November 2021

Spin Coupling in Magnetic Core - Shell Nanoparticles

Corisa Kons
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Spin Coupling in Magnetic Core - Shell Nanoparticles

by

Corisa Kons

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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Date of Approval:
October 29, 2021

Keywords: Nanostructures, Neutrons, X-ray, Spin Canting, Spinels

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This dissertation is dedicated to my cats, Upgrade and Thunder Paws, who taught me the importance of saving this document repeatedly and often. Their unconditional love and support was invaluable during this time, as were the constant dinnertime reminders.
Acknowledgments

First and foremost, I would like to thank my advisor Prof. Darío A. Arena for his patience and guidance throughout the Ph.D process and helping me to develop my skills as a researcher. I talk too much and ask a lot of questions but he always (patiently) took the time to answer them. He didn’t share my passion for cheesy horror movies but I didn’t enjoy his green tea flavored mints so we’ll call it even. I would also like to thank my committee members Dr. Manh-Huong Phan, Dr. Sherwin Kouchekian, and Dr. Sarath Witanachchi for evaluating my progress as a Ph.D candidate and a researcher. Thank you to Dr. Kouchekian for supporting my dream of becoming a ”mediocre” scientist and never letting me give up on that over the years. Jenae Shoup and I were the first students in the lab, she was instrumental in getting the lab setup as well as providing her friendship and knowledge over the years; I wish her the best of luck in her own endeavors.

I would be remiss to not acknowledge our collaborators over the years, especially Dr. Julie Borchers and Dr. Kathryn Krycka at NIST. They have been invaluable in their assistance with the neutron measurements and analysis. The amount of patience and knowledge they’ve shared with me over the years is humbling; I hope one day to be the kind of inspiration and scientist they are. Credit to our Uppsala collaborators, Dr. Nikolaos Ntallis and Dr. Manuel Pereiro, who did all the micromagnetic simulations for the Fe and Co-ferrite project that lead to very interesting results. I would also like to thank Dr. Raja Das who assisted Supun and I with the doped Co ferrite project all the way from Vietnam and has always taken the time to answer my questions about the synthesis process. I would also like to thank my sample growers from Dr. Phan and Dr. Srikanth’s lab for providing me with things to measure over the years, would’ve been very dull otherwise; Dr. Zohre Nemati, Joshua Robles, and Supun B. Attanayake were all instrumental in the projects over the years.

Send all my appreciation to the USF Physics department faculty; Daisy Matos, Jimmy Suarez and James Kersey for their hard-work and dedication to keeping this department operating at peak efficiency. I also enjoyed James’ emails along the way and seriousness he brought to the program. They all provided me
with the tools I needed to successfully complete my PhD. I would also like to thank old and new friends for their support during my time in graduate school. We have a nice little community in the physics department and I’m very appreciative of the time spent getting to know everyone. I liked most of you. In no particular order of importance and based solely on who I remembered first; Danish, Jaspreet, Nivarthena, Terry, Noah, Joshua, Abibat (best dressed), Alok, Arup, Domingo, different Greg, Yen, Kai, Qixing, Sookie, Kristen Repa (sweetest lady alive and great baker), Mahesh, Maja, Manuel, Mark, Nalaka, Noha, Paul, Temitope (almost best dressed), Vijay, and the duo Hana & Zach. I’m sure I’ve forgotten some people but all of you, named or not, had an impact on my time at USF and I will forever be grateful for the time we spent together. I’ve only just meet Yasith but I think he’ll be a good replacement for Jaspreet.

Special shout outs go to Dr. Yamil Nieves, Dr. (Juan) Sebastian Gomez Velez, Greg Salazar, Olga Harrington, and Dr. Brian Casas who I met early on in graduate school and shared many classes and informative discussions with. The social bee of the department, Dr. Ellie Clements, who always made sure our social calendars were full and for her roll as patron saint of Castle. Dr. Zohre Nemati, Dr. Richa Madhogaria, Dr. Ghanim Ullah, (soon to be Dr.) Valery Ortiz Jimenez, (soon to be Dr.) Varun Mapara, and Kanchana (too many last names) Karunarathne for their friendship over the years; I couldn’t imagine graduate school without their support and Dr. Ullah’s infinite cow wisdom. Although a relatively recent addition to my life I would like to thank Farjad Shafighi who provided support when I needed it most; whether that was in the form of comforting words, sweet cheeks, or labneh I’m grateful for it all.
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<td>CoFe$_2$O$_4$</td>
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<td>FC</td>
<td>Field Cooled</td>
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<tr>
<td>FO</td>
<td>Fe$_3$O$_4$</td>
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<tr>
<td>HF</td>
<td>High Field</td>
</tr>
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<td>mSLD</td>
<td>Magnetic Scattering Length Density</td>
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<tr>
<td>NP</td>
<td>Nanoparticle(s)</td>
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<td>RT</td>
<td>Room Temperature</td>
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<td>SLD</td>
<td>Scattering Length Density</td>
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<td>SPM</td>
<td>Superparamagnetic</td>
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<td>$T_B$</td>
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<td>X-Ray Magnetic Circular Dichroism</td>
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<td>ZF</td>
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Abstract

Magnetic nanoparticles (NPs) have garnered much interest due to the unique properties that emerge when compared to their bulk counterparts. In particular, core-shell (CS) NPs offer the ability to tailor the magnetic properties of the system through careful selection of core and shell constituent materials. In this work, the magnetic ordering of CS NPs with contrast in core/shell features (moment, anisotropy, coercivity, etc.) have been investigated using a combination of X-ray magnetic circular dichroism spectroscopy (XMCD) and polarized small angle neutron scattering (SANS). First, temperature-dependent analyses of XMCD and SANS studies were carried out for CS NPs featuring a core composed of metallic α-Fe paired with an Fe-oxide shell, and a variant NP structure with a reduced α-Fe core followed by a partial void layer surrounded by an Fe-oxide shell (CVS).

Next, the effect magnetically hard and soft materials have on spin coupling throughout a NP was explored by means of fully polarized SANS analyses of NPs with a hard CoFe\textsubscript{2}O\textsubscript{4}-core and soft Fe\textsubscript{3}O\textsubscript{4}-shell (core @ shell, CFO@FO) as well as the inverted structure with a Fe\textsubscript{3}O\textsubscript{4}-core and CoFe\textsubscript{2}O\textsubscript{4}-shell (FO@CFO). Large anisotropy differences between the core and shell will play a significant role in the degree of spin canting across the NP. The existence of a Bragg peak for neutron scattering perpendicular to the applied magnetic field (H) suggests the presence of spin canting in both CFO/FO NP variants with the peak persisting up to applied fields of 0.4 T for CFO@FO and 0.1 T for FO@CFO NPs.

Whereas prior worked sought to find a balance between anisotropy and saturation magnetization, the final project focused on keeping anisotropy in the core constant for various shell anisotropy values all while maintaining a constant moment. This was achieved by using NPs with a FO core and doping a CFO shell with increasing amounts of Zn; recent work has shown that while saturation magnetization is similar for various doping levels the shell anisotropy increases linearly with Co concentration. The magnetic ordering was explored using polarized SANS to probe spin distributions throughout the NP as a function of Zn doping concentration.
Chapter 1
Introduction

1.1 Motivation

Advances in synthesis techniques allow for a high degree of control over the size, shape, structure and composition of particles in the nanometer region which has greatly expanded interest in materials at this size [1, 2, 3, 4]. Composite nanoparticles (NPs) composed of an inner material and at least one surrounding layer are known as core-shell (CS) structures; they come in a variety of sizes and shape but are most common with a spherical structure. Such nanostructures offer the unique advantage of being able to tune a range of properties through selection of the constituent materials in the core and shell (C@S) making them useful for many applications [5, 6, 7]. Most notable of those would be in the biomedical area where magnetic CS NPs are commonly investigated for hyperthermia cancer therapy [8, 9]. Although these layered NPs can overcome many challenges posed by single particles such as low magnetic moments or poor heating efficiency, new challenges arise due to the interaction of the two or more layers [10, 11].

It’s not easy to predict what the magnetic properties of a CS NP will look like, for example, it’s not as simple as adding the magnetic moment of the core material plus the moment of the shell material. The interaction of spins near the interface between the two layers can lead to phenomena such as exchange bias, spin canting, or spin glass behavior that will affect the overall properties of the entire NP. In the case of spin canting, individual moments are not fully aligned in the direction of an external field leading to a reduction in magnetization throughout the NP volume which is often an undesirable byproduct of composite nanostructures. Spins may be uniformly canted leading to a net, albeit reduced, magnetic moment in the volume or incoherently canted such that the spins are randomly oriented resulting in no net moment. Understanding the interfacial spin coupling effects and spin ordering in general is crucial to optimizing or enhancing the magnetic properties in CS NPs. The focus of this dissertation is to explore such spin coupling behavior by means of various experimental methods in order to gain a better understanding of magnetization in the core and shell regions and how that contributes to the overall magnetic properties.
1.2 Magnetism

The basis of magnetism centers around current sources and magnetic dipoles; a loop of current (magnetic dipole) will produce a magnetic field \( H \) oriented perpendicular to the plane of the loop \([12]\). The strength of this magnetic dipole is known as the magnetic moment and is proportional to the amount of current passing through the loop. However, there is also a second source of magnetic moments due to the intrinsic angular momentum of electrons, also called spin \([13]\) so the total moment of a magnet is due to both orbital and spin angular momentum. In some materials, an electron orbiting within the atom behaves just like a loop of current thus magnetizing the material without the need for current sources. The vector sum of all those atomic dipole moments in a given volume is known as magnetization, for most materials these dipoles are randomly oriented so the net moment is zero \([14]\).

The degree of electron pairing will also determine magnetization in the atom. Based on the Pauli exclusion principle and Hund’s rule, if an orbital is filled the two electrons will pair in such a way that they have opposite spins leading to a cancellation of the induced magnetic moments resulting from the spin or orbital motion of each electron \([15]\). If two electrons are paired they will always spin and rotate in opposite
directions of each other. If electron pairing does not occur (i.e. there is only one electron in the orbital) then the atom will have an overall magnetic moment based on the motion resulting from the unpaired electrons. The orientation of these magnetic dipoles can be tuned by placing the material in an external magnetic field where they will rotate to align or anti-align with the field thus leading to non-zero magnetization, and the magnetic response can be broadly categorized into five major groups: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism [12, 14, 16].

Another metric by which magnetic materials are classified is known as magnetic susceptibility, it is a measure of how much a material will become magnetized when placed in an applied field [17].

1.2.1 Diamagnetism

Within a material, the orbital motion of an electron around the nucleus can be viewed classically as a loop of current resulting in a magnetic moment and field. The presence of an external applied field will result in a counteraction by the internal induced field to oppose the change in magnetic flux serving to reduce the effective magnetic field of the orbiting electron [18]. In the absence of an external field, the overall magnetic moment will be zero and the magnitude of the moment will generally increase linearly with higher fields. In such situations, the magnetization induced is oppositely aligned with the external field in a phenomenon known as a diamagnetism; since it results from electron motion all materials exhibit diamagnetic response although the effect is much weaker than other forms of magnetism [19].

Diamagnetic materials have no net magnetic moment due to filled orbitals with no unpaired electrons, in the presence of an applied field the dipole moments will align anti-parallel to the field resulting in negative magnetization, as seen in Fig. 1-2.

1.2.2 Paramagnetism

Unlike diamagnetism, materials with unpaired electrons in partially occupied orbitals can experience a cooperative effect in the presence of an external applied field in a phenomenon known as paramagnetism [12]. In such substances there is no interaction between individual atomic moments and no intrinsic long range ordering of spins; the presence of an applied field will partially align the atomic dipoles leading to a net magnetic moment oriented in the direction of the field, in the absence of a field the net magnetic moment is zero. A comparison of paramagnetic and diamagnetic responses to an external field is shown in Fig. 1-2; paramagnetism leads to higher magnetization values compared to diamagnetism as well as a positive moment due the spins now being aligned in the direction of the applied field. The ability of a field
to align the atomic moments is temperature-dependent; at higher temperatures it will take a larger field (Zeeman energy) to overcome the randomizing effects of thermal energy on spin orientation and rotate the magnetic moments in the direction of the applied field [16].

1.2.3 Ferromagnetism

While paramagnetism is associated with weak or non-interacting electrons another form of magnetic response can occur when the exchange forces between atoms is quite strong. As a result of the close proximity of atoms within the crystal lattice there is an overlap of electron orbitals leading to a strong interaction between neighboring atoms known as exchange coupling. This spin-spin interaction can lead to atomic moments aligned parallel or anti-parallel to each other; the former results in non-zero magnetization even in the absence of an external field resulting in ferromagnetism [20]. Application of an external field serves to increase the degree of alignment between the moments and the field until complete collinearity is achieved and the highest induced moment is reached, known as saturation magnetization. Although the exchange forces that govern these atomic interactions are quite large, at high enough temperatures there is enough thermal energy to overcome them and weaken the degree of spin alignment; eventually, spin ordering collapses entirely and the material becomes paramagnetic; the temperature at which this occurs in known as the Curie temperature ($T_C$) [12, 16].
In the absence of a field, the alignment of atomic moments will not happen uniformly throughout the material but rather in clusters; areas where spins are in the same direction are known as domains [21]. While magnetization is uniform within the domain, each domain is not aligned with another; the number and configuration of domains will occur in such a way as to minimize the magnetostatic energy of the system [22]. Despite this spontaneous magnetization a demagnetized state is still possible for ferromagnetics if the domains are randomly oriented such that the total moment is zero. Application of higher field strengths will lead to rotation of these regions until parallellity with the field is achieved for each domain resulting in the largest induced moment possible, this is known as a magnetically saturated state as any additional field increase will not result in higher magnetization.

Unlike para- or diamagnetism, ferromagnetic materials do not display a linear relationship of magnetization with applied magnetic field, instead, a field history dependent trend known as hysteresis is observed [16]. Removal of a field after a ferromagnetic material is magnetized to saturation ($M_s$) does not lead back to the initial demagnetized state but instead the spins retain some degree of alignment at zero field, this is known as remnant magnetization ($M_r$). The field at which the net magnetization returns to zero is known as the coercive field ($H_c$), a typical hysteresis loop is shown in Fig. 1-3. Similar to paramagnetism the magnetic ordering in ferromagnets is also temperature dependent; at low temperatures, the exchange forces are much greater than the thermal energy so parallel alignment of atomic moments is easier to achieve while at higher temperatures the increased thermal energy leads to more disorder and less coherent orientation of moments. The temperature at which the exchange forces and thermal energy are balanced is known as the Curie temperature ($T_c$) and is the point at which the material is no longer ferromagnetic, above this temperature the material will act as a paramagnet [18].

### 1.2.4 Antiferromagnetism

Compared to diamagnetism or paramagnetism a ferromagnetic system has strong magnetic ordering due to the high degree of spin alignment present; in more complex crystal structures, such as ionic compounds, unique ordering can occur. In such structures the various ions sit at different sites in the compound and each sublattice features a unique coordination geometry. Similar to ferromagnetism a single sublattice has moments oriented in a uniform direction but now the sublattices are antialigned to each other; the ordering is said to be antiferromagnetic if the sublattice spins are equal in magnitude but opposite in direction resulting in no net moment [23]. Analogous to the Curie temperature, antiferromagnetic
ordering is temperature dependent and beyond the Néel temperature \((T_N)\) the material will be in a paramagnetic state. A unique form of antiferromagnetism can occur if the spins are slightly canted resulting in a very small net moment, not to be confused with ferri- and ferromagnetics which exhibit much larger magnetization.

1.2.5 Ferrimagnetism

For materials where the magnetic sublattices are oppositely aligned but not equal in magnitude such that a non-zero net moment is present belong to a group known as ferrimagnetism. This class of magnetism is more closely related to ferromagnetism than antiferromagnetism and will exhibit a spontaneous magnetization, similar irreversible hysteresis behavior in the presence of an applied field, and a Curie magnetic ordering temperature. Although scientific understanding of ferromagnetism came first, the role of ferrimagnetics in history cannot be understated. One of the most recognized magnetic materials, lodestone (magnetized form of maghemite), was used for centuries in compasses due to its ability to align with the earth’s magnetic field and "point" North [24]. A summary of the differences in magnetic ordering for ferro-, ferri- and anti-ferromagnetic systems is shown in Fig. 1-4.
1.2.6 Superparamagnetism

Although not technically a unique form of magnetism, a special form of paramagnetism will occur in ferro- and ferri-magnetic nanoparticles (NP) when the NP size is small enough to enter a single domain state where all the individual moments are aligned in the same direction [12]. In such a state the NP is regarded as having a single magnetic moment that is comprised of all the atomic dipoles within and behaves paramagnetically, since the paramagnetic response is no longer that of a single atom but rather a collective behavior is known as superparamagnetism (SPM) [14, 16]. Although there is no net moment in the absence of a field, a SPM NP will exhibit a much higher magnetization than that of a typical paramagnetic due to the combined contributions of all atoms in the NP. It is a temperature dependent effect as there must be sufficient thermal energy to prevent ordering of the magnetic moments, the temperature at which a ferro- or ferrimagnet becomes SPM is known as the blocking temperature ($T_B$) [25].

1.3 Spinel Ferrites

Spinel ferrites, also known as cubic ferrites, are an important class of ferrimagnetic materials. These transition metal oxides have a chemical formula of $MFe_2O_4$ where $M$ is a divalent 3d metal such as Mn, Zn, Co, Ni, etc [26]. In this material group, the oxygen atoms form a close-packed face-centered cubic structure while the metal cations are distributed across two crystallographic sites with either tetrahedral ($T_d$) or octahedral ($O_h$) oxygen coordination [27]. Local symmetries are different at each site; tetrahedral (A sites) are surrounded by four oxygen atoms while octahedral (B sites) have six nearest oxygen neighbors [28]. A schematic of the cubic ferrite crystal structure is shown in Fig. 1-5 along with $T_d$ and $O_h$ geometries.

The distribution of $M^{2+}$ and $Fe^{3+}$ cations across $T_d$ and $O_h$ sites gives rise to 3 distinct spinel structures; normal, inverted, and mixed [26, 27, 29, 28]. In a normal structure the cation distribution is often written as $[M]^A[Fe_2]^B O_4$ as the divalent $M$ cations exclusively occupy $T_d$ crystallographic sites while

![Figure 1-4. Magnetic ordering in (a) ferromagnetic, (b) antiferromagnetic, and (c) ferrimagnetic materials.](image-url)
the trivalent Fe cations are found at $O_h$ ones. Common examples of normal spinels include ZnFe$_2$O$_4$ and CdFe$_2$O$_4$, both of which are antiferromagnetic below the Néel temperature in their bulk form [14] but have shown ferri- or ferromagnetic behavior in nanoparticles [30, 31, 32]. An inverted spinel structure has the divalent cations located at $O_h$ (B) sites while Fe$^{3+}$ ions are evenly distributed across both $T_d$ and $O_h$ (A and B sites, respectively) sublattices; this is commonly represented as [Fe]$^3$[MFe]$^3$O$_4$. Some of the most common spinel ferrites have this inverted structure, e.g. CoFe$_2$O$_4$, Fe$_3$O$_4$, and NiFe$_2$O$_4$ and are all ferrimagnetic substances. Intermediate states may also exist where the M$^{2+}$ and Fe$^{3+}$ cations are randomly distributed across $T_d$ and $O_h$ sites, noted as $(M_{1-x}Fe_x)^3[Fe_{2-x}O_4$. Ferrites in a mixed structured state include MnFe$_2$O$_4$ (most notably when $x = 0.2$), MgFe$_2$O$_4$ ($x = 0.9$, mostly inverse), and CuFe$_2$O$_4$.

As a result of oxygen-mediated superexchange, or indirect, interactions an antiferromagnetic alignment of spins between A and B sublattices will be energetically favorable, in contrast, spins within a single sublattice will be parallel to each other [29, 33, 14]. If the magnetic moments on each sublattice are not equal then a net moment will occur leading to a ferrimagnetic system. In the case of inverse spinels, since Fe$^{3+}$ cations are equally distributed on A and B sites and the sublattices are antiferromagnetically aligned to each other, the saturation magnetization is only dependent on the moment of the divalent metal ion [14]. The interaction of the 3d cations across the oxygen anion is known as superexchange owing to the large distance between the metal ions, the Goodenough-Kanamori-Anderson (GKA) rules governing such interplay can be used to classify the resulting magnetic ordering. Looking at the configuration of three atoms can determine the ordering type; if the 1st magnetic ion-ligand-2nd magnetic ion bond angle is $180^\circ$.
then the superexchange interaction will result in antiferromagnetism while $90^\circ$ leads to ferromagnetic ordering [34, 35] although the overall system can still be ferrimagnetic [36]. The basis of these rules is elaborated upon in Ref. [37].

A common crystal structure, and relatively similar atomic radii and densities result in comparable lattice parameters for cubic ferrites, an important aspect for chemical synthesis that allows for synthesis of high quality NPs [38, 39]. Aside from common structural parameters, spinel ferrites span a wide range of physical properties. These ferrites can be either antiferromagnetic (e.g. ZnFe$_2$O$_4$ and CdFe$_2$O$_4$) or ferrimagnetic; saturation magnetizations that range from $\approx 25 - 95$ Am$^2$/kg near room temperature, anisotropy constants that different by three orders of magnitude, and can be magnetically hard (e.g. CoFe$_2$O$_4$) or soft (e.g. Fe$_3$O$_4$, NiFe$_2$O$_4$) [16, 14]. Mixed ferrites containing two different transition metals (i.e. $[M_1]_{1-x}[M_2]_x$Fe$_2$O$_4$, $M_1 \neq M_2$) are possible due to aforementioned structural similarities and can produce properties unique to those of the individual spinels.

1.4 Magnetic Nanoparticles

Nanoparticles are materials with dimensions in the nanometer range ($< 100$ nm) but can vary in shape, composition and physical properties [3]. At such length scales, nanomaterials often exhibit novel properties compared to those of the bulk and have been subjects of much interest in a variety of disciplines. For example, in its bulk form gold is an easily recognizable metal but at the nanoscale both size and shape determine the optical properties such that gold NPs appear as different colors [40]. A similar effect has been exploited in CdS NPs where smaller radii lead to increased band gap widths that offer a way to control the fluorescence color of the system [41]. Plasmonics is one area that makes use of the size/shape dependency of optical properties in nanoparticles to drive next generation biological and chemical sensors as well as photovoltaics [42].

Owing to their small size quantum effects now become major driving forces in determining physical properties, this is one reason why nanomaterials are distinct compared to their bulk counterparts; the miniaturization of materials also leads to an increase in the surface-to-volume ratio meaning surface atoms now play a key role in property effects [3]. Considerable attention has also been paid to the effect of shape-dependence in nanoparticles [43] as it can impact physical and chemical factors such as melting point [44], transport [45], optical properties [46, 47], antibacterial impact [48], or even hydrophobic forces during self-assembly [49]. Proximity effects can also lead to unique properties in multi-component
systems, such as core-shell NPs, where now interfacial exchange coupling plays a role in determining physical properties. Whether it’s size, shape or composition NPs offer a multitude of options through which physiochemical properties can be tailored for a specific application.

Magnetic NPs are an often studied class of materials owing to their suitability in a wide range of applications and research areas such as bio-technology [50, 51], data storage [52, 53, 54], or environmental applications including organic and inorganic decontamination [55, 56, 57, 58]. Unlike bulk counterparts, magnetic NPs tend to exhibit low Curie temperatures; high magnetic susceptibility; changes in magnetic moment per atom, anisotropy, and coercivity; and a unique temperature-dependent state of magnetization, superparamagnetism [59]. In ferri- and ferromagnetic materials, domain size is also strongly tied to NP dimensions and below a critical size (typically < 100 nm) the structure will convert from a multi-domain to a single domain state [60, 61].

Domain formation is a result of the system trying to minimize the free energy of the material leading to a balancing act of different energy sources; exchange energy, magnetocrystalline anisotropy, and magnetostatic energy (also known as magnetic dipolar energy) [62, 55]. In general, the exchange energy favors unidirectional alignment of all the magnetic moments in the material, the magnetocrystalline anisotropy favors alignment along certain crystallographic axes and will try to ”push” spins in those directions, and the magnetostatic energy is related to the demagnetizing effects experienced by all magnetic materials [63, 64, 12]. The critical size of a material is affected by many factors such as saturation magnetization, competition of the three domain formation energies, and NP shape [55]. In bulk materials the atomic magnetic moments within an individual domain are aligned in a single direction but each domain has its own direction so that the net magnetization is a sum of the all the different magnetization of each domain. In a single domain particle all the moments point in a single direction such that there are no regions with spins pointed in different directions; in these cases, magnetization can be thought of as arising from a single macro-spin rather than the summation of moments in various regions. Once in a single domain state, SPM becomes possible and the magnetic response of the material is dictated by temperature (i.e. SPM above $T_B$, ferri- or ferromagnetic below).

Another important distinction with NPs comes from the role of surface atoms in the overall magnetization and disordering effects that change the environment at the surface of the particle compared to interior atoms. Surface effects arise from breaking the symmetry of the crystal structure at the surface along with changes in oxidation state, atomic vacancies, unsatisfied valence states, broken bonds, or lattice
Figure 1-6. A demonstration of the effects of adding a shell layer to magnetic NPs and the impact it has on magnetic properties. Image reprinted from M. Abdolrahimi et al., Magnetism of Nanoparticles: Effect of the Organic Coating, Nanomaterials 2021, 11, 1787. CC-BY. Reprinted with permission.
defects that can lead to disordered spins at the surface resulting in a magnetic volume unlike that of the interior [62, 65]. The weaker coupling between surface spins with those of the interior often lead to lower $M_S$ values in NPs, hindering there suitability for many applications [66, 67]. To some extent, surface contributions to magnetization can be tuned by exploiting interfacial effects through the addition of another layer to the NP resulting in a core/shell structure [68]. Exchange coupling between between the core and shell regions can serve to prevent spin disordering at the surface thereby increasing magnetic properties; capping magnetic materials with an organic coating has been shown to restore the crystal symmetry at the surface and ease spin canting that would otherwise reduce $M_S$ or other magnetic effects, this is shown schematically in Fig. 1-6 [69, 70, 71].

Aside from surface stabilization, a core/shell structure provides an additional way to tailor NP properties and broaden their usage in various applications; e.g. pairing a NP composed of both soft and hard magnets can experience the best of both worlds by maintaining the high moment from the softer material and the larger coercivity of the harder magnet [72, 73]. Adding a bio-compatible outer layer to magnetic NPs, which are often toxic, has enabled their usage in bio-medicine opening up potential new lines of cancer treatment and drug delivery [74, 75, 76]. Exchange coupling at the interface can lead to complex behavior that is unlike that of the constituent materials making core/shell NPs an attractive option in the design of new magnetic nanostructures with tunable properties [77, 78, 79, 80].

1.5 Instrumentation Techniques

1.5.1 Transmission Electron Microscopy

Morphological characterization has long been accomplished using various types of microscopy of which there are three main categories; light, electron, and scanning probe types. While optical microscopes have existed for centuries to observe microstructures, they lack the resolution to see features at the nano-level. Ernst Abbe was the first to formulate the resolving power of optical microscopes (assuming negligible aberration):

$$R = \frac{\lambda}{2nsin(\theta)}$$

where $R$ is the resolution of the microscope, $\lambda$ is the wavelength of light, $n$ is the index of refraction of the medium between the sample and lens, and $\theta$ is the aperture angle [81]. The denominator ($nsin(\theta)$) is also known as the numerical aperture, a quantity describing the range of optical angles the lens setup allows
To date, the best light microscopes are capable of resolutions near 0.2 $\mu m$ or 200 nm [83], this is of course far too great to view even the largest of nanoparticles. Optimizing the resolution, that is finding a minimum value for Eq. 1.1, would require shorter wavelengths or increasing the numerical aperture; in general, there is greater variation in electromagnetic wavelengths ($10^{-14} > 10^4$) available than index of refraction ($\sim 1.0-2.4$) so the former is a more practical choice for tuning resolution.

Advances in microscopy have enabled characterization of increasingly smaller samples with sub-nanometer resolution; Fig. 1-7 shows how resolution capabilities have evolved over the years since Abbe first calculated diffraction limits in optical microscopes. Electron microscopes rely on electrons with wavelengths nearly 4 orders of magnitude smaller than the visible light spectrum enabling resolutions less than 1 nm and the ability to characterize nanoparticle morphology [84]. There are two common types of electron microscopy: scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM is a useful tool for probing the surface of nanostructures and provides 3D images of the sample, it is typically lower resolution than TEM and prone to surface charging that can distort images [85]. Being a transmission technique, TEM has the potential to "see" within the structure at near-atomic resolution and
can also be used to characterize shape and size in addition to crystallinity and atomic arrangement [86]; it can only produce 2D images of the samples and the higher resolution comes at the expense of higher electron beam requirements that can damage or destroy samples [87]. There are advantages and drawbacks to either electron microscopy method, however, the ability to see both crystal structure, size and shape with TEM can be invaluable with NP studies and is the technique used for morphological characterization in this dissertation.

As implied by the name, in TEM a beam of electrons must pass through (transmittance) a thin sample in order to form an image on the fluorescent screen or charge coupled device (CCD) camera below the sample holder. Similar to how a glass lens focuses light in optical microscopes, an electromagnetic coil is used to manipulate the electron beam in TEM prior to interacting the sample. Within the sample volume, the electrons can either pass through without a change in transmission direction or scatter resulting in two possible imaging methods; bright/light field and dark field imaging modes. In bright field imaging, the intensity of unscattered electrons that reach the phosphor screen produce the sample image; more deflected electrons lead to dark spots while less scattering results in bright spots [88]. Dark field mode is made possible by imaging the scattered electrons instead of the transmitted/unscattered ones. Now, the area around the sample will be dark while the sample itself will be appear lighter. Although bright field mode is more common in TEM, dark field is useful due to its crystalline contrast that allows for clearer visualization of fine features, crystal lattice, crystal defects and grain size [89, 90].

For both imaging modes, there are two main contributors to image formation; mass-density and diffraction contrast. When electrons pass through the sample volume they come into contact with the much heavier atomic nucleus, this collision leads to deflected electrons; the heavier the nucleus (i.e. denser the material) the greater the chance of electrons being scattered [88]. As such, different materials will appear at dissimilar intensity levels with less dense materials being brighter since electrons can more readily pass through. This Z-sensitivity underscores one limitation of TEM, particularly when studying layered samples composed of similar materials (i.e. spinels), but in those cases it can still provide size and shape characterization. Diffraction contrast arises form the fact electrons can be scattered from parallel lattice planes according to Bragg’s Law. Selected area diffraction (SAD) can be imaged with TEM, this crystallographic analysis can provide insight into the crystalline nature of a sample (single crystal, polycrystalline, or amorphous); identify material or crystal phases; measure lattice parameters; or identify crystal symmetry and orientation [91].
In order for electrons to be transmitted the sample volume must be thin so preparation is key for well defined TEM images. For all presented TEM images throughout this dissertation, the sample was diluted in a small amount of hexane and ultrasonicated to prevent agglomeration of the NPs. One drop of the well-dispersed NP solution was then placed on a copper TEM grid and dried in air to evaporate the hexane. As mentioned previously, TEM contrast is density-dependent since hexane is a very light organic compound (~ 10X lighter than any measured sample) the presence of it will not significantly change the observed morphology of the NPs from TEM micrographs.

1.5.2 Magnetometry

A common method for obtaining field or temperature dependent magnetization data is from a vibrating sample magnetometer (VSM) [92]. In such a method, a sample is placed in a constant uniform magnetic field that will begin to align moments within the sample leading to an induced magnetization. The sample environment is then moved up and down vertically at a fixed frequency (i.e. vibrated) that leads to changes in the magnetic flux density. Relying on Faraday’s Law of Induction, a set of pickup coils or magnetic field sensors placed near the sample can detect these perturbations in field as the changing flux will induce a measurable voltage in the coils or sensors [93, 94]. The generated emf will be proportional to the magnetization within the sample and can be measured as a function of external applied field or temperature. Standard magnetization curves shown in Fig. 1-8 are examples of what magnetic properties are obtainable by VSM.

Since both ferro- and ferrimagnetic systems retain a memory of an external field even after it’s been removed they exhibit a nonlinear magnetization response to applied fields known as a hysteresis loop. This

Figure 1-8. Example of (a) field- and (b) temperature dependent magnetization curves for ferro- and ferrimagnetic materials obtained by VSM.
field dependent magnetization can be measured with VSM; a common magnetic hysteresis (MH) loop for ferri- and ferromagnetic materials is shown in Fig. 1-8(a). Initially, the system is unmagnetized but spin ordering gradually increases with higher fields until it reaches a magnetically saturated state ($M_S$) where additional field strength does not produce any changes in the number of moments aligned with the field. If the field is removed the magnetic moments maintain some degree of ordering but overall alignment degrades resulting in a lower magnetization, the residual moment in zero field is known as remanent magnetization [95]. If the field direction is then reversed there exists such a field where the material loses its magnetization, this is known as coercivity ($H_C$). Increasing the field beyond this point will cause the moments to orient themselves in the negative field direction until negative saturation is achieved. Repeating the field reduction and reversal completes the hysteresis loop.

Temperature dependent magnetization (MvT) is another measurement possible with VSM that probes magnetic ordering across a range of temperatures; characteristics such as blocking temperature, Néel temperature, or Verwey transition can be explored with MvT [96]. Two curves are generally measured, as shown in Fig. 1-8(b); one in which the sample is cooled in an external applied field (FC) or in the absence of a field (ZFC). In both cases, the sample is cooled to some minimum desired temperature, then, a constant external field is applied while measuring the magnetization as the sample is slowly heated [97]. In ZFC measurements, without Zeeman energy the spins will be randomly oriented and upon cooling will become "locked" in this disordered arrangement as the thermal energy is reduced leading to a lower measured magnetization once the field is turned on. In comparison, FC measurements will retain some degree of magnetic ordering as the temperature is lowered due to the applied field and so will retain a higher moment overall but will not experience as drastic changes in magnetization with temperature as the ZFC curve since the FC curve will be much closer to the maximum possible magnetic ordering. In short, the ZFC curve goes from randomly oriented spins to ordered while the FC measurement already starts somewhat ordered and ends a bit more ordered.

Temperature dependent magnetization is often performed in conjunction with hysteresis for a broader understanding of a sample’s magnetic properties; both measurements are particularly useful when studying small NPs that undergo changes in their magnetic behavior (e.g. ferrimagnetic to SPM) and have been performed for all projects discussed in this dissertation. Magnetic measurements were primarily completed using a Quantum Design DynaCool Physical Property Measurement System (PPMS) equipped with a VSM probe provided through USF Physics. This PPMS is capable of magnetic fields up to $\pm 9 \, T$.
and a temperature range of 1.8 K – 400 K. Each sample was prepared for measurements by first weighing a small amount of powder into a gel cap, packed into place using teflon tape, and inserted into a straw that was then connected to the VSM probe that is inserted into the PPMS. It’s important to keep the NPs in place otherwise in the presence of a field they will migrate away from the measured area so that the total signal is no long reflective of the measured mass, adding a layer of uncertainty when calculating mass magnetization. In short, there is no such thing as too much teflon.

1.5.3 X-ray Spectroscopy

X-ray Absorption Spectroscopy (XAS) is a powerful technique where X-rays resonant with core level electrons are used to study the electronic, chemical, and magnetic structure of a sample. In this process an X-ray is absorbed by an atom leading to an interaction with core level electron; if the energy of the incident photon is close to but larger than the binding energy of the electron, the electron will be excited into an unoccupied energy level, if the binding energy is greater then no absorption will occur [98, 99]. The likelihood of absorption is governed by the absorption coefficient, $\mu_E$, that is primarily dependent on the sample composition and X-ray energy; XAS is fundamentally a measure of the energy dependence of $\mu_E$ at and near the binding energy of core-level electrons [100]. Binding energies for a given atom are well known allowing for element-specific selectivity with XAS measurements; this is illustrated in Fig. 1-10 for common transition metals where it can be seen that the absorption profile and energy is unique for each element.

For a given element, multiple absorption edges are possible due to the quantum mechanical processes that govern such electron transitions. The names for these edges derive from the principal quantum number associated with the excited core level transition; e.g. in Fe a K-edge corresponds to $1s \rightarrow 4p$ transition while an L$_{2,3}$ edge indicates a $2p \rightarrow 3d$ transition [101]. In particular, X-ray absorption on 3-d transition metals along the L-Edges have been well researched. For such materials, XAS is related to the transition of electrons from an electronic configuration of $2p^63d^\mu \rightarrow 2p^53d^{\mu+1}$ [102], the corresponding energy span for this transition is known as the L-edge. Due to dipole selection rules electrons initially in a $p$-state can only transition to $s$ or $d$-states, since the absorption coefficient for final $s$-state transitions is significantly weaker than that of $d$-states those transition states are often neglected [100, 103]. Spin-orbit coupling in the 2p configuration leads to splitting in the L-edge; a photoelectron initially in a $2p_{\frac{1}{2}}$ state will require a higher photon energy for absorption to occur resulting in the L$_2$ edge while an initial $2p_{\frac{3}{2}}$ state
leads to the L₃ edge at lower energy [104, 100]. The shape and probability of the absorption edge is determined by the spin direction of the photoelectron, as shown in Fig. 1-9.

While other X-ray spectroscopy techniques lead to the creation of a core-hole what sets XAS apart is that the ejected core electron now resides in unoccupied sites near the Fermi level. There are a few common measurement modes to probe this electron transition event with XAS using soft X-rays including total electron yield (TEY) and fluorescence detection. During the absorption process secondary electrons can be emitted from near the surface of the sample; in TEY mode absorption can be discerned by measurement of this photocurrent of electrons throughout the sample [100, 102]. Since the escape depth of the electrons is on the order of a few nanometers TEY is a surface sensitive measurement best used with thin samples or for studying surface properties. While TEY mode measures the photocurrent generated as a result of X-ray absorption, fluorescence detection measures the secondary (fluorescent) X-rays post-absorption and is better suited for thick samples as the penetration depth can extend up to 100 nm [100, 99, 102].

X-ray magnetic circular dichroism (XMCD) is the absorption difference between left and right circularly polarized X-rays of a magnetized sample [105]. The energy dependence of the absorption...
coefficient varies when the polarization direction is parallel or anti-parallel to the sample’s magnetization [100, 99]. Any material is capable of absorbing a photon so long as the X-ray energy is in the appropriate range making XAS a useful tool for characterizing all elements present in the sample while XMCD can provide insight into the contributions of magnetic sources. The shape of XAS and XMCD features are often explained using two different models; band theory for metallic samples and multiplet theory for transition metal complexes [102]. Band theory takes the one electron approach where weak interaction between the core hole and valence electrons results in a spectrum representative of the Density of States [102, 106]. In multiplet theory for transition metals the interaction in the final state between the $2p^5$ and $3d$ shells must be taken into consideration along with the crystal field dependence, resulting in a spectrum that reflects the splitting and degeneracy of these multiplets [103, 102]. The electronic and oxidation state of the sample will also play a role in the shape of the resulting spectra. In a ferrimagnetic system oppositely aligned spins located on different lattice sites can be distinguished with XAS and XMCD based on the direction of the absorption edge. Different cations for a given element can also be distinguished since higher oxidation states mean fewer valence electrons and shielding of core electrons from the nucleus, the more tightly bound core electrons will require a higher photon energy for absorption to occur [107]. The elemental and cationic sensitivity of XAS and XMCD can provide a better compositional and spatial understanding of the magnetic nature of the sample.

The relative contribution to absorption edges can be determined by fitting the experimental data with spectra of known reference materials. This can be achieved by assuming a linear combination of reference spectra for each element present:

$$\sigma_{\text{fit}} = \sum_{i=1}^{n} \alpha_i \sigma_i$$

(1.2)

where $\alpha$ and $\sigma$ represent the fitting parameter and spectra for each reference material, respectively, with the fitting parameters determined computationally [108]. In mixed material samples, such as CS NPs, such analyses can make it possible to separate relative contributions from each layer. For compounds or metallic samples reference spectra are often comprised of previously measured experimental data, model ionic spectra can also be generated using various XAS multiplet programs. The latter is useful for samples that are in mixed stoichiometric states, such as metal oxides that are a mix of different oxidation states.
1.5.4 Neutron Scattering

Small angle scattering is a widely used diffraction technique to study the structure of materials with resolution capabilities down to the nanometer scale and suitable for a variety of sample types (e.g. thin films, nanoparticles, polymers, etc.) [109]. Such a method requires a beam of radiation with wavelengths on the order of a few Angstroms [109], this is achieved by use of X-rays, thermal neutrons, or electrons. Although more commonly available, the use of non-resonant X-rays poses a few challenges to scattering measurements; it is often a destructive measurement that permanently damages or alters the measured material due to the large amount of energy delivered to the sample and the amplitude of the scattering interaction using X-rays is proportional to the electron density of the sample meaning there is little contrast for elements that are close to each other on the periodic table [110, 109, 111]. Small angle scattering with neutrons does not face these restrictions and has the added benefit of directly interacting with the magnetic moments within the sample making it a suitable technique to characterize the magnetic microstructure in addition to the physical structure [109].

A neutron is a subatomic particle with no net charge, nuclear spin of 1/2, and a magnetic moment of \(-1.91 \mu_N\) [112]. During the scattering process, neutrons interact with nuclei in the sample resulting in what is known as nuclear scattering; since neutrons also have an associated spin they are able to interact with the magnetic moments of unpaired electrons, the scattering from these dipoles is known as magnetic scattering [109, 110, 113, 114]. The amount of scattering per volume is characterized by the scattering length density
(SLD), it is the summation of scattering lengths (Å) from each atom within the sample volume (Å³).

Nuclear SLDs are a function of the material composition and density while magnetic SLD is tied to the magnetic moment of a material [115]. For scattering experiments cold (slow) neutrons are often used due to their lower energies (< 3 meV) and longer wavelengths leading to improved spatial resolution [113, 116]. Neutron spins can be aligned along a quantization axis with a spin projection of ±\frac{1}{2} allowing for polarization of the neutron beam for SANS measurements of magnetic systems. The expected SANS magnetic SLD can be calculated from the following equation if the magnetic saturation of the material is known:

\[
\rho_m = M_S \times 2.853 \times 10^{-6} \frac{m}{Å^{-2}}
\]

where \(M_S\) (A/m) can be known bulk values for saturation magnetization or taken from measured M(H) loops (refer to section 1.5.2) [114].

SANS measurements generally fall within 3 levels of polarization depending on the sample, neutron beam optics, and desired information; an un-polarized neutron beam, half-polarized, or fully-polarized setup (shown in Fig. 1-11). Neutron spin orientation and selection happens at various points along the beam path; the various equipment shown in Fig. 1-11 can be removed depending on the polarization level of the measurement. The neutron beam is initially un-polarized before passing through an FeSi super mirror upstream from the sample that orients the spins in a uniform spin up direction, this incident spin
state can be reversed by use of an electromagnetic coil, more commonly known as a neutron spin flipper. After scattering off the sample a 3He container can preferentially allow neutrons in a specific spin direction to pass through thus allowing only neutrons in a certain orientation to be detected, the preferred direction of the 3He atoms can be changed by a nuclear magnetic resonance pulse. The final destination for scattered neutrons is a 2D detector oriented in the plane perpendicular to the neutron beam.

In an un-polarized setup the neutron spin direction is never preferentially selected and, under the presence of an applied field, half the spins will align with the field and the other half antiparallel to the field; although this technique contains both nuclear and magnetic scattering contributions the magnetic component is weak compared to nuclear scattering, in the case of Fe$_3$O$_4$ the magnetic scattering intensity is less than 5% of the total signal at saturation [110, 117]. An unpolarized measurement is similar to a fully-polarized setup (shown in Fig. 1-11) without the neutron spin flipper and 3He spin analyzer; although commonly used for soft matter it is still a popular form of magnetic SANS.

A half-polarized setup refers to when the spin state of incident neutrons is selected prior to the sample but the orientation after scattering off the sample is not analyzed; such a technique makes use of the neutron spin flipper but not the 3He spin analyzer. In half-polarized measurements the magnetic scattering intensity is much higher compared to un-polarized setups allowing for better analyses and the possibility of modeling the nuclear and magnetic microstructures to quantify scattering length densities and physical parameters such as size and shape of the sample [118]. Since only the initial neutron spin state is known the magnetic information represents the magnitude and lacks any directional information. For samples where spin canting is not expected a half-pol technique is preferred due to shorter measurements times and simplified scattering calculations [117, 114].

A fully-polarized SANS measurement (shown in Fig. 1-11) will make use of both the neutron spin flipper upstream from the sample and the 3He container behind it, in this setup the spin state is known before and after interacting with the sample. The neutron spin may initially be selected as spin up (↑) or spin down (↓) via the electromagnetic coil while the 3He container selects the spin orientation after scattering; cases where the spin changes direction after interacting with the sample are known as spin-flip cross sections while spins that remain in the same direction are known as non-spin flip cross sections. A spin up indicates positive alignment with the applied field while a down spin lies anti-parallel to the field direction. The detection of initial and final spin states opens up the ability to not only separate nuclear and magnetic scattering contributions (as can be done in a half-pol setup) but to further resolve the magnetic
scattering in all directions for 3D spatial resolution [110, 114]. This is crucial for samples were spin canting may be present as magnetic moments parallel and perpendicular to the field can be detected; non-spin flip scattering contains only nuclear (structural) and parallel magnetic contributions whereas spin-flip scattering is purely magnetic.

The difference between the scattered and incident wave directions is known as the scattered wave vector, $Q$, and is captured as a 2D scattering profile by a detector placed behind the sample, as illustrated in Fig. 1-11. The resulting intensity map is a function of $Q$ that reflects both magnetic and nuclear scattering contributions. The quantum mechanical processes that govern these scattering interactions result in well defined scattering ‘rules’: only the component of magnetization that is perpendicular to $Q$ ($M_\perp Q$) may contribute to scattering, the projection of ($M_\perp Q$) that is parallel to the neutron polarization axis (i.e. parallel to the applied field) results in a non-spin flip (NSF) interaction while the perpendicular projection leads to spin flips (SF) [119]. The angular dependence of both nuclear and magnetic scattering results in the so called spin selection rules that allow for individual scattering contributions. The detector used in SANS measurements provides a 2D scattering profile, by taking sector cuts along the appropriate axes and applying the spin selection rules each individual scattering contribution can be determined, as illustrated in Fig. 1-12. These angle-dependent polarization rules were calculated as followed:

$$\text{Nuclear/Structural : } N^2(Q) = (I_{\theta=0^\circ}^{++} + I_{\theta=0^\circ}^{--})$$ (1.4)

$$M^2_{\|}(Q) = \frac{(I_{\theta=90^\circ}^{-+} - I_{\theta=90^\circ}^{++})^2}{4N^2}$$ (1.5)

$$M^2_{\perp}(Q) = \frac{1}{3} \left[ (I_{\theta=0^\circ}^{+-} + I_{\theta=0^\circ}^{-+}) + (I_{\theta=90^\circ}^{+-} + I_{\theta=90^\circ}^{-+}) \right]$$ (1.6)

where (+,-) indicate scattering from spin up and down neutrons, respectively, and $I^{pq}$ corresponds to the scattering intensity along that sector cut for initial spin direction, $p$, and the spin direction after scattering, $q$, [110, 120, 121]. For all SANS measurements presented in this dissertation the external field is in the $\hat{X}$ direction, the neutron beam along the $\hat{Z}$ axis, with $\hat{Y}$ representing the vertical direction; the collected 2D profiles are measurements of scattering in the XY plane. Each equation assumes isotropic nuclear scattering ($N^2$), $M^2_{\|} = M^2_X$, and $M^2_{\perp} = M^2_Y = M^2_Z$ [114], as indicated by the coordinate geometry shown in Figs. 1-11 and 1-12. There are other methods to calculate $M^2_{\|}$ but they come at the risk of high statistical...
uncertainties and low intensity, especially when the nuclear contribution is quite large, as was seen for all measured samples in this dissertation [122]. It should also be noted that Eq. 1.5 represents the net parallel scattering along the $X$ axis while Eq. 1.6 is sensitive to the total magnetic perpendicular scattering contributions.

Spin polarization rules can also be carried out for half-polarized measurements although the information is limited to nuclear and primarily parallel magnetic scattering. Without the the 3He cell only the initial neutron spin is known (either $\uparrow$ or $\downarrow$) so instead of four cross-sections only two can be directly probed with half-polarized SANS:

$$I^\pm = I^{\pm\pm} + I^{\pm\mp}$$  \hspace{1cm} (1.7)

where now a single (+,-) refers to measurement of a neutron initially in a spin up or down orientation, respectively, with no selection of the final state after scattering off the sample [123]. Here a simplified notation of magnetic SANS cross-sections are presented:

$$I^\pm = N^2 + M_Z^2 + M_Y^2 \cos^2(\theta) + M_X^2 \sin^2(\theta)$$

$$-2M_X M_Y \sin(\theta) \cos(\theta) \mp 2MN_X M_Y \sin(\theta) \cos(\theta)$$  \hspace{1cm} (1.8)

Figure 1-12. Schematic of 2D scattering profiles for spin flip and non-spin flip cross sections. The dashed arrows indicate the scattering contributions along that viewing angle.
individual terms have been discussed above (i.e. $N^2$ = nuclear scattering, $M||$ collinear with $\hat{X}$, $M_\perp$ lies in YZ plane) and $\theta$ refers to the angle between the applied field direction ($X$) and momentum transfer vector ($Q$). As with fully-polarized SANS the cross-sections simplify at key angles, namely in directions parallel and perpendicular to the applied field. Successful application of these cross-sections to experimental data relies on the assumption the sample is in a magnetically saturated state such that only the $M^2_\parallel$ and $N^2$ terms exist [124, 125]. Since the introduction of perpendicular magnetic scattering comes from the SF cross-sections such assumptions about saturation conditions (i.e. $M^2_\perp = 0$) are limited to only half-polarized and un-polarized SANS measurements as they cannot distinguish SF from NSF scattering. Applying magnetic saturation conditions leads to a reduced form of Eq. 1.8:

$$ I^\pm = N^2 + M^2_\parallel \sin^2(\theta) \mp 2M_X N \sin^2(\theta) \tag{1.9} $$

where each term can be uniquely isolated by appropriate maths and modeled independently of other scattering contributions [126, 110]. In the direction parallel to the field ($\theta = 0^\circ$) only nuclear scattering is present allowing for structural and compositional studies of the sample while perpendicular to the field introduces the magnetic terms. The inclusion of the nuclear-magnetic cross-term exists for both half- and fully-polarized SANS measurements and is useful because it’s the only term that preserves phase information as the purely nuclear and magnetic ones are squared values. This is helpful in multi-layered systems where magnetization in a single layer can be anti-aligned with another; modeling of the $M^2_\parallel$ term can indicate two regions are oppositely aligned but not specifics as to which layer is reversed, such information though is accessible by analysis of the nuclear-magnetic cross-term [118]. Looking at Eq. 1.8 there are two nuclear-magnetic terms but in practice only the parallel one is considered as perpendicular magnetic scattering intensity is usually quite low compared to nuclear scattering.

Regardless of polarization, the scattering intensity for all SANS experiments is comprised of two different contributions that span all scattering sources; the form factor and the structure factor [127]. Broadly, scattering intensity can be expressed as:

$$ I(Q) = P(Q)S(Q) \tag{1.10} $$

where $P(Q)$ represents the form factor and $S(Q)$ the structure factor. Also known as the single particle form factor, $P(Q)$ is scattering that arises from intra-particle interactions and is strongly dependent on the size,
and shape of the particle [127]. The most common form factors are those of spheres and cylinders with majority of other forms being a variation of those two shapes [128]. Intensity related to the spatial ordering of particles and their interactions with each other gives rise to the inter-particle structure factor, it is also know as the interference factor since it is a result of interference from multiple scattering particles [129]. In dilute systems where the particles do not ”see” each other (i.e. they are too far away to interact), $S(Q) \rightarrow 1$ and the total scattering intensity is now dependent only on the form factor.

The low Q scattering behavior is illustrative of the long-range interactions present in the measured sample and primarily governed by the structure factor; in dilute systems where particles are isolated from each other a flat scattering profile is expected at low Q since this region would correspond to characteristic length scales greater than that of a single particle [130]. If the particles experience attractive forces the low Q intensity increases as a result of the non-uniform distribution of particles [131] and the long-range interactions between them (greater the distance, lower the Q value in reciprocal space). In general, the sharper the low Q slope the more correlated or interacting the particles are. In the intermediate Q range, the structure factor introduces a peak corresponding to inter-particle spacing, the average distance between particles; in concentrated samples this peak position is often similar to the individual particle size but in dilute or isolated systems this peak is noticeably absent since inter-particle spacing is often much larger (i.e. much lower Q) than that of the intra-particle dimensions [113].
Chapter 2

Fe@γ-Fe₂O₃ Core-Shell Nanoparticles: High Moment + Passivating Oxide Layer Investigations

2.1 Introduction

Magnetic NPs have been employed in various bio-medical applications but their potential has been limited due to the lower saturation magnetization of bio-compatible materials, such as iron oxides, whereas high moment metals like Fe are strongly reactive in the presence of water or oxygen and may oxidize completely [133, 134]. A core / shell structure makes it possible to preserve the high moment of Fe NPs by incorporating an oxide shell around the Fe to prevent oxidation and increase stability in both air and aqueous solutions [135, 136]. Such structures face a new set of challenges due to the Kirkendall effect where diffusion of the Fe core through the shell leads to changes in magnetic properties and structure as a result of the different diffusion rates between the various Fe species [137, 138].

The first core/shell (CS) system investigated focused on NPs featuring a high moment bcc - Fe core, also known as α - Fe, and a bio-compatible γ Fe₂O₃, or maghemite, shell. An intermediate particle was also studied where the Kirkendall effect lead to a void region between the Fe core and oxide shell, known as a core-void-shell (CVS) structure. The reduction of the core and introduction of a void layer in CVS NPs should lead to differences in spin coupling at the interface and magnetic distribution across the NP compared to the CS system. Through a combination of X-ray absorption spectroscopy (XAS) and half polarized small angle neutron scattering (SANS) these differences may be probed. The Kirkendall effect eventually leads to NPs with a hollow center (H) leaving only the oxide shell behind, such NPs were used as a reference for XAS and XMCD measurements. A detailed summary of this work can be found in [132].

2.2 Synthesis

All three NP variants investigated in this project were derived from the same synthesis process involving thermal decomposition of metallic precursors. While the details have been published elsewhere

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1 Portions of this chapter have been previously published [132] and have been reprinted with permission from [C. Kons et al., Physical Review Materials, 4, 034408, 2020] Copyright 2021 by the American Physical Society.
but, in short, it involves heating a mixture of oleylamine (70%) and 1-octadecene (90%) to 140 °C in a combination of Ar (95%) and \( \text{H}_2 \) (5%) for two hours. Temperature was increased to 220 °C at which point iron pentacarbonyl, \( \text{Fe(CO)}_5 \), was injected into the solution and allowed to reflux for 20 minutes before cooling to room temperature. This stage of synthesis produces NPs with an \( \alpha \)-Fe core surrounded by a \( \gamma \)-Fe\( _2 \)O\( _3 \) shell and an average diameter of 15 ± 2 nm, as determined from TEM. In order to obtain CVS and H morphology the as-synthesized NPs were annealed at 180 °C for up to one hour under a flow of \( \text{O}_2 \). After the desired structure was achieved the NPs were then washed with ethanol followed by hexane and centrifuged between washing. A portion of each NP was set aside for magnetometry and TEM studies. This synthesis is known to produce NPs with a core 12 nm in diameter surrounded by a 2 nm thick shell [139].

2.3 Structural and Magnetic Studies

Shape morphology and size distributions (not shown) of each NP were confirmed from TEM micrographs shown in Fig. 2-1. A darker core and lighter shell can be seen in Fig. 2-1(a) for the CS NPs while a faint halo can be seen between those two regions in the CVS NPs indicating the presence of the void layer in Fig. 2-1(b). The H NPs, lacking the dense Fe core, have an inverted contrast scheme compared to the CS structure with the oxide shell being darker in contrast to the empty interior, as seen in Fig. 2-1(c). Size distributions derived from these TEM micrographs show a similar overall size of 15 ± 1-2 nm for CS and CVS NP variants and slightly larger H NPs that are 17.5 ± 3.5 nm in diameter.

Temperature and field-dependent magnetometry were performed for each NP and compared to Langevin generated magnetization curves (shown in Fig. 2-2 for CS and CVS NPs). For an assembly of non-interacting NPs in a SPM state, hysteresis loops generated using a Langevin function can be compared to experimental results for a better understanding of how ordered the spins are in the system. Both field cooling in a 5 mT field and zero field cooled conditions were measured for temperature-dependent magnetization (\( M \) vs \( T \)) of each NP. Blocking temperatures of 111 K and 94 K for the CS and CVS NPs, respectively, from prior work [138] are in close agreement with the results of the \( M \) vs \( T \) curves shown in Fig. 2-2(a) and Fig. 2-2(c). Magnetic hysteresis curves shown in the insets of Fig. 2-2(a) and Fig. 2-2(c) confirm the transition from SPM at room temperature to ferrimagnetic below the blocking temperature. A decrease in coercive field from 95 mT for CS NPS to 75 mT for CVS variants can be observed, possibly indicating a weaker average exchange interaction between the high moment/high anisotropy Fe core and
Figure 2-1. Representative TEM images for the NPs used in x-ray spectroscopy study of (a) CS, (b) CVS and (c) H NPs. The darker Fe core can be seen in the CS TEM image alongside a smaller core in the CVS sample both surrounded by a light shell representing the oxide layer. The H NPs are reversed with the shell being darker than the empty core region.

lower moment/ softer oxide shell. Saturation magnetization for the CS NPs is $\approx 70 \text{ Am}^2/\text{kg}$ and decreases to $\approx 50 \text{ Am}^2/\text{kg}$ for CVS samples. It is worth noting that differences in synthesis batches between x-ray and neutron measurements can lead to variations in $M_s$ up to 15% due changes in the size of void layer in CVS NPs and overall diameter of the NPs.

The magnetic response of noninteracting NPs in a SPM phase can be approximated using a Langevin function to generate $M(H)$ curves. Hysteresis curves in Fig. 2-2(b) and Fig. 2-2(d) were generated using an equation of the following form:

$$M(H) = n\mu L\left(\frac{\mu_0 H \mu}{k_B T}\right)$$  \hspace{1cm} (2.1)

where $n$ is the total number of particles, $\mu$ is the magnetic moment per particle, $\mu_0H$ is the applied field, $k_B$ is the Boltzmann constant, and $T$ is for temperature [141, 142]. A Langevin function of the following form is used in Eq. 2.1:

$$L(x) = \frac{1}{\tanh(x)} - \frac{1}{x}$$  \hspace{1cm} (2.2)

A value of $\mu$ was assigned for each NP based on structural parameters determined from SANS fittings and $M_s$ derived from experimental $M(H)$ curves. As can be seen in Fig. 2-2(b) and Fig. 2-2(d) there are deviations between the experimental and Langevin generated curves below 0.5 T for CS NPs and 0.6 T for CVS. Equation 2.1 assumes each NP is uniformly magnetized and so the independently found value for $\mu$ would describe magnetic correlations at both low and high fields. Around 0.1 T each NP sees $\approx 20\%$
Figure 2-2. Field cooled (FC) and zero-field cooled (ZFC) $M$ vs. $T$ curves are shown for (a) CS and (c) CVS NPs. The insets to (a) and (c) show magnetic field hysteresis loops at 5 K and RT. Corresponding magnetization curves generated from a Langevin fit for the RT hysteresis are shown in (b) and (d) for CS and CVS NPs, respectively.
reduction in the experimental magnetic moment, the difference in behavior at low field indicates a reduction in the component of $\mu$ parallel to the applied field likely as a result of spin canting perpendicular to the field direction [141].

2.4 XAS

XAS of the CS, CVS, and H NPs were acquired at beam line 4-ID-C at the Advanced Photon Source, Argonne National Laboratory. Spectra were obtained in total electron yield (TEY) mode and field cooled at +5 T for three temperatures (7 K, 95 K, and 150 K). Both left and right circularly polarized data sets were acquired in a ± 5 T field where the average is XAS while the difference between the two polarization directions gives the XMCD spectra. Measurements probed the energy range from 700-730 eV corresponding to the Fe$\text{L}_{2,3}$ edges, and as TEY mode is a surface sensitive measurement with a probing depth of a few nanometers such a technique is well suited to characterize the electronic structure of the shell as well as the relative magnetic contributions of all Fe species for each NP [108, 143, 144].

Measured XAS and XMCD spectra for CS, CVS, and H NPs at 95 K are shown in Fig. 2-3. The double peak featured along the L$_3$ edge (703-713 eV) in the XAS spectra of all three NPs is indicative of $\gamma$-Fe$_2$O$_3$ [103], however, the reduced intensity of the lower energy peak and broadening of the overall L$_3$ structure reveal contributions from the $\alpha$-Fe and other Fe cations not present in maghemite [108, 145]. Similar studies on Fe/Fe-oxide core-shell systems have reported a shell layer that is more Fe$_3$O$_4$-like at the inner surface with a shift to more $\gamma$-Fe$_2$O$_3$-like at the outer edge [108, 143, 144]. The three peaks in each XMCD spectra are good indicators of the presence of Fe-oxides but the drastic reduction of peak B is unlike that found in $\gamma$-Fe$_2$O$_3$ or Fe$_3$O$_4$ [145, 108]. In pure $\gamma$-Fe$_2$O$_3$ the $A$ peak would be would be half the intensity of peak $C$ however the spectra in Fig. 2-3 show an enhanced lower energy peak that is also wider than expected. The difference in the shape of peak $A$ can be attributed to the presence of metallic Fe and Fe$^{2+}$ cations both of which have overlapping peaks at lower energy [108].

Stoichiometric $\gamma$-Fe$_2$O$_3$ contains only Fe$^{3+}$ cations on both octahedral (O$_h$) and tetrahedral lattice sites while Fe$_3$O$_4$ also contains Fe$^{2+}$ cations on O$_h$ sites. Fitting of XMCD spectra took into consideration the presence of these various Fe cations to account for various iron oxide species as well as $\alpha$-Fe. Reference cation spectra were calculated using CTM4XAS, a charge transfer multiplet program used for modeling XAS and XMCD spectra of transition metal 2p core level excitations [146]. All cation data were calculated assuming reduction of the $d - d$ and $p - d$ Slater integrals to $k = 0.7$ and 0.8, respectively; a
Figure 2-3. Experimental total electron yield (TEY) data of XAS (top) and XMCD (middle) at 95 K in a 5T field with calculations of XMCD of Fe$_{2+}^{Oh}$, Fe$_{3+}^{T_d}$, Fe$_{3+}^{Oh}$ and $\alpha$-Fe for (a) CS and (b) CVS NPs. The experimental spectra are shown in comparison with a normalized sum of calculated spectra (bottom).

Crystal field of 10$D_q$ = 1.2 eV was used for the Fe$_{Oh}$ cations while 10$D_q$ = -0.6 eV was for Fe$_{T_d}$ cations; and an exchange field of g$\mu$BH = ± 0.01 eV for O$_h$ and T$_d$ sites, respectively. Lorentzian broadening values of 0.3 (0.5) eV were used for the $L_3$ ($L_2$) edge to correct for intrinsic linewidth broadening along with a Gaussian broadening of 0.25 eV to account for instrumental effects [147]. These parameter values are similar to previous reports [147, 102, 103]. The reference $\alpha$-Fe spectra came from previously acquired XMCD of a thick Fe film deposited on a silicon substrate and capped with Al.

XMCD spectra were first fit assuming a linear combination of reference spectra based on Eq. 1.2 resulting in the following equation:

$$\sigma_{\text{fit}} = a\sigma_{\alpha-Fe} + b\sigma_{Fe^{2+}_{Oh}} + c\sigma_{Fe^{3+}_{T_d}} + d\sigma_{Fe^{3+}_{Oh}},$$  

(2.3)

where a,b,c, and d are coefficients determined from least squares regression. As seen in the bottom of Fig. 2-3 there is close spectral overlap of $\alpha$-Fe and the lower energy Fe$^{2+}$ peak leading to an over-estimate in the contribution of the Fe cation to overall XMCD signal. Since the H NPs (shown Fig. 2-3c) have no Fe core present it is possible to determine an Fe$_{Oh}^{3+}$ / Fe$_{Oh}^{2+}$ ratio of the oxide shell to serve as a fitting constraint in the CS and CVS NPs. It is assumed the oxide shell size and composition is consistent across NPs, as shown by TEM and SANS results. The Fe$^{3+}_{Oh}$ / Fe$^{2+}_{Oh}$ ratio was determined to be $\approx$ 0.82 and used as a
constraint in Eq. 2.3 for CS and CVS fitting. Fits using the H constraint for CS, CVS, and H NPs are shown in the middle of Fig. 2-3 in solid blue.

The normalized sum of magnetic contribution from each of the reference spectra is shown at the bottom of Fig. 2-3 for each NP at 95 K. As mentioned above, stoichiometric $\gamma$-Fe$_2$O$_3$ does not contain Fe$^{2+}$ ions, however, fitting results show a large contribution from these cations on $O_h$ sites indicating a shell that is more Fe$_3$O$_4$-like. The enhanced Fe$^{2+}$ contribution can also explain the reduction in Peak B intensity; the minor secondary peak of Fe$^{2+}$ around 709.3 eV is close in energy to the peak of the Fe$^{3+}_{T_d}$ cation spectra however the two peaks are antiferromagnetically aligned leading to a significant cancellation in $T_d$ site contribution to the XMCD signal. There is also some overlap of spectral contribution from Fe$^{3+}_{O_h}$ with Fe cations on the $T_d$ sublattice that also serves to diminish the intensity of Peak B. The presence of $\alpha$-Fe serves to broaden Peak A due to the energy offset between the metallic Fe peak and that of Fe$^{2+}_{O_h}$ compared to Peak C. As a result of the surface sensitivity of TEY measurements the shorter penetration depth results in a signal where the dominant contribution comes from the Fe-oxide shell layer, as such, the reduction in $\alpha$-Fe contribution is to be expected. In both the CS and CVS (Fig. 2-3a and Fig. 2-3b, respectively) a less intense metallic Fe peak can be seen compared to any of the Fe cation constituents.

Data were collected at three temperatures corresponding to below, near, and above the blocking temperatures (7 K, 95 K and 150 K, respectively) for each of the 3 CS variant NPs. A summary of the XMCD fit results are shown in Fig. 2-4. The lack of variation in fitted values with temperature in the H NPs reveal stable magnetic contributions from all Fe cations composing the oxide shell. CS material constituents also see relatively little change in magnetic contribution from the Fe cations across temperature. At 95 K, near the blocking temperature, CVS NPs see significant change compared to 7 K or 150 K. Both cations on $O_h$ sites shows a decrease in magnetic contribution while $\alpha$ - Fe and Fe$^{3+}_{T_d}$ see an increase.

2.5 SANS

Half-polarized SANS measurements were performed at NIST Center for Neutron Research using NG-7, a 30 m small angle neutron scattering instrument [148]. In a half-pol setup only the incident neutron beam is polarized, this is accomplished by an FeSi super mirror upstream from the sample that allows neutrons in a spin up ($\uparrow$) orientation to pass through. The neutron direction can be changed to spin down ($\downarrow$) by use of an electromagnetic flipper coil. Both CS and CVS samples were mounted in an aluminum
sample holder in a He environment to prevent further oxidation of the shell layer and core degradation via the Kirkendall effect. SANS data were measured for both CS and CVS NPs at 4 temperatures (15K, 75 K, 125 K, 250 K) probing magnetic configurations below, near, and above the blocking temperature. Field cooling was performed in a 1.5 T field along with zero field cooled measurements for each temperature.

Each field cooling protocol was accompanied by zero field (ZF) and high field (HF) measurements leading to four field conditions per temperature: ZFC ZF, ZFC HF, FC ZFC, and FC HF. The standard high field setup on NG-7 uses the TITAN magnet which is capable of fields up to $\approx 1.5$ T, our HF measurements used the maximum field possible.

Applying spin selection rules to polarized SANS experiments allows for separation of nuclear (structural) scattering components from magnetic scattering cross sections [110]. Scattering in directions parallel to the applied field ($Q \parallel H$) contain only nuclear scattering information while the perpendicular direction ($Q \perp H$) is a combination of nuclear and magnetic contributions [149]. The structural parameters can be determined by first taking sector averages at $0^\circ$ of the 2D scattering with sector widths of $\pm 10^\circ$ and fitting the averaged scattering data. Magnetic scattering parameters can be extracted by repeating the sector averaging process for $90^\circ$ and applying the fitted structural parameters to the perpendicular scattering data.
Data reduction for 2D scattering distributions were done using an NCNR data analysis package for IGOR Pro [150] and analyzed in SASView 4.2.0 [151] using a custom core/multi-shell model.

Reduced SANS data collected in the scattering direction perpendicular to the applied field ($Q \perp H$) and the corresponding fits for FC-HF conditions at 75 K are shown in Fig. 2-5 for both polarization directions. Here, spin up is taken to mean neutrons polarized in the direction parallel to the applied field [$I^+(Q)$] while spin down indicates neutrons aligned antiparallel to the applied field [$I^-(Q)$]. Scattering for $Q \perp H$ contain both structural and magnetic contributions, differences between $I^+(Q)$ and $I^-(Q)$ are readily seen for each spin direction. These differences can be attributed to magnetic scattering rather than nuclear interactions as the scattering cross sections are spin dependent and so will vary when the neutron spin is reversed [113].

2.5.1 Nuclear Scattering

Due to the similarities in overall size and composition for CS [Fig. 2-5a] and CVS [Fig. 2-5b] NPs, both data sets show Bragg peaks at $Q \approx 0.045, 0.078, \text{ and } 0.12 \text{ Å}^{-1}$. The peak at lower $Q$ corresponds to the overall size of each NP while subsequent peaks are the result of higher order diffraction. The defined peaks are due to a narrow size distribution as shown in TEM images (Fig. 2-1) and are better resolved for CS NPs than the CVs counterparts. As SANS is a volume averaged measurement it is expected that the void layer in CVS NPs would lead to less scattering seen by the detector this is reflected by the overall lower intensity seen in the CVS spectra. Each of the three Bragg peaks are accompanied by a crossover in $I^+(Q)$ and $I^-(Q)$ scattering intensity, such a phenomena is commonly seen in the magnetic scattering of composite nanoparticles and reflects the core/shell structure of these NPs [152, 153, 154].

As mentioned previously, structural scattering parameters must first be determined in order to separate nuclear and magnetic contributions for scattering perpendicular to the field direction. Although TEM can provide size analysis, it is limited to a small sampling region and low density materials like organic surfactants can be hard to ”see” with electron microscopy whereas SANS is a volume averaged measurement that can provide structural and material information for each layer of the NP [155]. An angle-dependent core + multi-shell model was developed to account for both scattering directions and similarly used for each NP variant. The model assumed a smooth core centered at the middle of the structure surrounded by varying number of shell with no surface roughness between layers. Due to the nature of synthesis and cleaning routine the outermost layer was assigned as an organic layer due to leftover
Figure 2-5. SANS scattering intensities for (a) CS and (b) CVS NPs at 75K for FC HF measurements. Data for incident neutron spins antiparallel (I\(^{-}\), red) and parallel (I\(^{+}\), blue) to the horizontal field were obtained by having the flipper off and on, respectively. The solids lines show the best fit for each NP using a core + multi-shell model. The inset of each plot shows the evolution of magnetic scattering length density (SLD) as a function of distance from the center of the NP.

Surfactants or other materials left behind when handling the samples. Modeling of the void layer in the CVS NPs was adapted to account for surface roughness from the core and surrounding Fe-oxide layer that may extend into this empty space. The model assumes concentric layers placing the core at the center of the nanoparticle but presence of the void layer could allow for the core to become off-centered in relation to the shell layers. As such, non-zero SLD values were used during analysis of all scattering directions for CVS NPs to account for such possibilities. Another important parameter, polydispersity, can also be derived from the SANS model that is related to size distribution; it is a measure of the range of different particle sizes present in the sample with values ranging from 0, meaning a monodisperse system where only one particle size is present, to 1 indicating a broad size distribution [156]. Although size distributions were included in the model the Fe-core produced the only sizable contribution to polydispersity.

Fitting of nuclear scattering determined the CS NPs had an average overall \(\alpha\)-Fe core diameter of 12.8 \(\pm 0.24\) nm with a polydispersity of 7.6% surrounded by an Fe-oxide layer 1.4 \(\pm 0.06\) nm thick, and a 1.2 \(\pm 0.05\) nm thick surface layer. As expected, CVS NPs see a reduced core 12.2 \(\pm 0.34\) nm in diameter with a higher polydispersity of 11.4%, the dissipation of the core formed a void region 1.0 \(\pm 0.01\) nm thick, and slightly thicker shells for the oxide and surface layers (1.7 \(\pm 0.16\) nm and 1.5 \(\pm 0.18\) nm, respectively). The increased overall diameter and shell thicknesses are consistent with reports of other CS NPs that undergo void formation due to the Kirkendall Effect [157, 77, 158]. While dissipation of the core
reduces its size the overall composition remains unaffected so the core nuclear SLD was fixed to the SLD of bulk Fe \( (8.05 \times 10^{-6} \text{Å}^{-2}) \). In light of the XMCD results and previous reports suggesting a mixed Fe-oxide shell SLDs in the oxide and surface layers were allowed to vary. This lead to nuclear SLDs up to 20\% lower than known values for \( \gamma \)-Fe\(_2\)O\(_3\) or Fe\(_3\)O\(_4\) [159] in the oxide shell and structural SLDs much greater than those of possible surface contaminants [110]. Although nuclear SLDs are material dependent it difficult to differentiate between Fe-oxide compositions as their SLDs are very similar and, while the model assumes each NP layer is composed of one material, any interfacial or surface roughness would lead to SLDs that deviate from known values to reflect the mixed composition of the layer.

### 2.5.2 Magnetic Scattering

With the nuclear contributions known, magnetic parameters could be found by fitting of \( Q \perp H \) scattering. The insets to Fig. 2-5 show the evolution of magnetic SLD (mSLD) with radial distance for CS and CVS data sets at 75 K for FC-HF measurements. Both NPs see a large mSLD coming from the high-moment \( \alpha \)-Fe core of \( \approx 2.4 \times 10^{-6} \text{Å}^{-2} \), followed by negative mSLD in the adjacent layer, and positive mSLDs in the outer layer(s). A negative mSLD indicates the direction of the net magnetic moment is antiparallel to the applied field while a positive SLD would be aligned in the field direction. In the CS NPs, this negative mSLD region corresponds to the Fe-oxide layer with a magnitude much lower than reported values for \( \gamma \)-Fe\(_2\)O\(_3\) or Fe\(_3\)O\(_4\) [160, 110]. The strong, positive mSLD of the outer layer is uncharacteristic of surfactants or other organic materials but any surface roughness from the preceding oxide layer would result in a mSLD in this region. In the CVS NPs the layer immediately adjacent to the core is the void region; although any SLD in this hollow layer would be unexpected a negative mSLD is possible if interfacial roughness or an off-centered core are considered. As with the CS, the outer shells all have positive mSLDs including the oxide and surface layers. Restricting mSLDs to only positive values when fitting lead to negligible mSLDs in the shell layer adjacent to the core and reduced scattering intensities at each of the Bragg peaks.

A summary of mSLDs for all four field conditions and temperatures is shown in Fig. 2-6 for CS NPs and Fig. 2-7 for CVS. In CS variants magnetic scattering from the \( \alpha \)-Fe core is relatively stable across all temperatures; temperature dependent magnetometry shown in Fig. 2-2 show a continuous decrease in magnetization after the blocking temperature that is reflected by a small decrease in mSLD at 250 K for HF measurements compared to lower temperatures. Much weaker magnetic scattering from the core is seen for
Figure 2-6. Temperature dependence of magnetic SLDs and field conditions in each layer in CS NPs. For the core of the NP, there is considerable overlap of the mSLDs for the ZFC HF and FC HF conditions.

ZF measurements with a peak at 15 K. Moving into the oxide layer the negative mSLDs show the spins have a preference to align antiparallel to the applied field with a peak near the blocking temperature for all field conditions. In the outer surface the moment is again with the field with less change occurring near the blocking temperature; at HF there is greater consistency in scattering while ZF shows greater variation with temperature.

Similarly, magnetic scattering from the core in CVS NP variants also show little change with temperature for both HF and ZF conditions, as shown in the top left graph of Fig. 2-7. The FC ZF case deviates from ZFC ZF measurements at both temperature extremes (15 K and 250 K) with mSLDs values closer to the HF cases while near the blocking temperature (75 K and 125 K) magnetic scattering drops. SANS scattering intensities for \((Q \perp H)\) show greater splitting between \(I^+(Q)\) and \(I^-(Q)\) for the high and low temperatures, indicating greater magnetic contributions for those temperatures. Again, a negative mSLD is seen for the layer adjacent to the core corresponding to the void region; a larger scattering amplitude and temperature variation is seen compared to the negative region of CS NPs. The larger mSLDs beyond known values for any Fe-oxides lends credibility to the assumption of surface roughness or an off-center core where the higher moment of the \(\alpha\)-Fe would increase scattering in the void layer. From there, subsequent outer shell layers have a positive mSLDs; both the oxide and surface layer see splitting of values between HF and ZF measurements with greater variability near the blocking temperature.
2.6 Discussion & Conclusions

Through regression analysis of Eq. 2.3 for the XMCD spectra, temperature dependent changes in relative magnetic contributions from the metallic Fe core and Fe cation species of the shell were studied. All XAS measurements were performed and field cooled in a +5 T applied field, based on magnetometry results shown in Fig. 2-2. FC measurements would be expected to have little change in magnetic state with increasing temperature. From Fig. 2-4 it can seen that there is little to no change in the relative contributions from either of the Fe cation species that comprise the hollow NP (shown in green). Fit coefficients for CS NPs (shown in blue) also show little variation across temperature for all material constituents. As to be expected, the presence of the $\alpha$-Fe core in the CS NPs reduced the contributions from the Fe cations compared to the H samples.

Unlike both CS and H NPs only the CVS sample sees significant changes in magnetic contribution but only at 95 K near the blocking temperature (shown in red, Fig. 2-4). Relative contributions from $O_h$ sites weaken while those from Fe$^{3+}_{Td}$ and $\alpha$-Fe see sizable increase. At temperatures above (150 K) or below (7 K) the blocking temperature the fit values are similar to those of CS NPs. Results from polarized SANS also show a tendency for greater magnetic variation near the blocking temperature that is enhanced.
in CVS NPs compared to the CS counterpart. In particular for the CS variants, a splitting in magnetic scattering is clearly seen between HF and ZF measurements in the core and surface layer. A similar story arises for the core in the CVS NPs where mSLDs for HF and ZF measurements that have a tendency for aligning parallel to the applied field, with some deviations for FC ZF at either temperature extreme. In general for ZFC ZF measurements of the CVS NPs, without alignment to an external field the core spins become randomly oriented leading to a reduction mSLD. For FC ZF measurements in the core at 15 K and 250 K the mSLDs are comparable to both HF cases but overlap with ZFC ZF near the blocking temperature. Splitting between field measurements can also be seen in the oxide layer of both NPs but weakens as temperature increases to 75 K. While the mSLDs are negative in the oxide layer of CS NPs, near the blocking temperature all field conditions see weaker scattering contributions with ZF measurements very close to zero. The smaller mSLDs suggest enhanced spin disorder or canting in the oxide shell near the blocking temperature.

From SANS a common story emerges for both NPs of a higher moment Fe core aligned in the direction of the horizontal field surrounded by a layer whose spins preferentially align opposite the core and external field. In CS NPs the layer adjacent to the core is the oxide shell while in CVS NPs the anti-aligned layer is a partial void region with considerable overlap from the Fe core and surrounding oxide layer. Modeling of both NPs assumed smooth concentric layers built outwards from the core with zero surface roughness and an outer layer composed of leftover surfactants. This meant abrupt transitions from one layer to the next with well defined densities for each region, in reality these interfaces within each NP are going to be far more complex with surface roughness and variations in chemical composition along the

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<tr>
<td>250 K</td>
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$M^2_{\text{Total}}$
interfaces, as has been reported in similar Fe/Fe-oxide CS NP studies [108, 143, 144]. Such assumptions would mean the void region in the CVS NPs should have no nuclear or magnetic scattering contributions to the overall SANS signal, however, fitting determined non-zero SLDs in this region supporting the idea of interface mixing between layers with the Fe core and oxide shell contributing to scattering in the void layer. Surface roughness from the outer edge of the oxide layer can also explain the higher nuclear and magnetic SLDs in the surfactant layer that would be expected for organic materials. This is especially evident in CS NPs where the surface mSLD at HF is similar to reported values for $\gamma$-Fe$_2$O$_3$ [160].

Consistent with the Kirkendall process that results in only smaller core layer, the Fe-oxide and surfactant shell layers maintain relatively similar volume fractions between the two NP types while the core+void region is nearly equal in volume to that of the core in CS NPs; 29% for the oxide layer in CS and CVS NPs, and 36-38% for the outer layer. In the CS NP, the Fe core occupies nearly 35% of the total volume and, after undergoing the Kirkendall process, the reduced core + void regions occupy a volume 33% of the total with a 21/12 core/void split. A summary of the radial distribution of mSLDs for each NP variant can be seen in the inset to Fig. 2-5a,b. For pure Fe a magnetic SLD of $4.97 \cdot 10^{-6} \text{Å}^{-2}$ is expected [161], while the Fe oxide layer can vary between 1.09 and $1.46 \cdot 10^{-6} \text{Å}^{-2}$ for maghemite [160] and magnetite [114], respectively.

Combining the volume fractions with known bulk values for mSLD results in a tabulated maximum value for the total parallel mSLD; this leads to a value of $\sim 2.3-2.4 \cdot 10^{-6} \text{Å}^{-2}$ for CS NPs depending of the composition of the oxide layer and a mSLD of $\sim 1.5-1.6 \cdot 10^{-6} \text{Å}^{-2}$ for CVS NPs. Using $M_S$ values from magnetic hysteresis loops and Eq. 1.3 results in an experimental mSLD of $\sim 1.2 \cdot 10^{-6} \text{Å}^{-2}$ for CS NP variants and $\sim 0.70 \cdot 10^{-6} \text{Å}^{-2}$ for CVS NPs, regardless of the Fe oxide composition. At HF, the CVS NPs have mSLDs near those expected from the hysteresis loops while CS values are $\sim 15-20\%$ less than $M_S$, while VSM and SANS are very different methods for determining magnetic properties they yield consistent, albeit, not identical results. It is worth reiterating that with half-pol measurements such as these magnetic SANS modeling assumes saturation in only the field direction so fitted mSLDs are representative of moments aligned with the field ($M_2^\parallel$) meaning any perpendicular magnetization would be unaccounted for [126]. Ideally, at saturating fields all moments would point in the direction of the field such that the fitted parallel mSLDs and theoretical mSLDs would be the same, however, as already indicated by the Langevin fits (Fig. 2-2(b,d)), there are deviations between experimental and theoretical results; for both NPs, $M_S$ were about half those using known bulk values Fe and Fe-oxides.
The intent of pairing a high-moment $\alpha$-Fe with a bio-compatible Fe-oxide shell to bolster overall saturation magnetization is undermined by the region of reversed magnetization that lies adjacent to the core leading to partial cancellation of core spins. While half-polarized SANS lacks the sensitivity required to spatially resolve spin alignment the lower mSLDs compared to bulk could be to due spin canting throughout the NPs [118, 160]. Prior studies on the H NPs revealed enhanced spin disorder in the shell with spins at the surface being most susceptible to spin canting [162]. Hysteresis loops generated from Langevin fits shown in Fig. 2-2 reveal a significant reduction in the experimental moment at low fields that has been attributed to spin canting within NPs for other core-shell systems [141]. Although SANS measurements were taken at ZF and HF conditions, it is expected that intermediate fields would see a reduction in mSLD corroborating the story of spin disorder at lower fields. Fully polarized SANS studies would need to be performed in order to shed light on the degree of spin canting at both the surface and various interfaces.
3.1 Introduction

This work expands past core/shell studies to focus on bi-magnetic spinel structures composed of soft (S) and hard (H) materials. While Fe@γ-Fe₂O₃ NPs experienced a void formation due to atomic diffusion via the metal/insulator interface, insulating magnetic oxide interfaces such as CoFe₂O₄/Fe₃O₄ are a possible solution to preventing such structural defects that alter the overall magnetic properties of the NP. Two NPs are considered; first, S@H CS NPs where anisotropy is lower in the core than the shell and then the reversed H@S system where anisotropy decreases from the core to the shell. Although the constituent materials making up the core/shell interface will be the same for both NP variants there are many factors that can influence the spin alignment between the two layers. CoFe₂O₄ (CFO) was selected as the hard magnet while Fe₃O₄ (FO) is the soft material. While surface spins are more susceptible to spin canting than interior ones [120], the higher anisotropy of CFO will limit the degree of canting as spins are more tightly bound to the crystal lattice [163].

In this work, SANS analysis is performed for both CFO@FO and the reversed structure, FO@CFO, to evaluate the spin and magnetic structures of both NPs. CoFe₂O₄ was selected for its high anisotropy compared to other ferrimagnetic cubic spinels and tendency to establish uniformly canted layers meaning majority of spins will be ordered at the same angle away from the field instead of each spin pointing in a different direction [163]. An ordered canted layer preserves magnetization while a disordered canted layer results in a zero moment. Amongst spinel ferrites, magnetite has long been favored for hyperthermia treatments due to its relatively high magnetic moment and strong bio-compatibility thus increasing the potential for biomedical applications.

3.2 Synthesis

A similar seed mediated thermal decomposition process, with appropriate modifications, was used to grow both FO@CFO and CFO@FO NPs. A typical Fe₃O₄ synthesis involved mixing 1,2 hexadecanediol,
Figure 3-1. HR-TEM images for (a) CoFe$_2$O$_4$@Fe$_3$O$_4$ and Fe$_3$O$_4$@CoFe$_2$O$_4$ NPs.

oleic acid (90%), oleylamine (70%), and benzyl ether (98%) with iron (III) acetylacetonate while adding cobalt (II) acetylacetonate to the mix would produce CoFe$_2$O$_4$ instead. For FO cores, the mixture was heated to 200°C for 2 hours in a nitrogen gas environment before increasing temperature to 300°C and refluxing for 1 hour. For the CFO cores, after the initial heating at 200°C for 2 hours temperature is slowly increased at a ramping rate of 3°C/min to 300°C and refluxed for 30 minutes. The mixture is then cooled to room temperature where the cores are washed and collected by centrifuging with ethanol and hexane.

The cores were then dispersed in hexane to be used as seeds for the shell layer growth; 85 mg of synthesized core were added to the above mixtures for Fe$_3$O$_4$ or CoFe$_2$O$_4$, depending on the desired shell composition. The core-mixture was then heated to 100°C for 30 minutes to evaporate the hexane before refluxing at 300°C for 1 hour. The now synthesized core/shell NPs were cooled to room temperature before being washed in ethanol and collected by centrifuging the mixture. The NPs were mixed with a small amount of hexane to prevent further oxidation or side reactions from occurring. This synthesis is known to produce NPs with a core 6 nm in diameter surrounded by a roughly 1 nm thick shell. A detailed account of the synthesis procedure has been published previously [164].

3.3 Structural and Magnetic Studies

High resolution TEM was used to characterize the size and shape of each NP variant from the synthesis procedure described above. Unlike in previous work, TEM cannot resolve the core and shell
regions due to low mass density contrast but can still be used for other morphology analysis. In TEM, a powerful magnetic field (often > 2 T) is generated from the objective lens and this can lead to imaging distortion of magnetic samples making it difficult to obtain accurate size estimates but can still provide qualitative dimensional results [165, 166, 167]. From Fig. 3-1, a spherical shape with narrow size distributions are confirmed for both NP types; bearing in mind lens effects, micrographs show diameters of ∼12 nm for CFO@FO and ∼10 nm for FO@CFO NPs confirming the small size but additional dimensional analysis will be confirmed with SANS modeling.

Temperature and field-dependent magnetometry were performed for each NP alongside hysteresis curves generated from a Langevin model given Eq. 2.2 and are shown in Fig. 3-2. Field cooling and other temperature-dependent magnetometry were performed in a 10 mT field for each NP. From Fig. 3-2(c) it can be seen that the blocking temperature for the CFO@FO NPs is well above room temperature and exceeds the measured temperatures, whereas, the FO@CFO NPs have a blocking temperature of ≈275 K, as can be seen in Fig. 3-2(f). The differences between hysteresis loops at 100 K and 300 K confirm the transition from nearly SPM at RT to ferrimagnetic at lower temperatures.
The 100 K hysteresis loop in Fig. 3-2(a) and Fig. 3-2(d) show a saturation magnetization of \( \approx 78 \) Am\(^2\)/kg and 60 Am\(^2\)/kg for the CFO@FO and FO@CFO NPs, respectively. Only FO@CFO hysteresis loops show an additional structure between 0 and 1 T indicating a two-step switching process where the core and shell spins change direction at different fields. A change in coercive field is also seen between the two NP variants suggesting differences in exchange coupling depending on the choice of hard or soft materials for the core and shell constituents. When magnetically hard CoFe\(_2\)O\(_4\) is in the core and paired with a softer Fe\(_3\)O\(_4\) shell there is a coercive field \( \sim 0.5 \) T (Fig. 3-2(a)), the inverted variant (Fe\(_3\)O\(_4\)@CoFe\(_2\)O\(_4\)) has a smaller coercive field of nearly 0.35 T (3-2 (d)). The red dots represent the fields where SANS measurements were made; note that the SANS setup is only capable of fields up to \( \approx 1.5 \) T so measurements were likely made close to but somewhat off the major loop.

Reflecting the lower blocking temperature FO@CFO NPs are superparamagnetic at 300K while CFO@FO NPs have a small coercive field on the order of 70 mT with a remnant magnetization of \( \sim 3.5 \) Am\(^2\)/kg at the same temperature. As each NP was in or near the SPM state a similar Langevin analysis was performed based on Eq. 2.2 and Eq. 2.1, the results are shown in Fig. 3-2(b,e). A value of \( \mu \) was assigned for each NP based on structural parameters determined from SANS fittings and \( M_\text{S} \) derived from experimental M(H) curves. For field values less than 0.5 T there are significant deviations between the experimental and generated hysteresis loops, around 0.1 T each NP sees nearly a 25% decrease in predicted magnetization compared to experimental results. The difference in low field behavior could indicate a reduction in the component of \( \mu \) parallel to the applied field likely as a result of spin canting perpendicular to the field direction [141].

3.4 SANS

Fully-polarized SANS measurements were performed at NIST Center for Neutron Research using NG-7, a 30 m small angle scattering instrument [148]. A full-pol setup differs from half-pol in that now the neutrons are polarized before and spin analyzed after scattering off the sample so that all four spin cross sections can be measured (↑↑, ↑↓, ↓↓, ↓↑). An FeSi super mirror allows spin up (↑) incident neutrons to pass through with spin down (↓) made possible by use of an electromagnetic flipper coil. Both CFO@FO and FO@CFO NPs were mounted in an aluminum sample holder that was backfilled with He to prevent oxidation or degradation of the samples. After interacting with the sample a \(^3\)He cell will allow neutrons aligned with the \(^3\)He nuclear spins to pass through, the direction of the \(^3\)He spins can be reversed with a
nuclear magnetic resonance pulse [110]. The neutrons that make it to the detector are therefore a result of the spin orientations selected prior to scattering off the sample and afterward. A variable horizontal magnet (TITAN) was used to achieve fields up to $\sim 1.5$ T during measurements. All measurements were ZFC in order to observe changes in the magnetic state since FC $M$ vs T curves [see Fig. 3-2(c,f)] for both samples showed little change in magnetization. Measurement temperatures ranged from 5 - 300 K for both NPs and were collected at a variety of fields between 0 T and 1.5 T to probe the magnetic state during the switching process that appears in the hysteresis loops well below the blocking temperature [refer to Fig. 3-2(a,d)].

SANS results in 2D scattering profiles of each spin cross section; non-spin flip (NSF) channels are cross sections where the incident and scattered neutron have the same spin direction ($\uparrow \uparrow$ or $\downarrow \downarrow$) whereas when incident and scattered neutrons spins are anti-aligned ($\uparrow \downarrow$, $\downarrow \uparrow$) the cross sections are said to have spin-flips (SF). Area normalized sector slices of $\pm 10^\circ$ are taken from the 2D scattering data at prescribed angles and applying spin selection rules to these sector cuts allow for separation of scattering contributions. These angle-dependent polarization rules simplify at several angles to allow quantification of nuclear scattering ($N^2$) and magnetic contributions parallel ($M^2_\parallel$) and perpendicular to the applied field ($M^2_\perp$) [110]. Here, $\theta$ is the angle between the X axis (parallel to the applied field) and the projection of $\vec{Q}$ onto the X − Y plane of the detector; the z-direction is parallel to the neutron beam. Refer to Figs. 1-11 and 1-12 for a schematic of the coordinate system used in SANS and how this correlates to the measured scattering profiles. The polarization spin selection rule calculations can be found in Ch. 1.5.4. Data reduction of the 2D scattering distributions were completed using a custom Python script and analyzed in SASView 4.2.2 [168] using a custom core/multi-shell model.

3.4.1 Nuclear Scattering

Structural parameters were obtained by fitting nuclear scattering data calculated from Eq. 1.4, representative fits at 5 K are shown in Fig. 3-3. Only NSF channels contribute to nuclear scattering so by fitting scattering data parallel to the applied field ($Q \parallel H$) structural information can be extracted. Error bars representing $1-\sigma$ distributions are shown in the graph although most are smaller than the marker size. The overall scattering profiles are strongly correlated to the close-packing and morphology of the NPs [120] with peaks representing the overall size of each NP variant. A narrow size-distribution results in well-defined Bragg peaks seen around $Q \sim 0.055 \, \text{Å}^{-1}$ at all temperatures for CFO@FO NPs and near $\sim 0.07 \, \text{Å}^{-1}$ for the FO@CFO variants. A similar core + multi-shell model as described in Ch. 2 was used to
fit the calculated nuclear scattering; in short, it assumes smooth, concentric layers with no interfacial roughness or mixing between layers. The outermost layer was again assigned as an organic layer composed of leftover surfactants or other materials after cleaning of the NPs was performed. Size distribution of each layer was included in the fits with only the core of each NP having any sizable contribution to this parameter.

The FO@CFO NPs have an average overall diameter of 10.3 ± 0.3 nm; the Fe$_3$O$_4$ core has a radius of 3.5 ± 0.05 nm with a polydispersity value of 15.2%, a CoFe$_2$O$_4$ layer 1.3 ± 0.05 nm thick, and a surface layer on the order of 0.3 ± 0.04 nm. While the average diameter of the CFO@FO NPs (10.5 ± 0.15 nm) is similar to the inverted system the size of each layer differs; a smaller core radius of 2.9 ± 0.03 nm was found for the CoFe$_2$O$_4$ layer, the adjacent shells were each larger than found for the inverted systems at 1.7 ± 0.03 nm and 0.6 ± 0.02 nm, respectively, for the Fe$_3$O$_4$ and surface layers. Fitting the nuclear scattering of each NP variant found a SLD of 6.5 ± 0.1 ×10$^{-6}$Å$^{-2}$ when Fe$_3$O$_4$ is in the core and 6.8 ± 0.1 ×10$^{-6}$Å$^{-2}$ when in the shell, both values differ by less than 5% of known nuclear SLDs for Fe-oxides [159]. Variations in SLD are seen for CoFe$_2$O$_4$ as well; in CFO@FO NPs it has a SLD of 5.9 ± 0.1 ×10$^{-6}$Å$^{-2}$ and 5.5 ± 0.2 ×10$^{-6}$Å$^{-2}$ in the inverted system. Again, both values are within 10% of tabulated values [114] and agree well with reported values of similar NP systems [169, 170]. Values for SLD in the surface layer range from -0.5 to -0.8 ± 0.2 ×10$^{-6}$Å$^{-2}$; the weakly negative SLDs match well...
with hexane, supporting the assumption of leftover surfactants or other organic materials [171]. The negative SLDs and thin outer layer indicate a relatively smooth surface with little roughness that would otherwise lead to higher nuclear SLDs due to interfacial mixing at the oxide/surface boundary, as was seen in the CS and CVS NPs.

3.4.2 Magnetic Scattering

One advantage of fully-polarized SANS is the ability to resolve magnetic ordering in all directions providing insight into complex spin structures at the nano-level [125]. Parallel and perpendicular magnetic scattering cross sections calculated from spin selection rules summarized in Eqs. 1.5 and 1.6 at 100 K are shown in Fig. 3-4 for each NP. A similar story unfolds for perpendicular magnetic scattering of both NP variants [3-4(a,c)] whereby a well defined Bragg peak is seen at low fields and decreases with increasing field strength. At low field (0.02 T) the peak is still prominent, near $H_c$ the intensity is greatly diminished and reappears slightly at high field (1.56 T) near saturation. For both $\text{CoFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$ NP variants the perpendicular magnetic scattering peak is centered at the same Q-value as the nuclear Bragg peak indicating that this perpendicular spin alignment is coherent across the entire NP volume. The presence of a small peak at high field suggests spin canting even near saturation, possibly due to structural disorder, or reduced exchange interactions at the surface of the NPs allowing spins to more freely cant, or spin frustration at the core/shell interface [172, 173]

To reiterate, $M_\parallel^2$ calculations based on Eq. 1.5 are representative of the net scattering between magnetic moments aligned both anti-parallel and parallel to the applied field. Fig. 3-4(b) shows parallel magnetic ordering for CFO@FO NPs; a small Bragg peak is observed at 0.02 T while increasing the field near coercivity shows a breakdown in parallel ordering (0.41 T - 0.51 T) and a strong Bragg peak is observed at high field (1.56 T). For fields close to coercivity the neutron intensity drops by nearly two orders of magnitude indicating much weaker magnetic scattering, this coupled with the lack of a Bragg peak does not imply that individual magnetic moments tend to zero but rather the length of coherent spin alignment between NPs is drastically reduced.

In FO@CFO NPs parallel spin ordering, shown in Fig. 3-4(d), reveal a more complex ordering process; the development of a Bragg peak at very low field (0.02 T) is consistent with the inverted variant but for intermediate field values corresponding to just below (0.33 T), near (0.41 T), and slightly above (0.51 T) coercivity a shift in Bragg peak position is seen until 1.56 T where the peak returns to its original
Figure 3-4. SANS magnetic scattering contribution calculated from Eq. 1.6 and Eq. 1.5 for (a,b) CFO@FO and (c,d) FO@CFO NPs at 100 K for various field measurements. The field evolution for magnetic scattering perpendicular to the field is shown in (a) and (c) while parallel can be seen in (b) and (d).
low field location. At low fields and near $H_C$ where spin alignment is weaker, less defined Bragg peaks are to be expected as a result of higher signal-to-noise. This can be seen in Fig. 3-4(b) where the 0.41 T scattering curve shows evidence of some parallel ordering but the Bragg peak is distorted and has a higher noise level compared to higher field data.

The 100 K magnetic SANS data and corresponding fits are shown in Fig. 3-5 while a summary of the fit values are provided in Table 3-1. As with the nuclear data, a correlated core-shell model detailing long-range ordering between NPs was used to fit the magnetic data. This worked well for data with sharp low-Q slopes and well defined Bragg peaks, both evidence of long-range interactions [174, 175, 176], but failed to capture the magnetic behavior for field conditions that lacked those features. A correlated-only core-shell model was used for $M^2_{\parallel}$ scattering at all field values other than those nearest to $H_C$ (0.41 T for CFO@FO and 0.33 T for FO@CFO); for all $M^2_{\perp}$ measured fields and $M^2_{\parallel}$ scattering near coercivity a core-shell correlated + spherical uncorrelated model was used to describe the scattering behavior of the NP ensemble. Correlated contributions account for long-range ordering where spin alignment is consistent across multiple particles while uncorrelated comprises scattering resulting from particles that are still magnetically ordered but with little to no coherence between particles [177]. The uncorrelated portion assumes a net moment for each particle and returns the overall diameter of the non-interacting spherical NPs whereas the correlated scattering is sensitive to the core/shell structure and can provide individual dimensions.

The corresponding magnetic scattering data and fits are shown in Fig. 3-5 for each CFO/FO NP variant while Table 3-1 summarizes the obtained magnetic scattering length density (mSLD) fit results. Italicized values indicate measurements where modeling suggests anti-alignment between NP layers although the exact reversal region(s) cannot be determined. At 1.56 T when both samples are near saturation and spins are well aligned the parallel magnetic scattering signal is comprised of long range interactions with no detected contribution from uncorrelated scattering and this trend continues as the field decreases. Near coercivity, the parallel scattering signal decreases and the flatness of the low-Q region is reminiscent of systems with little to no inter-particle interactions [163, 130], however, the SANS signal is only partially accounted for by a single particle spherical form factor with no magnetic correlations between nanoparticles and so the system still retains some long-range ordering [178, 179]. At low field near remanence (0.02 T) the parallel spin ordering is again highly correlated between individual particles and modeling of experimental data resulted in no evidence of non-interacting spheres.
Figure 3-5. Magnetic SANS data and fits for each CS NP variant as a function of the scattering vector $Q$ for 100 K and a variety of applied magnetic field conditions. Presented data are normalized to the highest intensity values (i.e. the scattering peak near 0.06 - 0.08 Å$^{-1}$ for $M_2^\parallel$ and the low Q scattering at 0.04 Å$^{-1}$ for $M_2^\perp$) and offset from each other on either a linear (a,c) or log (b, d) scale. Open circles represent experimental scattering data while solid lines show the best fit.
For parallel magnetic ordering in both variants, as the field nears coercivity the scattering signal is comprised of both correlated and uncorrelated contributions; this is in contrast to perpendicular spin alignment where both contributions are present at all field values. Fits near $H_C$ for parallel magnetic scattering contributions show greater deviation with experimental results indicating the model doesn’t fully capture the magnetic reversal behavior of the NPs. Perpendicular magnetic moments consistently showed both uncorrelated and correlated interactions at all field values with the size of the non-interacting spheres increasing near coercivity suggesting changes to the magnetic ordering within a single NP rather than across several particles. From Table 3-1, near coercivity the core and shell layers of FO@CFO NPS have parallel and perpendicular mSLD values with opposite signs indicating spins in the two regions are anti-aligned with each other. In comparison, CFO@FO NPs do not show this tendency for anti-ferromagnetic alignment at any field value or spin orientation.

Fitting of magnetic scattering indicates anti-alignment of the core and shell at certain field values but due to the fact these cross sections are proportional to the squared magnetic scattering, phase information is lost. Micromagnetic simulations completed on both NP variants support the idea of nucleation starting in the FO region regardless of which layer it is in [180]. Looking at the nuclear-magnetic cross term can allow for identification of the flipped region since phase information is preserved in this cross section. Given that the direction of nuclear scattering will not change for these spherically symmetric NPs it will contribute a constant sign to the overall scattering intensity, therefore, only the magnetic scattering direction is responsible for modulation of the nuclear-magnetic cross term sign in this NP system; a non-zero cross term is indicative of a phase difference between long-range nuclear and magnetic ordering that does not average out across the measured sample [181]. The shape of the difference of NSF scattering cross sections in Fig. 3-6 also suggests the assumption that both nuclear and magnetic structure factors are equal is not valid for any measured field, as would be expected if the samples were uniformly saturated. This reinforces the need for two different models to accurately capture nuclear and magnetic scattering behavior; differences between the models used have been discussed previously in this chapter. Although Eq. 1.9 is specifically for half-polarized measurements the means of obtaining the nuclear-magnetic cross term is similar for fully-polarized SANS:

$$NM_X = I_{\theta=90^\circ}^{-} - I_{\theta=90^\circ}^{++}$$
Table 3-1. Fitted magnetic scattering length density (mSLD) values in units of $10^{-6} \times \text{Å}^{-2}$ for correlated core and shell layers, and non-interacting spheres of each NP variant at 100 K. Italicized values indicate the core and shell regions are anti-aligned with each other but the model is unable to determine which region is reversed with the field.

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where $NM_X$ is the nuclear-magnetic cross term for moments parallel to the applied field, $I_{\theta=90}^{\pm}$ refers to the scattering intensity perpendicular to the applied field for neutrons in an $\uparrow \uparrow$ and $\downarrow \downarrow$ orientation, respectively [182, 183, 184]. Calculations of the nuclear-magnetic cross term for both NPs at all measured fields are shown in Fig. 3-6; if the intensity is always positive that means both core and shell are aligned in the direction of the field while all negative scattering means the entire NP volume is anti-parallel to the field, a change in sign strongly implies one region flips with respect to the field while the other maintains alignment. Fields 0.02 T and 1.56 T for both samples agree well with magnetometry in Fig. 3-2; from hysteresis loops it is already known that the moment is negative at low field and then saturated in the positive direction by 1.56 T. Coercivity is where the nuclear-magnetic cross term takes an interesting turn where now there is a Q-dependency in the sign of the nuclear-magnetic cross term for both samples; for CFO@FO a sign change occurs at both 0.41 T and 0.51 T, in FO@CFO only for 0.33 T. Challenges in fitting the magnetic scattering for fields near $H_C$ to extract mSLDs hinder the potential to model the nuclear-magnetic cross term but the change in signs supports the idea of core-shell regions with spins that do not point in the same direction.

3.5 Discussion and Conclusions

TEM micrographs of each CoFe$_2$O$_4$/Fe$_3$O$_4$NP variant shown in Fig. 3-1 reveal nearly spherical NPs on the order of 10 nm in diameter. From Fig. 3-3, nuclear SANS scattering for each NP are well fitted.
using a spherical core + multi-shell model, corroborating the morphology determined from the TEM micrographs. Magnetometry of CFO@FO NPs [Fig. 3-2(a-c)] indicate a blocking temperature well above room temperature while hysteresis loops at 5 and 100 K reveal $H_C$ increasing at lower temperatures. FO@CFO NPs, shown in Fig. 3-2 (d-f), have a lower blocking temperature around 275 K and smaller coercive fields values compared to CFO@FO variants. Magnetic ordering of the harder CoFe$_2$O$_4$ compared to the softer Fe$_3$O$_4$ can lead to a phenomena known as the magnetic proximity effect in which the NP structure exhibits new properties unlike those of the constituent materials due interfacial effects of the dissimilar core and shell materials [185]. Experimental reports note a $T_B$ of $\sim$50 K in FO core NPs and a $T_B$ of $\sim$200 K [186] meaning the core and shell may not be in the same magnetic state, depending on the measurement temperature. Below $T_B$ ferrimagnetic ordering will occur while above $T_B$ it will be SPM, such differences in the magnetic ordering are sure to play a role in the overall magnetic properties of the system and may be associated with the knee-like feature seen in hysteresis loops as well as the spin flipping observed in SANS and micromagnetic simulations.

Neutron scattering analysis of each CoFe$_2$O$_4$/Fe$_3$O$_4$NP variant reveal the complex nature of magnetic ordering in these core/shell systems. The presence of parallel and perpendicular magnetic Bragg peaks in Fig. 3-4 for both NP systems is indicative of a coherent spin structure that persists across NPs.

Figure 3-6. Plots of the nuclear-magnetic cross terms calculated from the difference of UU and DD cross sections at 100 K for various field values of (a) CFO@FO and (b) FO@CFO NPs.
instead of an isolated particle magnetic structure [122, 120, 163]. Referring to Fig. 3-4, at 0.33 T for FO@CFO NPs the parallel scattering Bragg peak shifts to higher Q with the peak location slowly decreasing back to lower Q values as the field increase; as scattering experiments probe samples in reciprocal space a trend towards higher Q value is correlated with a smaller scattering volume. At low and high fields the parallel magnetic Bragg peaks overlap with those arising from nuclear scattering indicating that the magnetic domains occur on the same length-scale as the overall NP structure, while at intermediate fields spin ordering is confined to a smaller region of the NP characterized by a $M^2_\parallel$ peak at higher Q. Correlating differences in magnetic scattering volume with the step-like features of the measured MH loops (Fig. 3-2(a,d)) suggest that the spins in the core and shell do not become aligned in unison; spins in the magnetically soft magnetite core may align with an external field at a lower field than those in the harder shell layer.

The knee-like features seen in the hysteresis loops of Fig. 3-2 have been reported in other hard/soft systems for both NPs and thin films alike as a result of exchange spring coupling across the hard/soft interface [187, 188, 189, 190]. Exchange spring coupling is strongly tied to the dimensions of the soft phase; when the size of the soft region is less than twice the length of the domain wall of the hard phase ($2\delta_H$) the system will see strong exchange coupling and a smooth hysteresis curve [191, 192, 72]. If the soft region is larger than this critical size the system will see coupling only at the core/shell interface and the soft layer will nucleate spin reversal at a lower field than the hard phase [188]. In core/shell NPs with overall dimensions below that of $2\delta_H$ magnetic properties are still tied to the dimension of the soft phase; structures where the volume fraction of the soft material dominate have also been shown to exhibit two-phase hysteresis loops similar to those seen in Fig. 3-2 [193, 190, 189, 194, 195, 196]. In the CFO@FO NPs the softer magnetite shell comprised nearly 75% of the overall NP volume and the magnetic effects are well explained by exchange spring coupling that pins spins near the core/shell interface while allowing spins near the surface to rotate freely as the external field is increased. In a strongly coupled system the spins in the core and shell regions behave coherently and so the spin state switching process will happen uniformly throughout the NP. Weaker coupling between core/shell layers can lead to pinning of shell spins near the interface while those closer to the surface are free to rotate independently of core and interface spins.

With a blocking temperature between 40-50 K the magnetite layer (3.5 nm radius for FO@CFO NPs, 1.7 nm shell thickness for CFO@FO NPs) will enter a SPM state long before the harder CoFe$_2$O$_4$
layer. In the FO@CFO variants the NP volume will be dominated by the shell layer (≈ 61% total volume); above $T_B$ of FO the large stray field of the CFO shell can lead to ordering of spins in the magnetite core while in the inverted CFO@FO structure CFO now occupies only 25% of the total volume and the stray field may not be sufficient to influence ordering in the FO shell [162, 164].

The structural arrangement for systems of non-dilute magnetic NPs eventually leads to aggregation due to dipolar, van der Waals, and repulsive interactions resulting in nuclear and magnetic interparticle correlations [197]. This adds an additional layer of complexity in estimating the structure factor at lower fields where the spins are not fully aligned and the assumption that the nuclear and magnetic factors are equal may not be valid due to differences in spatial particle arrangement and pair distance functions [198]. Especially for dense powders this can lead to magnetic scattering interference from spin misalignment that is not accounted for [199]. In this project, a core-shell model assuming collinear magnetic regions with dimensions equal to that of nuclear parameters was used leaving only the mSLDs as field-dependent variables. On going attempts to better model the magnetic system for each NP variants, especially near coercivity, combine the form factor for a raspberry-like cluster of NPs with the spatial ordering of hexagonal packed layers. Such a model allows for more detail into how the NPs self-aggregate and how that long-range ordering changes with field.

The spin evolution with field is more complex in the inverted FO@CFO system where the NP is no longer dominated by the soft phase as the magnetite core occupies only ≈ 39% of the core/shell volume. From Fig. A-1 the knee-like features common in hysteresis loops of exchange-spring magnets are present at 5 K in both NPs but noticeably absent at 100 K for FO@CFO NPs and, despite a greater hard phase volume fraction, the coercivities are lower than those seen for the CFO@FO NPs. In the conventional hard@soft variant the CoFe$_2$O$_4$ layer only has one interface for coupling to occur whereas in the inverted system when CFO is in the shell now interfacial effects can happen at the core/shell boundary and at the surface. As the Zeeman energy increases, spins in the FO core can easily switch direction while those in the CFO shell face competing spin disordering effects at both the core/shell interface and at the surface. A larger core also means more CFO spins will be located at the core/shell interface due to the increased surface area, in combination with disordering at two interfaces could result in a smaller measured coercive field.

In summary, the spin distributions in core/shell NPs composed of CoFe$_2$O$_4$ and Fe$_3$O$_4$ were studied with fully-polarized SANS and conventional magnetometry. Magnetic scattering of both CFO@FO and
FO@CFO NPs reveal multi-particle correlations in directions parallel and perpendicular to the field, spin canting is present at low fields but disappears at intermediate and higher applied fields. The shift of Bragg peaks with increasing field for parallel magnetic ordering strongly suggests the system behaves as an exchange-spring magnet where spins in the soft layer nucleate at lower fields compared to those coupled at the interface or in the harder CoFe$_2$O$_4$ layer. Evidence of a more complex spin reversal mechanism is reflected in the hysteresis of each NP variant where a knee-like feature can be seen. Results indicate that in addition to properties such as material selection (which establishes the bulk magnetization and anisotropy of the constituents) and overall nanoparticle size, additional parameters including core / shell volume ratios and number of interfaces of the magnetically hard component (core to shell vs. shell to core + shell to surfactant layer) greatly affect the spin canting and overall spin ordering within the nanoparticles. Control over these parameters will facilitate development of magnetic NPs with desired properties.
Chapter 4

Fe₃O₄@CoₓZn₁₋ₓFe₂O₄ Core-Shell Nanoparticles: Studies of Anisotropy Tuning on Spin Ordering

4.1 Introduction

While past work focused on tuning saturation magnetization by choice of core and shell constituents and exploring material anisotropy differences on magnetic properties, this work sought to find a balance between $M_S$ and anisotropy. It has been demonstrated that saturation magnetization and magnetic anisotropy are key factors in optimizing NPs for magnetic hyperthermia [200, 201, 202] but lower anisotropy can result in greater spin canting that reduces magnetic properties, such as $M_S$ [163, 203, 204]. Reports of doping ferrites with other metallic elements have demonstrated the ability to preserve saturation magnetization while at the same time increasing anisotropy [205, 206, 207, 208]. This affords a new opportunity for optimizing intrinsic properties of CS NPs beyond size or shape morphology and enhancing their suitability for biomedical applications.

Expanding on previous work, which saw a notable perpendicular magnetic component for FO@CFO NPs, various amounts of Zn would partially replace Co in the CFO layer to create a mixed Co/Zn- ferrite shell (CZFO). The higher anisotropy of Co-ferrite allows for a greater range of anisotropy tuning when doped with Zn as well as modifying potential spin canting effects than would be possible with Fe₃O₄. Mixed ferrites containing Zn have been shown to undergo changes in both saturation magnetization and anisotropy allowing such materials to be optimally tuned for hyperthermia applications. As such anisotropy changes should lead to variations in spin canting [209], fully polarized SANS is one technique suited to probe these effects as well as other structural and magnetic changes with increasing Zn concentration. Increasing Zn concentration has a limited positive effect on $M_S$ values where further addition of Zn cations results in lower saturation magnetization due to replacement of Co and Fe ions with dopant ions in octahedral and tetrahedral sites [210, 211]; this would lead to differences in magnetic scattering from the shell detectable by SANS. This work would serve as an expansion of the FO@CFO NPs by doping the Co-ferrite shell with Zn concentrations ranging from 0 - 100% in order to track magnetic properties as a
Figure 4-1. HR-TEM images for the doped core/shell Fe$_3$O$_4$/Co$_X$Zn$_{1-X}$Fe$_2$O$_4$ NPs with cobalt fractions (a) X = 0.25, (b) X = 0.50, and (c) X = 0.75.

function of doping concentration and anisotropy. The continued trend of using the core-shell structure will allow for optimal magnetic properties due to the higher magnetic moment of a soft material and the high coercivity afforded by hard magnets.

4.2 Synthesis

The Fe$_3$O$_4$ cores were synthesized in a similar fashion as described in section 3.2 by mixing iron (III) acetylacetonate, oleylamine, oleic acid and benzyl ether. The initial synthesis of the 6 nm oxide NPs served as seeds for further synthesis routines to produce 12 nm cores. About 100 mg of the 6 nm core NPs were added to the precursor solution and heated to 200°C for 1 hour before increasing the temperature to 300°C for 30 minutes, this procedure results in 8 nm cores. The reaction using the now synthesized 8 nm cores was carried out once more to produce 12 nm spherical Fe$_3$O$_4$ NPs. Once the desired core size is grown, the obtained NPs serve once again as seeds for growth of the variable Co/Zn ferrite shell. A similar precursor solution is used but with the inclusion of Co (II) acetylacetonate and Zn (II) acetylacetonate; by varying the amounts of the latter two reagents a different shell composition ranging from pure Co or Zn ferrite can be achieved. The as-synthesized CS NPs were then cleaned and centrifuged in the presence of ethanol and hexane. This synthesis produces nominal 12 nm Fe$_3$O$_4$ cores surrounded by a 3 nm thick shell of variable Co/Zn - ferrite composition [212].

4.3 Structural and Magnetic Studies

Size and shape morphology of NPs produced from the synthesis routine described above have been studied using HR-TEM for shell compositions with Co fraction X = 0.25, X = 0.50, and X = 0.75.
Figure 4-2. Field dependent magnetometry for the doped core/shell Fe$_3$O$_4$@Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ NPs with various Zn concentrations. Magnetic hysteresis loops at 5 K and 300 K are shown for the (a) undoped NPs (Co fraction $X = 1.0$); intermediate doping levels (b) $X = 0.25$, (c) $X = 0.50$, and (d) $X = 0.75$; and (e) fully Zn doped ($X = 0.0$) shells with a constant Fe$_3$O$_4$ core.
Consistent with the expected synthesis the NPs are primarily hexagonal in shape although size variations exist between samples with different Co fractions. Due to possible image distortion from using a non-Lorenztian lens, quantitative size analysis will not be presented based on TEM micrographs. As can be seen in Fig. 4-1(b,c), smaller NPs are present in the TEM images likely as a consequence of the multi-step synthesis process; e.g. the third step of the reaction should yield NPs 12 nm in diameter but may also initiate growth of new 6 nm cores. Estimating the size of these smaller NPs from TEM show most are $\sim 12$ nm in diameter while some 6 nm cores are also produced.

Field and temperature magnetometry of the as-synthesized samples were collected for shells with Co concentrations ranging from $X = 0.0$ (fully Zn doped) to $X = 1.0$ (undoped); Fig. 4-2 shows magnetic hysteresis loops measured at 5 K and 300 K for each sample while Fig. 4-3 shows the FC M vs. T curve. Field cooling temperature-dependent magnetometry were performed in a 10 mT field for all measurements. At room temperature (blue curve, Fig. 4-2), all samples are superparamagnetic except the undoped sample ($X = 1.0$) which has a small coercive field of $\sim 20$ mT. At 5 K (orange curve, Fig. 4-2), the widened hysteresis loops highlight the shift from a SPM state above the blocking temperature to a ferrimagnetic one below $T_B$. In the fully Zn-doped sample [Co concentration $X = 0.0$, Fig. 4-2(a)] the shell is now antiferromagnetic so the hysteresis shape is a reflection of the magnetite core; since Fe$_3$O$_4$ is a soft magnetic material a smaller coercive field is expected. As the Co fraction is increased, a steady rise in coercivity and remanence is seen as a result of the shift from an antiferromagnetic shell to a magnetically hard one. Unlike prior work on FO / CFO NPs, there is no evidence of a knee-like feature present in the magnetic hysteresis loops this is a good indication that the core and shell layers are strongly coupled. Hysteresis loops following the SANS experimental conditions for the three measured samples are shown in Appendix B.3.

Field cooled M vs T loops shown in Fig. 4-3 all show an interesting feature between 100 - 125 K where a jump in magnetization can be seen. This spike is attributed to the Verwey Transition ($T_V$) which is a spontaneous crystallographic change in Fe$_3$O$_4$ accompanied by deviations in the magnetic, electronic, and thermal signatures of the material [213, 214]; since this feature is unique to magnetite it also confirms the composition of the core for each NP variant. The transition is most noticeable in the samples with shells composed of pure Zn-ferrite shell [$X = 0.0$, Fig. 4-3(a)] where the magnetic moment will be dominated by the ferrimagnetic Fe$_3$O$_4$ core. As CoFe$_2$O$_4$ is added to the system [Fig. 4-3(b-e)] the M vs T graphs change in shape but always retain a magnetization jump near $T_V \sim 125$ K.
Figure 4-3. Field cooled temperature dependent magnetization for the doped core/shell Fe$_3$O$_4$@Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ NPs with various Zn concentrations. Magnetization curves are shown for the (a) undoped NPs (Co fraction X = 1.0); intermediate doping levels (b) X = 0.25, (c) X = 0.50, and (d) X = 0.75; and (e) fully Zn doped (X = 0.0) shells with a constant Fe$_3$O$_4$ core. The abrupt change in magnetization near $\sim$ 125 K is indicative of the Verwey Transition arising from the magnetite core.
4.4 SANS

Fully-polarized SANS measurements were performed at NIST Center for Neutron Research using NG3 VSANS, a 45 m very small angle scattering instrument capable of achieving lower Q range than prior measurements. Measurements were completed for Fe$_3$O$_4$@Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ NPs with Co fractions X = 0.25, X = 0.50, and X = 0.75; with additional beam time, future work would focus on SANS measurements of the undoped (X = 1.0) and fully Zn-doped (Co fraction = 0.0). To briefly recap polarized SANS, neutrons are polarized before scattering off a sample and spin analyzed after interacting with the material making all four spin cross-sections accessible for analysis (↑↑, ↑↓, ↓↓, ↓↑). For a complete discussion of polarized SANS refer to Ch. 1.5.4. An FeSi super mirror controls the spin direction by only allowing neutrons in a single orientation to pass through, an electromagnetic flipper coil is used to reverse the allowed spin direction (i.e. ↑ to ↓). All samples were mounted in an aluminum sample holder that was backfilled with He to prevent oxidation or degradation of the samples during measurement. Situated behind the sample holder is a $^3$He cell that allows neutrons aligned with the $^3$He nuclear spins to pass through, the direction of the spins can be flipped using a nuclear magnetic resonance pulse [110]. The last stop is the 2D detector, the neutrons that make it this far are a result of the spin directions selected before and after interacting with the sample; since each of the four cross-sections have unique spin arrangements they require individual measurements. A variable horizontal magnet (TITAN) was used to achieve fields up to $\sim$ 1.6 T during measurements.

As was done previously for polarized SANS, all measurements were ZFC in order to observe the greatest changes in magnetization since FC M vs T graphs (Fig. 4-3) show little change in moment for the three Co fractions measured with SANS. The presence of the Verwey Transition means the system will undergo structural changes at $T_V$ leading to disruptions in electronic and magnetic configuration; SANS measurements were performed at 5 K well below $T_V$, 100 K slightly below $T_V$, 150 K corresponding to slightly above the transition, and at room temperature far away from $T_V$. At each temperature, four field values were investigated; near zero field (-0.007 T), low field (0.019 T), $H_C$, and high field ($\sim$ 1.63 T). Based on hysteresis loops in Fig. 4-2, each measured sample will be saturated at the field value corresponding to high field. The samples were again magnetically trained by first applying a field for positive saturation, reversed to negative saturation, and then brought to the measurement field where the SANS measurements started; this allowed the opportunity to probe various states of magnetic ordering for each temperature.
Neutron scattering results in 2D profiles for each spin cross-section that can be categorized in 2 groups; if the incident and scattered neutrons have the same spin orientation it is considered a non-spin flip (NSF) cross-section and contains both nuclear and magnetic information while a neutron that changes spin direction after interacting with the sample results in spin-flip (SF) scattering and arises from purely magnetic scattering. From the 2D scattering profiles, area normalized sector slices of ± 20° are taken at key angles where application of spin selection rules to these sector cuts will allow separation of scattering components (nuclear vs magnetic). Angle-dependent spin selection rules simplify at certain angles and allow for quantification of nuclear scattering ($N^2$) and magnetic contributions parallel ($M^2_{\parallel}$) and perpendicular to the applied field ($M^2_{\perp}$) [110]. Note, $\theta$ is the angle between the $X$ axis (parallel to the applied field) and the projection of $\vec{Q}$ onto the $X-Y$ plane of the detector; the $z$-direction is parallel to the neutron beam. The polarization spin selection rule calculations can be found in Ch. 1.5.4. Data reduction of the 2D scattering distributions were completed using custom Python scripts and analyzed in SASView 4.2.2 [168] using various custom core/multi-shell models.

### 4.4.1 Nuclear Scattering

Three samples of the Fe$_3$O$_4@$ Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ NPs were measured with SANS, those with Co concentrations in the shell equal to 25%, 50%, and 75%. Fitting of calculated nuclear scattering based on Eq. 1.4 allows for quantitative analysis of important structural and chemical composition details; representative fits at 5 K for HF (1.6 T) measurements are shown in Fig. 4-4 for each of the three NP variants with Co fraction in the shell ranging from $X = 0.25$ to $X = 0.75$. Error bars equal to 1-$\sigma$ distributions are shown in the graph although most are smaller than the marker size. A sizable Bragg peak is observed for NPs with a mixed-ferrite shell consisting of 25% Co [Fig. 4-4(a)] but becomes less pronounced as the Co fraction is increased [Fig. 4-4(b,c)]. Reflective of the differences in overall diameter between NP variants, first-order Bragg peak locations also shift between samples; for Co fraction $X = 0.25$ a nuclear peak is centered at $Q = 0.35 \, \text{Å}^{-1}$ at all temperatures, the larger $X = 0.50$ NPs see a shift to $Q \sim 0.021 \, \text{Å}^{-1}$, and near $Q = 0.02 \, \text{Å}^{-1}$ for NPs with 75% Co-ferrite shells. For $X = 0.25$ NPs, two more Bragg peaks were noted in the nuclear scattering (not shown in Fig. 4-4); a second-order peak located at $Q = 0.065 \, \text{Å}^{-1}$, and a third near $Q = 0.095 \, \text{Å}^{-1}$. For NPs with a 50% CoFe$_2$O$_4$ shell, a second peak was observed at $Q = 0.043 \, \text{Å}^{-1}$ and the last one at $0.065 \, \text{Å}^{-1}$. In $X = 0.75$ NPs, these subsequent peaks were noted at $Q = 0.039 \, \text{Å}^{-1}$ and $0.055 \, \text{Å}^{-1}$, respectively.
Figure 4-4. Nuclear SANS profiles and fits measured at 5 K in a 1.6 T field for NPs with an Fe$_3$O$_4$ core and Zn-doped CoFe$_2$O$_4$ shell with Co fractions (a) X = 0.25, (b) X = 0.50, and (c) X = 0.75. Orange solid line represents the best fit to the experimental data (blue circles) using a correlated core/multi-shell model for each NP variant.

In SANS, Bragg peaks are a function of instrumental resolution and consistent morphology of the NPs with peak location a measure of the overall size of the NPs in the sample [215, 120]. Since measurement conditions (neutron wavelength, sample-detector distances, etc.) were consistent for each NP variant it’s unlikely Bragg peak broadening is a result of the experimental setup. Referring to the TEM images in Fig. 4-1 smaller NPs can be seen for samples with Co fractions X = 0.50 and X = 0.75 that would serve to increase the size dispersity within each sample and broaden the Bragg peak as now scattering occurs across a wide range of NP diameters leading to a spread in Q-values. By comparison, TEM shows NPs with a 25% Co fraction shell have a narrower size distribution and this is reflected in the width of the nuclear Bragg peak. A similar correlated spherical core + multi-shell model detailed in Ch. 2 and Ch. 3 was used to fit the calculated nuclear scattering; in short, it assumes smooth, concentric layers with no interfacial roughness or mixing between layers. The outermost layer was prescribed as an organic layer composed of leftover surfactants or other materials after cleaning of the NPs was performed. Size distribution of each layer was included in each fit although only the core of each NP had any sizable contribution to this parameter.

As mentioned previously, a greater size variation in NPs will widen the nuclear Bragg peak and reduce its intensity to accommodate the distribution of characteristic length scales. Nuclear scattering for sample X = 0.75 [Fig. 4-4(c)] is an example of this effect as the scattering peak is quite diminished.
compared to the $X = 0.25$ and $X = 0.50$ peaks. This poses a challenge to modeling the data since the nuclear profile appears almost feature-less across the full $Q$-range meaning a range of fit parameters can appear to give an identical fit quality. Subsequent Bragg peaks are always less intense than first order ones and were drastically reduced for the 75% Co fraction shell samples, adding further complications to the fitting process. To avoid physically unlikely results, tighter fitting constraints and a narrower $Q$-range that focused only on the area around the first peak were used.

Referring to earlier discussion TEM also indicates the presence of much smaller NPs, particularly for samples with shell Co fraction $X = 0.50$ and $X = 0.75$ [Fig. 4-1(b,c)]. In great enough quantities these smaller sized NPs can lead to a bimodal size distribution and scattering from these two size groups can result in multiple first-order Bragg peaks located at different $Q$-values [216]. Since SANS measurements take place in reciprocal space the particle diameter and momentum transfer vector ($Q$) will be inversely related so the larger sized NPs will have a primary Bragg peak at lower $Q$ while peaks from the smaller sized NPs will appear at higher $Q$-value. The net effect is that secondary and tertiary Bragg peaks for the larger NPs can overlap with those resulting from the smaller NPs leading to smeared out intensity profile. Data fitting was limited to the region around the first peak since the model could reliably detail the first peak but the fit would always undershoot the second and third-order ones as it assumed a single size distribution.

The FO@CZFO ($X = 0.25$) NPs have an overall average diameter $20.1 \pm 0.6$ nm with a $6.1 \pm 0.1$ nm Fe$_3$O$_4$ core radius with a polydispersity of 19%, $3.3 \pm 0.1$ nm doped Co/Zn-ferrite shell, and a $0.6 \pm 0.1$ nm outer layer. NPs with a shell Co concentration of 50% were found to have an average diameter of $29.6 \pm 0.6$ nm with up to 20% size variation; a $10.2 \pm 0.1$ nm magnetite core followed by a $4.0 \pm 0.1$ nm shell layer, and a $0.6 \pm 0.1$ nm surfactant layer. The final FO@CZFO ($X = 0.75$) NPs were the largest samples with an overall diameter of $32 \pm 0.7$ nm distributed amongst a $7.5 \pm 0.1$ nm FO core with 25% size dispersity, a mixed ferrite layer of $7.9 \pm 0.1$ nm, and a $0.6 \pm 0.15$ nm outer shell.

In addition to dimensional analysis, fitting of nuclear scattering can also provide information regarding chemical composition in the form of nuclear SLD values. Since neutrons interact with nuclei the corresponding scattering lengths are uniquely tied to atomic number and quantitative analysis of SLD values can provide a blueprint of the various scattering materials present [113]. Since the Verwey Transition was present for all three samples the core SLD was fixed to the known value of $6.97 \times 10^{-6}$ Å$^{-2}$ for Fe$_3$O$_4$ while subsequent shell layer SLDs were modeled to confirm layer composition. Pure
CoFe$_2$O$_4$ has a known nuclear SLD of 6.07 · 10$^{-6}$ Å$^{-2}$ [114] while 6.21 · 10$^{-6}$ Å$^{-2}$ is expected for Zn-ferrite [217] so for increased Zn doping a higher SLD is expected. In general, all measured samples showed higher than expected nuclear SLDs for the mixed CZFO layer while the outermost layer was on par with values expected of common surfactants. For the X = 0.25 samples, fitting of the mixed ferrite layer produced an average SLD of 6.30 ± 0.05 · 10$^{-6}$ Å$^{-2}$ and -0.46 ± 0.16 · 10$^{-6}$ Å$^{-2}$ for the outer organic layer. For a 50% Co/Zn-ferrite shell layer a fitted SLD of 6.37 ± 0.08 · 10$^{-6}$ Å$^{-2}$ was found with a surface SLD of -0.68 ± 0.22 · 10$^{-6}$ Å$^{-2}$. The highest Co fraction X = 0.75 has a SLD of 5.58 ± 0.04 · 10$^{-6}$ Å$^{-2}$ with an surfactant layer of -0.61 ± 0.30 Å$^{-2}$.

In a typical spinel ferrite of the form MFe$_2$O$_4$ where M is a divalent transition mental ion there is a 1:2 ratio of M to Fe, however, recent reports on the chemical analysis of NPs produced with this synthesis method have suggested the presence of Zn deficiencies for samples with X ≤ 0.5 leading to non-stoichiometric amounts of Co:Zn:Fe while significant Co deficiencies were not observed [212]. The same report found that for X = 0, ZnFe$_2$O$_4$ is the expected chemical formula but mass spectrometry placed it closer to Zn$_{0.6}$Fe$_{2.4}$O$_4$, in that case, the expected nuclear SLD would be closer to 6.51 · 10$^{-6}$ Å$^{-2}$. Overall, Zn deficiencies in the lower Co fraction NPs would serve to increase the SLD; e.g. using reported density values for Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ [218] the calculated SLD is ∼ 6.1 · 10$^{-6}$ Å$^{-2}$ but a deficiency that reduces the Zn ratio by 0.1 would raise the SLD to ∼ 6.2 · 10$^{-6}$ Å$^{-2}$. Based on the published mass spec results [212], the X = 0.25 NPs had a chemical formula closer to Co$_{0.25}$Zn$_{0.6}$Fe$_{2.15}$O$_4$ that yields ∼ 6.28 · 10$^{-6}$ Å$^{-2}$ nuclear SLD that matches well with the fitted SANS SLD of 6.30 ± 0.05 · 10$^{-6}$ Å$^{-2}$. While the SLDs for X = 0.25 and X = 0.50 are higher than both pure Co or Zn-ferrite, the values are reasonable when using Zn$_{0.6}$Fe$_{2.4}$O$_4$ SLD as an upper bound instead of stoichiometric ZnFe$_2$O$_4$ and taking Zn deficiencies into account.

Shape and structure also play a large role in neutron scattering and can lead to deviations in expected scattering lengths. Vacancies in the crystal lattice essentially remove atoms for neutrons to scatter off leading to a change in the collected 2D scattering profile as the remaining atoms will no longer destructively or constructively interfere with the absent nuclei [219]. Deviations in shape can also lead to incorrect modeling regions; while the model assumes concentric spherical layers TEM (Fig. 4-1) also reveals hexagonal or cubic shapes, particularly for X = 0.75 NPs. The shape mismatch between model and reality can lead to fitting regions that incorporate multiple layers resulting in an volume averaged SLD that is reflective of the constituent regions. Due to the non-spherical shape of the NPs with a 75% Co fraction

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shell and the low SLD it is likely this layer encompasses both the Co/Zn-ferrite shell as well as part of the surfactant shell and possibly empty space. A schematic of this is depicted in Fig. 4-5; the shape dictated by the model is shown on the left while next to that is a more realistic shape based on TEM micrographs, the dashed circles represent where the Co/Zn shell layer would be based on the model and how they correspond to a cubic shape. In such a scenario, the SLD in between the dashed lines would lead to a value lower than that of mixed Co/Zn-ferrite since it also encompasses the negative surfactant layer as well as “empty” space (SLD $\sim 0.1 \cdot 10^{-6} \text{Å}^{-2}$). For stoichiometric Co$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ the calculated nuclear scattering density is $\sim 6.04 \cdot 10^{-6} \text{Å}^{-2}$, the experimental value shows less than a 10% deviation from the expected despite shape assumptions by the core/shell model. To a lesser degree as they are more spherical, both the X = 0.25 and X = 0.50 NP samples may also experience this model shape limitation.

4.4.2 Magnetic Scattering

Taking advantage of the ability to isolate differences in magnetic orientation using fully-polarized SANS provides a glimpse into the 3D spin arrangement within these NPs. Since the Verwey transition is linked to modifications in magnetization, temperatures very far (5 K), slightly below (100 K), slightly above $T_V$ (150 K), and room temperature (300 K) were probed to explore these changes in magnetic ordering. At each temperature four fields were measured; HF (1.63 T), $H_C$, low field (0.019 T), and near zero field (NZF) field. As a result of magnetically training the NPs by cycling around the hysteresis loop a direct zero field measurement wasn’t possible, at 0 V there was a remanence field of -0.007 T. Parallel and
perpendicular magnetic scattering cross sections were calculated from spin selection rules summarized in Eqs. 1.5 and 1.6. Data at 5 K are shown in Fig. 4-6 for each NP variant. Additional magnetic scattering data at the other three temperatures can be found in Appendix B.3 along with the magnetic hysteresis loops at all four measured temperatures.

Referring to Fig. 4-6, at NZF a perpendicular ($M^2_\perp$) magnetic Bragg peak can be seen for each sample; for the 25% Co-ferrite shell NPs there is a corresponding Bragg peak in the parallel ($M^2_\parallel$) direction indicating strong ordering along both $M^2_\parallel$ and $M^2_\perp$ directions while $X = 0.50$ and $X = 0.75$ NPs do not show any net parallel ordering. As the field is increased to 0.019 T a weaker perpendicular Bragg peak is seen for $X = 0.25$ and $X = 0.75$ NPs, some ordering is noted for $X = 0.50$ at this field but the data intensity is weaker and noisier; no change in parallel scattering is seen for $X = 0.25$ NPs compared to NZF, 50% Co-ferrites NPs now exhibit a scattering profile reflective of parallel arrangement of spins as seen by the ordering of the data and the small Bragg peak, although $X = 0.75$ data show a flat line it’s hard to determine if absent Bragg peak is due to lack of coherence in spin direction or peak broadening as a result of the large size distribution.

Once coercivity is reached, no net parallel ordering is seen for any sample but small differences exists in perpendicular scattering; note that due to instrument related challenges there is no measured coercive field for $X = 0.75$. For 25% CoFe$_2$O$_4$ shell NPs both perpendicular Bragg peaks are drastically diminished and the low-Q slope is slightly different, the absence of peaks coupled with the shape of the scattering does not suggest the magnetic moment goes to zero but rather the NPs lose their correlation such that the magnetization is non-zero but points in different directions for each NP. Interestingly, for $X = 0.50$ NPs the scattering from low field to coercivity actually increases and returns to a similar level as the NZF condition. For both $H_C$ and NZ there is no definitive peak present in $M^2_\perp$ scattering, it’s unclear if this is due to peak broadening related to large size disparity or if the magnetization of the NPs are uncorrelated. At saturating fields (1.63 T), no perpendicular scattering occurs from any sample while parallel ordering is at its highest. For all measured fields and spin orientations, any observed magnetic Bragg peaks coincide with those from nuclear scattering meaning the magnetic volume is of the same characteristic length scale as the NP structure.

As the temperature is increased to slightly below $T_V$ little change in magnetic scattering is seen at 100 K (shown in Fig. B-7 in Appendix B.3). Again, negligible spin alignment is seen for moments aligned perpendicular to the field for any sample, as the field is decreased to coercivity a magnetic moment remains
Figure 4-6. SANS magnetic scattering contribution calculated from Eq. 1.6 and Eq. 1.5 for samples with magnetite core and Co/Zn-ferrite shells with Co fractions (a,b) $X = 0.25$, (c,d) $X = 0.50$, and (e,f) $X = 0.75$ at 5 K for various field measurements. The field evolution for magnetic scattering perpendicular to the field is shown in (a,c,e) while parallel can be seen in (b,d,f).
but long-range ordering disappears as indicated by the lack of Bragg peaks. At 0.019 T improved perpendicular ordering is seen for X = 0.25 and X = 0.50 samples compared to 5 K as evident by the slightly increased intensity and smoother peaks; no discernible change is seen in X = 0.75 NPs at this temperature and field condition compared to 5 K. Scattering in this direction at NZF seems to be on par with observations at 5 K.

In the parallel direction, only X = 0.50 NPs show a slight improvement in long range ordering NZF, as noted by the intensity increase, while the other two samples appear the same. This enhancement for the 50% Co-ferrite doped NPs continues as the field is raised to 0.019 T; the improvement in perpendicular scattering at this field for X = 0.25 seems to come at the expense of parallel arrangement where weaker intensity and more diffuse Bragg peaks are now present, no change is seen for X = 0.75 NPs. At coercivity, only the 25% again show any noticeable changes; now, the parallel ordering that seemed to suggest a Bragg peak at 5 K definitively shows long range alignment at 100 K. At HF where all samples are saturated the greatest parallel ordering is observed, as expected.

Increasing the temperature beyond \( T_V \) to 150 K (Fig. B-8) shows an overlap in the perpendicular magnetic scattering at the lowest three field values for X = 0.25 and X = 0.50 samples without any significant first order Bragg peaks. At all four field values, Bragg peaks are seen for parallel moments in the X = 0.25 NPs; for the 50% Co fraction sample an increase in intensity is noted for NZF alongside small formation of a peak indicating more spins are pointing in the field direction compared to lower temperatures but with little to no long-range ordering. In the highest Co fraction sample the only observable change is more coherent ordering in parallel spins near coercivity.

At RT when all the measured samples are SPM or very close to SPM ordering, interesting changes in the magnetic arrangement are seen in the SANS data for X = 0.25; \( M^2 \) SANS data at 300 K are shown in Fig. B-9 for all samples. The perpendicular and parallel Bragg peaks are better defined and an increase in intensity compared to other fields is noted for NZF; at coercivity, no parallel peaks is seen although the data is nearly 1-2 orders of magnitude weaker than other field conditions at RT however the rise in intensity as Q decreases is indicative of some kind of interaction amongst NPs but it’s not clear if it is correlated or uncorrelated. For X = 0.50 NPs, the magnetic scattering shows the emergence of a Bragg peak at coercivity for parallel ordering that did not exist at lower temperatures. Peaks are seen at the three lowest fields for perpendicular scattering in the 75% Co fraction samples; near coercivity there seems to be some suggestion of a Bragg peak but the data is not well defined at higher Q and, overall, the intensity is 2-3 orders of magnitude weaker than other field conditions at RT.
magnitude lower, however, the possible peak appears to be located at the same Q-value as peaks from HF magnetic scattering and those resulting from nuclear contributions.

Corresponding magnetic scattering data and fits at 5 K are shown in Fig. 4-7 for each measured FO@CZFO variant. Any fields not shown in the graphs fall below the plotted intensity range and, generally, do not indicate any significant scattering structures; this is also true for experimental data that do not have lines of best fit. Fits for both $M_\parallel^2$ and $M_\perp^2$ used a similar core-shell model as described in the nuclear scattering section but also allowed for uncorrelated interactions when necessary. Pure Fe$_3$O$_4$ has an expected mSLD of $1.46 \cdot 10^{-6} \text{Å}^{-2}$ while CoFe$_2$O$_4$ is $1.42 \cdot 10^{-6} \text{Å}^{-2}$ [114], since ZnFe$_2$O$_4$ is antiferromagnetic a magnetic SLD is not expected for that material so as the Co fraction increases it is expected that the shell mSLD will as well.

For $X = 0.25$ NPs, in the field direction a Bragg peak is seen at all fields showing strong contribution from a correlated magnetic structure while the smaller slope at low Q and reduced peak intensity for perpendicular scattering showed contributions from both correlated and uncorrelated moments. When the NPs are saturated at 1.63 T the shell mSLD is close to the expected value for a shell composed of 25% CFO but the FO core mSLD is significantly lower than that of bulk values. Near coercivity, the parallel spins in the core and shell become anti-aligned with each other although it was not possible to determine the exact reversal region with the model used; due to the decreased intensity, refinement of the modeling parameters couldn’t be performed so the fit and subsequent mSLD are representative of best approximations based on trends from other field conditions.

In the perpendicular direction, the flattening of the slope at low Q but the curvature near the nuclear Bragg peak region is reminiscent of correlated and uncorrelated scattering contributions; the correlated core mSLD is nearly the same in the parallel and perpendicular direction while the perpendicular shell mSLD is much higher. The uncorrelated sphere mSLD is much lower at $0.21 \cdot 10^{-6} \text{Å}^{-2}$ although this isn’t surprising given that the core and shell are anti-aligned so the volume averaged moment would be lower than the individual regions. This anti-alignment may also indicate that the core and shell do not reverse at the same field, this could be a result of a magnetic reversal process akin to exchange-spring magnets [187]. At low field, parallel and perpendicular core/shell mSLD values are again similar while the uncorrelated sphere mSLD reaches it’s highest value. At the lowest field, perpendicular core and shell mSLDs are much greater than those in the parallel direction while the uncorrelated moments are similar to those of the correlated spins.
Figure 4-7. Magnetic SANS data and fits for each measured FO@CZFO NP variant as a function of the scattering vector Q for 5 K and a variety of applied magnetic field conditions. Presented data are offset from each other on a log scale. Open circles represent experimental scattering data while solid lines show the best fit.
From Table 4-1 a story begins to emerge about the magnetic ordering in the X = 0.25 NPs; after the sample is saturated in the negative direction and then lowered to almost 0 T the spins favor a perpendicular arrangement, as indicated by the higher $M_2^⊥$ mSLDs; some of these moments rotate from the negative field direction to the orthogonal direction in clusters (correlated core-shell values) while a slightly smaller amount rotate as individuals (uncorrelated sphere mSLD). As the field is increased to 0.019 T some of the correlated orthognals spins continue their rotation into the positive field direction (higher $M_2^∥$ SLD compared to NZF) while others remain perpendicular and some clusters lose their long-range ordering (seen by increase in uncorrelated sphere values). Interestingly, the correlated moments parallel and perpendicular to the field have nearly similar magnetic moments. At coercivity, either the core or shell region flips and is anti-aligned with the other; long range interaction is maintained at this field (Bragg peaks still present) and the core actually sees a significant jump in scattering in both directions while the non-interacting core/shells see a reduction in their overall moment. At saturation, no evidence of spin canting is present (no perpendicular scattering), however, mSLDs are considerably smaller than known bulk values of $1.42 \times 10^{-6} \text{Å}^{-2}$ for CoFe$_2$O$_4$ and Fe$_3$O$_4$, respectively.

In X = 0.50 NPs, at NZF the parallel scattering data is weak and reflective of noise; although the data could not be fit this does not mean there is no parallel moment present but rather the net parallel ordering could be such that there are equal amount of moments lying parallel and anti-parallel to the field. Since magnetometry [Fig. 4-2(b)] shows non-zero magnetization the latter is a more physically reasonable interpretation of the NZF SANS data than assuming a zero mSLD. As the field is slightly increased to 0.019 T, the NP system does not show evidence of uncorrelated interaction meaning long-range ordering of spins is favored and exists for both parallel and perpendicular scattering directions. At this field, the lower mSLDs for $M_2^⊥$ indicate smaller spin canting compared to at NZF and the shell mSLD also decreases with the increasing field while the core mSLD remains relatively the same. Increasing to coercivity reveals a drop in mSLDs for the parallel field orientation as well as the existence of uncorrelated interactions for both $M_2^∥$ and $M_2^⊥$. At high field, the perpendicular contributions vanish and parallel spins do not show evidence of uncorrelated interactions. At all fields where perpendicular scattering exist, the core mSLD stays relatively constant with field changes while the shell varies up to 20%.

Similar to the 50% Co-fraction, for X = 0.75 NPs only correlated perpendicular moments are present at NZF suggesting the NPs form widespread clusters of spins rotated from negative saturation in a common fashion and the NPs maintain those long-range interactions once the field approaches 0 T. At 0.019 T a net
parallel spin arrangement exists alongside the perpendicular ordering and, as with X = 0.50, correlated interactions seem to dominate the scattering profile with no evidence of non-interaction NPs. Values for mSLDs seem to indicate strong spin canting as parallel mSLDs are nearly half of those orthogonal to the field. At HF when the NPs are saturated the perpendicular components again disappear and the correlated parallel magnetic contributions more than double compared to 0.019 T. Although the coercive field could not be measured at 5 K both correlated and uncorrelated parallel and perpendicular scattering is expected based on $H_C$ measurements for X = 0.75 NPs at three other temperatures (refer to Appendix B.3).

Comparison of parallel and perpendicular mSLDs for correlated NPs allows for calculation of spin canting in the core and shell regions based on values in Table 4-1. For all samples and temperatures, the absence of any scattering perpendicular to the field at 1.63 T seems to indicate negligible amounts of spins oriented in this direction and further supported by hysteresis loops showing the samples are magnetically saturated it is assumed little to no spin canting is present at HF. At -0.007 T for samples X = 0.50 and X = 0.75, where the net parallel scattering was essentially noise, it wasn’t possible to calculate spin canting, however, it would prudent to assume the moments only lie in the perpendicular plane as individual parallel and anti-parallel moments can still exist at NZF while the net parallel moment is essentially not present.

For NPs X = 0.25, spin canting angles in the core at various fields were calculated to be 62° ± 0.1° at NZF, 45° ± 0.1° at 0.019 T, and 46° ± 0.3° at coercivity; in the 25% CFO shell, canting was found to be 57° ± 0.1° at NZF, 48° ± 0.1° at 0.019 T, and 60° ± 0.6° near $H_C$. For sample X = 0.50, spin canting could

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Table 4-1. Fitted magnetic scattering length density (mSLD) values in units of $10^{-6} \times \text{Å}^{-2}$ for FO@CZFO NPs at 5 K using a correlated core-shell model that also includes contributions from non-interacting spheres. Uncertainty is on the order of 10-15% for each parameter aside from values for X = 0.25 near coercivity where the scattering intensity was too low for determination of exact values. Italicized values indicate the core and shell regions are anti-aligned with each other but the model is unable to determine which region is reversed with the field.
not be ascertained for core or shell regions at NZF, at 0.019 T the core had a canting angle of 25° ± 0.3° while the shell was 22° ± 0.2°, and near coercivity canting angles of 34° ± 0.1° and 24° ± 0.1° were calculated for the core and shell, respectively. For X = 0.75 NPs spin canting could only be determined for the measured field 0.019 T; canted angles of 67° ± 0.2° in the core and 61° ± 0.1° in the shell were calculated from fitted mSLDs.

For the ∼ 20 nm spherical X = 0.25 correlated NPs, canting angles between the core and shell tend to be relatively similar except near coercivity where the shell is rotated much closer to the perpendicular plane. For the larger ∼ 30 nm hexagonal X = 0.50 NPs similar core-shell canting angles exist at low field but now the core is more canted at $H_C$ although, overall, angles are about half those compared to the lower Co fraction sample. The larger (∼ 32 nm), more cubic samples with a 75% CFO shell show strong tendencies for spin canting in both the core and shell compared to lower Co fraction samples.
Chapter 5
Summary & Future Outlook

5.1 Summary

The research presented in this dissertation focused on exploring the spin dynamics in bimagnetic core-shell NP systems. Choice of constituent materials were exploited to explore the magnetic ordering of CS NPs with contrast in core/shell features (moment, anisotropy, coercivity, etc.) using a combination of x-ray and neutron based studies. In early work, the high moment of metallic Fe was paired with a bio-compatible Fe-oxide shell, however, due to differences in diffusion rates of the various Fe ions the core will slowly migrate outward through the oxide shell until a hollow region forms in a process known as the Kirkendall effect. Magnetic ordering at various stages of the core diffusion were studied including when the core was fully intact (CS), early stages of void formation (CVS), and complete dissipation of the Fe core (H). XAS measurements of magnetically saturated samples showed little change in individual Fe-species contributions with temperature, as expected from the FC $M_vT$ curve. Only CVS NPs see a significant change in magnetic contribution but this is limited to near the blocking temperature, in line with neutron results that show a similar tendency for greater changes in magnetic variation near $T_B$.

Half-polarized SANS revealed anti-aligned layers adjacent to the core in each NP type that serve to reduce the overall magnetization within each particle. Deviations between expected mSLDs and fitted ones, as well as Langevin fits, for CS and CVS NPs strongly suggest the presence of spin canting however fully-polarized SANS measurements would need to be performed to explore this possibility.

Careful selection of core and shell materials can ease or eliminate the Kirkendall effect [220] while inclusion of a harder magnetic material may offer resistance against spin canting [163, 141]. To this end, NPs composed of CoFe$_2$O$_4$ and Fe$_3$O$_4$ were studied to explore the role of anisotropy in spin ordering. Two variants were studied; one in which the harder CFO was placed in the core surrounded by the magnetically softer FO (CFO@FO) and the reversed structure (FO@CFO). Spin canting was again present in both samples and persisted even up to $\sim 1.5$ T; parallel spins primarily displayed long-range ordering with
characteristic lengths scales beyond that of a single NP while perpendicular moments showed tendency for both correlated and uncorrelated interactions at all fields. The knee-like feature present in the hysteresis loops below $T_B$ may suggest exchange spring coupling behavior in which the hard and soft magnetic layers are not rigidly coupled and, therefore, may nucleate reversal at different fields. Micromagnetic simulations point to the FO layer as flipping first regardless of location (core or shell) [180]; this was corroborated by SANS fitting for FO@CFO where an anti-aligned FO region was found for field values near coercivity. Although fitted mSLD values for CFO@FO NPs did not show this trend the nuclear-magnetic cross term [shown in Fig. 3-6(a)] at 0.41 T seemingly supports the idea of anti-aligned regions. Additional models are being explored to better capture the magnetic behavior in both NPs, especially near coercivity where the uncorrelated magnetic ordering becomes more prominent.

Continuing the trend of developing magnetic NPs with high saturation magnetization and large anisotropy, NPs with an Fe$_3$O$_4$ core and a Zn-doped CoFe$_2$O$_4$ shell were synthesized. Typically, there is a trade-off between magnetization and anisotropy, one usually comes at the expense of the other but the addition of Zn to the shell provides a way to maintain $M_S$ alongside increasingly larger shell anisotropy. This project explored the effect of Zn-doping on the overall anisotropy and spin ordering throughout the NP using fully-polarized magnetic SANS in conjunction with other magnetometry. Although synthesis of various Zn concentrations resulted in NPs of different sizes and shapes all FC $MvT$ curves feature a sharp increase in magnetization near $\sim 115$ K corresponding to the Verwey Transition, a feature present in magnetite, indicating all samples highly crystalline. Perpendicular magnetic moments were observed at low fields for all samples and temperatures but were not present at saturating fields indicating that spins do not cant at lower fields but become fully aligned by HF, unlike the undoped counterparts previously described. Interestingly, near ZF at 5 K the NP variants with a 50% and 75% Co fraction did not have any distinguishable net parallel ordering meaning an equal amount of spins were oriented parallel and anti-parallel to the field direction. Magnetic reversal in the doped FO@CFO NPs seemed to be more straightforward; fitting of magnetic cross sections found regions of anti-alignment only near coercivity and mSLDs increased with field, as expected based on MH results. All NP types measured with SANS seemed to be well described by a correlated + uncorrelated core-shell model; some deviations at $H_C$ were encountered due to the low scattering intensity (2-4 orders of magnitude lower than other fields) but the model still accurately represented peak location but may have over-estimated the polydispersity of the system.
5.2 Future Outlook

Magnetic NPs are of considerable importance in next generation biotechnology for applications such as drug delivery, magnetic hyperthermia, data storage, or biosensors. To meet the demands for such applications suitable nanostructures should have high saturation magnetization and/or effective anisotropy but potential for the CS NPs presented in this dissertation is hampered by the presence of spin canting that leads to a reduction in magnetic properties. Current research has shown that organic coatings of CS NPs can reduce canting at the surface providing an additional avenue to tune the magnetic properties of bi-magnetic nanostructures [65, 221, 222]. NPs composed of CoFe$_2$O$_4$ and Fe$_3$O$_4$ have been shown to be good candidates for advanced magnetic hyperthermia [223] owing to their sizable $M_S$ and coercivity values but the pervasiveness of perpendicular spins even up fields of $\sim 1.5$ T (see Fig. 3-4) can hinder such applications. Future work would focus on further tuning of magnetic properties by coating the as-synthesized NPs in an organic film such as oleic acid (a common choice for spinel ferrites [224]) and studying the spin structure using fully-polarized magnetic SANS alongside conventional magnetometry. In addition to the capping layer, the FO@CZFO NPs would benefit from a more controlled synthesis process that produces CS NPs of similar morphology for each of the various Co fractions; this would allow for a more direct study of the effects of Zn doping on the overall magnetic properties as well as the spin orientation in the individual CS layers. Mossbauer spectroscopy would also allow for better compositional analysis of the Zn-doped CFO layer in each NP as recent reports have indicated Zn deficiencies as low Co fractions [212]. It also has the added benefit of providing a way to quantify spin canting angles as a function of magnetic sublattices instead of by core-shell region providing additional insight into the spin arrangement for each CS nanostructure.
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Appendix A

Fe$_3$O$_4$ / CoFe$_2$O$_4$ Core-Shell Nanoparticles: Supplementary Materials

A.1 Magnetometry

Selected magnetic hysteresis loops at various temperatures for both CoFe$_2$O$_4$/ Fe$_3$O$_4$ samples.
Figure A-1. Magnetic hysteresis loops for (a-c) CFO@FO and (d-f) FO@CFO NPs at various temperatures.
Appendix B

Fe$_3$O$_4$@Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ Core-Shell Nanoparticles: Supplementary Materials

B.1 Magnetometry

Selected magnetic hysteresis loops for Fe$_3$O$_4$@Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ samples also measured with fully-polarized SANS.
Figure B-1. Magnetic hysteresis loops for sample X = 0.25 at temperatures corresponding to SANS measurements.

Figure B-2. Magnetic hysteresis loops for sample X = 0.5 at temperatures corresponding to SANS measurements.

Figure B-3. Magnetic hysteresis loops for sample X = 0.75 at temperatures corresponding to SANS measurements.
B.2 Nuclear Scattering

Additional nuclear SANS graphs for Fe$_3$O$_4$@Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ Core-Shell Nanoparticles supplemental to Ch. 4 are shown below.
Figure B-4. SANS nuclear scattering contribution calculated from Eq. 1.4 for sample with a magnetite core and $\text{Co}_{0.25}\text{Zn}_{0.75}\text{Fe}_2\text{O}_4$ shell at various fields and temperatures.
Figure B-5. SANS nuclear scattering contribution calculated from Eq. 1.4 for sample with a magnetite core and Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ shell at various fields and temperatures.
Figure B-6. SANS nuclear scattering contribution calculated from Eq. 1.4 for sample with a magnetite core and $\text{Co}_{0.75}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ shell at various fields and temperatures.
B.3 Magnetic Scattering

Additional magnetic SANS graphs for Fe$_3$O$_4$@Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ Core-Shell Nanoparticles supplemental to Ch. 4 are shown below.
Figure B-7. SANS magnetic scattering contribution calculated from Eq. 1.6 and Eq. 1.5 for samples with magnetite core and Co/Zn-ferrite shells with Co fractions (a,b) $X = 0.25$, (c,d) $X = 0.50$, and (e,f) $X = 0.75$ at 5 K for various field measurements. The field evolution for magnetic scattering perpendicular to the field is shown in (a,c,e) while parallel can be seen in (b,d,f).
Figure B-8. SANS magnetic scattering contribution calculated from Eq. 1.6 and Eq. 1.5 for samples with magnetite core and Co/Zn-ferrite shells with Co fractions (a,b) X = 0.25, (c,d) X = 0.50, and (e,f) X = 0.75 at 5 K for various field measurements. The field evolution for magnetic scattering perpendicular to the field is shown in (a,c,e) while parallel can be seen in (b,d,f).
Figure B-9. SANS magnetic scattering contribution calculated from Eq. 1.6 and Eq. 1.5 for samples with magnetite core and Co/Zn-ferrite shells with Co fractions (a,b) \( X = 0.25 \), (c,d) \( X = 0.50 \), and (e,f) \( X = 0.75 \) at 5 K for various field measurements. The field evolution for magnetic scattering perpendicular to the field is shown in (a,c,e) while parallel can be seen in (b,d,f).
Appendix C
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Magnetism of Nanoparticles: Effect of the Organic Coating

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Abstract

The design of novel multifunctional materials based on nanoparticles requires tuning of their magnetic properties, which are strongly dependent on the surface structure. The organic coating represents a unique tool to significantly modify the surface structure through the bonds between the ligands of the organic molecule and the surface metals. This work presents a critical overview of the effect of the organic coating on the magnetic properties of nanoparticles through a selection of papers focused on different approaches to control the surface structure and the morphology of nanoparticles' assemblies. View Full Text

Keywords: magnetic nanoparticles; molecular coating; magnetic properties

Figure 1

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Correlated spin canting in ordered core-shell $\{\text{Fe}_3\text{O}_4\}_x\{\text{Mn}_x\text{Fe}_{3-x}\text{O}_4\}_{1-x}$ nanoparticle assemblies

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