Structural and Magnetic Investigations of Magnetic Nanoparticles and Core-Shell Colloids

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Abstract

The main interest of this thesis relies on the structural and magnetic investigation of magnetic particles with dimensions in the nano- and micrometer range. Three types of particles have been investigated, namely: aqueous-based Fe₃O₄ nanoparticles, with an average diameter of 12±3 nm, as well as, core-shell particles and composite particles, both with diameters ranging from 680 nm to 1000 nm.

The Fe₃O₄ nanoparticles are negatively charged and tetrabutylammonium hydroxide-stabilized. The core-shell particles consist of an anionic polystyrene core, with a diameter of 640 nm coated with multilayers of Fe₃O₄ nanoparticles and polyelectrolytes. The composite particles have the same polystyrene core coated with Fe₃O₄ nanoparticles, polyelectrolytes and silica-encapsulated gold nanoparticles with a diameter of 15 nm. The core-shell and composite particles were prepared by using a recently developed method, called layer-by-layer technique [10]. Alternate adsorption of layers of positively and negatively charged specimens is the basic idea of the layer-by-layer method.

The uniformity and regularity of the coating has been confirmed by Transmission Electron Microscopy and Atomic Force Microscopy measurements. The structure of the Fe₃O₄ nanoparticles has been investigated by High Resolution Transmission Electron Microscopy, X-ray Diffraction, X-ray Absorption Spectroscopy and X-ray Photoelectron Spectroscopy.

The pattern formation of the core-shell and composite particles in water solution under applied magnetic field has been studied. An in-plane magnetic field arranged the microspheres into a chain-like structure. Chains up to 2 mm in length have been observed. The motion of the magnetic colloids in an aqueous solution when a magnetic field is applied has been visualized in real-time by Optical Microscopy.

Ferromagnetic Resonance, SQUID-magnetometry and Magnetic Force Microscopy have been used to investigate the magnetic properties of the nano- and micrometer-size particles. The polar angular dependence of ferromagnetic resonance for Fe₃O₄ nanoparticles reveals an effective anisotropy field of 0.12 T and a negative out-of-plane anisotropy constant at 300 K. In comparison with the bulk value for Fe₃O₄ (M_r/M_s = 0.5) a small ratio between remanence and saturation magnetization M_r/M_s = 0.08 at 300 K is revealed by magnetometry measurements. The magnetic measurements on the core-shell particles aligned into a chain-like structure confirm a long-range dipolar order at room temperature, an in-plane easy axis of the magnetization along the chains and a reduction of the magnetic moment of Fe₃O₄ (∼ 0.3 bulk value).
Chapter 1

Introduction

1.1 Motivation and applications

Magnetic particles with dimensions in the nano- and micrometer range represent a particularly interesting class of material from both a scientific and technological point of view [22], [24], [54]. Magnetic nanoparticles show a wide variety of anomalous magnetic properties as compared to the respective bulk materials. The magnetic properties of small particles are strongly influenced by finite-size effects [46]. The relevance of these effects increases with decreasing particle size. Finite size effects result, for example, from quantum confinement of the electrons, whereas typical surface effects are related to the symmetry breaking of the crystal structure at the boundary of each particle [6], [54], [73]. Small magnetic particles exhibit unique phenomena such as superparamagnetism [54], quantum tunnelling of magnetization [83], and unusual large coercivities. Due to their large coercivity, low saturation magnetization and high anisotropy, certain magnetic nanoparticles (CoPt [53], FePt) are of high interest for future high-density recording media.

Magnetic nanoparticles are also used in medicine. For example, iron oxide colloids have a very low toxicity and show good biocompatibility, which makes them suitable in various areas of medicine. One application is to use them for the hyperthermic treatment of cancer [11]. It is well established that by exposing cancer tissue to elevated temperatures (above 42 °C), the viability of the cancer cells is reduced and an enhancement of their sensitivity to radiation and chemotherapy is observed.

Colloidal systems would be very advantageous for drug targeting. Controlled and site-specific drug delivery have shown considerable advances. The release mechanism of drugs, the diffusion coefficient and the biodegradation rate are the main factors which govern the drug release rate. Here, drugs may be bound to the nanoparticles either within the production process of nanoparticles or by adsorption of drugs to nanoparticles. Site-specific delivery of drugs would
not only adjust the amount of drugs at the site to an ideal concentration but it would also decrease the amount of drugs being distributed to other parts of the body, thus reducing unwanted side-effects. The successful incorporation of magnetic Fe$_3$O$_4$ particles with diameters of 10-12 nm into albumin was already reported [56]. Particles were injected into a certain part of the body and a magnet was placed close to the point of injection, such that the particles were retained at the location of the magnet. Moreover, by placing the magnet in the vicinity of some organs or extremities it was possible to increase the concentration of the drugs at that position. Another field of medical applications where magnetic nanoparticles are very useful is magnetic resonance imaging [25]. Because of their tendency to accumulate with different density at different tissue compositions, one can use magnetic nanoparticles as contrast agents for the localization and diagnostics of e.g. brain tumors.

Recently there has also been much interest in the fabrication of composite particles, such as core-shell structured materials [9], [10]. These core-shell materials produced by controlled coating of core particles with organic or inorganic layers are exploited in the areas of electronics, catalysis and separations [9]. Caruso et al. reported on the creation of hollow magnetic spheres by removing the diamagnetic core through calcination or by exposure to a solvent [7]. Such empty core-shell particles may be used as capsules for drug delivery, catalysis, coatings, etc.

Because of their size and ability to self-organize, colloidal crystals are very attractive for the fabrication of optical photonic crystals. Photonic crystals are periodic structures in 1-, 2- or 3-dimensions which exhibit a modulation of the dielectric constant in the micrometer range, resulting in a periodic band-gap [87].

Another point of interest is to explore the optical anisotropy (linear dichroism and birefringence) of the ferrofluids subjected to a magnetic field [86]. Optical devices which employ the strong magneto-optical effects of magnetic fluids are still under development. In Ref.[26] the magnetochromatic behavior of magnetic fluids subjected to dynamic magnetic fields are investigated. The authors claim that the diffracted light can be manipulated via external magnetic fields, which makes magnetic spheres attractive for applications as optical switches, optical modulators, etc.

The organization of magnetic nano- and micrometer particles in ordered array, have a great impact on numerous branches of applied science as well. Ordered arrays of magnetic nanostructures are very interesting to investigate due to their wide spread applications, such as magnetic random access media memory (MRAM), storage data, magnetic switches, etc [28]. On the other hand, the self-assembly of micrometer size particles is one route for the fabrication of photonic band gap materials at optical wavelengths. Another interesting aspect is given by
the fact that one can study both the individual and collective behavior of magnetic nano- and micrometer particles. A number of techniques have been developed to obtain ordered arrays of nano- and micrometer particles, for example, spin coating [34], vertical deposition [87], deposition on patterned substrates [88], or simply evaporating the colloidal suspensions onto a flat substrate. Also, a control over the colloidal self-assembly can be achieved by applying external magnetic [27], [40], [45], [89] or electric fields (electrophoretic deposition) [43].

Outline of the thesis

The present thesis is organized as follows:

In chapter 2 the theoretical background related to the present work is discussed. The first part of this chapter deals with a brief introduction to colloidal systems and their stability. The second part focuses on the magnetic properties and the magnetic anisotropy of ferro- and ferrimagnetic systems. The ferrimagnetism of iron oxides is also discussed.

In chapter 3 two of the experimental techniques used to characterize magnetic particles, namely ferromagnetic resonance and scanning force microscopy, are presented.

Chapter 4 presents a summary of the experimental results. It includes the structural and magnetic investigations of three types of particles: Fe\textsubscript{3}O\textsubscript{4} nanoparticles, as well as core-shell and composite micrometer particles. The preparation of the particles is also described.

The self-assembly of micrometer sized particles into 1D and 2D structure is described in chapter 5. The magnetophoretic deposition and resulting field-induced chain-like structures of particles are discussed in detail.

The summary of the current work is presented in chapter 6.
Chapter 2

Theoretical considerations

2.1 Colloids

In general, a colloidal system consists of a particulate substance which is finely dispersed in a continuous medium [64]. Usually, the size of the dispersed particles is in the range of 1-1000 nm. Thus, colloidal systems cover the range between the size of molecules and macroscopic bulk phases. The stability of colloids against aggregation is of particular importance as will be discussed in the following section.

2.2 Stability of Colloids

The most important forces that determine the stability of the colloidal suspensions are attractive and repulsive van der Waals forces, electrostatic forces and forces resulting from adsorbed polymers[64]. There are two major ways to stabilize colloidal particles in an aqueous solution, namely electrostatic and/or steric stabilization. The electrostatic stabilization results from the interplay between the attractive van der Waals force and the electrical double layer repulsion (DLVO theory). The steric stabilization is described by the balance between the attractive van der Waals force and the steric repulsive forces.

2.2.1 Van der Waals forces

Inside an atom, the nucleus carries a positive charge and negatively charged electrons are located at off-center positions. Statistical displacement of positively and negatively charges gives rise to the formation of the fluctuating dipole moment, which results in attractive interatomic forces, at large distances. These forces are identified as van der Waals forces. At large distances the most important contribution to the total van der Waals interaction results from the so-called "London dispersion" force.
One can estimate the strength of the van der Waals force between two polystyrene spheres of radius \( a = 320 \text{ nm} \) separated by a distance \( D = 10 \text{ nm} \), suspended in water according to

\[
F = A \frac{a}{12D^2} \sim 3.46 \times 10^{-12} \text{ N}
\]

(2.1)

where \( a \) is the particle radius, \( A \) Hamaker constant, and \( D \) the surface-to-surface interparticle separation. The Hamaker constant \( A \), depends on the density of the particle and the medium. The Hamaker constant for polystyrene spheres interacting across water is reported to have the value \( A = 1.3 \times 10^{-20} \text{ J} \) \([69]\). Calculating the interaction energy using the follow formula

\[
V_A = -A \frac{a}{12D}
\]

(2.2)

one finds that the interaction energy is \( 3.4 \times 10^{-20} \text{ J} \) for 320 nm radius and 10 nm interparticle separation. \( V_A \) is about 8 kT (at 300 K) the energy of thermal motion. At first glance one can argue that van der Waals forces would cause attractive collisions between the particles, leading to the formation of aggregates. In order to avoid the aggregation phenomenon and to ensure the colloidal stability, one needs a counterbalance to the attractive forces, i.e., repulsive forces. These repulsive forces will be discussed in the following.

### 2.2.2 Electrical double layer repulsion

The electrical double layer model was first introduce by Stern by combining the Helmholtz and Gouy-Chapman models \([20]\). In general the colloidal particles possess an electrostatic charge in a disperse medium. This surface charge of the colloidal particles has two important roles:

\( a) \) it causes a repulsion between particles when they approach each other, thus preventing the particles to stick together.

\( b) \) it attracts ions to the vicinity of the particles.

These oppositely charged ions form a so-called electrical double layer around each colloidal particle. One can say that a "cloud" of ions is associated with each colloidal particle. A schematic illustration of an electrical double layer is shown in Figure 2.1. Because of the electrostatic interactions the electrical double layer contains an excess of counterions (of opposite charge to that on the colloidal particle) and a deficiency of co-ions (of the same charge). The inner (compact) layer is called Stern layer and the outermost is called the diffuse layer. To understand the interaction between charged colloidal particles one has to understand the behavior of the electrical double layer. The thickness of the electrical double layer around colloidal particles determines how close two particles can get to each other before they start feeling repulsive
forces.
The electrical potential for a spherical particle of radius $a$, at a distance $r$ from the center of the sphere can be written as [65]:

$$\psi = \psi_0 \frac{a}{r} \exp \left[-\kappa (r - a)\right]$$ (2.3)

where $\psi_0$ represents the surface potential and $\kappa$ is the so-called "Debye length", which identifies the inverse thickness of the electrical double layer. In the case of two spherical particles of radii $a$, separated by a distance $D$ (surface-to-surface), the repulsive interaction energy is:

$$V_R = 2\pi \varepsilon_0 \varepsilon_r a \psi_0^2 \ln[1 + \exp (-\kappa D)]$$ (2.4)

where $\varepsilon_0$ is the permittivity of vacuum and $\varepsilon_r$ is the relative permittivity of the medium in the diffuse layer.

Eq. 2.4 is valid for large particles and small electrical double layer overlap i.e. $(\kappa a) \ll 1$. For small particles and $(\kappa a) \gg 1$ the interaction energy between nanosized particles is given by [65]:

$$V_R = 2\pi \varepsilon_0 \varepsilon_r a \psi_0^2 \exp (-\kappa D)$$ (2.5)

### 2.2.3 Derjaguin-Landau-Verwey-Overbeek (DLVO) theory

The theory of Derjaguin, Landau [21], Verwey and Overbeek [78] (DLVO) explains the qualitative features of colloid stability. According to this theory, the sum of Van der Waals forces
and the electrostatic double layer interaction determines the stability of the colloidal particles. In the model one calculates the energy of interaction $V_{\text{int}}$ between colloidal spherical particles as a function of interparticle separation and other parameters, for example the Debye length. The energy of interaction is related to the force by

$$F_{\text{int}} = -\frac{\partial V_{\text{int}}}{\partial r}$$

(2.6)

The interaction energy between two small spherical particles at short separation can be expressed as:

$$V_{\text{int}} = 2\pi\varepsilon_0\varepsilon_r a \psi_0^2 \exp(-\kappa D) - Aa/12D$$

(2.7)

A barrier of 15-20 kT is usually enough to ensure colloidal stability [65]. The height of the energy barrier can be controlled by changing the ionic strength (which affects the Debye length), the surface potential, $\psi_0$, and radius of the particle. The surface charge can be controlled by the pH of the solution and solvent polarity. The interaction energy is plotted as a function of the particles surface separation for various particle sizes, surface potentials and ionic strengths in Figure 2.2, Figure 2.3, Figure 2.4. For all the calculations the Hamaker constant $4 \times 10^{-20}$ J reported for magnetite particles interacting through water [48] was used. From the examination of Eq. 2.7 it is clear that both the attractive and repulsive interaction energies increase with particle radius. This is visible below (Figure 2.2), where the barrier height increases as the particle size increases. Figure 2.3 shows the total interaction energy between two spherical particles in an aqueous solution as a function of the separation of the particles for several ionic strengths (different electrolyte concentrations). The enhancement of the ionic strength promotes flocculation by allowing the colloids to come together in the region where the Van der Waals interactions dominate. As we can see (Figure 2.4) the surface potential (an estimate of this potential is obtained by the zeta potential $^1$) plays also an important role in the stability of the colloids. A large surface potential implies a high energy barrier. The colloids with a large value of the Hamaker constant require a high zeta potential value, as well. For example, for metal gold particles with a diameter of 10 nm interacting in aqueous solution and a Hamaker constant of $A = 2.5 \times 10^{-19}$ J, a zeta potential larger than 50 mV is necessary to ensure the stability of the colloids [54].

---

$^1$Zeta potential ($\zeta$) is calculated from the electrophoretic mobility measurements using the relation $\zeta = u\eta/\epsilon$, where $u$ is the electrophoretic mobility, $\eta$ and $\epsilon$ are the viscosity and permittivity of the solution, respectively.
2.2.4 Steric stabilization

Another mechanism to ensure the colloidal stability and to protect particles against coagulation is the so-called **steric stabilization** [20]. Layers of large molecules, for example long chain polymers, are adsorbed on the particle surface. These polymers can either stabilize or destabilize the colloidal particles. An illustration of these phenomena is shown in Figure 2.5. For uncovered particles the electrical double layer establishes the repulsive interactions (Figure 2.5 a). For small quantities of polymer, the configuration of the polymer layer is rather flat and the electrostatic repulsion continues to determine the stability of colloidal suspension (Figure 2.5 b). When the particles are only partly covered with polymer, the adsorbed polymer can form a macromolecular bridge by adsorbing on both colloids at the same time. This phenomenon is called bridging flocculation (Figure 2.5 c). When there is an excess of polymer, the particles are saturated and repeal each other via steric repulsion (Figure 2.5 d). A good colloidal stability is reached by using polymers with low molecular weight. In this case the thickness of the polymer layer is much less than the Debye length and the colloidal particles are repulsive at long range by the electrostatic forces and at short distances by the steric repulsion (Figure 2.5 e). Polymers such as polyelectrolytes ensure both electrostatic and steric stabilization, while uncharged...
Figure 2.3: The effect of ionic strength on the total interaction energy between two identical magnetite particles with radius 6 nm, $\psi_0 = -50$ mV, $A = 4 \times 10^{-20}$ J.

Figure 2.4: The effect of the surface potential on the total interaction energy ($a = 6$ nm, $\kappa = 0.05$ nm$^{-1}$, $A = 4 \times 10^{-20}$ J).
polymers provide steric stabilization.

2.3 Ferrofluids

Ferrofluids have been reported for the first time in 1938 by W. C. Elmore [23]. They are stable colloidal suspensions of magnetic single domain particles dispersed in an organic or aqueous medium [74]. These particles are often referred to as magnetic colloids or magnetic fluids. The colloidal suspensions consist of permanent magnetic moments (in contrast to magnetorheological suspensions which are formed by superparamagnetic particles of micrometric size, dispersed in a non magnetic medium). The Brownian motion keeps the particles randomly dispersed throughout the carrier in the absence of a magnetic field. The particles are coated with a surfactant to prevent clumping due to the attractive Van der Waals forces. A schematic drawing of a ferrofluid is shown in Figure 2.6. Such magnetic colloids attract more and more interest because of their behavior in a magnetic field [74], [45], [89], [44], [47].

The magnetic colloids experience besides van der Waals and electrostatic interaction a magnetic dipole-dipole interaction. Because the particles are single domain they can be considered as point dipoles with a magnetic moment proportional to the volume. In SI units,

\[ m = \frac{\pi}{6} \times M_s D^3 \]  

(2.8)

where \( M_s \) represents the saturation magnetization and \( D \) is the diameter of the particle. The magnetic interaction between two particles with magnetic moments \( \vec{m}_1 \) and \( \vec{m}_2 \) at a distance \( \vec{r}_{12} \)
Figure 2.6: Schematic representation of a ferrofluid; to prevent the particles from sticking to each other they are coated with a surfactant.

In the energetically most favorable configuration, the magnetic moments point in the same direction and lie head-to-tail.

2.4 Iron oxides

An interesting class of magnetic materials are iron oxides such as Fe₃O₄, γ-Fe₂O₃ and MO·Fe₂O₃ (where M is Mn, Co, Ni, Cu) [14], because they display ferrimagnetism. Some general properties of the iron oxides are tabulated in Appendix. Magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃) and hematite (α-Fe₂O₃) are the most common iron oxides and they are discussed in the next sections.

2.4.1 Magnetite (Fe₃O₄)

Magnetite (Fe O · Fe₂O₃) is the oldest known magnetic material [14]. At room temperature, bulk magnetite crystallizes in the inverse spinel structure² as is shown in Figure 2.7. The oxygen atoms form the close-packed face-centered-cubic (fcc) lattice with the irons atoms occupying interstitial sites [50]. Each cubic spinel contains eight oxygen (fcc) cells. The so-called A sites

²in a spinel structure the Fe³⁺ ions are located on the B sites, while the divalent ions M²⁺ on the A sites.
are characterized by tetrahedral oxygen coordination around the Fe ions and B sites which have octahedral oxygen coordination. The A sites are occupied by Fe$^{3+}$ and the B sites are occupied by equal numbers of Fe$^{2+}$ and Fe$^{3+}$. Below 851 K magnetite is ferrimagnetic with A-site moments aligned antiparallel to the B-sites. Magnetite undergoes a first-order phase transition at 120 K (Verwey transition), with a change of crystal structure, latent heat and decrease of the dc conductivity. The distribution of Fe$^{3+}$ and Fe$^{2+}$ in B sites changes from a dynamic disorder to a long-range order with an orthorhombic symmetry below 120 K [16]. At room temperature, Fe$_3$O$_4$ very easily undergoes a transformation to maghemite.

### 2.4.2 Maghemite (γ-Fe$_2$O$_3$)

The γ-Fe$_2$O$_3$ has the same spinel structure as magnetite but has no divalent ions. The magnetic Fe$^{3+}$ ions are positioned in two sublattices with different oxygen coordination. The ferrimagnetism arises from the unequal distribution of these ions in A and B sites. γ-Fe$_2$O$_3$ is still used for magnetic recording media. Maghemite has a good chemical stability and can be prepared involving low prices and cheap technology. It was found that small γ-Fe$_2$O$_3$ nanoparticles exhibit a strong exchange interaction and a magnetic training effect [61]. Recently, a low tempera-
ture spin-glass transition was found at $T = 42 \text{ K}$ [61]. In the dry state, $\gamma$-Fe$_2$O$_3$ transforms to $\alpha$-Fe$_2$O$_3$ (hematite) at temperatures ranging from 370-600°C.

2.4.3 Hematite ($\alpha$-Fe$_2$O$_3$)

The hematite has a corundum crystal structure and has an antiferomagnetical order below the Néel temperature (955 K). At 260 K a spin-flip transition occurs which is known as Morin transition (the spins of the two sublattices are not perfect parallel but slightly canted or tilted [17]). Below $T_M$ the two magnetic sublattices are oriented along the rhombohedral [111] axis. This spin canting results in a weak ferromagnetism in the (111) plane. Hematite is the most stable iron oxide.

2.5 Magnetism

2.5.1 Ferrimagnetism

The first who proposed the concept of ferrimagnetism was Néel [66]. The ferrimagnetism is characterized by the existence of two sublattices in which the magnetic moments are not the same. It occurs either because the atoms are of different elements, or because the ions have not the same charge. For example, in the case of Fe$_3$O$_4$, there is Fe$^{2+}$ in one sublattice and Fe$^{3+}$ in the other. The resulting total magnetization is the difference between the magnetization of the two sublattices which do not cancel out.

The most important ferrimagnetic materials are the so-called ferrites (oxides of iron mixed with another metal ion [12]). To gain deeper insight into the mechanism of a ferrimagnet let us examine the magnetic structure of Fe$_3$O$_4$. As illustrated above, the magnetic ions in Fe$_3$O$_4$ are arranged in tetrahedral and octahedral sites. In Figure 2.8 the Fe$^{3+}$ ions on the A and B sites are aligned anti-parallel so that the net magnetic moment comes from the Fe$^{2+}$ ions, with a magnetic moment of $4\mu_B$ per atom.

The net magnetization can have a very complicated temperature dependence. Because the magnetization of the sublattices can dominate at different temperatures, the net magnetization can be reduced to zero and change sign at a certain temperature called the compensation point [5]. In a ferrimagnet the magnetic ions experience two types of interactions [17]. The strongest is the antiferromagnetic superexchange interaction which involves the oxygen p orbital; the second one is a ferromagnetic interaction called double exchange interaction which takes place just in the case when a mixed valency is present (like in Fe$_3$O$_4$).

\footnote{The term ferrite denotes a group of iron oxides which have the general formula MO·Fe$_2$O$_3$, where M is a divalent ion.}
2.5.2 Magnetism in single-domain particles

As the size of the particle is reduced, the particle cannot longer gain a favorable energy configuration by breaking up into domains, hence it remains in a single domain state. Single-domain particles with all the spins aligned in a single direction are desirable for the applications in magnetic recording media [75]. Magnetic nanoparticles are in a single-domain state if the energy needed to create a domain wall exceeds the reduction of magnetostatic energy. The critical radius $r_c$ below which a particle acts as a single domain particle [13] was found:

$$r_c \approx 9 \frac{(AK_u)^{1/2}}{\mu_0 M_s^2}$$

(2.10)

where $A$ is the exchange constant, $K_u$ is the uniaxial anisotropy constant and $M_s$ is the saturation magnetization. According to Eq. 2.10, for magnetite with $A = 1.28 \times 10^{-11}$ J/m, $K_u = -1.1 \times 10^4$ J/m$^3$ and $\mu_0 M_s^2 = 4 \times 10^5$ J/m$^3$, a critical radius of 84 nm, at room temperature, is calculated [14]. For $\gamma$-Fe$_2$O$_3$, a critical radius of 30 nm has been estimated [13]. Thus, since there are not domain walls to move, the magnetization reversal in a single-domain particles involves the rotation of the total magnetic moment.

There are various models to explain the magnetization reversal of small particles. Stoner and Wohlfarth [76] have developed a model for the coherent rotation of the magnetization. They assume non-interacting particles with uniaxial anisotropy in which the spins are parallel and rotate at unison. Following this assumption the energy density of a single domain particle with
volume $V$ and an anisotropy $K_u$ can be written as [5]:

$$e = E/V = K_u \sin^2(\theta - \phi) - \mu_0 H M_s \cos(\theta - \phi)$$  \hspace{1cm} (2.11)

where $\phi$ is the angle between the direction of the applied field and the easy axis. $\theta$ represents the angle between the magnetization vector of the particles and the easy axis.

The magnetization can rotate also by an incoherent motion of the spins [17]. It was also reported that the magnetization in a single domain particle can reverse by macroscopic quantum tunnelling through the barrier created by the magnetic anisotropy [83].

### 2.5.3 Relaxation mechanism of ferrofluids

Two distinct rotational relaxation mechanisms may occur in ferrofluids: the Brownian (or Debye relaxation), corresponding to the rotation of the particles inside the fluid [35] and the Néel relaxation, by which the magnetic moment of the particle rotates with respect to the lattice of the particle. The Brownian relaxation is characterized by an extrinsic particle rotation and the time associated with the rotational diffusion is given by:

$$\tau_B = \frac{3V\eta}{k_BT}$$  \hspace{1cm} (2.12)

where $V$ is the hydrodynamic volume of the particle, $\eta$ represents the viscosity of the liquid carrier and $k_BT$ is the thermal energy [22]. For 12 nm Fe$_3$O$_4$ nanoparticles dispersed in water ($\eta = 0.001$ Pa·s) the rotational diffusion time has the value $\tau_B = 6.44 \times 10^{-7}$ s.

The intrinsic reversal mechanism is the Néel mechanism [17]. In this case, the magnetization may reverse the direction within the particle by overcoming an energy barrier. The relaxation time, in this case, has the expression:

$$\tau_N = \tau_0 \exp \left( \frac{E_B}{k_BT} \right) = \tau_0 \exp \left( \frac{K_u V}{k_BT} \right)$$  \hspace{1cm} (2.13)

where $\tau_0$ usually has a value of $10^{-9}$ s, $V$ is the volume of the particle and $E_B$ represents the energy barrier.

For the spherical particles with an uniaxial anisotropy the energy is [1]:

$$E = K_u V \sin^2 \theta$$  \hspace{1cm} (2.14)

where $K_u$ is the anisotropy constant and $\theta$ the angle between the easy axis and the magnetization. The energy barrier ($E_B = E_{max} - E_{min} = K_u V$) separates the two minima at $\theta = 0$ and $\theta = \pi$ corresponding to a magnetization parallel and antiparallel to the easy axis (Figure 2.9). For small particles at 300 K the energy barrier becomes comparable to the thermal energy. Thus the
magnetization will fluctuate between the two energy minima. This results in a superparamagnetic relaxation. This fluctuation of magnetization due to the thermal activation between two easy-axis orientations is called \textit{superparamagnetism}.

![Figure 2.9: Schematic illustration of the energy of a single-domain particle with uniaxial anisotropy as a function of magnetization direction. $E_B$ is the energy barrier for the rotation of the magnetization and $\theta$ is the angle between $M$ and the easy axis.](image)

The temperature dependence of the Néel-type superparamagnetic relaxation time $\tau$, can be written as [54]:

$$\tau = \tau_0 \exp \left( \frac{K_u V}{k_B T} \right)$$

(2.15)

where $k_B$ is Boltzmann’s constant and $\tau_0 = 10^{-9}$ s. Using $\tau=100$ s (typical time to observe the magnetic transitions with a SQUID-magnetometer), one obtains:

$$T_B = \frac{E_B}{25k_B} = \frac{K_u V}{25k_B}$$

(2.16)

where $T_B$ is called the blocking temperature. Below $T_B$ the free movement of the spins is blocked by the anisotropy, while above $T_B$ the thermal energy will disrupt the bonding of the total moment of the particles and the system turns to be superparamagnetic.

For example, according to Eq. 2.16 the magnetite particles (assuming that they possess just uniaxial anisotropy) with 12 nm diameter will be blocked at 29 K, while the magnetite particles with 20 nm diameter at 132 K. At this point we should mention that the determination of the blocking temperature according to Eq. 2.16 does not work for all the systems. This equation
is valid for individual particles or a system of non-interacting particles with the same size and anisotropy. If the particles are not monodisperse, the distribution of particle sizes results in a blocking temperature distribution. Magnetic interactions between nanoparticles have a strong influence on the superparamagnetic relaxation, as well [75].

2.6 Magnetic anisotropy

Magnetic anisotropy energy is the energy difference between two directions of the magnetization with respect to a crystallographic axis [12]. The total magnetization of a system will prefer to lie along a certain direction called the easy axis. The energetic difference between the easy and hard axis results from two microscopic interactions only: the spin-orbit interaction and the long range dipolar coupling of magnetic moments. The spin-orbit coupling is responsible for the intrinsic (magnetocrystalline) anisotropy, surface anisotropy, and magnetostriction, while the dipole-dipole coupling is responsible for shape anisotropy [36]. In the following we discuss three contributions to magnetic anisotropy: magnetocrystalline anisotropy, shape anisotropy and surface anisotropy.

2.6.1 Magnetocrystalline anisotropy

The magnetocrystalline anisotropy is related to the crystal symmetry of the material and, originates from the spin-orbit interaction. The energy (magnetocrystalline anisotropy energy) necessary to reverse the magnetization from an easy direction to a hard direction depends on the crystal symmetry.

For crystals with cubic symmetry, the anisotropy energy can be written in terms of the direction cosines \((\alpha_1, \alpha_2, \alpha_3)\) of the internal magnetization with respect to the three cube edges [12]:

\[
E^{\text{cubic}}_a = K_1 V (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 V \alpha_1^2 \alpha_2^2 \alpha_3^2 + ... \tag{2.17}
\]

where \(\alpha_i\) are defined through \(\alpha_1 = \cos \alpha, \alpha_2 = \cos \beta, \alpha_3 = \cos \gamma, \alpha, \beta, \gamma\), being the angles between the magnetization and the crystal axes. \(K_1, K_2, ...\) are the anisotropy constants and they are temperature dependent [36].

In the case of hexagonal symmetry the anisotropy energy can be expressed as:

\[
E^{\text{hexagonal}}_a = K_1 V \sin^2 \theta + K_2 V \sin^4 \theta + ... \tag{2.18}
\]

where \(\theta\) is the angle between the magnetization and the \(c\) axis and \(V\) is the particle volume. This kind of anisotropy is usually referred to as uniaxial anisotropy.
2.6.2 Shape anisotropy

Another source of magnetic anisotropy results from the shape of the specimen. In the case of a nonspherical sample it will be easier to magnetize along a long axis than along a short direction. This is due to the demagnetizing field, which is smaller in the long direction, because the induced poles at the surface of the sample are further apart. For a spherical sample there is no shape anisotropy. The magnetostatic energy density can be written as [17]:

\[ E = \frac{1}{2} \mu_0 N_d M^2 \]  

(2.19)

where \( N_d \) is a tensor and represents the demagnetized factor (which is calculated from the ratios of the axis). \( M \) is the saturation magnetization of the sample. Demagnetizing factors for the general ellipsoid were calculated by Osborn [68]. For example the shape anisotropy energy of an uniform magnetized ellipsoid is [36]:

\[ E = \frac{1}{2} \mu_0 V (N_x M_x^2 + N_y M_y^2 + N_z M_z^2) \]  

(2.20)

where the tensors satisfied the relation : \( N_x + N_y + N_z = 1 \).

2.6.3 Surface anisotropy

In small magnetic nanoparticles a major source of anisotropy results from surface effects [58], [38]. This can be easily understood, if one considers that 10 mg of a powder of 3 nm Co particles contain roughly 5 mg of Co surface atoms. Hence, in a nanoscale particle the ratio between surface atoms and bulk atoms is large (~50% for 3 nm) and the surface effects can dominate the magnetic properties of the nanoparticles [54]. The surface anisotropy is caused by the breaking of the symmetry and a reduction of the nearest neighbor coordination. The protective shell or ligand molecules which cover the small particles play an important role as well, leading to a change of the electronic environment on the particles surface.

Phenomenologically, the effective magnetic anisotropy for a thin film, can be described as the sum of a volume and a surface terms [53]:

\[ K_{eff} = K_v + \frac{2}{t} K_s \]  

(2.21)

where \( t \) is the thickness of the film, \( K_s \) is the surface contribution, and \( K_v \) is the volume contribution consisting of magnetocrystalline, magnetostriction and shape anisotropy. In the case of small spherical particles with diameter \( d \) the effective magnetic anisotropy can be expressed as:

\[ K_{eff} = K_v + \frac{S}{V} K_s = K_v + \frac{6}{d} K_s \]  

(2.22)

where \( S = \pi d^2 \) and \( V = \frac{1}{6} \pi d^3 \) are the surface, respective the volume of the particle [6].
Chapter 3

Experimental techniques

3.1 Ferromagnetic resonance

Ferromagnetic resonance (FMR) is a very powerful technique for the investigation of the magnetic properties of magnetic samples. It is a very sensitive technique, where a number of $10^{10}$ paramagnetic moments can be detected. The energy resolution for the determination of the magnetic anisotropy is on the order of $0.1 \, \mu eV$ [36].

The principle of ferromagnetic resonance is similar to electron spin resonance (ESR) and relies on the transition between Zeeman components of the electronic levels. The splitting at a given external magnetic field yields information on the magnetic moment of the atoms or ions involved in the resonance transitions. The illustration of the Zeeman splitting is shown in Figure 3.1. However, one important phenomenon will distinguish FMR from ESR, namely that in FMR we are not dealing with individual isolated atoms, but with atoms which are coupled together by the exchange interaction. In a magnetic resonance experiment, the magnetization of the sample precesses around the direction of a static local magnetic field $B_0$, at the Larmor frequency. The energy of a transverse magnetic field will be absorbed when the rf-frequency is equal to the Larmor frequency. In this case the resonance condition can be expressed as

$$h \nu_0 = g \mu_B B_0$$

where $h$ is Plank’s constant, $\nu_0$ is the resonance frequency, $g$ is the Landé factor $^1$ (also called the spectroscopic splitting factor), $B_0$ is the external applied magnetic field and $\mu_B$ is the Bohr magneton. This resonance condition (Eq. 3.1) is valid just for the paramagnetic regime. For a ferromagnet, it is not only the external Zeeman field that affects the resonance condition; the anisotropy fields and exchange fields play an important role as well.

In order to derive the resonance condition for ferromagnetic samples, one has to solve

---

$^1$for a free electron $g = 2$ and for pure orbital momentum $g = 1$. 
Figure 3.1: a) Energy level of a single free electron in a magnetic field $B_0$. In an external magnetic field, the electron from the lower energy level will be excited into the upper one and it will absorb $h\nu_0 = E_2 - E_1 = g\mu_B B_{\text{res}}$. b) The precession of the magnetization of the sample.

the Landau-Lifshitz-Gilbert equation, which describes the motion of the magnetization vector around the direction of an effective static magnetic field (see Figure 3.1 b) [29]:

$$\frac{d\vec{M}}{dt} = -\gamma (\vec{M} \times \vec{B}_{\text{eff}}) + \alpha \left( \frac{\vec{M}}{M} \times \frac{d\vec{M}}{dt} \right)$$

(3.2)

where $\alpha$ is the dimensionless damping parameter and $\gamma$ is the gyro-magnetic ratio defined as $\gamma = g\mu_B/h$. For a free electron $\gamma = 1.7588 \times 10^7$ Hz/Oe. The damping parameter $\alpha$ in SI system is related to the Gilbert damping factor in CGS units by the equation:

$$\alpha = \frac{4\pi G}{\mu_0 M \gamma}$$

(3.3)

$B_{\text{eff}}$ is a sum of the driving rf-microwave magnetic field, the external magnetic field, the demagnetization field and the magnetocrystalline anisotropy field.

Usually, the equation of motion is expressed in terms of the total free energy density $F$, instead of effective fields [29], [59].

$$dF = \vec{B}_{\text{eff}} \cdot d\vec{M}$$

(3.4)
The contribution to the free energy density, in an external magnetic field, is coming from:

\[ F = F_{Zee} + F_{dem} + F_{anis} + F_{ex} \]  \hspace{1cm} (3.5)

where \( F_{Zee} \) describes the energy contribution of the external magnetic field, \( F_{dem} \) is the energy of the demagnetizing field of the sample, \( F_{anis} \) depends on the crystalline structure of the investigated sample (and it is caused by the spin-orbit coupling) and \( F_{ex} \) represents the energy of exchange interaction [29], [36]. The easy direction of the magnetization can be determined by the minimum of the free-energy density. For example, for a thin film with tetragonal symmetry and an additional in plane uniaxial anisotropy \( K_{2\|} \), the free energy per unit volume has the expression [59]:

\[
F = -MH_{res} \cos(\theta - \theta_H) + (2\pi M^2 - K_{2\perp}) \cos^2 \theta - 1/2 K_{4\perp} \cos^4 \theta \\
- 1/8 K_{4\perp}(3 + \cos 4\varphi) \sin^4 \theta - K_{2\|} \cos^2(\varphi - \varphi_H) \sin^2 \theta \]  \hspace{1cm} (3.6)

where \( \theta \) and \( \theta_H \) are the polar angles of the magnetization and the external magnetic field is measured from the film to normal and \( \varphi \) and \( \varphi_H \) are the azimuthal angles measured with respect to the [100] in-plane direction. \( K_{2\perp} \) is the out-of-plane anisotropy constant and \( K_{4\|} \) is the in-plane anisotropy constant. \( K_{4\|} \) and \( K_{4\perp} \) are the fourfould in-plane and out-of-plane anisotropy constants respectively. \( M \) is the magnetization of the sample and \( H_{res} \) is the resonance field.

The resonance conditions derived from Eq. 3.6 neglecting \( K_{2\|} \) is written for polar geometry in the form:

\[
\left( \frac{\omega}{\gamma} \right)^2 = \left[ H_{res} \cos(\theta - \theta_H) + \left( M_{eff} + \frac{K_{4\perp}}{M} - \frac{K_{4\|}}{2M} \right) \cos 2\theta + \left( \frac{K_{4\perp}}{M} + \frac{K_{4\|}}{2M} \right) \cos 4\theta \right] \\
\times \left[ H_{res} \cos(\theta - \theta_H) + \left( M_{eff} + \frac{K_{4\perp}}{M} - \frac{K_{4\|}}{2M} \right) \cos^2 \theta + \left( \frac{2K_{4\perp}}{M} + \frac{K_{4\|}}{M} \right) \cos 2\theta - \frac{2K_{4\|}}{M} \right] \]  \hspace{1cm} (3.7)

For azimuthal geometry one finds the follow resonance condition:

\[
\left( \frac{\omega}{\gamma} \right)^2 = \left[ H_{res} \cos(\varphi - \varphi_H) + \frac{2K_{4\|}}{M} \cos 4\varphi \right] \left[ H_{res} - M_{eff} + \frac{2K_{4\|}}{2M}(3 + \cos 4\varphi) \right] \]  \hspace{1cm} (3.8)
A typical FMR spectra is shown in Figure 3.2. The spectra was recorded at 300 K, 9.51 GHz for 12 nm Fe$_3$O$_4$ nanoparticles. The derivative of the absorptive part of the complex rf susceptibility is recorded as a function of the applied magnetic field at constant microwave frequency [36].

From a careful analysis of the width and shape of the resonance information about the magnetic anisotropy, the relaxation of the magnetization, the g-factor, Curie temperature, and magnetocrystalline anisotropy coefficients can be extracted [62], [79]. We denote by $B_{\text{res}}$ the resonance field (the zero crossing of the absorption derivative) and by $\Delta B_{\text{pp}}$ the peak-to-peak linewidth (the field between the minimum and the maximum of the absorption derivative). The magnitude of $B_{\text{res}}$ and its dependence on the orientation of the field, the sample thickness and the temperature provides information about the magnetic anisotropy of the sample.

For a ferromagnetic sample the resonance field is shifted from its paramagnetic value by the intrinsic anisotropy fields resulting from different magnetic anisotropies. Thus a precise determination of the easy axis of the magnetization is possible.

From multi-frequency measurements the $g$-factor is determined. In 3d elements, the $g$-factor is
related to the ratio of the orbital moment to the spin momentum, via:

$$\frac{\mu_l}{\mu_s} = \frac{g}{2} - 1$$  \hspace{1cm} (3.9)

The peak-to-peak resonance linewidth, $\Delta B_{pp}$, yields information about the relaxation rate of the magnetization. Two mechanisms are responsible for this relaxation, namely the intrinsic damping of the magnetization and the magnetic inhomogeneities of the sample [36]. The inhomogeneous contribution is caused by the inhomogeneous local field distribution. The frequency-dependent resonance linewidth can be expressed as [70]:

$$\Delta B_{pp}(\omega) = \Delta B_{inhom} + \Delta B_{hom} = \Delta B_{inhom} + \frac{2}{\sqrt{3}} \frac{G}{\gamma^2 M} \omega$$  \hspace{1cm} (3.10)

where the term $\Delta B_{inhom}$ is due to the magnetic inhomogeneities in the magnetic sample. The second term describes the intrinsic damping of the precession of the magnetization $M$, and $\gamma$ is the gyromagnetic ratio. The Gilbert parameter has values on the order of $10^{-8}$ s$^{-1}$. By making multi-frequency measurements it is possible to determine the Gilbert damping parameter (it is obtained from the slope of the frequency variation of the peak-to-peak line width of the FMR signal). The intensity of the absorption signal can be used to estimate the magnetization of the sample. For signal derivatives with a Lorentzian lineshape the intensity is proportional to the product: $A \times \Delta B_{pp}^2$ [36]. In order to get a correct value of the magnetization, one needs a perfect calibration of the FMR spectrometer because the amplitude of the signal is very sensitive to the location of the sample within the cavity.

### 3.2 Atomic force microscopy

Part of the present work has been carried out by using a scanning force microscope in the AFM mode (atomic force microscopy) and in the MFM mode (magnetic force microscopy). Both a "Q-Scope™ 250" from Quesant Instrument Corporation and a "Dimension 3000" from Digital Instruments were utilized to perform experimental studies.

#### 3.2.1 Basic principles

The scanning force microscope has been invented by Binning et al. in 1986 [2]. Scanning force microscopy measures the forces acting between a fine tip and a sample. Figure 3.3 schematically shows the basic concept of scanning force microscopy. The tip is attached to the free end of a cantilever and is brought very close to a surface. Attractive or repulsive forces resulting from interactions between the tip and the surface will cause a positive or negative bending of the
Cantilever which is detected by means of a laser beam which is reflected from the back side of the cantilever.

Forces of the order of $10^{-13}$ to $10^{-14}$ N can be measured by using a scanning force microscope with a lateral resolution of a few nm down to atomic resolution.

### 3.2.2 Detection techniques

There are several techniques which allow to detect the very small deflections of the cantilever: electron tunnelling, optical interferometry, capacitance method and laser beam deflection [85]. Within the instrumentation used, the laser beam deflection technique is utilized (Figure 3.4). The beam from a laser diode is reflected from the back size of the cantilever, onto a photodiode arrangement and the output signal of the photodiode is directed to a differential amplifier. Bending of the cantilever generates a large signal in one photodiode as compared to the other photodiode. The difference average normalized to the sum is proportional to the deflection of the cantilever. Using this detection method a resolution smaller than 1 Å can be achieved.
3.2.3 Modes of operation

- **Contact mode**
  In the so-called contact-AFM mode, the tip makes soft "physical contact" with the surface of the sample. Due to e.g. short range repulsive van der Waals forces the cantilever is bend away from the surface. The deflection of the cantilever $\Delta x$ is proportional to the force acting on the tip, via Hook’s law, $F = -k \Delta x$, where $k$ is the spring constant of the cantilever. In contact-mode the tip either scans at a constant small height above the surface or under the condition of a constant-force. In the constant-height mode the height of the tip is fixed, whereas in the constant-force mode the deflection of the cantilever is fixed and the motion of the scanner in z-direction is recorded. By using contact-mode AFM, even "atomic resolution" images are obtained.

- **Tapping mode**
  The forces measured by AFM can be classified into long-range forces and short-range forces. The first class dominates when we scan at large distances from the surface and they can be Van der Waals forces, capillary forces (due to the water layer often present in an ambient environment). When the scanning is in contact with the surface the short range forces are very important, in particular the quantum mechanical forces.
  In tapping mode-AFM the cantilever is oscillating close to its resonance frequency. It is brought close to the surface so that at the bottom of its travel it lightly hits the surface periodically. An electronic feedback loop ensures that the oscillation amplitude remains constant, such that a
constant tip-sample interaction is maintained during scanning. By using this mode of operation a lateral resolution of 1-5 nm can be achieved. Importantly, because lateral forces (for example, friction forces) are almost fully eliminated, the operation of an AFM in the tapping mode results in less damage to the sample than in contact mode.

3.3 Magnetic force microscopy

For magnetic force microscopy (MFM) investigations an AFM-tip is coated with a ferromagnetic thin film, which in most cases is a CoCr film of ~50 nm thickness. MFM senses surface magnetic fields of magnetic samples with a lateral resolution of ~40 nm. A simple model for MFM is shown in Figure 3.5a) [85]. In MFM a ferromagnetic tip is scanned across a sample and the interaction of the magnetic tip with the sample stray field is detected. The magnetic tip is usually magnetized in a direction perpendicular to the sample surface. The typical interaction between the tip and the sample stray field is schematically shown in Figure 3.5a) for a sample with a magnetization in plane. The resulting force upon the magnetic tip can be either repulsive, translated into a bright image contrast, or attractive, translated into a dark image contrast. Thus, the magnetic transitions in Figure 3.5 b) will appear as either dark or bright stripes, depending on whether the tip magnetization is oriented parallel (dark) or antiparallel (bright) to the direction of the stray field. In a simple model, the tip is approximated by a point-dipole with a magnetic moment $m$.

The resulting force upon the tip is [85]:

$$ F = \nabla(m \cdot B) $$

(3.11)

where $B$ is the magnetic induction outside. When the tip is scanned across the surface of the sample only vertical forces on the tip will be detected, since the tip is magnetized in z-direction. Forces in z-direction are proportional to the field gradient in z direction:

$$ F_z = m_z \frac{dB_z}{dz} $$

(3.12)

Minimum forces of down to $10^{-13}$ N can be detected [85]. Forces of magnetic origin acting upon the tip will shift the resonance frequency of the cantilever. They also modify the amplitude and the phase of the tip oscillation. Thus, in MFM either the amplitude of the cantilever vibration, the phase shift, or the shift in resonance frequency is measured while the tip is scanned across the surface.
CHAPTER 3. EXPERIMENTAL TECHNIQUES

Figure 3.5: A simple model for MFM. a) A magnetic tip is used to detect the magnetic stray field from the sample; b) the MFM contrast during scanning of an in-plane magnetized sample.

By using the so-called "lift-mode" MFM allows to correlate the magnetic properties of the sample with its topographic features. In lift-mode the tip passes twice over each scan-line. During the first scan the tip is located very close to the surface. This yields information about the topography of the surface (AFM). In the second scan the tip is moved along the same scan-line, but at a larger tip to sample distance (typically 50-90 nm). During this scan the respective changes of the amplitude are related to only the magnetic properties of the sample. Figure 3.6 shows typical AFM (left) and MFM (right) images of a magnetic disk. The magnetic image was obtained at a lift height of 90 nm. It clearly shows alternating black and white lines which correspond to magnetic stray fields from bit-transitions directed in +z and -z directions, respectively.

Thus, MFM allows the determination of the direction of the magnetization within the sample, once the direction of the tip-magnetization is fixed. This information can be related to the topography of the sample surface. Any quantitative information about the sample magnetization or stray-field can only be obtained in special sample geometries and with calibrated MFM-tips [82].
Figure 3.6: A topographic (a) and a lift-mode image (b) of a magnetic disk sample. The images have been recorded with the AFM -"Dimension 3000".
Chapter 4

Characterization of nano- and micron-size particles

4.1 Characterization of Fe$_3$O$_4$

4.1.1 Synthesis of magnetite nanoparticles

In this section the preparation of the nanoscale Fe$_3$O$_4$ particles is discussed. The magnetite nanoparticles used in the present work were prepared by M. Hilgendorff at Hahn-Meitner-Institute in Berlin. There are two important steps in synthesizing a ferrofluid which one should take into account. The first one ensures the chemical stability of the magnetic nanoparticles, and the second one disperses the nanoparticles into a liquid carrier. Surfactants are added during the synthesis of ferrofluids in order to overcome their attractive tendencies.

In our case, the magnetite nanoparticles are synthesized in water and are tetrabutylammonium hydroxide-stabilized. The synthesis procedure of magnetite nanoparticles is as follow: a solution of 50 mL 1-propanol and 8 mL tetrabutylammoniumhydroxide was deaerated for 45 min using N$_2$. Following this, 0.3244 g of FeCl$_3$ was added to the solution and heated to reflux while stirring with a magnetic stirrer. After that 0.1988 g of FeCl$_2$·4H$_2$O were added to this solution and heated under N$_2$ reflux while stirring with a magnetic stirrer. The two solutions (while still hot) were then mixed rapidly and heated to reflux for 30 min. After cooling to room temperature, the black-brown colloidal particles were collected using a permanent magnet and separated from liquid. The colloid was redispersed in 100 mL deaerated ethanol, sonificated for 10 min, and separated again from the liquid. Finally, the magnetite particles were redispersed in 100 mL H$_2$O to give a negatively charged colloidal solution. Electrophoresis measurements showed a $\xi$ potential of about - 30 mV for magnetite nanoparticles [9]. At the end, a colloidal solution of $\approx 1 \times 10^{15}$ particles mL$^{-1}$ was obtained.
The structural and magnetic characterization of these 8-15 nm in diameter Fe$_3$O$_4$ nanoparticles are presented in the following sections.

### 4.1.2 Structural investigations of Fe$_3$O$_4$ nanoparticles

It is well known that the iron forms several stable iron oxides, e.g. Fe$_3$O$_4$, $\alpha$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$, FeO. In order to distinguish what type of iron oxide is present in our nanoparticles we have investigated them by various techniques like X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM). The results are presented below.

The particle-size distribution and morphology was examined by TEM imaging. Figure 4.1 a) shows a TEM micrograph of magnetite nanoparticles while Figure 4.1 b) represents a HRTEM for the same particles. We can see that the particles are well isolated, with spherical and facetted shape. The average particle size is about 12 nm, ranging from 8 to 15 nm. Based on the TEM images we have represented the size distribution of our magnetite nanoparticles in Figure 4.2. The Fourier transformation reveals the typical lattice plane for magnetite ($a = 8.39$ Å). Calculating the number of particles with the corresponding lattice planes found in HRTEM measurements, we can argue that there is about 20% $\gamma$-Fe$_2$O$_3$ in our nanoparticles.

![Figure 4.1](image)
Figure 4.2: The size distribution of the Fe$_3$O$_4$ nanoparticles.

Figure 4.3: X-ray spectra of the magnetite nanoparticles; the main peaks for Fe$_3$O$_4$ are indicated by arrows.
Figure 4.3 shows the XRD pattern for the magnetite powder nanoparticles. The measurements were done with monochromated CoK$_\alpha$ radiation. The peaks (220), (311), (400), (422), (511), (440) correspond to the face centered cubic phase of Fe$_3$O$_4$. The x-ray diffraction patterns for different iron oxides are presented in appendix A4. One can see that $\gamma$-Fe$_2$O$_3$ has an x-ray diffraction pattern that is almost identical to the Fe$_3$O$_4$. The additional peaks associated to $\gamma$-Fe$_2$O$_3$ ((213), (210) (113); see appendix) are not distinguishable in Figure 4.3. Thus, based on this measurement one cannot rule out the existence of $\gamma$-Fe$_2$O$_3$ in our sample. However, it is clear that we do not have $\alpha$-Fe$_2$O$_3$ in our nanoparticles.

Combining TEM data analyzes with X-ray information, the assumption that there is a content of 20% of $\gamma$-Fe$_2$O$_3$ in our nanoparticles is reasonable.

Further, x-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) were used to investigate the structure of magnetite nanoparticles, as well. These two techniques are the most widely used core electron spectroscopies. Figure 4.4 represents an illustration of the principle for each technique. In XAS (Figure 4.4 a), an electron is excited from the core level to an empty valence state while in XPS the photons interact with the atoms by the photoelectric effect, causing electrons to be emitted.
The XAS and XPS measurements were done at beam line D1011 at the Max-Laboratory synchrotron facility in Lund, Sweden. This beam line utilizes bending radiation in the energy range of 20-1500 eV. The sample was prepared as follow: 8 µL very concentrated colloidal magnetite solution, was dried on the 5 × 5 mm² Si/Cr(20 Å)/Au(1040 Å) substrate in the presence of an in plane, applied magnetic field of 0.4 T.

The XAS measurements were performed with linear polarized light at normal incidence and room temperature. The spectra were recorded by means of total electron yield detection. This detection mode makes XAS a surface sensitive method with a probe depth of about 20 Å. The measurements were done under ultrahigh vacuum with a base pressure of about 1.1 × 10⁻⁹ mbar. At that time it was not possible to measure the I₀ section, so we could not normalize the spectra to the flux of the photons. Because of this just a qualitative interpretation of the XAS spectra can be given.

In a typical XAS spectrum the absorption is measured as a function of energy of the photon radiation. As we can see in the absorption spectra (see Figure 4.6) there are two main peaks which correspond to 2p³/₂ → 3d (L₃ edge) and 2p¹/₂ → 3d (L₂ edge) transitions. In principle, the total intensity of the peaks is proportional to the number of empty 3d valence states.

First, in order to observe the major absorption edges in our sample an extended energy scan has been performed. The spectra were recorded in the energy range from 80 eV to 1200 eV at room temperature and normal incidence. In Figure 4.5 one can see clearly the very pronounced Fe L-edge and O K-edge. The Au N-edge peak is due to the substrate which was used. The broad peak at 138 eV is an artificial feature due to the shape of the grating in the monochromator which makes the light "more linear" at high energy values than at very low energy values. If it would be an element edge, this feature should be sharper.

The second step was to scan at the Fe L-edge. As we can see from Figure 4.6 a, b), the XAS spectra for magnetite nanoparticles at the Fe edge yield clearly the existence of the oxidic environment. The indication that we are dealing with an oxide is the multiplet or fine structure, which is clearly visible at both edges. This multiplet structure is due to the fact that the empty oxide states are more localized than metal states and their energies are determined by crystal field and multiplet effects. Multiplet effects arise from the spin and orbital momentum coupling of different 3d valence holes (or electrons) in the electronic ground state, and from coupled states formed after x-ray absorption between the 3d valence holes and the 2p core hole.

The next task is to establish if this oxidation state can be identified as magnetite. Two arguments have to be considered in order to proof that we have mostly Fe₃O₄ in our sample. First, the peak at 709.7 eV (see Figure 4.6) corresponds to magnetite, as it was found also in many other works [32], [52]. The second proof is the shift of the L₃ intensity (the difference between the oxide L₃
Figure 4.5: Overview XAS spectrum. The absorption edges of Fe, O, Au, C are indicated.

Figure 4.6: Fe $L_{3,2}$-edges X-ray absorption spectra for magnetite nanoparticles (a); The fine structure of Fe-$L_3$ edge (b); the arrows show the oxide peak (2) and the metallic peak (1).
maximum and the metal L₃ maximum). We observed a value of 1.4 eV which is in a very good agreement with the one reported by Regan et al. [32]. This can be seen in Figure 4.6 b) which is an expanded scale of Fe-L₃ edge. For comparison, the XAS spectra of two other iron oxides, FeO and α-Fe₂O₃, are shown in Figure 4.7, as reported in [32]. For α-Fe₂O₃ a shift of 1.7 eV of the Fe-L₃ peak intensity was obtained. FeO oxide yields no shift of the Fe-L₃ peak intensity.

\[ E = h \nu - E_B - \phi \]  \hspace{1cm} (4.1)

where \( h \nu \) is the incident photon energy, \( E_B \) is the binding energy and \( \phi \) is the work function. The electron binding energies depend on the chemical environment of the atom. XPS is therefore useful to identify the oxidation state and the presence of ligands of an atom. Every spectrum was calibrated by determining the zero of the binding energy scale from the measurement of the Fermi edge of a Au reference sample. In Figure 4.8 the XPS spectra for
Fe\textsubscript{2p}, Fe\textsubscript{3p}, and O\textsubscript{1s} core-levels are shown. All the spectra were taken at a pass energy of 200 eV. Prior to the photoemission experiments the sample was sputtered for 95 minutes, with an acceleration voltage 3 kV, current 5 µA and Ar pressure 2 × 10\textsuperscript{-5} mbar, in order to remove the surface contamination due to the exposure to air.

![Figure 4.8](image)

Figure 4.8: XPS Fe\textsubscript{2p}, Fe\textsubscript{3p}, O\textsubscript{1s} core-level spectra for the magnetite nanoparticles.

For Fe 2p spectra, the excitation energy was 1270 eV, hence, we are bulk-sensitive. The kinetic energy distribution for Fe 2p electrons is shown in Figure 4.8 a). The binding energy of about ∼708 eV for Fe 2p \textsubscript{3/2} and ∼721 eV for Fe 2p\textsubscript{1/2} are observed. The difference between the 2p\textsubscript{3/2} peak and 2p\textsubscript{1/2} peak is 13.2 eV. The Fe 3p peak has a binding energy of ∼53.9 eV (Figure 4.8b)). To excite the Fe 3p electrons we used an energy of 703 eV. O 1s binding energy is represented in Figure 4.8 c). One can distinguish a main peak at 527.6 eV and a shoulder at 528.8 eV. A theoretical and an experimental work on the XPS investigations in various iron oxides has been done by T. Fujii et al. [31]. They claim that by doing XPS one can distinguish between Fe\textsuperscript{2+} and Fe\textsuperscript{3+} ions in the octahedral sites. For the magnetite they found the main peak of Fe 2p (2p\textsubscript{3/2}) at 709 eV (which is characteristic for the formation of Fe\textsuperscript{2+} ions) and the Fe 2p\textsubscript{1/2} peak at 722 eV which is in a good agreement with our results. For the other two iron oxides the following values of the binding energy were found at the main peak Fe 2p\textsubscript{3/2}: for γ-Fe\textsubscript{2}O\textsubscript{3} the binding energy of about 710.7 eV and for α-Fe\textsubscript{2}O\textsubscript{3} at 710.9 eV. The differences in XPS spec-
tra for the iron oxides arise from the different environment of the iron ions and different type of iron ions. For example, in $\gamma$-Fe$_2$O$_3$, the Fe$^{3+}$ ions occupy both octahedral and tetrahedral sites. In the case of $\alpha$-Fe$_2$O$_3$, all the Fe$^{3+}$ ions occupy octahedral sites while in Fe$_3$O$_4$ one-third are Fe$^{2+}$ in octahedral sites, one-third are Fe$^{3+}$ ions in octahedral sites and the remaining being Fe$^{3+}$ in tetrahedral sites. Another interesting aspect in the XPS spectra of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ is a satellite structure, visible between the Fe 2p$_{3/2}$ peak and Fe 2p$_{1/2}$ peak [31]. This satellite peak is not present in the XPS spectrum of magnetite, which is in agreement with our results, as well.

In conclusion, the above XAS and XPS spectra can be used as fingerprints to identify the phase of magnetite in our nanoparticles. Moreover, the X-ray absorption and X-ray emission spectroscopy measurements proof the feasibility of the core-level investigations of nanoscale particles under ultra-high-vacuum conditions and after bakeout.

4.1.3 Magnetic properties

The magnetic properties of the magnetite nanoparticles were investigated by means of SQUID-magnetometry, ferromagnetic resonance (FMR) and magnetic force microscopy (MFM).

SQUID-magnetometry

For the magnetometry measurements two types of SQUID devices have been used: a home-build and a commercial one. The commercial SQUID was used in the temperature range of 5 to 300 K with a maximum applied field of 5 T.

With the home-build SQUID-magnetometer (see for details [72]) the $B_z$ component of the dipolar magnetic stray field of the in-plane magnetized sample is measured at a constant height as a function of the lateral position of the SQUID sensor over the sample (the measurement geometry is shown in chapter 4, Figure 4.20). A stray-field of 24 nT, at room temperature, for the magnetite nanoparticles deposited on a quartz substrate ($4 \times 4$ mm$^2$) and magnetized in plane in 1.2 T was measured. This shows that the magnetite nanoparticles are remanently magnetized at room temperature. The distance between the SQUID sensor and the sample plane is 6.2 mm.

By using a model of an homogeneous in-plane magnetized film (a detailed description of this model is given in the next section), a remanent magnetization, $M = 0.11$ T (for a film thickness of 24 nm) is estimated. This value is larger than the remanence magnetization of bulk magnetite $M_{r,bulk} = 0.024$ T, at 300 K ($M_{s,bulk} = 470$ Oe; $M_r/M_s = 0.52$ [16]; for a system of noninteracting, randomly oriented single-domain magnetite particles one expects $M_r/M_s = 0.5$ [41]). Possible reasons for this discrepancy are the lack of the correct determination of the sample thickness and the deviation from an homogeneous in-plane magnetized film. One has to take in account that particles are not monodisperse and have not the same shape.
Further, in Figure 4.9, the magnetization curves (taken with a commercial SQUID) of the Fe$_3$O$_4$ nanoparticles are shown. The diamagnetic contribution from the substrate was subtracted. The sample is prepared by drying in air a 5 µl highly concentrated solution of water-based Fe$_3$O$_4$ nanoparticles on a SiO$_2$ substrate. The values of the saturation magnetization, the coercive field and remanence magnetization were extracted from the hysteresis loops and are presented in Table 4.1. At room temperature, the nanoparticles yield a very small remanence magnetization. The coercivity decreases with increasing temperature (from 240 Oe at 5 K to 20 Oe at 300 K). Possible explanations for the reduced magnetization are: i) the presence of the γ-Fe$_2$O$_3$ in our nanoparticles (γ-Fe$_2$O$_3$ has a smaller saturation magnetization than magnetite; see appendix A.3); ii) the presence of the surfactant layer on the surface of the nanoparticles.

By simulating the experimental magnetization curves, at 5 K, an effective anisotropy constant, $K_{\text{eff}} = 0.21 \times 10^5$ J/m$^3$ could be determined (see Figure 4.10). To simulate, the Landau-Lifshitz-Gilbert equation is solved for a system of 1600 interacting particles, with an average diameter of 12 nm. A filling factor of 0.8 is used. It is considered that the effective field applied to each particle is given by the sum of the interaction field and the external magnetic field. A detailed description of the model is given in [84]. The calculated effective anisotropy constant is larger than the first-order magnetocrystalline anisotropy constant reported for bulk magnetite at 5 K (see Table 4.2). This result suggests that besides magnetocrystalline anisotropy, other anisotropies contribute to the total anisotropy of the particles. Similar investigations on magnetite nanoparticles with 4 nm diameter yield an anisotropy constant of $K_{\text{eff}} = 0.4 \times 10^5$ J/m$^3$ at 5 K. [41].

Several contributions to this magnetic anisotropy are important, for example, the effective magnetic anisotropy of the individual particle and the interaction between particles. The effective magnetic anisotropy of the individual particles includes shape anisotropy (a spread of demagnetizing fields due to a spread of particle shapes), volume and surface anisotropy contributions. The only interaction between the coated magnetite nanoparticles is the long-range dipolar magnetic coupling. Because we are dealing with coated-nanoparticles the existence of an exchange interaction between nanoparticles is ruled out (due to the surfactant layers the particles are not able to come together in order to overlap the orbital of the surface atoms). One can assume that the magnetic anisotropy of each particle averages to zero due to a random orientation of the crystallographic axes and a spherical shape. In this case, the enhancement of the anisotropy is mainly related to the effect of dipolar interactions between nanoparticles. Note that, the first-order magnetocrystalline anisotropy constant for the bulk magnetite has a negative value at room temperature and passes through positive values around 120 K (see Table 4.2). The reason for this change of sign of the magnetocrystalline anisotropy is the so-called Verwey transition,
when a phase transition from the cubic to monoclinic symmetry occurs [50].

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>5</th>
<th>120</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_c$ (Oe)</td>
<td>240</td>
<td>85</td>
<td>20</td>
</tr>
<tr>
<td>$M_r$ (Am$^2$)</td>
<td>$2.04 \times 10^{-7}$</td>
<td>$1.3 \times 10^{-7}$</td>
<td>$3.24 \times 10^{-8}$</td>
</tr>
<tr>
<td>$M_s$ (Am$^2$)</td>
<td>$4.25 \times 10^{-7}$</td>
<td>$4.13 \times 10^{-7}$</td>
<td>$3.7 \times 10^{-8}$</td>
</tr>
<tr>
<td>$M_r/M_s$</td>
<td>0.48</td>
<td>0.31</td>
<td>0.087</td>
</tr>
</tbody>
</table>

Table 4.1: Coercivity, remanence and saturation magnetization for the magnetite nanoparticles at 5, 120 and 300 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_1 \times 10^5$ (J/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-0.11</td>
</tr>
<tr>
<td>154</td>
<td>-0.063</td>
</tr>
<tr>
<td>144</td>
<td>-0.037</td>
</tr>
<tr>
<td>114</td>
<td>0.054</td>
</tr>
<tr>
<td>5</td>
<td>0.11-0.13</td>
</tr>
</tbody>
</table>

Table 4.2: First order magnetocrystalline anisotropy constant for bulk magnetite at various temperatures [41], [57].
Figure 4.9: Hysteresis loops measured at three temperatures for 5 µl Fe₃O₄ nanoparticles deposited on a quartz substrate.

Figure 4.10: Experimental (squares) and simulated (circles) magnetization loops, at 5 K.
Ferromagnetic resonance

To better understand the magnetic properties of the magnetite nanoparticles ferromagnetic resonance (FMR) measurements have been done. We mention that both SQUID and FMR techniques measure the collective response, so they average over the magnetic properties of the particles with different sizes, shapes and surfaces.

The magnetic resonance has been measured at room temperature using an X-band (9.51 GHz) Varian electron-spin-resonance spectrometer in the microwave power range of about 5 mW. The sample is prepared by drying a drop of colloidal solution on a carbon-coated copper TEM grid and is mounted in the middle of the cylindrical microwave cavity. We have performed a polar angular dependence when the applied field was rotated in a plane normal to the film plane. The results are shown in Figure 4.11 and Figure 4.12. All the spectra were normalized to the factor $Q \times \sqrt{P}$, where $Q$ represents the quality factor of the microwave cavity (indicates how efficiently the cavity stores the microwaves) and $P$ is the power of microwave. The gain factor, $6.32 \times 10^3$, and modulation amplitude 1 G, were kept constant during the measurements.

![Ferromagnetic resonance spectra](image)

Figure 4.11: Ferromagnetic resonance spectra taken at 300 K and 9.51 GHz for magnetite nanoparticles. $B_{||}$ indicates the resonance field corresponding to the geometry when the magnetic field is parallel to the film plane, respective at the resonance field $B_{\perp}$, the magnetic field is perpendicular to the grid plane.
In Figure 4.11 one can see that the resonance field depends strongly on the orientation of the external magnetic field. When the magnetic field is applied parallel to the substrate plane, a resonance field of 0.26 T is found, while a resonance at 0.44 T is observed when the static magnetic field is perpendicular to the substrate plane. The lowest resonance field is found when the external magnetic field is applied parallel to the grid plane. It is smaller than the paramagnetic resonance field $\omega/\gamma = 0.319$ T (this value is calculated assuming a magnetite bulk-like g-factor equal to 2.12), which shows that an additional intrinsic magnetic field due to an effective magnetization is present and that the easy axis of magnetization is lying in-plane of the substrate.

In order to get a quantitative value of the effective anisotropy field for our system of interacting particles at 300 K, a full polar angular dependence of the resonance field is recorded. The experimental and simulated results are presented in Figure 4.12. To fit the experimental data we have used the resonance conditions (Eq. 3.7, see chapter 3) for a homogeneous thin film with tetragonal symmetry [59]. The resonance condition yields an effective anisotropy field
$H_{\text{eff}} = 0.12 \, \text{T}$ with the effective anisotropy field defined as:

$$H_{\text{eff}} = -\frac{2K_{2\perp}}{M_s} + 4\pi f M_s$$  \hspace{1cm} (4.2)

where $M_s$ is the saturation magnetization, $K_{2\perp}$ is the intrinsic out-of-plane anisotropy constant and $f$ the volumetric filling factor. For a paramagnetic sample $H_{\text{eff}} = 0$ or very small. A negative $K_{2\perp}$ indicates an easy axis in plane, whereas a positive value shows a preferential orientation normal to the film plane. A good fit is obtained without including in-plane or out-of-plane fourth-order contributions. An isotropic $g$ factor, $g = 2.12$ (reported for magnetite single crystal, at 300 K, along the easy axis $<111>$ [57]) is assumed. This value of the effective anisotropy field is smaller than $4\pi M_s = 0.59 \, \text{T}$, where $M_s$ is the bulk magnetization value of magnetite at 300 K. By using a filling factor of 0.8 (the same filling factor is used for the magnetization simulations), a value of the average magnetization of 0.47 T is obtained, which is still larger than $H_{\text{eff}}$. In order to explain this difference, probably one has to take into account the contribution from a perpendicular anisotropy field. With $M_{\text{bulk}}$, $f = 0.8$, $g = 2.12$ the intrinsic out-of-plane anisotropy constant, $K_{2\perp} = -1.64 \times 10^5 \, \text{J/m}^3$ is calculated. The negative value of $K_{2\perp}$ is an additional proof of the existence of an in-plane easy axis of magnetization.

Another interesting aspect is the variation of the peak-to-peak linewidth with the orientation of the magnetic field. When the magnetic field is parallel to the substrate plane a value of $\Delta B_{\text{pp}} = 0.06 \, \text{T}$ is found. This value is smaller than the peak-to-peak linewidth of bulk single crystal magnetite (0.07 T) [14]. This narrowing of the linewidth can be attributed to the dipolar interaction between particles [39]. For a system of particles which are dipolar coupled the dipolar forces between the moments of the individual particle couple their motions so that the resultant peak-to-peak linewidth is less than what would be expected for a random isolated particles. When the magnetic field is perpendicular to the substrate plane, $\Delta B_{\text{pp}} = 0.09 \, \text{T}$. One possible explanation is that the easy axis of magnetization for the individual nanoparticles are not completely aligned in the direction of the magnetic field.

For comparison, FMR measurements on a system of hexane-based Fe$_3$O$_4$ nanoparticles are presented in Appendix A.1. It was shown that these nanoparticles have a strong dipolar interactions which dominate the magnetic properties of the arrays over the anisotropy of the individual particle [71]. The role of the dipolar interaction is clearly visible in the FMR signal, where narrow peak-to-peak linewidth are measured. For example, for one monolayer nanoparticles a larger effective anisotropy field of $H_{\text{eff}} = 0.17 \, \text{T}$ is found. This value can be associated with the dipolar interparticle interactions. Hence, by modifying interparticle interactions through an exchange of e.g. the surfactant which protects against agglomeration, one could tune the interparticle dipolar interactions.
The above magnetic investigations yield that the magnetite nanoparticles are ferromagnetic at room temperature and reveal a small coercivity at 300 K, which increases at lower temperatures. At 5 K, a larger effective magnetic anisotropy constant as compared to the bulk value is found. This result indicates that for small particles other terms than magnetocrystalline anisotropy contribute to the effective anisotropy. The polar angular dependence of the resonance field shows that the easy axis of the magnetization has an in-plane orientation.
Magnetic force microscopy

The magnetite nanoparticles, have been investigated by means of magnetic force microscopy (MFM) as well. MFM experiments were performed in the lift mode, in air, with a standard magnetic tip (purchased from Digital Instruments) having a radius of about 30 nm. In Figure 4.13, AFM and MFM images of a “cluster” of magnetite nanoparticles deposited on quartz substrate are shown. The scan size is $20 \times 20 \mu m^2$. The direction of the tip magnetization is illustrated. The lift height was 90 nm. As one can see in Figure 4.13 there is still a very pronounced influence from the topography on the magnetic signal. A clear dark and bright contrast is not visible in the MFM response. Different tries, for example, MFM measurements with two opposite polarities of the tip at the same location of the sample or measurements of a sample which was a priori magnetized in a magnetic field of 2 T out-of-plane, did not bring an improvement of the magnetic contrast. One possible explanation for the lack of the magnetic contrast is the small remanence of the nanoparticles at room temperature. In this case a possible perturbation of the magnetic structure of the nanoparticles by the stray-field of the magnetic tip is reasonable to take into account. We mention that at 90 nm lift height the stray-field of the magnetic tip has a value of about 100 Oe, while the coercivity of the sample at room temperature is about 20 Oe.
4.2 Core-shell particles

4.2.1 Synthesis using layer-by-layer technique

In this section the preparation, structural and magnetic investigations of the so called "core-shell" particles are discussed. The core-shell particles were prepared by Dr. M. Spasova at Max-Planck Institute of Colloids and Interfaces in Potsdam. The preparation of coated colloidal particles was possible by using layer-by-layer technique. Layer-by-layer (LbL) self-assembly represents an elegant method to create functional materials and core-shell structures [9], [10]. The idea of the process is a strong electrostatic attraction between a charged surface and an oppositely charged molecules in the solution. Consecutively alternating adsorption of anionic and cationic polyelectrolytes from aqueous solution leads to the formation of multilayer assemblies. The principle of the multilayer assembly is represented in Figure 4.14. In contrast to Langmuir-

![Diagram of layer-by-layer absorption technique]

Blodgett technique, in which monolayers are formed on a water surface and then transferred onto a solid substrate, there are no restriction with respect to the substrate size and topology. The method is highly controllable in terms of the properties of the constructed materials. Latex particles, inorganic spheres, organic crystals and solid biomaterials with charged surfaces
are suitable to act as templates in the layer coating process. Hence, many different materials can be incorporated in the individual multilayers films and the film architectures are completed determined by the deposition sequence.

We have used this approach to coat anionic polystyrene (PS) spheres with 640 nm diameter, with $\text{Fe}_3\text{O}_4$ nanoparticles, described above. In the first step the anionic PS spheres were primed with three layers of polyelectrolytes: positively charged, PDADMAC (poly(diallyldimethylammonium chloride)), negatively charged, PSS (polystyrenesulfonate) /positively charged, PDADMAC, as this provides a uniformly and positively charged, smooth surface that supports the subsequent uniform deposition of anionic nanoparticles. In Figure 4.15 are the chemical formulas of these two polyelectrolytes. A considerable improvement in the growth, uniformity and regularity of the core-shell particles it was observed when the anionic core was not coated with one positively charged polyelectrolyte (PDADMAC) layer but with three polyelectrolyte layers. The outermost layer was PDADMAC, making the coated particles positively charged. This was verified by electrophoresis measurements in which a $\zeta$ potential of +50 mV for the primed latex core was found. As is shown in Figure 4.14 the excess polyelectrolyte was removed by four centrifugation/wash/redispersion cycles. The next step consisted in coating the primed template core with negatively charged magnetite 13 nm nanoparticles. The nanoparticles were adsorbed on the PS core by adding 0.3 mL of the magnetite solution ($\sim 3 \times$...
10^{14} \text{ particles}) to the precoated template (\sim 5 \times 10^9 \text{ particles}) dispersed in 0.5 \text{ mL of water}. The nanoparticles were allowed to absorb for 20 min, and excess Fe$_3$O$_4$ nanoparticles were removed by repeated centrifugation/dispersion cycles. Electrophoretic measurements reveal a \zeta \text{ potential of } -30 \text{ mV} for magnetite nanoparticles. The next step involves another electrolyte PDADMAC / PSS / PDADMAC deposition. We can continue this process until the desired number of magnetic layers is achieved. A very detailed description of the preparation of magnetic core-shell particles has been presented in [9]. We have prepared such core-shell particles with one to five magnetic layers. This sequential layering approach gives us the flexibility to tune the thickness and composition (see next section) of the deposited multilayers with nanoscale precision, either by varying the number of adsorption cycles or the number of polyelectrolyte layers deposited between each nanoparticle layer.

In order to avoid confusions the following notation concerning the terminology of the core-shell particles is adopted: latex2Fe$_3$O$_4$ means: the latex core (640 nm in diameter) is covered with two magnetic shells.

### 4.2.2 Structural characterization of the core-shell particles

To monitor the assembly of the nanoparticles/polyelectrolyte multilayers on the PS core and to examine the morphology of the coated particles we have used transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). We can see in Figure 4.16 a) a PS core (640 nm in diameter), pre-coated with three layers of polyelectrolyte (PDADMAC / PSS / PDADMAC) which exhibits a smooth surface and a spherical shape. Figure 4.16 b) shows this pre-coated PS core exposed to two depositions of Fe$_3$O$_4$ nanoparticles /polyelectrolyte. The presence of magnetic nanoparticles and polyelectrolyte shells clearly result in increased surface roughness and particle diameter. As we can see in Figure 4.17, the diameter increases with the number of the Fe$_3$O$_4$ nanoparticle /polyelectrolyte layers. The error in the determination of the core-shell particle diameter is \pm 30 \text{ nm}. The average diameter increment for each deposition step varies between 50 nm and 80 nm, meaning that the layer thickness after each deposition is about 25 nm-40 nm. It is known that the thickness of three layers of polyelectrolyte is approximative 5 nm. That is an indication that after each adsorption cycle the magnetite layer has a thickness of about 20-35 nm. If one considers the 10 nm diameter of the magnetite particles, we can estimate that 2-3 monolayers of magnetite particles are adsorbed at each step.

The core-shell particles prepared by a sequential layering approach, were also visualized by SEM and AFM. Figure 4.18 represents an image of the PS core after one step of Fe$_3$O$_4$ nanoparticles /polyelectrolyte adsorption. A drop of 5 \text{ \mu L solution is deposited on quartz pat-
Figure 4.16: a) TEM image of the PS core pre-coated with three layers of polyelectrolyte and b) followed by two cycles of Fe$_3$O$_4$ nanoparticles /polyelectrolyte adsorption, with an average diameter of 770 nm.

Figure 4.17: TEM micrographs of PS core covered with one (a), three (b), four (c) and five (d) layers of Fe$_3$O$_4$ nanoparticles /polyelectrolyte. The average diameters of the core-shell particles are 680, 810, 940 and 1000 nm, respectively.
terned substrate. Details about the preparation of the patterned substrates are described in [82]. One can see that the particles have still spherical shape. For the AFM measurement a normal quartz substrate was used. In both cases core-shell particles (latex1Fe₃O₄) with 680 nm in diameter were visualized.

Figure 4.18: SEM micrographs (different magnifications) of the dried latex1Fe₃O₄ deposited on a patterned substrate.

In Figure 4.19 AFM images recorded in air in the tapping mode for core-shell particles are shown. No special features can be resolved, confirming thus the homogeneity of the coating. Some characteristics of the core-shell particles are tabulated in Table 4.3.

By using the layer-by-layer technique, uniform multilayer assemblies composed of polymers and magnetite nanoparticles can be grown on the colloidal template. The thickness of the core-shell particles can be controlled by varying the number of the deposition cycles, while the size and the shape can be tuned by the dimensions of the colloid template. By calcination or decomposition after exposure to solvents, the latex and/or polymers layers were removed and so called "hollow magnetic spheres" were produced [7].
<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter of the core-shell particle (nm)</th>
<th>Thickness of the magnetic shell (nm)</th>
<th>Number of Fe₃O₄ particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>latex1Fe₃O₄</td>
<td>680 ± 30</td>
<td>20</td>
<td>1.1 × 10⁴</td>
</tr>
<tr>
<td>latex2Fe₃O₄</td>
<td>750 ± 30</td>
<td>55</td>
<td>3.8 × 10⁴</td>
</tr>
<tr>
<td>latex3Fe₃O₄</td>
<td>810 ± 30</td>
<td>85</td>
<td>6.5 × 10⁴</td>
</tr>
<tr>
<td>latex4Fe₃O₄</td>
<td>940 ± 30</td>
<td>150</td>
<td>1.4 × 10⁵</td>
</tr>
<tr>
<td>latex5Fe₃O₄</td>
<td>1000 ± 30</td>
<td>180</td>
<td>1.8 × 10⁵</td>
</tr>
</tbody>
</table>

Table 4.3: Some characteristics of the core-shell particles. To estimate the number of the magnetite nanoparticles, a diameter of 12 nm has been assumed. The diameter of the core-shell particles and the average magnetic shell thickness have been determined from TEM measurements. The error in the determination of the number of magnetite nanoparticles is about 30%.
Figure 4.19: AFM-tapping mode images of core-shell particles (680 nm in diameter) deposited on a quartz substrate. a) $15 \times 15 \, \mu m^2$; the height variation is $2 \, \mu m$; b) $2 \times 2 \, \mu m^2$; the height variation corresponds to 500 nm. The topography was imaged with a tip with a radius of 60 nm. The spring constant of the cantilever was 42 N/m and the resonant frequency 190 KHz.
4.2.3 Magnetic properties

SQUID-magnetometry

In this section the magnetic properties of the above described magnetic core-shell colloids are investigated by means of SQUID-magnetometry, FMR and MFM.

The magnetic measurements have been performed for two types of the samples: the so-called "random" core-shell particles which have been prepared by letting a drop of the colloidal solution slowly evaporate and the "chain" core-shell particles, where the colloidal solution is dried in the presence of an in-plane magnetic field (we refer to this field as the drying magnetic field).

More details about the drying of the colloidal solution in the presence of an applied magnetic field are presented in the chapter "Self-assembly into 1D, 2D structure".

For the magnetometry measurements a home-built SQUID and a commercial SQUID device have been used.

A schematic of the home-build SQUID setup is shown in Figure 4.20 b). With such a set-up the stray field \((B_z)\) of the in-plane magnetized sample is recorded while the SQUID sensor is scanned above the sample along the \(x\)-direction. The sample is prepared as follow: a drop of a 6 \(\mu\)l water-based core-shell particles solution, latex\(\text{Fe}_3\text{O}_4\) (with a diameter of 1000 nm), is dried in the presence of an applied 0.2 T magnetic field. A priori to the measurement the sample is magnetized in-plane in 1.2 T. The measurements have been done along the \(x\)-axis.

The stray field of the sample can be calculated by integrating the stray fields produced by elementary magnetic moments in the sample using the following assumptions: a) the sample behaves as a thin film; b) all the particles have the same shape and size; c) the sample is in a single domain state, so all the magnetic moments have the same orientations. The result is shown in Figure 4.20a), where the measured and the calculated \(B_z\) component of the stray field of the sample at room temperature are represented. A stray field of 9.4 nT is measured. By applying the respective model to calculate the vertical component of the stray field using the remanent magnetization for bulk magnetite one expects a value of 240 nT. For a square sample \((4\times4\text{mm}^2)\) with 1 \(\mu\)m thickness, at 6.2 mm distance from the SQUID sensor a remanence magnetization of 11 G is calculated. This value is smaller than the remanence magnetization of bulk magnetite. This difference can be explained by taking into account the deviation from the model assumptions. These are: a) the approximation of a continuous film is not reasonable; b) the magnetic moments of the individual particles are not all aligned in-plane as in model; c) due to the size and shape distribution the particles do not have the same magnetic moment. Two other reasons can be proposed for the reduction of the magnetization. First, due to the assembly process of the magnetite nanoparticles on the polystyrene spheres, possible particle surface modifications have
occurred. Second, the packing factor of the magnetite nanoparticles can have an influence on the magnetization loops, as well. In order to find out the sources for the reduction of the magne-

tization further magnetization measurements with a commercial SQUID device have been done. The measurements have been carried out in a magnetic field of up to 5 T and temperatures between 5 K and 350 K. The magnetic field is applied parallel to the substrate plane. The quartz substrate response is measured separately, and its diamagnetic contribution to the total signal is subtracted in the data. Due to the fact that the volume of the substrate is considerably larger than the volume of the polyelectrolyte spheres (which also have a diamagnetic contribution to the magnetic signal) the major diamagnetic contribution is from the substrate. In Figure 4.21 the hysteresis loops for the random core-shell particles are shown. The remanent magnetization, the saturation and coercivity of the random core-shell particles at various temperatures are tabulated in Table 4.21. The error in the determination of the saturation magnetic moment per ball is about 30%. The source of error comes from the determination of the number of particles in the sample and from the calculation of the number of magnetite nanoparticles within the shell. The determination of the number of core-shell particles in the sample has been done by means

Figure 4.20: a) The vertical component \( B_z \) of the dipolar magnetic stray field of the magnetized sample, at 300 K. For the simulation, a model of an homogeneous in-plane magnetized film has been used [67]. b) The illustration of the scanning principle of the home-build SQUID.
of an optical microscope. For the investigated sample a number of core-shell (balls) particles in the sample of about $3.1 \times 10^6$ is estimated. The number of the magnetite nanoparticles in the shell could be estimated only roughly from TEM image analysis using a packing factor of the nanoparticles in the shell of about 0.3. Assuming $1.8 \times 10^5$ magnetite particles to be in one ball with 1000 nm diameter and the density of magnetite 5.18 g/cm$^3$, the saturation magnetization for the magnetite nanoparticles is estimated (see Table 4.4). In comparison to the saturation magnetization of bulk magnetite ($M_s = 92-100$ Am$^2$/kg at 300 K) [14], the $M_s$ of the nanoparticles in the shell is about three times less. The possible explanation is due to the chemical preparation of the colloidal particles, where the surface magnetic properties of the particles are strongly modified leading to a reduction of the effective particle size. It is worthwhile to note that as compared to magnetite nanoparticles studied in the previous section, smaller $M_r/M_s$ and coercivity are obtained at room temperature. Besides the above mentioned reason, the influence of the packing density on the behavior of magnetization can also explain the reduction of the magnetization. A smaller packing density implies a smaller coercivity and ratio between the remanence and saturation magnetization. This is in agreement with theoretical simulations of magnetization loops (data no shown) for the core-shell particles with a different packing density of the magnetite nanoparticles [51].

![Magnetization curves measured on the random core-shell particles (latex5Fe$_3$O$_4$) at 5 and 300 K. The particles have been deposited on a quartz substrate.](image-url)
CHAPTER 4. RESULTS

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>5</th>
<th>42</th>
<th>120</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hc (Oe)</td>
<td>245</td>
<td>133</td>
<td>64</td>
<td>12</td>
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<tr>
<td>Mr × 10^{-8} (Am^2)</td>
<td>3.24</td>
<td>2.21</td>
<td>1.25</td>
<td>0.18</td>
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<tr>
<td>Ms × 10^{-8}(Am^2)</td>
<td>9.80</td>
<td>9.75</td>
<td>9.54</td>
<td>8.52</td>
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<tr>
<td>Mr/Ms</td>
<td>0.33</td>
<td>0.23</td>
<td>0.13</td>
<td>0.02</td>
</tr>
<tr>
<td>Mr/ball (10^{-14} × Am^2)</td>
<td>3.16</td>
<td>3.14</td>
<td>3.07</td>
<td>2.74</td>
</tr>
<tr>
<td>Ms/Fe_3O_4 (Am^2/kg)</td>
<td>36.44</td>
<td>36.21</td>
<td>35.40</td>
<td>31.60</td>
</tr>
</tbody>
</table>

Table 4.4: Coercivity, remanence and saturation magnetization for the random core-shell particles at 5, 42, 120, 300 K. The average saturation magnetic moment per core-shell particles (ball) and per magnetite nanoparticle were also estimated.

For the core-shell particles assembled in chains the magnetization curves are represented in Figure 4.22, at 5 and 300 K. The values of the magnetization and coercivity are tabulated in Table 4.5. Comparison of the magnetization curves for the aligned and randomly oriented core-shell particles showed relatively few differences. The aligned particles displayed a slight increase in the remanence magnetization and coercivity.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>5</th>
<th>42</th>
<th>120</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hc (Oe)</td>
<td>253</td>
<td>138</td>
<td>67</td>
<td>15</td>
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<tr>
<td>Mr_{rem} × 10^{-8} (Am^2)</td>
<td>3.83</td>
<td>2.69</td>
<td>1.49</td>
<td>0.30</td>
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<tr>
<td>Ms_{sat} × 10^{-8}(Am^2)</td>
<td>9.80</td>
<td>9.52</td>
<td>9.27</td>
<td>8.21</td>
</tr>
<tr>
<td>Mr_{rem} / Ms_{sat}</td>
<td>0.39</td>
<td>0.28</td>
<td>0.16</td>
<td>0.03</td>
</tr>
<tr>
<td>Mr/ball (10^{-14} × Am^2)</td>
<td>3.16</td>
<td>3.07</td>
<td>2.99</td>
<td>2.64</td>
</tr>
<tr>
<td>Ms/Fe_3O_4 (Am^2/kg)</td>
<td>36.44</td>
<td>35.40</td>
<td>34.48</td>
<td>30.44</td>
</tr>
</tbody>
</table>

Table 4.5: Coercivity, remanence and saturation magnetization for the chains core-shell particles at 5, 42, 120, 300 K. The average saturation magnetic moment per core-shell particles (ball) and per magnetite nanoparticle were also estimated.

In order to determine the transition temperature (blocking temperature) to the superparamagnetic state, ZFC and FC measurements have been performed. Figure 4.23 shows the magnetization as a function of temperature obtained in the ZFC and FC processes for randomly
oriented core-shell particles. The temperature dependence of the magnetization is measured after cooling the sample without a magnetic field (zero-field cooling (ZFC) curve) and after cooling in a magnetic field of 5 T (field-cooled (FC) curve) from 350 K to 5 K. Then a magnetic field of 20 G is applied and the magnetization is recorded with increasing temperature. As seen from Figure 4.23 a distinct magnetic cooling effect is observed for ZFC and FC curves. The ZFC magnetization curves increase monotonically with temperature while FC curves do not change dramatically with changing temperature. Thus, in the temperature range 5-300 K, no superparamagnetic behavior of the ensemble of particles is observed.

**Ferromagnetic resonance**

To study the magnetic anisotropy of these core-shell colloids ferromagnetic resonance has been employed. The FMR measurements have been carried out at 9.51 GHz and 300 K. The random (see Figure 4.24 a)) and the aligned (see Figure 4.24 b)) core-shell particles have been measured. The samples consist of core-shell particles (latex5Fe₃O₄) with 1 µm diameter, dried on a quartz substrate with and without an applied magnetic field [3]. The results are shown in Figure 4.24. The measurements have been done for two different orientations of the magnetic
Figure 4.23: a) Magnetization versus temperature measured in 20 Oe in the zero-field-cooled and field-cooled states. The measurements have been done for randomly distributed particles with 1 µm diameter (latex5Fe$_3$O$_4$).

field with respect to the substrate plane (parallel and perpendicular to the substrate plane). One can observe that for the random core-shell particles the resonance field yields a small angular dependence of about 0.01 T. For the aligned core-shell particles (chain-like structure) a larger angular dependence 0.05 T is measured. The values of the resonance fields for both samples and orientations are tabulated in Table 4.6.

<table>
<thead>
<tr>
<th>sample</th>
<th>$B_{\text{res} \parallel}$ (T)</th>
<th>$B_{\text{res} \perp}$ (T)</th>
<th>$B_{\text{res} \parallel} - B_{\text{res} \perp}$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>random</td>
<td>0.28</td>
<td>0.29</td>
<td>0.01</td>
</tr>
<tr>
<td>aligned</td>
<td>0.26</td>
<td>0.31</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 4.6: The resonance fields for random and aligned core-shell particles.

Several features of the spectra are important to discuss. First, the angular dependence of the resonance field for the chain-like sample, indicates a long-range magnetic order due to dipolar coupling between the core-shell particles within the chain at 300 K. Second, the lowest resonance field occurs when the external field is applied parallel to the substrate plane and the chains. This reveals an easy axis of magnetization in-plane along the chains. Moreover, the lowest resonance field (0.28 T for random and 0.26 T for aligned core-shell particles) is smaller
Figure 4.24: FMR spectra measured at 9.5 GHz and 300 K for the sample dried without magnetic field a) and in a magnetic field of 1 T b). The full curves are recorded when the magnetic field is applied perpendicular to the substrate and dotted curves when the magnetic field is applied parallel to the substrate.

than the paramagnetic resonance field (0.319 T), which shows that there is an additional intrinsic anisotropy field. Third, in comparison with random magnetite nanoparticles (see Figure 4.11), the FMR spectra for the core-shell particles do not yield a large angular dependence of the resonance field. It seems that by assembling the magnetite nanoparticles on the polystyrene spheres a reduction of the magnetic anisotropy is obtained.

In order to find out the magnitude of the effective anisotropy field, a polar angular dependent FMR measurement for the aligned core-shell particles has been performed. The magnetic field is rotated in a plane normal to the film plane. The result is shown in Figure 4.25. The polar angle is measured from the normal to the sample plane. A fit according to Eq. 3.7 yields an effective anisotropy field $H_{eff} = 0.03$ T ($H_{eff}$ is defined in the previous section). This value is four times smaller than the effective anisotropy field calculated for the magnetite nanoparticles in the previous section. At this point one remark should be made. To fit the polar angular dependence of the resonance field for the aligned core-shell particles a g-factor equal to 2.4 and a frequency equal to 9.5 GHz are assumed. This enhanced value of g-factor is unclear (g = 2.12 for bulk magnetite). Anomalies in the g-factor values for thin film magnetite have been reported
in the literature [77]. For example, a $g = 2.8$ for 9.3 nm Fe$_3$O$_4$ film and a $g = 2.8$ for 1.5 nm Fe$_3$O$_4$ film are found. It was established that a very high effective g-factor for magnetite can occur when a compensation temperature is approached [77], [81]. However, the magnetometry measurements show no indication for the magnetic compensation point. One can speculate that a larger g value can imply a high orbital moment (see Eq. 3.9). This can be due to the surface anisotropy which is very sensitive to the nature of the bonding at the particle surface. However, the large g-factor used to fit the experimental data has no influence on the magnitude of $H_{\text{eff}}$. For the reduction of the effective anisotropy field, as compared with the magnetite nanoparticles studied in the previous section, two sources are considered:

1) the strength of the dipolar interaction between nanoparticles. Assembling the nanoparticles on the diamagnetic core the dipolar coupling between them became weaker due to the presence of polyelectrolytes multilayers;

2) by using the layer-by-layer technique to produce core-shell particles an additional surface modification for the magnetite nanoparticles could have occurred. Moreover, the difference in spectra between random (Figure 4.24 a)) and aligned (Figure 4.24 b)) core-shell particles indicates that not only the dipolar coupling between the nanoparticles within the shell of one microsphere plays an important role on the magnetic anisotropy but also the dipolar coupling between the microspheres.

By doing an azimuthal angular dependence of the resonance field, another interesting aspect is observed. The result is plotted in Figure 4.26. Different resonance fields have been measured when the magnetic field was perpendicular to the chains, in plane (0.28 T; see Figure 4.26) and perpendicular to the chains, out-of-plane (0.31 T; see Figure 4.25). This shows that there is not only dipolar coupling between the core-shell particles within one chain, but also individual chains might interact via dipolar forces. In order to check the role played by the dipolar interactions between nanoparticles FMR measurements for the core-shell particles with different numbers of magnetic layers have been performed. The results are shown in Figure 4.27. The core-shell particles with the number of magnetic shells ranging from 2 to 5 have been dried in the presence of 0.2 T on $4 \times 4$ mm$^2$ quartz substrate. The applied magnetic field was rotated in a plane normal to the substrate plane. A small increase of the difference between resonance fields with the increase of the number of magnetic layers has been measured. This can be associated with the enhancement of the dipolar coupling between nanoparticles. Note, that FMR investigations on samples prepared in different drying magnetic fields ranging from 0.2 T until 1 T have been done. In the dependence of the resonance fields and the peak-to-peak linewidths on the drying magnetic fields no special features could be observed.

We focus now on the behavior of the peak-to-peak resonance linewidth. A polar angular
dependence of $\Delta B_{pp}$ is displayed in Figure 4.28. The sample was dried in 0.2 T. A change from $\Delta B_{pp} = 0.08$ T when the static magnetic field is applied along the chain direction to $\Delta B_{pp} = 0.13$ T when the static magnetic field is perpendicular to the chain axis has been measured. For random core-shell particles a value of 0.11 T for the peak-to-peak linewidth was observed. These values are larger than the peak-to-peak linewidths observed for the magnetite nanoparticles in the previous section. One source of the line broadening is due to the distribution of the particle orientation. If one assumes that the particles are not strongly dipolar coupled, a random orientation of the easy axis will generate a large $\Delta B_{pp}$. In [70] it was reported that structural homogeneity is strongly correlated with the linewidth as well.

**Magnetic force microscopy**

The core-shell particles were investigated by means of MFM as well. The procedure was the same as that used for the magnetite nanoparticles. On the first pass, the topography was recorded using tapping mode. On the second pass, the tip was raised to a selected height and phase shifts in the cantilever oscillation (caused by gradients in the magnetic force on the tip) were recorded. The MFM probe had a silicon pyramidal tip coated with a Co-Cr alloy, having a radius of...
The magnetization of the magnetic tip has a value of 749 emu/cm$^3$ [60]. From the SQUID measurements we know that one "ball" has an average saturation magnetic moment of $2.74 \times 10^{-14}$ Am$^2$. A typical value for the spring constant of the cantilever is 2.39 N/m.

In Figure 4.29 AFM and MFM images of an identical magnetic chain, for the two polarities of the magnetic tip (the tip was magnetized up and down with a permanent magnet) are shown. A strong topographic influence in the magnetic image is visible. The small difference in the magnetic response for the two directions of the tip magnetization is induced by the magnetization of the tip.

In an attempt to get rid of the topographic influence of the magnetic response, the scans at different lift-heights ranging from 90 nm to 2 µm were done. On the one hand, one should expect to have a decrease of the topographic contrast with an increase of the distance between the tip and the sample. On the other hand, to achieve high resolution in the magnetic image, the stray field has to be measured at a distance close to the surface. The resulting MFM images are shown in Figure 4.30. No improvement of the magnetic contrast has been observed.

An explication for the fake of a clear dark and bright contrast in the MFM image could be that

Figure 4.26: The angular dependence of the in-plane resonance field at 300 K for aligned core-shell particles. The azimuthal angle was measured from the direction parallel to the chains.
the magnetization of the tip strongly influences the magnetization of the sample. During the measurements several problems were encountered, e.g. the core-shell particles are very soft and one can easily move them on the substrate, or they are attached to the apex of the tip (note that, by scanning at very high frequency, for example 20 Hz, it is possible to drop the "captured" particle back on the substrate).

The above-presented magnetic experiments on the core-shell particles may be summarized as follows: i) SQUID-magnetometry investigations show a reduction of the magnetization for the magnetite nanoparticles assembled on the diamagnetic core as compared with the magnetite nanoparticles studied in the previous section. Surface effects and the packing factor seems to be responsible for this reduction; ii) FMR-angular dependence reveals a long-range order at 300 K, an easy axis of magnetization along the direction of the chains and a smaller effective anisotropy field; iii) The strength of the dipolar interaction can be used to tune the magnetic response of the particles.

Figure 4.27: The difference between the resonance fields measured with the magnetic field applied normal to the chains and with the magnetic field applied along the direction of chains plotted as a function of the number of magnetic layers.
Figure 4.28: The angular dependence of the peak-to-peak linewidth for the latex$5F_3O_4$. The measurements have been performed in the xz-plane.
Figure 4.29: AFM (height mode) and MFM images of a part of a dried chain of the core-shell particles. The sample was dried in a magnetic field of 0.2 T. The scan size was 15×15 µm². The MFM tip was magnetized vertically (perpendicular to the sample surface) upward and downward and the tip-sample separation was 240 nm.
Figure 4.30: AFM height image (the top left) and MFM images recorded at different lift heights for the magnetic balls. A very strong topographic influence is present even very far from the surface. The scan size (8.92 × 8.92 µm²) is identical for all the images.
4.3 Composite particles

4.3.1 Preparation of the composite microspheres

The interest to create core-shell particles with multifunctional properties was already discussed before. In this section, we show that by using the layer-by-layer technique it is possible to fabricate core-shell particles not just with tailored thickness but also with tailored composition. We refer to this type of core-shell particles as "composite" particles (see Figure 4.31). One composite microsphere consists of a polystyrene (PS) core (640 nm diameter), coated with consecutive shells of Fe$_3$O$_4$ nanoparticles (~12 nm diameter)/polyelectrolytes/Au nanoparticles encapsulated in a thin layer of silica (15 nm). The use of the silica encapsulated gold nanoparticles has several advantages [8]. For example, the surface characteristics of silica can be exploited to control and achieve a dense packing of gold nanoparticles on the colloidal template. This is often desired, particularly for the preparation of so-called "hollow" spheres. Another reason to construct such composite particles with Au shells is their size-dependent optical properties. Due to the strong plasmon absorption band of gold nanoparticles, one can exploit not just the magnetic properties of magnetite but also, the optical properties of Au nanoparticles [63].

The composite microspheres were fabricated in a similar manner as the core-shell particles, i.e., using the self-assembly strategy and the colloidal template. Shortly, the preparation was as follows. The anionic PS cores were primed with

![Figure 4.31: Schematic of a composite microsphere.](image-url)
three layers of polyelectrolytes: PDADMAC$^1$/PSS$^2$/PDADMAC. In the second step tetrabutylammoniumhydroxide-stabilized magnetite nanoparticles with an average diameter of $12 \pm 3$ nm are adsorbed, followed by another PDADMAC/ PSS/ PDADMAC deposition. After each adsorption the suspension was subjected to repeated centrifugation/water-wash cycles to remove unabsorbed materials.

For the formation of the gold shell we had to use negatively charged Au nanoparticles encapsulated in a very thin layer of silica [63]. Only these special Au particles allow to achieve a dense packing of encapsulated nanoparticles on the template colloids. The presence of silica helps in preventing aggregation of the coated colloids, confers optical transparency and assures the control over the interparticle spacing. For the details on preparation and characterization of Au nanoparticles see [55]. It should be noted that the Au nanoparticle/PE multilayer shell was fabricated using only one polyelectrolyte (PE) layer (PDADMAC) as the spacer layer between nanoparticles. The average incremental diameter increase for each Au / PE layer is $36 \pm 10$ nm, corresponding to a layer thickness of approximately 18 nm. This value is in a close agreement with the diameter of the Au nanoparticles (gold core $\sim 15$ nm + SiO$_2$ shell $\sim 2$ nm). This indicates that a single monolayer of gold nanoparticles is deposited with each adsorption step. The thickness of each PE layer is 1-2 nm.

Similar to the core-shell particles the following notation is used: "latex2Fe$_3$O$_4$3Au" means that the latex core is covered with two layers of magnetite and three layers of gold.

### 4.3.2 Structural characterization of the composite microspheres

The composite microspheres were characterized using atomic force, transmission and optical microscopy techniques. Samples for TEM measurements were prepared by drying an aqueous solution of the composite particles on a carbon-coated copper grid, while for the optical and atomic force microscopy, a drop of the solution was dried on the silica substrates.

The uniform coverage is shown by the transmission electron microscopy (TEM) images in Figure 4.32, which represent a 640 nm PS microsphere covered (a) with two shells of magnetic Fe$_3$O$_4$ nanoparticles (overall diameter $750 \pm 20$ nm) and (b) after additional coverage with three layers of Au nanoparticles (overall diameter is $860 \pm 20$ nm). The same polystyrene spheres as for the core-shell particles (a TEM image of the polystyrene sphere was shown in Figure 4.16) have been used. In comparison with the PS spheres coated just with magnetite nanoparticles, the composite particles exhibit an increase of surface roughness, probably due to the aggregation of gold nanoparticles.

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$^1$poly(diallyldimethylammonium chloride)
$^2$polysteresulfonate
Figure 4.32: TEM images of 640 nm PS microspheres covered (a) with two layers of magnetic Fe₃O₄ nanoparticles (overall diameter 750 ± 20 nm) and (b) after additional coverage with three layers of Au nanoparticles (overall diameter is 860 ± 20 nm).

Figure 4.33: a) and c) Optical microscopy images of randomly distributed microspheres (latex2Fe₃O₄2Au) with different volume fraction; b) 40 × 40 μm² 3D AFM-tapping mode of some particles from image a);
A 10 µl colloidal solution with a different volume fraction \( \sim 4.9 \times 10^6 \) microspheres for Figure 4.33 a),b) and \( \sim 10^7 \) microspheres for Figure 4.33 c) were dried in air on a Si substrate. Figure 4.33 exhibits the optical and AFM images of the composite microspheres consisting of a latex core covered with two layers of magnetite and two layers of Au. The average diameter of these composite particles is 810 nm \( \pm \) 20 nm, in good agreement with the TEM analysis. As we can see in Figure 4.33, at low concentration, the distribution of the composite particles is random over a wide area of the Si wafer. At high concentration they form two-dimensional clusters. The pattern formation as a function of various parameters will be discussed in the next chapter in more detail.

Thus, uniform and densely packed layers of gold nanoparticles encapsulated in a very thin layer of silica and magnetite nanoparticles on polystyrene microspheres were created.

### 4.3.3 Magnetic properties

Magnetic measurements on the composite microspheres were carried out with an X-band (9.5 GHz) electron paramagnetic resonance (EPR) and SQUID-magnetometry.

#### Ferromagnetic resonance

Below, the ferromagnetic resonance measurements are discussed. The polar angular dependence of the resonance field for aligned composite microspheres (latex2Fe\(_3\)O\(_4\)2Au) at 300 K is shown in Figure 4.34 [4]. In the same figure the angular dependence of the peak-to-peak linewidth and an optical micrograph of the investigated sample are presented. The sample is dried in a magnetic field of 0.2 T.

The larger resonance field is observed when the magnetic field is applied perpendicular to the film plane (0.32 T). This yields that the easy axis of magnetization is in the film plane. A comparison between the FMR response of the composite microspheres (latex2Fe\(_3\)O\(_4\)2Au) and the core-shell particles (latex2Fe\(_3\)O\(_4\)) is presented in Table 4.7. The values of the resonance fields when the magnetic field is parallel to the substrate (\( B_{\text{res} \parallel} \)) and perpendicular to the substrate (\( B_{\text{res} \perp} \)) are displayed. By analyzing the features of the FMR spectra for the sample "latex2Fe\(_3\)O\(_4\)" and "latex2Fe\(_3\)O\(_4\)2Au", the role of the gold shells on the magnetic properties can be investigate. One can see that the microspheres with Au shells reveal a smaller angular dependence of the resonance field and a shift to higher values of the resonance field. This shift of the resonance field to higher fields at 300 K is due to the reduction of the magnetic anisotropy. A fit according Eq. 3.7 reveals a value of the effective anisotropy field six times smaller (\( H_{\text{eff}} = 0.02 \) T) than \( H_{\text{eff}} \) found for the magnetite nanoparticles. One possible reason
for that is the dipolar coupling between the composite microspheres within the chain. It seems that by surrounding the magnetic nanoparticles with the diamagnetic shells a weaker dipolar coupling between the composite microspheres is obtained. Thus, by adding the gold shells (enlarge the distance between magnetic nanoparticles) one can tune the strength of the dipolar interaction between the aligned composite microspheres. Of course, the different chemical surrounding can influence the magnetic properties, as well.

Concerning the peak-to-peak linewidth, both, yield a large value of the linewidth in comparison with the magnetite nanoparticles ($\Delta B_{pp} = 0.06 \, \text{T}$) investigated before. The larger value ($\Delta B_{pp} = 0.14 \, \text{T}$) is obtained for the composite microspheres when the magnetic field is normal to the film plane. The broadening of $\Delta B_{pp}$ has, in principle, the same origin as the one for the core-shell particles namely, the variation of the local magnetic resonance fields across the sample. Inhomogeneities in the structural composition, distribution of the particle size and shape are possible effects which can lead to the distribution of the local magnetic field of the whole sample.

Figure 4.34: a) Polar angular dependence of the resonance field for the chain-like sample. The external field was rotated in the xz plane. The chains are parallel to the x axis; b) Angular dependence of the peak-to-peak linewidth; c) Optical image of the sample dried in 0.2 T.
Table 4.7: The values of the resonance fields and peak-to-peak linewidth for latex2Fe$_3$O$_4$ and latex2Fe$_3$O$_4$2Au.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$B_{res∥}$ (T)</th>
<th>$B_{res⊥}$ (T)</th>
<th>$B_{res∥}$ - $B_{res⊥}$ (Oe)</th>
<th>$\Delta B_{pp∥}$ (T)</th>
<th>$\Delta B_{pp⊥}$ (T)</th>
</tr>
</thead>
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<tr>
<td>latex2Fe$_3$O$_4$</td>
<td>0.26</td>
<td>0.3</td>
<td>475</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>latex2Fe$_3$O$_4$2Au</td>
<td>0.29</td>
<td>0.32</td>
<td>270</td>
<td>0.11</td>
<td>0.14</td>
</tr>
</tbody>
</table>

In Figure 4.35 a) the characteristic FMR spectra at four different temperatures are illustrated. The measurements were done for the chain-like sample consisting of two layers of magnetite and two layers of gold. The magnetic field for drying was 0.2 T. The temperature dependence of the resonance position is shown in Figure 4.35 b). It is observed that the resonance field shifts to lower magnetic fields. This behavior of the resonance field is expected. If one looks at the resonance condition (Eq. 3.7) can see that $B_{res}$ should shift to lower magnetic fields with decreasing temperature. Upon cooling a narrowing of the linewidth ($\Delta B_{pp} = 0.09$ T at 230 K) is observed. These features of the linewidth are explained as a result of the effects of super-paramagnetism. From magnetometry measurements one can see that the blocking temperature lies slightly above room temperature, so fluctuations of the direction of magnetization lead to a larger linewidth at 300 K. At lower temperatures than 170 K the signal become indistinguishable and unmeasurable.

**SQUID-magnetometry**

For a further investigation of the magnetic properties of the composite microspheres, SQUID-magnetometry measurements have been performed. The hysteresis loops were taken at 5 and 300 K in applied fields of up to 5 T, for the sample with two layers of magnetite and two layers of gold deposited on a quartz substrate. The magnetic field is applied parallel to the plane of the substrate and parallel to the direction of chains. The magnetization curves are shown in Figure 4.36. The composite microspheres show a small remanence magnetization at room temperature ($3.19 \times 10^{-9}$ Am$^2$). At low temperature (5 K) a coercivity of 300 Oe and a remanent magnetization of 48% of the saturation value were found.

Based on the estimation of the number of the composite microspheres we have determined the average magnetic moment per composite microsphere, respective per magnetite nanoparticle. At 300 K, the saturation magnetic moment per composite microsphere was $1.24 \times 10^{-15}$ Am$^2$ while at 5 K a value of $1.62 \times 10^{-15}$ Am$^2$ was estimated. Assuming that in one microsphere with two magnetite shells are $3.8 \times 10^4$ Fe$_3$O$_4$ nanoparticles we found that the value of
Figure 4.35: a) The FMR spectra at different temperatures; b) the resonance field as a function of temperature; The measurements were done at $\nu = 9.31$ GHz, $P = 5$ mW, gain factor $= 10^4$, modulation amplitude 10 G.

Figure 4.36: SQUID measurements of composite microspheres (latex$2Fe_3O_42Au$) at 5 and 300 K.
the average magnetic moment of the magnetite nanoparticles ($\sim 8 \pm 3 \text{ Am}^2/\text{kg} \text{ at } 300 \text{ K}$) is four times smaller than the saturation magnetic moment of magnetite nanoparticles from core-shell particles. An error of about 30% in the estimation of the number of magnetite nanoparticles is assumed. The weight of the 12 nm magnetite nanoparticles is $4.67 \times 10^{-18}$ g. As it was mentioned before, the interparticle interactions play an important role on the reduction of the magnetic moment. Another approach for the reduction of the magnetization of magnetite nanoparticles covered with silica-encapsulated gold nanoparticles is reported in [65]. The authors claim that silica coating is likely to eliminate poorly coordinated bonds of surface iron atoms, which reduces the total spin and decreases the magnetic moment of the magnetite nanoparticles [65]. In Figure 4.37 the magnetization versus temperature curves measured under zero-field cooling (ZFC) and field cooling (FC) are shown. The temperature ranges from 5 to 300 K. The cooling field was 5 T, while the measured field was 20 Oe. Above 300 K a shallow maximum is observed which may indicate that the blocking temperature lies in this range. It is established that the blocking temperature increases with increases the strength of the interaction (in our case the dipolar interaction) between particles. This means that the weaker dipolar coupling, which we assumed for the composite particles, induces a lower blocking temperature. By comparing Figure 4.37 with Figure 4.23 one can say that the composite particles have a tendency to block at lower temperature (close to 300 K). It is clear that for both, core-shell and composite particles one does not expect a sharp transition to superparamagnetism. The distribution of the particle sizes causes a distribution of the blocking temperature.

![Figure 4.37: Magnetization as a function of the temperature after field cooling and zero-field cooling. The cooling field was 5 T. The sample consists of composite microspheres (latex2Fe$_3$O$_4$2Au), dried in 0.2 T on a quartz substrate.](image)
4.3.4 Optical properties

Another interesting feature of these composite particles with a metallic Au particle shell is related to their optical properties. In particular, gold nanoparticles exhibit a strong plasmon absorption band feature which make them very attractive candidates to build up photonic band gap materials. Surface plasmon effects are due to the coupling of surface electrons (conduction electrons) with incident electromagnetic waves. It was shown that the absorption spectrum of the metal particles is very sensitive to particle size, shape, composition, temperature and dispersion medium [65].

Here are some preliminary results on the optical properties of the composite particles. The evolution of the absorption spectra with the number of the gold shells for composite particles is shown in Figure 4.38.

![Absorption spectra of PS spheres coated with 2 Fe₃O₄ layers (black curve) and after further coverage with 2 (red curve) and 3 Au nanoparticles layers (blue curve). The right graph represents the absorption spectra of the silica encapsulated gold nanoparticles in aqueous solution.](image)

Figure 4.38: Absorption spectra of PS spheres coated with 2 Fe₃O₄ layers (black curve) and after further coverage with 2 (red curve) and 3 Au nanoparticles layers (blue curve). The right graph represents the absorption spectra of the silica encapsulated gold nanoparticles in aqueous solution. The absorption spectra reveal a plasmon resonance peak at $\lambda_{max} = 520$ nm.

As we can see in Figure 4.38a), the PS sphere covered with two magnetite layers exhibits a single peak at 425 nm. The origin of this peak can be due to light scattered by the particles. The PS spheres covered with two gold shells (red curve) and with three gold shells (blue curve) show additional peaks due to a plasmon resonance[65]. The peaks are indicated by arrows.
Figure 4.38 b shows the absorption spectra of gold nanoparticles in aqueous solution. The spectrum of this system displays a maximum at $\lambda_{\text{max}} = 520$ nm, which is the standard result for gold colloids. We mention that the gold nanoparticles are encapsulated in small silica nanoparticles. However, due to the electronic inertness of the silica, there is not charge transfer with gold nanoparticles.

With the deposition of gold nanoparticles on PS/magnetite spheres, the plasmon resonance starts to red-shift. For two layers of Au nanoparticles $\lambda_{\text{max}} = 565$ nm was found, while for three gold shells the peak was observed at $\lambda_{\text{max}} = 575$ nm. One explanation for the red shift can be given by the coupling of the surface plasmon between neighboring particles [65].

One of the advantages of such composite particles is that we are able to tune the optical resonance by changing the gold thickness.

To conclude the discussion about the composite colloids, it has been shown that magnetic microspheres with a multilayer shell of Au and magnetite nanoparticles can be prepared. FMR measurements reveal an effective anisotropy field, $H_{\text{eff}} = 0.02$ T and an easy axis of magnetization in-plane. A reduction of the magnetic moment of magnetite ($\sim 0.1$ bulk value) is estimated. The reduction is related to the dipolar interactions between particles and to the surface effects. It was observed that one can use the dipolar interactions between particles to tune the magnetic response of the particles.
Chapter 5

Self assembly into 1D, 2D structure

In this section, a few methods such as magnetophoretic deposition and deposition on patterned substrates used to obtain regular structure of micrometer particles are presented.

5.1 Drying process without magnetic field

First, to have a better understanding of pattern formation in an external magnetic field, we present the pattern formation in the absence of the external magnetic field. When a drop of a colloidal solution is spread onto a substrate two basic questions arise: What kind of pattern is formed? Which parameters determine the pattern formation?

In a very simple way, the drying of a colloidal solution deposited on a flat substrate can be described as shown in Figure 5.1. Surface and interfacial energies will determine how the liquid droplets deform when they adhere to a surface. Of course, for a complex study additional forces must be taken into account, mainly gravitational, capillary and hydrodynamic forces [33].

For a spherically shaped droplet deposited on a flat substrate, the contact angle between the droplet and substrate can be calculated by using:

\[
\frac{\gamma_{13} - \gamma_{12}}{\gamma_{23}} = \cos \theta 
\]

(5.1)

where \(\gamma_{12}\) is the interfacial energy between the solution and the substrate, \(\gamma_{13}\) between the substrate and atmosphere and \(\gamma_{23}\) between the drop and atmosphere. The angle \(\theta\) is the contact angle between the drop and the substrate. It was observed [48], that the contact angle can be changed by modifying the surface chemistry or changing the medium. For example, by preheating the quartz substrate above 300° C, the contact angle increases from 0° to about 60° [48].

In our case the wettability played a very important role. An important aim of the present work has been to observe, in real-time, the dynamics of the patterns formation from the colloidal

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1\(\gamma\) is given in units of energy per unit area mJm\(^{-2}\) or in units of tension per unit length mNm\(^{-1}\).
water-based solution. To achieve this a high wettability (small contact angle) between the substrate and the solution is necessary. A small contact angle (10°-15°) has been obtained by depositing a drop of colloidal solution (2-5 µl) on a glass substrate covered with polymethylmethacrylate (PMMA). The direct visualization by means of a CCD camera attached to an optical microscope is then possible. The use of quartz or silica substrates leads to a high contact angle and the examination of the pattern formation is not possible.

In the following we examine the effect of the particle concentration and the substrate on the pattern formation from the colloidal solution in the absence of external magnetic fields. The effect of the particle concentration is shown in Figure 5.2. For all the experiments a drop consisting 10 µl colloidal solution was evaporated in the ambient atmosphere. It was observed that at low concentration (∼ 4.9×10^5 microspheres/µl), the particles are randomly distributed on the substrate and just a few dimers or trimmers are formed (Figure 5.2a). At high concentration (∼ 10^6 microspheres/µl), small chains randomly oriented appeared (Figure 5.2b). Moreover, when the particles concentration is high, very large parts of the substrate are occupied with bilayers or trilayers.

The influence of the substrate on the pattern formation is clearly illustrated in Figure 5.3, where the microspheres were deposited on a silica (Figure 5.3 a), respectively silica covered with PMMA substrate (Figure 5.3 b). When a silica substrate is covered with PMMA the friction forces are reduced, thus a greater mobility of the particles on the substrate can be achieved. This is shown in Figure 5.3 b), where the particles have a tendency to form small chains and
a netlike structure. The smaller mobility of the microspheres is achieved by using a quartz substrate (SiO$_2$), which is negatively charged. This will enhance the electrostatic attraction between the substrate and the particles. We mention that all the composite and core-shell particles used in the experiments, are positively charged. In the absence of an external magnetic field we notice a intense Brownian motion of the particles during the water evaporation. The mech-

Figure 5.2: a), b) Optical microscopy of dried composite microspheres (latex2Fe$_3$O$_4$2Au), with a diameter of 810 nm, on silica substrate in the absence of an external field. The images represent the final pattern for two different concentrations. At low concentration (a) the particles are randomly distributed, while at high concentration (b) the particles form an open loop structure with no particular spatial orientation.
anism of pattern formation from micrometer spheres on a flat substrate is explained in [30] in
detail. According to [30], the ordering starts when the thickness of the water layer containing
microspheres becomes approximatively equal to the particle diameter.

Figure 5.3: Dried core-shell particles (latex5Fe₃O₄) deposited on silica substrate a) and on silica
covered with PMMA b).
5.2 Pattern formation under in-plane magnetic field

The next step was to study the pattern formation in the presence of an external magnetic field. This section presents the results for the samples exposed to an in-plane magnetic field. The magnetophoretic deposition technique has been used, where a drop of colloidal solution is dried on a flat substrate in the presence of an homogeneous magnetic field. Several substrates such as silica, quartz and patterned glass substrates were used. In Figure 5.4 the formation of linear chains in the presence of an applied magnetic field is shown. In this case the colloidal solution is deposited on a patterned glass substrate covered with PMMA in ambient atmosphere. The image (a) represents the microspheres in water solution in zero magnetic field. These are in thermal motion and have no tendency to agglomerate. This is an indication that the net magnetic dipole moment carried by the microspheres either is zero or has a very small value. The Brownian motion leads to the statistical arrangement of the colloidal microspheres. The situation changes when an external magnetic field is applied (frames b, c, d). The particles start to attach to each other to form small chains along the direction of the external magnetic field. For the above described measurement and for the others were the dynamics of the particles was recorded a bar magnet with a field strength of approximatively 0.1 T was used. For the rest of the experiments, the samples were prepared first and investigated after the drying process in a dried state. To dry the samples a Brucker electromagnet with a magnetic field of up to 1.2 T was used. By applying an external magnetic field, the magnetic moments of the magnetite nanoparticles in the shell are aligned and the microspheres carry a net magnetic moment. The attractive dipolar interactions between the microspheres are then sufficiently large to overcome the thermal motion and to induce the formation of chains. The chains start to form in the moment when the magnetic field is applied. We assume that as soon as two or more microspheres are attracted they form a larger dipole moment and create a local inhomogeneous magnetic field, which pulls nearby particles to the front and back ends depleting the region around the ends. Under an applied in-plane magnetic field, the chains grow until the area at their ends is completely depleted. This process occurs as long as the particles move in the liquid carrier.

A pattern of a dried, field-induced structure is shown in Figure 5.5. A 10 µl drop of latex5Fe₃O₄ with a concentration corresponding to a coverage $c \ll 0.5 \text{ML}/25 \text{mm}^2$ was deposited on a quartz substrate ($5 \times 5 \text{ mm}^2$) and slowly evaporated while an external magnetic field was applied parallel to the plane of the substrate. Figure 5.5a) displays the dried microspheres in zero applied magnetic field, while Figure 5.5 b) displays the field-induced chains in 0.4 T. In this way chains with an average length of 600 µm were formed. For some of the chains the total length exceeded 2 mm. The chain width is on the order of one, two, or at most three microsphere diameters. The
Chapter 5. Self assembly into 1D, 2D structure

Figure 5.4: Optical micrograph (top view) of the microspheres (latex5Fe3O4) dispersed in water solution: a) without any applied magnetic field and b) after 2 s, c) 4 s, d) 6 s from the application of the magnetic field. The direction of the external magnetic field is illustrated.

The complexity of the pattern is found to depend on several parameters, e.g., the field strength, the volume fraction and the type of the substrate. It was observed that by increasing the strength of the drying field, the spacing between chains becomes larger. For example, for the core-shell particles with 1 μm diameter, dried on the quartz substrate, at $B_{\text{dry}} = 0.2$ T the average distance between chains was 30 μm. The enhancement of the field strength by a factor of 3 ($B_{\text{dry}} = 0.6$ T) determines the increase of the separation between chains with a factor of 2.3 (70 μm).

Moreover there is a direct correlation between the length of the chains and the concentration of particles in the solution. For example, when the concentration of the particles varies from $5.6 \times 10^5$ balls/μl to $8.4 \times 10^5$ balls/μl the average length increases from 100 μm to 400 μm.

At this point, some remarks about magnetic field-induced structures have to be made. First, we observed that two or more chains of dipolar coupled microspheres have a tendency to clump together, even at very low volume fraction. This process is shown in Figure 5.6. The sequential frames a, b, c show the chains behavior in water solution in the presence of an external magnetic field. At first glance the lateral coalescence of the chains is very surprising. The reason is that even for very long chains, the dipole-dipole interaction between uniform and parallel chains is always repulsive for chains more than two particle diameters apart [42]. However, we have clearly seen that some of the chains were sticking together. One has to keep in mind that even if
Figure 5.5: Optical images (top view) of dried core-shell particles (latex5Fe₃O₄) deposited on quartz substrate: a) without applied magnetic field and b) in an external, in-plane, homogeneous magnetic field of 0.4 T. The scale bar corresponds to both images; A schematic of the experimental setup is shown in c).

the chains are aligned with the magnetic field, the chains are also exposed to thermal fluctuations and the external fluid flow. The competition between these has an influence on the movement of the chains.

Another interesting behavior of the dipolar chains has been observed during the drying process, when the magnetic field was flipped in plane by 180°. Two extreme situations have been tested: slow and rapid variation of the magnetic field. When the magnetic field is rotated slowly the chains of microspheres follow the field direction, remaining unbreakable and rotating as a rigid chain. During the rotation some of the chains seemed to have a very strong contact point with the substrate, and the rotation took place around this point. A rapid variation of the field orientation splits the chains into small chains. These small chains are able to follow the field direction. When the small chains are again parallel to the applied field (in stationary conditions) they join together. This degree of flexibility is related to the strength of the magnetic field, the volume fraction, the viscosity of the solvent and the sweep rate of the magnetic field.

By inspecting a dried sample we noticed that the microspheres do not form a straight line. By means of the optical and atomic force microscopy it was possible to observe the arrangement
Figure 5.6: a) Optical images (sequential frames) of the chains in water solution; b) after 2 s; c) after 7 s. The aggregation of two chains is marked.

of the microspheres within one chain. The arrangement is shown in Figure 5.7 a,b, where chains of about 15 μm and 30 μm length were imaged with AFM and with optical microscopy, respectively. Two interesting aspects should be mentioned. First, a slight angular deviation from the direction of the external magnetic field was observed. Second, it seems that the particles
are not linear and not uniformly coupled, but they tend to coupled in pairs or triples within one chain. The fluctuations in the separation between spheres is up to 30% of a diameter.

The aggregation process and the chain-like structure formation in an externally applied magnetic field of various ferrofluids were intensively studied [19], [27], [44], [90]. In our case, each $\text{Fe}_3\text{O}_4$ magnetite nanoparticle corresponds to a single domain and therefore, has a permanent magnetic moment. In the absence of an external magnetic field the magnetic moments of the individual nanoparticle are randomly oriented on the spheres, thereby giving a zero net magnetic moment for each sphere or a very small one (a schematic is shown in Figure 5.8). Experimentally, at a certain volume fraction the absence of the chain-like structure (see Figure 5.5 a)) supports the above assumption. The hypothesis of zero net magnetic moment is consistent with the result of the simulations presented in [51]. In order to find out the spin configuration of one microsphere numerical calculation have been performed. The results are shown in Figure 5.9. The simulation were done by using the conjugate gradient method. This method is based on the minimization of the total magnetic energy (the sum between dipole energy and Zeeman energy). The model considers: i) the lattice magnetic anisotropy is negligible; ii) the particles are perfectly spherical. Hence, there is no shape anisotropy per particle and no indirect exchange interactions between particles. The simulations were done for a value of a packing factor of 0.78, and 300 magnetic particles deposited on a surface of a sphere have been assumed.
The result is shown in Figure 5.9. We notice that there are many random orientations of the magnetic moments on the surface of the sphere and only a very small degree of local order. The calculations predict that there is no net magnetic moment for one sphere in zero applied magnetic field. The same result has been obtained by using the model described in [84] to simulate the magnetization curves for randomly distributed core-shell particles.

![Figure 5.8: Schematic illustration of the magnetic moments of single-domain Fe₃O₄ nanoparticles covering the polystyrene sphere, in the absence and in the presence of the applied magnetic field.](image)

When a magnetic field is applied, a magnetic dipole moment \( m \) is induced in each sphere by aligning the magnetic moments of Fe₃O₄ nanoparticles partially with the magnetic field. Thus, two magnetized spheres with their magnetic dipole moments aligned along the direction of the magnetic field will interact with each other via the dipole-dipole interaction energy. This interaction is given by the following expression, in SI units:

\[
U_d(r, \theta) = \frac{\mu_0 m^2}{4\pi} \left( \frac{1 - 3 \cos^2 \theta}{r^3} \right)
\]  

(5.2)

where \( \theta \) is the angle between the direction of the external applied magnetic field and the line joining the center of mass of particles, and \( r \) is the distance between the center of the spheres. Note that Eq. 5.2 neglects the multipole contributions.
Figure 5.9: Spin configuration of a magnetic sphere in zero applied magnetic field. The arrangement of the particles on one sphere was considered regular a-b) and random c).

The calculation of the dipole-dipole interaction energy for two microspheres which are in contact (r = 2a; a is radius of one microsphere) and aligned head-to-tail (θ = 0°) yields the value: $1.4 \times 10^{-16}$ J, which is large in comparison with the thermal energy at 300 K $^2$. A value of the magnetic moment of $2.64 \times 10^{-14}$ Am$^2$ is used.

Basically, there are two dimensionless parameters which determine the ordering of our system [44]. The first reflects the competition between the dipole-dipole interaction (which aligns the droplets together) and thermal energy (which tries to randomized the droplets),

$$K_{dd} = \frac{U_{dd}}{k_B T} \quad (5.3)$$

The second, called Langevin parameter, determines the strength of Zeeman energy of the dipole in the magnetic field relative to the thermal energy $k_B T$:

$$K_{df} = \frac{\mu_{eff} B_{dry}}{k_B T} \quad (5.4)$$

where $B_{dry}$ designates the magnetic field used to form the chain-like structures. At a fixed temperature, $K_{dd}$ can be controlled by adjusting either the magnetization or the diameter of

$^2k_B T = 4 \times 10^{-21}$ J
the particles. Taken a magnetic moment of $2.64 \times 10^{-14}$ Am$^2$ at room temperature, the value $K_{dd} = 3.5 \times 10^4$ is obtained. As expected, the magnetic interactions will dominate over the thermal motion. When the dipolar interaction between particles exceeds the thermal energy, the particles aggregate into chains of dipoles aligned with the field direction. For the range of fields used in our measurements, we find $K_{df} = 13 \times 10^5$ at 0.2 T and $3 \times 10^5$ at 1.2 T. $K_{df}$ tends to infinity corresponds to the case where all dipoles are aligned parallel to the external field. We calculated also, the magnetic forces between particles resulting from dipolar interactions using the follow formula [90]:

$$F_{pair} = \frac{6\mu_0\mu^2_{eff}}{d^4}$$

(5.5)

where $d$ is the center-to-center distance between particles. The attractive dipole force within a long chain reads as:

$$F_{chain} = -\xi(3)\frac{6\mu_0\mu^2_{eff}}{d^4}$$

(5.6)

where $\xi(3) = 1.202$ is the Riemann function. For example, for two particles within a chain, with center-to-center distance of 1000 nm, a dipole force of about $6.96 \times 10^{-9}$ N could be estimated. In [90], the magnetic forces both between the individual particles and within a chain are calculated in detail. They observed that a mutual induction of particles within a chain enhances their magnetization by up to 34% beyond the magnetization of an identical droplet in isolation. This enhancement is not observed in our case.


5.3 Pattern formation under perpendicular magnetic field

In this section the pattern formation of the micrometer particles subjected to an applied perpendicular magnetic field is discussed. Several studies have been done on the phase behavior of the different magnetic colloids under perpendicular magnetic field [19], [45], [47].

By applying a magnetic field perpendicular to the plane of the substrate, the induced magnetic moment of the microspheres is normal to the substrate and the microspheres will repel each other. This leads to a columnar structure of the particles in the carrier solution. The final pattern of the magnetic colloids subjected to a perpendicular magnetic field can exhibit various phases, from highly ordered [49] such as hexagonal, rectangular, triangular, to a disordered structure [80], for example, labyrinthes, branched or net-like structure. This transition phase is strongly correlated with the volume fraction, the strength of the magnetic field, the sweep rate of the magnetic field, the viscosity of the medium.

The structure which is observed in our case is disordered. The microspheres arrange in glassy or labyrinthine structures rather then hexagonal or triangular structures. Two representative examples are displayed in Figure 5.10, where the optical images of the final pattern of the core-shell particles dried in a perpendicular magnetic field of 4 and 12 T are shown. For a drying field of 4 T a net-like structure was observed, while for 12 T one can see the appearance of so-called "branched" structure. A systematic dependence of the pattern formation as a function of perpendicular applied magnetic field was not observed. Some short range ordering is observed as one can see in Figure 5.11 but this was not a well controlled process. The sample was prepared by drying a drop of composite microspheres in a perpendicular magnetic field of 8 T. In Figure 5.11 AFM images taken in tapping mode, in air, for a this sample are presented.

The origin of the disorder structure is not entirely clear. Possible explanations are:

i) it might be that the particles have not enough time to reach the equilibrium state; another carrier with a larger evaporation time should be use e.g kerosene.

ii) the columns which are formed when the magnetic field is normal to the substrate plane are longer then the thickness of the colloidal drop, thus they break up and drop down after the evaporation of the solvent.
Figure 5.10: Optical micrographs of latex$5\text{Fe}_3\text{O}_4$, dried on the quartz substrate in perpendicular magnetic field of a) 4 T and b) 12 T.

Figure 5.11: AFM-tapping mode of composite microspheres (latex$2\text{Fe}_3\text{O}_4\text{3Au}$) dried in a perpendicular magnetic field of 8 T, on a quartz substrate. For the left above image the scan size is $30 \times 30 \ \mu m^2$, while for the lower image is $4 \times 4 \ \mu m^2$. The height variation for the large image scan corresponds to 2 $\mu m$. 
5.4 Structure on patterned substrate

Another promising approach to self-assemble colloidal particles into ordered structure is to use patterned substrates [30].

Figure 5.12: a) AFM image of a patterned substrate with a periodicity of 1 \( \mu m \); b) SEM image of polystyrene spheres covered with one magnetic layer deposited on this substrate; c), d) Different magnification of SEM image of polystyrene spheres deposited on the same substrate.

We have used for this a patterned glass substrate covered with PMMA. The patterned substrates were prepared by means of optical lithography and are described in details in [82]. An AFM image of the substrate is shown in Figure 5.12a. The idea was to use the patterned substrate which has the same periodicity as the particles diameter in order to push the particles to arrange in the holes of the substrate. The results are shown in Figure 5.12 b), where a scanning electron microscopy (SEM) of the core-shell particles (latex\( \text{Fe}_3\text{O}_4 \)) with 680 nm in diameter deposited on this patterned substrate is presented. One can see that the particles have a tendency to agglomerate (due to the magnetic interactions) and do not self-assemble into regular arrays. On the other hand using non-magnetic polystyrene spheres (with a diameter of 640 nm) one gets an array which exhibits some degree of 2D order, alternating a rectangular with a hexagonal structure, on a large scale (Figure 5.12 c), d)).

In this section the pattern formation of the core-shell and composite particles has been inves-
tigated. By applying an in-plane magnetic field an induced self-assembly of the particles into linear chains is demonstrated. A perpendicular magnetic field induces mainly a disordered structure. Using patterned substrates a good assembly of the charged polystyrene spheres is achieved. Due to the magnetic interaction between the core-shell particles an ordered array on the patterned substrate was not observed.
Chapter 6

Conclusions

This work presented a detailed investigations of the structure and the magnetic properties of three systems: Fe$_3$O$_4$ nanoparticles, core-shell and composite particles. The water-based chemically synthesized Fe$_3$O$_4$ nanoparticles have an average diameter of 12±3 nm while the size of the core-shell and composite particles ranges from 680-1000 nm. Various experimental techniques, such as TEM, AFM, XAS, XPS, XRD, SQUID, FMR, MFM have been employed to study the above systems.

The main results for the Fe$_3$O$_4$ nanoparticles can be summarized as follow:

- The X-ray diffraction pattern revealed that the phase of α-Fe$_2$O$_3$ does not exist in our particles. Due to the almost identical X-ray diffraction pattern of γ-Fe$_2$O$_3$ and Fe$_3$O$_4$, the existence of γ-Fe$_2$O$_3$ can not be ruled out.

- According to HRTEM investigations, the chemically synthesized nanoparticles consist of 80% Fe$_3$O$_4$ and 20% γ-Fe$_2$O$_3$. The TEM investigations have shown that the nanoparticles are well isolated, mostly with spherical shapes and only a few with faceted shapes.

- The fine structure of the Fe L-edge found in XAS spectra for Fe$_3$O$_4$ shows an oxidic environment. The peak at 709.5 eV found at Fe L$_3$-edge and the difference between the oxidic peak and the metallic peak of 1.4 eV are in a very good agreement with the literature values reported for the magnetite [32]. The XPS results concord well with data reported on magnetite [31].

- With a home-build SQUID, the vertical component of the dipolar magnetic stray field of the in-plane magnetized magnetite nanoparticles has been measured. This indicates that the nanoparticles have a remanence magnetization at room temperature.

- The magnetometry measurements show a small coercivity (20 Oe) at 300 K. The coercivity value increases with decreasing temperature. By fitting the magnetization curves at
5 K, an effective anisotropy constant \( K_{\text{eff}} = 0.21 \times 10^5 \text{ J/m}^3 \) is calculated. The obtained value is larger than the magnetocrystalline anisotropy constant reported for bulk Fe\(_3\)O\(_4\).

- At 300 K, the FMR polar angular dependence measurements yield an effective anisotropy field of \( H_{\text{eff}} = 0.12 \text{ T} \). We associate the presence of the intrinsic magnetic anisotropy field to the interparticle interactions and to an effective anisotropy of the individual particle. The only interaction between coated particles has a dipolar character. This observation has been confirmed by the relative narrow peak-to-peak linewidth \( \Delta B_{pp} = 0.06 \text{ T} \). An out-of-plane anisotropy constant \( K_{2,\perp} = -1.64 \times 10^5 \text{ J/m}^3 \) has been determined. The lowest resonance field occurred when the static magnetic field was applied parallel to the sample plane, confirming the in-plane orientation of easy axis of magnetization.

- Due to a small remanence magnetization of the magnetite nanoparticles, a MFM contrast could not be resolved.

By using the recently developed layer-by-layer deposition technique, the Fe\(_3\)O\(_4\) nanoparticles have been used to create novel core-shell and composite particles. This method offers the flexibility to tune and to control the thickness and the composition of the deposited multilayers on the nanoscale level. The resulted core-shell particles consist of a 640 nm diameter polystyrene spherical colloidal core covered with a shell of Fe\(_3\)O\(_4\) and polyelectrolyte multilayers. Bellow, the results obtained for the core-shell particles are presented.

- The TEM, SEM and AFM investigations reveal that uniform micrometer-size magnetic core-shell particles with defined shape, composition and multilayer shell thickness have been produced.

- The AFM and Optical Microscopy methods have been employed to investigated the magnetic field-induced pattern formation of water-based core-shell colloids. The experiments show that an in-plane applied magnetic field induces a chain-like structure. Chains with lengths up to 2 mm and width on the order of one, two or at most three particle diameters have been observed. The strength of the applied magnetic field, the volume fraction of the solution and the charge of the substrate influence the separation between the chains and their length. In a perpendicular magnetic field a mainly disordered structure has been observed. Note that, by using a proper substrate with a high wettability, the pattern formation has been visualized in real-time.

- The FMR angular dependence measurements on aligned core-shell particles indicate a long-range order due to dipolar coupling between particles within the chain and an
effective anisotropy field $H_{eff} = 0.03$ T at 300 K. The easy axis of magnetization is found in-plane, along the direction of the chains.

- The calculations predict that there is no net magnetic moment coming out from one core-shell sphere in zero applied magnetic field.

- SQUID-magnetometry studies at 300 K, exhibit a reduction of the magnetic moment of Fe$_3$O$_4$ ($\sim 0.3$ bulk value). The origins for this reduction of the magnetization are the surface effects and the packing factor. No superparamagnetic behavior at room temperature was observed.

The composite particles have the same polystyrene core covered with consecutive shells of Fe$_3$O$_4$, polyelectrolyte and 15 nm diameter Au nanoparticles.

The main results for the composite particles are:

- It was shown that magnetic composite microspheres with tailored optical properties can be prepared via manipulation of the silica-encapsulated gold nanoparticles multilayer shell thickness.

- The composite microspheres were self-assembled into chain-like structure by using magnetophoretic deposition technique.

- The FMR polar angular dependence investigations on the aligned composite particles reveal a smaller value for the effective anisotropy field $H_{eff} = 0.02$ T. A broad peak-to-peak linewidth $\Delta H_{pp} = 0.14$ T has been measured.

- The magnetometry studies reveal a small magnetic moment of Fe$_3$O$_4$ ($\sim 0.1$ bulk value). This reduction is related to the interparticle interactions and surface effects.

- It was observed that the presence of the silica-encapsulated gold shells leads to a weaker dipolar interaction between microspheres within the chains.
Appendix A

A.1 Ferromagnetic resonance on magnetite hexane-based nanoparticles

In this section the ferromagnetic resonance measurements for hexane-based magnetite nanocrystals coated with oleic-acid are presented. The particles were obtained from Dr. Gil Markovich from School of Chemistry, Tel Aviv University-Israel. A detailed description about preparation, structure and magnetic properties is given in [37], [71].

The particles are near spherical in shape with an average size of 8.5±1.4 nm. The nanoparticles were assembled into close-packed monolayer as well as multilayer arrays. Both monolayer and multilayers were investigated.

<table>
<thead>
<tr>
<th>sample</th>
<th>$B_{res∥}$ (T)</th>
<th>$B_{res⊥}$ (T)</th>
<th>$B_{res∥} - B_{res⊥}$ (T)</th>
<th>$ΔB_{pp∥}$ (Oe)</th>
<th>$ΔB_{pp⊥}$ (Oe)</th>
</tr>
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<tr>
<td>one monolayer</td>
<td>0.27</td>
<td>0.49</td>
<td>0.22</td>
<td>480</td>
<td>400</td>
</tr>
<tr>
<td>four monolayers</td>
<td>0.27</td>
<td>0.51</td>
<td>0.24</td>
<td>460</td>
<td>513</td>
</tr>
</tbody>
</table>

Table A.1: The resonance fields and peak-to-peak linewidth for one monolayer and four monolayers hexane-based magnetite.

Both spectra show a large angular dependence of the resonance field. In Table A.1 the resonance fields for two geometries and the peak-to-peak linewidth are tabulated. $B_{res⊥}$ means that the applied magnetic field was perpendicular to the grid plane and at $B_{res∥}$ the magnetic field was parallel to the grid plane.
Figure A.1: FMR angular dependence for four monolayers magnetite deposited on a carbon-coated copper grid at room temperature. The lower and the larger resonance field values $B_{\text{res}}=0.27$ T and $B_{\text{res}}=0.51$ T were observed when the magnetic field has been applied in the substrate plane and perpendicular to the substrate plane, respectively.

Figure A.2: FMR angular dependence for one monolayer magnetite deposited on a TEM grid at room temperature.
A.2 General properties of iron oxides

<table>
<thead>
<tr>
<th></th>
<th>Goethite</th>
<th>Lepidocrocite</th>
<th>Akaganite</th>
<th>Feroxyhyte</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>$\alpha$-FeOOH</td>
<td>$\gamma$-FeOOH</td>
<td>$\beta$-FeOOH</td>
<td></td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>tetragonal</td>
<td>hexagonal</td>
</tr>
<tr>
<td><strong>Cell dimension</strong></td>
<td>$a = 0.460$, $b = 0.995$, $c = 0.302$</td>
<td>$a = 0.388$, $b = 1.254$, $c = 0.307$</td>
<td>$a = 1.000$, $b = 0.303$, $c = 0.307$</td>
<td>$a = 0.293$, $c = 0.460$</td>
</tr>
<tr>
<td><strong>Density (g/cm$^3$)</strong></td>
<td>4.26</td>
<td>4.09</td>
<td>3.56</td>
<td>4.20</td>
</tr>
<tr>
<td><strong>Color</strong></td>
<td>yellow-brown</td>
<td>orange</td>
<td>yellow-brown</td>
<td>red-brown</td>
</tr>
<tr>
<td><strong>Type of magnetism</strong></td>
<td>antiferromag.</td>
<td>antiferromag.</td>
<td>antiferromag.</td>
<td>ferrimag.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ferrihydrite</th>
<th>Haematite</th>
<th>Magnetite</th>
<th>Maghemite</th>
<th>Wüstite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>$\delta$-FeOOH</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>Fe$_3$O$_4$</td>
<td>$\gamma$-Fe$_2$O$_3$</td>
<td>FeO</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>hexagonal</td>
<td>trigonal</td>
<td>cubic</td>
<td>cubic or tetragonal</td>
<td>cubic</td>
</tr>
<tr>
<td><strong>Cell dimension</strong></td>
<td>$a = 508$, $c = 0.94$</td>
<td>$a = 0.503$, $c = 1.375$</td>
<td>$a = 0.839$</td>
<td>$a = 0.834$</td>
<td>$a = 4302$</td>
</tr>
<tr>
<td><strong>Density (g/cm$^3$)</strong></td>
<td>3.96</td>
<td>5.26</td>
<td>5.18</td>
<td>4.87</td>
<td>5.9</td>
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<tr>
<td><strong>Color</strong></td>
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<td>red</td>
<td>black</td>
<td>reddish-brown</td>
<td>black</td>
</tr>
<tr>
<td><strong>Type of magnetism</strong></td>
<td>speromag.</td>
<td>weakly ferromag. or antiferromag.</td>
<td>ferrimag.</td>
<td>ferrimag.</td>
<td>antiferromag.</td>
</tr>
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Table A.2: General properties of iron oxides
### A.3 Magnetic properties of bulk Fe$_3$O$_4$, α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$

<table>
<thead>
<tr>
<th></th>
<th>Fe$_3$O$_4$</th>
<th>α-Fe$_2$O$_3$</th>
<th>γ-Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic structure</td>
<td>ferrimagnetic</td>
<td>weakly ferromagnetic</td>
<td>ferrimagnetic</td>
</tr>
<tr>
<td>Temperature (K)$^a$</td>
<td>850 $T_C$</td>
<td>956 $T_C$</td>
<td>820-986 $T_C$</td>
</tr>
<tr>
<td></td>
<td>120-Verwey transition</td>
<td>260 $T_M$</td>
<td></td>
</tr>
<tr>
<td>Saturation magnetization at 300 K (Am$^2$/Kg)</td>
<td>92-100</td>
<td>0.3</td>
<td>60-80</td>
</tr>
<tr>
<td>Magnetostriction constant $\lambda_s$</td>
<td>35x10$^{-6}$</td>
<td>8x10$^{-6}$</td>
<td>35x10$^{-6}$</td>
</tr>
</tbody>
</table>

Table A.3: Magnetic properties of bulk Fe$_3$O$_4$, α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$.

$^a$) $T_N$ - Néel temperature, $T_C$ - Curie temperature, $T_M$ - Morin temperature.
A.4 X-ray diffraction of the iron oxides

Figure A.3: X-ray diffraction pattern for several iron oxides. Taken from Ref. [14].
Figure A.4: X-ray diffraction pattern for several iron oxides. Taken from Ref. [14].
A.5 AFM-tips

A brief description of the cantilevers used for the AFM and MFM measurements is presented below [15]. The cantilevers with a spring constant around 40 N/m (for tapping mode) along with very sharp tips are desirable for achieving best lateral resolution in AFM. They are micro-fabricated from silicon or silicon nitride waves by using photolithographic techniques. V-shaped cantilevers are the most popular ones, providing low mechanical resistance to vertical deflection and high resistance to lateral torsion.

The tips usually have either pyramidal, conical or tetrahedral geometries. Nominal tip radii at the tip apex are around 20-60 nm. The main characteristics of the cantilevers used in the present work are tabulated below. Figure A.5 represents optical micrographs of typical cantilevers used for contact mode, tapping mode and magnetic force microscopy.

<table>
<thead>
<tr>
<th></th>
<th>width ($\mu$m)</th>
<th>length ($\mu$m)</th>
<th>thickness ($\mu$m)</th>
<th>resonance frequency (kHz)</th>
<th>spring constant (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>contact mode</td>
<td>50 ± 3</td>
<td>460 ± 5</td>
<td>2 ± 0.5</td>
<td>12 ± 3</td>
<td>0.15 ± 0.1</td>
</tr>
<tr>
<td>tapping mode</td>
<td>28 ± 8</td>
<td>225 ± 10</td>
<td>7 ± 1</td>
<td>190 ± 44</td>
<td>48 ± 27</td>
</tr>
<tr>
<td>MFM-tips</td>
<td>28 ± 8</td>
<td>225 ± 10</td>
<td>3 ± 1</td>
<td>75 ± 30</td>
<td>2.8 ± 2</td>
</tr>
</tbody>
</table>

Table A.4: Some characteristics of the cantilevers which were used.

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<th>Description</th>
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<td>5.12</td>
<td>a) AFM image of a patterned substrate with a periodicity of 1 $\mu m$; b) SEM image of polystyrene spheres covered with one magnetic layer deposited on this substrate; c), d) Different magnification of SEM image of polystyrene spheres deposited on the same substrate.</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>A.3</td>
<td>X-ray diffraction pattern for several iron oxides. Taken from Ref. [14].</td>
</tr>
<tr>
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</tr>
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1) TMR Euroconference-school, "From nanoscopic to mesoscopic magnetic systems-1", Spetses, Greece, 27.08-01.09.2000;
Poster Session: "Magnetic Wires Made from Submicron Spheres with a Multilayered Fe$_3$O$_4$ shell".

2) 1st Workshop on "Correlation of Structure and Magnetism in Novel Nanoscale Magnetic Particles", Smolenice, Slovakia, 27. 10 - 30. 10. 2000;
Oral Presentation and Poster: "Magnetic Wires Made from Submicron Spheres with a Multilayered Fe$_3$O$_4$ shell".

3) 2nd Workshop on "Correlation of Structure and Magnetism in Novel Nanoscale Magnetic Particles", Braunschweig, Germany, 23. 03 - 24. 03. 2001;
Oral Presentation: "Magnetically directed self-assembly of quasi 1-D structure with Fe$_3$O$_4$ core-shell particles".

4) Summer Workshop on Mesomagnetism, Spin Dynamics and Spin Electronics, Santorini, Greece, 30.06-5.07.2001;
Poster Session: "Magnetically directed self-assembly of submicron spheres with a Fe$_3$O$_4$ nanoparticle shell".

5) 5th Workshop on "Correlation of Structure and Magnetism in Novel Nanoscale Magnetic Particles", Thessaloniki, Greece, 03.10-06.10.2002;
Oral Presentation: "Ferromagnetic resonance of magnetic multi-shell composite colloids".

6) AVS 49th International Symposium, Denver, Colorado, USA, 03.11-08.11.2002;
Oral Presentation: "Self-assembly and magnetism in novel magnetic composite microspheres".

7) Workshop "Struktur und Magnetismus ultradünner Metallfilme VI", Chandolin, Schweiz, 25.01-01.02.2003;
Oral Presentation: "Structural and magnetic characterization of ferrimagnetic microspheres".

8) 6th Workshop on "Correlation of Structure and Magnetism in Novel Nanoscale Magnetic Particles", Duisburg, Germany, 21.03-22.03.2003;
Poster Session: "Structural and magnetic characterization of ferrimagnetic microspheres".

9) DPG-Frühjahrstagungen, Dresden, Germany, 24.03-28.03.2003,
Oral Presentation: "Structural and magnetic characterization of ferrimagnetic microspheres".

Poster Session: "Self-Assembly and Magnetic Properties of Core-Shell Colloids".

**Invited talks**

"Magnetic Wires Made from Submicron Spheres with a Multilayered Fe$_3$O$_4$ shell"
Free University Berlin, Prof. Dr. P. Fumagalli ’s group, December 2000;
Publications in International Journals

1) E. L. Bizdoaca, M. Spasova, M. Farle, M. Hilgendorff, F. Caruso
M magnetically Directed Self-assembly of Submicron Spheres with a Fe₃O₄ nanoparticle shell,

Self-assembly and magnetism in core-shell microspheres,

3) M. Broschwitz, S. Knetsch, A. Borgschulte, L. Bizdoaca, J. Schoenes
Size effects of optical and magneto-optical properties of epitaxial CrPt₃ films

Ratio of orbital-to-spin magnetic moment in Co core-shell nanoparticles