The origin of the magnetism of maghemite $(\gamma$ -Fe₂O₃)-based core/shell nanoparticles

by

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Abstract

The study of core/shell nanoparticles has gained considerable interest due to the potential to engineer interactions at interfaces to provide a rich variety of properties which are not achievable with single phase counterparts. However, an open question remains: What is the precise nature of the core/shell interface and how does it produce the nanoparticle properties? For magnetic systems this is exemplified by interfacial spin disorder and exchange interactions that determine the magnetic coupling between the core and shell. To answer this question necessitated a detailed understanding of interfacial intermixing effects.

In this work, these questions are addressed by describing in detail the relationship between interfacial intermixing, interfacial magnetic interactions, and the overall magnetism of γ -Fe₂O₃-based core/shell nanoparticles with NiO, MnO and CoO shells. Using element-specific techniques (Mössbauer spectroscopy, x-ray absorption spectroscopy, and x-ray magnetic circular dichroism spectroscopy) interfacial intermixed layers were identified as being formed by transition metal ions from the shell that migrated into the octahedral and tetrahedral sites within the surface layers of the γ -Fe₂O₃. A detailed analysis of the element and site-specific magnetism revealed a clear relationship between the nature of core/shell intermixing, interfacial spin disorder and exchange interactions that modified directly all aspects of the nanoparticle magnetism (e.g. relaxation, anisotropy, and exchange bias). Furthermore, chemical changes induced by intermixing resulted in a temperature dependent transition that modified the interfacial metal-oxygen bonding and that was correlated with the onset of the exchange bias. By disentangling the element- and site-specific magnetism of each species at the core/shell interface, this work provides a clear description of the origin and the variability of the core/shell nanoparticle magnetism based on a precise understanding of interfacial intermixing, and reveals the critical role of the interfacial superexchange pathway responsible for the magnetism.

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Chapter 1

Introduction

The understanding of the physics of the magnetism of nanoparticles has evolved substantially over the past sixty years, developing from a viewpoint that considered nanoparticles as bulk-like magnetic structures with small-scale boundaries [1] to entirely more complex systems that are dominated by surface, disorder, and finite-size effects [2–6]. Whereas in the bulk the magnetism is determined by interactions among 10^{23} atoms in a regular structural environment, in nanoparticles the magnetism is a result of the interactions between 100s–1000s of atoms of which a significant fraction reside on the surface (e.g. ~70 % for a ~5 nm diameter Fe-oxide particle). As such, the magnetism of nanoparticles is of particular fundamental importance because it displays aspects of both atomic and bulk physics. However, a complete understanding of nanoparticle magnetism remains elusive since it is a product of the interplay between atomic and collective behaviours that are not easily disentangled experimentally.

Nanoparticles of transition-metal oxides such as maghemite (γ -Fe₂O₃) have been

of significant continuous interest, most recently due to their biocompatibility and the exceptional variability of their magnetic and electronic properties [7,8]. However, the surface and disorder effects intrinsic to nanoparticles suppress the useful magnetic properties and complicate the interpretation of the nanoparticle magnetism. As a result, substantial research effort is aimed at understanding the origin and manipulation of the magnetism of nanoparticles to optimize the overall properties for use in applications such as drug delivery, cancer treatment via magnetic hyperthermia, magnetic resonance imaging, ultra-high density data storage, and green energy [9,10]. The development of the layered core/shell type nanoparticle has stemmed from the need to achieve overall properties superior to those of single phase or passively oxidized nanoparticles [11–13], in particular through interfacial interactions which can lead to a variety of interesting physical phenomena. The combination of distinctly different core and shell materials, interfacial magnetic interactions, and finite-size and disorder effects act cooperatively to produce overall properties that are not accessible to the individual core and shell materials.

The research challenge I will address is to understand how the overall magnetism of a series of maghemite (γ -Fe₂O₃)-based core/shell nanoparticles with antiferromagnetic shells arises from the interplay between the intrinsic magnetism of the core and shell materials, and finite-size, interface, surface, and disorder effects. This system is an ideal candidate for elucidating the nature of the magnetism of core/shell nanoparticles since the effects of ferrimagnetic γ -Fe₂O₃, antiferromagnetic shells, and dopant ions (i.e. from intermixing) can be distinguished, which is critical to understanding the nature of the magnetism at the core/shell interface. The organization of this Thesis is as follows. The Introduction provides a brief description of magnetic interactions, the magnetism of bulk materials and nanoparticles, and highlights the basic properties of maghemite (γ -Fe₂O₃) structure and nanoscale magnetism. Chapter 2 describes the experimental techniques that were used to characterize nanoparticle properties including structural, atomic, and elementspecific techniques which together enable a clear discussion of the interfacial magnetism. Chapters 3, 4, and 5 describe the magnetism of γ -Fe₂O₃ nanoparticles with NiO, MnO, and CoO shells, including a comprehensive discussion of the occurrence of interfacial intermixing and its relationship to the unique overall magnetism of each system. A summary of the results for the series of core/shell nanoparticles which provides a discussion of the implications of the nature of intermixing and role in determining the magnetic properties is provided in Chapter 6. Conclusions and suggestions for future work are provided in Chapter 7.

1.1 Bulk Magnetism

1.1.1 Magnetic states

In many bulk materials there are magnetic interactions between the atomic magnetic moments that result in spontaneous magnetic order (i.e. without an externally applied magnetic field) when the thermal energy k_BT is less than a critical temperature due to the interaction energy. As shown in Fig. 1.1, in a ferromagnetic (FM) material all of the magnetic moments have the same orientation below the Curie temperature T_C . Alternatively, in an antiferromagnetic (AF) material, the magnetic moments within a unit cell compensate each other, resulting in zero net magnetic moment below the



(a) Ferromagnetic (FM) $T < T_C$



(b) Antiferromagnetic (AF) $T < T_N$



(c) Ferrimagnetic (FiM) $T < T_C$

(d) Paramagnetic (PM) $T > T_C$, T_N

Figure 1.1: Illustration of the spontaneous (zero applied field) magnetic moment configurations for different types of magnetic materials.

Néel temperature T_N . For magnetic materials with antiparallel coupling but where the magnetic moments do not fully compensate, a ferrimagnetic (FiM) material is obtained. Above the critical temperature, the spontaneous ordering of the magnetic moments is lost and the net magnetic moment vanishes; a material at $T > T_C$ or T_N is in the paramagnetic (PM) state.

1.1.2 Exchange Interactions

Magnetic order describes the correlation of magnetic moments of a material. The inter-atomic interactions responsible for this effect are exchange interactions. Exchange interactions are a purely quantum mechanical effect resulting from the Coulomb repulsion between electrons and the Pauli exclusion principle which forbids two electrons from having the same quantum number, which together lead to different energies for parallel and antiparallel spin alignment. The effective coupling between the spins of two atoms a and b $(\vec{S}_a \text{ and } \vec{S}_b)$ can be described by the Hamiltonian

$$\mathcal{H} = -2J\vec{S}_a \cdot \vec{S}_b \tag{1.1}$$

where the exchange integral J describes the exchange direction and strength, and J > 0 for parallel spin alignment, and J < 0 for antiparallel spin alignment; J is often expressed in units of energy or Kelvin. Exchange interactions require effective overlap of the electron wavefunctions (electron orbitals) to correlate the electron spins. In the simplest case, when two atoms are sufficiently close for the electron orbitals to overlap directly, a "direct exchange" interaction results. In many magnetic materials, however, the magnetic atoms or ions are too far apart for the electron orbitals to overlap directly and the magnetism is due to "indirect exchange" interactions. In metals, indirect exchange can be mediated by the conduction electrons; a localized magnetic moment on one metal atom or ion polarizes the conduction electrons which then transfer the interaction on to a second localized magnetic moment some distance r away. This type of exchange interaction is referred to as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction or itinerant electron exchange, and results in an oscillatory sign of J, depending on r [14–16].

In ionic solids, magnetic ions interact indirectly through an intermediate nonmagnetic anion, called the "superexchange" interaction. For example, in transition metal oxides the superexchange interaction is a result of the overlap between the transition metal 3d orbitals and the oxygen 2p orbitals, which enables the transfer of spin polarized electrons. As shown in Fig. 1.2, the magnetic coupling between the valence 3d transition metal cations is mediated by the 2p electrons of a central O^{2-}



Figure 1.2: Illustration of the superexchange interaction mediated by an oxygen anion coupling the spins of two transition metal ions in an octahedral ligand field. Interaction is shown for (a) AF coupling of two d^3 cations, (b) AF coupling of two d^8 cations, and (c) FM coupling of a d^3 and d^5 cation.



Figure 1.3: Illustration of the double exchange interaction mediated by an oxygen anion coupling the spins of two transition metal ions in an octahedral ligand field. Interaction is shown for (a) Mn-ions $(d^4 - d^3)$, and (b) Fe-ions $(d^6 - d^5)$.

anion, and the sign of J is determined by the Pauli exclusion principle and Hund's rules coupling of the 3d and 2p spins. For example, for two transition metal ions both having less than half filled or more than half filled valence shells, such as the d^3-d^3 and $d^8 - d^8$ configurations, shown in Fig. 1.2a and b, AF coupling occurs, whereas a combination of $d^3 - d^5$ configurations results in FM coupling (Fig. 1.2c). The sign and strength of J depends on the degree of metal-oxygen orbital overlap, bond length and symmetry, metal valence, degree of covalency, and the bonding geometry. The superexchange interaction is described empirically through the Goodenough-Kanamori rules [17-19], which describe the relative effects of these factors. In some oxides, the magnetic ions may also couple via the "double exchange" interaction The double exchange requires a mixed valence system, and occurs through [20].the virtual hopping of an electron of a given spin from one ion to the other. As depicted in Fig. 1.3, it is more energetically favourable for the delocalized electron to transfer between ions with identical electronic configurations [20, 21], so that the double exchange interaction favours FM alignment of the two magnetic ions.

1.1.3 Magnetic anisotropy

The magnetic anisotropy K refers to the tendency of the magnetization \vec{M} to lie in a particular direction. There are several contributions to K such as the magnetocrystalline, shape, strain, and exchange anisotropy.

The magnetocrystalline anisotropy K_u is the anisotropy that is intrinsic to a material and is a result of the spin-orbit interaction which couples the direction of the spin moment to the crystalline lattice. If an anisotropy energy E_A is the energy required to rotate the magnetization from an "easy" crystalline direction to a "hard" direction, the anisotropy energy may be described by [21]

$$E_A = K_{u,1} \sin^2(\theta) + K_{u,2} \sin^4(\theta) + K_{u,3} \sin^6(\theta) + \cdots$$
(1.2)

where $K_{u,i}$ are the anisotropy constants and θ is the angle between the magnetization and the easy direction.

There is also a shape anisotropy, resulting from the demagnetization field. For nanoparticles, small deviations from a perfectly spherical shape result in the easy axis lying parallel to the longest axis of the particle. A surface anisotropy K_s may also contribute to the total effective anisotropy of nanoparticles (discussed in Sec. 1.3.4). Also, the broken symmetry and loss of full coordination at the surface of a nanoparticle can impart some strain on the surface layers. In core/shell systems this may also result in surface or interface strain that can depend on the shell crystallinity and thickness. As a result, for spherical nanoparticles E_A is approximated using the first term of Eq. 1.2, and a total effective anisotropy K is used [2, 22] which is understood to contain contributions from the magnetocrystalline, shape, and surface anisotropies.

1.1.4 Bulk magnetic properties

In a bulk ferromagnetic material, the strong and short-ranged exchange interactions between atoms favour parallel alignment of magnetic moments, while demagnetization effects favour antiparallel alignment of the magnetic moments at grain boundaries. This competition results in a domain structure, shown in Fig. 1.4, where regions of uniform magnetization are formed (domains) that are separated by boundaries (walls). A hysteresis loop, shown in Fig. 1.4, describes the magnetization of a material at a



Figure 1.4: The domain structure and hysteresis loop of a bulk ferromagnet, showing the saturation magnetization (M_S) and coercivity (H_c) .

fixed temperature in a varying applied magnetic field, and is a conventional method to characterize magnetic properties. At the largest applied fields the macroscopic magnetization \vec{M} shows a plateau when all of the magnetic moments are aligned with the applied field, providing the saturation magnetization, M_S . As the applied field is lowered, \vec{M} decreases since all of the magnetic moments are no longer aligned along the field direction and the domains move. The coercivity H_c is the applied field required to reverse the direction of the overall magnetization. In a bulk material, magnetization reversal is determined by the formation (nucleation) and motion of domain walls. The temperature dependence of M_S of a bulk magnet is determined by the approach to the magnetic ordering temperature T_C or T_N , and the temperature dependence of H_c is dominated by micromagnetic effects such as internal grain structure, which determines the domain wall reversal mechanisms. This is contrasted with the properties of single-domain nanoparticles where H_c is determined by the anisotropy, K, and superparamagnetism.

1.2 Maghemite $(\gamma$ -Fe₂O₃) and spinel ferrites

The magnetism of spinel-oxides (e.g. γ -Fe₂O₃) are well known to be strongly dependent on the identity and distribution of cations within the structure [23]. This results in variability that is practically useful, but also leads to a critical need to determination precisely the cation distribution to understand the intrinsic magnetism. This is of particular importance for iron-oxide based core/shell nanoparticles, since the magnetism at the core/shell interface may be altered substantially by chemical intermixing that can produce a layer of substituted iron-oxide with intrinsic properties that are distinct from the core and shell.

1.2.1 Structure

Maghemite is a spinel iron-oxide that is one of a diverse group of materials that are based on a close packed lattice of oxygen ions with interstitial octahedral O_h and tetrahedral T_d -sites that are able to accommodate a wide variety of cations. The spinel structure is based on a unit cell of 32 O²⁻ ions and where 16 of 32 available octahedral (B), and 8 of 64 available tetrahedral (A) sites may be occupied, as shown in Figure 1.5. For a fully occupied inverse spinel, the cation distribution can be described as $(Y)_A[XY]_BO_4$, where X is a divalent (e.g. Fe²⁺) ion and Y is a trivalent (e.g. Fe³⁺) ion that occupies the tetrahedral () and octahedral [] A- and B-sites. Maghemite $(\gamma$ -Fe₂O₃) may be considered as a B-site deficient magnetite (Fe₃O₄). Whereas the fully occupied inverse spinel magnetite is (Fe³⁺)_A[Fe²⁺Fe³⁺]_BO₄, γ -Fe₂O₃ contains no divalent ions and to maintain charge balance has some octahedral site vacancies. Hence, the cation distribution for maghemite can be written as (Fe³⁺)_A[Fe³⁺_{5/3}□_{1/3]_BO₄;}



Figure 1.5: Unit cell of the spinel structure, showing the oxygen lattice (O^{2-} , grey), and the tetrahedral (A-site, green), and octahedral (B-site, red) cation sites.

each unit cell contains 32 O^{2-} ions, 8 tetrahedral (A-site) Fe³⁺ ions, 40/3 octahedral (B-site) Fe³⁺ ions, and 8/3 vacant (\Box) octahedral sites.

The versatility of the structure arises from the stability available over a wide range of stoichiometry; compositions that span the entire range intermediate to Fe₃O₄ and γ -Fe₂O₃ are possible. In addition, a wide variety of cations are accepted readily into the octahedral and tetrahedral sites [7, 24], which allows the formation of cationsubstituted iron-oxides with accessible compositions ranging from pure iron-oxide to fully substituted spinel ferrites, such as CoFe₂O₄.

1.2.2 γ -Fe₂O₃ and spinel ferrite magnetism

Spinel ferrites are ferrimagnetic materials, as shown in Fig. 1.6. Within the B sublattice of the O_h -sites the magnetic moments are coupled ferromagnetically via the double exchange (DE) interaction, and the A and B sublattices are coupled antiferromagnetically via the superexchange (SE) interaction [21]. The total magnetization is a result of the imbalance between the number of A-site and B-site ions.



Figure 1.6: The magnetic interactions between the A- and B-sites of spinel ferrites. Reprinted with permission from [21]. Copyright 2006 Springer Science and Business Media.

The intrinsic magnetism of a spinel-oxide is strongly dependent on the type of cation or the distribution of cations among the A and B-sites. For example, for Fe₃O₄, which has no vacant B-sites, $(Fe^{3+})_A[Fe^{2+}Fe^{3+}]_BO_4$, the total B-site magnetization is larger than γ -Fe₂O₃, despite the slightly lower moment for Fe²⁺ (4 μ_B). As a result, the slight change in cation distribution results in a larger saturation magnetization for Fe₃O₄. A wide variety of transition-metal cations are also readily incorporated into the spinel structure. For example, Co²⁺ has a high affinity for the octahedral B-sites, often producing the cation distribution (Fe³⁺)_A[Co²⁺Fe³⁺]_BO₄. Since the magnetic moment for Co²⁺ (3.8 μ_B) is lower than that of Fe³⁺ (5.9 μ_B), CoFe₂O₄ has a lower saturation magnetization than γ -Fe₂O₃. However, Co²⁺ has a large orbital moment and hence produces a large anisotropy and coercivity (by contrast Fe³⁺ $m_{\ell} \sim 0$). Thus, by varying the amount of Co²⁺ in the structure, the total magnetization and the magnetic hardness of the material can be altered. For most spinel ferrites, the relative strengths of the exchange pathways is $|J_{AB}| > |J_{BB}| >> J_{AA}$; however the strength of J depends on the distribution of magnetic ions in the structure. For example, for Fe₃O₄, $J_{AB} = -2.88$ K (for Fe^{2+/3+}_O-O²⁻-Fe³⁺_{Td}), $J_{BB} = +0.83$ K (for Fe²⁺_{Oh}-O²⁻-Fe³⁺_{Oh}), and $J_{AA} = -0.18$ K (for Fe³⁺_{Td}-O²⁻-Fe^{3+/2+}_{Td}) [25]. By comparison, for γ -Fe₂O₃ the exchange constants are [26, 27] $J_{AB} = -28.1$ K (for Fe³⁺_{Oh}-O²⁻-Fe³⁺_{Td}), $J_{BB} = -8.6$ K (for Fe³⁺_{Oh}-O²⁻-Fe³⁺_{Oh}), and $J_{AA} = -21.0$ K (for Fe³⁺_{Td}-O²⁻-Fe³⁺_{Td}). Similar changes in magnetism are possible using other substituting ion distributions.

1.3 Nanoparticle Magnetism

The magnetism of nanoparticles differs substantially from that of a bulk material. In addition to the intrinsic magnetism of the material, the overall magnetism of a nanoparticle is determined by a combination of finite size effects that are a consequence of the geometrical restrictions of the nanoparticle and surface effects due to the broken coordination of atoms near the particle surface. To date, there is still considerable debate regarding the relative importance of each of these effects, and work is ongoing to determine precisely the spin configuration within nanoparticles.

1.3.1 Superparamagnetism

If the volume of the material is made sufficiently small (below a critical size D_C), then domain wall formation is no longer energetically favourable, and a single-domain particle is obtained. For typical magnetic materials, $D_C = 20 - 800$ nm, depending on the intrinsic magnetism of the material (spontaneous magnetization, anisotropy K, and exchange energies) [2], and for iron-oxides $D_C \sim 50$ nm [28]. A nanoparticle with



Figure 1.7: (a) A single-domain nanoparticle with a uniaxial anisotropy. (b) The dependence of the total energy E on the angle θ between the nanoparticle magnetization \vec{M} , and the easy-axis direction in zero applied field, and showing the energy barrier ΔE to magnetization reversal and the associated relaxation time τ . (c) Example of the energy barrier and related relaxation time definitions for the case where the total energy has unequal minima.

size $D < D_C$ is considered in the most simple picture as a single domain wherein all of the atomic moments are ordered and behave collectively as one "super moment" of magnitude M_S (in analogy to an atomic moment μ). In a nanoparticle, the magnetization \vec{M} is determined to first order by the coherent rotation of all of the spins forming the nanoparticle magnetization over an energy barrier and activated by thermal energy.

The Stoner-Wohlfarth model [29] is the simplest model to describe the magnetism of a nanoparticle. As shown in Fig. 1.7, in the absence of an applied magnetic field the energy associated with magnetization reversal of a non-interacting assembly of single domain particles with a uniaxial anisotropy is described by

$$E = KV\sin^2(\theta) \tag{1.3}$$



Figure 1.8: Illustration of the region within the total energy landscape that a singledomain uniaxial particle is able to sample within a fixed timeframe (red curve) for a system beginning with the magnetization \vec{M} oriented parallel to the easy-axis. (a) For T = 0 $\vec{M}(t)$ is fixed since no thermal fluctuations are possible and a maximum magnetization M_S occurs. (b) $0 < T < T_B$, where fluctuations due to collective excitations reduce the magnetization, but the particles are still blocked. (c) The particle is unblocked for $T \ge T_B$ and spontaneous superparamagnetic (180°) reversals occur resulting in $\langle \vec{M}(t) \rangle = 0$.

where K is the anisotropy (determined by the magnetocrystalline and shape anisotropies) and V is the volume of a nanoparticle. Energy minima for the orientation of the nanoparticle's magnetization \vec{M} relative to the easy axis are located at $\theta = 0$ and 180° . The energy barrier to magnetization reversal from one easy direction to the other is $\Delta E = KV$ (Fig. 1.7). As shown in Fig. 1.8a, at T = 0 the nanoparticle magnetization is trapped in one of the wells and is unable to fluctuate, and the measured magnetization is $\langle \vec{M}(T) \rangle = M_S$ (where $\langle \rangle$ indicates an average over the timesale of the measurement). As the temperature is increased, the nanoparticle magnetization may undergo thermal fluctuations and $\langle \vec{M}(T) \rangle < M_S$ due to collective excitations [4,30]. If the temperature is sufficiently high for the thermal energy $k_B T$ to overcome ΔE , nanoparticle magnetization is able to reverse spontaneously resulting in $\langle \vec{M}(T) \rangle = 0$. This spontaneous magnetization reversal of a nanoparticle results in a behaviour analogous to an atomic paramagnet, but with a (very) large effective total magnetization, and so the phenomenon is called "superparamagnetism", shown in Fig. 1.8c. The threshold temperature that describes the onset of spontaneous 180° reversal is the superparamagnetic blocking temperature T_B , and below T_B the nanoparticle is "blocked".

The superparamagnetic fluctuations of an assembly of non-interacting nanoparticles can be described most simply by the Néel relaxation model [31, 32]. When the system is at some finite temperature the nanoparticle magnetization can fluctuate about the minimum energy direction. As shown in Fig. 1.7b, there are two energy minima in the absence of an applied field and the nanoparticle magnetization has two equilibrium positions $\phi_i = 0^\circ$ and $\phi_j = 180^\circ$ separated by an energy barrier ΔE . At finite temperatures, thermal energy allows the direction nanoparticle magnetization to fluctuate and there will be some probability w_{ij} that a particle in state ϕ_i will change to ϕ_j within a given time interval. The relaxation time $\tau = 1/w_{ij}$ is described by the Néel-Arrhenius equation

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right) \tag{1.4}$$

where $\Delta E = KV$ when H = 0 (described by Eq. 1.3) and τ_0 is the attempt frequency (~ $10^{-9} - 10^{-12}$ s [33]). The relaxation time τ is obtained from the probabilities of a transition from ϕ_i to ϕ_j ($w_{ij} = 1/\tau^+$) and from ϕ_j to ϕ_i ($w_{ji} = 1/\tau^-$), as shown in
Fig. 1.7

$$\frac{1}{\tau} = \frac{1}{\tau^+} + \frac{1}{\tau^-}.$$
(1.5)

In the case of H = 0, ϕ_i and ϕ_j have the same energy and ΔE is equal for jumping from ϕ_i to ϕ_j or from ϕ_j to ϕ_i , so $\tau^+ = \tau^- = 2\tau$. In that case, it takes a time 2τ for a nanoparticle magnetization to flip once. Thermal equilibrium is achieved for times $t \gg \tau$. In cases where ϕ_i and ϕ_j have different energies, such as $H \neq 0$, described below and shown in Fig. 1.7c, $1/\tau^+$ is the probability of a jump occurring from the lower energy minimum to the higher energy minimum over an energy barrier ΔE^+ , and $1/\tau^-$ is the probability of the reverse over an energy barrier ΔE^- . Thus, the superparamagnetic relaxation and measured T_B is dependent on the timescale over which the system is averaged τ_m (i.e. the measurement time). According to Eq. 1.4, the blocking temperature T_B is given by

$$T_B = \frac{KV}{k_B} \ln\left(\frac{\tau_m}{\tau_0}\right). \tag{1.6}$$

For two different measuring times $\tau_{m,1}$ and $\tau_{m,2}$, T_B scales according to

$$\frac{T_{B,1}}{T_{B,2}} = \frac{\ln(\tau_{m,2}/\tau_0)}{\ln(\tau_{m,1}/\tau_0)}.$$
(1.7)

 T_B for a system is of particular practical importance since applications generally require the system to be near or below T_B during use. Significant research efforts have been directed towards simply elevating T_B for nanoparticles [34]; for example, for the iron oxides of typical sizes, a $T_B < 100$ K is obtained for a typical $\tau_m \sim 10 - 100$ s.

1.3.2 Nanoparticle anisotropy and coercivity

When a magnetic field \vec{H} is applied at an angle ϕ relative to the particle easy axis, the field will rotate \vec{M} an angle θ away from the easy axis and an angle $\psi = \phi - \theta$



Figure 1.9: (a) A single-domain nanoparticle with a uniaxial anisotropy, with particle magnetization \vec{M} at an angle ψ relative to the applied magnetic field \vec{H} . (b) The dependence of the total energy $\mathcal{E} = \frac{E}{2KV}$ on the angle ψ and the field $h = \frac{M_SH}{2K}$ on the decreasing field branch of a hysteresis loop for the case when $\theta = 0$. (c) The dependence of the total energy \mathcal{E} on the angle ψ and the field h on the decreasing field branch of a hysteresis loop for the case when $\theta = 0$. (d) Hysteresis loop for the scenario shown in (a) - (c) when T = 0.

towards \vec{H} , as shown in Fig. 1.9a. The magnetization with respect to the direction of the field is then

$$M = M_S \cos(\psi) \tag{1.8}$$

where, as above M_S is the total nanoparticle magnetization. Adding the field energy to Eq.1.3 and writing in terms of ϕ and ψ gives the total energy

$$E(\phi, \psi, H) = KV \sin^2(\phi - \psi) - HM_SV \cos(\psi).$$
(1.9)

A change of variables $\mathcal{E} = \frac{E}{2KV}$ and $h = \frac{M_S H}{2K}$ provides

$$\mathcal{E}(\psi,\theta) = \frac{\sin^2(\phi - \psi)}{2} - h\cos(\psi). \tag{1.10}$$

Choosing $\theta = 0$, the behaviour of M(H) that would be obtained from a hysteresis loop measurement of such a nanoparticle can be illustrated from $\mathcal{E}(\psi, H)$, shown in Fig. 1.9. The hysteresis loop is obtained from the nanoparticle magnetization Mat a fixed temperature as the field is swept from $+H_{max} \rightarrow -H_{max}$ (the decreasing field branch) followed by $-H_{max} \rightarrow +H_{max}$ (the increasing field branch). At T = 0, beginning the M(H) cycle from the largest H will trap the nanoparticle magnetization at $\psi = 0$ (aligned parallel to \vec{H}). For large enough H there will be no other energy minimum. As shown in Fig. 1.9b, as H decreases, a second minimum at $\psi = 180^{\circ}$ appears; however, at T = 0, the nanoparticle magnetization may not fluctuate from the minimum energy, and no superparamagnetic relaxation to the second minimum is possible. As shown in Figs. 1.9c and d, at h = 0 the magnetization becomes unstable at $\psi = 0$ and jumps to $\psi = 180^{\circ}$, resulting in $H_c = 2K/M_S$. Hysteresis loops for the same model with $\theta \neq 0$ are shown in Fig. 1.10a, and the loop resulting from a



Figure 1.10: Hysteresis loops of $m_h = M/M_S$ versus $h = \frac{M_SH}{2K}$ calculated for singledomain nanoparticles with a uniaxial anisotropy. (a) Hysteresis loops for different orientations of the particle easy axis relative to \vec{H} (labeled on the central vertical axis). The parameters ϕ_0 and ϕ'_0 are the angles between the field \vec{H} and the direction of the magnetization \vec{M} before and after the nanoparticle magnetization jump, respectively. (b) Hysteresis loop calculated for a randomly oriented assembly of particles.

non-interacting assembly of particles with randomly oriented easy axes (a randomized θ) is shown in Fig. 1.10b.

At intermediate temperatures, $H_c(T)$ is determined by the competition between superparamagnetic relaxation (thermal energy) and the field energy. A simple description of $H_c(T)$ is obtained by combining the Néel relaxation model (Eq. 1.4) with the Stoner-Wohlfarth model (Eq. 1.3) [22]. In an applied field, the energy barriers to magnetization reversal are obtained from Eq. 1.9

$$\Delta E = KV \left(1 \pm \frac{HM_S}{2K} \right)^2 \tag{1.11}$$

where \pm indicates the energy barrier is raised or lowered if H is parallel or antiparallel to the nanoparticle magnetization. Since H_c is the field that reduces the magnetization to zero within the timeframe of the measurement, this occurs when ΔE in Eqs. 1.11 and 1.4 are equal, which provides

$$\mu_0 H_c(T) = \frac{2K}{M_S} \left(1 - \sqrt{\frac{T}{T_B}} \right). \tag{1.12}$$

1.3.3 Nanoparticle magnetization

Thermal fluctuations also modify the nanoparticle magnetization, $M_S(T)$, due to collective spin-wave excitations. In the bulk, the temperature dependence of the magnetization is described by the successive reversals of single spins in an assembly, wherein spin deviations are spread out over the entire assembly via "spin waves" as shown in Fig. 1.11. This is described by the Bloch $T^{3/2}$ law [35]

$$\frac{M_S(T)}{M_S} = \left[1 - \frac{0.0587}{\nu} \left(\frac{k_b T}{2SJ}\right)^{3/2}\right] = 1 - BT^{3/2}$$
(1.13)

where ν is an integer that equals 1, 2, or 4 for a simple cubic, bcc, or fcc lattice, respectively, S is the atomic spin, and J is the exchange constant. In many nanoparticles $M_S(T)$ is well described by the Bloch $T^{3/2}$ law. However, there are also many cases where $M_S(T)$ is better described in the form

$$\frac{M_S(T)}{M_S} = 1 - BT^{\alpha} \tag{1.14}$$



Figure 1.11: Illustration of a spin wave.

with $\alpha = 1.5 - 2$, due to the finite size of the nanoparticle becoming comparable to the spin wave length for low-lying excitations [36, 37]. In some other cases, the expression for $M_S(T)$ must be modified to include additional terms due to disordered spins at a nanoparticle's surface [38] (described below).

1.3.4 Surface Effects

At the surface of the nanoparticle the atomic coordination environment is incomplete, causing broken exchange bonds and a reduced site symmetry. As a result, the nanoparticle volume is not truly single-domain, but contains a surface spin population whose moments are highly anisotropic and which can have a distinctly different behaviour from the moments within the interior of the particle. Depending on the type of exchange interactions present, the surface spin population is described as variations on a "hedgehog"-like or "throttled" configuration with different effects on the overall nanoparticle magnetism [39]. In ferromagnetic nanoparticles, the spins tend to orient along a preferred axis, causing an enhanced saturation magnetization. In ferrimagnetic nanoparticles competing AF exchange interactions between magnetic sublattices can produce a disordered spin population. Surface disorder effects are particularly important in nanoparticles of spinel ferrites (e.g. γ -Fe₂O₃, NiFe₂O₄, $CoFe_2O_4$, and $CuFe_2O_4$) and have been described in several detailed studies using a wide variety of experimental techniques and simulations [36, 40-44]. In antiferromagnetic nanoparticles a weak ferromagnetism is observed due to uncompensated surface spins and a surface anisotropy that produce a net magnetization 5. The existence of a large surface anisotropy that is up to an order of magnitude larger than the bulk



Figure 1.12: Exchange bias loop shift H_{ex} .

counterpart [6] can contribute to the total nanoparticle anisotropy.

1.3.5 Exchange Bias

To understand the types of interactions which occur when a nanostructured material contains two distinct types of magnetic layers such as the ordered core and disordered shell (described in Sec. 1.3.4) consider first the simplest prototypical case of a FM/AF layered system where T_C of the FM layer is larger than T_N of the AF layer. When the system is cooled from $T_C > T > T_N$ in the presence of a saturating magnetic field, the magnetization direction of the FM is determined by the field. On cooling through T_N , the interfacial spin configuration and domain structure that is established in the AF layer is influenced by interfacial exchange interactions with the ordered FM layer. While the energy profile is equal for the increasing and decreasing field branches of a hysteresis loop for the single-phase system with a uniaxial anisotropy, described in Sec. 1.3.2, the FM/AF exchange coupled system has a unidirectional anisotropy that produces a single preferred direction for the magnetization of the FM layer due to the interfacial exchange interactions. As shown in Fig. 1.12, this results in a shift in the hysteresis loop along the field axis called the "exchange bias" loop shift, $H_{ex} = (H_{c,1} + H_{c,2})/2.$

Intense research to determine the nature of the interface magnetism of exchangebias systems has been a subject of ongoing investigation since the phenomenon was first discovered in 1956 [45]. Some relationships between exchange bias behaviour, AF layer thickness, interface roughness, and pinned interfacial spins have been observed (primarily using thin-film systems); however, a complete description of the phenomenon remains to be established, particularly when applied to nanoparticles [46,47]. In addition, exchange bias effects are not limited to FM/AF systems and have been observed in FiM/AF, FiM/FM, and hard/soft FiM/FiM coupled systems. Importantly for the ferrites, interactions between the ordered interior and disordered surface spin populations in "single phase" nanoparticles results in an exchange bias, with prominent examples being NiFe₂O₄ [48] and γ -Fe₂O₃ [44, 49].

1.4 γ -Fe₂O₃ nanoparticle magnetism

At the nano-scale γ -Fe₂O₃ is the most stable iron-oxide and is the natural product of Fe-based synthesis when oxygen is available. Due to the variability, stability, and significant technological relevance γ -Fe₂O₃ it is also one of the most well characterized nanoparticle systems, and remains a promising candidate for use in applications. In addition, the magnetism of γ -Fe₂O₃ nanoparticles is well representative of the issues that are of concern for other nanoparticle systems. The surface and disorder effects that are common to other nanoparticle systems have been identified clearly in γ -Fe₂O₃ using overall ("bulk") characterization techniques, and atomic ⁵⁷Fe studies [40, 43, 49, 50], and simulations [42, 51]. The surface spin disorder results in a variety of "anomalous" magnetic properties. The magnetization of the nanoparticles is significantly reduced due to a loss of effective magnetic volume. However, when the nanoparticles are cooled to low temperature ($\sim < 2-5$ K) in a large applied field, the disordered spins will become "frozen" in with the magnetization of the nanoparticle. Interactions between the core and surface spins result in an exchange bias and an enhanced coercivity, and the temperature dependence of the magnetization decreases quickly with warming as the disordered spins "thaw". The ordered core and disordered surface spin populations are also observed clearly in experiments that probe the atomic magnetism, which can distinguish the magnetic relaxation of the two spin populations.

1.5 Core/shell nanoparticle magnetism

The magnetic interactions at the core/shell interface are well known to have a substantial effect on the overall magnetism of the nanoparticle. The first instance of core/shell magnetism was measured in passively oxidized Co/CoO nanoparticles in which the exchange bias phenomenon was discovered [52]. The interface magnetism may be modified by combining different FM or FiM materials. For example, the combination of hard (high coercivity) and soft (low coercivity) materials can produce an "exchange spring" system wherein the overall magnetization reversal is altered by the interface coupling [12]. The addition of non-magnetic shells also alters the surface magnetism by completing the coordination environment of the magnetic ions at the surface of the core nanoparticle [53–55]. In nanoparticles, the addition of finite-size effects, disorder, and potential chemical intermixing all significantly complicate the development of a clear understanding of how the overall properties of the core/shell nanoparticle arise from the choice of core and shell materials. There have been numerous studies of a large variety of magnetic core/shell nanoparticles [13, 47] which have resulted in a very large variety of overall magnetic properties, even for nominally similar core and shell materials.

1.6 Progress and open questions

To date, much research on magnetic core/shell nanoparticles has centered on the realization and measurement of the overall properties of new combinations of core and shell materials and in the reproduction of properties of layered thin-films in core/shell nanoparticle analogues with a substantial fraction of studies using iron-oxide or ferrite-based materials [11–13]. Currently, the magnetism of core/shell nanoparticles is considered primarily a combination of intrinsic material properties and interfacial interactions across a sharp core/shell phase boundary. This interpretation is used to account for experimentally observed properties and forms the basis for simulations of core/shell nanoparticle magnetism [12,56]. However, the current description does not account for the details of the surface magnetism or disorder of the core, core/shell interface roughness, and intermixing effects. Such effects are known to alter substantially the magnetism of thin-films [47] for which large lateral length scales facilitate characterization, but have yet to be applied to core/shell nanoparticles due to the added complication of finite-size effects and the practical challenge of characterization over atomic length scales. To this end, some recent work to examine the nature of the structure of some Fe-oxide/Mn-oxide core/shell nanoparticles has identified a change in composition at the interface that suggests a complex interface [57, 58].

This work aims to further the understanding of core/shell nanoparticles by describing the nature (magnetism, composition) of the interfacial intermixed layer and determining its role in producing the overall properties of the nanoparticle. To disentangle the variety of effects that contribute to the magnetism of core/shell nanoparticles, experiments to characterize the composition and magnetism over a range of time and length scales (i.e. 10^{-8} s to 100 s, and from overall to atomic, and element-specific), temperatures, and applied magnetic fields will be used to provide a self-consistent and comprehensive description of the core/shell nanoparticle magnetism. I will characterize the overall magnetic properties (e.g. T_B , $M_S(T)$, $H_c(T)$, and $H_{ex}(T)$) of the nanoparticles using magnetometry and susceptometry experiments. Using Mössbauer spectroscopy I will determine atomic Fe magnetic and electronic environments to determine whether core/shell intermixing occurs, to examine the temperature dependent magnetic relaxation, and to identify disorder in the nanoparticles. I will examine the core and shell composition and the element and site-specific magnetism using xray absorption and x-ray magnetic circular dichroism spectroscopy. The elemental magnetism will identify how the core and interface magnetizations are coupled, identify core/shell mixing, and identify changes in the orbital moments of the magnetic ions. The effects of intermixing will also be examined with a series of γ -Fe₂O₃/CoO core/shell nanoparticles, where the synthesis conditions have been modified to alter deliberately the interface mixing amounts. The nature of the interfacial intermixed layer in γ -Fe₂O₃/CoO core/shell nanoparticles will also be examined in depth using atomic and element-specific measurements that probe the local metal-oxygen bonding and exchange interactions.

Chapter 2

Experimental Methods

To understand the origin of the magnetic properties of nanostructured materials is often a complex task due to the substantial sensitivity of all aspects of the properties to small changes in structure, composition, morphology, and atomic-scale magnetism. To disentangle the precise role of interfacial microstructure and magnetism requires an in-depth examination of the entire nanoparticle. This necessitates not only measurement of the overall ("bulk") properties which are the sum-total of all factors, but also the element-specific and atomic properties which can probe separately each region and spin population of the nanoparticle. In addition, measurements which probe a variety of length and time-scales, temperature, and field-dependent behaviour are necessary to separate intrinsic (material) properties from the effects of superparamagnetism. The complement of experimental techniques described in this chapter allows the requisite analysis. The structure and morphology of the nanoparticles was determined using powder x-ray diffraction and transmission electron microscopy. The overall magnetic properties were characterized using magnetometry and susceptometry measurements. Mössbauer spectroscopy identified each unique ⁵⁷Fe-site, providing the Fe-based composition, and the temperature evolution provided a Fe site-resolved approach to superparamagnetism. X-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) identified the Fe and shell transition metal ion sites, while temperature and field-dependent measurements provided the element and site-specific magnetism.

2.1 Nanoparticle synthesis

Core/shell nanoparticles were synthesized using a two-part seed-mediated approach based on the thermal decomposition of metal-precursors in hot organics. The γ -Fe₂O₃ seed nanoparticles were synthesized following the method described in Ref. [59]. A metal-cupferronate was prepared for each shell transition-metal from CoCl₂·6H₂O (98%, Alfa Aesar), MnCl₂·4H₂O (99%, Arcos Organics), Ni(CH₃COO)₂·4H₂O (99%, Acros Organics) and cupferron (NH₄[C₆H₅N(O)NO], 99%, Acros Organics) using the procedure described in Ref. [60]. A solution of 1.8 mmol of metal-cupferronate in octylamine (99%, Acros Organics) was prepared, and heated to 100°C under Ar for 1 h. To create core/shell nanoparticles, 7 mL of γ -Fe₂O₃ nanoparticle solution was heated under Ar 250°C to which 4 mL of precursor solution was rapidly injected. The entire mixture was allowed to react at 225°C K for 30 minutes, after which heat was removed and the reaction flask was allowed to cool to room temperature. In addition, a series of three γ -Fe₂O₃/CoO core/shell nanoparticles was prepared using the same procedure described above, but with final reaction temperatures of 100°C, 150°C and 235°C to create each sample. Nanoparticles of the shell transition metal-oxides were also synthesized using a similar procedure described for the shell addition step; 7 g of tri-n-octylamine (95%, Alfa Aesar) was heated to 100°C for 1 h under Ar atmosphere. The tri-n-octylamine was heated to 250°C, and 4 mL of metal-cupferronate precursor solution was rapidly injected. The entire mixture was allowed to react at 225°C K for 30 minutes, after which heat was removed and the reaction flask was allowed to cool to room temperature.

Nanoparticle powders were isolated from solution by washing with alcohols and air-drying.

2.2 Powder x-ray diffraction (XRD)

X-rays incident on a lattice will scatter from the electrons surrounding each atom, and scattered wavefronts from points in the lattice interfere, creating a diffraction pattern from which the lattice symmetry can be determined. The relationship between the spacing of a set of (hkl) planes d_{hkl} , the diffraction angle θ , and x-ray wavelength λ is given by Bragg equation

$$n\lambda = 2d_{hkl}\sin\theta_{hkl} \tag{2.1}$$

where n is an integer number. For an infinitely large number of diffracting planes, the width of a given reflection will be determined by instrumental factors (neglecting strain effects). For small crystallites, however, reflections will be broadened due to the finite number of planes from which the diffracted x-rays are scattered. Broadening



Figure 2.1: Diagram of the Bragg condition geometry. Reprinted with permission from [62]. Copyright 2003 Springer Science and Business Media.

due to crystallite size effects is described by the Scherrer formula [61]

$$D_{XRD} = \frac{K\lambda}{\beta\cos(\theta)} \tag{2.2}$$

where D_{XRD} is the volume weighted crystallite size, K is the Scherrer constant (K = 0.9 for a spherical particle), λ is the wavelength of the x-rays, and β is the integral breadth of the reflection (in radians 2θ).

X-ray diffraction patterns were collected to determine the nominal core and shell structures of the nanoparticles. All patterns were collected using a Bruker D8 DaVinci with Cu K radiation using a Bragg-Brentano geometry under ambient conditions. A schematic diagram of the diffractometer in Bragg-Brentano geometry used for powder XRD is shown in Fig. 2.2. X-rays are generated by use of an x-ray tube consisting of a cathode, anode and Be windows. Electrons are emitted from the cathode that is an electrically heated tungsten filament. A large potential difference is applied across the cathode and anode, causing the electrons to accelerate towards the cathode. Typically a potential difference between the cathode and anode of 40 kV, and a tube current



Figure 2.2: Bruker D8 DaVinci diffractometer using a Bragg-Brentano geometry showing the x-ray tube, primary and secondary optics, and detector.

of 40 mA is used. The tube current strikes the anode Cu target, and the emitted x-ray spectrum consists of characteristic x-rays of the anode metal superimposed on a continuous background of Bremsstrahlung radiation. The primary and secondary x-ray optics focus the x-rays on the sample surface and are optimized to maximize the pattern quality and sample illumination. A secondary set of optics consisting of physical and electronically controlled slits re-focused the diffracted x-rays onto the detector. Programmable slits control the equatorial divergence of the x-rays (i.e. along the sample length) and the sample illumination. The Soller slits are a collimating optic consisting of parallel foils separated by spacers which limit the axial divergence of the x-rays (i.e. along the sample width). A Ni filter on the secondary optics strongly attenuates the Bremsstrahlung and Cu K_{β} x-rays. X-rays

were detected with a Lynxeye linear Si strip detector. X-rays which impinge on the Si detector create electron-hole pairs by x-ray photoionization. A bias voltage attracts charge carriers, which are detected following a photoionization event. The number of photoelectrons generated is proportional to the energy of the detected radiation. The minimum threshold energy of the detected signal is controlled with the diffractometer software which enables minimization of florescence radiation in Fe-based samples due to excitation of electrons from the Fe K-shell (7 keV) by the Cu K_{α} x-rays (8.04 keV), to minimize background.

XRD patterns were collected using dried nanoparticle samples on a zero-background quartz slide using a rotating stage. For γ -Fe₂O₃/CoO nanoparticles described in Ch. 5 XRD patterns were measured from 50 K to 300 K using a Phenix stage with a closedcycle refrigerator. Lattice parameters, average crystallite sizes, and estimates of the core and shell structure volume fractions were obtained using Rietveld refinements with FullProf [63].

2.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is an essential technique to characterize nanostructures. The transmission electron microscope focuses a beam of electrons onto a nano-scale region of a sample which allows many types of measurements to be carried out either by detecting the transmission of electrons through the sample or diffracted electrons. In the TEM, detection of the diffracted electrons provides a pattern similarly to XRD, but with the substantial advantage of providing area selectivity via the focused electron beam. Powder-like average diffraction patterns may be obtained

from low-magnification images and indexed similarly to powder XRD patterns, and diffraction images measured from regions within a single nanoparticle can identify atomic-scale changes in structure. Much of the functionality of the TEM is based on the detection of electrons as they are transmitted through the sample. At low magnification, a TEM image will show contrast due to the absorption of electrons by the sample. The contrast is proportional to the sample thickness and the atomic number Z of the atoms. High-resolution TEM (HRTEM) allows the observation of the atomic-scale structure of materials by virtue of the wave-like nature of electrons. A full description of the highly complex nature of the behavior of transmitted electrons through a material is beyond the scope of this work and may be found elsewhere [64]; however, the physical principles behind the technique can be given through a simple phenomenological description. A parallel beam of electrons incident on the sample can be considered as a plane wave. As an electron penetrates the sample it will be attracted to the atomic potential of the atoms that make up the lattice and will travel along the lattice, resulting in waves which are transmitted through the sample. At the same time, electrons are scattered by nearby atoms, resulting in diffracted waves. Since the diffracted and transmitted waves travel different distances through the sample, an interference pattern results. The resulting "phase contrast" depends on the strength and the spacing of the periodic potential of the lattice along a given crystallographic orientation. The HRTEM image is obtained from mapping the phase contrast, and requires careful accounting of microscope focus conditions and aberrations to reconstruct the final image, and detailed analysis to account for the 2D-generated projection of the oriented 3D structure. Also highly useful is the ability to measure the loss of electron energy during transmission. The electrons used to generate TEM images have sufficient energy (typically 50 - 800 keV) to eject core electrons from the atoms in the sample. The electron energy loss spectrum (EELS) provides the energy loss in the transmitted electron beam due to such core-level excitations. Since the energy levels and hence the energy required to excite core electrons is element-specific, EELS mapping provides the element-specific distribution of atoms in the sample.

Transmission electron microscopy (TEM) images were collected to determine the nanoparticle size distribution and morphology. EELS mapping was also done to ascertain the distribution of transition-metals to confirm core/shell morphology. All of the TEM images and their structural analysis presented herein were collected by Prof. Hao Ouyang and his students C. C. Chi, T. T. Su, and H. S. Hsiao from National Tsing Hua University, using either a JEOL-ARM200F microscope at National Tsing Hua University or a JEOL 2100F microscope at the Material and Chemical Research Laboratories, Industrial Technology Research Institute, Taiwan. To prepare TEM samples, nanoparticles were washed with alcohols to remove excess organics then diluted with hexanes and dropped onto a 400-mesh carbon-coated copper grid. Prior to image collection the TEM samples were plasma cleaned three times for ten seconds to remove the excess organic coating from the nanoparticle surfaces.

Low and medium-magnification images containing a large sample of nanoparticles were used to determine the particle size distributions. The nanoparticle size distributions were determined using the image processing software ImageJ [65] to measure the 2D projected size of the 3D particle via the Feret diameter by measuring 300 - 500 nanoparticles. The distribution was fitted to a log-normal expression

$$p(D) = \frac{1}{\sqrt{2\pi\sigma D}} \exp\left[-\frac{1}{2\sigma^2} \left(\ln\frac{D}{D_0}\right)^2\right]$$
(2.3)

where σ is the standard deviation and D is the particle diameter.

To examine structural changes due to core/shell intermixing in γ -Fe₂O₃/CoO nanoparticles discussed in Chapter 5, extensive analysis of HRTEM and electron diffraction images were done by Prof. H. Ouyang, C. C. Chi, and H. S. Hsiao. HRTEM was used to measure the CoO shell thickness directly. Also, an in-depth characterization of the core/shell interface was done using highly focused electron diffraction, with analysis supported by simulations of potential interfacial structures.

2.4 Overall magnetism

The magnetic properties of a nanoparticle are usually determined with a combination of dynamic and static measurements using a magnetometer. The use of a superconducting quantum interference device (SQUID)-based magnetic properties measurement system (MPMS) is required due to the small magnetic responses of nanoparticles dispersed in non-magnetic media which is required to ensure comparable interparticle separations. A SQUID consists of a superconducting ring containing two Josephson junctions, as shown in Fig. 2.3a, and provides essentially a conversion between magnetic flux and voltage. The SQUID's functionality is based on two physical phenomena: 1) the wavefunction of the superconductor around the ring must be single-valued, so that a phase change of multiples of 2π are allowed for a closed path around the loop, imposing a flux quantization condition, and 2) the Josephson



Figure 2.3: a) A SQUID containing two Josephson junctions, b) the relationship between bias voltage and current, and c) periodic voltage response due to flux quantization. d) Schematic of a gradiometer used to measure the sample magnetization.

junction, a thin insulator which interrupts the superconducting ring, allows tunneling of the super-current up to a maximum critical value, and determines the phase change of the wavefunction across the junction. The combination of the two phenomena provides a sensitive flux-to-voltage conversion, as illustrated in Fig. 2.3a-c. A bias current is applied that is divided among the two Josephson junctions. In the absence of a change in flux through the ring, the maximum current which can pass the SQUID is the sum of the two critical currents of each Josephson junction, shown in the top curve of Fig. 2.3b. When the flux through the SQUID changes, an additional current is induced in opposition, and with increasing flux the current through the SQUID decreases due to the interference of the wavefunctions across the two Josephson junctions, with a minimum occurring for one-half flux quantum. This interference behaviour has a periodicity of one flux quantum, as shown in Fig. 2.3c.

The magnetic properties of the nanoparticles were characterized using a Quantum Design SQUID-based magnetic properties measurement system (MPMS-XL5). In an MPMS, the SQUID is connected to a gradiometer made of a set of superconducting pickup coils. The sample is transported through the coil and the current induced in the coils is inductively coupled to the SQUID, as shown in Fig. 2.3d. The gradiometer coil configuration is arranged with high symmetry to eliminate any contributions from the uniform field applied by the superconducting magnet. A magnetic field is applied to the sample using a superconducting magnet in a solenoid configuration that surrounds the SQUID detection coils. The sample region, SQUID detection coils, and magnet are within the main body of the MPMS, shown in Fig. 2.4. The entire magnet is shielded by a permalloy shroud to reduce the magnetic field external to the MPMS and the entire assembly housed in a liquid helium dewar. The magnet is charged with a given current to achieve the desired applied field. The temperature is controlled by helium gas flow from a reservoir at the bottom of the dewar and a heater above the sample. The sample motion is controlled by a reciprocating sample measurement system (RSO). Measurement with the RSO uses a small amplitude periodic displacement of the sample through a gradiometer to produce an oscillating ac signal in the SQUID. This measurement technique provides increased sensitivity and noise reduction over typical dc measurement techniques, allowing measurements



Figure 2.4: The Quantum Design MPMS-XL5.

of sample signals as small as 5×10^{-9} emu [66]. All aspects of the SQUID electronics, sample measurement parameters, field, and temperature were controlled via the MPMS Multi-View software.

Many measurements of nanoparticles require that the samples be cooled in the absence of any external magnetic field. This can be a particular issue if such measurements are done immediately after the magnet been charged to high fields, since fields may induce some magnetization in the permalloy shield surrounding the superconducting magnet, and some remanent field may remain in the magnet when it is charged back to zero from a high field state. To address this, prior to to each measurement that requires a zero-field initial configuration the degauss shield and magnet reset options were used. The degauss shield option alternates positive and negative field polarity from the maximum 5 T to zero in sequentially smaller field steps. Following this, a magnet reset causes a heater to warm the superconducting magnet windings above their critical temperature to expel any remanent fields. Following this procedure reduced the magnetic field at the sample region to $< 10^{-3}$ mT (checked with field profiling using a fluxgate magnetometer [67]).

The magnetic properties of a nanoparticle are usually determined with a combination of dynamic and static measurements. This is often necessary since the intrinsic material properties and superparamagnetic relaxation both contribute to the overall magnetism of the nanoparticle. In addition, for systems consisting of multiple distinct spin populations (i.e. magnetically soft and hard, or ordered and disordered components) a complement of measurements probing different timescales and external conditions (i.e. applied field and temperature) is necessary. The static magnetism was characterized by measuring the magnetic response in a fixed non-saturating field as a function of temperature to provide the *dc*-susceptibility, or by measuring the magnetization versus the applied field with a fixed temperature (hysteresis loop measurements) to characterize the anisotropy and saturation magnetization of the nanoparticle.

Hysteresis loop measurements were done by cooling while applying a saturating field (typically 5 T), to base temperature (typically 5 K), and measuring the magnetization at a fixed temperature while changing the field from +5 T to -5 T and -5 T to +5 T.

The overall dynamical response of the nanoparticle was obtained by measuring

the response of the nanoparticles to a small (0.25 mT) ac applied magnetic field as a function of temperature. This provides the complex ac-susceptibility,

$$\chi_{ac}(\nu, T) = \chi'_{ac}(\nu, T) - i\chi''_{ac}(\nu, T)$$
(2.4)

where $\chi'_{ac}(\nu, T)$ and $\chi''_{ac}(\nu, T)$ are the in-phase and out-of-phase components, respectively, to an *ac* field oscillating with frequency ν . χ_{ac} measurements were done by removing the remanent magnetization of the magnetometer, cooling the sample to base temperature in zero applied magnetic field, and measuring $\chi'_{ac}(\nu, T)$ and $\chi''_{ac}(\nu, T)$ with $\nu = 10$ Hz to 1000 Hz and 0.25 mT while warming to 300 K.

The dc-susceptibility ($\chi_{dc}(T)$) of the nanoparticles was obtained by using zerofield-cooled (ZFC)-field-cooled (FC) measurements. After quenching the remanent magnetization of the magnetometer, the sample was cooled from room temperature to base temperature in zero applied field. A small field was applied (typically ~10 mT, well below the field required to reach magnetic saturation) and the zero-field-cooled susceptibility is obtained from the magnetic response $\chi_{dc,ZFC}(T) = M_{dc,ZFC}(T)/\mu_0 H$ measured while warming. Similarly, the field-cooled dc-susceptibility was obtained by measuring the magnetic response in the same applied field while cooling, e.g. from 300 K to base temperature. Compared to ac-susceptibility measurements (10 Hz -1 kHz), the dc-susceptibility measurement occurs on a significantly longer time-scale of ~ 0.01 - 0.1 Hz.

Both *ac*- and *dc*-susceptibility measurements are used typically to detect the onset of superparamagnetism and to provide an estimate of T_B . Being a dynamical phenomenon, T_B depends on the timescale of the measurement; however, a qualitative comparison of T_B for different samples is possible when obtained from the same measurement. The *dc*-susceptibility is a measure of the magnetization of the nanoparticles which are blocked (have a static component of magnetization over the measurement timescale). A maximum magnetization at a given temperature (T_{max}) and onset of ZFC/FC reversibility (convergence of the ZFC and FC responses) marks the onset of superparamagnetic relaxation, but does not necessarily provide a measure of T_B (e.g. $T_{max} \propto \beta T_B$, where β up to 2 in FM and FiM nanoparticles [2,68,69]). The *ac*susceptibility measures the frequency-dependent dynamical response of the nanoparticle magnetization to a small applied field, and provides a maximum $\chi''_{ac}(\nu, T)$ (related to the energy dissipation) followed by a maximum $\chi'_{ac}(\nu, T)$ (the magnetic response) and an onset of reversibility (loss of frequency dependence to the magnetic response) as T_B is approached while warming. Both $\chi_{dc}(T)$ and $\chi_{ac}(\nu, T)$ measurements require an applied field which may also perturb the energy landscape of the system. Thus, while susceptometry provides a good qualitative comparison of the anisotropy when all other factors are equal (size distribution, interaction strength, etc.) care should be taken when extracting quantitative information.

2.5 Mössbauer Spectroscopy

In 1958, R. L. Mössbauer discovered that for nuclei bound in a lattice, there is a finite probability for emission and absorption to occur with no recoil [70]. Mössbauer spectroscopy provides a sensitive measure of the local electronic and magnetic environments surrounding probe nuclei, and leads to valuable insight of the site-specific magnetism. Furthermore, by virtue of the fast measurement time (due to the lifetime of the nuclear excited state) spectra reflect the entire range of dynamical processes from fully static to superparamagnetic magnetism for Fe-based nanoparticles. This provides an excellent complementary technique to magnetometry, which has significantly slower measurement timescales and lacks site-specificity. By far the most widely used transition is that of the ⁵⁷Fe nucleus.

When a free nucleus undergoes radioactive decay from an excited state, E_e , to a ground state, E_g , and emits a γ -ray with energy $E_0 = E_e - E_g$, momentum conservation requires that the nucleus experiences a recoil with resultant energy loss, E_R , descried by

$$E_R = \frac{E_\gamma^2}{2Mc^2} \tag{2.5}$$

where $E_{\gamma} = E_e - E_g$ is the energy of the γ -ray corresponding to the difference in the excited and ground states of the decaying nucleus, M is the mass of the recoiling nucleus, and c is the speed of light. As depicted in Fig. 2.5, the energy of the emitted γ -ray will then be

$$E_{\gamma} = E_0 - E_R. \tag{2.6}$$

The γ -ray energy will have a certain uncertainty $\Gamma_{nat} = \hbar/t_{1/2}$ due to the lifetime



Figure 2.5: Illustration of momentum conservation during γ -ray emission, resulting in a recoil energy imparted to the nucleus. Reprinted with permission from [71]. Copyright 2010 Springer Science and Business Media.



Figure 2.6: Illustration of the emission and absorption lines for a free nucleus. The recoil energy E_R for the emission and absorption processes results in a separation of $2E_R$ between absorption and emission lines. Reprinted with permission from [71]. Copyright 2010 Springer Science and Business Media.

of the excited state. For a system at finite temperature, the energy of the emitted γ ray will be further modulated by the thermal motion of the nuclei, which contributes an additional Doppler energy

$$E_D = \frac{v_n}{c} E_\gamma \tag{2.7}$$

that results in a γ -ray energy broadening

$$\Gamma_D = 2\sqrt{E_R \cdot k_B T} \tag{2.8}$$

due to a distribution of nuclear velocities, v_n , at a given temperature, T, and with k_B the Boltzmann factor. The total energy of an emitted γ -ray is then given by

$$E_{\gamma} = E_0 - E_R + E_D.$$
 (2.9)

The Mössbauer effect is based on the emission and resonant absorption of γ -rays so that recoil and thermal broadening effects must be considered for both the emission and absorption processes. Shown in Fig. 2.6, the recoil energy and thermal broadening



Figure 2.7: ⁵⁷Co decay scheme. The ⁵⁷Fe $I = 3/2 \rightarrow I = 1/2$ transition with energy separation 14.4 keV and excited state lifetime $\tau = 97.8$ ns labeled " γ -ray" is used for ⁵⁷Fe Mössbauer spectroscopy.

affect both the emission and absorption processes, so that a γ -ray emitted from one nucleus has energy $E_{\gamma} = E_0 - E_R$, and the energy of an incoming γ -ray required to excite the same free nucleus is $E'_{\gamma} = E_0 + E_R$. The difference between the energy of the emitted γ -ray and the energy required for a resonant absorption process is $2E_R$. For γ -ray transitions $\Gamma_D \ll 2E_R$ and there is negligible overlap between emission and absorption processes. As an example, the decay scheme of ⁵⁷Co provided in Fig. 2.7 shows the γ -ray used for ⁵⁷Fe Mössbauer spectroscopy, and the relevant properties of the resonance transition for ⁵⁷Fe are provided in Table 2.1.

Table 2.1: Numbers regarding the 14.4 keV nuclear transition of ⁵⁷Fe [71, 72].

	Abundance	E_0	Γ_{nat} (eV)	E_R	$\Gamma_D(300 \ K)$
	[%]	$[\mathrm{keV}]$	[eV]	[eV]	[eV]
$^{57}\mathrm{Fe}$	2.19	14.41	4.55×10^{-9}	1.95×10^{-3}	$\sim 10^{-2}$

In 1958, during his Ph.D. work on γ -ray absorption in ¹⁹¹Ir, R. L. Mössbauer discovered that for nuclei bound in a solid the recoil energy is transferred to the entire lattice [70]. Since the energy required to eject the nucleus from the lattice is much greater than the free atom recoil energy, the recoil energy is transferred to the lattice, and M becomes the mass of the entire crystal. The recoil energy may be transferred to the lattice by exciting vibrations (phonons). As phonons are quantized, when the recoil energy is less than the lowest energy vibrational mode a recoil-free event will occur. The probability of such a zero-phonon process is given by the recoilless fraction f, and is described by

$$f = \exp[-\langle x^2 \rangle E_{\gamma}^2 / (\hbar c)^2]$$
(2.10)

where $\langle x^2 \rangle$ is the expectation value of the squared vibrational amplitude of the nucleus in the γ -ray direction over the timescale of the Mössbauer measurement.

Mössbauer spectra are measured by directing γ -rays, typically from a radioactive source, towards a sample containing the corresponding probe nuclei. The source is moved relative to the absorber to produce a Doppler-shifted γ -ray to excite transitions in the probe nuclei whose energies deviate from E_0 due to hyperfine interactions. The γ -rays with energy equal to the nuclear transitions in the probe nuclei are absorbed, and the Mössbauer spectrum is obtained by detecting the absorbed γ -rays as a function of Doppler-shifted source velocity equivalent to the incident γ -ray energy relative to E_{γ} .

The experimentally measured centroid of the Mössbauer spectrum is the isomer shift, δ , that consists of contributions from the intrinsic isomer shift δ_I due to the electric monopole interaction, and the second-order Doppler shift δ_{SOD} : $\delta = \delta_I + \delta_{SOD}$. The electric monopole interaction provides δ_I and arises due to the finite size of the nucleus and the Coulombic interaction with *s*-electrons at the nucleus. The intrinsic isomer shift (Fig. 2.8a) is proportional to the difference in the electron density at the nucleus between the γ -ray absorber and source, $|\psi_A(0)|^2 - |\psi_S(0)|^2$, and is described by

$$\delta_I = \frac{2}{5}\pi Z e^2 (R_e^2 - R_g^2) (|\psi_A(0)|^2 - |\psi_E(0)|^2)$$
(2.11)

where R_e and R_g are the radii of the excited and ground states of the probe nucleus, respectively. For ⁵⁷Fe, $R_e^2 < R_g^2$, so an increase in *s*-electron density at the nucleus will result in a lower δ [71]. The second order Doppler shift is related to the mean squared velocity of the absorber atom

$$\delta_{SOD} = -\frac{\langle v^2 \rangle}{2c}.$$
(2.12)

For Mössbauer spectra measured at different temperatures δ_{SOD} will decrease with increasing temperature due to an increase in $\langle v^2 \rangle$ with warming. For these reasons δ is usually reported with respect to a standard at a given temperature. The current convention is to report the measured δ relative to α -Fe at room temperature (e.g. 300 K).

A nucleus with I > 1/2 has a non-spherical charge distribution and a quadrupole moment eQ which quantifies the magnitude of the charge distribution deformation. If the nucleus also experiences an electric field gradient due to a non-spherical surrounding charge environment the degeneracy of the nuclear energy level will be lifted by the electric quardupole interaction. This splits the nuclear energy levels into doubly degenerate m_I sublevels with energy [72]

$$E_Q = \frac{eQV_{zz}}{4I(2I-1)} [3m_I^2 - I(I+1)] \left(1 + \frac{\eta^2}{3}\right)^{1/2}$$
(2.13)

where $V_{zz} = \partial^2 V / \partial z^2$ is the principal component of the electric field gradient tensor, η is the asymmetry parameter given by

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \tag{2.14}$$

and $|V_{zz}| \ge |V_{yy}| \ge |V_{xx}|$ and $V_{zz} + V_{yy} + V_{xx} = 0$. As shown in Fig. 2.8c, for ⁵⁷Fe, this results in a doublet due to the splitting of the I = 3/2 level with an energy given by

$$\Delta = \frac{eQV_{zz}}{2} \left(1 + \frac{\eta^2}{3}\right)^{1/2}.$$
 (2.15)

The nuclear spin \vec{I} and magnetic moment $\vec{\mu}$ will interact with a local magnetic field \vec{B}_{hf} at the nucleus via the magnetic dipole, or nuclear Zeeman interaction, described by the Hamiltonian

$$\mathcal{H} = -\vec{\mu}_N \cdot \vec{B}_{hf} = -g\mu_N \vec{I} \cdot \vec{B}_{hf} \tag{2.16}$$

where g is the nuclear g-factor. The energies of the nuclear energy levels are then given by

$$E_M = -g\mu_N B_{hf} m_I \tag{2.17}$$

where m_I is the z-component of I. This interaction lifts the degeneracy of the nuclear level resulting in (2I + 1) equally spaced $m_I = I, I - 1, ..., -I$ sublevels. For ⁵⁷Fe, the transition of interest is from the I = 1/2 ground state to the I = 3/2 (14.4 keV) excited state. This causes the nuclear level splitting as shown in Fig. 2.8b. The allowed transitions are determined by the selection rules for magnetic dipole transitions $\Delta I = 1, \ \Delta m_I = 0, \pm 1$, which provides six possible transitions for ⁵⁷Fe, with



Figure 2.8: The nuclear energy level splitting and Mössbauer spectra due to the hyperfine interactions. a) The intrinsic isomer shift δ_I , b) the hyperfine field B_{hf} , and c) the electric quadrupole splitting ΔE_Q . Reprinted with permission from [72]. Copyright 1975 Springer Science and Business Media.

the relative transmission probabilities of a randomly oriented powder of 3:2:1:1:2:3 determined by the Clebsch-Gordon coefficients.

The B_{hf} contains contributions from the Fermi contact term (due to the net spin polarization of *s* electrons at the nucleus arising due to unpaired valence electrons), an orbital contribution due to the total orbital moment *L* of the valence electrons, and a dipolar contribution from the non-spherical distribution of the electron spin density. For transition metals, the dominant contribution to B_{hf} is the Fermi contact term described by (in the one electron case) [71,73]

$$B_{con} = 2\mu_B \frac{8}{3}\pi [\rho_s^{\uparrow}(0) - \rho_s^{\downarrow}(0)]$$
 (2.18)

where $\rho_s^{\uparrow}(0)$ and $\rho_s^{\downarrow}(0)$ are the spin up and down densities, respectively, at the nucleus; shown for Fe to be directly proportional to the number of 3*d* electrons [74].

Importantly, for the study of nanoparticles, B_{hf} is proportional to the total spin moment on the Fe atoms averaged over the timescale of the Mössbauer transition $(\sim 10^{-8} \text{ s})$. In nanoparticles, thermal fluctuation of the local magnetic moment of the atoms increases with warming due to collective excitations and 180° spin flips due to superparamagnetic relaxation, and $B_{hf} \rightarrow 0$ as $T \rightarrow T_B$. Thus, the thermal evolution of the sextet splitting and relative spectral line intensities can be used to describe the nanoparticle relaxation over a timescale which is significantly faster than magnetometry measurements. Further, by virtue of the unique hyperfine parameters for each Fe-site, the behaviour of different spin populations (i.e. interior vs surface spins) can be disentangled, providing significant advantage over bulk measurements which provide only an averaged response.

A diagram depicting a typical Mössbauer spectrometer is shown in Fig. 2.9. In an 57 Fe Mössbauer experiment, a 57 Co source in a Rh matrix is mounted on Wissel MDU MR-360 transducer. The motion of the transducer is controlled by a Wissel DFG-1200 digital function generator which provides a triangle voltage (constant acceleration) waveform that produces Doppler-shifted γ -rays which are used to excite transitions of 57 Fe nuclei in the sample. γ -rays passing through the sample that are not absorbed were detected using an LND model 45431 Ar/Xe proportional counter and amplified before reaching an ORTEC single channel analyzer (SCA). The SCA has upper and lower discriminators, and the SCA generates a pulse when it receives a signal within a set voltage window, adjusted to detect only the 14.4 keV transition. The signal is sent



Figure 2.9: Schematic diagram of a transmission Mössbauer spectrometer.

to the PC with an ORTEC multi-channel scaler (MCS) that sorts the incoming data into channels corresponding to specific drive velocities. The Mössbauer spectrum is recorded as the number of absorbed γ -rays measured as a function of the drive velocity.

The velocity scale of the measured Mössbauer spectra were calibrated using a 6 μ m-thick α -Fe foil at room temperature using the known $B_{hf}(300 \text{ K}) = 33 \text{ T}$, and all δ are relative to α -Fe at 300 K. Spectra were measured from 10 K to 300 K using a Janis SHI-850 closed cycle refrigeration system (CCR). Powder nanoparticle samples were dried and dispersed in BN powder and held between two x-ray mylar films mounted on a brass holder.

A non-linear least squares analysis was applied to all of the Mössbauer spectra, with each Fe-site characterized by a Lorentzian line-shape sextet with a set of hyperfine parameters described above. In some cases (γ -Fe₂O₃ and γ -Fe₂O₃/MnO, described in Chapter 4), the spectra were described using a full multi-level relaxation
model to describe the B_{hf} and line-shape evolution due to collective excitations and superparamagnetism.

2.6 X-ray Spectroscopy

X-ray spectroscopic techniques have grown to provide invaluable information in nanostructured magnetic materials due to the element specificity, range of detection, and with control of the sample temperature and applied magnetic field. In particular, when the core and shell materials are based on different elements with different magnetic properties, x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) spectra provide a unique window to detect changes in core and shell-ion valence, coordination, and magnetism due to intermixing effects. Importantly, detailed studies with temperature and field for each element provide an excellent comparison with atomic ⁵⁷Fe studies and magnetometry studies that provide the overall nanoparticle magnetic response. XAS and XMCD, although requiring synchrotron x-ray sources, have become vital and increasingly utilized experimental techniques to study nano-magnetism due to the ability to measure separately the magnetism of each site and hence provide a description of the contributions of different spin populations to the overall magnetism.

X-ray absorption spectroscopy (XAS) is the absorption of monochromatic x-rays (often from a synchrotron source) to excite a core electron of an atom or ion of interest in a material. In an XAS experiment an incoming x-ray excites a core electron to an empty state in the valence band when the x-ray photon has sufficient energy to overcome the binding energy. Shown in Fig. 2.10, the x-ray absorption edges are



Figure 2.10: Labels for various core-electron excitations and their corresponding energies for Fe metal. Also shown is an illustration of an x-ray absorption spectrum showing the L and K-absorption edges.

labeled after the core electron. Since the absorption edge energy is unique for each element, x-ray absorption spectroscopy is an element-specific technique.

The x-ray absorption intensity is described by the probability of exciting an electron from an initial state Φ_i to a final state $\Phi_f(W_{i\to f})$ by Fermi's Golden Rule [75]:

$$W_{i \to f} = \frac{2\pi}{\hbar} |\langle \Phi_f | T | \Phi_i \rangle |^2 \delta(E_f - E_i - \hbar\omega)$$
(2.19)

where T is the transition operator, and E_f , E_i , and $\hbar\omega$ are the energies of the final and initial states and the x-ray photon energy, respectively. In the case of one-photon transitions and energies $<\sim 10$ keV (such as XAS of transition metal L and oxygen K edges used in this Thesis) T is (from the electric dipole approximation) [75]

$$T \propto \vec{e}_q \cdot \vec{r}$$
 (2.20)

where $\vec{e_q}$ is the unit vector of the x-ray photon electric field polarization and \vec{r} is the

position operator. Thus,

$$W_{i\to f} \propto \sum_{q} |\langle \Phi_f | \vec{e}_q \cdot \vec{r} | \Phi_i \rangle |^2 \delta(E_f - E_i - \hbar\omega).$$
(2.21)

Dipole selection rules require that $\Delta L = \pm 1$ and $\Delta S = 0$ so that transitions from a core s-state can only reach p-final states and transitions from core p-states can only access final s and d-states.

The advantage of x-ray absorption experiments for magnetic studies arises through the use of polarized x-rays. Due to the selection rules for the x-ray absorption process, transitions from a core level to a spin polarized valence state will occur with different probabilities for left and right-circularly polarized x-rays (i.e. carrying opposite angular momentum). The XMCD signal is the difference between the absorption cross sections with left and right-circularly polarized light, which provides a direct measure of the difference in the density of spin up and spin down valence states that is directly proportional to the magnetization. This process is equivalent to using a fixed photon helicity and reversing the magnetization by measuring the absorption cross section an applied magnetic field with positive and negative polarity [21]. This is illustrated in Fig. 2.11 for the L_3 and L_2 -edge transitions of Fe metal. Since the L_3 and L_2 transitions (corresponding to the excitation of a $2p_{3/2}$ and $2p_{1/2}$ core electron, respectively) have opposite spin orbit coupling $(\ell + s \text{ and } \ell - s)$ the spin polarization is antiparallel at the two edges. At the L_3 -edge, left circularly polarized x-rays have a larger probability of exciting a spin-up electron (62.5 %) versus right circularly polarized x-rays (37.5%), whereas the opposite occurs at the L_2 -edge [21]. The difference provides the XMCD, which is proportional to the magnetization along the x-ray propagation direction. In addition, due to the selection rules, the x-ray does not interact with



Figure 2.11: X-ray magnetic circular dichroism for Fe metal, showing the different in absorption intensities for positive (blue) and negative (yellow) x-ray helicity. Reprinted with permission from [21]. Copyright 2006 Springer Science and Business Media.

the electron spin directly; however, the angular momentum of the x-ray may interact with the electron spin indirectly through the spin-orbit interaction, further affecting the absorption intensities. This provides a measure of the orbital and spin moments through L_3 and L_2 -edge integrated XMCD intensities via spectral sum-rules [76–78].

In a single electron approximation the XAS spectrum reflects the unoccupied symmetry-projected density of states; e.g. the O K-edge absorption as a function of photon energy measures the unoccupied density of p states. This is quite useful for examining bonding and magnetism in oxides since it provides a direct measure of the nature of metal-oxygen bonding (i.e. covalency, valence changes, etc.). However, for L-edge transitions there are additional effects which modify substantially the measured spectrum that arise due to wavefunction overlap between the core-hole (created after absorption) and the valence electrons, and valence electron correlations called "multiplet effects". A proper description of the L-edge spectrum features thus requires a many-body description to account for the Coulombic (electron-electron) and spin-orbit interactions. These interactions result in a large number of possible initial and final states for a single electronic configuration. For example, for an excitation of a core electron to a $2p^53d^5$ final state configuration of a free ion (e.g. for Mn³⁺), there are 1512 possible final states [75]. Hence, XAS for *L*-edge transitions of oxides consist of complex multi-line spectra. The problem is complicated further by electrostatic interactions with the surrounding lattice which result in further modifications to the energy-levels. This is in fact useful, since the XAS spectrum features are characteristic of the metal valence and coordination environment symmetry and hence enables in many cases a fairly reliable identification of all ionic species.

XAS and XMCD experiments were done at beamline 4-ID-C of the Advanced Photon Source. Samples were measured in a helium flow cryostat with a 7 T (maximum) superconducting magnet to obtain temperature and field-dependent properties. Powder samples were mounted onto a carbon tape on a Cu holder and were oriented at a grazing angle to the applied field and x-ray direction, as shown in Fig. 2.12. An electromagnetic undulator provided left and right-circularly polarized x-rays. Details of the x-ray optics can be found in Ref [79]. The x-rays pass through a spherical grating monochromator which can provide x-rays from 500 eV to 3000 eV with an energy resolution of 0.1 eV. The incident x-rays were alternated between left and right-circular polarization at each energy interval, and the raw XAS and XMCD are the sum and difference, respectively, of the absorption of the polarized x-rays. The raw x-ray absorption was normalized to the beam current I_0 that was monitored using an Au mesh upstream of the cryostat. A diagram of the cryostat showing the



Figure 2.12: (a) Photo showing the 7 T magnet at 4-ID-C at the Advanced Photon Source, and (b) illustration of the relative orientations of the sample, incident x-rays and applied field H inside the cryostat.

sample orientation, x-ray and applied field directions is shown in Fig. 2.12. Spectra were measured in total-electron yield (TEY) mode, as shown in Fig. 2.13, by monitoring the drain current. TEY mode measurements are surface-sensitive, and probe approximately the topmost ~ 5 nm, with $\sim 60\%$ of the signal resulting from the topmost 2 nm [21, 80] for transition-metal oxides. XMCD spectra were normalized to the maximum XAS intensity. XMCD spectra are an average of both field polarity measurements (to eliminate possible non-magnetic artifacts), and were normalized to the maximum XAS intensity.

To identify species in the core/shell nanoparticles, reference spectra of individual



Figure 2.13: Illustration of the total-electron-yield (TEY) measurement of x-ray absorption. Reprinted with permission from [21]. Copyright 2006 Springer Science and Business Media.

sites were compared directly with experiment. When reference spectra were not available XAS and XMCD spectra were modeled using ligand field multiplet (LFM) calculations based on the method of van der Laan and Thole [81] using the CTM4XAS 5.5 program [82]. The CTM4XAS program is based on the well established methods that were first applied to optical spectra developed by Cowan [83,84] to calculate the energies of the terms of an electronic configuration due to electron-electron repulsion (i.e. the Slater parameters F_{pd} , G_{pd} and F_{dd}) and spin-orbit interactions, and transition probabilities which provide the XAS line intensities. The program also includes code developed by Thole and Ogasawara [85–87] to account for charge transfer effects, and ligand field effects based on group theory analysis by Butler [88] which describe the lifting of degeneracies of electronic levels due to the electrostatic field from a surrounding lattice. The simulations of transition-metal spectra in this Thesis were done with parameters typical of transition metal-oxides (usually ferrites) available in the literature. The symmetry and strength of the ligand field (10Dq) was typically -0.6 eV for a T_d -site and 1.2 eV for an O_h -site. The Slater parameters were reduced to 80 % of the atomic values to approximate the effects of covalency, which allows the electrons to drift farther from the nucleus compared to the free atom case, and hence reduced the electron-electron repulsion. Additionally, Lorentzian and Guassian line broadening were added to account for the lifetime of the excited state, and instrumental broadening, respectively, to better approximate measured spectra.

The use of sum-rules established by Carra and Thole [76–78] that describe the different contributions of the orbital moment m_{ℓ} and spin moment m_s to the total magnetization responsible for the XMCD signal at the L_3 and L_2 edges, can be used to obtain the quantity m_{ℓ}/m_s . According to the sum rules, $m_{\ell}/m_s = 2p/(3p - 6q)$, where p is the integrated XMCD intensity over the L_3 -edge, and q is the integrated intensity over the L_3 and L_2 -edges.

Chapter 3

γ -Fe₂O₃/NiO core/shell nanoparticles

3.1 Introduction

 γ -Fe₂O₃ nanoparticles form the basis of the series of core/shell nanoparticles investigated. In particular, the aim is to verify the occurrence of core/shell intermixing, identify changes to the γ -Fe₂O₃-surface spin disorder, and understand precisely the role of the intermixed layer in determining the overall nanoparticle magnetism. This chapter presents a comprehensive comparison of the overall, atomic and elementspecific magnetism of γ -Fe₂O₃/NiO core/shell nanoparticles. The NiO shell, despite being incomplete, results in clear reduction of γ -Fe₂O₃ surface spin disorder, and changes to the nanoparticle coercivity. The changes are due to new exchange pathways with Ni²⁺ ions which have migrated from the NiO shell into the surface layers of the γ -Fe₂O₃ core to form an interfacial Ni-ferrite.

3.2 Composition, structure and morphology

X-ray diffraction (XRD) patterns for the γ -Fe₂O₃ and γ -Fe₂O₃/NiO nanoparticles are shown in Fig. 3.1. A Rietveld refinement identified the Fd3m spinel structure for both the seed and core/shell nanoparticles, and indicated additional reflections due to the Fm3m rock-salt structure of the NiO shell. The unit cell of γ -Fe₂O₃ is based on a cubic lattice of 32 O^{2-} ions with 8 interstitial tetrahedral T_d -sites (A-sites) occupied by Fe³⁺ ions and 13 $^{1}\!/\!_{3}$ of 16 available interstitial octahedral $O_{h}\text{-sites}$ (Bsites) occupied by Fe^{3+} ions, with vacancies on remaining 2 $^2/_3 O_h$ -sites. Refinements indicated a lattice parameter for the spinel phase of 0.8380 ± 0.0002 nm for both γ -Fe₂O₃ and γ -Fe₂O₃/NiO that is typical for γ -Fe₂O₃ or doped- γ -Fe₂O₃ nanoparticles [24, 89]. For the rock-salt phase, a lattice parameter of 0.4190 ± 0.0002 nm was observed for γ -Fe₂O₃/NiO consistent with NiO [90]. By including Scherrer broadening into the refinements, an average crystallite diameter of the spinel phase of γ -Fe₂O₃ and γ -Fe₂O₃/NiO nanoparticles of $D_{XRD} = 6.5 \pm 0.5$ nm indicated no change in core crystallite size. For the rock-salt phase of the core/shell nanoparticle a crystallite diameter of ~ 3 nm was observed. Overall weight fractions of 46%/54% spinel/rock-salt were measured for the core/shell nanoparticles.

The lattice parameter of NiFe₂O₄ (~0.834 nm) [91] is nearly identical to the pure Fe-oxides (0.833 nm and 0.839 nm for bulk γ -Fe₂O₃ and Fe₃O₄, respectively), and Ni and Fe electron scattering is similar. Also, significant broadening of the reflections was observed, so the XRD patterns did not indicate a change in spinel lattice parameter or O_h -site occupancy that would indicate a change in composition or structure due



Figure 3.1: Powder x-ray diffraction pattern of (a) γ -Fe₂O₃ and (b) γ -Fe₂O₃/NiO nanoparticles, with the results of the refinement (black line). The black Bragg markers and (hkl) labels index the γ -Fe₂O₃ (Fd $\bar{3}$ m) structure, and the red Bragg markers and (hkl) labels index the NiO (Fm $\bar{3}$ m) structure. The residuals of the refinements are indicated by the solid blue lines.

to core/shell intermixing.

Transmission electron microscopy images of γ -Fe₂O₃ cores prepared using the same synthesis procedure [54] and γ -Fe₂O₃/NiO core/shell nanoparticles are shown in Fig. 3.2a-c. The nanoparticle size distributions, shown in Fig. 3.3, obtained from ImageJ [65] analysis of TEM images provided an average diameter $D_{TEM} =$ 6.61 ± 0.04 nm and distribution with $\ln(\sigma_{D_{TEM}}) = 0.05 \pm 0.01$ for γ -Fe₂O₃ [54], and a bi-modal distribution for γ -Fe₂O₃/NiO with one population characterized by $D_{TEM} =$ 6.52 ± 0.04 nm, $\ln(\sigma) = 0.03 \pm 0.01$, and a second population with $D_{TEM} = 2.34 \pm$



Figure 3.2: (a) Transmission electron microscopy (TEM) image of (a) γ -Fe₂O₃ nanoparticles (b) and (c) γ -Fe₂O₃/NiO core/shell nanoparticles



Figure 3.3: Size distribution for γ -Fe₂O₃ and γ -Fe₂O₃/NiO nanoparticles determined form ImajeJ analysis of TEM images.

0.03 nm, $\ln(\sigma) = 0.07 \pm 0.01$, consistent with the crystallite sizes indicated by XRD. Elemental mapping using electron energy loss spectroscopy (EELS) shown in Fig. 3.4 identified clearly that the two size populations were due to small NiO nanoparticles that formed an incomplete surrounding layer on the surface of the γ -Fe₂O₃ nanoparticles. No isolated clusters of γ -Fe₂O₃ or NiO nanoparticles were observed, indicating all of the γ -Fe₂O₃ was decorated with the NiO.



Figure 3.4: (a) A typical transmission electron microscopy image showing the γ -Fe₂O₃/NiO nanoparticles and (b) the corresponding elemental map of Fe (red) and Ni (green).

3.3 Overall magnetism

The overall magnetic properties of the γ -Fe₂O₃ cores and γ -Fe₂O₃/NiO core/shell nanoparticles were determined from magnetometry and susceptometry measurements. These measurements provide an overall response of the nanoparticle that results from all (atomic, interfacial, intrinsic) properties. To compare the magnetic properties of γ -Fe₂O₃ and γ -Fe₂O₃/NiO, magnetic measurements were done using nanoparticles embedded in paraffin wax with similar interparticle separation, and where the same temperature and field histories were used.

The temperature dependent magnetic properties of γ -Fe₂O₃ and γ -Fe₂O₃/NiO were examined using zero-field-cooled (ZFC) and field-cooled (FC) *dc*-susceptibility measurements, shown in Fig. 3.5. The ZFC configuration was obtained by cooling nanoparticles in the absence of any applied magnetic field, from 300 K to 5 K. By using the ZFC procedure from above the T_B of the nanoparticles, a random orientation of the nanoparticles' magnetizations was obtained at 5 K. A *dc* magnetic field of 10 mT

was then applied and the magnetization was measured with warming. The rapid increase in the dc-susceptibility, $\chi_{dc}(T) = M_{dc}(T)/\mu_0 H$, is a result of the ability of the nanoparticles' magnetizations to align with the applied field due to thermal fluctuations away from their initial random orientations. With further warming, thermal energy becomes sufficient for the nanoparticles to undergo superparamagnetic 180° magnetization reversals resulting in a decrease in $\chi_{dc}(T)$. For the FC measurement, the same 10 mT field was used, and the nanoparticles magnetizations were measured while cooling from 300 K to 5 K. When the nanoparticles are superparamagnetic, there is the same response for $\chi_{dc,ZFC}(T)$ and $\chi_{dc,FC}(T)$. With further cooling, as the nanoparticles become blocked, the magnetizations remain aligned with the applied field, causing the divergence between $\chi_{dc,ZFC}(T)$ and $\chi_{dc,FC}(T)$. A precise determination of T_B of the nanoparticles from dc-susceptibility is problematic due to the influence of interparticle interactions, particle size distribution, and the use of an applied field which may perturb the spontaneous magnetization reversal. Typically, T_B is found to scale with temperature at which the maximum $\chi_{dc,ZFC}(T)$ occurs (T_{max}) according to $T_B = \beta T_{max}$, where the scale factor $\beta \sim 1 - 2$ [2,68,69]. T_B is also related to the onset temperature of $\chi_{dc,ZFC}(T)$ and $\chi_{dc,FC}(T)$ irreversibility. For samples which are prepared with comparable interparticle spacings and measured with the same temperature and field history, a qualitative change in T_B that describes the overall anisotropy of the nanoparticle is possible. Shown in Fig. 3.5, the dc-susceptibility for γ -Fe₂O₃ and γ -Fe₂O₃/NiO nanoparticles is quite similar. The energy barrier to magnetization reversal which determines T_B is dependent on KVof the nanoparticle, where K is the effective anisotropy and V is the volume. The



Figure 3.5: Zero-field cooled (ZFC) (black \bigcirc) and field-cooled (FC) (red \Box) dc susceptibility measurements of (top) γ -Fe₂O₃ and (bottom) γ -Fe₂O₃/NiO nanoparticles measured in $\mu_0 H = 10$ mT.

dc-susceptibility measurements indicate that the overall anisotropy of the γ -Fe₂O₃ core is either not significantly altered by the NiO shell, or that there are other factors which are predominant in determining the core/shell relaxation properties.

To investigate further the temperature dependent properties, ZFC *ac*-susceptibility was measured to probe the time-dependent response. For the *ac*-susceptibility measurement, the nanoparticles were first cooled to 5 K in the absence of any applied field to obtain randomly oriented magnetizations. A small 0.25 mT applied field oscillating at a $\nu = 10 - 1000$ Hz was applied at each temperature interval, and the *ac*response was measured to obtain the in-phase ($\chi'_{ac}(\nu, T)$) and out-of-phase ($\chi''_{ac}(\nu, T)$) *ac*-susceptibilities. At 5 K, prior to applying a magnetic field, the nanoparticle mag-



Figure 3.6: The in-phase (top) and out-of-phase (bottom) *ac*-susceptibilities $\chi'_{ac}(\nu, T)$ and $\chi''_{ac}(\nu, T)$ measured in 0.25 mT drive field oscillating at 10 Hz to 1 kHz for (a) γ -Fe₂O₃ and (b) γ -Fe₂O₃/NiO nanoparticles prepared using the same interparticle spacings. The inset of (a) shows the same measurement for γ -Fe₂O₃ nanoparticles with a larger interparticle spacing.

netizations lie along the easy axis of the nanoparticles. In an ac applied magnetic field, the nanoparticle magnetization oscillates around the easy axis direction. At the lowest temperatures, the magnetization responds only weakly to the ac field, since the anisotropy energy, KV, is large compared to the thermal energy, k_BT , of the system. At higher temperatures, the magnetization responds strongly to the ac field, and a maximum response is obtained when temperatures are near T_B according to the measurement time of the ac drive field frequency. As shown in Fig 3.6, there is a frequency dependent maximum in $\chi'_{ac}(\nu, T)$ with warming that is preceded by a maximum in $\chi''_{ac}(\nu, T)$ that indicates a maximum energy dissipation by the nanoparticles occurring at temperatures just below the onset of superparamagnetism. For temperatures above T_B , there is sufficient thermal energy in the system for superparamagnetic magnetization reversal to occur spontaneously, and a decreasing response that is independent of the applied field frequency is observed. By comparing $\chi_{ac}(\nu, T)$ of the same γ -Fe₂O₃ nanoparticles with a larger interparticle separation (inset of Fig. 3.6a), we can conclude that there are some interparticle interactions which influence the observed susceptibility. However, for the same interparticle separation, there is clearly a much more broad temperature dependent response of γ -Fe₂O₃ cores than for the γ -Fe₂O₃/NiO nanoparticles.

Interestingly, despite nearly identical $\chi_{dc}(T)$, a clear difference in $\chi_{ac}(\nu, T)$ was observed for γ -Fe₂O₃ and γ -Fe₂O₃/NiO nanoparticles. The differences in *ac* response between the two nanoparticle systems and between *ac* and *dc* responses of the same system indicate a change in the magnetism affecting various spin populations that are reflected differently in the *ac* and *dc* measurement, and in different applied fields. Clearly, the overall properties of the core/shell nanoparticles do not directly shed light on the origin of the differences between dynamical magnetism of the two systems, motivating the use of atomic and element-specific experiments, described below. However, γ -Fe₂O₃ and γ -Fe₂O₃/NiO having nearly identical $\chi''_{ac}(\nu, T)$ and $\chi_{dc}(T)$ suggests that the T_B 's (describing the total magnetic response of the nanoparticle) are comparable in the two systems and $T_B \sim 75 K$.

Hysteresis loops were measured for γ -Fe₂O₃ and γ -Fe₂O₃/NiO nanoparticles from 5 K to 300 K, with ±5 T fields, after cooling to 5 K in 5 T. As shown in Fig. 3.7 below $T_B \gamma$ -Fe₂O₃/NiO nanoparticles show hysteresis, and the energy barrier to magneti-



Figure 3.7: Typical hysteresis loops for γ -Fe₂O₃/NiO measured from ±5 T after cooling to 5 K in an applied field $\mu_0 H = 5$ T. The low-field region shows clearly H_c at low temperatures, and the inset shows the temperature variation of the high-field magnetization.



Figure 3.8: Temperature dependence of the coercivity $(H_c(T))$ for γ -Fe₂O₃ (red \Box) and γ -Fe₂O₃/NiO (black \bigcirc). The inset shows $H_c(T^{1/2})$ with the lines indicating a fit as described in the text.

zation reversal is described by the coercivity $H_c(T)$. The temperature dependence of H_c for γ -Fe₂O₃ and γ -Fe₂O₃/NiO nanoparticles is shown in Fig. 3.8. The similarity of T_B for γ -Fe₂O₃ and γ -Fe₂O₃/NiO indicated by susceptometry was also reflected in the H_c onset temperature of $T_{B,H_c} = 75$ K that was the same for γ -Fe₂O₃ and

 γ -Fe₂O₃/NiO. Interestingly, H_c was nearly doubled with the addition of NiO; compare $H_c = 60 \pm 1$ mT for γ -Fe₂O₃/NiO versus $H_c = 33 \pm 0.5$ mT for γ -Fe₂O₃ at 5 K. At the lowest temperatures H_c is determined by the energy barrier to magnetization reversal, KV. For nanoparticles, the temperature dependence of H_c is dominated by superparamagnetic relaxation, and may be described in the simplest model of a uniaxial single domain particle, as described in Sec. 1.3.2. Fits to expression 1.12 (shown in the inset of Fig. 3.8) provide an estimate of $K = 2.5 \times 10^4$ J/m³ for γ -Fe₂O₃, consistent with previous measurements, and $K = 5.3 \times 10^4$ J/m³ (assuming an $M_S = 3.65 \times 10^5$ A/m for γ -Fe₂O₃) indicating an increase in the overall anisotropy of the core/shell nanoparticles. Also quite interestingly, whereas γ -Fe₂O₃ nanoparticles have $H_{ex} = 5.0 \pm 0.5$ mT at 5 K, it is nearly eliminated in γ -Fe₂O₃/NiO nanoparticles ($H_{ex} = 1.5 \pm 1$ mT at 5 K). Since the two systems have the same T_B , a lower H_{ex} is most likely a result of a change to the γ -Fe₂O₃ spin disorder.

The magnetization of a nanoparticle is affected by surface disorder and magnetization dynamics such as spin-wave excitations. For γ -Fe₂O₃ nanoparticles, disordered spins at the nanoparticle surface contribute to the nanoparticle magnetization only at the lowest temperatures and largest fields [49]. In core/shell nanoparticles, this spin population lies at the core/shell interface and may be altered. To examine this, the saturation magnetization ($M_S(T)$) of γ -Fe₂O₃ and γ -Fe₂O₃/NiO was determined by fitting the high-field region of the hysteresis loops at each temperature interval with the law of approach to saturation

$$M(H) = M_S \left(1 - \frac{a}{H} - \frac{b}{H^2} \right) \tag{3.1}$$

where the constant a is typically interpreted as due to stress from imperfections and

dislocations, and b is due to the magnetocrystalline anisotropy $K_{u,1}$ [92]. $M_S(T)$ was cross-checked with a linear fit of M versus $1/\mu_0 H$ for each hysteresis loop. Measurements for γ -Fe₂O₃/NiO showing clear hysteresis for $T < T_B$, and a large change in M_S between 5 K and 10 K are shown in Fig. 3.7, and $M_S(T)$ for γ -Fe₂O₃ and γ -Fe₂O₃/NiO is shown in Fig. 3.9. The temperature dependence of nanoparticles is well described by a Bloch $T^{3/2}$ law [38]

$$M_S(T) = M_0(1 - BT^{3/2}) \tag{3.2}$$

where M_0 is the is the magnetization as T tends to zero, and B is the Bloch constant $(\propto 1/J)$. To describe the magnetism of γ -Fe₂O₃-based nanoparticles, $M_S(T)$ was fitted using a modified Bloch law [38, 49]

$$M_S(T) = M_0 \left[(1 - A)(1 - BT^{3/2}) + A \exp^{-T/T_f} \right]$$
(3.3)

that includes an additional term $A \exp^{-T/T_f}$ that describes qualitatively "freezing out" of disordered surface spins at the lowest temperatures, where A quantifies the contribution of the disordered spins to M_S for temperatures $T < T_f$. As shown in Fig. 3.9 the modified Bloch law describes $M_S(T)$ well, and provided $A = 0.21 \pm 0.04$, $T_f = 3.3 \pm 0.4$ K and $B = 3.19 \pm 0.06 \times 10^{-5}$ K^{-3/2} for γ -Fe₂O₃, and $A = 0.42 \pm 0.05$, $T_f = 3.2 \pm 0.5$ K and $B = 3.31 \pm 0.05 \times 10^{-5}$ K^{-3/2} for γ -Fe₂O₃/NiO. Thus, the $M_S(T)$ behaviour indicated that the core/shell nanoparticles contain a disordered spin population which contributes a slightly larger relative fraction of the magnetization at 5 K and that has the same T_f compared to the disordered surface spins of γ -Fe₂O₃. In addition, the nanoparticle J is lower for γ -Fe₂O₃/NiO versus γ -Fe₂O₃ indicated by the lower Bloch constant B. It is possible that intermixing causes the disordered spins



Figure 3.9: Temperature dependence of the saturation magnetization $M_S(T)$ for (a) γ -Fe₂O₃ and (b) γ -Fe₂O₃/NiO. The solid lines are a fit to a modified Bloch $T^{3/2}$ law as described in the text.

to be partially recaptured into the core and that those spins contribute to $M_S(T)$ for $T > T_f$ in the core/shell nanoparticle. If interfacial spins contribute to $M_S(T)$ for $T > T_f$ yet do not have a completed coordination environment similar to that of the ordered core spins an increase in B would result from a lower average J for the ferrite-based interior.

It is interesting that the addition of a NiO shell (although incomplete) increases H_c , yet decreases H_{ex} and J and increases A. The exchange bias observed for γ -Fe₂O₃ cores, which is a result of interactions between the (ordered) core and disordered surface spin populations [49], is essentially eliminated in the γ -Fe₂O₃/NiO. This may be expected for a system where the completion of the surface structure resolves disorder; however it appears contradictory to the $M_S(T)$ behaviour, which presented a larger low temperature upturn. In FiM/AF systems that are typical exchange bias systems any interfacial coupling would be expected to increase both H_c and H_{ex} . Our result

suggests that the NiO is able to alter the surface magnetism of the γ -Fe₂O₃ cores but does not provide a sufficient interfacial AF/FM exchange coupling to produce a unidirectional anisotropy. This may be due to the relatively low anisotropy of NiO [47] or the lack of large enough structural coherence (below the critical AF size to induce a unidirectional anisotropy). The occurrence of a larger K and lower J, however, provide a clear indication of changes to the intrinsic magnetism that would be consistent with an interfacial NiFe₂O₄-like layer due to intermixing. In order to verify this possibility, we have examined the changes in atomic Fe magnetism using Mössbauer spectroscopy.

3.4 Atomic magnetism

To ascertain the presence of interfacial chemical intermixing, the atomic Fe environments and magnetism of the nanoparticles was examined using Mössbauer spectroscopy at 10 K ($\langle T_B \rangle$), where superparamagnetism does not alter the hyperfine parameters. For γ -Fe₂O₃, the Mössbauer spectrum at 10 K consists of two sextet components with hyperfine parameters typical of octahedral Fe³⁺ B-sites, and tetrahedral Fe³⁺ A-sites with the expected 62%/38% abundance. In addition, γ -Fe₂O₃ nanoparticles contain a component with $B_{hf} = 0$ at 5 K due to disordered surface spins which fluctuate quickly even at the lowest temperatures [50]. As shown in Fig. 3.10, the Mössbauer spectrum of γ -Fe₂O₃/NiO nanoparticles at 10 K shows clear asymmetry, indicating a multi-component spectrum which exhibits significant spectral overlap, indicative of subspectra due to Fe-sites with small differences in hyperfine parameters; an overall spectral shape that is typical of γ -Fe₂O₃-based

nanoparticles [93]. Each unique magnetic and electronic environment (site) is described by a sextet characterized by a Lorentzian with FWHM linewidth Γ , hyperfine field B_{hf} , isomer shift δ , and quadrupole splitting Δ , with the relative abundance of each site proportional to the relative spectral area of the representative component. For γ -Fe₂O₃/NiO, the majority of the spectrum is described by components (labeled A and B_I) which have hyperfine parameters typical of the octahedral Bsites $(B_{hf,B_I} = 53.32 \pm 0.06 \text{ T}, \delta_{B_I} = 0.532 \pm 0.007 \text{ mm/s})$ and tetrahedral A-sites $(B_{hf,A} = 50.93 \pm 0.05 \text{ T}, \delta_A = 0.393 \pm 0.007 \text{ mm/s})$ with $\Gamma = 0.26 \pm 0.01 \text{ mm/s}$ of γ -Fe₂O₃. The relative abundance of the sites was obtained from spectral areas under the assumption that the recoil-free fractions of the spinel A and B-sites are equal at 10 K [94] and indicate approximately 30 % and 44 % for the γ -Fe₂O₃ B- and A-sites, respectively (versus 62 % and 38 % for stoichiometric γ -Fe₂O₃). An additional component with $B_{hf,B_{II}} = 49.7 \pm 0.1 \text{ T}, \delta_{B_{II}} = 0.70 \pm 0.03 \text{ mm/s}$ and $\Gamma = 0.45 \pm 0.05 \text{ mm/s}$ was necessary to fully describe the spectrum, indicating a change in the environment of some of the Fe-ions in the core had occurred after adding the NiO shells, and which comprised 22 % of the Fe-sites. The hyperfine parameters of the new B_{II} component are consistent with the B-sites of a non-stoichiometric Ni-ferrite at the core/shell interface. The larger δ represents a lower Fe-valence, so that the B_{II} -site is from Fe^{2+} -ions, and the lower B_{hf} is consistent with a site with fewer or weakened nearest-neighbour exchange interactions expected for sites within the surface layers of the γ -Fe₂O₃-based core. Also, while γ -Fe₂O₃ nanoparticles have a significant absorption at v = 0 mm/s due to paramagnetic surface spins [50], no such component was observed in γ -Fe₂O₃/NiO. Instead, for γ -Fe₂O₃/NiO the disordered surface spin



Figure 3.10: Mössbauer spectrum for γ -Fe₂O₃/NiO nanoparticles measured at 10 K, showing each subspectrum component due to individual Fe-sites.

component was replaced with an interfacial component (observable most clearly as absorption ~ -3 mm/s) indicating that $B_{hf,surf} = 0 \rightarrow B_{hf,int} = 22.1 \pm 0.01 \text{ T}$, where the increase in B_{hf} is due to a slowing down of the fluctuation rate of the interfacial spins. However, since $B_{hf,int}$ is still significantly lower than B_{hf} of the interior Fesites; the interfacial spin population retained some degree of disorder. The interfacial Fe-sites were also characterized by a $\Delta = 0.40 \pm 0.05 \text{ mm/s}$ due to an asymmetric local electric field that is also observed for the surface spins of γ -Fe₂O₃.

Mössbauer spectra were measured at 100 K intervals to compare the thermal evolution of the B_{hf} and overall spectral collapse due to the onset of superparamagnetism. As shown in Fig. 3.11, the overall collapse of B_{hf} for γ -Fe₂O₃/NiO nanoparticles was also comparable to that of the γ -Fe₂O₃ cores (i.e. similar overall line asymmetry and broadening, and B_{hf} reduction with increasing temperature). By contrast, the absorption near v = 0 is due to a change in relaxation of the γ -Fe₂O₃ disordered surface spins. These results indicate clearly that there is a change in Fe-based composition



Figure 3.11: Mössbauer spectra measured at various temperatures for (a) γ -Fe₂O₃/NiO and (b) γ -Fe₂O₃ [50].

of the nanoparticle due to Ni-ions from the shell migrating into the surface layers of the γ -Fe₂O₃ nanoparticle to form a Ni-ferrite interfacial layer. By virtue of the new exchange interactions between surface Fe-ions and Ni-ions, the total exchange interactions to the Fe-surface ions is increased, which to some degree recaptures the (previously) disordered, paramagnetic surface spins.

3.5 Element-specific magnetism

X-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) measurements were used to confirm composition changes due to intermixing and to examine the nature of magnetic coupling at the core/shell interface. The element-specificity of XAS and XMCD enables characterization of both Fe and Ni-sites, and by virtue of the characteristic spectral features resulting from different ion valence and coordination environments, XAS and XMCD also provide site-specificity.

Spectra measured over the $L_{2,3}$ -edges of Fe and Ni at 10 K and in ± 5 T applied fields (where $T < T_B$ and $\mu_0 H$ is well above the field required to saturate the magnetization) were used to determine the Fe and Ni-sites configuration, and the relative magnetic coupling. To identify the Fe and Ni-sites, XAS and XMCD spectra were simulated using ligand field multiplet calculations of the $2p^63d^5 \rightarrow 2p^53d^6$ and $2p^63d^6 \rightarrow 2p^53d^7$, and $2p^63d^8 \rightarrow 2p^53d^9$ transitions for Fe³⁺ and Fe²⁺, and Ni²⁺, respectively, and by specifying the crystal field splitting 10Dq of O_h and T_d -sites. The spectra were simulated using the CTM4XAS software interface [82] with all sites described using parameters typical of the literature on similar systems [95, 96]. As shown in Fig. 3.12, the Fe XAS and XMCD spectra were typical of a spinel Feoxide. In the XMCD spectrum, two peaks with negative XMCD intensities are due to octahedral Fe^{2+} and Fe^{3+} sites whose magnetization aligns parallel to the applied magnetic field, while a third peak with positive XMCD intensity is due to tetrahedral Fe^{3+} -sites which are AF coupled to the O_h -sites via a superexchange interaction. The relative O_h -site intensities provided a clear indication that the Fe ion distribution was intermediate to γ -Fe₂O₃ and Fe₃O₄ [97, 98]. The relative abundances of the Fe-sites was found to be 31% Fe²⁺ O_h , 32% Fe³⁺ T_d , and 37% Fe³⁺ O_h from a best weighted sum of simulated Fe-sites. However, it should be kept in mind that spectra collected using TEY mode, although able to detect ~ 5 nm from the surface of transition metaloxides [80], will preferentially detect layers closer to the surface due to the attenuation



Figure 3.12: XAS and XMCD measured over the Fe $L_{2,3}$ -edges of γ -Fe₂O₃/NiO at 10 K and 5 T compared with and ligand field multiplet (LFM) simulations of Fe²⁺ O_h , Fe³⁺ T_d , and Fe³⁺ O_h sites. (a) Simulations of the XAS of Fe-sites, (b) measured XAS (black \circ) and sum of simulated sites with 31 % Fe²⁺ O_h , 32 % Fe³⁺ T_d , and 37 % Fe³⁺ O_h (grey line), (c) simulations of the XMCD of Fe-sites, and (d) measured XMCD (black \circ) and sum of simulated sites with 31 % Fe²⁺ O_h , 32 % Fe³⁺ T_d , and 37 % Fe³⁺ O_h with antiparallel O_h and T_d -site magnetizations (grey line).

of electron escape through the sample. Thus, for Fe-spectra, the interfacial layers will be over-represented. The occurrence of a large fraction of Fe^{2+} via XAS and XMCD compared to the Mössbauer spectra is a direct result of this sensitivity difference between the two techniques. However, the Fe XMCD spectra also clearly do not match a pure NiFe₂O₄, which is consistent with a multi-phase system.

For Ni, the XAS and XMCD spectra could be identified [96, 99, 100] clearly as being from octahedral Ni²⁺ with a magnetization aligned with the Fe O_h -sites of the spinel core and interface layers. These results are consistent with the formation



Figure 3.13: (a) XAS and (b) XMCD measured over the Ni $L_{2,3}$ -edges of γ -Fe₂O₃/NiO at 10 K and 5 T compared with and ligand field multiplet (LFM) simulations of Ni²⁺ O_h .

of a Ni-ferrite intermixed layer from Ni²⁺-ions from the NiO shell migrating into the surface layers of the spinel core. This is also consistent with the tendency of Ni²⁺ to occupy preferentially the octahedral sites of the spinel structure [7, 101]. The Ni XAS is due to all Ni²⁺ O_h -sites while the XMCD is a result only of the net magnetization of Ni²⁺ sites induced by the applied magnetic field along the direction of x-ray propagation. The relatively small Ni²⁺ XMCD measured compared to NiFe₂O₄ is likely a result of a under-representation of the normalized XMCD (representing the magnetic fraction) intensity due to compensated Ni²⁺ O_h -sites within the AF NiO particles that contribute to the XAS but not the XMCD.

Sum-rules (described in Sec. 2.6) were used to obtain the quantity $m_{\ell}/m_s = 2p/(3p - 6q)$, where p is the integrated XMCD intensity over the L_3 -edge, and q is the integrated intensity over the L_3 and L_2 -edges, as shown in Fig. 3.14. For Fe, $m_{\ell}/m_s = -0.02 \pm 0.02$ which provides an total effective m_{ℓ}/m_s for all Fe-sites, and $m_{\ell}/m_s = 0.13 \pm 0.02$ for Ni. Keeping in mind the limitations of applying sumrules to transition metal-oxide systems [102] to obtain a precise absolute value of m_{ℓ}/m_s (e.g. due to $L_3 - L_2$ -edge mixing, sensitivity to data normalization, etc.)



Figure 3.14: XMCD of the L_3 and L_2 -edges of (a) Fe and (b) Ni for γ -Fe₂O₃/NiO at 10 K and 5 T. The integrated XMCD intensities are shown in dashed lines and p and q are the integrated XMCD of the L_3 and $(L_3 + L_2)$ -edges, respectively.

the results are consistent with the expected m_{ℓ}/m_s for the Fe and Ni-sites of spinel ferrites [96]. Nevertheless, a reliable comparison of the relative changes in m_{ℓ}/m_s for data sets which are treated with equal normalization and integration procedures can obtained, so that these values may be compared with the results for other core/shell nanoparticles described in this Thesis.

Field and temperature dependent measurements of the Fe and Ni L_3 XMCD demonstrate a clear coupling of all sites within the intermixed layer, and provide further insight to the overall magnetism indicated by magnetometry measurements. Fig. 3.15a shows the temperature and field variation of the maximum XMCD signal of each site, plotted such that the site magnetizations parallel to the applied field



Figure 3.15: (a) Field dependence (at 10 K) and (b) temperature dependence (in $\mu_0 H = 1$ T) of the magnetization of the Fe and Ni-sites determined from the maximum XMCD intensity.

are positive. Fig. 3.15a shows the change in magnetization versus applied field measured at 10 K showing a saturating behaviour for all sites, and 3.15b exhibits the temperature variation in site-specific magnetization measured in $\mu_0 H = 1$ T that shows a similar modified Bloch-like behaviour as $M_S(T)$ from magnetometry. The field-dependent magnetization of the Ni-sites clearly shows the same field-dependent behaviour as the Fe-sites, confirming that the Ni behaves magnetically as part of a ferrite layer. This also validates the interpretation that the Ni magnetic response is not due to the typical NiO, which is a simple AF and should have no significant XMCD. The similar Bloch-like temperature variation was observed for the Fe-sites with a stronger and more linear temperature variation for Ni, which may be a result of a weakened J of the interfacial sites, consistent with the larger B of γ -Fe₂O₃/NiO versus γ -Fe₂O₃, and the results from Mössbauer spectroscopy at 10 K.

3.6 Summary

In summary, the presence of an intermixed layer wherein the Ni²⁺ ions are coupled to the octahedral B-site sublattice of the γ -Fe₂O₃ core is likely the mechanism which enables the increase in coercivity for the γ -Fe₂O₃/NiO system relative to the uncoated γ -Fe₂O₃ cores. That is, since the XMCD results indicate that the Ni spins are exchange coupled to the Fe spins at the interface, the increase in H_c is likely due to the higher anisotropy NiFe₂O₄ layer [91, 103]. The elimination of H_{ex} is from the interfacial layer recapturing the disordered Fe surface spins in concert with the NiO crystallites being too small to provide a fully resolved AF component, thus not able to provide a fixed "effective field" for a measurable H_{ex} . In addition, we have shown that the NiO surface particles and γ -Fe₂O₃ cores are structurally and magnetically coupled. Although the NiO particles do not form a complete shell layer, the surface modification provides a mechanism to resolve the surface spin disorder of the γ -Fe₂O₃ nanoparticle cores.

Chapter 4

γ -Fe₂O₃/MnO core/shell nanoparticles

4.1 Introduction

Chapter 3 established the existence of core/shell intermixing in a relatively "simple" case; only the O_h sites were affected, and the intermixed layer formed was magnetically similar to the core γ -Fe₂O₃ so that the interface disorder was affected primarily. This chapter discusses the significantly more complex case of γ -Fe₂O₃/MnO core/shell nanoparticles. Fe-oxide/Mn-oxide systems have been important in establishing the existence of core/shell intermixing [57, 58, 104]; however, due to the tendency of Mnions to adopt a variety of valences (+2, +3, +4), and to occupy O_h and T_d -sites readily in a variety of structures, it is challenging to identify precisely the role of intermixing in determining the overall magnetism. In this chapter we show that core/shell intermixing can alter substantially the dynamical magnetism of the nanoparticle. This is a result of more extensive core/shell intermixing into the O_h and T_d -sites of the γ -Fe₂O₃-based core which fully integrates disordered spins at the γ -Fe₂O₃ surface and creates an intermixed layer with different anisotropy, exchange strength, and spin structure than γ -Fe₂O₃.

4.2 Composition, structure and morphology

The x-ray diffraction pattern of γ -Fe₂O₃/MnO nanoparticles is shown in Fig. 4.1. In addition to the spinel structure (Fd3m) with lattice parameter $a = 0.8404 \pm 0.0002$ nm and crystallite size $D_{XRD} = 6.0 \pm 0.5$ nm, refinements identified additional reflections due to the rock-salt (Fm $\bar{3}$ m) MnO structure with $a = 0.4401 \pm 0.0002$ nm, and volume fractions of 73%/27% spinel/rock-salt were observed. The spinel lattice parameter was consistent with γ -Fe₂O₃ or doped- γ -Fe₂O₃ nanoparticles [24, 89], but is larger than a for γ -Fe₂O₃/NiO and other γ -Fe₂O₃-based core/shell nanoparticles prepared with the same cores [54, 105]. While it is not uncommon for a to be slightly different for a nanostructured material versus the bulk, the slightly larger a is consistent with a larger degree of core/shell intermixing (discussed below). The lattice parameter of the rock-salt phase was consistent with MnO [106]. An MnO crystallite size of $D_{XRD} = 4.2 \pm 0.5$ nm was obtained from the refinement; however, it should be noted that reflection broadening effects for a shell material have not yet been described quantitatively, and it is not clear what physical meaning is obtained from crystallite sizes extracted using conventional Scherrer analysis for shell structures. There are several examples of reflection broadening for hollow nanoparticles which do not necessarily correspond to a crystallite size on the scale of the shell thickness alone if examined via simple Scherrer analysis [107].

Attempts to include a secondary tetragonal structure $(Mn_3O_4 \text{ or } FeMn_2O_4)$ did not improve the residuals of the refinements. Despite the significant reflection broadening



Figure 4.1: Powder x-ray diffraction pattern of (a) γ -Fe₂O₃/MnO, with the results of the refinement (black line). The black Bragg markers and (*hkl*) labels index the γ -Fe₂O₃ (Fd $\bar{3}$ m) structure, and the red Bragg markers and (*hkl*) labels index the MnO (Fm $\bar{3}$ m). The residuals of the refinement are indicated by the solid blue line.

intrinsic to nanostructured materials, the cubic and tetragonal structures can be distinguished from intense reflections which do not overlap significantly. While the addition of a small amount of tetragonal structure improves the refinement slightly by adding intensity at ~60 deg. 2θ , the residuals become worsened at lower 2θ . It is possible that the background due to the organic surfactants which remain on the particles is problematic for describing properly the background function for the XRD pattern refinement. By comparison reflections due to the MnO are clearly visible, and we can reliably identify the MnO shell structure. The lack of evidence of surface passivization in γ -Fe₂O₃/MnO nanoparticles is consistent with samples prepared using an inert atmosphere [108] (i.e. versus samples which were exposed to air while hot, or which have been stripped of protecting surfactants or stored in air). However, we can not definitively exclude the existence of some thin secondary Mnoxide surface layer. For this reason, element-specific and atomic characterization that describe the Mn and Fe magnetism are used to ascertain the interfacial magnetism



Figure 4.2: Typical TEM images of γ -Fe₂O₃/MnO core/shell nanoparticles showing different magifications.



Figure 4.3: Particle size distribution of γ -Fe₂O₃ and γ -Fe₂O₃/MnO core/shell nanoparticles obtained from ImageJ analysis of TEM images.

and identify changes in Fe-based magnetism due to intermixing.

The nanoparticle size distribution (Fig. 4.3) was determined from TEM images. The particle size distribution provided an average diameter $D_{TEM} = 7.34 \pm 0.07$ nm and distribution with $\ln(\sigma_{D_{TEM}}) = 0.04 \pm 0.01$. An increase in D_{TEM} indicated a shell thickness ~0.4 nm. Fig. 4.4 shows elemental mapping using EELS that confirms the



Figure 4.4: (a) A typical transmission electron microscopy image showing the γ -Fe₂O₃/MnO nanoparticles and (b) the corresponding elemental map of Fe (red) and Mn (green).

core/shell morphology, and indicated that the MnO shell covered the γ -Fe₂O₃ cores.

4.3 Overall magnetism

The *dc*- and *ac*-susceptibilities of γ -Fe₂O₃/MnO nanoparticles are shown in Figs. 4.5 and 4.6. The *dc*-susceptibilities of γ -Fe₂O₃ and γ -Fe₂O₃/MnO nanoparticles are quite similar, although the maximum of $\chi_{dc,ZFC}(T)$ is more broad in γ -Fe₂O₃/MnO, and the onset of irreversibility is slightly lower. For γ -Fe₂O₃/MnO nanoparticles, the *ac*susceptibility shows a maximum in $\chi'_{ac}(\nu, T) \sim 75$ K and a maximum in $\chi''_{ac}(\nu, T) \sim$ 40-50 K due to the onset of superparamagnetism. While the comparable maxima in $\chi_{ZFC}(T)$ and $\chi''_{ac}(\nu, T)$ for γ -Fe₂O₃ and γ -Fe₂O₃/MnO nanoparticles indicate similar $T_B \sim 75$ K, $\chi'_{ac}(\nu, T)$ increases much more rapidly for γ -Fe₂O₃/MnO, and has a significantly more narrow maximum, suggesting a substantial change to the dynamical magnetism of the core/shell nanoparticle.

Hysteresis loops of γ -Fe₂O₃/MnO are shown in Fig. 4.7. At 5 K, both H_c and H_{ex} of γ -Fe₂O₃/MnO were larger ($H_c = 49 \pm 1 \text{ mT}$ and $H_{ex} = 7 \pm 1 \text{ mT}$) than γ -Fe₂O₃


Figure 4.5: Zero-field cooled (ZFC) (black \bigcirc) and field-cooled (FC) (red \Box) dc susceptibility measurements of (top) γ -Fe₂O₃ and (bottom) γ -Fe₂O₃/MnO nanoparticles measured in $\mu_0 H = 10$ mT.



Figure 4.6: The in-phase (top) and out-of-phase (bottom) *ac*-susceptibilities $\chi'_{ac}(\nu, T)$ and $\chi''_{ac}(\nu, T)$ measured in 0.25 mT drive field oscillating at 10 Hz to 1 kHz for (a) γ -Fe₂O₃ and (b) γ -Fe₂O₃/MnO nanoparticles prepared using the same interparticle spacings. The inset of (a) shows the same measurement for γ -Fe₂O₃ nanoparticles with a larger interparticle spacing.



Figure 4.7: Typical hysteresis loops for γ -Fe₂O₃/MnO measured from ±5 T after cooling to 5 K in an applied field $\mu_0 H = 5$ T. The low-field region shows clearly H_c at low temperatures, and the inset shows the temperature variation of the high-field magnetization.



Figure 4.8: Temperature dependence of the coercivity $(H_c(T))$ for γ -Fe₂O₃ (red \Box) and γ -Fe₂O₃/MnO (black \bigcirc). The inset shows $H_c(T^{1/2})$ with the lines indicating a fit as described in the text.

 $(H_c = 33.0 \pm 0.5 \text{ mT} \text{ and } H_{ex} = 5.0 \pm 0.5 \text{ mT} \text{ at 5 K})$, as shown in Figs. 4.8 and 4.9. The fit shown in the inset of Fig. 4.8 using Eq. 1.12 provided an estimate of $K = 4.15 \times 10^4 \text{ J/m}^3$. An enhanced H_{ex} in γ -Fe₂O₃/MnO compared to γ -Fe₂O₃ was consistent with interfacial coupling between the FiM γ -Fe₂O₃ core and the AFM



Figure 4.9: Temperature dependence of the exchange bias $(H_{ex}(T))$ for γ -Fe₂O₃ (black \bigcirc) and γ -Fe₂O₃/MnO (red \triangle).



Figure 4.10: Temperature dependence of the saturation magnetization $M_S(T)$ for (a) γ -Fe₂O₃, where the The solid line is a fit to a modified Bloch $T^{3/2}$. (b) $M_S(T) \gamma$ -Fe₂O₃/MnO, where solid lines are a fit with a linear T dependence modified to include a term to describe surface spins.

MnO shell, typical of exchange bias systems. The loop measured at 5 K shows saturation only at the largest fields. The non-saturating component might indicate some contribution due to Mn-spins which were not present in γ -Fe₂O₃. $M_S(T)$ for γ -Fe₂O₃/MnO shows a sharp upturn at the lowest temperatures and deviated clearly from the Bloch $T^{3/2}$ dependence, following instead a linear dependence, providing another indication of some significant change to the dynamical magnetism of the nanoparticle.

4.4 Atomic magnetism

To determine precisely the changes in dynamical magnetism for the different spin populations within the γ -Fe₂O₃/MnO nanoparticles relative to γ -Fe₂O₃ seeds, Mössbauer spectra were collected from 10 K to 300 K (shown in Fig. 4.11). Mössbauer spectroscopy provides an excellent complementary technique by virtue of the siteselective measurement of the Fe dynamics. In addition, the faster measurement time $\tau_{m,Moss.} \sim 10^{-8}$ s versus $\tau_{m,Magnet.} \sim 10$ s typical of dc-magnetometry and susceptometry results in T_B observed at significantly higher temperatures, as described by Eq.1.7, thus enabling a more detailed measure of the onset of superparamagnetism through gradual changes in spectrum lineshape and B_{hf} (that is a measure of the time-averaged local magnetic field). To describe the dynamical atomic magnetism, consider the Stoner-Wohlfarth model (Sec. 1.3.1) that describes the energy of a uniaxial single-domain particle. At the lowest temperatures, thermal energy is not sufficient for the nanoparticle magnetization to fluctuate about the easy axis. With increasing temperature, the nanoparticle magnetization oscillates (via collective excitations) and will deviate by θ from the easy axis, causing the time-averaged magnetization to decrease. For sufficiently high thermal energy there is a probability that the magnetization will flip completely by 180° so that the time averaged magnetization is zero and the nanoparticle is superparamagnetic. When $T \ll T_B$, there is little relaxation, and the Mössbauer spectrum consists of a sharp sextet with B_{hf} near the typical bulk value. With warming $B_{hf} \rightarrow 0$ as fluctuations increase in frequency. As shown in Fig. 4.11, at 10 K γ -Fe₂O₃/MnO core/shell nanoparticles show no absorption at v = 0 that is observed clearly in γ -Fe₂O₃, due to disordered surface spins [50]. Interestingly, there is no additional component in γ -Fe₂O₃/MnO with a $B_{hf} \sim 20$ T, as occurred in γ -Fe₂O₃/NiO due to the partial recapture of the disordered Fe spins, indicating a more complete recapture of the surface spin population into the ordered γ -Fe₂O₃-based core.

To characterize the spins within the γ -Fe₂O₃/MnO core-shell nanoparticles spectra shown in Fig. 4.11c were fitted using a multi-level relaxation model. The model describes the oscillation frequency of the fluctuations of the Fe spins of the nanoparticle magnetization as a function of temperature [110]. The relaxation model describes different spectral lineshape effects of static spins and those undergoing different amounts of collective excitations and 180° spin flips when superparamagnetic to provide the energy barrier to magnetization reversal and thus the spin relaxation rate for the core and surface populations separately. The results of the fits provided a component describing the core spin population that was characterized by $B_{hf,core} = 51.8 \pm 0.09$ T, isomer shift $\delta_{core} = 0.410 \pm 0.008$ mm/s, quadrupole splitting $\Delta_{core} = 0.017 \pm 0.002 \text{ mm/s}$, and anisotropy $K_{core} = 2.8 \times 10^3 \text{ J/m}^3$. The interface spin population was characterized by $B_{hf,int} = 50.4 \pm 0.4 \text{ T}, \ \delta_{int} = 0.44 \pm 0.02 \text{ mm/s},$ $\Delta_{int} = 0.028 \pm 0.004 \text{ mm/s}$, and $K_{int} = 5.8 \times 10^5 \text{ J/m}^3$. Shown Fig. 4.11d at the lowest temperatures no magnetic relaxation was observed ($\nu_0 = 0$). With increasing temperature, the relaxation frequency for the core and surface spin populations increased, with a faster change occurring in the surface spins. We observed a substantial reduc-



Figure 4.11: (a) Mössbauer spectra collected from 5 K to 300 K for γ -Fe₂O₃ nanoparticles, with the lines indicating fits using a multi-level relaxation model, as described in the text, and (b) the relaxation rated for the core and surface ⁵⁷Fe spins [50]. (c) Mössbauer spectra collected from 10 K to 300 K for γ -Fe₂O₃/MnO core/shell nanoparticles, with the lines indicating fits using a multi-level relaxation model, as described in the text, and (d) the relaxation rated for the core and surface ⁵⁷Fe spins. Reprinted with permission from [109]. Copyright 2017 Springer Science and Business Media.

tion in the relaxation rate for the interface spins in γ -Fe₂O₃/MnO ($\nu_{0,int} = 40$ MHz) in comparison to the surface spins [50] of γ -Fe₂O₃ ($\nu_{0,surf} = 185$ MHz). Interestingly, by comparison, the core spin population within γ -Fe₂O₃/MnO was found to have a faster relaxation rate at 300 K ($\nu_{0,core} \sim 100$ MHz) than the core spins within γ -Fe₂O₃ seeds [50] ($\nu_{0,core} \sim 40$ MHz). The large reduction of Δ_{int} in γ -Fe₂O₃/MnO versus $\Delta_{surf} = 0.423 \pm 0.086$ mm/s for γ -Fe₂O₃, indicated that the asymmetric electronic environment due to broken surface coordination and surface O_h -site vacancies in the γ -Fe₂O₃ seeds is essentially resolved for interfacial Fe-sites in γ -Fe₂O₃/MnO, further confirming the strong effect of the core/shell intermixing.

Typically, in a FiM/AF exchange coupled system interfacial exchange interactions with the AF layer increase the anisotropy of the coupled system, which results in an H_{ex} and increased H_c versus the uncoupled FiM layer [46, 47]. The increase in $\nu_{0,core}$ and $\nu_{0,surf}$ for γ -Fe₂O₃/MnO occurs only above 100 K, consistent with this behaviour since stabilizing interfacial interactions between the ferrimagnetic core and the MnO shell will be effective only below the MnO $T_N = 119$ K. Also, T_N may be reduced from the bulk value due to finite-size effects [111]. Above 100 K, we observe a somewhat contrary result, since the Mössbauer relaxation provided a larger $\nu_{0,core}$ for γ -Fe₂O₃/MnO versus γ -Fe₂O₃ indicating a less stable FiM layer magnetization. The closer correlation of the relaxation rates of the $\nu_{0,core}$ and $\nu_{0,int}$ in γ -Fe₂O₃ versus ν_{core} and $\nu_{0,surf}$ indicated a significantly more uniform dynamical behaviour among the Fe spins in the core/shell nanoparticle, although some difference ($\nu_0(T)$ and K) between the two spin populations remains. Thus, the more uniform overall relaxation rate for γ -Fe₂O₃/MnO nanoparticle is consistent with a more narrow maximum in $\chi'_{ac}(\nu, T)$ versus γ -Fe₂O₃. This is likely a result of intermixing effects which recapture the disordered surface spins into an Mn-ferrite layer, similar to the results obtained for γ -Fe₂O₃/NiO. However, the more marked change in $\chi'_{ac}(T)$ and clear loss of the disordered interfacial spin population indicated by the Mössbauer spectra for γ -Fe₂O₃/MnO shows a more substantial effect of core/shell intermixing than γ -Fe₂O₃/NiO nanoparticles.

Since Mössbauer spectra results indicate a very clear reduction of the surface spin relaxation that is consistent with substantial intermixing effects, and Fe-oxide/Mnoxide systems are expected to contain some degree of intermixing [57, 58, 104], the interpretation of the changes in Fe-atomic magnetism requires further knowledge of the nature of the intermixed layer. In particular, the faster spin relaxation at high temperatures, and the lower core K determined for γ -Fe₂O₃/MnO from Mössbauer fits ($K = 2.8 \times 10^3 \text{ J/m}^3$) than is typical for γ -Fe₂O₃ ($\sim 2 \times 10^4 \text{ J/m}^3$) may be due to a reduced K from Mn ion substitution into the Fe-oxide core. K for mixed Fe/Mnoxides may be lower than the pure Fe-oxide counterpart (although it is dependent on the ion distribution). Conversely, a change in the exchange interactions within the interfacial intermixed layer may alter the relaxation behaviour, or a lowered core volume due to the formation of a magnetically distinct interfacial ferrite.

4.5 Element-specific magnetism

To investigate the origin of the large change in dynamics XAS and XMCD were used to determine the element-specific magnetism. XAS and XMCD spectra measured over the $L_{3,2}$ edges of Fe and in ± 5 T are shown in Fig. 4.12. Spectra contained multiplet structure typical of spinel Fe-oxides, containing octahedral (O_h) Fe²⁺ and Fe³⁺-sites with parallel magnetization, and tetrahedral (T_d) Fe³⁺-sites with magnetization antiparallel to the O_h -sites, evident in the three peak structure in the L_3 -edge XMCD [97, 113]. The Fe-ion distribution was determined using a best weighted sum



Figure 4.12: XAS and XMCD measured over the Fe $L_{2,3}$ -edges of γ -Fe₂O₃/MnO at 10 K and ±5 T compared with and ligand field multiplet (LFM) simulations of Fe²⁺ O_h , Fe³⁺ T_d , and Fe³⁺ O_h sites. (a) Simulations of the XAS of Fe-sites, (b) measured XAS (black \circ) and sum of simulated sites with 30 % Fe²⁺ O_h , 31 % Fe³⁺ T_d , and 39 % Fe³⁺ O_h (grey line), (c) simulations of the XMCD of Fe-sites, and (d) measured XMCD (black \circ) and sum of simulated sites with 30 % Fe²⁺ O_h , 31 % Fe³⁺ T_d , and 39 % Fe³⁺ O_h with antiparallel O_h and T_d -site magnetizations (grey line).

of the simulated individual Fe-sites to the L_3 -edge XMCD. XAS and XMCD of γ -Fe₂O₃/MnO was best described by a sum of 30 % Fe²⁺ O_h , 31 % Fe³⁺ T_d , and 39 % Fe³⁺ O_h .

The Mn $L_{2,3}$ -edge XAS and XMCD reveal clearly multiple Mn-sites. The XAS, shown in Fig. 4.13a, differs clearly from the XAS of MnO (containing only Mn²⁺ O_h sites) [114–116] and indicates a mixture of Mn²⁺ and Mn³⁺-sites [114,116–119] (I(A)and I(B)). The relative intensities I(A)/I(B) did not match any single Mn-oxide or typical stoichiometric Mn-ferrite system. Due to the tendency for Mn³⁺ O_h -sites to



Figure 4.13: XAS and XMCD measured over the Mn $L_{2,3}$ -edges of γ -Fe₂O₃/MnO at 10 K and 5 T. (a) Measured XAS, (b) simulated Mn²⁺ O_h (38%) and T_d (62%)-sites, and (c) difference plot between the experimental XAS and Mn²⁺ sites, which can be identified as Mn³⁺ O_h -sites. (d) Measured XMCD, (e) a reference spectrum of MnFe₂O₄ containing Mn²⁺ O_h (20%) and T_d (80%)-sites [112], (f) difference plot between the experimental XMCD and Mn²⁺ sites, which can be identified as Mn³⁺ O_h -sites.

be involved in significant charge transfer with the anions of the lattice and to undergo Jahn-Teller [120] distortions, simulations of the Mn³⁺ O_h -sites using a simple ligandfield multiplet model prove inadequate, and more complex models which incorporate charge transfer (interactions) with the surrounding ligands are more commonly used to simulate XAS of such sites [118, 120–122]. To help identify the individual sites, Mn²⁺-sites were simulated using CTM4XAS program [82] with parameters typical of Mn²⁺ in O_h and T_d -sites [123–125], and subtracted from the experimental XAS of γ -Fe₂O₃/MnO at the Mn $L_{2,3}$ -edges, as shown in Fig. 4.13. The difference spectrum, shown at the bottom of Fig. 4.13 identifies clearly that the remaining sites are Mn³⁺



Figure 4.14: XMCD of spinel MnFe₂O₄ measured at 10 K in ±1 T [112], (a) LFM calculations of Mn²⁺ T_d and Mn²⁺ O_h -sites (b) a sum of 80% Mn²⁺ T_d and 20% Mn²⁺ O_h -sites compared with the measured XMCD.

 O_h -sites by comparison with experimental spectra of Mn₂O₃ (containing only Mn³⁺ O_h -sites) [114, 118, 119, 126]. By comparison, the Mn XMCD of γ -Fe₂O₃/MnO is quite complex and unique. Among the Fe/Mn-oxide-type nanostructures reported, no similar Mn XMCD has been observed [12,127,128], and the XMCD differs also from that of spinel MnFe₂O₄ [125,129,130] and of Mn₃O₄ [131]. By comparing the energies of the Mn²⁺ and Mn³⁺-sites identified in the XAS, the prominent features in the L_3 edge XMCD (labeled I(A) and I(B)) are due to magnetic Mn²⁺ and Mn³⁺-sites. To resolve the spectra of the individual sites, the experimentally measured spectrum of MnFe₂O₄ (containing 80% Mn²⁺ T_d and 20% Mn²⁺ O_h -sites, Fig. 4.14) was subtracted from the XMCD of γ -Fe₂O₃/MnO, revealing the XMCD due to Mn³⁺ O_h -sites. A similar spectrum has been identified in the intermixed layer of Fe-oxide/Mn-oxide nanoparticles [127, 132].

Using sum rules (described in Sec. 2.6) m_{ℓ}/m_s was obtained from the XMCD



Figure 4.15: XMCD of the L_3 and L_2 -edges of Fe in γ -Fe₂O₃/MnO at 10 K and 5 T. The integrated XMCD intensities are shown in dashed lines and p and q are the integrated XMCD of the L_3 and $(L_3 + L_2)$ -edges, respectively.

spectra of Fe and Mn. As shown in Fig. 4.15, an $m_{\ell}/m_s = -0.10 \pm 0.02$ was measured for Fe. The negative sign indicates an orbital moment that is antiparallel to the spin moment, and the magnitude of m_{ℓ}/m_s of Fe in γ -Fe₂O₃/MnO was clearly larger than was observed for Fe in γ -Fe₂O₃/NiO. For Mn²⁺ and Mn³⁺, the spin sum rule deviates significantly from the actual spin moment due to to multiplet effects and core-valence interactions, which mix the L_2 and L_3 -edges. For example, as shown in Fig. 4.15, these interactions result in no clear separation of the L_2 and L_3 -edge XMCD features (or plateau in the integrated XMCD), which is particularly problematic for systems with Mn³⁺-ions. In some cases, corrections may be applied to obtain precise values of m_s [102]. However, this is challenging for spectra which contain a mixture of sites. To address this, the spectra due to the Mn²⁺ and Mn³⁺ were analyzed separately, as shown in Figs. 4.16b and c. For Mn²⁺-sites $m_{\ell}/m_s = 0$, indicating that the m_{ℓ}/m_s is due entirely to the Mn³⁺-sites, for which $m_{\ell}/m_s = -0.14 \pm 0.02$. While the uncertainty reflects the reliability of the XMCD integration, the m_s correction for Mn³⁺ depends strongly on local environment of the ion (e.g. the crystal fields strength



Figure 4.16: XMCD of the L_3 and L_2 -edges of Mn for γ -Fe₂O₃/MnO at 10 K and 5 T. The integrated XMCD intensities are shown in dashed lines and p and q are the integrated XMCD of the L_3 and $(L_3 + L_2)$ -edges, respectively. The full XMCD spectrum measured for γ -Fe₂O₃/MnO is shown in (a), (b) is the XMCD due to the Mn²⁺ sites only, and (c) is the XMCD due to the Mn³⁺-sites only.

10Dq, charge transfer effects, and Jahn-Teller distortion) so despite isolating the m_{ℓ} to a single site we can only reliably determine that $m_{\ell} \neq 0$ for the Mn³⁺-site. However, the coinciding enhanced Fe m_{ℓ} is consistent with an intermixed layer containing both species.

The field and temperature dependence of the Fe and Mn-site magnetizations were determined from XMCD spectra measured over the Fe and Mn L_3 -edges with



Figure 4.17: (a) Field dependence (at 10 K) and (b) temperature dependence (in $\mu_0 H = 1$ T) of the magnetization of the Fe and Mn-sites determined from the maximum XMCD intensity.

 $\mu_0 H = 0.1 - 5.0$ T at 10 K, and from 10 K to 200 K in 1 T. The magnetizations of each site were obtained from the maximum intensities of each characteristic feature. Shown in Fig. 4.17a, the field dependent magnetization of the Fe-sites and the Mn²⁺-sites displayed typical approach to saturation behaviour. By contrast, the Mn³⁺-site magnetization first increased then decreased with increasing applied field. This is consistent with the changes in exchange interactions among a highly substituted Mn-ferrite layer; the Mn²⁺_{Td}-O²⁻-Fe^{2+/3+}_{Oh} exchange interaction is nearly half that of Fe³⁺_{Td}-O²⁻-Fe^{2+/3+}_{Oh} and the Mn²⁺_{Td}-O²⁻-Mn³⁺_{Oh} interaction is even weaker [7, 101, 133, 134]. γ -Fe₂O₃ and Fe₃O₄ have a collinear spin arrangement due to the strong AF O_h -T_d superexchange interaction. In an intermixed layer containing the Mn-ion distribution described above, the significantly weakened exchange coupling to the Mn³⁺ O_h -sites could result in a

canted spin arrangement [12,101] which would produce the field-dependent behaviour shown in Fig. 4.17a. The significantly weaker $Mn^{3+} O_h$ -site magnetization reversal for γ -Fe₂O₃/MnO than was observed for Fe-oxide/Mn₃O₄ core/shell nanoparticles (where the Mn-site magnetization reverses sign) is consistent with the behaviour of an intermixed Mn/Fe-ferrite layer which contains more (stronger) $\operatorname{Fe}_{T_d}^{3+}-\operatorname{O}^{2-}-\operatorname{Mn}_{O_h}^{3+}$ exchange interactions versus the pure Mn_3O_4 layer, containing weak $Mn_{T_d}^{2+}-O^{2-}-Mn_{O_h}^{3+}$ interaction tions, and hence enabling a larger spin canting in the same applied fields [12]. The temperature dependence of the Fe-sites in Fig. 4.17b, shows that the Fe-sites exhibit a Bloch-like behaviour, similar to that of γ -Fe₂O₃/NiO nanoparticles, which is clearly different from the overall behaviour reflected in the linear $M_S(T)$ of γ -Fe₂O₃/MnO indicated by magnetometry. By comparison with the temperature dependence of the Mn-site magnetization we can conclude that the Mn-ions contribute significantly to the linear $M_S(T)$ dependence observed in magnetometry. The contribution of Mnsites to the XMCD up to 200 K was is in keeping with an intermixed layer (i.e. versus an oxidized Mn-shell) since an Mn_3O_4 shell which would contain the same Mn-sites sites, with $T_N = 40$ K would not contribute significantly to the XMCD up to these temperatures [131, 132].

The unique Mn XMCD that is clearly distinct from any possible pure Mn-oxide phases indicates that the γ -Fe₂O₃/MnO contains an interfacial intermixed Mn/Feoxide layer formed by a substantial amount of intermixing between the Mn-oxide and Fe-oxide layers.

4.6 Summary

In summary, we have shown that γ -Fe₂O₃/MnO nanoparticles have a very different dynamical magnetism compared to γ -Fe₂O₃. The significant changes in the overall and atomic magnetism are a result of a substantial core/shell intermixing wherein Mn²⁺ and Mn³⁺ substitute into the O_h and T_d -sites in the surface layers of the γ -Fe₂O₃ core. The intermixing fully recaptured the disordered surface spins of the γ -Fe₂O₃ core into the ferrimagnetic core of the γ -Fe₂O₃/MnO core/shell nanoparticle, and produced an intermixed layer with magnetism and spin structure that are distinctly different from either the nominal core or shell materials. However, γ -Fe₂O₃/MnO also displays properties of a typical exchange bias system. This naturally leads to the new question of how exchange interactions, now mediated by a magnetically distinct interface layer, affect this important magnetic phenomenon.

Chapter 5

γ -Fe₂O₃/CoO core/shell nanoparticles

5.1 Introduction

 γ -Fe₂O₃/CoO core/shell nanoparticles provide an ideal system to elucidate the role of the intermixed layer on the overall nanoparticle properties. The effects of the antiferromagnetic CoO shell, γ -Fe₂O₃ interior, and a Co-doped interfacial layer can be distinguished by virtue of the substantially different intrinsic magnetism of each layer. This Chapter consists of three studies of γ -Fe₂O₃/CoO magnetism which show precisely how the intermixed layer dominates all aspects of the nanoparticle magnetism. In Sec. 5.2, a self-consistent description of the magnetism and composition at "bulk"/overall, atomic, and elemental scales identifies definitively an intermixed layer formed by Co²⁺ migration into the γ -Fe₂O₃ core, primarily the octahedral sites. Further, it is shown that overall magnetic properties are dominated by this interfacial layer. Sec. 5.3 provides a detailed and direct measurement of the intermixed layer thickness and ion distribution to reveal clearly an intimate relationship between the intermixed layer, interfacial disorder, and exchange bias properties. Finally, Sec. 5.4 describes temperature dependent element-specific and atomic magnetism to reveal an abrupt change in the interfacial metal-oxygen bonding which provides the mechanism responsible for the exchange bias onset in the core/shell nanoparticles.

5.2 Core/shell intermixing to determine the nanoparticle magnetism

This section describes the basic structure, composition, and magnetism of γ -Fe₂O₃/CoO nanoparticles and demonstrates clearly that the intermixed layer dominates the magnetism of the nanoparticle. This also confirms the advantageous properties necessary to disentangle the characteristics of the intermixed layer from the overall nanoparticle magnetism.

5.2.1 Composition, structure and morphology

To determine the core and shell structures, a Rietveld refinement of the x-ray diffraction patterns of the γ -Fe₂O₃/CoO was done using Fullprof [63]. As shown in Fig. 5.1, the refinement identified the spinel (Fd3m) structure of the γ -Fe₂O₃ [89] core and the rock-salt (Fm3m) structure of the CoO shell. Lattice parameters of $a = 0.8362 \pm$ 0.0003 nm and $a = 0.4212 \pm 0.0002$ nm were ascertained for the spinel and rock-salt phases, respectively, consistent with the expected lattice parameters for γ -Fe₂O₃ and CoO [89, 90]. An estimate of the crystallite size for the spinel phase of $D_{XRD} =$ 7.1 ± 0.5 nm was obtained from Scherrer broadening. The refinement to the XRD pattern also provided an estimate of the relative volume fractions of 72%/28% spinel to rock-salt.



Figure 5.1: Powder x-ray diffraction pattern of γ -Fe₂O₃/CoO nanoparticles with the results of the Rietveld refinement (black line). The black Bragg markers and (*hkl*) labels index the γ -Fe₂O₃ (Fd $\bar{3}$ m) structure and the red Bragg markers and (*hkl*) labels index the CoO (Fm $\bar{3}$ m) structure. The residuals of the refinement are indicated by the solid blue line.



Figure 5.2: Typical transmission electron microscopy images of γ -Fe₂O₃/CoO nanoparticle.

Typical transmission electron microscopy images of γ -Fe₂O₃/CoO nanoparticles are shown in Fig. 5.2. The clear bright and dark fringes are due to the atoms within the nanoparticle's highly crystalline structure aligned parallel to the electron beam. The particle size distribution obtained from ImageJ [65] analysis of the TEM im-



Figure 5.3: Size distribution for γ -Fe₂O₃ and γ -Fe₂O₃/CoO nanoparticles determined by ImageJ analysis of TEM images.



Figure 5.4: Selected area electron diffraction image obtained from low magnification TEM of γ -Fe₂O₃/CoO nanoparticles. The rings are labeled with the corresponding *d*-spacing and according to the corresponding (*hkl*) planes of the spinel (γ -Fe₂O₃) and rock-salt (CoO) structures.



Figure 5.5: (a) A typical transmission electron microscopy image showing the γ -Fe₂O₃/CoO nanoparticles, and the corresponding EELS mappings of (b) Fe (red) and (c) Co (green).

ages, shown in Fig. 5.3, provided a log-normal size distribution with mean diameter $D_{TEM} = 7.9 \pm 0.1$ nm, and size distribution $\ln(\sigma) = 0.07 \pm 0.01$ [105]. The increase in particle size versus γ -Fe₂O₃ cores ($D_{TEM} = 6.6 \pm 0.1$ nm) [54] provides a first confirmation of core/shell morphology. Electron diffraction, shown in Fig. 5.4, also identified the spinel and rock-salt structures confirming the results from the XRD refinements. Elemental mapping using EELS (Fig. 5.5) confirmed the core/shell morphology (i.e. versus a nanoparticle mixture), revealing clearly Fe and Co in each nanoparticle. The CoO shell thickness was determined directly from a high-resolution TEM image. As shown in Fig. 5.6, the intensity of the lattice fringes differs between the core and shell structures. To determine the shell thickness, a line from the core across the shell was chosen (indicated in Fig. 5.6a) and the image intensity profile was analyzed, as shown in Fig. 5.6b. The core structure was first confirmed by determining the spacing between fringes and comparing with the γ -Fe₂O₃ structure relative to the electron beam direction. The average intensity of the core and shell structure areas



Figure 5.6: (a) A HRTEM image of a γ -Fe₂O₃/CoO core/shell nanoparticle and (b) the analysis to determine the CoO shell thickness from the HRTEM image intensity profile with the lattice fringes.

was measured, and the interface threshold was obtained form the inflection point. The shell thickness was determined by examining the Fast-Fourier-Transform (FFT) obtained from a segment of the image, moving from the grid region into the core at 60 intervals (0.075 nm step sizes). By observing the FFT intensity corresponding to the Co-O bond distance in CoO, the thickness of the shell to the interface was found to be 0.7 ± 0.2 nm [105]. The CoO shell thickness of 0.7 nm was consistent with the increase in mean particle diameter obtained from the size distribution analysis.

5.2.2 Overall magnetism

The susceptibility of γ -Fe₂O₃/CoO nanoparticles, shown in Figs. 5.7 and 5.8, indicates a substantial change in the magnetic properties of the nanoparticle. Considering only the increase in magnetic volume due to the 0.7 nm thick CoO shell, an increase in T_B from 75 K to 135 K would be expected (a volume increase of 1.8×). However, $\chi_{dc,ZFC}(T)$ shows clearly a maximum at ~ 200 K, the $\chi'_{ac}(\nu, T)$ maximum is ~ 225 K,



Figure 5.7: Zero-field cooled (ZFC) (black \bigcirc) and field-cooled (FC) (red \Box) dc-susceptibility measurements for (a) γ -Fe₂O₃ and (b) γ -Fe₂O₃/CoO nanoparticles measured in $\mu_0 H = 10$ mT.

and the maximum in $\chi_{ac}''(\nu, T)$ is at ~ 150 K, indicating a $T_B > 150$ K. In addition, there is clear irreversibility in $\chi_{dc}(T)$ and $\chi_{ac}'(\nu, T)$ up to nearly 300 K. Notably, the changes in susceptibility for γ -Fe₂O₃/CoO versus γ -Fe₂O₃ are markedly different from those of γ -Fe₂O₃/NiO and γ -Fe₂O₃/MnO, despite the comparable increases in magnetic volume. Altogether, this indicates that the anisotropy, K, of the nanoparticle was increased substantially with the addition of a CoO shell, in a manner which does not simply stabilize the magnetism of the γ -Fe₂O₃ core, suggesting instead that the intrinsic properties have changed. The clear discrepancy between the $\chi_{ac}'(10\text{Hz}, \text{T})$ and $\chi_{dc,ZFC}(T)$, which show different curve maxima and shapes (inset of Fig. 5.8b) also suggests contributions from multiple spin populations which respond differently



Figure 5.8: The in-phase (top) and out-of-phase (bottom) *ac*-susceptibilities $\chi'_{ac}(\nu, T)$ and $\chi''_{ac}(\nu, T)$ measured in 0.25 mT drive field oscillating at 10 Hz to 1 kHz for (a) γ -Fe₂O₃ and (b) γ -Fe₂O₃/CoO nanoparticles prepared using the same interparticle spacings. The inset of (a) shows the same measurement for γ -Fe₂O₃ nanoparticles with a larger interparticle spacing. The inset of (b) shows a comparison of $\chi'_{ac}(T, 10\text{Hz})$ and $\chi_{dc,ZFC}(T)$.

to the different applied fields and time-scales of the two measurements.

There is further evidence of a clear change in the magnetism from hysteresis loop measurements, shown in Fig. 5.9, measured from 5 K to 300 K after cooling in an applied field of 5 T. For example, the hysteresis loops show a clear two-phase shape, observed as a loop narrowing as H_c is approached (Fig 5.9) that persists until H_c becomes zero at 200 K. This was not observed in the uncoated γ -Fe₂O₃ nanoparticles, and in γ -Fe₂O₃/CoO could be due to the existence of two magnetically distinct core and intermixed phases, each with a different anisotropy. As shown in Fig. 5.10, the exchange bias H_{ex} and coercivity H_c are both substantially increased with the



Figure 5.9: Typical hysteresis loops for γ -Fe₂O₃/CoO measured from ±5 T after cooling to 5 K in an applied field $\mu_0 H = 5$ T. (a) Low $\mu_0 H$ for selected temperatures, and (b) the temperature variation of the high-field magnetization for selected temperatures.

addition of a CoO shell. Since the energy barrier that determines H_c is proportional to KV/k_BT_B , H_c may be increased by increasing the intrinsic anisotropy of the nanoparticle, K, or extrinsically by enhancing T_B . By comparing the temperature dependencies of H_c for γ -Fe₂O₃/CoO and γ -Fe₂O₃ the systems, which do not coincide even when re-scaled to the respective T_B values for the onset of H_c (Fig. 5.11) we can conclude that the H_c increase was due to the intrinsic anisotropy K and not the relative T_B differences. Using an estimate of the volume normalized M_S (where the same nanoparticle volume fraction is expected for both the γ -Fe₂O₃ and γ -Fe₂O₃/CoO mag-



Figure 5.10: Temperature dependence of the (a) coercivity $(H_c(T))$ and (b) exchange bias $(H_{ex}(T))$ for γ -Fe₂O₃/CoO. The inset shows the $H_c(T)$ for T > 140 K, showing $T_{B,H_c} = 200$ K.



Figure 5.11: Temperature dependence of the coercivity $(H_c(T))$ for γ -Fe₂O₃ (red \Box) and γ -Fe₂O₃/CoO (black \bigcirc), normalized to the onset temperature, T_{B,H_c} . The lines indicate a fit as described in the text.

netometry samples) $K = 2.5 \times 10^4 \text{ J/m}^3$ was measured for γ -Fe₂O₃, consistent with our previous work [49], and a value typical of γ -Fe₂O₃ nanoparticles. By comparison, a substantially enhanced $K = 1.2 \times 10^5 \text{ J/m}^3$ was measured for γ -Fe₂O₃/CoO. Since K of a composite system is typically determined by the component with the largest K, this represents a larger overall increase in K than would be expected from CoOalone (with $K = 5 \times 10^4 \text{ J/m}^3$) [135]. Overall, the increase in H_c and T_B that we observed were significantly higher than has been reported for other mixed γ -Fe₂O₃ and Co nanoparticle systems such as surface Co-doped γ -Fe₂O₃ [136, 137] and composites of similar size γ -Fe₂O₃ and CoO nanoparticles [138]. Since surface doping has a maximum effect at approximately the Co amount required to form a monolayer of (Co,Fe)-oxide at the nanoparticle surface [137], this suggested that the properties we observed were due to a combination of interfacial exchange with CoO and intermixing effects. To compare the temperature dependent properties, a substantial H_{ex} due to the CoO shell was observed up to 140 K (Fig. 5.10b). It is possible for the T_N of the CoO shell to be reduced substantially relative to the bulk T_N of 290 K considering the shell thickness of ~ 0.7 nm [111]. However, as discussed in Sec. 5.4, the H_{ex} onset can be related directly to a change the Fe-O bonding within the interfacial layer, which influences the interfacial exchange interaction. This also indicates that interactions with the CoO did not contribute to the persisting H_c above 140 K, further demonstrating the existence of an additional magnetic phase. By comparison, no H_{ex} or H_c was observed above 100 K for the uncoated γ -Fe₂O₃ cores.

The temperature dependence of the saturation magnetization, $M_S(T)$, for γ -Fe₂O₃/CoO shows clearly an exponential-like behaviour at the lowest temperatures



Figure 5.12: Temperature dependence of the saturation magnetization $M_S(T)$ for (a) γ -Fe₂O₃ and (b) γ -Fe₂O₃/CoO. The solid lines are a fit to a modified Bloch $T^{3/2}$ law as described in the text.

that is also observed in the uncoated γ -Fe₂O₃ cores due to the freezing out of disordered surface spins [49]. In the γ -Fe₂O₃/CoO core/shell nanoparticles the similar $M_S(T)$ behaviour indicates that the surface spin disorder from the core persisted in the core/shell nanoparticle; however, it is also possible that there is some additional contribution from other phases in the core/shell nanoparticle (i.e due to Co). A fit to the modified Bloch law provided $A = 0.15 \pm 0.02$, $T_f = 7.0 \pm 0.5$ K and $B = 3.55 \pm 0.04 \times 10^{-5}$ K^{-3/2} for γ -Fe₂O₃/CoO; a slightly larger T_f , and increased B, indicating a weakened J compared to the bare γ -Fe₂O₃ nanoparticles.

5.2.3 Atomic magnetism

To describe the origin of the magnetism changes observed in γ -Fe₂O₃/CoO nanoparticles, Mössbauer spectra characterized the atomic ⁵⁷Fe magnetism. As shown in Fig. 5.13 the spectrum at 10 K identifies the Fe-sites. Approximately 75 % of the spectrum consisted of two components with hyperfine parameters typical of the tetra-



Figure 5.13: (a) 10 K Mössbauer spectrum of γ -Fe₂O₃/CoO nanoparticles. The numbers mark the spectral lines from the transitions between the $\pm \frac{3}{2} \rightarrow \pm \frac{1}{2}$ nuclear spin states and (b) 300 K Mössbauer spectrum of γ -Fe₂O₃/CoO. Subspectra labeled I indicate pure γ -Fe₂O₃, and II indicate Co-doped γ -Fe₂O₃.

hedral Fe³⁺ A-site ($B_{hf,A} = 51.25 \pm 0.05 \text{ T}$, $\delta_A = 0.402 \pm 0.005 \text{ mm/s}$), and octahedral Fe³⁺ B-site of γ -Fe₂O₃ ($B_{hf,B_I} = 53.42 \pm 0.03 \text{ T}$, $\delta_{B,I} = 0.500 \pm 0.004 \text{ mm/s}$) [93] with line width $\Gamma(\text{FWHM}) = 0.26 \pm 0.01 \text{ mm/s}$ relative to $\Gamma_{\text{nat}} = 0.13 \text{ mm/s}$ for the source. The broadened linewidth identified chemical and structural disorder about the Fe sites, typical for γ -Fe₂O₃ nanoparticles. An additional $\sim 5 \%$ of the spectrum area was described by a component with $B_{hf} = 21.7 \pm 0.5 \text{ T}$, $\Delta = 0.49 \pm 0.05 \text{ mm/s}$ which

accounted for the low velocity features ($\sim \pm 3 \text{ mm/s}$) from interfacial disordered spins with an incomplete local coordination that results in an electric field gradient, Δ , not present in bulk γ -Fe₂O₃ [139], similar to that observed in γ -Fe₂O₃/NiO. An additional site, comprising $\sim 20\%$ of the Mössbauer spectrum at 10 K could not be described by stoichiometric γ -Fe₂O₃. The occurrence of a magnetically distinct component not belonging to γ -Fe₂O₃ was also observable clearly at 300 K as a static component (shown in Fig. 5.13b) consisting of two sextets with significantly different hyperfine parameters and Γ 's (inconsistent with γ -Fe₂O₃ A and B-sites which have similar hyperfine parameters). The change in spectral symmetry (visible most clearly by comparing lines 1 and 6 between the 10 and 300 K spectra) indicated clearly a temperature variation inconsistent with a simple stabilization of the γ -Fe₂O₃-sites, which would show a much more symmetric spectrum even under temperature changes [50, 93]. As described further in Sec. 5.4.1, B_{hf} and δ of each component were obtained by incorporating a broad singlet to describe the superparamagnetic component (labeled SP in Fig. 5.13b) to account for the lineshape effects of magnetic relaxation (although the physics of the process is not described, e.g. magnetic relaxation [50] masked with $\Gamma ~\sim~ 0.8~{\rm mm/s}$ vs Γ_{nat} = 0.13 mm/s). In fact, relaxation models could not describe the spectral evolution of γ -Fe₂O₃/CoO nanoparticles indicating additional factors (described in Sec. 5.4) affecting the temperature dependence of the atomic magnetism. Examining the evolution of the Mössbauer spectra in this way ensured a consistent description of the hyperfine parameters with temperature for each spectral component. The pure γ -Fe₂O₃ component exhibited similar temperature evolution to that of the γ -Fe₂O₃ seed particles [50]. This allowed the identification of the broad singlet labeled SP in the 300 K spectrum as from a superparamagnetic pure γ -Fe₂O₃ core, and the second magnetically distinct phase was confirmed. The remaining ~20% at 10 K, and the change in spectral lineshape asymmetry required a component with significantly larger δ and smaller B_{hf} ($B_{hf} = 47.7 \pm 0.1$ T, $\delta = 0.68 \pm 0.03$ mm/s, $\Gamma = 0.6 \pm 0.1$ mm/s) than the A- and B-sites of pure γ -Fe₂O₃ that were strikingly similar to the B-site of a Co-doped Fe₃O₄ [140, 141], and is hence labeled B_{II} in Fig. 5.13.

This result would be expected for an interfacial intermixed layer of Co-doped γ -Fe₂O₃, since the two structures would differ only by the amount of octahedral site vacancies. The large $\delta_{B,II}$ determined for the Co-doped Fe-oxide phase indicated the presence of Fe²⁺ which would be required to maintain charge balance within the structure. As the spectral area represented by each component is proportional to the number of Fe atoms, the A/B site occupancy for each phase can be ascertained; the pure γ -Fe₂O₃ components were in good agreement with the expected A/B of 0.375/0.625, and the A/B occupancy of the Co-doped Fe-oxide phase was unchanged from that of the core. The identical site occupancies indicated that Co²⁺ substituted into the vacant octahedral sites in γ -Fe₂O₃ at the γ -F₂O₃/CoO interface, rather than displacing Fe³⁺. Assuming the Fe content was unchanged throughout the core, from the relative spectral areas for the components we estimate the interfacial cobalt-doped layer thickness to be ~0.3 nm, indicating that only the first few monolayers of the core were affected.

The Mössbauer spectrum at 300 K also provides some insight to the temperaturedependent magnetism in γ -Fe₂O₃/CoO (indicated by magnetometry and susceptometry) by providing a site-specific relaxation of the pure γ -Fe₂O₃ interior and the interfacial intermixed layer separately through the variation of B_{hf} of each Fe-site. The onset of superparamagnetism results in a collapse of the sextet to a singlet as $B_{hf} \rightarrow 0$ with increasing 180° spin flip rates which can be observed for each Fe-site separately by virtue of the differences hyperfine parameters unique to each. For example, magnetometry and susceptometry measurements provide only the total sample magnetization and can not distinguish the effects of multiple phases, but rather a distribution of anisotropy barriers within the sample are observed as a broadened maximum in the $\chi'_{ac}(T)$ and $\chi_{dc,ZFC}(T)$. In multiple-phase systems where several distinct magnetic components exist attributing a single T_B to the composite system can be problematic. Mössbauer spectroscopy, however, measures directly the contribution from magnetically distinct phases that are characterized by different hyperfine parameters. The Mössbauer spectrum for γ -Fe₂O₃/CoO (Fig 5.13b) shows a clear static magnetic component at 300 K. Since this is above the T_N of CoO, this effect can not be due to a straightforward exchange interaction with the CoO shell.

Having identified two Fe-oxide phases with clearly different temperature dependent properties, the temperature regimes where the interior and intermixed layers influence the overall magnetism indicated by magnetometry can be described by considering the different measuring times for Mössbauer spectroscopy (10^{-8} s) and magnetometry measurements (1-10 s). Using the simple arguments based on the Néel relaxation model described in Sec. 1.3.1, and assuming a typical moment reversal attempt time of $\tau_0 = 10^{-9} - 10^{-11}$ s, a conservative estimate of $T_{B,DC}/T_{B,Moss} \sim 2-4$ is expected, based on Eq. 1.7. Since a similar temperature evolution was observed for the B_I and A-sites of γ -Fe₂O₃/CoO as for γ -Fe₂O₃ (with $T_B \sim 75 \ K$), re-scaling of the dynamical freezing behaviour of γ -Fe₂O₃/CoO reveals clearly that H_c persisting up to 200 K was not due to the pure γ -Fe₂O₃ core. That is, for a magnetometry T_B of 200 – 250 K (a lower estimate for the γ -Fe₂O₃/CoO system), a completely magnetically split Mössbauer spectrum should be observed at 300 K. However, Fig 5.13b shows clearly that the pure γ -Fe₂O₃ component was collapsed. By comparison, the Fe-sites within the intermixed layer showed almost no line broadening (e.g. observed clearly in line 1, with a sharp A-site linewidth) or significant B_{hf} reduction that would indicate significant relaxation effects resulting from a near proximity to T_B . This means that, in addition to altering the basic characteristics of the nanoparticle magnetism at low temperatures by enhancing H_{ex} and altering the surface spin disorder of the core, the intermixed layer can also completely determine the magnetism at high temperatures when the low anisotropy γ -Fe₂O₃ core is superparamagnetic.

5.2.4 Element-specific magnetism

To determine the magnetic sites within the intermixed layer and to characterize the element-specific magnetism, x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) were collected over the Fe (700–740 eV) and Co (770–815 eV) $L_{2,3}$ ($2p \rightarrow 3d$ transition) edges at 10 K and in a applied fields of ± 1 T using total electron yield (TEY) mode. The Fe XAS and XMCD spectra were typical of a spinel Fe–oxide. The Fe L_3 -edge XAS reveals two unresolved peaks due to a mixture of octahedral O_h (B)-sites and tetrahedral T_d (A)-sites, with relative intensity intermediate to that expected for γ -Fe₂O₃ and Fe₃O₄ [97,97,98]. The XMCD reveals



Figure 5.14: XAS and XMCD measured over the Fe $L_{2,3}$ -edges of γ -Fe₂O₃/CoO at 10 K and 1 T compared with and ligand field multiplet (LFM) simulations of Fe²⁺ O_h , Fe³⁺ T_d , and Fe³⁺ O_h sites. (a) Simulations of the XAS of Fe-sites, (b) measured XAS (black \circ) and sum of simulated sites with 31 % Fe²⁺ O_h , 33 % Fe³⁺ T_d , and 36 % Fe³⁺ O_h (grey line), (c) simulations of the XMCD of Fe-sites, and (d) measured XMCD (black \circ) and sum of simulated sites with 31 % Fe²⁺ O_h , 32 % Fe³⁺ T_d , and 37 % Fe³⁺ O_h with antiparallel O_h and T_d -site magnetizations (grey line).

clearly a typical Fe L_3 -edge splitting due to a mixture of Fe²⁺ and Fe³⁺ O_h -sites with parallel magnetizations, and an Fe³⁺ T_d -site with antiparallel magnetization that occurs in spinel ferrites. The relative intensity of the two negative XMCD features due to the O_h -sites resembled more closely that of γ -Fe₂O₃ than Fe₃O₄; however XMCD also indicated clearly some Fe²⁺ O_h -sites, not observed in γ -Fe₂O₃, in agreement with the Mössbauer spectra. As shown in Fig. 5.14, an estimate of the Fe-ion distribution was obtained using ligand-field multiplet (LFM) simulations of the individual sites. The LFM simulations were done using ligand field strengths 10Dq used typically to



Figure 5.15: XAS and XMCD measured over the Co $L_{2,3}$ -edges of γ -Fe₂O₃/CoO at 10 K and 1 T compared with and ligand field multiplet (LFM) simulation of Co²⁺ T_d -sites and reference spectra of Co³⁺ O_h , and Co²⁺ O_h sites. (a) The XAS of Co-sites, (b) measured XAS (black \circ) and sum of individual sites with 83 % Co²⁺ O_h , 6 % Co²⁺ T_d , and 11 % Co³⁺ O_h (grey line), (c) the XMCD of Co-sites, and (d) measured XMCD (black \circ) and sum of individual sites with 84 % Co²⁺ O_h and 16 % Co³⁺ T_d with antiparallel O_h and T_d -site magnetizations (grey line).

describe ferrites [95], and with standard reduction of the Slater parameters to 80% of the atomic values. Keeping in mind that the interfacial ion distribution will be over-represented for XMCD measured in TEY mode [80], an estimate of the Fe-ion distribution of 31 % Fe²⁺ O_h , 33 % Fe³⁺ T_d , and 36 % Fe³⁺ O_h was obtained by using a best weighted sum of the simulated Fe-sites to the Fe L_3 -edge XMCD, as shown in Fig. 5.14.

The Co XAS was very similar to that of $\text{Co}^{2+} O_h$ -sites such as in CoO or the O_h sites of a Co-doped spinel Fe–oxide [142], and differed clearly from that of Co_3O_4

which contains only $\operatorname{Co}^{2+} T_d$ and $\operatorname{Co}^{3+} O_h$ -sites [143]. Due to the strong overlap of spectral features of Co sites, a precise identification of all Co species was made by considering reference spectra of Co^{2+} and $Co^{3+} O_h$ -sites measured previously at the same beamline [144], and $\operatorname{Co}^{2+} T_d$ -sites simulated using parameters typical of oxides [95]. As shown in Fig. 5.15a, the XAS was described predominantly by $\operatorname{Co}^{2+} O_h$ -sites with a small amount of $\operatorname{Co}^{2+} T_d$ and $\operatorname{Co}^{3+} O_h$ -sites. For a simple antiferromagnet, no significant XMCD signal is expected since there is no overall magnetization. However, a clear Co XMCD signal indicated a measurable Co magnetization aligned with the Fe O_h -sites. This would be expected for Co ions incorporated into the O_h sites of the ferrimagnetic γ -Fe₂O₃. While the Co XMCD looks quite similar to that of Co²⁺ O_h -sites, there is a clear difference in the shape of the L_2 -edge XMCD. As with the XAS, which identified the magnetic and non-magnetic Co-sites, to describe the XMCD, reference spectra of $\operatorname{Co}^{2+} O_h$ and $\operatorname{Co}^{3+} O_h$ -sites with intermediate spin state from experiment [144], and simulated $\operatorname{Co}^{2+} T_d$ -sites were considered. No indication of any contribution to the XMCD due to Co³⁺-sites was observed, and the XMCD was best described as predominantly due to $Co^{2+} O_h$ -sites with magnetization parallel to the Fe O_h -sites and a small amount of $\operatorname{Co}^{2+} T_d$ -sites with magnetization parallel to the Fe³⁺ T_d -sites. This is consistent with the strong preference for Co²⁺ ions to occupy O_h -sites and indicates an ion distribution typical of a cobalt-ferrite-like layer [7, 101, 145]. However, the magnitude of the Co XMCD of γ -Fe₂O₃/CoO is significantly smaller than expected for cobalt-ferrite [146] where the maximum XMCD intensity is $\sim 0.5 - 0.6$ (when normalized to the XAS intensity maximum). This is consistent with a large contribution of non-magnetic $\operatorname{Co}^{2+} O_h$ sites to the XAS from


Figure 5.16: XMCD of the L_3 and L_2 -edges of (a) Fe and (b) Co for γ -Fe₂O₃/CoO at 10 K and 1 T. The integrated XMCD intensities are shown in dashed lines and p and q are the integrated XMCD of the L_3 and $(L_3 + L_2)$ -edges, respectively.

the CoO shell.

Fig. 5.16 shows the Fe and Co XMCD and the integrated XMCD. Using sum-rule analysis [76–78], the relative contribution of the spin and orbital moments, averaged among the Fe and Co-sites is provided by $m_{\ell}/m_s = 2q/(9p - 6q)$, where p and qare the integrated XMCD intensities over the L_3 edge, and the combined L_3 and L_2 edges, respectively. Interestingly, total integrated Fe XMCD (q) does not equal zero indicating a non-zero orbital moment $(m_{\ell}/m_s)_{\rm Fe} = 0.05 \pm 0.02$ that is clearly larger than observed in γ -Fe₂O₃/NiO. For Co, a large m_{ℓ} is indicated clearly by the large q, which provided $(m_{\ell}/m_s)_{\rm Co} = 0.53 \pm 0.02$. These results are consistent with a mixture of Co^{2+} in T_d sites (with low m_ℓ) and O_h sites (m_ℓ/m_s expected between ~ 0.4 - 0.6) [147-149]. The relatively large Co m_ℓ/m_s may also be in part due to uncompensated Co^{2+} from lower coordination at the interface or CoO shell [148], or local strain in the interfacial layer [149]. The presence of coupling was also reflected in the enhanced Fe (m_ℓ/m_s)_{Fe} (m_ℓ is essentially zero for Fe-oxides, even at the nanoscale [150, 151]), that has been observed in strained Co-substituted Feoxides [149], and was consistent with the observation of a canted spin population in the Mössbauer spectra. While the presence of some Fe²⁺ O_h -sites might be expected provide a small m_ℓ , $m_\ell/m_s = 0$ was observed for γ -Fe₂O₃/NiO, despite a similar interfacial Fe²⁺ amount. This further supports that the (m_ℓ/m_s)_{Fe} changes are related to magnetic coupling at the interface due to intermixing effects, and not an intrinsic behaviour of the Fe-ions.

All of the information shows clearly that the γ -Fe₂O₃/CoO core/shell nanoparticles do not have a simple two layer structure. By characterizing the composition in detail, we identified clearly the presence of an interfacial cobalt doped γ -Fe₂O₃ layer that arose predominantly from Co²⁺ migration into O_h sites at the γ -Fe₂O₃ surface. We have shown that the combined effects of the single ion anisotropy of Co²⁺ in the spinel structure and exchange bias (interfacial coupling) effects have acted cooperatively to increase the total anisotropy of the nanoparticle. In γ -Fe₂O₃/CoO nanoparticles, the static magnetism at 300 K above CoO's T_N is fully consistent with a cobalt–ferrite–like layer that would have a substantially higher intrinsic anisotropy (due to the unquenched m_ℓ of Co and Fe ions) [145,147,152,153], and the substantially enhanced H_{ex} relative to the uncoated γ -Fe₂O₃ core is typical of an exchange bias system. In particular, the substantial differences between the intrinsic magnetism of γ -Fe₂O₃ interior and the cobalt-ferrite-like intermixed layer in combination with the high T_B provides an excellent system to examine in greater depth the precise role of the intermixed layer in determining the magnetism of the nanoparticle, described in the following Sections.

5.3 Intermixed layer thickness effects on core/shell nanoparticle magnetism

For magnetic systems, interfacial interactions which lead to exchange bias effects are of the utmost importance, and a large fraction of work surrounding multi-layered nanostructured systems is aimed at understanding and controlling exchange bias properties. Despite persistent investigation over decades, the precise and quantitative description of the interface and exchange bias effects in nanostructured systems remains unresolved in large part due to the atomic-scale characterization required to describe fully the interface. While recent technological advances have allowed the detection of interfacial intermixed layers which mediate the magnetic interactions of the layer system, a comprehensive description of the relationship between the nature of the intermixed layer (e.g. thickness, composition, internal magnetic structure) has yet to be incorporated into the understanding of interfacial properties such as exchange bias. Thus, to date, despite the clear consensus that exchange bias phenomena are determined by the magnetic configuration at the interface, the potential magnetic effects of intermixed layers which determine the interfacial magnetism and mediate the overall layer coupling must often be inferred from *a posteriori* expected chemical behaviour of the nominal core and shell materials, rather than ascertained from a known interfacial structure, leaving a gap in fundamental understanding.

The less than one nm-thick interfacial intermixed layer in γ -Fe₂O₃/CoO core/shell nanoparticles is similar to those described in thin films that has been shown to have substantial implications on the interfacial exchange [154–156], motivating further examination of these effects in the core/shell nanoparticles. In addition, the interfacial intermixed layer of a core/shell nanoparticle comprises a significant fraction of the total magnetic volume (i.e. compared to thin films), providing improved sensitivity that is advantageous for the study of interfacial phenomena. To expand on this and probe quantitatively the relationship between the interfacial microstructure and H_{ex} , we have synthesized a series of γ -Fe₂O₃/CoO nanoparticles with controlled interfacial layer thickness [157].

5.3.1 Composition, structure and morphology

A series of γ -Fe₂O₃/CoO core/shell nanoparticles were synthesized by a seed-mediated thermal decomposition of Fe and Co-cupferronates, as described in Section 2.1. The reaction temperature used during the CoO shell addition step was 100°C, 150°C, and 235°C. X-ray diffraction (XRD) patterns for the γ -Fe₂O₃ seeds and γ -Fe₂O₃/CoO core/shell nanoparticles synthesized using different CoO reaction temperatures are shown in Fig. 5.17. Refinements to the XRD patterns indicated the spinel (Fd3m) and rock-salt (Fm3m) structures of the Fe-oxide core and CoO shell, respectively. The crystallite sizes, lattice parameters, relative volume fractions were determined by Rietveld refinement and are provided in Fig. 5.18. A gradual increase in the lattice



Figure 5.17: Powder x-ray diffraction pattern of γ -Fe₂O₃/CoO nanoparticles synthesized using different reaction temperatures for the shell addition step, with the results of the Rietveld refinement (black line). The black Bragg markers and (*hkl*) labels index the γ -Fe₂O₃ (Fd $\bar{3}$ m) structure, and the red Bragg markers and (*hkl*) labels index the CoO (Fm $\bar{3}$ m).

parameter a of both phases was observed with increasing shell reaction temperature consistent with vacancy filling within the γ -Fe₂O₃ core resulting from intermixing. Changes in lattice parameter for the CoO shell (vs. the bulk [90] a = 0.4263 nm) may be related to strain [157]. No change in the crystallite size of the spinel phase of $D_{XRD} \sim 5$ nm was observed, while the CoO crystallite size increased from ~ 10 nm to 14 nm accompanied by an increase in CoO volume fraction from $\sim 21\%$ to $\sim 35\%$.

TEM images of the 150°C and 235°C reaction samples are shown in Fig. 5.19. Also provided in Fig. 5.19 are the size distributions obtained from imageJ analysis of TEM images. The 150°C reaction nanoparticles provided a lognormal distribu-



Figure 5.18: Structural parameters the spinel and rock-salt (CoO) structures of γ -Fe₂O₃/CoO core/shell nanoparticles synthesized using different shell reaction temperatures.



Figure 5.19: Transmission electron microscopy images of γ -Fe₂O₃/CoO synthesized using a shell reaction temperature of a) 150°C and b) 235°C, and c) particle size distributions of γ -Fe₂O₃ and γ -Fe₂O₃/CoO. The size bar in (a) and (b) is equal to 20 nm.

tion with $D_{TEM} = 8.6 \pm 0.2$ nm with $\ln(\sigma) = 0.31 \pm 0.01$, and for the 235°C reaction nanoparticles we observed a bi-modal distribution, with one population with $D_{TEM} = 7.9 \pm 0.2$ nm, $\ln(\sigma) = 0.28 \pm 0.01$, and a second with $D_{TEM} = 10.9 \pm 0.3$ nm,

 $\ln(\sigma) = 0.28 \pm 0.01$. Energy dispersive electron spectroscopy and structural analyses of the same areas of the TEM images indicated that higher reaction temperatures led to the formation of some isolated CoO particles, which may also account for the observed change to a bi-modal size distribution, and the increase in CoO for the 235°C reaction that was indicated by XRD.

5.3.2 Intermixed layer thickness variation

To determine the intermixed layer thickness, detailed analysis of the core and shell structures, including changes due to O_h -site vacancy filling resulting from Co²⁺ substitution in the surface layers of the γ -Fe₂O₃ core, was done by Prof. Hao Ouyang, and his research group at National Tsing Hua University [157, 158]. To distinguish the γ -Fe₂O₃ interior from the intermixed layer, electron diffraction images of the oriented γ -Fe₂O₃ spinel structure (containing O_h -site vacancies), Co-doped γ -Fe₂O₃ and CoO were simulated. Fig. 5.20a shows the Co-doped γ -Fe₂O₃ structure oriented along [111], and simulations of the diffraction patterns of [111] oriented γ -Fe₂O₃ and Co-doped γ -Fe₂O₃. Additional reflections due to the newly occupied O_h -sites (highlighted in Fig. 5.20c) were used to determine the Co^{2+} diffusion depth into the surface layers of the γ -Fe₂O₃ core. Fig. 5.20d shows an example of the electron diffraction pattern for the oriented rock-salt structure of the CoO shell. The HRTEM images of γ -Fe₂O₃/CoO core/shell nanoparticles synthesized using different shell reaction temperatures were mapped onto multislice simulations [159-161] to ascertain the atomic Co, Fe, and O arrangements and obtain the zone axis. The spinel and rock-salt structure boundaries were mapped by measuring the diffraction at intervals across the



Figure 5.20: a) Structure of γ -Fe₂O₃ with O_h -site vacancies filled with Co²⁺ ions (yellow), representing the interfacial intermixed layer of γ -Fe₂O₃/CoO core/shell nanoparticles. The structure is oriented along the (111) direction. Also shown are the simulated diffraction images of (b) γ -Fe₂O₃ and (c) Cobalt-doped γ -Fe₂O₃ oriented along the [111] zone axis. (d) The electron diffraction pattern for CoO oriented along the [101] zone axis. (e) An example of the measured electron diffraction pattern for an area selected the γ -Fe₂O₃ interior of the nanoparticle. (f) An example of the electron diffraction obtained near the γ -Fe₂O₃/CoO structural boundary with the reflections due to the spinel structure highlighted in yellow, and the reflections due to the rocksalt CoO structure highlighted in green.

core/shell boundary, and detecting the changes in electron diffraction patterns due to the two structures (e.g., as shown in Fig. 5.20f). The intermixed layer thickness t_{int} was then measured directly using this same procedure, by examining the diffraction along and across the core/shell interface, and mapping the appearance of reflections due to Co²⁺ dopant ions in the spinel structure. Fig. 5.21 shows the results of this



Figure 5.21: High resolution TEM images of γ -Fe₂O₃/CoO synthesized using a) 100°C, b) 150°C, and c) 235°C shell reaction temperature. The yellow line indicates the limit of Co diffusion into the γ -Fe₂O₃ core, and the red line indicates the outer boundary of the γ -Fe₂O₃ core, so that the intermixed region is represented by the gap in between the two boundaries (the same size bar applies to all images). The relationship between the Co ion diffusivity and shell reaction temperature is shown in d), with the line indicating a fit as described in the text.

approach to tracking the Co²⁺ diffusion path [157]. The red line marks the location where the structure changed from spinel to rock-salt, and the yellow line indicates the change from pure γ -Fe₂O₃ to cobalt-doped γ -Fe₂O₃. The region in between the red and yellow lines indicates the thickness of the intermixed layer. This provided $t_{int} = 0.34, 0.47$, and 0.67 nm for CoO shell reaction temperatures of 100°C, 150°C, and 235°C, respectively. To support the analysis, a simulation structure consisting of γ -Fe₂O₃ and Co-doped γ -Fe₂O₃ was built and simulations of multislice HRTEM images were made and analyzed using the same method, and provided an uncertainty of 5 % in the t_{int} measurement.

The activation energy for Co diffusion was calculated from the relation between the diffusion depth d and the diffusivity D, according to $d = a\sqrt{Dt}$ (where a is a constant [162], and t is the diffusion time). The relationship between the diffusivity and the activation energy is described by the Arrhenius relation [163] $D = D_0 \exp(-E/RT)$ (where D is the diffusivity, E the activation energy, R the ideal gas constant, and T the temperature). The results of the diffusivity relationships from the measured Co diffusion depths (Fig. 5.21d) provide a Co E = 15797 J/mol, which is within the same order of magnitude as Co diffusion in CoO [164] and vacancy diffusion in Fe₃O₄ [163], and an order of magnitude lower than Fe diffusion in Fe-oxide [165, 166], further indicating that Co has better mobility than Fe within the structure, and consistent with Co's preference for O_h sites in substituted Fe-oxides.

5.3.3 Intermixed layer composition and magnetism

To determine precisely the changes in ion distributions, XMCD spectra were measured over the $L_{2,3}$ transition $(2p \rightarrow 3d)$ edges of Co and Fe at 10 K in ±1 T applied fields. The Fe and Co-sites were determined using the same simulations and reference spectra as Sec. 5.2.4. As shown in Fig. 5.22, the occupancy of Fe²⁺ in O_h sites, Fe³⁺ in T_d sites, and Fe³⁺ in O_h sites was 20%, 22%, and 46%, respectively, and did not reveal significant changes, due to a large contribution from the un-doped γ -Fe₂O₃ interior¹. The amount of each Co site in an XMCD spectrum (Figure 5.23) was estimated by correlating the experimental intensity with LFM calculations [167, 168].

¹The closer correspondence of the XMCD and Mössbauer spectra at 10 K (below), compared to γ -Fe₂O₃ described in Sec. 5.2 are likely a result of the larger incident angle used during the XMCD measurements, which will be more sensitive to the γ -Fe₂O₃-based interior



Figure 5.22: The changes in the site-specific Fe magnetization in γ -Fe₂O₃/CoO synthesized using shell addition temperatures of 100°C (top) and 235°C (bottom).

The L_2 -edge of XMCD spectra revealed a departure from Co²⁺ O_h sites due to the presence of Co²⁺ T_d sites (highlighted in the inset of Fig. 5.23). The Co magnetization was predominantly due to Co²⁺ O_h sites. The Fe and Co XMCD spectra together confirmed that the magnetization of the O_h sites were FM aligned and that the magnetization of the O_h and T_d sites were AF aligned, as expected for Co substitution into the spinel structure forming Co/Fe-ferrite [23, 101].

A uniform interfacial composition would result in a constant $\text{Co}^{2+} O_h/T_d$ XMCD intensity. However, as shown in Fig. 5.24, a change in the O_h/T_d magnetization occurs for different reaction temperatures. From a comparison of the t_{int} from TEM and the Co^{2+} -sites from XMCD, we find that higher reaction temperatures allow more Co^{2+} diffusion into the structure, since Co^{2+} -ions are better able to reach the energetically more favourable vacant O_h -sites [169–171], this results in a larger O_h/T_d Co^{2+} fraction.



Figure 5.23: X-ray magnetic circular dichroism spectra (XMCD) of γ -Fe₂O₃/CoO synthesized using shell addition temperatures of 100°C (top) and 235°C (bottom). The inset shows the L_2 -edge of the XMCD spectra.



Figure 5.24: The changes in the site-specific Co magnetization in γ -Fe₂O₃/CoO for different shell reaction temperatures.



Figure 5.25: 10 K Mössbauer spectrum of γ -Fe₂O₃/CoO nanoparticles synthesized using shell reaction temperatures of 100°C, 150°C, and 235°C. Subspectra labeled I indicate the octahedral B-site γ -Fe₂O₃, and II indicate octahedral B-site Co-doped γ -Fe₂O₃.

These results support the occurrence of core/shell intermixing identified by TEM, and reveal that the ion distribution departed substantially from pure γ -Fe₂O₃ within the intermixed layer, and could be altered through changes in synthesis conditions.

Mössbauer spectra collected at 10 K (Fig. 5.25) were fitted with several sextet components, each describing a unique Fe-site with the same hyperfine parameters as described in Sec. 5.2.3 with a variable spectral weight, consistent with a mixture of γ -Fe₂O₃ and Co-substituted Fe-oxide [140, 141]. Fits to the Mössbauer spectra at 10 K revealed little change in Fe-based composition versus reaction temperature, consistent with the Fe XMCD spectra and the preference for Co²⁺-ions to occupy O_h site vacancies primarily. Interestingly, the hyperfine field of the interfacial disordered spins, $B_{hf,int}$, was found to increase slightly with increasing reaction temperature (and hence t_{int} , discussed below).

5.3.4 Relationship between the intermixed layer and overall magnetism

The magnetism of the core/shell nanoparticles was determined from *ac*-susceptibility and hysteresis loop measurements of nanoparticle powders. As shown in Fig. 5.26 *ac*-susceptibility was measured from 10 K to 400 K using a 0.25 mT drive frequency oscillating from 10 Hz to 1 kHz. The interpretation of $\chi_{ac}(\nu, T)$ data for an interacting system of nanoparticles (such as a powder) will include effects due to superparamagnetism, and due to collective dynamics of the assembly [172–174]. Two maxima in $\chi''_{ac}(\nu, T)$ at ~150 K and ~ 250 K indicated two dynamical regimes. Since hysteresis loop measurements indicated H_c onset between 100 K and 200 K, the maximum of $\chi''_{ac}(\nu, T)$ occurring ~150 K likely corresponds to the superparamagnetic blocking temperature of the individual particles and the dynamics > 200 K are likely due to the collective dynamics of the interacting nanoparticle assembly. The maximum of $\chi''_{ac}(10\text{Hz}, \text{T})$ (occurring at 140 K, 145 K, and 165 K for γ -Fe₂O₃/CoO synthesized using shell reaction temperatures of 100°C, 150°C, and 235°C, respectively) suggests that T_B was comparable for all samples and increased slightly with increasing shell



Figure 5.26: *ac* measurements of the in-phase (top) and out-of-phase (bottom) *ac*susceptibilities $\chi'_{ac}(\nu, T)$ and $\chi''_{ac}(\nu, T)$ measured in 0.25 mT drive field oscillating at 10 Hz to 1 kHz for γ -Fe₂O₃/CoO nanoparticles synthesized using shell reaction temperatures of (a) 100°C, (b) 150°C, (c) and 235°C.

reaction temperature, keeping in mind the limitations of a precise description of T_B for multicomponent systems using a bulk susceptometry measurement.

Hysteresis loops were measured from 10 K to 400 K, and from ±5 T after cooling in an applied field of 5 T. As shown in Fig. 5.27, $M_S(T)$ was well described by a Bloch $T^{3/2}$ law, and revealed $B \propto 1/J$ (from Eq. 1.13) that decreased with increasing t_{int} . This trend was likely due to an increasing number of exchange interactions with progressive intermixing filling O_h -site vacancies. The exchange bias, H_{ex} , varied from 19 mT to 29 mT, and decreased with with increasing t_{int} (Fig. 5.28). H_{ex} is a result of the coupling between FM(FiM)/AF layers, and is proportional to an interfacial pinning energy ΔE , which provides the unidirectional anisotropy, and the magnetization of the FM layer M_{FM} , in an expression² of the form [47, 56]

²Various expressions of this form have been used to describe systems, such as the classical Meiklejohn-Bean model used to describe FM/AF thin films, $H_{ex} = J_{eb}/\mu_0 M_{FM} t_{FM}$, see Refs [47,56].



Figure 5.27: (a) Temperature dependence of the saturation magnetization $M_S(T)$ for γ -Fe₂O₃/CoO nanoparticles synthesized using different shell reaction temperatures. The solid lines are a fit to a modified Bloch $T^{3/2}$ law as described in the text. (b) Change in $B \propto 1/J$ from $M_S(T)$ for γ -Fe₂O₃/CoO for different intermixed layer thicknesses resulting from different shell reaction temperatures.



Figure 5.28: The exchange bias H_{ex} versus intermixed layer thickness t_{int} for γ -Fe₂O₃/CoO core/shell nanoparticles, measured at 10 K after cooling in a field of $\mu_0 H = 5$ T.

 $H_{ex} = \Delta E/2M_{FM}t_{FM}$. Fig. 5.29a shows the relationship between ΔE calculated from $\Delta E = 2H_{ex}M_{FiM}t_{FiM}$, from the values of the exchange bias, saturation magnetization measured at 10 K (after accounting for the volume fraction of CoO, obtained from XRD), and thickness $(t_{FiM} \sim D_{spinel}/2 = 3.3 \text{ nm})$ of the ferrimagnetic spinel-based core of the nanoparticle. Interestingly, there is a clear linear relationship between ΔE and t_{int} . A relationship between the interfacial disorder or the number of pinned



Figure 5.29: a) Change in the interfacial energy $\Delta E = 2H_{ex}M_{FiM}t_{FiM}$ obtained from hysteresis loop measurements at 10 K with the thickness of the interfacial intermixed layer t_{int} . b) The change in spin disorder within the interfacial CoFe₂O₄-like intermixed layer is proportional to the hyperfine field B_{hf} , which decreases as t_{int} increases.

interfacial spins has been well established both in models and experiment of thin films [155, 156, 175, 176] and nanoparticles [56, 177–179]. In nanoparticles, for example, it has been shown that the energy barrier $\Delta E \propto S_F$ where S_F is the number of frozen interfacial spins [177, 178, 180]. Hence, it is likely that the linear decrease in H_{ex} with progressively deeper intermixing causes a recapture of surface spin disorder that is intrinsic to the γ -Fe₂O₃ nanoparticle. It should be noted that this relationship can not be accounted for by other factors; $\chi_{ac}(T)$ indicated an increasing T_B (if any significant change), so that any re-scaling according to the respective T_B would only enhance the trend shown in Fig. 5.29a. Further, after accounting for the volume fraction of CoO obtained from XRD results, M_S does not vary significantly, and could not account for the ΔE variation. As shown in previous Chapters, the effectiveness of the recapture of (previously) disordered interfacial spins can be correlated to the magnitude of the $B_{hf,int}$. As shown in Fig. 5.29b, $B_{hf,int}$ of the disordered interfacial spin population increases in proportion to t_{int} , indicating clearly that the extent of intermixing progressively lessens the interfacial disorder. This is also consistent with the increase in J indicated by $M_S(T)$, and reveals directly the mechanism of H_{ex} variation in this system.

5.4 Intrinsic magnetism of the intermixed layer

In the previous Sections, the existence of an intermixed layer was established clearly, and the important role in the magnetism was highlighted by showing that the intermixed layer anisotropy determined the properties at high temperatures. Results which confirm structurally, and quantified the thickness of the intermixed layer were also provided. By comparison with established interfacial disorder concepts derived from the study of thin-film systems we found that H_{ex} not only depends on the existence of the intermixed layer, but also on the interfacial microstructure, even considering changes on monolayer-length scales. This clear sensitive dependence on interfacial microstructure and composition leads naturally to the question of whether the intrinsic properties of this interfacial region (which differ in composition, magnetism, ion distribution) also play a role in the layer coupling. This Section establishes clearly that the exchange coupling is not purely interfacial, but is translated from FiM to AF layer through the interfacial layer which has distinct composition, microstructure and magnetism, and wherein changes to the interfacial metal-oxygen bonding reflect directly in the exchange bias onset.



Figure 5.30: Representative Mössbauer spectra of $\gamma\text{-}\mathrm{Fe_2O_3/CoO}$ core/shell nanoparticles, measured from 10 K to 300 K

5.4.1 Atomic Fe magnetism

To gain insight to the intrinsic magnetism of the nanoparticle Mössbauer spectra of the nanoparticles shown in Sec. 5.2 were measured from 10 to 300 K to probe the atomic ⁵⁷Fe electronic and magnetic environments of the Fe-sites within the core and interfacial layers of the nanoparticle (shown in Fig. 5.30). As described in Sec. 2.5, since the recoil energy associated with γ -ray absorption is much larger than the natural line width of the nuclear level, nuclear resonance occurs only for events for which no phonons are excited, with the probability of such recoilless events quantified by the recoilless fraction f. f is affected by any temperature dependent transition which modifies the local bonding strength (e.g. via a change in spin state, structural changes or distortions, or bonding stiffness) thus providing a means to gain insight directly to the Fe bonding behaviour through the local lattice vibrations. Regardless of the model, f decreases monotonically with increasing temperature when no changes to the lattice occur. The recoil-free fraction is temperature dependent, with $\langle x^2 \rangle$ increasing as the temperature increases, resulting in lower f. Since f depends on the nature of the lattice strength to which the ⁵⁷Fe nuclei are bound, an abrupt change in f reflects a change to the lattice rigidity surrounding the probe nuclei.

The temperature dependence of f is often described by the simple Debye model, in which the upper limit frequency vibration $(\hbar\omega_D)$ of the lattice determines the Debye temperature $\Theta_D = \hbar\omega_D/k_B$, so that

$$f = \exp\left[\frac{-3E_{\gamma}}{k_B\Theta_D M c^2} \left\{\frac{1}{4} + \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\Theta/T} \frac{x}{e^x - 1} dx\right\}\right]$$
(5.1)

where E_{γ}^2/Mc^2 is the free-atom recoil energy E_R , k_B is the Boltzmann factor.



Figure 5.31: Temperature variation of the *f*-factor for γ -Fe₂O₃ (seeds) and γ -Fe₂O₃/CoO core-shell nanoparticles. The lines indicate the expected temperature dependence for systems with a Debye temperature (Θ) of 250 K for γ -Fe₂O₃ and 450 K for γ -Fe₂O₃/CoO, respectively.

While the complexity of most structures, including the spinel, makes it so that the Debye model is not strictly appropriate, Θ_D may be used to provide a qualitative comparison of the total lattice stiffness when compared with similar analysis on other materials. As shown in Fig. 5.31a, for γ -Fe₂O₃ a monotonic temperature dependence is indeed observed, and the *f*-factor variation is well described by a Debye model with $\Theta_D \sim 250$ K. By contrast, in γ -Fe₂O₃/CoO core/shell nanoparticles, we observe $\Theta_D \sim 450$ K, and a clear anomaly ~150 K, indicating some type of transition.

To examine in more detail the Fe atomic electronic and magnetic environment of the spinel-based core in the vicinity of this transition, Mössbauer spectra from 10 K to 200 K were fitted by varying B_{hf} and δ with temperature³. The spectra were fitted

³We found no evidence of line broadening or lineshape changes resulting from significant relaxation within this temperature range that would necessitate a full dynamical model including collective excitations and superparamagnetic (180°) fluctuations.



Figure 5.32: Temperature dependence of (a) the hyperfine field (B_{hf}) and (b) isomer shift (δ) for γ -Fe₂O₃/CoO core/shell nanoparticles.



Figure 5.33: Mössbauer spectrum of γ -Fe₂O₃/CoO measured at 162.5 K, showing the fit line from the spectrum at 150 K to highlight the abrupt change in spectral features occurring between 150 K and 162.5 K.



Figure 5.34: Mössbauer spectra of γ -Fe₂O₃/CoO nanoparticles measured at (a) 150 K and (b) 162.5 K. Subspectra labeled I indicate pure γ -Fe₂O₃, and II indicate Co-doped γ -Fe₂O₃.

using three sites [105] that describe the O_h -sites of γ -Fe₂O₃, the O_h -sites of cobaltdoped γ -Fe₂O₃ for the intermixed layer, and one common T_d -site. An additional site at 10 K with a reduced $B_{hf} \sim 22$ T due to surface spins was included, but the low spectral area prevented a reliable estimate of any potential temperature variation in the associated hyperfine parameters, and only the spectral area was allowed to vary. The hyperfine parameters at 10 K are given in Sec. 5.2.3. As shown in Fig. 5.32, we observed an discontinuity in δ of the O_h -sites between 150 K and 162.5 K, accompanied by an abrupt decrease in B_{hf} of all Fe-sites. This is also clearly observable as an abrupt change in the spectrum features, for example, shown in Fig. 5.33, which provides the spectrum measured at 162.5 K with the fit obtained for the spectrum measured at 150 K, and in Fig. 5.34, which includes the component fits for the two spectra.

Similarly to the f-factor, δ will necessarily decrease as a result of an in increase in δ_{SOD} with increasing temperature due to an increase in $\langle v^2 \rangle$, with the rate of change being dependent on Θ_D . However, the abrupt decrease in δ shown in Fig. 5.32 must arise either (i) from an abrupt decrease in Θ_D that changes δ_{SOD} (e.g. as has been observed in the ferroelectric transition in 57 Fe-doped PbTiO₃ [181]), or (ii) a change in the intrinsic isomer shift δ_I (described in Eq. 2.11) via an increase in selectron density at the Fe nucleus [71]. By comparing f(T) to the line indicating a Debye model with a single $\Theta_D = 450$ K, there does not appear to be an abrupt change in Θ_D across the transition; however a difference in Θ_D as large as 50 K would not provide a substantially different f(T) that would eliminate this possibility directly. To discern the origin of the change in $\delta(T)$ requires considering also the changes in $B_{hf}(T)$. The dominant contribution to B_{hf} is the Fermi contact term which, according to Eq. 2.18, is related to the polarized spin density at the nucleus and is proportional to the number of 3d electrons. We consider also that B_{hf} is proportional to the time average of the total spin moment on the Fe atoms, and in the case of nanoparticles, as thermal fluctuation of the local magnetic moment of the atoms increases with warming (due to collective excitations and 180° spin flips due to superparamagnetic relaxation), $B_{hf} \rightarrow 0$ as $T \rightarrow T_B$. However, there is no significant line broadening or decrease in B_{hf} from thermal fluctuation effects. Also, models of $B_{hf}(T)$ approaching T_B describe a gradual reduction, indicating that the observed $B_{hf}(T)$ change is inconsistent with magnetic relaxation effects. Instead, there is an intrinsic change in B_{hf} due to local bonding, affecting changes to the 3d electron populations. Thus, the Mössbauer data indicate clearly some temperature dependent transition occurring in the nanoparticle, that is driven by a change in the electronic environment of the O_h -sites. An abrupt decrease in both δ and B_{hf} with warming could be accounted for by an increase in the *s*-electron density due to an decrease in the effective *d*-electron number (i.e. via diminished *d*-electron screening). This may be a result of a change in Fe valence, or a change in the degree of Fe-O hybridization.

5.4.2 Interfacial metal-oxygen bonding

In order to investigate the nature of the Fe-oxygen bonding, we have examined the temperature dependence of the oxygen K-edge by x-ray absorption spectra (XAS). XAS is especially well suited probe the nature of interfacial exchange as it provides a direct measure of the oxygen-metal hybridization [182]. XAS measurements of the O K-edge were done from 10 K to 200 K using the total electron yield (TEY) mode that provides preferential measurement of the surface and interfacial region of our core/shell nanoparticle due to the intrinsic surface sensitivity. Fig. 5.35a shows the O K-edge XAS at 200 K. Since the O K-edge is due to transitions from the O 1score states to unoccupied O states with p character, it is described by two parts; the first from ~ 530 - 543 eV contains a double peak due to transitions from the O 1s state to hybridized O 2p-(Fe/Co) 3d states, and the second region at higher energies contains a broad multi-peak structure that is due to transitions from the O 1s states to O 2p-(Fe/Co) 4s and 4p hybridized states. Shown Fig. 5.36, a comparison of the O K-edge XAS for γ -Fe₂O₃/CoO with other Fe and Co-oxides [182–186] reveals that only the surface Co-oxide and interfacial $CoFe_2O_4$ -like layer contribute significantly to the spectra, consistent with the γ -Fe₂O₃/Co-doped γ -Fe₂O₃/CoO structure [105].



Figure 5.35: X-ray absorption spectra of the oxygen K-edge of γ -Fe₂O₃/CoO core/shell nanoparticles measured at 200 K in total electron yield (TEY) mode. b) The O K-edge spectra measured in the energy region corresponding to transitions from O core-states to hybridized O 2*p*-Fe/Co 3*d* valence states, with features due to the transition metal t_{2g} and e_g states of the O_h -sites labeled. c) Integrated O K-edge XAS spectral area of the O 2*p*-Fe/Co 3*d* region (529-834 eV), and d) the change in relative XAS intensity of the t_{2g}/e_g features of the O_h -sites.

The O 2p-Fe/Co 3d region of the XAS spectrum for Fe-oxides includes contributions from the 3d states of Fe and Co in O_h and T_d sites. The 3d levels are split by the ligand field into lower lying t_{2g} and higher energy e_g sublevels for O_h -sites, and opposite splitting for T_d -sites. The states lying closest to the Fermi level (and hence appearing at the lowest energy in the O K-edge spectrum) are the minority t_{2g} states of the O_h -sites. According to band structure calculations, and comparisons of O K-edge XAS of other Fe-oxides, the O_h -site states contribute to two resolved peaks, while the T_d state splitting (being smaller) contributes broad features at intermediate energies [184, 189].

As shown in Fig. 5.35, there is a clear change in the XAS in the O 2p–Fe/Co 3d region of γ -Fe₂O₃/CoO. Since the abrupt change in $\delta(T)$ indicates a decrease in the effective d-electron count on the O_h -sites with warming, the prominent features



Figure 5.36: Oxygen K-edge spectrum of γ -Fe₂O₃/CoO nanoparticles measured at 200 K (black line) compared to reference spectra [187,188] of Co-oxides. The difference (red line) matches well with O K-edge data of CoFe₂O₄ nanoparticles [188].

of the O 2p-Fe/Co 3d region have been labeled as indicating the t_{2g} and e_g states of the O_h -sites to describe clearly the change in spectral weight amongst the features in Fig. 5.35b. The origin of the O_h -site t_{2g}/e_g spectral weight may either be a result of a change in valence (i.e. possibly among O_h and T_d -sites, or Fe and Co-ions) or due to a change in the degree of metal-oxygen hybridization which affects different states differently. For the first, a change in valence that results in an increase of O_h -site t_{2g} intensity with warming would suggest a decrease in the d electron count into the O_h sites (creating more holes in the valence band). Although this is consistent with the changes in Fe O_h -sites indicated by δ and B_{hf} , charge conservation would ultimately require an increase valence of Fe T_d -sites, or of the Co-sites. Such a charge transfer would result in a transfer of spectral weight in the O XAS, which was not observed. There is also no abrupt increase in the e_g XAS to suggest a change in spin state, and thus we conclude that the change in t_{2g} vs. e_g intensity is due to a change in bond covalency rather than a change in Fe or Co valence.

5.4.3 Element-specific magnetism

Finally, to confirm whether the changes in local bonding are a result of a changing degree of hybridization rather than a valence change, x-ray magnetic circular dichroism (XMCD) was measured over the Fe and Co $L_{2,3}$ -edges between 10 and 200 K in ± 1 T, and over the L_3 -edge from 0.1 - 5.0 T at 10 K. The spectrum measured at 10 K over the $L_{2,3}$ -edges was described in Sec. 5.2.4 (to determine the Fe and Co-sites). The temperature and field dependence of the element and site-specific magnetization was determined from the variation in the XMCD intensity. The field dependent XMCD, shown in Fig. 5.37, shows a typical approach to saturation of the Fe and Co-sites, consistent with the expected behaviour for an intermixed layer. All of the Fe-sites showed the same change with increasing temperature, shown in Fig. 5.38c, which tracked well with the variation in the magnetization value at 1 T obtained from hysteresis loop measurements (keeping in mind that the interfacial region is overrepresented in XMCD, whereas magnetometry provides an overall bulk measure). By comparison, the Co XMCD spectra did not simply re-scale with temperature, indicating a slight difference the O_h and T_d -site magnetization temperature dependencies. By tracking the intensity of the features most clearly affected by the O_h and T_d -sites



Figure 5.37: Field variation of the element-specific magnetization measured at 10 K, determined from the maximum intensity of the feature representing each site in the L_3 -edge XMCD spectra.

(and checking the result against a re-scaling of the spectrum measured at 10 K) we obtained the site-specific magnetization variation, shown in Figs. 5.38b and c. Interestingly, the T_d sites show an anomalous variation with a maximum XMCD intensity at 130 K. More interestingly, the Co²⁺ T_d site maximum coincides with the anomaly in the overall metal-oxygen hybridization indicated by the oxygen XAS, confirming that the transition is driven by the intermixed Co-doped γ -Fe₂O₃ layer.

As shown in Fig. 5.16, no change in the $(m_{\ell}/m_s)_{\text{Fe}}$ was observed with changing temperature. However, $(m_{\ell}/m_s)_{\text{Co}}$ decreases between 130 – 150 K. This change in $(m_{\ell}/m_s)_{\text{Co}}$ may be either due to a transient decrease in m_{ℓ} , or increase in m_s of Co. However, a change in m_s would be inconsistent with the changes in Fe-sites described by Mössbauer spectroscopy. The variation is due to m_{ℓ} . Specifically, the



Figure 5.38: a) The Fe XMCD intensity (equal for all Fe-sites, b) the Co²⁺ O_h -sites, and the c) Co²⁺ T_d -sites.



Figure 5.39: Temperature dependence of a) m_{ℓ}/m_s of the Fe-sites, b) m_{ℓ}/m_s of the Co-sites.

abrupt decrease in δ and B_{hf} describe a reduction in the effective *d* electron count of the Fe-sites, for which a corresponding abrupt increase in the Co valence would be expected. In turn, this would produce an abrupt (and persistent) decrease in the Co spin moment due the pairing of electrons for the Co²⁺ (d^7)-ion, resulting in an increase of $(m_\ell/m_s)_{\rm Co}$. Since this is not observed, a change in m_ℓ occurring in the temperature regime of a local structural distortion which induces a change in the degree of metal-oxygen hybridization is more likely.

5.4.4 Interfacial magnetism and the superexchange pathway

Together, the discontinuous changes in δ and B_{hf} indicate a change in the *d* electron populations, and can be linked directly with metal-oxygen hybridization changes indicated by the O XAS. The anomalous variation in the *f*-factor is also indicative of changes in local bonding, as evidenced by the numerous similar occurrences in a many different systems, such as ferroelectrics, magnetoelectrics, intermetallics, and superconductors, due to changes in spin-phonon interactions, magnetostriction, and the influence of soft phonon modes across the relevant transitions [181, 190–196]. Its temperature dependence in Fig. 5.31 is consistent with this result.

Compared to the purely ionic case, the occurrence of metal-oxygen hybridization transfers back some electrons to the metal 3*d* population, and the valence state may be described by some linear combination of metal and ligand states (i.e., $\Psi_{3d} = (1 - \beta^2)^{1/2} |M_{3d}\rangle + \beta^2 |L_{2p}\rangle$). Thus, when the hybridization is reduced at a given temperature, one would expect this to coincide with an increased *s*-electron density at the nucleus (via weakened 3*d*-electron shielding), resulting in a decrease of δ . The relationship between δ and the effective *d*-electron count resulting from the degree of charge transfer with covalency has also been described in the literature [197–199]. Interestingly, only δ of the O_h sites shows a sudden change; however, B_{hf} of all sites is affected. The origin of the B_{hf} variation among the O_h and T_d -sites may be the impact of changes in the supertransferred hyperfine field, that affects the B_{hf} via a contact field from alterations to the local spin polarization through polarized metal-oxygen charge transfer, a mechanism directly related to the superexchange interaction, and dependent on the full Fe_{O_h} -O-Fe_{Td} pathway. Further, as the superexchange and supertransferred hyperfine field occur through the transfer of spin polarized O^{2-} p electrons, the phenomena are directly related to the covalency [74,200] and consistent with a temperature variation in the O XAS.

We can also note some interesting similarities in our results to the well known transitions which occur in Fe-oxides, and, although we are limited in the knowledge of the precise role of the Co²⁺ ions. For example, while Fe XMCD is insensitive to the Verwey transition [201, 202] it has been well documented that the Mössbauer spectra of Fe₃O₄ show a marked change in features through T_V , and there have been some reports of *f*-factor variation occurring near T_V which result from a strong electron-phonon interaction at the transition [203]. There have also been reports of a "Verwey-like" transition in bulk cobalt-substituted magnetite, where there was clear evidence of an electronic change via spectroscopy, despite the lack of evidence of the transition according to macroscopic measurements (magnetostriction, magnetization) [204]. The occurrence of a "Verwey-like" transition in Co-doped Fe-oxides was also discussed in detail elsewhere in later papers [140, 141]; however, in those cases no anomalous variation in B_{hf} or δ was observed. We postulate that the interfacial nature (and enhanced role of the interface in our core/shell nanoparticle system), plus interactions with the CoO shell may play a part in the observed transition.

Despite being quite a thin layer, there are reports of thin 1 nm magnetite being ferrimagnetic [205] (consistent with the possibility the thin intermixed layer can have "magnetite-like" properties), and interfacial interactions have been shown to stabilize T_V in Fe₃O₄ [206]. An interplay between hybridization of oxygen and the metal e_g and t_{2g} states may reflect the changes in metal e_g and t_{2g} population rearrangement related to the e_g screening effect occurring across the transitions in Fe₃O₄ [184]. There has also been a report of a relationship in the temperature dependent orbital moment in ϵ -Fe₂O₃ and the temperature dependent O 2*p*-Fe 3*d* hybridization accompanying the structural distortion that marks the onset of anisotropy changes in the structure 207. While we can identify the local structural change, an analogous local change due to the Verwey-like transition would be expected to shorten some O_h -O- O_h distances, while lengthening others below T_V . Our results appear consistent with the strengthening of the secondary $\operatorname{Fe}_{O_h}^{2+}$ -O-Fe $_{O_h}^{3+}$ double exchange interaction when warming through T_V in Fe₃O₄; it is possible that the lack of complete exchange pathway among the O_h sublattice is the cause of the relatively weakened $\operatorname{Fe}_{O_h}^{2+}$ -O-Fe $_{O_h}^{3+}$ double exchange below T_V , which results in a more effective dominant $\operatorname{Fe}_{O_h}^{2+/3+}$ -O-Fe $_{T_d}^{3+}$ pathway. The same distortion which diminishes the effectiveness of the double exchange pathway for $T < T_V$ may also result in a less effective Fe-O hybridization among the Fe t_{2g} states by virtue of small changes in the bond distances or angles which and enable more effective Fe-O interactions within the dominant $\operatorname{Fe}_{O_h}^{2+/3+}$ -O-Fe $_{T_d}^{3+}$ exchange pathway, which includes the e_g states.

In an attempt to discern possible structural changes, XRD patterns were measured from 15 K to 300 K. However, as shown in Fig. 5.41, there is no discernable change



Figure 5.40: Comparison of XRD patterns measured from 15 K to 300 K. The black lines indicate the results of a Rietveld refinement that provided the lattice paramerers of the spinel and rock-salt structures of γ -Fe₂O₃/CoO nanoparticles at various temperatures.



Figure 5.41: Lattice parameters for (a) the spinel phase, and (b) the rock-salt CoO phases of γ -Fe₂O₃/CoO core/shell nanoparticles for different temperatures.

in the XRD pattern. Refinements of the XRD patterns also could not identify any significant changes to the structure. However, considering that the changes in lattice parameters occurring for Fe-oxides at the characteristic transitions are quite small and on the order of the uncertainty for values reported in this Thesis (i.e. a change of ~ 0.0001 nm for Fe₃O₄ at the Verwey transition [208]), it would be unlikely to observe such subtle changes in the XRD of nanoparticles exhibiting such significant Scherrer broadening. Further investigation of the interfacial structure including possible strain would be necessary to determine precisely the local distortion responsible for the changes observed.

Finally, by examining the temperature-dependent intrinsic properties of the interfacial layer, we observe that the exchange bias onset shown in Fig. 5.10 correlates precisely with the the change in interfacial metal-oxygen hybridization. This is consistent with previous work in V₂O₃/Ni₈₀Fe₂₀ thin films where a coincidence between the Verwey transition in an interfacial Fe₃O₄ layer and H_{ex} was observed [209]. This work provides clear evidence of this phenomenon in a well described core/shell nanoparticle, including a consistent description of the changes in local magnetism of all interfacial species, and identifies the mechanism for the H_{ex} onset.

5.5 Summary

We have identified a temperature dependent metal-oxygen hybridization in γ -Fe₂O₃/CoO core/shell nanoparticles that (i) is an interfacial phenomenon (i.e. not occurring in the uncoated particles, directly influencing interfacial spins of the core/shell nanoparticle), and (ii) is a direct result of metal-oxygen hybridization, which mediates the

superexchange interaction. Hence, we postulate that this sudden weakening in the local hyperfine field reflects a weakened superexchange induced by a change in metaloxygen hybridization whose strength is transferred among the e_g and t_{2g} valence states. This temperature dependent transition alters the interfacial metal-oxygen bonding mediating the effective magnetic coupling of the interfacial spin population, responsible for effective interfacial coupling which produces H_{ex} . This work provides a clear confirmation of the types of important changes in H_{ex} due to intermixing and interfacial microstructure which have been proposed in the literature. Further, we believe that such a temperature dependent transition (i.e. occurring in Fe-oxides, and magnetostrictive materials) is a critically important factor to be considered in understanding the exchange bias phenomenon in oxides.
Chapter 6

Discussion

The γ -Fe₂O₃ cores of the nanoparticles investigated in this Thesis are characterized by a moderate T_B , low K, and significant surface spin disorder that leads to a H_{ex} . With the addition of AF NiO, MnO and CoO shells an interesting variety of overall magnetism is observed. Considering a simple core/shell description (excluding intermixing effects) all exchange bias systems (i.e. consisting of FM or FiM layers coupled to AF layers) should exhibit in an increased H_c and H_{ex} below T_N of the AF layer due to interfacial exchange interactions [47]. As shown in Fig. 6.1a and Table 6.1, for γ -Fe₂O₃/CoO and γ -Fe₂O₃/MnO H_c and H_{ex} were enhanced; however, for γ -Fe₂O₃/NiO H_{ex} was nearly eliminated while H_c was almost doubled and T_B was unchanged, indicating a clear increase in K of those core/shell nanoparticles. While the lack of H_{ex} increase in γ -Fe₂O₃/NiO could be understood as a result of the low K of NiO [47] and the lack of a complete shell, these factors can not account for the near elimination of H_{ex} compared to γ -Fe₂O₃. For γ -Fe₂O₃/CoO, there is also a large increase in K that is not due to a simple re-scaling according to the T_B



Figure 6.1: (a) Hysteresis loops for γ -Fe₂O₃ and core/shell nanoparticles measured from ±5 T after cooling to 5 K in an applied field, $\mu_0 H = 5$ T. (b) Temperature dependence of the saturation magnetization $M_S(T)$ for γ -Fe₂O₃ and core/shell nanoparticles. The solid lines are a fit to a modified Bloch $T^{3/2}$ law, with the exception of γ -Fe₂O₃/MnO which is a fit to a modified linear T dependence.

increase, and which is larger than expected for the magnetic volume increase due to the CoO shell when compared to γ -Fe₂O₃/NiO and γ -Fe₂O₃/MnO. Also interestingly, γ -Fe₂O₃/NiO and γ -Fe₂O₃/MnO, despite having similar T_B s indicated by susceptometry have clearly different $M_S(T)$ behaviour due to different magnetic relaxation of γ -Fe₂O₃/MnO compared to the other core/shell nanoparticles. The overall properties of the core/shell nanoparticles indicated that a simple core/shell (sharp interface) description was not sufficient to describe the overall magnetism of the nanoparticles.

The Mössbauer spectra of the nanoparticles at 10 K, shown in Fig. 6.2, also reveal

Table 6.1: Coercivity (H_c) and exchange bias (H_{ex}) measured at 5 K after cooling in an applied field of 5 T, estimates of the superparamagnetic blocking temperature (T_B) from *ac*- and *dc*-susceptibility measurements, an estimate of K from $H_c(T)$, and the Bloch constant obtained from $M_S(T)$ for γ -Fe₂O₃ and core/shell nanoparticles.

	$H_c (\mathrm{mT})$	H_{ex} (mT)	T_B (K)	$K (\mathrm{J/m^3})$	$B (K^{-3/2})$
γ -Fe ₂ O ₃	33.0 ± 0.5	5.0 ± 0.5	~ 75	2.5×10^4	3.17×10^{-5}
γ -Fe ₂ O ₃ /NiO	60 ± 1	1.5 ± 1	~ 75	5.3×10^4	3.31×10^{-5}
γ -Fe ₂ O ₃ /MnO	49 ± 1	7 ± 1	~ 75	4.5×10^{4}	/
γ -Fe ₂ O ₃ /CoO	298 ± 2	17 ± 2	~ 225	1.2×10^{5}	3.55×10^{-5}



Figure 6.2: Mössbauer spectrum of γ -Fe₂O₃ measured at 5 K and core/shell nanoparticles measured at 10 K.

clear changes to the atomic Fe magnetism, in particular, revealing changes to the Febased composition and to the spin disorder at the surface of the Fe-based core. For γ -Fe₂O₃ disordered surface spins (which fluctuate much more quickly than the ordered interior spins) contribute the Mössbauer spectrum at v = 0 due to a $B_{hf} = 0$ over the timeframe of the Mössbauer effect. In all of the core/shell nanoparticles no component at v = 0 was observed indicating that the fluctuation rate of the spins at the surface of the Fe-based core (at the core/shell interface) was slowed. For γ -Fe₂O₃/NiO and γ -Fe₂O₃/CoO, absorption at $v = \pm 3$ mm/s was due to a component with $B_{hf} \sim 21$ T indicating that interfacial disordered spins fluctuated more slowly than the surface spins of γ -Fe₂O₃ but more quickly than the ordered interior spins. In γ -Fe₂O₃/MnO no similar component was observed indicating that the disordered interfacial spins were incorporated more completely into the ordered interior spin population. Fits to the γ -Fe₂O₃/MnO Mössbauer spectra using a relaxation model confirmed that the fluctuation rate of the interfacial spin population was significantly lowered compared to γ -Fe₂O₃, and revealed much more uniform fluctuation rates for the interior and interfacial spins in γ -Fe₂O₃/MnO, consistent with the significant changes in dynamical magnetism indicated by magnetometry.

Core/shell intermixing was observed clearly from the spectral features measured at 10 K that revealed changes to the O_h and T_d Fe-sites. This is highlighted in Figs. 6.3a-c which shows the fits to the Mössbauer spectra of core/shell nanoparticles compared to that of γ -Fe₂O₃ (which has been re-scaled to the maximum absorption that would fall within the spectrum of each core/shell nanoparticle, with the exception of the v = 0feature that is clearly absent in the Mössbauer spectra of the core/shell nanoparticles).



Figure 6.3: (a) - (c) Fits to the Mössbauer spectra of γ -Fe₂O₃ and core/shell nanoparticles, with the γ -Fe₂O₃ spectrum re-scaled to the maximum that would fall within the spectrum of the core/shell nanoparticles. (b) - (d) Approximate spectra due to the interfacial ferrite phase obtained by subtracting the γ -Fe₂O₃ spectra from the core/shell spectra shown in (a) - (c). Two sites are visible in all of the difference spectra, as labeled in (d), that are due to the octahedral Fe B-sites and tetrahedral Fe A-sites of the interfacial ferrite.

Much of the Mössbauer spectra of the core/shell nanoparticles could be described by γ -Fe₂O₃, consistent with the existence of an un-doped interior for all core/shell nanoparticles. The difference plots between the core/shell and γ -Fe₂O₃ Mössbauer spectra shown in Figs. 6.3d-f are very similar to the spectra of the interfacial ferrites. The octahedral B-sites and tetrahedral A-sites of the interfacial ferrites are observed in the difference spectra (labeled for γ -Fe₂O₃/NiO in Fig. 6.3d). The changes in the composition of the interfacial layers are observed clearly by the different relative spectral weights of the A and B-sites, most visible in line 6 (at $v \sim 9$ mm/s) of the spectra. For γ -Fe₂O₃/NiO and γ -Fe₂O₃/CoO two resolved sites were observed with different relative weights due to different amounts of Ni²⁺ and Co²⁺ in O_h -sites; the larger B-site intensity for γ -Fe₂O₃/NiO indicated fewer O_h -sites were filled by Ni²⁺ ions whereas the lower *B*-site intensity for γ -Fe₂O₃/CoO indicated more O_h -sites were filled by Co²⁺ ions in the interfacial phase. For γ -Fe₂O₃/MnO the difference spectrum shows larger degree of overlap for the A and B-sites that is from a more similar Fe-ion distribution in the interfacial ferrite and the γ -Fe₂O₃-based core, consistent with Mnion substitution onto both the O_h and T_d -sites. A lower fraction of the Mössbauer spectrum of γ -Fe₂O₃/MnO was described by γ -Fe₂O₃ (shown in Fig. 6.3b) compared to γ -Fe₂O₃/NiO and γ -Fe₂O₃/CoO consistent with more extensive intermixing in γ -Fe₂O₃/MnO.

The different in interfacial ferrite compositions were also reflected in the Fe L_3 edge XAS and XMCD spectra shown in Fig. 6.4. Changes to I(A) in the XAS were due to different amounts of Fe O_h and T_d -sites. The L_3 -edge XMCD spectra of the core/shell nanoparticles resolved more clearly the different Fe-site mangetizations and indicated different Fe O_h and T_d -site amounts that were consistent with the Mössbauer results. The overall XMCD spectra were similar to that of γ -Fe₂O₃, where the feature proportional to the Fe²⁺ O_h -sites is less intense than that of the Fe³⁺ O_h sites, (i.e. versus Fe₃O₄, where the opposite is observed) indicating that the Fe-ion distributions could be described as transition-metal ion doped γ -Fe₂O₃-like layers. For γ -Fe₂O₃/NiO the largest Fe²⁺ amount was observed, consistent with the large Bsite intensity observed in the Mössbauer spectrum of the interfacial ferrite. A lower Fe³⁺ T_d -intensity for γ -Fe₂O₃/MnO compared to γ -Fe₂O₃/NiO and γ -Fe₂O₃/CoO was consistent with a significant T_d -site occupancy from shell dopant ions that did not



Figure 6.4: (a) XAS and (b) XMCD of the Fe L_3 -edges of γ -Fe₂O₃/NiO, γ -Fe₂O₃/MnO, and γ -Fe₂O₃/CoO nanoparticles.

occur in the other core/shell nanoparticles.

XMCD of the shell transition metal $L_{2,3}$ -edges identified clearly the interfacial magnetic species and provided temperature and field dependent behaviours that were compared with the overall magnetism. The XMCD indicated quite different ion distributions for each ferrite; for γ -Fe₂O₃/NiO Ni²⁺ O_h -sites were observed, and for γ -Fe₂O₃/CoO, predominantly Co²⁺ O_h -sites were observed with a small amount of Co²⁺ T_d -sites. By contrast, for γ -Fe₂O₃/MnO significant amounts of Mn²⁺ O_h and T_d -sites were observed in addition to a unique Mn³⁺ O_h -site with distorted coordination geometry or significant metal-ligand interactions. The XMCD indicated that the magnetization of each site was coupled with that of the corresponding Fe-sites as expected for an interfacial ferrite (i.e. parallel O_h -site magnetizations, parallel T_d site magnetizations, and antiparallel O_h and T_d -site magnetizations). In addition, the temperature dependencies of the shell-ion XMCD were inconsistent with the expected behaviours of the corresponding shell-oxides.



Figure 6.5: Powder x-ray diffraction patterns of (a) NiO, (b) Mn_3O_4 , and (c) CoO nanoparticles. Bragg markers indicate the structure reflections and the residuals of the refinement are indicated by the solid blue lines.



Figure 6.6: Transmission electron microscopy of CoO nanoparticles.

To examine this point in more detail, we describe the magnetism of transitionmetal oxide nanoparticles which most closely match the ion distribution of the interfacial ferrites, and we compare the results with the XMCD measured for the core/shell nanoparticles. XRD patterns for NiO, Mn₃O₄, and CoO nanoparticles are shown in Fig. 6.5. Refinements of the patterns identified the rock-salt (Fm $\bar{3}$ m) structure of NiO and CoO with $a = 0.4190 \pm 0.0003$ nm and $a = 0.4215 \pm 0.0002$ nm, consistent with NiO and CoO, respectively [90] and the I4₁/amd structure with $a = 0.5756 \pm 0.0002$ nm and $c = 0.9448 \pm 0.0001$ nm of Mn₃O₄ [210]. Crystallite sizes $D_{XRD} = 4.3$, 14.0, and 9.0 ± 0.5 nm were obtained for NiO, Mn₃O₄ and CoO, respectively. A TEM image of CoO nanoparticles (Fig. 6.6) indicated well crystallized particles with D_{TEM} consistent with D_{XRD} .

In nanoparticles of AF materials such as NiO and CoO, magnetism arises from uncompensated spins due to finite-size and surface effects, often resulting in hysteresis, exchange bias, superparamagnetism, and slow glass-like dynamics [211–213].



Figure 6.7: Susceptometry measurements for NiO nanoparticle powder showing (a) the in-phase (top) and out-of-phase (bottom) *ac*-susceptibilities $\chi'_{ac}(\nu, T)$ and $\chi''_{ac}(\nu, T)$ measured in 0.25 mT drive field oscillating at 10 Hz to 1 kHz and (b) zero-field cooled (ZFC) (black \bigcirc) and field-cooled (FC) (red \Box) *dc*-susceptibility measured in $\mu_0 H = 10$ mT.

Susceptometry experiments on powdered samples of NiO, Mn₃O₄, and CoO nanoparticles confirmed magnetism typical of transition-metal oxide nanoparticles. The *ac*susceptibilities were measured from 2 K to 75 K with an applied field of 0.25 mT oscillating with frequencies of $\nu = 10-1000$ Hz, and the ZFC and FC *dc*-susceptibilities were measured with an applied field of $\mu_0 H = 10$ mT. For NiO (Fig. 6.7) susceptometry indicated blocking below ~50 K, and glass-like slow dynamics due to interactions amongst surface spins at ~ 10-20 K [212,213]. For CoO (Fig. 6.8) two regimes were also observed in susceptometry experiments; $\chi_{ac}(\nu, T)$ and $\chi_{dc,ZFC}(T)$ show a sharp maximum at 5 K and $\chi_{dc,ZFC}(T)$ indicates broad maximum ~ 75 K and $\chi_{dc,ZFC}(T)$ and $\chi_{dc,FC}(T)$ irreversibility persist up to significantly higher temperatures. This behaviour is typical of AF nanoparticles with frozen and magnetically ordered regions



Figure 6.8: Susceptometry measurements for CoO nanoparticle powder showing (a) the in-phase (top) and out-of-phase (bottom) *ac*-susceptibilities $\chi'_{ac}(\nu, T)$ and $\chi''_{ac}(\nu, T)$ measured in 0.25 mT drive field oscillating at 10 Hz to 1 kHz and (b) zerofield cooled (ZFC) (black \bigcirc) and field-cooled (FC) (red \Box) *dc*-susceptibility measured in $\mu_0 H = 10$ mT.



Figure 6.9: Susceptometry measurements for Mn_3O_4 nanoparticle powder showing (a) the in-phase (top) and out-of-phase (bottom) *ac*-susceptibilities $\chi'_{ac}(\nu, T)$ and $\chi''_{ac}(\nu, T)$ measured in 0.25 mT drive field oscillating at 10 Hz to 1 kHz, and (b) zerofield cooled (ZFC) (black \bigcirc) and field-cooled (FC) (red \Box) *dc*-susceptibility measured in $\mu_0 H = 10$ mT.

of the surface shell [211, 213]. For Mn₃O₄, shown in Fig. 6.9, $\chi_{ac}(\nu, T)$ and $\chi_{dc}(T)$ reveal clearly $T_C \sim 40$ K [214].

Hysteresis loop measurements were done after cooling in an applied field of 5 T, and were measured from $\pm 5T$. Temperature and field-dependent magnetizations of CoO, Mn_3O_4 , and NiO can be compared with the XMCD of the core/shell nanoparticles to contrast the observed XMCD with the potential response of the shells or of isolated particles. For NiO, Mn_3O_4 , and CoO nanoparticles the field dependent magnetism was obtained from hysteresis loops measured at 10 K and $\mu_0 H = 0 - 5$ T, and the temperature dependent magnetism was obtained from the magnetization at $\mu_0 H = 1$ T from hysteresis loop measurements. These behaviours are compared with the temperature and field dependent magnetism of Ni, Mn, and Co in the core/shell nanoparticles obtained from XMCD. For the core/shell nanoparticles the Ni, Mn, and Co magnetism were obtained from the variation in the L_3 -edge XMCD intensity; the field dependent magnetism was obtained from the XMCD measured at 10 K from $\mu_0 H = 0.1 - 5$ T and the temperature dependent magnetism was measured from 10 K to 200 K in $\mu_0 H = 1$ T. The results are shown in Fig. 6.10. The field dependent magnetism of NiO, Mn_3O_4 , and CoO nanoparticles reveals a predominantly linear behaviour. This departed clearly from the field dependent XMCD obtained from the Ni and Co L_3 -edges of γ -Fe₂O₃/NiO and γ -Fe₂O₃/CoO nanoparticles. Combined with the different temperature dependent magnetism, this indicated that the Ni and Co XMCD were due to interfacial ferrites and not the response of the AF shells. For γ -Fe₂O₃/MnO, the change in Mn magnetization with applied field was obtained from the integrated L_3 -edge XMCD due to the different field-dependent behaviours of



Figure 6.10: Temperature (left) and field (right) dependent magnetism of transitionmetal oxide nanoparticles (obtained from hysteresis loop measurements) and the corresponding transition-metal ions in core/shell nanoparticles (obtained from the L_3 -edge XMCD). Field-dependent measurements were done at T = 10 K, and temperature dependent measurements were done using $\mu_0 H = 1$ T. Results are shown for the (a) magnetometry of NiO and the Ni XMCD of γ -Fe₂O₃/NiO, (b) magnetometry of Mn₃O₄ and the Mn XMCD of γ -Fe₂O₃/MnO, and (c) magnetometry of CoO and the Co XMCD of γ -Fe₂O₃/CoO.



Figure 6.11: Temperature (left) and field (right) dependent overall magnetism (obtained from hysteresis loop measurements) and site-specific magnetism (obtained from the L_3 -edge XMCD) of core/shell nanoparticles. Field-dependent measurements were done at T = 10 K, and temperature dependent measurements were done using $\mu_0 H = 1$ T. Results are shown for the (a) magnetometry compared to the Fe and Ni XMCD of γ -Fe₂O₃/NiO, (b) magnetometry compared to the Fe and Mn XMCD of γ -Fe₂O₃/MnO, and (c) magnetometry compared to the Fe and Co XMCD of γ -Fe₂O₃/CoO.

the Mn²⁺ and Mn³⁺-sites. For Mn₃O₄, a similar field-dependent magnetism was observed when compared with the Mn L_3 -edge XMCD of γ -Fe₂O₃/MnO nanoparticles that was likely due to a similar canted spin arrangement that occurs in ferrimagnetic Mn₃O₄; however, Mn₃O₄ shows clearly an abrupt decrease in the magnetization at T_C , whereas a gradual variation in the Mn XMCD was observed for γ -Fe₂O₃/MnO nanoparticles.

The temperature and field dependent magnetism of Ni, Mn and Co in the core/shell nanoparticles indicated by XMCD was much more in keeping with the behaviour of an interfacial ferrite. Fig. 6.11 provides a comparison of the site-specific magnetism obtained from XMCD to the overall magnetism obtained from magnetometry (measured in the same way as described above for NiO, Mn_3O_4 , and CoO). For γ -Fe₂O₃/NiO and γ -Fe₂O₃/CoO, the Fe, Ni and Co magnetizations show clearly an approach to saturation that is nearly identical to the magnetometry. The difference in the field dependence of the total Mn-magnetization compared to Ni and Co is a result of the different spin structure due to the weakened $Mn^{3+}-Mn^{2+}$ exchange that enables a noncollinear spin arrangements in large applied fields, discussed in Sec. 4.5. This results in a similar field dependent magnetism as observed in Mn_3O_4 . However, the clear difference in the temperature dependence of the Mn magnetism in γ -Fe₂O₃/MnO versus Mn_3O_4 is due to the existence of significantly stronger exchange interactions with Fe-ions which are also present in the interfacial Mn-ferrite. The temperature dependence of the Fe-site magnetism was similar to the overall magnetism obtained from magnetometry. For γ -Fe₂O₃/NiO a similar Bloch-like temperature dependence was observed clearly for the Fe-sites, but with a more pronounced temperature variation

than the total core/shell nanoparticle provided by magnetometry. The Ni XMCD also exhibited a larger variation with temperature than the total magnetization of the core/shell nanoparticle indicated by magnetometry. However, since J is strongly reduced for the surface-sites of γ -Fe₂O₃ due to broken coordination and surface vacancies, an interfacial ferrite would be expected also to have a lower J compared to the ordered interior of the nanoparticle and hence vary more strongly with increasing temperature. Since the interfacial phase is emphasized in the TEY XMCD due to the surface sensitivity of the measurement, this results in the more pronounced temperature variation of the XMCD compared to the magnetometry data. Interestingly, the Co XMCD of γ -Fe₂O₃/CoO nanoparticles shows a stronger temperature variation than the Ni XMCD of γ -Fe₂O₃/NiO, which is also consistent with the larger Bloch constant B for γ -Fe₂O₃/CoO that indicates a weaker J. By comparison, the temperature dependence of the Fe-site XMCD of γ -Fe₂O₃/MnO reveals a Bloch-like behaviour, whereas a linear M(T) was observed in magnetometry. By comparing the temperature variations of the Fe and Mn XMCD, it appears that the overall linear M(T) indicated by magnetometry is strongly influenced by the Mn magnetism, which has a more linear dependence.

The core/shell nanoparticle properties can be compared with typical properties of the interfacial ferrites (summarized in Table. 6.2). For γ -Fe₂O₃/NiO the interfacial ferrite contained Ni²⁺ O_h -sites and no indication of other Ni-sites was observed. This was consistent with the typical ion distribution of Ni-ferrites that results from the strong preference for Ni²⁺ to occupy O_h -sites exclusively [7, 215]. The formation of an interfacial Ni-ferrite resulted in a partial recapture of the interfacial disordered

	T_C (K)	$K (J/m^3)$	dopant ion distribution
γ -Fe ₂ O ₃	~ 900	2.5×10^4	/
$NiFe_2O_4$	858	$1-4 \times 10^4$	Ni ²⁺ O_h (100%)
$MnFe_2O_4$	585	2×10^{4}	${\rm Mn^{2+}} T_d (80\%) {\rm Mn^{2+}} O_h (20\%)$
$CoFe_2O_4$	790	$2-9 \times 10^5$	$\operatorname{Co}^{2+} T_d (20\%) \operatorname{Co}^{2+} O_h (80\%)$

Table 6.2: Typical magnetic properties of ferrites [7, 36, 49, 145, 215–219].

spins and H_{ex} was nearly eliminated. Since H_{ex} in γ -Fe₂O₃ is a result of interactions between the ordered core and disordered surface spin populations, H_{ex} reduction in γ -Fe₂O₃/NiO is a direct result of the changes to the spin disorder. The lack of H_{ex} due to interactions with NiO is likely due to the low K of NiO, which does not enable the effective pinning of interfacial NiO spins that is necessary to produce a unidirectional anisotropy [47] and the very small NiO particle size (i.e. versus a fully formed shell). It is likely that the enhanced H_c of γ -Fe₂O₃/NiO versus γ -Fe₂O₃ is due to a larger effective magnetic volume resulting from recapture of surface spins into a Ni-ferrite layer; however the lack of T_B enhancement indicates that the intermixed layer was not able to stabilize the magnetism of the core/shell nanoparticle, despite the changes in composition and Fe surface spin disorder.

For γ -Fe₂O₃/MnO a large change in the dynamical magnetism and the complete incorporation of the disordered spins of the γ -Fe₂O₃ core was consistent with the more extensive intermixing effects indicated by Mössbauer spectroscopy, XAS, and XMCD. Mn-ions are able to adopt a large variety of valences and to occupy both O_h and T_d sites. As a result, the intrinsic magnetism of Mn-ferrites can vary substantially; for

bulk MnFe₂O₄ prepared using ceramic methods the Mn-ions occupy the O_h and T_d sites as described in Table 6.2, resulting in a relatively low K and J (indicated by T_{C}). It is common for nanoparticles prepared using chemical techniques to contain Mn^{3+} O_h -sites [219, 220], as observed in γ -Fe₂O₃/MnO. Such Mn-ferrites typically have a large K up to 10^5 J/m³ [127]. It is possible that the coupling between the magnetically soft γ -Fe₂O₃ interior and the hard Mn-ferrite layer contributed to the H_{ex} enhancement, similarly to the hard/soft Fe/Mn-oxide core/shell nanoparticles [127], due to the lower K of MnO [221]. The Mn XMCD identified a non-zero m_{ℓ} for the Mn^{3+} O_h -sites that was consistent with a large anisotropy of the interfacial Mn-ferrite; however, further work is necessary to determine precisely the nature of the Mn³⁺-sites, for which no comparable XMCD was found in other Mn-oxide-based nanoparticles, and which could not be described by atomic multiplet simulations. The temperature dependence of the Fe core and interface spin fluctuation rates determined from Mössbauer spectroscopy in Sec. 4.4 indicated that interactions with the MnO shell stabilized the spins of the Fe-based core below T_N MnO. Together with the temperature dependence of the Fe and Mn magnetizations determined from XMCD. we can conclude that the deviation from Bloch $T^{3/2}$ behaviour in γ -Fe₂O₃/MnO to a linear dependence was a result of substantial changes to the Fe spin fluctuation rates and due to the important contribution of the Mn magnetization.

The occurrence of predominantly $\text{Co}^{2+} O_h$ -sites, and a small amount of T_d -sites in γ -Fe₂O₃ was consistent with typical ion distributions of Co-ferrites [7, 101, 145]. The relatively low fraction of T_d sites compared to typical Co-ferrites was likely due to the available O_h -site vacancies of γ -Fe₂O₃. A marked increase in K of γ -Fe₂O₃/CoO

versus γ -Fe₂O₃/NiO and γ -Fe₂O₃/MnO indicated by the large increase in T_B and H_c was consistent with the large single-ion anisotropy of Co²⁺-ions [147]. The large H_{ex} enhancement was also consistent with the behaviour of an FiM/AF exchange coupled system with a relatively large K of the CoO shell [47]. Interestingly, the Bloch constant B of γ -Fe₂O₃/CoO was larger than γ -Fe₂O₃/NiO (indicating weaker J) despite a complete CoO shell layer (Table 6.1). This is possibly a result of a weaker J_{AB} of $\operatorname{Fe}_A^{3+}-\operatorname{O}^{2-}-\operatorname{Co}_B^{2+}$ compared to $\operatorname{Fe}_A^{3+}-\operatorname{O}^{2-}-\operatorname{Ni}_B^{2+}$ indicated by the lower T_C of CoFe₂O₄. As shown in Sec. 5.3, there was also a clear relationship between the degree of core/shell intermixing and B, that indicated that J was strengthened as more surface sites were filled. This result was consistent with work which has established that $B_{\rm nano} > B_{\rm bulk}$ due to a reduced effective coordination number of surface atoms [36, 37]. The increased surface vacancy filling due to progressively deeper Co^{2+} diffusion was also directly related to a decrease in the interfacial spin disorder revealed by Mössbauer spectra at 10 K. This revealed a direct correlation between the interfacial disorder and H_{ex} , similar to the behaviour established in thin films yet which has not been fully described in a nanoparticle system. This also indicated clearly the overall magnetism is not only sensitive to the existence of an interfacial intermixed phase, but also on the interfacial magnetism, composition, and microstructure. The temperature dependent magnetism of the interfacial ferrite was also found to correlate with the onset of H_{ex} by virtue of changes in the interfacial metal-oxygen hybridization. This brings to light a new mechanism which should be considered in the broader understanding of exchange bias phenomena.

Overall, this work has confirmed that interfacial intermixed layers of ferrites were

formed naturally during the chemical core/shell nanoparticle synthesis process. Considering the high affinity for the shell transition metal ions to occupy the sites of the spinel core this is not a wholly unexpected result. However, due to the complexity of nanoparticle systems and the significant challenge in characterizing all aspects of core/shell magnetism, this has remained a relatively unexplored avenue to describe the origins of the properties of core/shell nanoparticles. This work has shown that the variety of magnetism observed in the core/shell nanoparticles can be well described by the degree of intermixing, the effect of intermixing on altering the interfacial disorder, and on the superexchange pathways which propagate through the interfacial ferrite.

Chapter 7

Conclusions and Future Work

The properties of multi-component nanostructured systems stem largely from interfacial phenomena. This has led to a significant opportunity to engineer a variety of interesting properties through interfacial interactions. At the same time, there is a pressing need to understand in better detail the nature of interfaces as a means of understanding the physical origins of such phenomena. In magnetic core/shell nanoparticles, interface spin disorder, anisotropy, and interfacial exchange interactions can alter all aspects of the overall properties (T_B, H_c, H_{ex}) , so that a large variety of properties are observed even for nominally similar core and shell material combinations. Systematic studies of core/shell nanoparticles examining factors such as core/shell combinations, geometry, shape effects, etc. have provided valuable insight to the origin of the nanoparticle magnetism. However, recent work has shown that interfacial intermixing does occur, yet to date there has been no systematic study to describe clearly the relationship between the properties of the interfacial layer and the overall nanoparticle magnetism, leaving an important gap in fundamental understanding.

To address this, the relationship between the overall magnetism and interfacial intermixing on γ -Fe₂O₃-based core/shell nanoparticles was examined. The overall properties were determined using magnetometry and susceptometry experiments, and the atomic and element-specific magnetism were characterized using Mössbauer spectroscopy, XAS and XMCD. For γ -Fe₂O₃/NiO, an interfacial Ni-ferrite was formed by Ni²⁺-ions migrating into the O_h -sites of the γ -Fe₂O₃ surface layers. A lower H_{ex} in γ -Fe₂O₃/NiO versus γ -Fe₂O₃ resulted from a partial recapture of the disordered spins at the γ -Fe₂O₃ surface into the interfacial ferrite layer by virtue of newly formed $\rm Fe^{3+}\text{-}O\text{-}Ni^{2+}$ superexchange interactions in the Ni-ferrite layer. For $\gamma\text{-}\rm Fe_2O_3/MnO$ a substantial change in the core/shell nanoparticle magnetism was a direct result of substantial core/shell intermixing. The interfacial Fe spin disorder was resolved in γ -Fe₂O₃/MnO through a large number of exchange interactions due to Mn-ion substitution into O_h and T_d -sites on the γ -Fe₂O₃ core. This resulted in much more uniform Fe spin relaxation in γ -Fe₂O₃/MnO versus γ -Fe₂O₃. The element-specific magnetism revealed that the intrinsic magnetism of the Mn-ferrite differed from γ -Fe₂O₃. To examine in further detail the implication of exchange core/shell interactions that are mediated the interfacial ferrite layer, further work was done using γ -Fe₂O₃/CoO nanoparticles that are a prototypical exchange bias system. In γ -Fe₂O₃/CoO, an interfacial Co-ferrite is formed consisting of predominantly $\operatorname{Co}^{2+} O_h$ -sites with a large anisotropy. Detailed studies using high-resolution transmission electron microscopy provided a direct relationship between the interfacial intermixed layer thickness, the degree of interfacial spin disorder, and the exchange bias of the core/shell nanoparticle. A comprehensive description of the interfacial ferrite magnetism provided further insight the origin of the magnetism by revealing a temperature dependent change in the metal-oxygen hybridization that provided the mechanism for the onset of interfacial magnetic coupling that enabled H_{ex} .

This work has shed light on the important and potential impact of different intermixed layers on the magnetism of core/shell nanoparticles. This has led to some questions which could be addressed further with further studies:

This work identified a close relationship between amount of interfacial intermixing and the interfacial spin disorder. Mössbauer spectra measured in an applied magnetic field would be better suited to observe the interfacial disordered Fe-spins, and would allow the spectral components due to different Fe A and B-sites to be resolved more clearly. When a magnetic field is applied parallel to the γ -ray direction, the effective field at the ⁵⁷Fe $\vec{B}_{eff} = \vec{B}_{hf} + \vec{B}_{ext}$. In a large applied field, the moments of the Fe atoms on the A and B-sites will lie parallel and antiparallel to B_{ext} . The relative intensities of the spectral lines are 3:R:1:1:R:3, where R is proportional to the angle between B_{eff} and the γ -ray direction. As a result, interfacial spins which are not able to align with \vec{B}_{ext} will result in $R \neq 0$ and can be resolved clearly from the bulk moments that align with the external field and have R = 0. Mössbauer spectra of γ -Fe₂O₃/NiO, γ -Fe₂O₃/MnO and γ -Fe₂O₃/CoO should be measured at 10 K in a large applied field (\geq 5 T) to better quantify disordered Fe spins and to observe their responses in an applied field.

Further work to describe the interfacial Mn^{3+} sites observed in XMCD spectra is necessary. Preliminary attempts to include local structural distortions typical of JahnTeller ions did not result reproduce the spectral features observed for γ -Fe₂O₃/MnO. As a result, further work using ligand field multiplet calculations including more substantial local Mn-site distortions should be explored. Also, Mn³⁺-ions are known to interact strongly with surrounding anions. Spectrum simulations including charge transfer effects should also be attempted. A better understanding of the interfacial Mn³⁺-sites would likely shed light on the origin of the Mn $m_{\ell}/m_s > 0$, which should be related to the anisotropy of the interfacial ferrite.

The observation of a temperature dependent change in the interfacial metaloxygen hybridization is an interesting result that deserves further examination. Similar measurements of the O K-edge XAS, and XMCD over the L_3 and L_2 -edges should be done for γ -Fe₂O₃, γ -Fe₂O₃/NiO and γ -Fe₂O₃/MnO. In addition, Mössbauer spectra for γ -Fe₂O₃/NiO and γ -Fe₂O₃/MnO should be collected in smaller temperature intervals to determine the temperature dependence of the *f*-factor in these systems. If the transition observed in γ -Fe₂O₃/CoO is related to a Verwey-like charge ordering, it is possible that no such transition was observed in γ -Fe₂O₃ (no *f*-factor anomaly was observed) since there are no Fe²⁺-ions. Since Fe²⁺-sites were observed in γ -Fe₂O₃/NiO and γ -Fe₂O₃/MnO, a similar transition may be observed. However, if the transition is related to some kind of magnetostrictive effect due to Co²⁺, no similar behaviour may be observed in γ -Fe₂O₃/NiO and γ -Fe₂O₃/MnO. Thus, such experiments done on the complete series of core/shell nanoparticles would shed light on the origin of the transition in γ -Fe₂O₃/CoO and on the universality of the phenomenon.

Bibliography

- C. P. Bean and J. D. Livingston. Superparamagnetism. J. Appl. Phys., 30:S120, 1959.
- [2] J. L. Dormann, D. Fiorani, and E. Tronc. Magnetic relaxation in fine-particle systems. Adv. in Chem. Phys., 98:283–494, 2007.
- [3] M. P. Morales, S. Veintemillas-Verdaguer, M. I. Montero, C. J. Serna, A. Roig,
 Ll. Casas, B. Martínez, and F. Sandiumenge. Surface and internal spin canting
 in γ-Fe₂O₃ nanoparticles. *Chem. Mater.*, 11:3058–3064, 1999.
- [4] S. Mørup and B. R. Hansen. Uniform magnetic excitations in nanoparticles. *Phys. Rev. B*, 72:024418, 2005.
- [5] S. Mørup, D. E. Madsen, C. Frandsen, C. R. H. Bahl, and M. F. Hansen. Experimental and theoretical studies of nanoparticles of antiferromagnetic materials. *J. Phys.: Condens. Matter*, 19:213202, 2007.
- [6] X. Batlle and A. Labarta. Finite-size effects in fine particles: magnetic and transport properties. J. Phys. D; Appl. Phys., 35:R15–R42, 2002.
- [7] A. Broese van Groenou, P. F. Bongers, and A. L. Stuyts. Magnetism, mi-

crostructure and crystal chemistry of spinel ferrites. *Mater. Sci. Eng.*, 3:317–392, 1969.

- [8] C. Altavilla and E. Ciliberto. Inorganic Nanoparticles: Synthesis, Applications, and Perspectives. CRC Press, Boca Raton, 2011.
- M. Colombo, S. Carregal-Romero, M. F. Casula, L. Gutiérrez, M. P. Morales,
 I. B. Böhm, J. T. Heverhagen, D. Prosperi, and W. J. Parak. Biological applications of magnetic nanoparticles. *Chem. Soc. Rev.*, 41:4306–4334, 2012.
- [10] P. Tartaj, M. P. Morales, T. Gonzales-Carreño, S. Veintemillas-Verdaguer, and C. J. Serna. The iron oxides strike back: From biomedical applications to energy storage devices and photoelectrochemical water splitting. *Adv. Mater.*, 23:5243–5249, 2011.
- [11] J.-H. Lee, J.-T. Jang, J.-S. Choi, S. H. Moon, S.-H Noh, J.-W. Kim, J.-G. Kim, I.-S. Kim, K. I. Park, and J. Cheon. Exchange-coupled magnetic nanoparticles for efficient heat induction. *Nature Nanotech.*, 6:418–422, 2011.
- [12] M. Estrader, A. López-Ortega, S. Estradé, I. V. Golosovsky, G. Salazar-Alvarez, M. Vasilakaki, K. N. Trohidou, M. Varela, D. C. Stanley, M. Sinko, M. J. Pechan, D. J. Keavney, F. Peiró, S. Suriñach, M. D. Baró, and J. Nogués. Robust antiferromagnetic coupling in hard-soft bi-magnetic core/shell nanoparticles. *Nature Commun.*, 4:2960, 2013.
- [13] A. López-Ortega, M. Estrader, G. Salazar-Alvarez, A. G. Roca, and J. Nogués.

Applications of exchange coupled bi-magnetic hard/soft and soft/hard magnetic core/shell nanoparticles. *Phys. Rep.*, 553:1, 2015.

- [14] M. A. Ruderman and C. Kittel. Indirect exchange coupling of nuclear magnetic moments by conduction electrons. *Phys. Rev.*, 96:99, 1954.
- [15] K. Yosida. Magnetic properties of Cu-Mn alloys. Phys. Rev., 106:893–898, 1957.
- [16] T. Kasuya. A Theory of Metallic Ferro- and Antiferromagnetism on Zener's Model. Prog. Theor. Phys., 16:45–57, 1956.
- [17] J B Goodenough. Theory of the Role of Covalence in the Perovskite-Type Manganites [La, M(II)]MnO₃. Phys. Rev., 100:564–573, 1955.
- [18] J. B. Goodenough. An interpretation of the magnetic properties of the perovskite-type mixed crystals La_{1-x}Sr_xCoO_{3-λ}. J. Phys. Chem. Solids, 6:287– 297, 1958.
- [19] J. Kanamori. Superexchange interaction and symmetry properties of electron orbitals. J. Phys. Chem. Solids, 10:87–98, 1959.
- [20] C. Zener. Interaction Between the d Shells in the Transition Metals. Phys. Rev., 81:440–444, 1951.
- [21] J. Stöhr and H. C. Siegmann. Magnetism: From fundamentals to nanoscale dynamics. Springer Science + Business Media, Berlin, Heidelberg, 2006.
- [22] E. F. Kneller and F. E. Luborsky. Particle size dependence of coercivity and remanence of single-domain particles. J. Appl. Phys., 34:656–658, 1963.

- [23] J. B. Goodenough. Magnetism and the chemical bond. Wiley & Sons, New York, 1963.
- [24] R. M. Cornell and U. Schwertmann. The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003.
- [25] M. Uhl and S. Siberchiot. A first-principles study of exchange integrals in magnetite. J. Phys.: Condens. Matter, 7:4227–4237, 1995.
- [26] R. H. Kodama and A. E. Berkowitz. Atomic-scale magnetic modleing of oxide nanoparticles. *Phys. Rev. B*, 59:6321–6336, 1999.
- [27] G. M. da Costa, E. De Grave, and R. E. Vandenberghe. Mössbauer studies of magnetite and Al-substituted maghemites. *Hyp. Int.*, 117:207–243, 1998.
- [28] K. M. Krishnan. Biomedical nanomagnetics: a spin through possibilities in imaging, diagnostics, and therapy. *IEEE Trans. Magn.*, 46:2523, 2010.
- [29] E. C. Stoner and E. P. Wohlfarth. A Mechanism of Magnetic Hysteresis in Heterogeneous Alloys. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, 240:599– 642, 1948.
- [30] S. Mørup and H. Topsøe. Mössbauer studies of thermal excitations in magnetically ordered microcrystals. Appl. Phys., 11:63–66, 1976.
- [31] N. Kurti. Selected Works of Louis Néel. CRC Press, New York, 1988.
- [32] W. F. Brown. Thermal Fluctuations of a Single-Domain Particle. Phys. Rev., 130:1677–1686, 1963.

- [33] D. P. E. Dickson and N. M. K. Reid and C. Hunt and H. D. Williams and M. El-Hilo and K. O'Grady. Determination of f₀ for fine magnetic particles. J. Magn. Magn. Mater., 125:345–350, 1993.
- [34] V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord, and J. Nogués. Beating the superparamagnetic limit with exchange bias. *Nature*, 423:850, 2003.
- [35] J. M. D. Coey. Magnetism and magnetic materials. Cambridge University Press, Cambridge, 2010.
- [36] R. H. Kodama. Magnetic nanoparticles. J. Magn. Magn. Mater., 200:359–372, 1999.
- [37] P. V. Hendriksen, S Linderoth, and P. A. Lindgard. Magnetic properties of Heisenberg clusters. J. Phys.: Condens. Matter, 5:5675–5684, 1993.
- [38] R. Aquino, J. Depeyrot, M. H. Sousa, F. A. Tourinho, E. Dubois, and R. Perzynski. Magnetization temperature dependence and freezing of surface spins in magnetic fluids based on ferrite nanoparticles. *Phys. Rev. B*, 72:184435, 2005.
- [39] Y. Labaye, O. Crisan, L. Berger, J. M. Greneche, and J. M. D. Coey. Surface anisotropy in ferromagnetic nanoparticles. J. Appl. Phys., 91:8715, 2002.
- [40] J. M. D. Coey. Noncollinear spin arrangement in ultrafine ferrimagnetic crystallites. *Phys. Rev. Lett.*, 27:1140, 1971.
- [41] E. Tronc, A. Ezzir, R. Cherkaoui, C. Chanéac, M. Noguès, H. Kachkachi, D. Fio-

- rani, A. M. Testa, J. M. Grenèche, and J. P. Jolivet. Surface-related properties of γ -Fe₂O₃ nanoparticles. J. Magn. Magn. Mater., 221:63–79, 2000.
- [42] J. Restrepo, Y. Labaye, and J. M. Greneche. Surface anisotropy in maghemite nanoparticles. *Phys. B Condens. Matter*, 384:221–223, 2006.
- [43] H. Kachkachi, A. Ezzir, M. Noguès, and E. Tronc. Surface effects in nanoparticles: application to maghemite γ-Fe₂O₃. Eur. Phys. J. B, 14:681–689, 2000.
- [44] B. Martínez, X. Obradors, Ll. Balcells, A. Rouanet, and C. Monty. Low Temperature Surface Spin-Glass Transition in γ-Fe₂O₃ Nanoparticles. *Phys. Rev. Lett.*, 80:181–184, 1998.
- [45] W. H. Meiklejohn and C. P. Bean. New Magnetic Anisotropy. Phys. Rev., 102:1413–1414, 1956.
- [46] J Nogués and Ivan K Schuller. Exchange bias. J. Magn. Magn. Mater., 192:203– 232, 1999.
- [47] J. Nogués, J. Sort, V. Langlais, V. Skumryev, S. Suriñach, J. S. Muñoz, and M. D. Baró. Exchange bias in nanostructures. *Phys. Rep.*, 422:65–117, 2005.
- [48] R. H. Kodama, A. E. Berkowitz, E. J. McNiff, and S. Foner. Surface spin disorder in ferrite nanoparticles (invited). J. Appl. Phys., 81:5552–5557, 1997.
- [49] T. N. Shendruk, R. D. Desautels, B. W. Southern, and J. van Lierop. The effect of surface spin disorder on the magnetism of γ-Fe₂O₃ nanoparticle dispersions. *Nanotechnology*, 18:455704, 2007.

- [50] R. D. Desautels, E. Skoropata, and J. van Lierop. Moment fluctuations in 7 nm γ-Fe₂O₃ nanoparticles probed at the atomic level using Mössbauer spectroscopy. J. Appl. Phys., 103:07D512, 2008.
- [51] Bassel Alkadour, J. I. Mercer, J. P. Whitehead, J. van Lierop, and B. W. Southern. Surface vacancy mediated pinning of the magnetization in γ-Fe₂O₃ nanoparticles: A micromagnetic simulation study. *Phys. Rev. B*, 93:140411, 2016.
- [52] W. H. Meiklejohn and C. P. Bean. A new magnetic anisotropy. *Phys. Rev.*, 105:904–913, 1957.
- [53] R. D. Desautels, E. Skoropata, Y.-Y. Chen, H. Ouyang, J. W. Freeland, and J. van Lierop. Tuning the surface magnetism of γ-Fe₂O₃ nanoparticles with a Cu shell. *Appl. Phys. Lett.*, 99:262501, 2011.
- [54] R. D. Desautels, E. Skoropata, Y.-Y. Chen, H. Ouyang, J. W. Freeland, and J. van Lierop. Increased surface spin stability in γ-Fe₂O₃ nanoparticles with a Cu shell. J. Phys.: Condens. Matter, 24:146001, 2012.
- [55] R. D. Desautels, Y.-Y. Chen, H. Ouyang, S.-C. Lo, J. W. Freeland, and J. van Lierop. Field dependence of the interfacial Cu in Cu-coated γ-Fe₂O₃ nanoparticles. J. Appl. Phys., 111:07B518, 2012.
- [56] O. Iglesias, A. Labarta, and X. Batlle. Exchange bias phenomenology and models of core/shell nanoparticles. J. Nanosci. Nanotechnol., 8:2761–2780, 2008.

- [57] S. Estradé, Ll. Yedra, A. López-Ortega, M. Estrader, M.D. Baró G. Salazar-Alvarez, J. Nogués, and F. Peiró. Distinguishing the core from the shell in MnO_x/MnO_y and FeO_x/MnO_x core/shell nanoparticles through quantitative electron energy loss spectroscopy (EELS) analysis. *Micron*, 43:30–36, 2012.
- [58] K. L. Krycka, J. A Borchers, G. Salazar-Alvarez, A. López-Ortega, M. Estrader, S. Estradé, E. Winkler, R. D. Zysler, J. Sort, F. Peiró, M. D. Baró, C.-C. Kao, and J. Nogués. Resolving material-specific structures within Fe₃O₄/γ-Fe₂O₃ core-shell nanoparticles using anomalous small-angle x-ray scattering. ACS Nano, 7:921–931, 2013.
- [59] J. Rockenberger, E. C. Scher, and A. P. Alivisatos. A new nonhydrolytic singleprecursor approach to surfactant-capped nanocrystals of transition metal oxides. J. Am. Chem. Soc., 121(49):11595–11596, 1999.
- [60] R. S. Bottei and R. G. Schneggenburger. Thermal and spectral study of some divalent metal chelates of cupferron and dicupferron. J. Inorg. Nucl. Chem., 32:1525–1545, 1970.
- [61] A. L. Patterson. The Scherrer Formula for X-Ray Particle Size Determination. *Phys. Rev.*, 56:978–982, 1939.
- [62] V. K. Pecharsky and P. Y. Zavalij. Fundamentals of powder diffraction and structural characterization of materials. Springer Science + Business Media, New York, 2003.

- [63] J. Rodriguez-Carvajal. Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B: Condens. Matt.*, 192:55–69, 1993.
- [64] B. Fultz and J. M. Howe. Transmission electron microscopy and diffractometry of materials. Springer Science-Verlag, Berlin Heidelberg, 2012.
- [65] W. S. Rasband. Image processing and analysis in java, 2005.
- [66] Quantum Design. Magnetic property measurement system (MPMS) Reciprocating sample option's user manual, November 2001.
- [67] Quantum Design. Magnetic property measurement system (MPMS) Low-field profiling user's manual, May 2000.
- [68] J. Gittleman, B. Abeles, and S. Bozowski. Superparamagnetism and relaxation effects in granular Ni-SiO₂ and Ni-Al₂O₃ films. *Phys. Rev. B*, 9:3891–3897, 1974.
- [69] D. E. Madsen, M. F. Hansen, and S. Mørup. The correlation between superparamagnetic blocking temperatures and peak temperatures obtained from ac magnetization measurements. J. Phys.: Condens. Matter, 20:345209, 2008.
- [70] R. L. Mössbauer. Kernresonanzfluoreszenz von gammastrahlung in Ir¹⁹¹. Z. Physik, 151:124 – 143, 1958.
- [71] P. Gütlich, E. Bill, and A. X. Trautwein. Mössbauer spectroscopy and transition metal chemistry: fundamentals and applications. Springer Science + Business Media, Berlin, Heidelberg, 2010.

- [72] U. Gonser. From a strange effect to Mössbauer spectroscopy. In U. Gonser, editor, *Mössbauer Spectroscopy*, pages 1–51. Springer Science + Business Media, Berlin, Heidelberg, 1975.
- [73] Y. Yoshida and G. Langouche. *Mössbauer spectroscopy: Tutorial book*. Springer-Verlag, Berlin Heidelberg, 2013.
- [74] G.A. Sawatzky and F. van der Woude. Covalency effects in hyperfine interactions. Le Journal de Physique Colloques, 35:C6–47, 1974.
- [75] F. de Groot and A. Kotani. Core level spectroscopy of solids. CRC press, New York, 2008.
- [76] B. T. Thole, P. Carra, F. Sette, and G. van der Laan. X-ray circular dichroism as a probe of orbital magnetization. *Phys. Rev. Lett.*, 68:1943–1946, 1992.
- [77] P. Carra, B. T. Thole, M. Altarelli, and X. Wang. X-ray circular dichroism and local magnetic fields. *Phys. Rev. Lett.*, 70:694–697, 1993.
- [78] C. T. Chen, Y. U. Idzerda, H.-J. Lin, N. V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin, and F. Sette. Experimental confirmation of the x-ray magnetic circular dichroism sum rules for iron and cobalt. *Phys. Rev. Lett.*, 75:152–155, 1995.
- [79] J. W. Freeland, J. C. Lang, G. Srajer, R. Winarski, D. Shu, and D. M. Mills. A unique polarized x-ray facility at the Advanced Photon Source. *Rev. Sci. Instrum.*, 73:1408, 2002.

- [80] J. M. Byrne, N. D. Telling, V. S. Coker, R. A. D. Pattrick, G. van der Laan, E. Arenholz, F. Tuna, and J. R. Lloyd. Control of nanoparticle size, reactivity and magnetic properties during the bioproduction of magnetite by *Geobacter sulfurreducens*. *Nanotechnology*, 22:455709, 2011.
- [81] G. van der Laan and B. T. Thole. Strong magnetic x-ray dishroism in 2p absorption spectra of 3d transition-metal ions. *Phys. Rev. B*, 43:13401–13411, 1991.
- [82] E. Stavitski and F. M. F. de Groot. The CTM4XAS program for EELS and XAS spectral shape analysis of transition metal L edges. *Micron*, 41:687, 2010.
- [83] R. D. Cowan. Theoretical calculation of atomic spectra using digital computers.J. Opt. Soc. Am., 58:808, 1968.
- [84] R. D. Cowan. The theory of Atomic structure and Spectra. University of California Press, 1981.
- [85] B. T. Thole, G. van der Laan, and P. H. Butler. Spin-mixed ground state of Fe phthalocyanide and the temperature-dependent branching ratio in x-ray absorption spectroscopy. *Chem. Phys. Lett.*, 149:295, 1988.
- [86] H. Ogasawara, A. Kotani, K. Okada, and B. T. Thole. Theory of x-rayabsorption spectra in PrO₂ and some other rare-earth compounds. *Phys. Rev. B*, 43:854, 1991.
- [87] H. Ogasawara, A. Kotani, P. Potze, G. A. Sawatzky, and B. T. Thole.

Praseodymium 3*d*- and 4*d*-core photoemission spectra of Pr_2O_3 . *Phys. Rev. B*, 44:5465, 1991.

- [88] P. H. Butler. Point Group symmetry, applications, methods, and tables. Plenum, New York, 1981.
- [89] C. Pecharromán, T. González-Carreño, and J. E. Iglesias. The infrared dielectric properties of maghemite, γ-Fe₂O₃, from reflectance measurement on pressed powders. *Phys. Chem. Minerals*, 22(1):21–29, 1995.
- [90] S. Sasaki, K. Fujino, and Y. Takeuchi. X-ray determination of electron-density distributions in oxides, MgO, MnO, CoO, and NiO, and atomic scattering factors of their constituent atoms. *Proc. Jpn. Acad.*, 55:43–48, 1979.
- [91] J. Smit and H. P. J. Wijn. *Ferrites*. N. V. Phillips' Gloeilampenfabrieken, Eindhoven, Holland, 1959.
- [92] B. D. Cullity and C. D. Graham. Introduction to magnetic materials. John Wiley & Sons, 2011.
- [93] J. Tuček, R. Zobril, and D. Petridis. Maghemite nanoparticles by view of Mössbauer spectroscopy. J. Nanosci. Nanotechnol., 6:926–947, 2006.
- [94] G. A. Sawatzky, F. van Der Woude, and A. H. Morrish. Recoilless-Fraction Ratios for Fe57 in Octahedral and Tetrahedral Sites of a Spinel and a Garnet. *Phys. Rev.*, 183:383–386, 1969.
- [95] V. S. Coker, C. I. Pearce, R. A. D. Pattrick, G. van Der Laan, N. D. Telling, J. M. Charnock, E. Arenholz, and J. R. LLoyd. Probing the site occupancies of
Co-, Ni-, and Mn-substituted biogenic magnetite using XAS and XMCD. Am. Mineral., 93:1119–1132, 2008.

- [96] G. van der Laan, C. M. B. Henderson, R. A. D. Pattrick, S. S. Dhesi, P. F. Schofield, E. Dudzik, and D. J. Vaughan. Orbital polarization in NiFe₂O₄ measured by Ni-2p x-ray magnetic circular dichroism. *Phys. Rev. B*, 59:4314–4321, 1999.
- [97] S. Brice-Profeta, M.-A. Arrio, E. Tronc, N. Menguy, I. Letard, C. Cartier dit Moulin, M. Noguès, C. Chanéac, J.-P. Jolivet, and Ph. Sainctavit. Magnetic order in γ-Fe₂O₃ nanoparticles: a XMCD study. J. Magn. Magn. Mater., 288:354– 365, 2005.
- [98] E. Pellegrin, M. Hagelstein, S. Doyle, H. O. Moser, J. Fuchs, D. Vollath, S. Schuppler, M. A. James, S. S. Saxena, L. Niesen, O. Rogojanu, G. A. Sawatzky, C. Ferrero, M. Borowski, O. Tjernberg, and N. B. Brookes. Characterization of nanocrystalline γ-Fe₂O₃ with synchrotron radiation techniques. *Phys. Stat. Sol. B*, 215:797–801, 1999.
- [99] B. B. Nelson-Cheeseman, R. V. Chopdekar, M. F. Toney, A. Arenholz, and Y. Suzuki. Interplay between magnetism and chemical structure at spinel-spinel interfaces. J. Appl. Phys., 111:093903, 2012.
- [100] J.-B. Moussy. From epitaxial growth of ferrite thin films to spin-polarized tunnelling. J. Phys. D: Appl. Phys., 46:143001, 2013.

- [101] G. A. Sawatzky, F. van Der Woude, and A. H. Morrish. Mössbauer Study of Several Ferrimagnetic Spinels. *Phys. Rev.*, 187:747–757, 1969.
- [102] C. Piamonteze, P. Miedema, and F. M. F. De Groot. Accuracy of the spin sum rule in XMCD for the transition-metal L edges from manganese to copper. *Phys. Rev. B*, 80:1–12, 2009.
- [103] C. Frandsen, C. W. Ostenfeld, M. Xu, C. S. Jacobsen, L. Keller, K. Lefmann, and S. Mørup. Interparticle interactions in composites of nanoparticles of ferrimagnetic (γ-Fe₂O₃) and antiferromagnetic (CoO, NiO) materials. *Phys. Rev. B*, 70:134416, 2004.
- [104] A. Juhin, A. López-Ortega, M. Sikora, C. Carvallo, M. Estrader, S. Estradé, F. Peiró, M. D. Baró, Ph. Sainctavit, P. Glatzel, and J. Nogués. Direct evidence for an interdiffused intermediate layer in bi-magnetic core-shell nanoparticles. *Nanoscale*, 6:11911, 2014.
- [105] E. Skoropata, R. D. Desautels, C.-C. Chi, H. Ouyang, J. W. Freeland, and J. van Lierop. Magnetism of iron oxide based core-shell nanoparticles from interface mixing with enhanced spin-orbit coupling. *Phys. Rev. B*, 89:024410, 2014.
- [106] B. Morosin. Exchange striction effects in MnO and MnS. Phys. Rev. B, 1:236– 243, 1970.
- [107] R. Popescu, P. Leidinger, C. Kind, C. Feldman, and D. Gerthsen. Structure of

hollow spheres analyzed by x-ray diffraction, transmission electron microscopy, and dynamic light scattering. J. Nanopart. Res., 15:1648, 2013.

- [108] A. Ullrich, S. Hohenberger, A. 'Ozden, and S. Horn. Synthesis of iron oxide/manganese oxide composite particles and their magnetic properties. J. Nanopart. Res., 16:2580, 2014.
- [109] E. Skoropata and J. van Lierop. Characterization of magnetism in core-shell nanoparticles. In Challa S.S.R. Kumar, editor, *Magnetic Characterization Techniques for Nanomaterials*, pages 375–412. Springer Science + Business Media, Berlin, Heidelberg, 2017.
- [110] J. van Lierop and D. H. Ryan. Mössbauer spectra of single-domain fine particle systems described using a multiple-level relaxation model for superparamagnets. *Phys. Rev. B*, 63:064406, 2001.
- [111] Y. J. Tang, D. J. Smith, B. Z. Zink, F. Hellman, and A. E. Berkowitz. Finite size effects on the moment and ordering temperature in antiferromagnetic CoO layers. *Phys. Rev. B.*, 67:054408, 2003.
- [112] S. A. Majetich. private communication.
- [113] P. Morall, F. Schedin, G. S. Case, M. F. thomas, E. Dudzik, G. van der Laan, and G. Thornton. Stoichiometry of Fe_{3-δ}O₄(111) ultrathin films on Pt(111). *Phys. Rev. B*, 67:214408, 2003.
- [114] S. P. Cramer, F. M. F. de Groot, Y. Ma, C. T. Chen, F. Sette, C. A. Kipke, D. M. Eichhorn, M. K. Chan, W. H. Armstrong, E. Libby, G. Christou, S. Brooker,

V. McKee, O. C. Mullins, and J. C. Fuggle. Ligand Field Strengths and Oxidation States from Manganese L-Edge Spectroscopy. J. Am. Chem. Soc., 113:7937–7940, 1991.

- [115] C. Mitra, Z. Hu, P. Raychaudhuri, S. Wirth, S. I. Csiszar, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng. Direct observation of electron doping in La_{0.7}Ce_{0.3}MnO₃ using x-ray absorption spectroscopy. *Phys. Rev. B*, 67:092404, 2003.
- [116] V. Bayer, R. Podloucky, C. Franchini, F. Allegretti, B. Xu, G. Parteder, M. G. Ramsey, S. Surnev, and F. P. Netzer. Formation of Mn₃O₄ (001) on MnO(001):
 Surface and interface structural stability. *Phys. Rev. B*, 76:165428, 2007.
- [117] L. A. J. Garvie, A. J. Craven, and R. Brydson. Use of electron-energy loss near-edge fine structure in the study of minerals. *Amer. Mineral.*, 79:411, 1994.
- [118] B. Gilbert, B. H. Frazer, A. Belz, P. G. Conrad, K. H. Nealson, D. Haskel, J. C. Lang, G. Srajer, and G. De Stasio. Multiple Scattering Calculations of Bonding and X-ray Absorption Spectroscopy of Manganese Oxides. J. Phys. Chem. A, 107:2839–2847, 2003.
- [119] M. Khan, E. Suljoti, A. Singh, S. A. Bonke, T. Brandenburg, K. Atak, R. Golnak, L. Spiccia, and E. F. Aziz. Electronic structural insights into efficient MnO_x catalysts. J. Mater. Chem. A, 2:18199–18203, 2014.
- [120] H.-J. Noh, S. Yeo, J.-S. Kang, C. L. Zhang, S.-W. Cheong, S.-J. Oh, and P. D.

Johnson. Jahn-Teller effect in spinel manganites probed by soft x-ray absorption spectroscopy. *Appl. Phys. Lett.*, 88:081911, 2006.

- [121] M. Ghiasi, M. U. Delgado-Jaime, A. Malekzadeh, R.-P. Wang, P. S. Miedema,
 M. Beye, and F. M. F. de Groot. Mn and Co Charge and Spin Evolutions in LaMn_{1-x}Co_xO₃ Nanoparticles. J. Phys. Chem. C, 120:8167–8174, 2016.
- [122] K. Kuepper, M. Raekers, C. Taubitz, M. Uhlarz, C. Piamonteze, F. M. F. de Groot, E. Arenholz, V. R. Galakhov, Ya M. Mukovskii, and M. Neumann. The x-ray magnetic circular dichroism spin sum rule for 3d⁴ systems: Mn³⁺ ions in colossal magnetoresistance manganites. J. Phys.: Condens. Matter, 24:435602, 2012.
- [123] F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky. $L_{2,3}$ x-ray absorption edges of d^0 compounds: K⁺ Ca²⁺, Sc²⁺, and Ti⁴⁺ in O_h (octahedral) symmetry. *Phys. Rev. B*, 41:928, 1990.
- [124] H. J. Lee, G. Kim, D. H. Kim, J.-S. Kang, C. L. Zhang, S.-W. Cheong, J. H. Shim, S. Lee, H. Lee, J.-Y. Kim, B. H. Kim, and B. I. Min. Valence states and occupation sites in (Fe,Mn)₃O₄ spinel oxides investigated by soft x-ray absorption spectroscopy and magnetic circular dichroism. J. Phys. Condens. Matter, 20:295203, 2008.
- [125] S. Matzen, J.-B. Moussy, R. Mattana, K. Bouzehouane, C. Deranlot, F. Petroff,
 J. C. Cezar, M.-A. Arrio, Ph. Sainctavit, C. Gatel, B. Warot-Fonrose, and
 Y. Zheng. Epitaxial growth and ferrimagnetic behavior of MnFe₂O₄(111) ul-

trathin layers for room-temperature spin filtering. *Phys. Rev. B*, 83:184402, 2011.

- [126] P. Ghigna, A. Campana, A. Lascialfari, A. Caneschi, D. Gatteschi, A. Tagliaferri, and F. Borgatti. X-ray magnetic-circular-dichroism spectra on the superparamagnetic transition-metal ion clusters Mn12 and Fe8. *Phys. Rev. B*, 64:132413, 2001.
- [127] A. López-Ortega, M. Etrader, G. Salazar-Alvarez, S. Estradé, I. V. Golosovsky, R. K. Dumas, D. J. Keaveny, M. Vasilakaki, K. N. Trouhidou, J. Sort, F. Pieró, S. Suriñach, M. D. Baró, and J. Nogués. Strongly exchange coupled inverse ferrimagnetic soft/hard Mn_xFe_{3-x}O₄/Fe_xMn_{3-x}O₄ core/shell heterostructured nanoparticles. *Nanoscale*, 4:5138, 2012.
- [128] C. L. Chen, C. L. Dong, G. Chern, K. Kumar, H. J. Lin, C. T. Chen, C. L. Chang, and A. Fujimori. Direct spectroscopic identification of the magnetic structure of the interface of Mn₃O₄/Fe₃O₄ superlattices. J. Alloys Compd., 614:177–181, 2014.
- [129] J.-S. Kang, G. Kim, H. J. Lee, D. H. Kim, H. S. Kim, J. H. Shim, S. Lee, Hangil Lee, J.-Y. Kim, B. H. Kim, and B. I. Min. Soft x-ray absorption spectroscopy and magnetic circular dichroism study of the valence and spin states in spinel. *Phys. Rev. B*, 77:035121, 2008.
- [130] S. Suga and S. Imada. Magnetic dichroism in core absorption and photoemission. J. Electr. Spec. Rel. Phenom., 92:1–9, 1998.

- [131] C. Chen, M. Wu, G. Chern, H. Lin, and C. Chang. Temperature Dependent XMCD Studies on the Magnetic Properties of Mn₃O₄/Fe₃O₄ Superlattice. In *INTERMAG 2006 - IEEE Int. Magn. Conf.*, pages 817–817. IEEE, 2006.
- [132] J. Nogués, G. Salazar-Alvarez, M. Estrader, A. Lopez-Ortega, and J. Sort. Magnetic coupling between layers of bi-magnetic core-shell nanoparticles. Technical report, European Synchrotron Radiation Facility, 01 2011.
- [133] P. J. van der Zaag, A. Noordermeer, M. T. Johnson, and P. F. Bongers. Comment on "Size-dependent Curie temperature in nanoscale". *Phys. Rev. Lett.*, 68:3112–3112, 1992.
- [134] I. S. Jacobs. Evidence for triangular moment arrangements in Mn·Mn₂O₃. J. Phys. Chem. Solids, 11:1–11, 1959.
- [135] R. C. O'Handley. *Modern magnetic materials*. Wiley, New York, 2000.
- [136] M. P. Sharrok, P. J. Picone, and A. H. Morrish. Mössbauer emission spectroscopy study of cobalt-surface-doped acircular magnetite particles. *IEEE Trans. Magn.*, MAG-19:1466, 1983.
- [137] G. Salazar-Alvarez, J. Sort, A. Uheida, M. Muhammed, S. Suriñach, M. D. Baró, and J. Nogués. Reversible post-synthesis tuning of the superparamagnetic blocking temperature of γ-Fe₂O₃ nanoparticle by adsorption and desorption of Co(II) ions. J. Mater. Chem., 17:322–328, 2007.
- [138] C. Fransden, C. W. Ostenfeld, M. Xu, C. S. Jacobsen, L. Keller, K. Lefmann, and S. Mørup. Interparticle interactions in composites of nanoparticles of ferri-

magnetic (γ -Fe₂O₃O) and antiferromagnetic (CoO, NiO) materials. *Phys. Rev.* B, 70:134416, 2004.

- [139] F. T. Parker, M. W. Foster, D. T. Margulies, and A. E. Berkowitz. Spin canting, surface magnetization, and finite-size effects in γ-Fe₂O₃ particles. *Phys. Rev. B*, 47:7885–7891, 1993.
- [140] E. De Grave, R. M. Persoons, R. E. Vandenberghe, and P. M. A. de Bakker. Mössbauer study of the high temperature phase of Co-substituted magnetites, $Co_x Fe_{3-x}O_4$. I. $x \leq 0.04$. Phys. Rev. B, 47:5881–5893, 1993.
- [141] R. M. Persoons, E. De Grave, P. M. A. de Bakker, and R. E. Vandenberghe. Mössbauer study of the high temperature phase of Co-substituted magnetites, Co_xFe_{3-x}O₄. II. x ≥ 0.1. Phys. Rev. B, 47:5894–5905, 1993.
- [142] F. M. F. de Groot, M. Abbate, J. van Elp, G. A. Sawatzky, Y. J. Ma, C. T. Chen, and F. Sette. Oxygen 1s and cobalt 2p x-ray absorption of cobalt oxides. *J. Phys.: Condens. Matter*, 5:2277–2288, 1993.
- [143] F. Zheng, S. Alayoglu, J. Guo, V. Pushkarev, Y. Li, P.-A. Glans, J.-L. Chen, and G. Somorjai. In-situ x-ray absorption study of evolution of oxidation states and structure of cobalt in Co and CoPt bimetallic nanoparticles (4nm) under reducing (H₂) and oxidizing (O₂) environments. *Nano Lett.*, 11:847–853, 2011.
- [144] J. W. Freeland. private communication.
- [145] E. Fantechi, G. Campo, D. Carta, A. Corrias, C. de Julián Fernández,D. Getteschi, C. Innocenti, E. Pineider, F. Rugi, and C. Sangregorio. Explor-

ing the effect of Co doping in fine maghemite nanoparticles. J. Phys. Chem. C, 116:8261–8270, 2012.

- [146] G. van der Laan, E. Arenholz, R. V. Chopdekar, and Y. Suzuki. Influence of crystal field on anisotropic x-ray magnetic linear dichroism at the Co²⁺ L_{2,3} edges. *Phys. Rev. B*, 77:064407, 2008.
- [147] J. C. Slonczewski. Origin of magnetic anisotropy in cobalt-substituted magnetite. *Phys. Rev.*, 110:1341, 1958.
- [148] A. M. Mulders, H. Loosvelt, A. Fraile Rodríguez, E. Popova, T. Konishi, K. Temst, O. Karis, D. Arvantis, and C. van Haesendonck. On the interface magnetism of thin oxidized Co films: orbital and spin moments. J. Phys.:Condens. Matter, 21:124211, 2009.
- [149] J. A. Moyer, D. P. Kumah, C. A. F. Vaz, D. A. Arena, and V. E. Henrich. Role of epitaxial strain on the magnetic structure of Fe-doped CoFe₂O₄. J. Magn. Magn. Mater., 345:180–189, 2013.
- [150] V. N. Antonov, B. N. Harmon, and A. N. Yaresko. Electronic structure and x-ray magnetic circular dichroism in Fe₃O₄ and Mn-, Co-, or Ni-substituted Fe₃O₃. *Phys. Rev. B.*, 67:024417, 2003.
- [151] H. Béa, M. Bibes, S. Fusil, K. Bouzehouane, E. Jacquet, K. Rode, P. Bencok, and A. Barthélémy. Investigation on the origin of the magnetic moment of BiFeO₃ thin films by advanced x-ray characterizations. *Phys. Rev. B.*, 74:020101(R), 2006.

- [152] R. A. McCurrie. Ferromagnetic Materials Structure and Properties. Academic Press, London, 1994.
- [153] G. A. Sawatzky, F. van der Woude, and A. H. Morrish. Cation distributions in octahedral and tetrahedral sites of the ferrimagnetic spinel CoFe₂O₄. J. Appl. Phys., 39:1204–1205, 1968.
- [154] H. Ohldag, T. J. Regan, J. Stöhr, A. Scholl, F. Nolting, J. Lüning, C. Stamm, S. Anders, and R. L. White. Spectroscopic identification and direct imaging of interfacial magnetic spins. *Phys. Rev. Lett.*, 87:247201, 2001.
- [155] A. E. Berkowitz, J.-I. Hong, S. K. McCall, E. Shipton, K. T. Chan, T. Leo, and D. J. Smith. Refining the exchange anisotropy paradigm: Magnetic and microstructural heterogeneity at the permalloy-CoO interface. *Phys. Rev. B*, 81:134404, 2010.
- [156] Y. Fan, K.J. Smith, G. Lüpke, A.T. Hanbicki, R. Goswami, C.H. Li, H.B. Zhao, and B.T. Jonker. Exchange bias of the interface spin system at the Fe/MgO interface. *Nature nanotechnology*, 8:438–444, 2013.
- [157] C.-C. Chi, C.-H. Hsiao, E. Skoropata, J. van Lierop, and H. Ouyang. Transmission electron microscopy and ab initio calculations to relate interfacial intermixing and the magnetism of core/shell nanoparticles. J. Appl. Phys., 117:17E135, 2015.
- [158] C.-C. Chi. Investigation of relations between the interface microstructures and

the magnetism of γ -Fe₂O₃/CoO core/shell nanoparticles. PhD thesis, National Tsing Hua University, 2014.

- [159] E. J. Kirkland. Advanced computing in electron microscopy. Springer, New York, USA, 2 edition, 2010.
- [160] G. D. Reid. Multislice simulation of TEM images. BSc thesis, Acadia University, 2012.
- [161] MacTempas, Total Resolution (www.totalresolution.com).
- [162] L. L. Chang. The junction depth of concentration-dependent diffusion. zinc in III-V compounds. Solid State Electron., 7:853–859, 1964.
- [163] A. Nakamura, S. Yamaguchi, K. Fueki, and T. Mukaibo. Vacancy diffusion in magnetite. J. Phys. Chem. Solids, 39:1203, 1978.
- [164] W. K. Chen, N. L. Peterson, and W. T. Reeves. Isotope effect for cation selfdiffusion in CoO crystals. *Phys. Rev.*, 186:887, 1969.
- [165] A. Atkinson and R. I. Taylor. Diffusion of ⁵⁵Fe in Fe₂O₃ single crystals. J. Phys. Chem. Solids, 46:469, 1985.
- [166] K. Hoshino and N. L. Peterson. Cation self-diffusion and the isotope effect in Fe₂O₃. J. Phys. Chem. Solids, 46:375, 1985.
- [167] F. Morales, F. M. F. de Groot, P. Glatzel, E. Kleimenov, H. Bluhm, M. Hävecker, A. Knop-Gericke, and B. M. Weckhuysen. In situ x-ray absorption of Co/Mn/TiO₂ catalysts for Fischer-Tropsch synthesis. J. Phys. Chem. B, 108:16201–16207, 2004.

- [168] R. Morrow, J. Yan, M. A. McGuire, J. W. Freeland, D. Haskel, and P. M. Woodward. Effects of chemical pressure on the magnetic ground states of the osmate double perovskites SrCaCoOsO₆ and Co₂CoOsO₆. *Phys. Rev. B*, 92:094435, 2015.
- [169] D. Carta, A. Corrias, A. Falqui, R. Brescia, E. Fantechi, F. Pineider, and C. Sangregorio. EDS, HRTEM/STEM, and x-ray absorption spectroscopy studies of Co-substituted maghemite nanoparticles. J. Phys. Chem. C, 117:9496–9506, 2013.
- [170] E. de Grave, R. Leyman, and R. Vanleerberghe. The coordination of Co²⁺ ions in Co substituted magnetites Fe_{3-x}Co_xO₄ with x ≤0.04. Phys. Lett., 97A:354– 356, 1983.
- [171] R. M. Persoons, E. De Grave, and R. E. Vandenberghe. Mössbauer study of Co-substituted magnetite. *Hyperfine Interact.*, 54:655–660, 1990.
- [172] R. Mathieu, J. A. De Toro, D. Salazar, S. S. Lee, J. L. Cheong, and P. Nordblad. Phase transition in a super superspin glass. *Europhys. Lett.*, 102:67002, 2013.
- [173] J. A. De Toro, S. S. Lee, D. Salazar, J. L. Cheong, P. S. Normile, P. Muñiz, J. M. Riveiro, M. Hillenkamp, F. Tournus, A. Tamion, and P. Nordblad. A nanoparticle replica of the spin-glass state. *Appl. Phys. Lett.*, 102:183104, 2013.
- [174] M. S. Andersson, R. Mathieu, P. S. Normile, S. S. Lee, G. Singh, P. Nordblad, and J. A. D. Toro. Particle size-dependent superspin glass behavior in ran-

dom compacts of monodisperse maghemite nanoparticles. *Mater. Res. Express*, 3:045015, 2016.

- [175] K. Takano, R. H. Kodama, A. E. Berkowitz, W. Cao, and G. Thomas. Interfacial uncompensated antiferromagnetic spins: Role in unidirectional anisotropy in polycrystalline Ni₈₁Fe₁₉/CoO bilayers. *Phys. Rev. Lett.*, 79:1130–1133, 1997.
- [176] H. Ohldag, A. Scholl, F. Nolting, E. Arenholz, S. Maat, A. T. Young, M. Carey, and J. Stöhr. Correlation between exchange bias and pinned interfacial spins. *Phys. Rev. Lett.*, 91:017203, 2003.
- [177] R. K. Zheng, G. H. Wen, K. K. Fung, and X. X. Zhang. Giant exchange bias and the vertical shifts of hysteresis loops in γ-Fe₂O₃-coated Fe nanoparticles. J. Appl. Phys., 95:5244–5246, 2004.
- [178] Q. K. Ong, X.-M. Lin, and A. Wei. Role of frozen spins in the exchange anisotropy of core-shell Fe@Fe₃O₄ nanoparticles. The Journal of Physical Chemistry C, 115:2665–2672, 2011.
- [179] D. De, O. Iglesias, S. Majumdar, and S. Giri. Probing core and shell contributions to exchange bias in Co/Co₃O₄ nanoparticles of controlled size. *Phys. Rev. B*, 94:184410, 2016.
- [180] E. C. Sousa, H. R. Rechenberg, J. Depeyrot, J. A. Gomes, R. Aquino, F. A. Tourinho, V. Dupuis, and R. Perzynski. In-field mossbauer study of disordered surface spins in core/shell ferrite nanoparticles. J. Appl. Phys., 106:093901, 2009.

- [181] V. G. Bhide and M. S. Hegde. Mössbauer effect for ⁵⁷Fe in ferroelectric lead titanate. *Phys. Rev. B*, 5:3488–3499, 1972.
- [182] F.M.F. De Groot, M. Grioni, J.C. Fuggle, J. Ghijsen, G.A Sawatzky, and H. Petersen. Oxygen 1s x-ray-absorption edges of transition-metal oxides. *Phy. Rev.* B, 40(8):5715–5723, 1989.
- [183] E. Goering, S. Gold, M. Lafkioti, G. Schütz, and V. A. M. Brabers. Oxygen K-edge shift at the Verwey transition of magnetite. *Phys. Rev. B*, 72:033112, 2005.
- [184] I. Leonov, A. N. Yaresko, V. N. Antonov, and V. I. Anisimov. Electronic structure of charge-ordered Fe₃O₄ from calculated optical, magneto-optical kerr effect, and O K-edge x-ray absorption spectra. *Phys. Rev. B*, 74:165117, 2006.
- [185] B. Gilbert, J. E. Katz, J. D. Denlinger, Y. Yin, R. Falcone, and G. A. Waychunas. Soft x-ray spectroscopy study of the electronic structure of oxidized and partially oxidized magnetite nanoparticles. J. Phys. Chem. C, 114(50):21994– 22001, 2010.
- [186] S. Zhou, K. Potzger, Q. Xu, K. Kuepper, G. Talut, D. Markó, A. Mücklich, M. Helm, J. Fassbender, E. Arenholz, and H. Schmidt. Spinel ferrite nanocrystals embedded inside ZnO: Magnetic, electronic, and magnetotransport properties. *Phys. Rev. B*, 80:094409, 2009.
- [187] J. van Elp, J. L. Wieland, H. Eskes, P. Kuiper, G. A. Sawatzky, F. M. F.

de Groot, and T. S. Turner. Electronic structure of CoO, Li-doped CoO, and LiCoO₂. *Phys. Rev. B*, 44:6090–6103, 1991.

- [188] C. A. Roberts. private communication.
- [189] Z. Y. Wu, S. Gota, F. Jollet, M. Pollak, M. Gautier-Soyer, and C. R. Natoli. Characterization of iron oxides by x-ray absorption at the oxygen K edge using a full multiple-scattering approach. *Phys. Rev. B*, 55:2570–2577, 1997.
- [190] G. Cao, Y. Li, R. Ma, and G. Wang. Study of lattice softening on a Bi-system superconductor. *Physica C: Superconductivity*, 205:133 – 138, 1993.
- [191] T. G. Reddy, A. Gupta, and K. R. Reddy. ¹⁵¹Eu Mössbauer studies on La_{0.46}Eu_{0.21}Ca_{0.33}MnO₃ CMR system. *Chem. Phys. Lett.*, 476:209–212, 2009.
- [192] L. Paolasini, G. H. Lander, S. M. Shapiro, R. Caciuffo, B. Lebech, L.-P. Regnault, B. Roessli, and J-M. Fournier. Magnetic excitations in the itinerant ferromagnet UFe₂. *Phys. Rev. B*, 54:7222–7232, 1996.
- [193] L. S. Lingam and K. N. Shrivastava. Reduction of the recoilless fraction of the Mössbauer spectra in superconductors. J. Phys.: Condens. Matter, 7(16):L231– L234, 1995.
- [194] A. Kozlowski, Z. Kackol, D. Kim, R. Zalecki, and J. M. Honig. Heat capacity of $\text{Fe}_{3-\delta}M_{\alpha}O_4$ (M = Zn, Ti, $0 \le \alpha \le 0.04$). *Phys. Rev. B*, 54:12093–12098, 1996.
- [195] K. Sharma, V. R. Reddy, A. Gupta, S. D. Kaushik, and V. Siruguri. Anomalous

variation of the Lamb–Mössbauer factor at the magnetic transition temperature in magnetoelectric GaFeO₃. J. Phys.: Condens. Matter, 24:376001, 2012.

- [196] H. J. Silverstein, E. Skoropata, P. M. Sarte, C. Mauws, A. A. Aczel, E. S. Choi, J. van Lierop, C. R. Wiebe, and H. Zhou. Incommensurate crystal supercell and polarization flop observed in the magnetoelectric ilmenite MnTiO₃. *Phys. Rev. B*, 93:054416, 2016.
- [197] F. Neese. Prediction and interpretation of the ⁵⁷Fe isomer shift in Mössbauer spectra by density functional theory. *Inorg. Chim. Acta*, 337:181–192, 2002.
- [198] A. Sadoc, R. Broer, and C. de Graaf. CASSCF study of the relation between the Fe charge and the Mössbauer isomer shift. *Chem. Phys. Lett.*, 454:196–200, 2008.
- [199] M. Filatov. First principles calculation of mössbauer isomer shift. Coordin. Chem. Rev., 253(5):594–605, 2009.
- [200] G.A. Sawatzky, W. Geertsma, and C. Haas. Magnetic interactions and covalency effects in mainly ionic compounds. J. Magn. Magn. Mater., 3:37–45, 1976.
- [201] R. J. Choudhary, Shailja Tiwari, D. M. Phase, Ravi Kumar, P. Thakur, K. H. Chae, and W. K. Choi. Magnetotransport, noise, and x-ray magnetic circular dichroism studies of pulsed laser deposited Fe₃O₄ film on Si substrates. *Appl. Phys. Lett.*, 92(7):072102, 2008.
- [202] E. J. Goering, M. Laftkioti, S. Gold, and G. Schuetz. Absorption spectroscopy

and XMCD at the Verwey transition of Fe₃O₄. J. Magn. Magn. Mater., 310:e249–e251, 2007.

- [203] D. Schrupp, M. Sing, M. Tsunekawa, H. Fujiwara, S. Kasai, A. Sekiyama, S. Suga, T. Muro, V. A. M. Brabers, and R. Claessen. High-energy photoemission on Fe₃O₄: Small polaron physics and the Verwey transition. *Europhys. Lett.*, 70:789, 2005.
- [204] R. M. Persoons and E. De Grave. On the Verwey transition in cobalt-substituted magnetite as determined by ⁵⁷Fe Mössbauer spectroscopy. *Solid State Commun.*, 72:977–980, 1989.
- [205] M. Monti, B. Santos, A. Mascaraque, O. Rodríguez de la Fuente, M. A. Niño,
 T. O. Menteş, A. Locatelli, K. F. McCarty, J. F. Marco, and J. de la Figuera.
 Magnetism in nanometer-thick magnetite. *Phys. Rev. B*, 85:020404(R), 2012.
- [206] G. Lavorato, E. Winkler, B. Rivas-Murias, and F. Rivadulla. Thickness dependence of exchange coupling in epitaxial Fe₃O₄/CoFe₂O₄ soft/hard magnetic bilayers. *Phys. Rev. B*, 94:054405, 2016.
- [207] Y.-C. Tseng, N. M. Souza-Neto, D. Haskel, M. Gich, C. Frontera, A. Roig,
 M. van Veenendaal, and J. Nogués. Nonzero orbital moment in high coercivity ε Fe₂O₃ and low-temperature collapse of the magnetocrystalline anisotropy. *Phys. Rev. B*, 79:094404, 2009.
- [208] B. Handke, A. Kozlowski, K. Parliński, J. Przewoźnik, T. Ślezak, A. I. Chumakov, L. Niesen, Z. Kakol, and J. Korecki. Experimental and theoretical

studies of vibrational density of states in Fe_3O_4 single-crystalline thin films. *Phys. Rev. B*, 71:143301, 2005.

- [209] J. De La Venta, M. Erekhinsky, S. Wang, K. G. West, R. Morales, and I. K. Schuller. Exchange bias induced by the Fe₃O₄ Verwey transition. *Phys. Rev. B*, 85:134447, 2012.
- [210] K. S. Irani, A. P. B. Sinha, and A. B. Biswas. Effect of temperature on the structure of manganites. J. Phys. Chem. Solids, 23(6):711–727, 1962.
- [211] E. Winkler, R. D. Zysler, M. Vasquez Mansilla, and D. Fiorani. Surface anisotropy effects in NiO nanoparticles. *Phys. Rev. B*, 72:132409, 2005.
- [212] E. Winkler, R. D. Zysler, M. Vasquez Mansilla, D. Fiorani, D. Rinaldi, M. Vasilakaki, and K. N. Trohidou. Surface spin-glass freezing in interacting core-shell NiO nanoparticles. *Nanotechnology*, 19:185702, 2008.
- [213] N. Rinaldi-Montes, P. Gorria, D. Martínez-Blanco, A. B. Fuertes, L. Fernández Barquín, I. Puente-Orench, and J. A. Blanco. Scrutinizing the role of size reduction on the exchange bias and dynamic magnetic behavior in NiO nanoparticles. *Nanotechnology*, 26:305705, 2015.
- [214] K. Dwight and N. Menyuk. Magnetic Properties of Mn₃O₄ and the canted spin problem. *Phys. Rev.*, 119:1470–1479, 1960.
- [215] D. Carta, M. F. Casula, A. Falqui, D. Loche, G. Mountjoy, C. Sangregorio, and A. Corrias. A Structural and Magnetic Investigation of the Inversion De-

gree in Ferrite Nanocrystals MFe_2O_4 (M = Mn, Co, Ni). J. Phys. Chem. C, 113(20):8606-8615, may 2009.

- [216] E. G. Sousa, M. H. Sousa, G. F. Goya, H. R. Rechenberg, M. C. F. L. Lara, F. A. Tourinho, and J. Depeyrot. Enhanced surface anisotropy evidenced by Mössbauer spectroscopy in nickel ferrite nanoparticles. J. Magn. Magn. Mater., 272-276:E1215–E1217, 2004.
- [217] H. Nathani, S. Gubbala, and R.D.K. Misra. Magnetic behavior of nanocrystalline nickel ferrite. *Mater. Sci. Eng. B*, 121:126–136, 2005.
- [218] G. Muscas, N. Yaacoub, G. Concas, F. Sayed, R. Sayed Hassan, J. M. Greneche, C. Cannas, A. Musinu, V. Foglietti, S. Casciardi, C. Sangregorio, and D. Peddis. Evolution of the magnetic structure with chemical composition in spinel iron oxide nanoparticles. *Nanoscale*, 7:13576–13585, 2015.
- [219] J. Chen, C. Sorensen, K. Klabunde, G. Hadjipanayis, E. Devlin, and a. Kostikas. Size-dependent magnetic properties of MnFe₂O₄ fine particles synthesized by coprecipitation. *Phys. Rev. B*, 54(13):9288–9296, 1996.
- [220] P. J. van der Zaag, V. A. M. Brabers, M. T. Jonson, A. Noordermeer, and P. F. Bongers. Comment on "Particle-size effects on the value of T_C of MnFe₂O₄: Evidence for finite-size scaling". *Phys. Rev. B*, 51:12009–12010, 1995.
- [221] F. Keffer and W. O'Sullivan. Problem of spin arrangements in MnO and similar antiferromagnets. *Phys. Rev.*, 108:637–644, 1957.