |M_r^-|}{2}$$  \hspace{1cm} (3.20)

where $M_r^+$ and $M_r^-$, indicated in figure 3.9b, were determined by linear regression of the data point nearest to $H=0$

The coercivity field was calculated as:

$$H_c = \frac{|H_c^+| + |H_c^-|}{2}$$  \hspace{1cm} (3.21)

where $H_c^+$ and $H_c^-$ \textbf{(Figure 3.9b)} was determined by linear regression of the data point nearest to $H=0$.

For the Hysteresis loop measured after field cooling of the samples the exchange field ($H_e$) was also measured:

$$H_e = \frac{|H_e^+| - |H_e^-|}{2}$$  \hspace{1cm} (3.22)

3.4.5 AC susceptibility

AC susceptibility measurements at different frequencies represent a very useful tool for studying dynamical properties of magnetic nanoparticles, as they have the advantage of covering a large time measuring time with the same technique. Moreover, as the strength of the used AC field is small, the barrier energy is very slightly modified and therefore the relaxation time value in absence of applied field can be used with good approximation.

The Magnetic field in the AC measurement is given by
\[ h(t) = h_0 \exp(i \omega t) \]  
(3.23)

where \( \omega \) is the angular frequencies.\(^{\text{VI}}\) The susceptibility is a complex quantity:

\[ \chi_{ac}(\omega, T) =\chi'(\omega, T) + i\chi''(\omega, T) \]  
(3.24)

where \( \chi' \) and \( \chi'' \) are respectively called in phase (or dispersion) component and out-phase (or absorption) component. A good expression for \( \chi_{ac} \) was proposed from Gittleman et al:\(^{\text{VII}}\)

\[ \chi = \frac{\chi_0 + i\omega t\chi_1}{1 + i\omega t} \]  
(3.25)

where \( \chi_0 \) is the superparamagnetic susceptibility and \( \chi_1 \) is the initial response of particle moments to both external field and anisotropy field in the “blocked state”.\(^{\text{VIII}}\)

The real part of AC susceptibility is given by:

\[ \chi' = \frac{\chi_0 + \omega^2 t^2 \chi_1'}{1 + \omega^2 t^2} \]  
(3.26)

When an external magnetic field is applied, the superparamagnetic system tend to reach an equilibrium distribution of the energetic levels which depends on the magnetic field strength. In this condition the equation (3.27) predicts:

- If \( \tau >> 1/\omega \), \( \chi' = \chi_0 \). The condition \( \tau >> 1/\omega \) is fulfilled for uniaxial particles at high temperature where \( KV << k_B T \) and the particle moments relax via thermal fluctuation.

\(^{\text{VI}}\) \( \omega = 2\pi \nu \), and \( \nu \) is the frequency of the applied magnetic field.

\(^{\text{VII}}\) \( \chi_0 \) at the thermal equilibrium is given by \( \chi_0 = \frac{M_s^2 V}{3k_B T} \)

\(^{\text{VIII}}\) \( \chi' \) is given by \( \chi' = \frac{M_s^2}{2K} \langle \sin^2 \theta \rangle \) where \( \theta \) is the angle between the applied field and the easy magnetization direction, the average being made over all the particles.

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• If $\tau >> 1/\omega$, $\chi' = \chi_1$. The condition $\tau >> 1/\omega$ is fulfilled for uniaxial particles at low temperature where $KV >> k_B T$. The particles are in the blocked state and the energy due to the magnetic field is not enough to reverse the particle moment in $\tau_m$.\(^{29}\)

The Gittleman expression for the susceptibility was derived under the assumption that the magnetization direction was at the energy minimum and the distribution of the easy axis orientation was random. Later, more accurate expression,\(^{35,36}\) that does not introduce significant errors in the Gittleman expression, have been proposed. Figure 3.10 show the thermal dependence of $\chi'$ and $\chi''$ for an assemblies of CoFe$_2$O$_4$ nanoparticles. Both the in phase and out of phase component present a well defined maximum, and the maximum in $\chi''$ corresponds approximately to the inflection point of $\chi'$.\(^{37}\) For an individual, isolated, particle the temperature of the maximum in $\chi'$ ($\chi_{\text{max}}$) should correspond to the blocking temperature $T_B$ at which $\tau = \tau_m$. For an assembly of particles with size distribution $T_{\text{max}}'$ is proportional to the average blocking temperature. Gittleman et al.\(^{21}\) suggest that the proportional constant $A$, is equal to 2 for rectangular distribution and to 1.8 for Poisson distribution.

The temperature of the maximum of the AC susceptibility increases with increasing frequency. The analysis of such frequency dependence allows to gain a useful insight on the dynamical properties. In particular an evaluation of energy barrier ($KV$) and relaxation time constant can be obtain from AC experiments. Considering the temperature corresponding to the maximum value of AC in-phase susceptibility, it is possible to rewrite the equation (2.18) as:

$$\tau_m = \tau_0 \exp \left( \frac{KV}{k_B T_{\text{max}}'} \right) \quad (3.27)$$

Utilizing the logarithm form equation (3.28) becomes:

$$\ln \tau_m = \ln \tau_0 + \frac{KV}{k_B T_{\text{max}}'} \quad (3.28)$$
The plot of \( \ln(\tau_n) \) vs \( 1/T_{\max}^{\epsilon} \) must then give a straight line with slope \( KV/k_B \) and intercept \( \tau_0 \). (Figure 3.11)\(^{38}\)

**Figure 3.11** Temperature dependence of the magnetization relaxation time estimated from AC susceptibility data for \( \gamma \)-Fe\(_2\)O\(_3\) nanoparticles\(^{38}\)

**Equipment**

AC susceptibility measurements were performed using a commercial susceptometer (Lakeshore).
REFERENCES


5. S. Mørup, *Mössbauer Spectroscopy and its applications in materials science*, note to the lessons of Mössbauer Spectroscopy, DTU, Lyngby, Denmark


# CHAPTER 4

CoFe$_2$O$_4$ prepared by sol gel autocombustion method:

Synthesis, structure and magnetic properties

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</tbody>
</table>
4.1 Introduction

Among the many synthetic methods proposed for the synthesis of nanoscaled spinel oxide particles, good results have been obtained by thermal decomposition of citrate precursor.\cite{1,2,3,4,5} Recently, this method has been modified so as to produce nanosized oxides through a process of sol-gel auto-combustion.\cite{6,7,8,9,10} The self-combustion procedure has the advantages of inexpensive precursors, simplicity, short preparation time, good quality of the powders and moderate heating; furthermore, it does not require specialised equipment, so that large quantities can be easily prepared. Therefore, such method was adopted to prepare cobalt ferrite (CoFe$_2$O$_4$).

In self combustion methods precursor gels are prepared from an aqueous solution of metal nitrates and an organic complexant such as citric acid,\cite{6,10,11,12,13,14} carboxylate azides,\cite{15,16} urea\cite{17} or glycine.\cite{18,19} Due to the good capability of chelating metallic ions and to low decomposition temperatures, citric acid is suitable for obtaining precursors of transition metal oxides.\cite{6,10,11,12,13,19} When heated on a hot plate many nitrate citrate gels burn in a self-propagating process, generating a large amount of heat and nontoxic gases in a short time, thus converting the precursors mixture directly to the product without any further calcination treatment.\cite{10,14} The Citric acid plays two important roles: on one hand, it is the fuel for the combustion reaction (the nitrate ion is the burning oxidizer). On the other hand, it forms complexes with metal ions preventing the precipitation of hydroxilated compounds. Moreover, among the various systems mentioned above, citrate gels appears to be the least explosive and, therefore, relatively safer.\cite{12}

An important step of this research, was devoted to verify whether the autocombustion process can be adjusted, so as to modify the features of the particles according to different requirements. In the investigations carried out so far, it was verified that many parameters affect the course of the reaction: composition of starting mixture, pH of the sol, modality of gel formation and starting combustion temperature. In consideration of the effect of the pH on the Citric acid speciation and complexing aptitude, it was believed that the acidity of the starting solution was the most important parameter to be controlled. In addition, it should be remarked that the pH conditions are extremely important in the traditional sol-gel process. Because the final aim was to combine sol-gel self combustion and sol-gel traditional method, a good control of the synthesis pH was believed fundamental.
4.2 Synthesis

The general synthesis procedure is shown in the flow diagram in figure 4.1. Four samples were prepared by mixing Fe(NO$_3$)$_3$·9H$_2$O (Aldrich, 98%), Co(NO$_3$)$_2$·6H$_2$O (Aldrich, 98%) and Citric acid (CA, Aldrich, 99.9%) aqueous solutions with a 1:1 molar ratio of metals (Co$^{II}$ + Fe$^{III}$) to citric acid.

The corresponding nitrate to citrate ratio was 0.37. The pH of the clear sol thus obtained resulted <1. Liquor ammonia (Aldrich, 30%) was then added drop by drop under constant stirring in order to adjust the pH. Four samples, at pH 7, 4, 2 and spontaneous (ammonia free) were so prepared. The samples will be indicated with the letter A, B, C and D respectively. The dark brown solutions were allowed to evaporate on a hot plate maintaining the solution temperature at 80-90°C. As a result of the increasing concentration, the viscosity raised due to the crosslinking of carboxylato-metal complexes into a three dimensional structure; on further dehydratation, a gel started to form. In figure 4.2 the possible gel structure for the

![Figure 4.1 Schematic representation of the procedure for the preparation of CoFe$_2$O$_4$ nanoparticles through sol-gel self combustion](image-url)

The corresponding nitrate to citrate ratio was 0.37. The pH of the clear sol thus obtained resulted <1. Liquor ammonia (Aldrich, 30%) was then added drop by drop under constant stirring in order to adjust the pH. Four samples, at pH 7, 4, 2 and spontaneous (ammonia free) were so prepared. The samples will be indicated with the letter A, B, C and D respectively. The dark brown solutions were allowed to evaporate on a hot plate maintaining the solution temperature at 80-90°C. As a result of the increasing concentration, the viscosity raised due to the crosslinking of carboxylato-metal complexes into a three dimensional structure; on further dehydratation, a gel started to form.
A, B and C samples is sketched. A sudden increase of the temperature (T>200°C) allowed to convert directly the gels into the corresponding nanocrystalline CoFe₂O₄ powders. However, the gels prepared at different pH showed different behaviour. In fact, the A, B, C gels gave a fast flameless autocombustion reaction with the evolution of large amounts of nontoxic gases (CO₂, H₂O, N₂): it started in the hottest zones of the beaker and propagated from the bottom to the top like the eruption of a volcano. The reaction was complete in 20-30 seconds giving rise to a dark grey voluminous product (figure 4.3). In the case of the D gel, the thermal treatment induced a slow reaction that led, in about 10 min, to a grey powder. In this case no volume increase was observed during the reaction. Elemental analysis by inductively coupled plasma - atomic emission spectroscopy (ICP-AES) confirmed the molar ratio between Fe and Co of 2:1 in all the samples.
4.3 Precursors characterization

In order to investigate the decomposition mechanism of the precursors and the formation mechanism of nanoparticles, the procedure was studied by thermal analysis. In addition, the precursors were studied by FT-IR spectroscopy.

4.3.1 Thermal analysis

In figure 4.4 TG and DTA curves of the dried citrate gel prepared at pH=7 (sample A) are compared with the ones of solid citric acid. The Citric acid exhibits two endothermic peaks at about 162°C and 207°C due to the conversion to Aconitic acid $\text{C}_6\text{H}_6\text{O}_6$ (-H$_2$O) and Itaconic acid $\text{C}_5\text{H}_6\text{O}_4$ (-CO$_2$), and an exothermic peak at about 460°C associated with the complete decomposition of the polymerised Itaconic acid.\textsuperscript{21} The TG curve of the dried gel shows, besides a weight loss of about 2-3 % in the 120-180°C temperature region attributable to water vaporization, only a vertical step at about 200°C accompanied by a drastic weight loss (about 80%). It corresponds to a sharp and intense exothermic peak in the DTA curve centred at 205°C. This behaviour indicates that the decomposition of the gel occurs suddenly as a single step, as observed in other systems.\textsuperscript{6,7,9,13,14,22} The absence of the pure citric acid exothermic peak at about 460°C in the gel curves indicate that the combustion reaction was already completed. Moreover, an experiment carried out on citrate gels containing Cl$\textsuperscript{-}$ ions instead of NO$_3$- did not exhibit auto-combustion; this corroborates the hypothesis that the reaction is attributable to the presence of nitrate ions, that induce strongly exothermic autocatalytic oxidation-reduction reaction.

![Figure 4.4 TG (a) and DTA (b) plots of the pure phase gel prepared at pH 7 (sample A, solid line) and of the pure citric acid (CA, dotted line)](image-url)
In figures 4.5 (a,b) TGd and DTA curves of the $A$, $B$, $C$ gels are reported.

The strong similarity of the curves confirms that the formation mechanism consists in a self combustion process in all the precursors.$^{6,11}$

Minor differences in the TG curves in the 25 -175 °C range among the three gels can be observed, due to the increase of weight loss from $A$ to $C$ sample. Such an effect can be due to the increasing amount of water trapped inside the gels. In fact, the decrease of the concentration of NH$_4^+$ ion leads to a lower degree of metal complexes polymerization and therefore to a more open structure which can accommodate higher percentage of water.$^9$

The figure 4.6 (a,b) shows TG and DTA curves of the sample $D$ prepared without ammonia. In the TG curve three weight loss steps can be observed. The first one of about 14% at low temperature is due to the adsorbed water removal. The second (at 150°C, about 30%) and the third (300°C; about 14%) ones are associated to exothermic processes due to the decomposition of the polymeric precursor. According to the literature$^1$ the second and the third steps can be ascribed to decomposition of the precursor to acetonedicarboxylate complex and to the final decomposition to cobalt ferrite respectively.

Figure 4.5 TG (a) and SDA (b) plots of the $A$ (dashed line), $B$ (dotted line) and $C$ (dashed-dotted line) samples.

Figure 4.6 TG (a) and DTA (b) plots of the $D$ (pH<1) sample.
4.3.2 FT-IR spectroscopy.

Figures 4.7 shows respectively the IR spectra in the range 400-2000 cm$^{-1}$ of the precursor gels. In table 4.1 the principal adsorptions bands, with corresponding wavenumbers and attributions are reported.

In the following the most important features of the precursor gels spectra are described. The spectrum of pure CA shows a doublet in the range 1700-1750 cm$^{-1}$ attributed to stretching vibrations absorptions bands of carboxylic groups, which can be ascribed to free carboxylic groups (1754 cm$^{-1}$) and carboxylic groups forming intramolecular hydrogen bonds (1704 cm$^{-1}$). In the spectra C, B and D the doublet is replaced by a broad absorption band at 1722 cm$^{-1}$ that decreases with the increase of pH. These absorptions are due to free carboxyl groups that form dimer compounds. Such absorption do not appear in the A sample, indicating that, with the increase of the pH, the quantity of free Citric acid decreases.

The band at 640 cm$^{-1}$ present in the IR spectra A, B and C is ascribable to symmetric stretching in the COO$^-$ group. The intensity of this band increases with the pH increase, because of the deprotonation of carboxylic groups and such absorption is not present in D spectra.

The D sample shows two band at 1570 cm$^{-1}$ e 1400 cm$^{-1}$ due respectively to $\nu_{\text{asym}}$ COO$^-$ and $\nu_{\text{sym}}$ COO$^-$. A separation energy of $\Delta=$ 170 cm$^{-1}$ between the bands indicated the formation of the bridging complex. In the A, B and C samples the broadening of absorption bands do not permit to determine precisely the separation energy. The two broad band at around 1400 cm$^{-1}$ and 1600 cm$^{-1}$ are typical of three-dimensional structure of a metal ammonium carboxilate gel.

The IR signal at low wavenumbers give information also about citrate metal complex in A, B and C samples. The very weak band present in the A, B and
C spectra at 960 cm\(^{-1}\) and 640 cm\(^{-1}\) are ascribed in literature to unidentate COO\(^-\) complex.\(^25\)

These bands increase with the increase of the pH and this fact suggest that also the interaction increases with the pH.

In the D sample the very sharp band at 1384 cm\(^{-1}\) is attributable to the stretching vibrations of NO\(_3^-\) ions; another sharp band clearly visible at 850 cm\(^{-1}\) is also ascribable to the NO\(_3^-\) ions.\(^26\) In the A, B and C samples sharp band at 1384 cm\(^{-1}\) is not visible because to broadening of the bands. The signal at 830 cm\(^{-1}\) is still visible and the presence of this sharp absorption indicates that NO\(_3^-\) exist as a free group in the structure of the citrate gels and it provides an in situ oxidizing environment for the combustion of the citrate component.\(^27\)

### Table 4.1 Principal adsorptions bands, with corresponding wavenumbers and attributions for A, B, C, and D samples

<table>
<thead>
<tr>
<th>D ((cm^{-1}))</th>
<th>C ((cm^{-1}))</th>
<th>B ((cm^{-1}))</th>
<th>A ((cm^{-1}))</th>
<th>Attributions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1720</td>
<td>1722</td>
<td>1722</td>
<td>---</td>
<td>COOH free groups that form dimer compounds</td>
<td>(^23), (^14)</td>
</tr>
<tr>
<td>1614</td>
<td>1614</td>
<td>1614</td>
<td>1614</td>
<td>(\delta(\text{HOH}))</td>
<td>(^1)</td>
</tr>
<tr>
<td>1570</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>(\nu_{\text{asym}} \text{COO}^-)</td>
<td>(^1)</td>
</tr>
<tr>
<td>1400</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>(\nu_{\text{sym}} \text{COO}^-)</td>
<td>(^1)</td>
</tr>
<tr>
<td>1390</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>(\nu \text{NO}_3^-)</td>
<td>(^26)</td>
</tr>
<tr>
<td>1300</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>(\nu \text{C-O})</td>
<td>(^1)</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>1250</td>
<td>--</td>
<td>(\nu \text{C-O})</td>
<td>(^1)</td>
</tr>
<tr>
<td>--</td>
<td>1200</td>
<td>1200</td>
<td>--</td>
<td>(\nu \text{C-O})</td>
<td>(^26)</td>
</tr>
<tr>
<td>--</td>
<td>1080-1040</td>
<td>1080-1040</td>
<td>1080-1040</td>
<td>(\nu \text{C-O} \alpha \text{OH})</td>
<td>(^26)</td>
</tr>
<tr>
<td>930</td>
<td>930</td>
<td>930</td>
<td>---</td>
<td>Dimeric Carboxil acid</td>
<td>(^24)</td>
</tr>
<tr>
<td>--</td>
<td>960</td>
<td>960</td>
<td>960</td>
<td>Unidentate complex</td>
<td>(^25)</td>
</tr>
<tr>
<td>---</td>
<td>640</td>
<td>640</td>
<td>640</td>
<td>Unidentate complex</td>
<td>(^25)</td>
</tr>
</tbody>
</table>

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4.4 Structural characterization

Structural Characterization was carried by XRD, TEM, IR spectroscopy and nitrogen physisorption. In addition CHN analysis and thermal analysis were performed.

XRD data of the as burnt samples (figure 4.8) show the presence of an ordered cobalt ferrite (CoFe$_2$O$_4$) phase with a spinel structure. Besides the main phase, low intensity reflections that can be ascribed to Co$_3$O$_4$ phase are observable. Since the nominal ratio Fe/Co in the samples is 2:1 and crystalline iron oxide phases are absent, the separation of a low quantity of cobalt oxide leads to a cobalt defective ferrite.

A broadening of the CoFe$_2$O$_4$ reflections is clearly visible for the $D$ sample if compared with the other samples, suggesting a decrease of the crystallite size. The mean particle sizes calculated by applying the Scherrer equation to the [400] reflection are reported in table 4.2 and result in the range 18 – 20 nm for $A$, $B$, $C$ samples and of about 10 nm for $D$ sample.

![Figure 4.8 XRD patterns of the $A$, $B$, $C$ and $D$ samples. The miller indexes reported for the $A$ sample are common to the other samples](image-url)
It is possible to observe the presence of spots and rings respectively, with larger spots for the $D$ sample, confirming the XRD indication of reduced

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area $(\text{m}^2/\text{g})$</th>
<th>BET average particle size $(\text{nm})$</th>
<th>XRD average particle size $(\text{nm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ ($\text{pH 7}$)</td>
<td>24(1)</td>
<td>49(2)</td>
<td>19(1)</td>
</tr>
<tr>
<td>$B$ ($\text{pH 4}$)</td>
<td>20(1)</td>
<td>58(2)</td>
<td>22(1)</td>
</tr>
<tr>
<td>$C$ ($\text{pH 2}$)</td>
<td>23(1)</td>
<td>51(3)</td>
<td>18(1)</td>
</tr>
<tr>
<td>$D$ ($\text{pH &lt;1}$)</td>
<td>76(1)</td>
<td>15(1)</td>
<td>10(1)</td>
</tr>
</tbody>
</table>

Table 4.2 BET surface area, BET average particle size and XRD particle size values. Uncertainties are given in parentheses as errors in the last digits.

The IR measurements in the region 400-1000 cm$^{-1}$ (figure 4.9) confirm the presence of the $\text{CoFe}_2\text{O}_4$ phase; in fact, a large band associated to the Fe-O stretching mode at 570, 572, 584 cm$^{-1}$ for $A$, $B$, $C$, $D$ samples respectively is present. Shoulder at about 660 cm$^{-1}$ is also visible in the $A$, $B$, $C$ spectra. In the literature the shift of the main band value (590 cm$^{-1}$) and the presence of the additional band have been ascribed to decreasing amount of cobalt on respect to the stoichiometric ratio.

These results suggest that in the $D$ sample the quantity of cobalt oxide is lower than that of $A$, $B$ and $C$ samples.

TEM micrographs of the as burnt powders indicate for all the samples their nanocrystalline nature. $A$, $B$, $C$ samples (figure 4.10a, 4.10b, 4.10c) are very similar: they show nanoparticles with an irregular morphology and with a broad particle size distribution ranging from around 4-5 nm to 55-60 nm, with a high percentage of small particles (4-15 nm). More regular spherical shape and narrower particle size (in the range 2 – 10 nm) distribution were observed for the $D$ sample (figure 4.10d). The SAD (Select Area Diffraction) patterns confirm the presence of
CoFe$_2$O$_4$ in all the samples. As an example, SAD images of $A$ and $D$ samples are reported (figures 4.11 and 4.12). In the tables, near the SAD images, the corresponding reflexes assignments are reported.

**Figure 4.10** Dark Field images of $A$ (a), $B$ (b), $C$ (c) and $D$ (d) samples

**Figure 4.11** SAD image of the $A$ sample. Sad assignments are reported in table

**Figure 4.12** SAD image of the $D$ sample. Sad assignments are reported in table

<table>
<thead>
<tr>
<th>$A$ (pH 7)</th>
<th>$A$ (pH 7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl</td>
<td>d$_{hkl}$ (nm)</td>
</tr>
<tr>
<td>111</td>
<td>0.49</td>
</tr>
<tr>
<td>220</td>
<td>0.296</td>
</tr>
<tr>
<td>311</td>
<td>0.256</td>
</tr>
<tr>
<td>400</td>
<td>0.211</td>
</tr>
<tr>
<td>331</td>
<td>0.188</td>
</tr>
<tr>
<td>422</td>
<td>0.172</td>
</tr>
<tr>
<td>511</td>
<td>0.160</td>
</tr>
<tr>
<td>400</td>
<td>0.149</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$D$ (pH 0)</th>
<th>$D$ (pH 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl</td>
<td>d$_{hkl}$ (nm)</td>
</tr>
<tr>
<td>111</td>
<td>0.49</td>
</tr>
<tr>
<td>220</td>
<td>0.30</td>
</tr>
<tr>
<td>311</td>
<td>0.25</td>
</tr>
<tr>
<td>400</td>
<td>0.21</td>
</tr>
<tr>
<td>422</td>
<td>-</td>
</tr>
<tr>
<td>511</td>
<td>0.172</td>
</tr>
<tr>
<td>400</td>
<td>0.161</td>
</tr>
<tr>
<td>400</td>
<td>0.148</td>
</tr>
</tbody>
</table>
It is possible to observe the presence of spots and rings respectively, with larger spots for the $D$ sample, confirming the XRD indication of reduced cobalt ferrite particle size.

The thermal analysis of the as burnt powders show a unique broad exothermic peak in the temperature region 280 – 400 °C due to the combustion of the carbonaceous residues associated with a weight loss of about 2-3%. This result is confirmed by elemental analysis, that revealed also a small percentage of nitrogen (1-2%). However, a mild treatment at about 400°C allowed to eliminate almost completely these impurities. All the samples were submitted to thermal treatment in the temperature range 300-900 °C. The XRD data indicate that the CoFe$_2$O$_4$ phase is stable until 550 °C; later on, the main reflex of $\alpha$-Fe$_2$O$_3$ appears.

N$_2$-physisorption measurements of the as burnt powders were also performed. The specific surface area values obtained by the BET method are summarized in Table 4.2 together with the average particles sizes, calculated as described in the experimental part. The particles size determined by BET technique, equation (3.3), shows values two times larger for the $A$, $B$, $C$ samples on respect to that calculated by XRD measurements: These results induce to believe that in these samples small clusters form. For the sample $D$ the particles size calculated by XRD and BET measurements are similar, indicating a lower degree of agglomeration of the crystallites.

4.5 Magnetic properties

The magnetic behaviour of all the samples was studied by DC magnetic measurement and Mössbauer spectroscopy at room temperature.

4.5.1 Magnetization measurements

The figure 4.12 shows the ZFC-FC magnetisation curves measured in the temperature range of 4.2-325 K under an external static magnetic field of 50 mT. These curves do not overlap at 325 K: this behaviour is characteristic of superparamagnetism and indicates the presence of a non negligible fraction of nanoparticles still in magnetic blocked state at this temperature. The most likely explanation of such a behaviour is connected with the large mean size of nanoparticles and the presence of interparticle interactions, that are exalted by the high nanoparticle magnetic moment and by the low mean distance among them.

The absolute difference between the ZFC and FC magnetization values taken at the minimum temperature is of the same order for the $A$, $B$ and $C$ samples, being this
related to the percentage of nanoparticles that have been oriented along the external magnetic field. This difference is two times larger in the D sample, indicating that in this case the percentage of oriented nanoparticles is greater than in the A, B and C samples. This appears in good agreement with the mean size of the nanoparticles observed by TEM and determined by XRD and BET complementary results. Moreover for the A, B and C samples a decrease of FC magnetization can be observed with lowering temperature in the thermal range within 325 K and 200 K, being also this behaviour very probably due to strong interparticle interactions. The interactions finally induce a collective magnetic ordered state, as suggested by the reaching of an about constant value of magnetisation below a certain temperature (<100K for A, B and C samples).\textsuperscript{30} The only sample that shows a different behaviour is once more the D one: in this case the FC curve shows firstly an

Figure 4.13 ZFC (empty circles) and FC (full circles) curves of the A (a), B (b), C (c) and D (d) samples
increase of FC magnetization with decreasing temperature. This fact can be probably ascribed to the lower strength of interparticle interactions due to the smaller mean size of the particles with respect to the ones in A, B and C samples. At lower temperatures (<40K) the FC magnetisation of D sample reaches a nearly constant value, following the same behaviour of the other samples.

Figure 4.14 shows the hysteresis loop of the A (4.14a), B (4.14b), C (4.14b) and D (4.14c) samples measured at T= 4.2K and T = 298 K respectively. Tables 4.3 and 4.4 report the $M_s$, $H_c$, $M_r$, and $M_r/M_s$ values obtained by these curves respectively at low (4.2 K) and high (298 K) temperature.

Figure 4.14 Hysteresis curves at 4.2K (empty circles) and at 298K (full circles) of the A (a), B (b), C (c) and D (d) samples

Both at 4.2K and 298 K the magnetization does not reach complete saturation but it is not too far from it for A, B and C samples. For the D sample the magnetization is instead less close to saturation even at H=5T. This behaviour is a direct consequence of the different nanoparticles mean size values and of the size distribution among the D sample and the A, B and C ones. The distance from
saturation is then due to the occurrence of a non-negligible fraction of small particles which are still relaxing at 5T.

For the A, B and C samples, both at 4.2K and 298 K, \( M_s \) is lower with respect to \( M_{bulk} \) (in the range 95.2 A m\(^2\) Kg\(^{-1}\) - 82.1 A m\(^2\) Kg\(^{-1}\))\(^{31}\), and this could be ascribed to the presence of small amounts of Co\(_2\)O\(_4\), as shown by XRD analysis. Moreover, some impurities as C and N were found to be contained in the samples by elemental analysis.

This fact could brings to a slight overestimation of the real amount of CoFe\(_2\)O\(_4\), lowering the effective value of \( M_s \) measured with respect to the total mass of magnetic phase. Considering that Co\(_2\)O\(_4\) and impurities are also contained in the D sample, the magnetization \( M_s \) value, well higher than that of the bulk either at 4.2

<table>
<thead>
<tr>
<th>Sample A (pH 7)</th>
<th>Sample B (pH 4)</th>
<th>Sample C (pH 2)</th>
<th>Sample D (pH &lt;1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_s ) (A m(^2) Kg(^{-1}))</td>
<td>74.8(2)</td>
<td>70.0(1)</td>
<td>76.3(3)</td>
</tr>
<tr>
<td>( H_c ) (T)</td>
<td>1.15 (1)</td>
<td>1.16(1)</td>
<td>1.16(1)</td>
</tr>
<tr>
<td>( M_r ) (A m(^2) Kg(^{-1}))</td>
<td>40.9 (1)</td>
<td>38 (2)</td>
<td>44.02 (1)</td>
</tr>
<tr>
<td>( M_r/M_s )</td>
<td>0.57</td>
<td>0.55</td>
<td>0.58</td>
</tr>
</tbody>
</table>

**Table 4.3** Values of Saturation Magnetization (\( M_s \)) Coercive field (\( H_c \)), remanent magnetization (\( M_r \)) and reduced remanent magnetization (\( M_r/M_s \)) at 4.2K. Uncertainties are given in parentheses as errors in the last digits

<table>
<thead>
<tr>
<th>Sample A (pH 7)</th>
<th>Sample B (pH 4)</th>
<th>Sample C (pH 2)</th>
<th>Sample D (pH &lt;1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_r ) (A m(^2) Kg(^{-1}))</td>
<td>65.9(2)</td>
<td>56.2(3)</td>
<td>67.4(1)</td>
</tr>
<tr>
<td>( H_c ) (T)</td>
<td>0.15(1)</td>
<td>0.15(1)</td>
<td>0.15(1)</td>
</tr>
<tr>
<td>( M_r ) (A m(^2) Kg(^{-1}))</td>
<td>25.8(2)</td>
<td>22.6 (3)</td>
<td>28.6 (1)</td>
</tr>
<tr>
<td>( M_r/M_s )</td>
<td>0.40</td>
<td>0.40</td>
<td>0.43</td>
</tr>
</tbody>
</table>

**Table 4.4** Values of Saturation Magnetization (\( M_r \)) Coercive field (\( H_c \)), remanent magnetization (\( M_r \)) and reduced remanent magnetization (\( M_r/M_s \)) at 298 K. Uncertainties are given in parentheses as errors in the last digits
K or at 298 K has to be explained differently. Some authors indicate that this behaviour can be ascribed to an off-stoichiometric composition\textsuperscript{32} or to the change in the inversion factor of CoFe\textsubscript{2}O\textsubscript{4}\textsuperscript{33}.

The $D$ sample shows, at low temperature, a $H_c$ value well higher than that of the other samples. This fact is probably caused by the reduced magnetic interparticle interactions strength due to the lower mean particle size.\textsuperscript{34} The $M_r/M_s$ values are of the same order for all the samples, indicating that the fraction of nanoparticles that contribute to the total magnetic moment even at zero field is similar for all the samples. As expected, the $M_r/M_s$ values are different when measured at $T=298K$, being in this case the fraction of the particles in superparamagnetic state quite larger than at low temperature. Furthermore, while for $A$, $B$, and $C$ samples the $M_r/M_s$ value, as already observed even at 4.2K, is of the same order at 298 K, this is not the case of $D$ sample. This different behaviour is explained considering the different nanoparticles mean size, that in $D$ sample is well lower than in the other samples. So, at 298 K the fraction of particles that are in superparamagnetic state is well higher than in $A$, $B$, and $C$ samples, and this fraction, when the external magnetic field is turned off, starts again to fast relax without contributing to the total magnetization. This has been confirmed by the difference between ZFC and FC magnetization values, as already shown, which is well higher than in the other ones. Due to the same reason, it is observed that at 298K the $H_c$ value, for the $D$ sample, is well lower than in the $A$, $B$, and $C$ samples: in fact the approach of the $D$ samples to an almost completely superparamagnetic behaviour determines the lowering also of the coercive field.

### 4.5.2 $^{57}$Fe Mössbauer spectroscopy: Data analysis

In order to complete the study of magnetic properties, Mössbauer spectra at 293 K were collected for all the samples. In particular, the Mössbauer characterization aimed at explaining the differences between the saturation magnetization values, $M_s$, deduced from the hysteresis loops. The starting hypothesis was to explain these differences in term of differences in inversion degree, as suggested by Jiang et al.\textsuperscript{33}

In spinel ferrite, Fe\textsuperscript{3+} ions have slightly different Mössbauer parameters according to their occurrence either in tetrahedral or in octahedral coordination.\textsuperscript{35} The superposition of the magnetic components due to iron ions located in $A$ and $B$ sites is higher in spectra of nanoparticles samples at high temperature due to relaxations effects;\textsuperscript{29} this superposition lead to some problems in the analysis of
Mössbauer data. In order to avoid these difficulties in the interpretation, a combined approach between Mössbauer spectra and magnetization measurement was adopted. Mössbauer spectra were interpreted in terms of the inversion degree obtained from magnetization values. The differences observed in this parameter were completely able to explain the different magnetic behaviour of the samples.

The inverse spinel ($\gamma=1$) has one Fe ion in the tetrahedral sites and one Fe and one Co ion in the octahedral sites. In the ferrimagnetic state the magnetic moments of the $A$ and $B$ sites are antiparallel; assuming the values of 3 $\mu_B$ for Co$^{2+}$ and 5 $\mu_B$ for Fe$^{3+}$ resulting from the electronic configuration, it is possible to calculate a magnetic moment per formula unit $m_{FU} = 3\mu_B$. The direct spinel ($\gamma=0$) has two Fe ions in the $B$ site and one Co ion in the $A$ site; therefore the moment is $m_{FU} = 7\mu_B$. The intermediate values of $m_{FU}$ correspond to partial inversion; from the value of the moment, the corresponding value of the inversion parameter may be calculated, using the relation

$$x = (1/4) \times [7 - (m_{FU}/\mu_B)]$$

(4.1)

It was supposed that in saturation condition the atomic moments of samples at 4.2 K were fully aligned; therefore the $m_{FU}$ value given in table 4.5, calculated starting from the saturation magnetization, is the true moment associated with one unit formula. By using the described procedure and equation (4.1), the inversion parameter ($\gamma$) of the four nanocrystalline samples was determined (table 4.5). The inversion parameter changes from sample $B$, which is a full inverse spinel, to sample $D$, which shows a strongly partial inversion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_S$ $(A m^2 Kg^{-1})$</th>
<th>$m_{UF}$ $(\mu_B)$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>74.8(2)</td>
<td>3.14</td>
<td>0.96</td>
</tr>
<tr>
<td>$B$</td>
<td>70.0(1)</td>
<td>2.94</td>
<td>1.01</td>
</tr>
<tr>
<td>$C$</td>
<td>76.3(3)</td>
<td>3.21</td>
<td>0.95</td>
</tr>
<tr>
<td>$D$</td>
<td>99.4(1)</td>
<td>4.18</td>
<td>0.71</td>
</tr>
<tr>
<td>bulk s.c.*</td>
<td>82.1</td>
<td>3.45</td>
<td>0.89</td>
</tr>
<tr>
<td>bulk q *</td>
<td>95.2</td>
<td>4.00</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Table 4.5 Saturation magnetization ($M_S$) at 4.2 K, magnetic moment per unit formula ($m_{FU}$) at 4.2 K and inversion parameter ($\gamma$) of the nanocrystalline samples ($A$-$D$). The magnetization data of two bulk samples s.c. (slow cooled) and q. (quenched) (marked with star) are taken from ref.31.
The spinel structure has one octahedral site with six nearest tetrahedral sites; the six \( A \) sites are occupied by six Fe ions in the full inverse spinel and by 6, 5, 4, or 3 Fe ions in the partially inverse. Therefore the Mössbauer spectrum of the fully inverse spinel has only two components corresponding to iron in \( A \) site and \( B \) site. Conversely, if the inversion is partial, the hyperfine magnetic field at the \( B \) site of the Fe\(^{3+}\) ion depends on the occupation of the six nearest \( A \) sites by iron and cobalt.\(^{31,36}\) Therefore, up to four components associated with the \( B \) site have been found in the spectrum of partially inverse bulk CoFe\(_2\)O\(_4\); the relative intensity of a \( B \) site component can be determined on statistical grounds by the relation\(^{31}\)

\[
I(n) = \frac{6!}{[n!(6-n)!]} \left(1 - x\right)^{6-n} x^n
\]  

(4.2)

where \( n \) is the number of iron ions in the nearest neighbor \( A \) sites. In the following the components with intensity \( I(n) \) associated with the octahedral sites will be named \( Bn \). The intensity of tetrahedral components, relative to the octahedral components, have to be corrected for the different recoil free fraction associated with the \( A \) and \( B \) sites \((f_A, f_B)\) measured in various ferrites, which gives a ratio \( f_B/f_A = 0.94 \) at room temperature\(^{31}\).

4.5.2\(^{57}\)Fe Mössbauer spectroscopy: Results

Figures 4.15a, 4.15b, 4.15c and 4.15d show respectively the spectra of samples \( A, B, C \) and \( D \).

\textbf{Figure 4.15} Mössbauer spectra (empty circles) and simulated spectra (line) of the samples \( A \) (a), \( B \) (b), \( C \) (c) and \( D \) (d) at 293 K.
The sample B spectrum shows a six-peaks structure, associated with a magnetically ordered blocked fraction of the sample, along with a two-peaks structure associated with a superparamagnetic fraction.\textsuperscript{37} The spectrum was fitted using two sextets for the blocked fraction (one for the tetrahedral site and one, named B6 because \(n=6\), for the octahedral site) and one doublet for the superparamagnetic fraction.

<table>
<thead>
<tr>
<th>Spectral Componen.</th>
<th>(\delta) (mm/s)</th>
<th>(B_{hf}) (T)</th>
<th>Sample A Area (%)</th>
<th>Sample B Area (%)</th>
<th>Sample C Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>0.26</td>
<td>48.9</td>
<td>49.6</td>
<td>51.6</td>
<td>49.1</td>
</tr>
<tr>
<td>(B6\ (n=6))</td>
<td>0.35</td>
<td>50.9</td>
<td>40.3</td>
<td>48.4</td>
<td>38.7</td>
</tr>
<tr>
<td>(B5\ (n=5))</td>
<td>0.31</td>
<td>50.1</td>
<td>10.1</td>
<td>0</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Table 4.6 Mössbauer parameters as obtained by fitting the spectra at 293 K of the samples \(A\), \(B\) and \(C\). The values of isomer shift (\(\delta\)), internal magnetic field (\(B_{hf}\)) and relative intensity of the components (Area) are reported.

The relative area of the sextets was fixed to the values calculated from the inversion parameter \(\gamma\) using equation (4.1) and given in table 4.5; the results of the fit are given in table 4.6 for the blocked fraction and in table 4.7 for the superparamagnetic fraction.

The isomer shift (\(\delta\)) and the quadrupole splitting (\(\epsilon\)) of the doublet are typical of superparamagnetic CoFe\(_2\)O\(_4\) at 293 K;\textsuperscript{38} this fraction corresponds to 3\% of the sample. The small amount of the superparamagnetic fraction at room temperature justifies the premise that at 4.2 K the sample is fully blocked and the atomic moments are fully aligned; in the following it will be seen that this is true also for the other three samples. The values of hyperfine magnetic field (\(B_{hf}\)) and isomer shift of the sextets \(A\) and \(B6\) are similar to those found in bulk CoFe\(_2\)O\(_4\);\textsuperscript{31} it points out that the average size of the nanoparticles is larger than the

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\delta) (mm/s)</th>
<th>(\epsilon) (mm/s)</th>
<th>Area sp %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>0.32</td>
<td>0.77</td>
<td>9</td>
</tr>
<tr>
<td>(B)</td>
<td>0.30</td>
<td>0.58</td>
<td>3</td>
</tr>
<tr>
<td>(C)</td>
<td>0.30</td>
<td>0.65</td>
<td>3</td>
</tr>
<tr>
<td>(D)</td>
<td>0.28</td>
<td>0.60</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4.7 Mössbauer parameters of superparamagnetic fraction as obtained by fitting the spectra at 293 K. The values of isomer shift (\(\delta\)), quadrupole splitting (\(\epsilon\)) and relative area of the superparamagnetic fraction (Area\(_{sp}\)) are reported.
critical dimension which causes a reduction of the $B_{hf}$ with respect to the bulk. In addition it should be remarked that the $\delta$ due to Fe$^{3+}$ in tetrahedral sites ($A$ component) is lower than the isomer shift due to the iron ions in octahedral sites. Also this result is in good agreement with previous Mössbauer studies on spinel ferrites.\textsuperscript{35,39}

Figures 4.14a and 4.14c show the spectra of the nearly inverse spinels (samples $A$ and $C$), which have $\gamma = 0.96$ and 0.95 respectively; equation 4.2 gives two octahedral components (named $B6$ and $B5$), neglecting the components with intensity less than 2%. The fits were performed by fixing the $B_{hf}$ and the $\delta$ of the components $A$ and $B6$ to the values found in the fully inverse spinel (sample $B$); this is reasonable because the average particle size is similar in the three samples and therefore a variation of the hyperfine magnetic field, due to the size of the nanoparticles, is not expected. The intensities calculated by equation (4.2), given in table 4.6, were also fixed in the fits. Table 4.6 also gives the $B_{hf}$ and the $\delta$ of the component $B5$ obtained by the fit, which are similar to those reported in literature for the bulk.\textsuperscript{31} At room temperature the superparamagnetic fraction amounts to 9% and 3% in the samples $A$ and $C$ respectively. The spectrum of the partially inverse spinel (sample $D$) is shown in figure 4.14d; the inversion parameter is $\gamma = 0.71$ and there are four octahedral components with non-negligible intensities, given in table 4.8. In this sample the different average particle size does not permit fixing $B_{hf}$ and $\delta$ values of the components $A$, $B6$ and $B5$ to those measured in the other samples. In the fit we fixed the ratio of the magnetic fields of the components as determined in the bulk;\textsuperscript{31} the ratio of the isomer shifts was fixed also. The results of the fit are given in table 4.8; the values of hyperfine magnetic field are smaller than in the other samples because of the reduction of the field in nanocrystalline materials, which confirms that sample $D$ has the smallest average particle size. The fit reproduces well the experimental data, except for a deviation due to the asymmetry of the peaks, which is caused by the distribution of $B_{hf}$'s typical of nanocrystalline samples; a small asymmetry of

<table>
<thead>
<tr>
<th>Spectral Comp.</th>
<th>$\delta$ (mm/s)</th>
<th>$B_{hf}$ (T)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>0.26</td>
<td>48.5</td>
<td>36.9</td>
</tr>
<tr>
<td>$B6$ ($n=6$)</td>
<td>0.34</td>
<td>50.5</td>
<td>8.6</td>
</tr>
<tr>
<td>$B5$ ($n=5$)</td>
<td>0.31</td>
<td>49.7</td>
<td>21.1</td>
</tr>
<tr>
<td>$B4$ ($n=4$)</td>
<td>0.35</td>
<td>47.0</td>
<td>21.6</td>
</tr>
<tr>
<td>$B3$ ($n=3$)</td>
<td>0.38</td>
<td>44.1</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Table 4.8 Mössbauer parameters as obtained by fitting the spectra at 293 K of sample $D$. The values of isomer shift ($\delta$), internal magnetic field ($B_{hf}$) and relative intensity of the components (Area) are reported.
the peaks is also visible in the other samples, due to the smallest blocked nanoparticles of each sample. The superparamagnetic fraction amounts to 2%.

The simulations performed by fixing the relative intensity of the components to the value calculated from the inversion parameter obtained by eq. (4.1) reproduce satisfactorily the experimental Mössbauer spectra. This demonstrates that the inversion parameter can be calculated from the saturation magnetization and strongly supports the starting hypothesis, that the differences in the saturation magnetization are due mainly to the different degree of inversion of the samples. This is rather believable, since the A, B and C samples differ from the D one both in the particle size and in thermal history, that is just in the factors usually indicated as responsible of the inversion degree attained by the ferritic spinels. It is likely that the different formation mechanism of the samples has given rise to a different growth of the particles and, in addition, has carried the reagents through a different thermal path, as regards both the maximum temperature and the cooling rate. Greater uncertainty exists concerning the absolute values of the inversion degree. In fact, the numbers reported in table 4.5 are among the highest reported in literature.\textsuperscript{40,41} This does not seem to be dependent on the method used for the calculation. In fact, the procedure adopted in the present work has been tested using the magnetization data of two bulk samples (s.c.-slow cooled, q.-quenched) reported by Sawatzky et al.;\textsuperscript{31} Table 4.5 gives the values of $\gamma$ calculated from eq. 4.1. These values have to be compared with those, determined by the same authors by a fitting of Mössbauer spectra taken with an applied magnetic field in order to separate the spectral contributions due to iron ions in tetrahedral and octahedral coordination (0.93 and 0.76 respectively). It is evident that the two methods provide results in almost complete agreement. Another possible reason for the differences with respect to literature information can be looked for in the uncertainty about the $M_s$ values to be introduced in equation 4.1. In fact, as mentioned in the introduction, some impurities are present in the samples. In particular, X-ray Diffraction patterns reveal the presence in the powders of a small percentage of Co$_3$O$_4$, whose contribution to the magnetization is negligible. Therefore, we tried to evaluate such a percentage by the use of the Rietveld analysis of diffractometric data. Then, the $M_s$ values to be used in equation 4.1 were corrected by attributing the observed magnetizations to the amounts of ferritic phase really present, and the inversion degrees were recalculated. These values were used as input for new simulations of the Mössbauer spectra. In all cases the best fits remained those obtained in the first calculations, when the
occurrence of Co$_3$O$_4$ was not taken into account. In particular, in the case of sample $B$, lowering the inversion degree under the value of 1%, resulted in an immediate worsening of the fit. This result can seem unexpected, but it cannot be considered a conclusive proof of the better quality of the first simulations. Perhaps it can be a consequence of the difficulty of comparing the quality of the fits that have been performed by using a different number of contributions. In fact, when lower inversion degrees are used, according to equation 4.2 it is necessary to introduce an increasing number of sextets and the convergence of the fits can be hampered. Since the Rietveld method meets with some difficulties in the determination of the abundance of a phase present in strong minority, these new calculations had the main aim of fixing the uncertainty to be ascribed to the $\gamma$ values, that turned out about 5%.

In spite of these uncertainties, the new calculations do not invalidate the conclusion that the differences between $A$, $B$ and $C$ samples and the $D$ one depend on the different inversion degree. In fact, also taking into account the presence of Co$_3$O$_4$, the $\gamma$ values of the first three samples differ from that of the fourth one more than the experimental uncertainty. Likewise, there is a confirmation that the inversion degrees of samples investigated are set among the highest values reported in literature.

4.6 Discussion and conclusions

All the four preparations give rise to the formation of nanosized cobalt ferrite, CoFe$_2$O$_4$, only slightly contaminated by Co$_3$O$_4$ phase. The samples $A$, $B$, and $C$ are quite similar as regards the size of the nanoparticles and their morphology; these properties are significantly different in the sample $D$, for which TG and DTA observations also point to a different formation mechanism. It can be affirmed that, as long as the nanoparticles are produced through an autocombustion reaction, essentially the same products are obtained. The IR investigation show that the precursor gels are similar for the samples $A$, $B$ and $C$, and quite different for the sample $D$.

The obtained results seem at variance with those presented by Yue et al., according to which the change of pH value of mixed precursor solutions from 2 to 7 greatly affects the size of the nanoparticles formed in the autocombustion reaction. It can be observed, however, that Yue et al. have synthesized a different ferrite (NiCuZn ferrite) and that their systems behave differently from those here presented in many aspects (i.e: XRD patterns of the gel precursors and TG-DTA
traces). Furthermore, some parameters of the procedure, like the ignition temperature, have been differently fixed in the present and Yue et al. works and also these parameters are known to be important for the characteristic of the products. Therefore, it is highly probable that both results are correct.

In any case, as regards the present study, differences between $A$, $B$, $C$ samples and the $D$ one are observed also in the magnetic measurements. All the four samples are superparamagnetic with high blocking temperature, but both ZFC-FC and hysteresis cycles show the differences that are expected when different particles sizes and interactions are accounted for. Mössbauer analysis indicate that the differences in the value of $M$, can be explained in terms of different inversion degree.
REFERENCES

CHAPTER 5
Synthesis and characterization of CoFe$_2$O$_4$/SiO$_2$
prepared by a new sol gel autocombustion method

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5.3 Precursor characterization 86
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5.1 Introduction

Magnetic nanoparticles tend to agglomerate, not only because of their large surface energy, but also due to strong magnetic interactions. Consequently, both in basic and applied investigations, magnetic properties are more profitably studied by preparing the samples in form of nanocomposites, that is by diluting the magnetic particles in inert matrices (frequently amorphous SiO₂, but also polymers and resins). Moving along this line, the sol-gel auto-combustion method used for synthesized CoFe₂O₄ was combined with traditional sol-gel method in order to prepare cobalt ferrite-silica nanocomposites in a wide range of composition.

5.1.1 Traditional sol-gel technique

Sol-gel method was first discovered in 1846 by M. Ebelmen who observed that under the influence of atmospheric humidity a silicon alkoxide changed from a clear liquid into a transparent solid which, on heating, formed silicon dioxide. In these processes a molecular solution is converted by chemical reactions into a sol, which reacts further to form a gel; this, in turn, on firing gives rise to a polymeric inorganic solid.

Typically, metal alkoxides of general formula Mⁿ(OR)ₙ are added to water in presence of an organic solvent, usually an alcohol, which is necessary in order to reach miscibility in the starting reaction solution. In fact, when the quantity of water is great, solvents or mixture of solvents are necessary to prevent liquid-liquid phase separation of alkoxide and water. M can be a metal, but also an other element like silicon, phosphorus or boron. In the case of preparation of silica networks the alkoxides used more frequently are tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS).

The fundamental reactions that take place during sol-gel process are shown in the following scheme:

\[
M(OR)₄ + H₂O \quad \xleftrightarrow{\text{Reesterification}} \quad M(OH)(OR)₃ + ROH
\]

\[
\text{Hydrolysis}
\]
Generally speaking, the hydrolysis reaction, through the addition of water, replaces alkoxide groups (OR) with hydroxyl groups (OH). Under normal conditions, the hydrolysis reaction is very slow. It is more rapid and complete when acids or bases are employed as catalysts. In both cases, however, the reaction mechanism responsible of the hydrolysis of the alkoxy groups results in the formation of a penta-coordinate transition state with a significant SN2-type character. Normally, base-catalyzed hydrolysis proceeds much more slowly than acid-catalyzed hydrolysis, under the same catalyst concentration. Subsequent condensation reactions involving M-OH groups produce M-O-M bonds, plus water or alcohol as by-products. In this way, dimeric, oligomeric and polymeric species form, depending on the rate of hydrolysis and of condensation. Under most conditions, condensation begins before hydrolysis is complete.

However, several other factors affecting the rate of hydrolysis and condensation reactions, such as pH, temperature and time of reaction, nature and concentration of reagents, H₂O/M molar ratio, nature and amount of solvent, temperature of gelation have to be considered. By controlling these factors, it is possible to vary the structure and properties of the sol-gel derived inorganic network.² Among the factors listed above, pH, nature and concentration of catalyst, H₂O/Si ratio and temperature have been identified as the most important in determining the characteristics of the final inorganic network.

5.2 Synthesis

Five (CoFe₂O₄)ₓ(SiO₂)₁₋ₓ nanocomposites, with x = 50, 30, 15, 10, 5, were synthesized with a procedure in which a traditional sol-gel technique is combined
with the sol-gel autocombustion. The general synthesis procedure set up in order to prepare CoFe₂O₄ powder is schematised in form of a flow diagram in figure 5.1.

Tetraethoxysilane (TEOS, Aldrich 98%) was used as precursor for SiO₂, whereas metal nitrates (Fe(NO₃)₃·9H₂O, Aldrich 98% and Co(NO₃)₂·6H₂O, Aldrich 98%) and citric acid were used as precursors for the CoFe₂O₄ nanoparticles. The iron and cobalt nitrates in 2:1 molar ratio were dissolved in water and Citric acid (CA, Aldrich, 99.9%) was added to the solution with 1:1 molar ratio of metals (Co²⁺ + Fe³⁺) to CA. The corresponding citrate to nitrate ratio resulted 0.37 for all the gels. The resulting clear purple solution had a spontaneous pH value <1. Liquor ammonia (Carlo Erba, 25%) was added dropwise to the aqueous solution in order to adjust the pH value to 2. A suitable amount of TEOS in ethanol was then added to the aqueous solution and few drops of ammonia were also added in order to bring back the pH to the value of 2. In all the cases the mixtures resulted clear and did not exhibit phase separation. After vigorous stirring for 30 minutes, the sols were poured into Teflon beakers and let to gel in static air at 40°C in an oven for 24 hours. Thermogravimetric analysis of the gels, described below, showed that the
decomposition of the precursors is completed at temperatures between 200 and 230°C. On this basis, the gels were submitted to thermal treatment at 300°C in a preheated oven. The gels started to eliminate large amounts of gases and burnt through a self-propagating process producing directly CoFe₂O₄/SiO₂ nanocomposites (as burnt samples). The process was complete after about 1-2 minutes leaving a collapsed branched-shape material.

The pH and preparation conditions reported in table 5.1 were selected as the best after a long series of experiments, by which the effect of several parameters was explored. In fact the preparation of composites meets with major difficulties if compared with the pure phases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TEOS (mol)</th>
<th>Et(OH) (mol)</th>
<th>H₂O (mol)</th>
<th>CA (mol)</th>
<th>Co(NO₃)₂ (mol)</th>
<th>Fe(NO₃)₃ (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe₂O₄/SiO₂</td>
<td>0.0130</td>
<td>0.76</td>
<td>1.29</td>
<td>0.0100</td>
<td>0.00340</td>
<td>0.00680</td>
</tr>
<tr>
<td>50% wt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoFe₂O₄/SiO₂</td>
<td>0.0304</td>
<td>0.76</td>
<td>1.29</td>
<td>0.0100</td>
<td>0.00340</td>
<td>0.00680</td>
</tr>
<tr>
<td>30% wt</td>
<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CoFe₂O₄/SiO₂</td>
<td>0.0746</td>
<td>1.18</td>
<td>1.29</td>
<td>0.0100</td>
<td>0.00340</td>
<td>0.00680</td>
</tr>
<tr>
<td>15% wt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoFe₂O₄/SiO₂</td>
<td>0.0304</td>
<td>0.76</td>
<td>1.29</td>
<td>0.00262</td>
<td>0.000881</td>
<td>0.00179</td>
</tr>
<tr>
<td>10% wt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoFe₂O₄/SiO₂</td>
<td>0.0304</td>
<td>0.76</td>
<td>1.29</td>
<td>0.00125</td>
<td>0.000417</td>
<td>0.000836</td>
</tr>
<tr>
<td>5% wt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.1** Preparation conditions of the starting sol

In order to obtain composites in which the active phase is well dispersed on the silica matrix, the gelation time of the silica precursor should be similar to the one of the metal citrate complex. At the pH conditions usually reported in the literature for the pure ferrite preparation (pH=7), TEOS hardly polymerises and is mostly eliminated during the self-combustion reaction leading to pure metal oxides. Nanocomposites with high load of active phase were successfully obtained at pH=4 and at gelation temperature of 40°C. The pH value of 2 and a gelation temperature of 40°C was found to be the best compromise in order to prepare homogeneous sols in a more extended range of compositions. In such conditions it was possible to obtain the desired nanocomposites, with good nanoparticles dispersion and size distribution.

The addition of ethanol as mutual solvent can lead to a phase separation due to the decreased solubility of the metal citrate complexes, therefore the amount of ethanol is a critical parameter. Then, in order to have homogeneous sols, when the
amount of TEOS is increased, it was necessary to increase the amount of ethanol going from \textit{N50} to \textit{N15}. However, the further increase of TEOS and ethanol for the diluted (\textit{N10} and \textit{N5}) samples would lead to great differences of the sol Surface/Volume ratio and therefore to different gelation time.\footnote{For this reason, in the diluted samples the amount of salts was decreased instead of increasing TEOS and ethanol amounts.}

The composition as well as the iron-to-cobalt ratio in all the composites were checked by Inductively Coupled Plasma analysis and the results confirmed the nominal composition and the iron to cobalt molar ratio of 2 within the experimental error (about 2\%). In the following, the (CoFe$_2$O$_4$)$_x$ (SiO$_2$)$_{1-x}$ as burnt samples, with $x= 50, 30, 15, 10, 5$, will be indicated by \textit{N50}, \textit{N30}, \textit{N15}, \textit{N10} and \textit{N5} acronyms respectively.

5.3 Precursor characterization

5.3.1 Thermal analysis

Figures 5.2(a, b) show the TG and DTA profiles of the \textit{N50}, \textit{N30}, \textit{N15} and \textit{N10}, \textit{N5} dried gels. All the gels show a weight loss from 7 to 17\% in the 50-190°C temperature range, related to the elimination of ethanol and water, and a drastic weight loss at 200-230°C, accompanied by an exothermic asymmetric peak in the DTA curves due to a self-combustion mechanism.\footnote{The total weight losses are due, besides the metal salts amounts, to the different amount of ethanol, water and citric acid entrapped inside the gel and even to the different quantity of ammonia used to adjust the pH. The weight loss at about 200°C is mainly affected by the metals content. It decreases by decreasing the metal content from a value of about 60-80\% in \textit{N15}, \textit{N30}, \textit{N50} down to 10-20\% in the \textit{N5} and \textit{N10} ones, while the sharp asymmetric exothermic peak centered at about 202-203 °C shifts to 223- 230°C, becomes broader and its intensity considerably decreases. This effect is due to the high content of silica that hampers the self-propagating combustion process. No other important}
transformation can be evidenced in the TG_DTA curves at temperature higher than 230°C, indicating that at this temperature the precursors are completely decomposed.

5.3.2 FT-IR spectroscopy

The Mid-IR spectra of the N5, N15, and N50 gels are reported in figure 5.3. Some important information are contained in the range 1300-1950 cm\(^{-1}\) region, in which the signals of the vibrational modes of the carboxyl groups are observable.

A small broad band at 1722 cm\(^{-1}\) is visible in the spectra of the gel precursors. Its incomplete disappearance indicates that a small amount of free citric acid is still present in the precursor gels.\(^{13}\) In addition to these, also four signals are present at about 1620 cm\(^{-1}\), 1560 cm\(^{-1}\), 1400 cm\(^{-1}\) and 1384 cm\(^{-1}\). The band at about 1620 cm\(^{-1}\) together with the shoulder at about 1560 cm\(^{-1}\) can be assigned to the asymmetric stretching O-C-O (\(\nu_{\text{asymm.}}\)) of the carboxylate anion, although at about 1630 cm\(^{-1}\) the bending of water intramolecular hydrogen can contribute;\(^{14}\) the intense signal at 1400 cm\(^{-1}\) is due to symmetric stretching of O-C-O group and to N-H stretching of NH\(_4^+\) ions. The large bands at around 1600 cm\(^{-1}\) and 1400 cm\(^{-1}\) are typical of a three dimensional structure of metal ammonium carboxylate gel,\(^{15}\) confirming the formation of metal complexes in all the samples. The very sharp band at 1384 cm\(^{-1}\) is attributable to the stretching vibration of NO\(_3^-\) ions; another sharp band is clearly visible at 830 cm\(^{-1}\) attributable to NO\(_3^-\) ions. The existence of these two signals indicates that the NO\(_3^-\) exists as a free group in the structure of the citrate gel and provides an in situ oxidizing environment for the decomposition of the citrate component.\(^{16}\)

The typical bands of silica gel (highlighted with arrows in figure 5.3) at about 1200 cm\(^{-1}\), 1080 cm\(^{-1}\), 960 cm\(^{-1}\), and 460 cm\(^{-1}\) are also present and their intensity
increases by decreasing the metal content, confirming the expected formation of silica network in higher amount in the diluted systems.\textsuperscript{12} These observations undoubtedly indicate that the precursor gels are formed by a silica network embedded by metal ammonium carboxylate complexes.

5.4 Structural characterization

In prevision of magnetic characterization the structure and morphology of the as burnt and 900 C° treated samples were careful investigated. Also the evolution of structural properties with the thermal treatment was followed, and here some results will be summarized.

5.4.1 As burnt nanocomposites

The XRD results for all the samples are reported in figure 5.4. In the case of diluted samples ($N15$, $N10$ and $N5$) only the amorphous pattern of the silica matrix is visible. With the increase of CoFe$_2$O$_4$ content, three broadened peaks appear ($N30$), then new and sharper reflexes with increased intensity emerge ($N50$) indicating the presence of a nanocrystalline phase.

The whole pattern can be ascribed to the CoFe$_2$O$_4$ spinel phase (PDF 22-1086) and no shift in the d-spacings was observed compared with theoretical card, confirming the formation of a stoichiometric cobalt ferrite. TEM observations show the presence of nanocrystalline particles dispersed over the silica matrix in all the samples. As an example, dark field micrographs of $N50$, $N15$ and $N5$ samples are reported in figure 5.5 (a,b,c).

The amount of visible particles increases with the CoFe$_2$O$_4$ content and their size
increases from an average of about 2 nm ($N5$) up to an average of about 8 nm ($N50$) and their size distribution becomes larger and larger. The small size and the low number of particles in the diluted samples justify the XRD results. Nanoparticles have rounded but irregular shape in the high CoFe$_2$O$_4$ content samples ($N50$, $N30$) and have spherical shape in the diluted ones ($N15$, $N10$, $N5$).

Figure 5.6 shows $N_2$ adsorption/desorption curves at 77K. Going from the diluted samples ($N5$ and $N10$) to the most concentrated ones a change of the textural features can be noticed. In fact, $N5$ and $N10$ show a type I isotherm with no hysteresis, indicating the presence of a totally microporous texture, as expected for silica gels prepared under acidic conditions. The $N15$ sample shows a type I-type IV composite isotherm, that could be due either to the presence of very narrow mesopores or to a bimodal distribution having one maximum in the micropore and another one in the mesopore range. Finally, the adsorption isotherms of the $N30$ and $N50$ samples are of type IV and present hysteresis loops of type H1 indicating that the structure is mainly mesoporous.

The surface area values, reported in table 5.2 together with the average pore size, increase from the $N50$ sample to the $N15$ one as consequence of the increasing porous silica content and then decrease as consequence of the reduced amount of $CA$ in the diluted gel precursors. These results are in agreement with literature data.

Figure 5.6 Nitrogen physisorption isotherms recorded at 77K of the as burnt samples

Figure 5.5 TEM Dark Field negative images of $N50$ (a), $N15$ (b) and $N5$ (c) as burnt samples
for silica samples prepared using citric acid.\textsuperscript{12} As an example in figure 5.7a and 5.7b the pore distribution for the sample N50 and N30 are reported respectively. In any case, the surface area values reported for these composites are quite high on respect to the results reported in literature for xerogel samples, while are similar to those observed for aerogel samples. This result can be explained by the formation mechanism of the texture; in fact, a self-combustion process induces an instantaneous loss of solvents similarly to the extraction in supercritical condition, leading to a preservation of the starting gel structure.

### Table 5.2 Textural Properties of the as burnt samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SA}^a ) (m(^2)/g)</th>
<th>Average Pore Size Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N50</td>
<td>221\textsuperscript{b}</td>
<td>40</td>
</tr>
<tr>
<td>N30</td>
<td>530\textsuperscript{b}</td>
<td>40</td>
</tr>
<tr>
<td>N15</td>
<td>823\textsuperscript{c}</td>
<td>6</td>
</tr>
<tr>
<td>N10</td>
<td>676\textsuperscript{c}</td>
<td>6</td>
</tr>
<tr>
<td>N5</td>
<td>495\textsuperscript{c}</td>
<td>6</td>
</tr>
</tbody>
</table>

\( ^a \) error 3% \( ^b \) BET surface area. \( ^c \) Dubinin surface area.

5.4.2 Evolution of structural properties with the thermal treatment

The temperature was raised up between 300°C and 900°C with steps of 100°C and the samples were kept for one hour at each temperature. In the following the samples treated at \( T \) °C will be indicated with the acronyms \( \text{NX}_T \) (\( X=50, 30, 15; T= 300, 400, ...900 \))

Figure 5.8 (a), (b), (c), (d), e show respectively the XRD patterns of N5, N10, N15, N30 and N50 at different temperatures. The progressive heating leads to the appearance of faint CoFe\(_2\)O\(_4\) X-ray diffraction peaks in the diluted samples (N5, N10, N15), while peaks intensity of the nanocrystalline phase increases and their broadening slightly decreases in the case of the high CoFe\(_2\)O\(_4\) content samples.
The amorphous background undergoes some modifications, indicating the structural rearrangement of the silica network. In fact, the silica halo at about $2\theta =11^\circ$ (as burnt sample) shifts towards lower $2\theta$ values ($9.5^\circ$) at 900°C.

In figure 5.9 $N_2$ adsorption/desorption curves at 77K for $N15$ sample treated at different temperature are reported.

**Figure 5.8** XRD patterns of the samples $N5$ (a), $N10$ (b), $N15$ (c), $N30$ (d) and $N50$ (e) at different thermal treatment temperature

In figure 5.9 $N_2$ adsorption/desorption curves at 77K for $N15$ sample treated at different temperature are reported.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_A$ $^a$ ($m^2/g$)</th>
<th>Average Pore Size Diameter $^b$ ($Å$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N15_{ab}$</td>
<td>823$^c$</td>
<td>6</td>
</tr>
<tr>
<td>$N15_{500}$</td>
<td>670$^c$</td>
<td>6</td>
</tr>
<tr>
<td>$N15_{700}$</td>
<td>678$^c$</td>
<td>6</td>
</tr>
<tr>
<td>$N15_{800}$</td>
<td>30$^c$</td>
<td>9</td>
</tr>
</tbody>
</table>

$^a$ error 3%  $^b$ BET surface area  $^c$ Dubinin surface area.

**Figure 5.9** Nitrogen physisorption isotherms recorded at 77K of the $N15$ sample treated at different temperature
The nitrogen adsorption-desorption isotherms of the sample calcined at different temperature indicate high surface area values up to 700°C; over this temperature a collapse of the structure is observed. In table 5.3 the results obtained for \( \text{N15} \) sample at various calcination temperatures are summarized. The highest surface area value is observed for the as burnt sample (823 m\(^2\)/g), although very high values are obtained also for the samples treated at 500°C and 700°C (670-680 m\(^2\)/g), while a collapse of the porous structure is observed for the sample heated at 900°C (30 m\(^2\)/g). Similar behaviour was displayed by the other samples.

5.4.3 Nanocomposites treated at 900°C

The XRD patterns of the samples treated at 900°C are reported in figure 5.8. The reflexes of the nanocrystalline phase increase in intensity with \( \text{CoFe}_2\text{O}_4 \) content and becomes sharper and sharper as a consequence of the increase of particle size. A determination of particles size from XRD measurement is difficult, particularly in the dilute samples, due to the presence of silica matrix.

TEM observations of the samples treated at 900°C (figure 5.10- left side) indicate the crystalline nature of the nanoparticles distributed over the silica support. Heating the samples leads to a progressive growth of the particles and to their structural ordering. Therefore, an higher number of particles can be evidenced in these images on respect to the as burnt samples. The HRTEM images (figure 5.10 – right side) confirm the irregular morphology of the particles for the samples with the highest concentration and spherical morphology of the nanocrystals for the diluted ones. Moreover, a great number of particles

\[ \text{Figure 5.10 TEM images (left side) of N50_{900} (a), N15_{900} (b) and N5_{900} (c) samples and HRTEM (right side) images of N50_{900} (a), N15_{900} (b)} \]
are in close contact in the $N_{50900}$ sample, while in the diluted samples the matrix avoid the aggregation. The set of fringes observed for the samples $N_{50900}$ and $N_{15900}$ correspond to the [3 1 1] lattice planes of cobalt ferrite phase.

Particle size distribution is represented with histograms and average particle size calculated with a log normal distribution.$^{19}$ The particle size distributions (figure 5.11) point out an increase of the average particle diameter from about 3 nm ($N_{5900}$) to 30 nm ($N_{50900}$) and a gradual broadening of the particle size distribution.

![Figure 5.11 TEM particle size distribution of the samples $N_{5900}$ (a), $N_{10900}$ (b), $N_{15900}$ (c), $N_{30900}$ (d) and $N_{50900}$](image)

#### 5.5 Conclusions

The preparation route reported here, that combines a traditional sol-gel technique (hydrolysis and condensation of alkoxide precursors) and the nitrate-citrate sol-gel auto-combustion, has been successful in providing nanoparticles of a unique CoFe$_2$O$_4$ spinel phase well spread in the silica amorphous matrix within a wide range of composition (from 5 to 50 wt%$^{20,21}$). In recent years other authors have attempted to prepare ferrites dispersed in silica matrices through a similar sol
gel auto-combustion synthesis; XRD, IR and NMR techniques indicated the difficulties found in the silica polymerization process and, as a consequence, in the ferrite dispersion in order to prepare homogeneous composites. Through a careful control of several preparation parameters (pH, amount of ethanol, gelation temperature, thermal treatments) the synthesis here proposed has allowed a clear improvement of the nanocomposites properties as regards active phase dispersion, particle shape and size and particle size distribution.

At all the investigated compositions thermal analysis has evidenced that the samples form through self-combustion mechanism. As consequence of the fast combustion process, the samples exhibit high surface area. The silica gel network, filled with amorphous cobalt iron ammonium citrate, do not shrink during the self-propagating combustion process, while condensation of silanols is not inhibited. Thus, a highly open structure is easily achieved in the whole range of composition; it is comparable to that obtained through a more complicate supercritical drying and is beneficial for the dispersion of the magnetic phase. This increases the interest for such materials, since they combine individual properties of the constituent phases, giving rise to new multifunctional materials. The silica open network allows fast diffusion of reactants and products and the large nanophase dispersion might provide a large number of active sites for catalytic applications.

The formation of the carboxylate-metal complexes during the gelation stage, which has been demonstrated by IR measurements, has been of great help in the regulation of nanoparticles properties. Interesting results have also been obtained monitoring the structural properties evolution of the samples as a function of the thermal treatment. A certain number of particles form through the self-combustion process (as burnt samples), then the thermal treatment gives rise to a progressive growth and structural ordering. As a consequence, a greater and greater number of nanocrystallites of CoFe₂O₄ is observed in TEM micrographs, CoFe₂O₄ reflections become increasingly evident in the XRD patterns, and the morphology becomes more regular as well the dispersion and particle size distribution.
REFERENCES


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CHAPTER 6
Magnetic Properties of CoFe₂O₄ nanoparticles dispersed in a silica matrix

6.1 Introduction

6.2 Magnetic properties of nanocomposites treated at 900 °C

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   6.3.1 Mössbauer investigation
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6.4 Magnetic properties of as burnt nanocomposites

6.5 Superparamagnetism and magnetic ordering phenomena
   6.5.1 Experimental results
   6.5.2 Discrimination between superparamagnetism and ordering phenomena
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References
6.1 Introduction

A systematic magnetic characterization of the nanocomposites in function of the silica content and of the thermal treatment was performed. In subsection 6.2 some of the results about the magnetic behaviour of all the nanocomposites treated at 900 °C are summarized. However for scope of brevity, the following of the chapter will report only the results obtained on the more concentrate nanocomposites.

In fact the nanocomposites $N15_{900}$, $N30_{900}$ and $N50_{900}$, will be used as model system in order to deepen the relation between crystalline structure (inversion degree) and magnetic properties and to give a contribution to the discussion about the real nature of spin canting phenomenon.

On the other hand the as burnt nanocomposites with high content of magnetic phase will be used in order to study the properties of strong interacting nanoparticles.

6.2 Magnetic properties of nanocomposites treated at 900°C

Figure 6.1 (a), (b), (c), (d) and (e) show magnetization measurements carried out with the ZFC FC protocol for the samples $N5_{900}$, $N10_{900}$, $N15_{900}$, $N30_{900}$ and $N50_{900}$ respectively.

![Graphs of magnetization measurements](image)

**Figure 6.1** ZFC (empty circles) and FC (full circles) DC magnetization for the $N5_{900}$ (a), $N10_{900}$ (b), $N15_{900}$ (c), $N30_{900}$ (d) and $N50_{900}$ (e)

The measurements show for all the samples an irreversible magnetic behaviour below a given temperature ($T_{irr}$), that is related to the blocking of the biggest
particles. All the ZFC curves exhibit a maximum and the corresponding temperature ($T_{\text{max}}$) is related to the blocking of particles with the mean particle size. The difference between $T_{\text{max}}$ and $T_{\text{irr}}$ provides a qualitative measure of the width of blocking temperature distribution. In table 6.1 $T_{\text{max}}$ and $T_{\text{irr}}$ for all the samples are reported.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acron.</th>
<th>$&lt;D_{\text{TEM}}&gt;$ (nm)</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$T_{\text{irr}}$ (K)</th>
<th>$T_{\text{mBT}}^\star$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe$_2$O$_4$/SiO$_2$ 5% wt</td>
<td>N5$_{900}$</td>
<td>2.8 (2)</td>
<td>41(2)</td>
<td>65(2)</td>
<td>25(1)</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/SiO$_2$ 10% wt</td>
<td>N10$_{900}$</td>
<td>2.9(2)</td>
<td>49(3)</td>
<td>73(3)</td>
<td>26(2)</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/SiO$_2$ 15% wt</td>
<td>N15$_{900}$</td>
<td>6.7(1)</td>
<td>53(1)</td>
<td>85(2)</td>
<td>26(1)</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/SiO$_2$ 30% wt</td>
<td>N30$_{900}$</td>
<td>16.3(7)</td>
<td>127(3)</td>
<td>231(4)</td>
<td>60(2)</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/SiO$_2$ 50% wt</td>
<td>N50$_{900}$</td>
<td>28.3(8)</td>
<td>207(4)</td>
<td>298(5)</td>
<td>134(4)</td>
</tr>
</tbody>
</table>

Table 6.1. Mean particles size obtained from TEM images ($<D_{\text{TEM}}>$), temperature corresponding to the maximum in ZFC Curve ($T_{\text{max}}$), irreversibility temperature ($T_{\text{irr}}$), blocking temperature from TRM measurement ($T_{\text{mBT}}^\star$).

$T_{\text{irr}}$ and $T_{\text{max}}$ increase with the increase of ferrite content and this trend can be explained by the increase of particle size and also by an increase of interparticle interactions, as they lead to an increase of the effective anisotropy energy. The behaviour of the FC magnetization (it increases with decreasing temperature even below $T_{\text{max}}$), indicates that the interparticle interactions are negligible in the most diluted sample ($N5_{900}$, $N10_{900}$, $N15_{900}$), and weak in the $N30_{900}$ and $N50_{900}$ samples. Indeed, for diluted samples, the FC magnetization shows a behaviour very close to that of an assembly of non interacting particles, i.e. a Curie-law behaviour. On the other hand, the low temperature progressive deviation from a Curie-type behaviour (downward curvature) observed in $N30_{900}$ sample and more marked in $N50_{900}$ sample, indicates that some weak interparticle interactions are present. Indeed, in case of strong interparticle interactions, the FC magnetization would exhibit a

\[^{1}\text{For the sample } N50_{900} T_{\text{irr}} \text{ may be slightly larger than the value given in the table 6.1, because the measurements were only made up to 325 K, and there is not clear coincidence of the FC and ZFC curves below this temperature.}\]
temperature independent behavior below $T_{\text{max}}$, as signature of a collective type blocking of particle moments.  

Figure 6.2 shows measurements of the magnetization as a function of temperature, carried out with the TRM procedure and the corresponding anisotropy energy barrier distribution ($\Delta E_a$, Continuous line); also the $\Delta E_a$ fits with a log-normal function (dotted line) for the $N5_{900}$, $N10_{900}$, $N15_{900}$, $N30_{900}$ samples are reported.

Figure 6.2 TRM measurements and distributions of magnetic anisotropy energy for $N5_{900}$ (a), $N10_{900}$ (b), $N15_{900}$ (c), $N30_{900}$ (d), $N50_{900}$ (e) samples

For all the samples, $M_{\text{TRM}}$ decreases with increasing temperature, and for $N5_{900}, N10_{900}, N15_{900}, N30_{900}$ it vanishes below 325 K, respectively, whereas $N50_{900}$ shows a non-zero value in the whole temperature range, indicating that the largest particles are blocked even at room temperature. Actually, the derivative of $M_{\text{TRM}}$ can be considered as representative of the $\Delta E_a$ distribution for the $N5_{900}$, $N10_{900}$, $N15_{900}$ and $N30_{900}$ samples, where the interparticle interactions are negligible and very weak, respectively, but not for the $N50_{900}$ sample. The decrease of ferrite content leads to a more regular distribution of anisotropy energy barrier, that

---

\[ \Delta E_a \]  

Because of the very irregular trends of the anisotropy energy barrier distribution in $N50_{900}$, it is not possible make a reliable fitting for this sample.
approaches more and more to log normal function. In Table 6.1 the values of the blocking temperatures ($T_B$) obtained with this method are reported. The blocking temperature obtained for $N50_{900}$ is less reliable, due to the presence of interparticle interactions, although weak, and in any case it is underestimated because the explored temperature range does not allow observation of the magnetic anisotropy for the biggest particles. The blocking temperature obtained from the measurements carried out with a cooling field of 5 mT are equal in $N5_{900}$ and $N10_{900}$ samples. These results indicate, compatibly with the TEM data, particles of the same size in both nanocomposites.

AC susceptibility measurements were carried out on the samples $N5_{900}$, $N10_{900}$ and $N15_{900}$. In Figure 6.3 the temperature dependence of the real part ($\chi'_{AC}$) of AC susceptibility measured at different frequency for samples $N5_{900}$ (Fig. 6.3a), $N10_{900}$ (Fig. 6.3b) and $N15_{900}$ (Fig. 6.3c) are reported.

At high temperature the real part of susceptibility is fairly consistent with the Curie–Weiss law. On decreasing temperature it deviates from this behaviour and a broad maximum appears. According to the superparamagnetic model, the temperature corresponding to the maximum of the AC susceptibility ($T_{\chi'_{max}}$) is

![Figure 6.3 Temperature dependence of the in-phase component of the ac susceptibility at different frequencies for the sample $N5_{900}$ (a), $N10_{900}$ (b), $N15_{900}$ (c)](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\chi'_{max}}$ (K)</th>
<th>$\tau_0$ (s)</th>
<th>$\Delta E_a$ (J)</th>
<th>$K$ (J/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N5_{900}$</td>
<td>85.4 (4)</td>
<td>3.77x10$^{11}$</td>
<td>1.94x10$^{-20}$</td>
<td>1.69x10$^{6}$</td>
</tr>
<tr>
<td>$N10_{900}$</td>
<td>84.7 (4)</td>
<td>9.37x10$^{11}$</td>
<td>1.80x10$^{-20}$</td>
<td>1.57x10$^{6}$</td>
</tr>
<tr>
<td>$N15_{900}$</td>
<td>98.9 (3)</td>
<td>3.9x10$^{13}$</td>
<td>1.5x10$^{-20}$</td>
<td>9.5x10$^{4}$</td>
</tr>
</tbody>
</table>

Table 6.2 Temperature corresponding to the maximum in AC susceptibility ($T_{\chi'_{max}}$). Time relaxation constant ($\tau_0$) and average energy barriers $\Delta E_a$ determined by AC magnetic measurements.
related to average blocking temperature\(^4\) for \(\tau_m = 1/\nu\), where \(\nu\) is the frequency. The position of the maximum is frequency dependent, moving to lower temperatures for lower frequencies. Such behaviour is characteristic of a superparamagnetic assemblies of nanoparticles.\(^5\)

Table 6.2 reports the \(T'_{\text{max}}\) values measured with a frequency of 5 kHz for all the samples. The higher value of \(N15_{900}\) is ascribable to bigger particle size, while the similar value (i.e.: within the experimental error) for \(N10_{900}\) and \(N5_{900}\) samples are in perfect agreement with TEM data and \(T''_b\) reported in table 6.1.

As described in subsection 3.4.5 AC measurement provided the most precise method of \(\Delta E_a\) and \(\tau_0\) evaluation. In fact, by varying the frequency (\(\omega\)) it was possible to change the experimental time windows (\(\tau_m = 1/\omega\)) and determine the blocking temperature for different \(\tau_m\). Finally, through the linear dependence between \(\ln \tau_m\) and \(1/T_B\), both \(\Delta E_a\) and \(\tau_0\) were determined (Figure 6.4).

![Figure 6.4](image)

In all the three samples the AC data follow very well the superparamagnetic model and in table 6.2 the values of \(\Delta E_a\) and \(\tau_0\) are reported. The experimentally determined \(\tau_0\) value for \(N15_{900}\) sample is lower than that usually reported for ferrimagnetic nanoparticles.\(^6\) This can be due to the effect of interparticle interactions, leading to lower \(\tau_0\) values with respect to non-interacting nanoparticles assemblies.\(^6\) Finally, by taking \(<V>\) from TEM analysis, it is possible to obtain the \(K\) values for all samples (last column table 6.2). The \(K\) values for the sample \(N5_{900}\) and \(N10_{900}\) are bigger with respect to the \(N15_{900}\) value and such behaviour can be correlated to an extra surface contribution due the reducing particle size in the most dilute nanocomposites.
6.3 Spin canting and inversion degree

Figure 6.5 (a), (b) and (c), shows the dependence of the magnetization on the field (hysteresis loops) in the range ± 5 T at 4.2 K, for the samples \( N_{15900}, N_{30900} \) and \( N_{50900} \) respectively.

In Table 6.3 the saturation magnetization \( (M_s) \) the coercive field \( (H_c) \), the remanent magnetization \( (M_r) \) and the reduced remanent magnetization \( (M_r/M_s) \) are reported.

![Image of hysteresis loops](image_url)

**Figure 6.5** Hysteresis loops of the \( N_{15900} \) (a), \( N_{30900} \) (b) and \( N_{50900} \) (c) at 4.2 K

In Table 6.3 the saturation magnetization \( (M_s) \) the coercive field \( (H_c) \), the remanent magnetization \( (M_r) \) and the reduced remanent magnetization \( (M_r/M_s) \) are reported.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_s ) ((A m^2 kg^{-1}))</th>
<th>( M_r ) ((A m^2 kg^{-1}))</th>
<th>( M_r/M_s )</th>
<th>( H_c ) ((T))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_{15900} )</td>
<td>20.0 (1)</td>
<td>78 (1)</td>
<td>0.26</td>
<td>0.87 (1)</td>
</tr>
<tr>
<td>( N_{30900} )</td>
<td>44.6 (1)</td>
<td>89.3 (2)</td>
<td>0.50</td>
<td>1.21 (1)</td>
</tr>
<tr>
<td>( N_{50900} )</td>
<td>44.5 (1)</td>
<td>89.5 (3)</td>
<td>0.50</td>
<td>1.31 (1)</td>
</tr>
</tbody>
</table>

**Table 6.3** Parameters obtained from the hysteresis loops: Saturation magnetization \( (M_s) \), coercive field \( (H_c) \), remanent magnetization \( (M_r) \), and reduced remanent magnetization \( (M_r/M_s) \). Uncertainties are given in parentheses as errors on the last digit.

For the samples \( N_{50900} \) and \( N_{30900} \), the values of \( M_s \) and \( H_c \) are very similar and the \( M_r/M_s \) ratio is very close to 0.5, the value expected, according to the Stoner-Wolfarth model, for an assembly of non-interacting particles with uniaxial anisotropy axes randomly distributed. This is coherent with the presence of weak interactions and the absence of multiaxial anisotropy as observed in other samples of CoFe\(_2\)O\(_4\) nanoparticles. For the \( N_{15900} \) sample, although the particles are not interacting, a lower \( M_r/M_s \) value is observed, probably due to the presence of very small particles still in the superparamagnetic state at 4.2 K. This is consistent with the size distribution discussed in subsection 5.4.3.
6.3.1 Mössbauer investigation

Figure 6.6 (a), (b) and (c) shows Mössbauer spectra for the samples $N15_{900}$, $N30_{900}$, $N50_{900}$, respectively, in zero applied magnetic field at different temperatures.

At low temperatures, the spectra show magnetically split sextets, but with increasing temperatures there is a gradual collapse of the six lines to a doublet component because of the fast superparamagnetic relaxation of the nanoparticles. The evolution of the spectra with temperature indicates that the magnetic anisotropy energy is predominant compared to the interaction energy.$^9$ The blocking temperature ($T^M_B$) can be defined as the temperature at which 50% of the spectral area is magnetically split.$^{11}$ The values of $T^M_B$ were estimated by fitting the spectra with sextets and doublets and are reported in table 6.4. The values of $T^M_B$ decrease with increasing silica content, in agreement with the trend of $T^m_B$ obtained from magnetization measurements.

The low-temperature spectra show an asymmetry due to a small difference in the Mössbauer parameters of ions in the $A$ and $B$ sites in the spinel structure. In the temperature range 45 K - 15 K for the $N15_{900}$ sample and between 60 K and 15 K for the $N50_{900}$ and $N30_{900}$ samples, it is possible to fit the spectra with sextets that
can be ascribed to the iron atoms in the A and B sites. However, because of the overlap of the lines, it was not possible to obtain reliable information about the cationic distribution from these spectra. As expected for small magnetic nanoparticles, we observe a decrease of the magnetic hyperfine field with increasing temperature due to collective magnetic excitations.

Figure 6.7 shows the thermal variation of the average hyperfine field $<B_{\text{hf}}>$ (weighted average over A and B components) at temperatures well below the blocking temperature. All the three samples show a linear trend in accordance with equation (3.9), and as expected the slope increases with decreasing particle size. The values of the anisotropy constants were estimated assuming spherical particle shapes with the diameters given in Table 6.4. The values of $K_a$, which are reported in Table 6.4, decrease with increasing particle size in accordance with earlier observations for nanoparticles of $\alpha$-Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$. The estimated values of $K$ may be influenced by interparticle interactions, which can result in apparently larger values of the estimated anisotropy constants.

Mössbauer spectroscopy and magnetization measurement have significantly different time scales and for this reason the blocking temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_B^M$</th>
<th>$T_B^M / T_B^m$</th>
<th>$T_B^M / T_B^m_{\text{max}}$</th>
<th>$K_a$ ($J/m^3$)</th>
<th>$K_b$ ($J/m^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N15900</td>
<td>127(10)</td>
<td>4.88</td>
<td>2.39</td>
<td>$6.8 \times 10^3$</td>
<td>$7.7 \times 10^3$</td>
</tr>
<tr>
<td>N30900</td>
<td>213(10)</td>
<td>3.55</td>
<td>1.67</td>
<td>$1.2 \times 10^3$</td>
<td>$9.5 \times 10^3$</td>
</tr>
<tr>
<td>N50900</td>
<td>236(10)</td>
<td>1.82</td>
<td>1.17</td>
<td>$8.2 \times 10^3$</td>
<td>$2.1 \times 10^3$</td>
</tr>
</tbody>
</table>

Table 6.4: Ratios of the blocking temperatures obtained from Mössbauer spectroscopy and the blocking temperatures from magnetization measurement ($T_B^M / T_B^m$) and the temperature corresponding to maximum in ZFC curve ($T_B^M / T_B^m_{\text{max}}$). Anisotropy constant obtained from the dependence $<B_{\text{hf}}>$ vs $T$ ($K_a$) and from a combined approach using Mössbauer and magnetization techniques ($K_b$).
estimated from the two techniques differ considerably. Inserting the time scales of magnetization measurement (\(\tau_m \approx 100 \text{ s}\)) and Mössbauer spectroscopy (\(\tau_M \approx 5 \times 10^{-9} \text{ s}\)) and values of \(\tau_0 \approx 10^{-10} - 10^{-12} \text{ s}\) typical for ferrimagnetic materials in Eq. (vd chapter1…..), one finds that the ratio \(T_B^M / T_B^\text{m}\) should be in the range 3-7.

Considering that the value of \(T_{\text{max}}\) in ZFC magnetization measurements may be larger than \(T_B^\text{m}\) by a factor \(\beta = 1-2\), the ratio \(T_B^M / T_B^\text{m}\) would be in the range 2-7.\(\uparrow\)

In table 6.4 the ratios \(T_B^M / T_B^\text{m}\) are reported. Considering the experimental errors, \(N15\text{900}\) and \(N30\text{900}\) show values that are in quite good agreement with the theoretical calculations, while for the sample \(N50\text{900}\) a lower value was obtained. This behaviour of the more concentrated sample can be due to some interparticle interactions (a lower measuring time dependence of the blocking temperature is expected in this case), but an underestimate of \(T_B^\text{m}\) may also play a role, since TRM measurement shows that there are still particles in the blocked state at 325 K, and the value of the blocking temperature obtained from the anisotropy energy barrier distribution does not take these particles into account. Anyway, both the trend of the FC curve and the Mössbauer data suggest that the interparticle interactions are weak in this sample.

Mössbauer spectra of ferrites in large applied field may allow a more reliable distinction between \(A\)- and \(B\)-site components than the zero-field spectra, because the applied field usually is added to the \(A\)-site hyperfine field and subtracted from the \(B\)-site hyperfine field. Therefore, there is less overlap between the two components in the high-field spectra. Furthermore, such spectra can also give information about the magnetic structure. In the presence of an external magnetic field parallel to the gamma-ray direction, the relative areas of the six lines give information about the degree of alignment of the magnetization with the applied field. Figure 6.8 shows Mössbauer spectra of the samples \(N15\text{900}\) and \(N30\text{900}\) at 6 K and of the sample \(N50\text{900}\) at 6 K and at 200 K, all obtained with a magnetic field of 6 T applied parallel to the gamma ray direction.

As expected, the spectra are clearly resolved in two main six-line components. Lines 2 and 5 have non-zero intensity and, as discussed in subsection 3.3.3, this suggests a non-collinear spin structure, i.e. some of the spins are not aligned parallel or antiparallel to the external magnetic field.

When fitting such spectra with partly overlapping components, it is necessary to apply some constraints on, for example, the relative areas. A finite absorber thickness will result in a ratio between lines 1, 6 and lines 3, 4 that is less than 3. In
In order to minimize the error due to the thickness of the absorbers in the fitting, each spectrum was first fitted with four doublets. For each doublet, the line intensity and line widths were constrained to be equal in pairs and we estimated an ratio $A_{1,6}/A_{3,4} \approx 2.8$ for all the spectra. This value was then used as a constraint in the fits with sextets. Several fitting procedures were used in order to investigate different possible models. In accordance with the presence of the iron atoms in tetrahedral ($A$ sites) and octahedral sites ($B$ sites), the spectra were first fitted with two sextets. The parameter $p = A_{2,5}/A_{3,4}$ was free, assuming that the canting angles for the magnetic moments in the $A$ and $B$ site are two independent parameters. The line widths and line intensities were fixed to be equal in pairs. However, this model seemed to be too simple, and in particular the fitting of the positions of lines 2 and 5 was not satisfactory, indicating that other components were present. The spectra were therefore fitted with three sextets. The best results were obtained utilizing a model similar to that used previously for maghemite nanoparticles, tin-doped maghemite\textsuperscript{15} and MnZn ferrite.\textsuperscript{16} Thus, it was assumed that some of the iron atoms were in perfect ferrimagnetic local environments and in accordance with this the relative areas of lines 2 and 5 were constrained to zero for two sextets (area ratio 2.8:0:1:0:2.8) corresponding to $A$ (sextet 1) and $B$ sites (sextet 2). A third sextet (sextet 3) was introduced to represent ions with canted spins and in this component

Figure 6.8 Mössbauer spectra in an external magnetic field of 6 T, recorded at 6 K for samples $N15_{000}$, $N30_{000}$ and at 6 K and 200 K for sample $N50_{000}$.

<table>
<thead>
<tr>
<th>N15 0K</th>
<th>N30 0K</th>
<th>N50 0K</th>
</tr>
</thead>
<tbody>
<tr>
<td>6K</td>
<td>6K</td>
<td>6K</td>
</tr>
</tbody>
</table>
the parameter $p = A_{2,5}/A_{3,4}$ was free (area ratio 2.8:$p$:1:1:$p$:2.8). In all three sextets the line widths and line intensities were constrained to be pair-wise equal. The Mössbauer parameters obtained from these fits are given in tables 6.5a and 6.5b.

### Table 6.5a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectral Comp.</th>
<th>$B_{\text{eff}}$ (T)</th>
<th>$\delta$ (mm/s)</th>
<th>$\varepsilon$ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N15000</td>
<td>Sextet 1 (Tetr.-A site)</td>
<td>55.8(2)</td>
<td>0.38(2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Sextet 2 (Octr.-B site)</td>
<td>46.9(2)</td>
<td>0.47(2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Sextet 3 (Canted Spin)</td>
<td>48.6(2)</td>
<td>0.50(3)</td>
<td>0.02</td>
</tr>
<tr>
<td>N30000</td>
<td>Sextet 1 (Tetr.-A site)</td>
<td>55.8(2)</td>
<td>0.38(3)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Sextet 2 (Octr.-B site)</td>
<td>47.3(2)</td>
<td>0.48(2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Sextet 3 (Canted Spin)</td>
<td>49.2(4)</td>
<td>0.50(5)</td>
<td>0.025</td>
</tr>
<tr>
<td>N50000</td>
<td>Sextet 1 (Tetr.-A site)</td>
<td>55.2(2)</td>
<td>0.38(3)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Sextet 2 (Octr.-B site)</td>
<td>47.2(2)</td>
<td>0.48(3)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Sextet 3 (Canted Spin)</td>
<td>49.6(3)</td>
<td>0.49(3)</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 6.5a Effective magnetic field ($B_{\text{eff}}$), isomer shift ($\delta$), quadrupole shift ($\varepsilon$). Uncertainties are given in parentheses as errors on the last digit.

### Table 6.5b

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area Ratio ($\alpha = A/B$)</th>
<th>$A_{2,5,\text{tot}}$ (%)</th>
<th>$\langle \theta \rangle$ (°)</th>
<th>Cationic Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>N15000</td>
<td>0.35(3)</td>
<td>15(1)</td>
<td>38(1)</td>
<td>(Co0.48Fe0.52)Fe1.48O4</td>
</tr>
<tr>
<td>N30000</td>
<td>0.39(3)</td>
<td>15(1)</td>
<td>37(1)</td>
<td>(Co0.48Fe0.52)Fe1.48O4</td>
</tr>
<tr>
<td>N50000</td>
<td>0.34(3)</td>
<td>22(1)</td>
<td>46(1)</td>
<td>(Co0.48Fe0.51)Fe1.48O4</td>
</tr>
</tbody>
</table>

Table 6.5b ratio between the $A$ and $B$ components ($\alpha$), relative area of the lines 2 and 5 for each component ($A_{2,5,\text{tot}}$)$^1$, canting angle ($\langle \theta \rangle$) and cationic distribution.

$^1$The area of the lines 2 and 5 is normalized by the total area of the spectrum.

In the high-field spectra, obtained at low temperature, the values of total field at the nuclei, $B_{\text{eff}}$, the isomer shifts ($\delta$), and the quadrupole shifts ($\varepsilon$), for each sextet are very similar for the three samples, and this indicates that the magnetic...
structure of the nanoparticles is quite similar for all of them. In all the samples, sextet 2 and sextet 3 show values of the isomer shifts typical for octahedrally coordinated Fe$^{3+}$ in spinels, but larger than that of sextet 1, which is typical for tetrahedrally coordinated Fe$^{3+}$. This indicates that the canted spins are mainly located in the $B$ sites.

At low temperatures the recoilless fraction for iron ions in the $A$ and $B$ sites are essentially equal\cite{18} and therefore the area of the different components can give information about the cationic distribution. The ratio between $A$ (sextet 1) and $B$ (sextet 2 and sextet 3) sites ($\alpha$) is remarkably similar for all the samples, indicating similar cationic distributions. The $\alpha$-values are lower than those of a previous Mössbauer study of CoFe$_2$O$_4$ nanoparticles, and this difference can be due to the preparation method of the material\cite{17} and in particular to the thermal treatment at high temperature. From these ratios, utilizing the formula $(\text{Co}_{1-x}\text{Fe}_x)[(\text{Co}_{1-x}\text{Fe}_x)]_{18}$, where the round and the square brackets indicate $A$ and $B$ sites, respectively, we can obtain the cationic distributions that are reported in Table 6.5b. It is quite clear that, within the experimental error, all the samples have the same cationic distribution.

The relative areas of lines 2 and 5 are quite similar for the samples $N15_{900}$ and $N30_{900}$ but clearly larger for the sample $N50_{900}$. Utilizing equation (3.13) it is possible to calculate the average value of the canting angles ($\langle \theta \rangle$), reported in Table 6.5b, that indicates a high degree of canting for all the samples, but most prominent in the sample $N50_{900}$.

We have also measured a spectrum of the sample $N50_{900}$ in a magnetic field of 6 T at 200 K in order to investigate the effect of temperature on the magnetic structure of the nanoparticles. Due to symmetry, a canted state with canting angle $\theta_c$ is commonly accompanied by another canted state with canting angle $-\theta_c$.\cite{18} At finite temperatures, the thermal energy may be sufficient to overcome the energy barrier separating these two canted states, and the ions may then perform relaxation between the two states (transverse relaxation).\cite{18,19,20} In sample $N50_{900}$ the area of the lines 2 and 5 in the sextet 3 decreases from $\sim22\%$ to $\sim17\%$, while the widths of the lines increase of the about 50% when the temperature is raised to 200 K. The decrease of $A_{2,3}$ indicates transverse relaxation with a relaxation time comparable to or shorter than the time scale of Mössbauer spectroscopy. In fact, under these conditions the effective magnetic field at the nucleus will be given by $B_{\text{eff}} \approx B_{hf} < \cos \theta_c >$,\cite{18,19} where $B_{hf}$ is the hyperfine field if the canting is static. A further confirmation that transverse relaxation mainly
affects the canted spins of the iron atoms located in the B site is revealed from a reduction of $B_{\text{eff}}$ by $\sim 4$ T at 200 K for sextet 3 and only $\sim 1$ T for sextet 1. In addition, the broadening of the lines 2 and 5 at 200 K can (at least partly) be attributed to transverse relaxation with relaxation times of the same order of magnitude as the time scale of Mössbauer spectroscopy.\textsuperscript{18,19}

6.3.2 Relation between inversion degree and magnetic properties

The magnetic properties of CoFe$_2$O$_4$ are strongly dependent on the distribution of the iron and cobalt ions in the A and B sites. As a rule, even small changes in the cationic distribution can result in substantial changes of magnetic moments and of the magnetic anisotropy\textsuperscript{21}. Usually, bulk cobalt ferrite has a partially inverse structure where the ratio $\alpha$ has been found to vary from 0.6 to 0.87, depending on the thermal history of the sample.\textsuperscript{16} In nanoscaled particles the ratio between iron atoms located in A sites and B sites has been found lower, in the range $0.67^{\textsuperscript{22}}$ - $0.5^{\textsuperscript{17}}$ for different synthesis methods. All the samples investigated in this work show $\alpha$-values around 0.36. The nearly constant value of $\alpha$ for all the samples is a very important result, because usually a reduction of the dimension leads to modification of the inversion degree and consequently to a variation of the magnetic properties. Instead the sol-gel autocombustion synthesis allows obtaining CoFe$_2$O$_4$ nanoparticles with cationic distribution independent of the particle size in a wide range of dimension (7 nm - 28 nm). This behaviour is probably an intrinsic feature of the synthesis procedure.

To confirm the values of the anisotropy constants obtained from the temperature dependence of $<B_{\text{obs}}>$, it was determined the $K$-values was determined combining TRM magnetometry and Mössbauer spectroscopy. Specifically, we inserted the blocking temperatures and the relaxation times corresponding to the time scales of the two techniques in eq. 3.9 and calculated values of $K$.\textsuperscript{11} For samples $N15_{900}$ and $N30_{900}$ the $K$-values obtained from the two methods (Table 6.3) are in reasonable agreement, considering the possible effect of the interactions. A larger discrepancy is observed in sample $N50_{900}$ and this behaviour may be due to an underestimate of $T_B^{\alpha}$.

It should be remarked that the $K$-values are considerably smaller than the bulk value for CoFe$_2$O$_4$ (1.8-3.0 x $10^5$ J m$^{-3}$).\textsuperscript{21} This is surprising, because the magnetic anisotropy usually is larger in nanoscaled particles.\textsuperscript{13,14,15,23} The lower anisotropy in our samples can be explained by the lower value of $\alpha$ in the nanoparticles. A reduction of magnetic anisotropy due to a high percentage of Co$^{2+}$ in tetrahedral
sites has been observed earlier.\textsuperscript{24} This can be explained by the smaller single ion anisotropy for Co\textsuperscript{2+} located in tetrahedral sites (\(^4A_2\) crystal field ground energy term) (-79×10\textsuperscript{-24} J/ion) compared to Co\textsuperscript{2+} in octahedral sites (+850×10\textsuperscript{-24} J/ion) (the larger magnetocrystalline anisotropy is related to the orbital contribution in the \(^4T_1\) ground energy term).\textsuperscript{25,26}

A change in the cationic distribution implies a variation in the saturation magnetization and, for a correct evaluation of magnetic properties in our samples, it is advisable to recalculate a new reference value of \(M_s\). Assuming that the Fe\textsuperscript{3+} and Co\textsuperscript{2+} ions have a moment of 5 \(\mu_B\) and 3 \(\mu_B\), respectively, and neglecting the spin canting, our samples have a magnetic moment per unit chemical formula of about 4.9 \(\mu_B\) that corresponds to a saturation magnetization of 116 A m\textsuperscript{2} kg\textsuperscript{-1}. All the samples show a significant reduction of \(M_s\) with respect to this theoretical value. The reduction of \(M_s\) can be explained by to the presence of a non-collinear spin structure, as shown by the high magnetic field Mössbauer spectra. The \(N15_{900}\) sample shows a larger reduction, probably due to the presence of particles still in the superparamagnetic state at low temperature.

6.3.3 Spin canting and particle size

The samples \(N30_{900}\) and \(N15_{900}\) show remarkably similar values of \(A_{2,5}\), within the experimental error, while sample \(N50_{900}\) present a slightly larger canting. This result is quite interesting in the general discussion about the non-collinear structure in the magnetic nanoparticles. In fact, the presence of similar canting in the three samples with the largest degree of canting in the largest particles indicates that the spin canting is not a surface phenomenon, but that it is an effect that is more or less uniform throughout the volume of the particles. In order to find a confirmation about this hypothesis, an \(MvsH\) measurement was recorded after the sample was very slowly field cooled with a positive field of 2T.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure69.png}
\caption{Hysteresis post ZFC (empty circles) and post FC (full circles) recorder at 4.2K for \(N15_{900}\) sample}
\end{figure}
The shift of hysteresis loop, as expected in samples with a shell of disordered atoms, was not observed.

6.3.4 Conclusions

The sol-gel autocombustion synthesis results in nanoparticles with a cationic distribution that is independent of the particle size (7 nm - 28 nm) and with a very low inversion degree that leads to important modifications of the magnetic properties of the materials. We have determined the magnetic anisotropy constants of cobalt ferrite nanoparticles from the temperature dependence of the magnetic hyperfine splitting in Mössbauer spectra at low temperatures and from the blocking temperatures estimated from Mössbauer spectroscopy and magnetization measurements. The values estimated by the two methods are in good agreement, and it is found that the anisotropy constant increases with decreasing particle size. However, surprisingly, it is found that the anisotropy constants are smaller than the bulk value. We show that this can be explained by a cationic distribution, which differs considerably from that usually found in bulk cobalt ferrite. Finally, the samples show large, but similar fractions of canted spins in the samples N15$_{900}$ and N30$_{900}$, indicating that the fraction of canted spins is only weakly dependent of the particle size in the range 6-17 nm. This result indicates that the spin canting is not simply a surface phenomenon, but also occurs in the interior of the particles.

6.4 Magnetic Properties of as burnt nanocomposites

In figure 6.10 Zero Field Cooled and Field Cooled curves of the samples N5, N15, N30 and N50 are reported.
FC and ZFC curves of the N5 sample coincide,\textsuperscript{III} showing a paramagnetic behaviour. A progressively irreversible magnetic behavior (separation of the two curves) was observed in N15, N30 and N50 samples indicating the presence of superparamagnetic particles as a consequence of the formation and growth of CoFe\textsubscript{2}O\textsubscript{4} nanoparticles within the matrix. This is in good agreement with the XRD and TEM results. In the N30 and N50 samples the irreversibility behaviour is observed in the whole investigated temperature range, indicating the presence of a not negligible fraction of nanoparticles still in a magnetic blocked state at 325K. No clear maximum is observed in ZFC curves, and this induce to believe that the blocking temperature of the samples are higher than 325 K. A paramagnetic behaviour at low temperature is clearly visible in ZFC and FC curve of N30, probably due not reacted metals and small particles. The FC curve of the N50 sample presents a slope variation below 40 K that corresponds in the ZFC curve to a very small maximum. This low temperature detail can be also due to the presence of a fraction of very small CoFe\textsubscript{2}O\textsubscript{4} nanoparticles.

\textbf{Figure 6.11} Mössbauer spectra of N15 as burnt sample recorder at 15K, 20K and 40 K

The Mössbauer spectra at 15K, 20K and 40K of sample N15 (Figure 6.11) are a superposition of quadrupolar component and six line magnetic component that decreases at increasing temperature and disappear at 40 K. The magnetic sextet at 15 K show $B_{hf}$ (46.80 T) and $\delta$ (0.461 mm/s) compatible with the CoFe\textsubscript{2}O\textsubscript{4} phase.\textsuperscript{22} Then, Mössbauer data confirm that the slight irreversibility behaviour observed in ZFC-FC curves can be ascribable to presence of small superparamagnetic nanoparticles of cobalt ferrite.

\textsuperscript{III} The ZFC FC curves of the N10 sample, note reported here, have the same trend of N5 sample
Figure 6.12a and 6.12b show the Mössbauer spectra at different temperature for N50 and N30 samples. At low temperatures, the spectra show magnetically split sextets, that gradual collapse to a doublet component with the increase of temperature. The \( T_B \)’s were estimated by fitting the spectra with sextets and doublets, and are 35 K for N50 and about 20 K for N30. In both cases the blocking temperature obtained for Mössbauer spectroscopy are well below the supposed blocking temperature (> 325 K). This behaviour is surprising, because \( T_B \) is expected higher than blocking temperature of magnetization measurements. In order to investigate this unpredicted behaviour, a deeper study was carried out on N50 sample.

6.5 Superparamagnetism and magnetic ordering phenomena

In order to have a reference, a system with interparticle interactions stronger than N50 was also studied (sample C, in chapter 4). In the chose of reference system fundamental condition was also that interparticle interactions were sufficient strong to lead to ordering of the magnetic moments. In figure 6.13 the FC curves of N50 and CoFe$_2$O$_4$ unsupported phase prepared from sol a pH 2 (sample C) are reported.
The FC magnetization of C sample decreases with the lowering of temperature between 325 K and 100 K, whereas, for temperatures below 100 K, it shows a constant trend; this indicates the presence of strong nanoparticles interactions, that could induce collective magnetic ordered state with high anisotropy. The high degree of aggregation, determined by previous BET measurements, suggest that there is an exchange coupling among surface atoms of neighbouring particles. In the N50 sample the FC susceptibility increases in the whole range of temperature and this indicates that the interparticle interactions are weaker than those present in the C sample. This is due to the presence of the matrix and by the reduced size of nanoparticles evidenced by XRD and TEM. In conclusion, N50 and C samples are both strong interacting systems, but the nanoparticles in sample C are certainly more interacting than in sample N50. In addition, in the unsupported CoFe\textsubscript{2}O\textsubscript{4}, the strong interparticle interactions lead to magnetic ordering phenomena, as indicated from the FC behaviour at low temperature. On this basis C sample was used as reference system.

6.5.1 Experimental Results

ZFC-FC measurements at high applied magnetic fields were carried out for C (figure 6.14a) and N50 (figure 6.14b) samples.

At magnetic fields above 0.2 T for the N50 sample and 1 T for the C sample, the ZFC curves exhibit a maximum and the corresponding temperatures ($T_{\text{max}}$) shift toward lower values by increasing the field. For both samples $T_{\text{max}}$ values show a good agreement with a linear dependence from $H^{2/3}$ (Figure 6.15);

**Figure 6.14** ZFC FC curves at different fields of the C (a; ZFC full squares, FC empty squares) and N50 (b; ZFC full circles, FC empty circles) samples
$T_{\text{max}}$ extrapolated for $H \to 0$ are 412 K for the C sample and 380 K for the N50 one. This kind of dependence can be ascribed both to superparamagnetic relaxation and to ordering phenomena due to strong interactions.\textsuperscript{30,31}

The measurements at different applied magnetic field also permit to obtain some information about the trend of the $M_{\text{ZFC}}$ and $M_{\text{FC}}$ at low temperature for N50 sample. Figure 6.16 reports FC (6.16a) and ZFC (6.16b) curves respectively in the range 4.2 – 150K, performed at 25 mT, 0.05 T and 0.2 T. The slope variation in FC measurements at low temperature increases with the field and the small maximum in the ZFC curves shifts to lower temperature. The slope variation of the FC susceptibility with the increase of the field is a first indication of the presence of a non collinear spin structure at the nanoparticles surface, as

Figure 6.15 Field dependence of $T_{\text{max}}$ for the C (squares) and N50 (circles) samples. The temperatures at zero field are obtained by extrapolation.

Figure 6.16 ZFC (a) and FC (b) curves of the S sample in the range 4.2 -160 K with external magnetic field of 25mT, 0.05 T and 0.2 T.
reported by some authors for $\gamma$-Fe$_2$O$_3$\textsuperscript{32} and CoFe$_2$O$_4$ nanoparticles.\textsuperscript{33} The temperature of the small maximum shows also in this case a linear dependence from $H^{2/3}$.

In order to obtain other information about the small ZFC susceptibility maximum present in the $N50$ sample, magnetization measurements according to the TRM protocol in the temperature range 4.2K-110K (figure 6.17a) were carried out. The TRM magnetization decreases with the temperature increase and at about 100K reaches a constant value. If all the nanoparticles were in the superparamagnetic state, $M_{TRM}$ should fall to zero, while in the present sample it becomes equal to 0.84 A m$^{-2}$ Kg$^{-1}$. This is explained by the presence of a large fraction of big nanoparticles still blocked at 100 K. By TRM it is possible to obtain information about the distribution of magnetic anisotropy energy of the nanoparticles. Figure 6.17b shows the distribution of magnetic anisotropy energies of small nanoparticles and, as a dotted line, the fitting of experimental data with log normal function. The temperature corresponding to the maximum of magnetic anisotropy distribution was used as blocking temperature ($T_B^c$) in SQUID magnetometry studies (Subsection 3.4.3) that, in this case turned out 13K.

To investigate the dependence of $M$ from $H$, the hysteresis loop of $N50$ sample was measured at 4.2 K; the results are shown in figure 6.18. Saturation Magnetization ($M_s$), calculated as reported in experimental section, magnetization at 5T ($M_{5T}$), Coercive Field ($H_c$), Remanent Magnetization ($M_r$) and Reduced Remanent Magnetization ($M_r/M_s$) are reported in table 6.6.

![Figure 6.17](image-url)
The Magnetization of N50 sample at 5T is very far from saturation, and, in this condition, it is quite difficult to obtain a reliable value of Saturation Magnetization with the equation (3.19). The lack of saturation, the drastic reduction of $M_r$ value (5 A m$^2$ kg$^{-1}$) and the important reduction of coercive field with respect to the value reported in literature for CoFe$_2$O$_4$ nanoparticles, probably are all due to the presence of very small particles that are still fast relaxing at 4.2K. Moreover, the presence of a non collinear spin structure can give a contribution to the observed reduction of $M_s$. Early studies on ferrite nanoparticles of $\gamma$-Fe$_2$O$_3$, NiFe$_2$O$_4$, and CoFe$_2$O$_4$ have reported such a reduction of $M_s$.

6.5.2 Discrimination between superparamagnetic and ordering phenomena

Many authors have shown that the temperature of the peak in ZFC susceptibility is directly proportional to the mean superparamagnetic blocking temperature in presence of weak interactions.$^4$ On the other hand in systems with strong interactions, the literature suggests that it is more correct to correlate the maximum in ZFC curve to ordering or spin-glass like phenomena.$^3$
For $T_{\text{max}}$ at high temperature ($T_{\text{MC},1}$) in the $C$ sample and for both $T_{\text{max}}$ at high ($T_{\text{MN50},1}$) and low ($T_{\text{MN50},2}$) temperature in the $N50$ sample, the temperature of the peak is found to decrease as the magnetic field increases, like already observed in other systems of nanoparticles\textsuperscript{16} in good agreement with a linear dependence from $H^{2/3}$\textsuperscript{34} Dormann et al.\textsuperscript{30} pointed out that in presence of a $T_{\text{max}}$ versus $H^{2/3}$ dependence, it is difficult to distinguish between magnetic ordering phenomena and superparamagnetic blocking process. At the same time, they suggested that a possible distinction criterion is, in $H^{2/3}$ versus $T_{\text{red}}$ (reduced Temperature)$^{IV}$ scaling, a shift of the line with respect to the origin, that occurs only in the superparamagnetic case. Figure 6.19 reports $H^{2/3}$ vs reduced temperature for $T_{\text{MC},1}$, $T_{\text{MN50},1}$ and $T_{\text{MN50},2}$. A shift of the line with respect to the origin is observed only for $T_{\text{MN50},2}$; this induces to believe that this peak in ZFC is due to superparamagnetic relaxation, while the ZFC maxima at high temperature in $N50$ and $C$ samples are due to ordering phenomena. The value of $T_{\text{max}}$ extrapolated at zero field can be then considered as the temperature below which the interactions among nanoparticles induce a transition from superparamagnetic to ordered state. The different strength of interactions in the $C$ and $N50$ samples is reflected in the different slope of the linear fitting of $T_{\text{max}}$ at high temperature. In fact, it has been demonstrated\textsuperscript{37} that the slope of the linear fit decreases with the particle interactions, that, in agreement with figure 6.15, result greater in the $C$ sample.

6.5.3 Superparamagnetic behaviour of small particles

As regards the very small nanoparticles in the $N50$ sample, from the distribution of magnetic anisotropy we obtain a $T_{B}^{*}$ value (13 K) that it is interesting to correlate with $T_{\text{max}}$ value extrapolated for $H\rightarrow0$ from $T_{\text{max}}$ vs $H^{2/3}$ dependence (figure 6.20.)

Figure 6.20 Field dependence of the temperature corresponding to the maximum at low temperature in $N50$ sample

Where the reduce temperature is defined as $T_{\text{red}}=1-(T_{\text{max}}(H)/T_{\text{max}}(0))$
and with blocking temperature estimated from Mössbauer spectroscopy (table 6.7).
As discussed in detail in subsection 3.4.2, for a random assembly of not interacting nanoparticles \( T_B^m = \beta T_{\text{max}} \) and \( \beta \) is typically of the order 1.5-2.0. For \( T_{\text{max}} = 29 \) K and \( T_B^m = 13 \) K, \( \beta \) is about 2.15, and this is a first confirmation that small nanoparticles have a superparamagnetic behaviour.\(^{33,37}\)

In this framework the blocking temperature obtained by Mössbauer spectroscopy can be ascribable to superparamagnetic relaxation of the small particles. Anyway the ratio \( T_B^M / T_B^m \) and \( T_B^M / T_{\text{max}} \) are lower than that expected (table 6.7). This behaviour can be due to overestimated of \( T_B^M \), because of the bigger interacting particles present in the sample. In order to give a rough evaluation of the big particles effect, a new value of Blocking temperature \( (T_B^M)_2 \) was calculated.

<table>
<thead>
<tr>
<th>( N50 )</th>
<th>( T_{\text{max}}/T_B^m )</th>
<th>2.015</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_B^M / T_{\text{max}} )</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>( T_B^M / T_B^m )</td>
<td>2.69</td>
<td></td>
</tr>
<tr>
<td>( (T_B^M)<em>2/T</em>{\text{max}} )</td>
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<td></td>
</tr>
<tr>
<td>( (T_B^M)_2/T_B^m )</td>
<td>4.15</td>
<td></td>
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</table>

**Table 6.7** Ratios of the blocking temperatures obtained from Mössbauer spectroscopy and the blocking temperature obtained from magnetization measurement \( [T_B^M / T_B^m, (T_B^M)_2 / T_B^m] \) and the temperature corresponding to the maximum in ZFC curve \( [T_{\text{max}} / T_B^m] \)

The variation of superparamagnetic fraction observed in Mössbauer spectroscopy (figure 6.21) show a strong decrease until 80-90K, then a small plateau around to 100 K; for higher temperature a slight decrease is shown. An exactly inverse behaviour is shown by blocked fraction of nanoparticles. Hypothesizing that the plateau observed at around 100K, indicate that all the small particles are in the superparamagnetic state, the value of \( (T_B^M)_2 \) was determined.

**Figure 6.21** Thermal variation of the superparamagnetic and blocked fraction of the N50 sample
With this approximation the values of $T_B^M / T_B^w$ and $T_B^M / T_{max}$ are in the expected range.

6.5.4 Conclusions

The magnetic data for the sample N50 are consistent with a model in which a fraction of small nanoparticles are able to fast relax in the whole measured range of temperature, while a fraction of big nanoparticles are responsible of ordering phenomena for $T<380K$. The presence of small particles explains the relative lower value of blocking temperature obtained by Mössbauer spectroscopy. The bigger particles are, indeed, responsible for irreversibility behaviour of ZFC FC measurement in all the temperature range.

In addition, it was developed an experimental approach in order to distinguish ordering and superparamagnetic phenomena and to study samples with strong interacting nanoparticles. It should be remarked that some extra experiment, like Mössbauer spectra at temperature higher than 325 K, can be useful in order to validate this approach.
REFERENCES

7 S. Morup and H. Topsøe, Appl. Phys. 11, 63 (1976)
Appendix: Terms and units in magnetism

The magnetic moment is the fundamental object in magnetism. A macroscopic approach involves a large number of atoms with magnetic moments, thus leading to use a more proper term: Magnetization ($\mathbf{M}$), defined as the magnetic moment for unit of volume:  

$$\mathbf{M} = \frac{m}{V}$$  

(a)

The magnetic fields can be described in terms of field strength ($\mathbf{H}$) and magnetic induction or magnetic flux density ($\mathbf{B}$). In the free space these quantities are linearly related by the equation:

$$\mathbf{B} = \mu_0 \mathbf{H}$$  

(b)

where $\mu_0$ is just the permeability of free space. However in other media the magnetic induction is no longer a linear function of field strength. $\mathbf{H}$ and $\mathbf{B}$ are related by the permeability of the medium $\mu$ through the equation:

$$\mathbf{B} = \mu \mathbf{H}$$  

(c)

but now the proportional constant, $\mu$, is not necessarily a constant and can vary with $\mathbf{H}$.

In an assemblies of magnetic moments $\mathbf{B}$ and $\mathbf{H}$ are also correlated with magnetization; the following is a general vector relationship between these three quantities:

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M})$$  

(d)

The equation (d) which relates these three basic magnetic quantities is true under all circumstances. Utilizing the equation (d), it possible rewrite the equation (c) as:

$$\mu = \mu_0 (1 + \frac{\mathbf{M}}{\mathbf{H}})$$  

(e)

In some special cases, magnetization is linearly related to the magnetic field:\footnote{These materials are called linear material.}

$$\mathbf{M} = \chi \times \mathbf{H}$$  

(f)
where $\chi$ is called magnetic susceptibility. $\chi$ is a measure of the effectiveness of an applied magnetic field for induce a magnetic dipole in the material. When the equation (f) is valid, the equation (e) can be rewrite as:

$$\mu = \mu_0 (1 + \chi)$$  \hspace{1cm} (g)

It’s useful to define the relative permeability of the medium; it’s given by:

$$\mu_r = \frac{\mu}{\mu_0}$$  \hspace{1cm} (h)

The relative permeability is closely related to the susceptibility and the following equation is always true.

$$\mu_r = (1 + \chi)$$  \hspace{1cm} (i)

Utilizing the equation (i) it is possible rewrite the (c) as:

$$\mathbf{B} = \mu_0 (1 + \chi) \mathbf{H}$$  \hspace{1cm} (f)

The field of magnetism has never been blessed with a clear system of quantities and units. The first unit system in magnetism were defined in the cgs (centimetres, grams, seconds) or Gaussian system. Such a system, based on magnetostatic, is again used for fundamental and primarily theoretical discussions. Since about the middle of the last century, the scientific world has gradually adopted a unit system which in its present form is known as International System (SI).\textsuperscript{2} Such system, based on an electrodynamic approach, actually it is used with three different convention. The two principal SI system are called “Sommerfeld system”\textsuperscript{II} (SI-1) and “Kennely system”\textsuperscript{III} (SI-2). The third one (SI-3) is very similar to Sommerfeld convention, except for magnetic field strength that is expressed in Tesla (T) instead of A/m\textsuperscript{3}. These three S.I. systems need not be contradictory or mutually exclusive.

The cgs system and each of the three versions of the SI system show advantages and advantages. For such reason all the systems are used in the literature, leading sometimes to inconsistencies and often generating confusion. The SI unit of the most important magnetic quantity with the cgs conversion factor, are reported in table Ia, Ib and Ic respectively for SI-1, SI-2 and SI-3 systems.

Great care has been given so as to keep notation and units as coherent and consistent as possible throughout the thesis and it’s used the third convention of SI.

\textsuperscript{II} Proposed in the 1936 from Kennely, was accepted first by electrical engineers.

\textsuperscript{III} Proposed in the 1948 from Sommerfeld.
There may be small deviations between the notation in the papers and the thesis, but the notation is consistent within each paper. Sometimes the magnetic moment will be expressed in Bohr magneton ($\mu_B$), defined in equation (2.2), where $1\mu_B = 9.274 \times 10^{-24}$ A m$^2$. Moreover, it’s important to underline that although it is a slight abuse of language, following common usage, it will refer both $\vec{H}$ and $\vec{B}$ will be referred as “magnetic fields” (knowing the equation c).

### Table Ia

<table>
<thead>
<tr>
<th>Magnetic Term</th>
<th>Sym.</th>
<th>cgs</th>
<th>SI-1 Kennel conv.</th>
<th>cgs Equiv.</th>
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<td>Field Strength</td>
<td>H</td>
<td>Oersted (Oe)</td>
<td>Ampere metre$^{-1}$ (A/m)</td>
<td>$4\pi \times 10^{-3}$ Oe</td>
</tr>
<tr>
<td>Magnetic induction</td>
<td>B</td>
<td>Gauss (G)</td>
<td>Tesla (T)</td>
<td>$10^6$ G</td>
</tr>
<tr>
<td>Mass - Magnetization</td>
<td>M</td>
<td>(emu g$^{-1}$)</td>
<td>(Wb m Kg$^{-1}$)</td>
<td>$10^{-4}/4\pi$ emu g$^2$</td>
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<tr>
<td>Basic Equation</td>
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<td>$\vec{B} = \mu_0 \vec{H} + \vec{M}$</td>
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### Table Ib

<table>
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<td>Oersted (Oe)</td>
<td>A/m</td>
<td>$4\pi \times 10^{-3}$ Oe</td>
</tr>
<tr>
<td>Magnetic induction</td>
<td>B</td>
<td>Gauss (G)</td>
<td>Tesla (T)</td>
<td>$10^6$ G</td>
</tr>
<tr>
<td>Mass - Magnetization</td>
<td>M</td>
<td>(emu g$^{-1}$)</td>
<td>A m$^2$ Kg$^{-1}$</td>
<td>1 emu g$^2$</td>
</tr>
<tr>
<td>Basic Equation</td>
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<td></td>
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<td>$\vec{B} = \mu_0 (\vec{H} + \vec{M})$</td>
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### Table Ic

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<td>Magnetic induction</td>
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<td>1 emu g$^2$</td>
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<tr>
<td>Basic Equation</td>
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<td></td>
<td></td>
<td>$\vec{B} = H + \mu_0 \vec{M}$</td>
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</table>

Table Ia, Ib, Ic: Units for magnetic quantities and conversion factors$^4$
REFERENCES