

UNDERSTANDING DOPANT SITE PREFERENCES IN DOPED IRON OXIDE
NANOPARTICLES: DOES A RELAXED UNIT CELL IN NANOPARTICLE ALTER
THE SITE PREFERENCE WITHIN THE SPINEL STRUCTURE?

by

Vanessa LaVelle Karandi Pool

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Physics

MONTANA STATE UNIVERSITY
Bozeman, Montana

July 2012

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DEDICATION

I would like to dedicate this to my family and my boyfriend Steven O' Neil for there support. Margaret Jarrett for being particularly helpful at a time when she hardly knew me and to all the people in the department that made it feel like a family. My high school physics teacher Mr. Lapp how introduced me to physics and with out whom I would likely never have gone into the field. To all the people and inspirations that made physics, and science in general, seem so cool. And last but not least my adviser Yves Idzerda, who is a constant inspiration and reminded of why I love physics, for all his support and guidance in this endeavor.

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ABSTRACT

The dopant behavior of spinels has been investigated for over half a century and yet new insight into this class of materials is still being made today. The dominating question has been “Into which site in the spinel structure does the dopant substitute?”. In this work, we will explore this question for the nanoparticle regime.

Through this work the potential for a relaxation of the normal strains that can arise in a bulk crystal structure is demonstrated in nanoparticles. The hypothesis that this relaxation can lead to unconventional dopant site preferences for dopants in an iron oxide spinel structure is demonstrated.

Nanoparticles ranging from 6 nm to 15 nm in diameter have been synthesized with vanadium, manganese, zinc and gallium doped into the iron oxide spinels. The size and structure of the nanoparticles was investigated with transmission electron microscope and X-ray scattering pair distribution functions. The dopant's valence state was investigated with X-ray absorption spectroscopy and the coordination and magnetic properties of the materials were investigated with X-ray magnetic circular dichroism. Alternating current magnetic susceptibility was used to determine the degree of interaction between the particles, and in the case of non-interacting particles, anisotropy energies were extracted. In this study the dopant atoms were found to behave similarly to their bulk counterparts, with the important exception of manganese and vanadium. Manganese doped iron-oxide nanoparticles show clear evidence of crystalline relaxation. Vanadium substituted into the preferred tetrahedral site in the nanoparticle form, unlike the bulk behavior. Both observations are attributed to the accommodating relaxation found in nanoparticles.

CHAPTER 1

INTRODUCTION AND MOTIVATION

Magnetite and other ferrite spinels have been investigated for over a half a century, but with the growing field of nanoparticles and other nanostructures, looking at these complex systems in the nanoscale is now of great interest. Ferrites are multiferroic and magneto-electric¹. In nanoparticle form ferrites have been investigated for a number of applications. In the biomedical field alone they have shown potential for cancer therapies such as hyperthermia²⁻⁶, MRI contrast agents⁷⁻¹⁴ and even as part of bio-detectors^{15, 16}. This is especially true for nanoparticles grown in a ferritin protein cage or other biocompatible organic vessel^{17, 18}. Additionally spinels can be used as catalysts^{19, 20}, optical switching detectors²¹, cathode materials^{22, 23}, microwave applications²⁴⁻²⁶ and more.

The breadth of properties exhibited by ferrites must be attributed to the way in which the multitude of dopants affects the iron-oxide spinel. Magnetite is a ferrimagnet. Doping can have a dramatic effect on the magnetic properties of the resulting ferrite. Due to the complex nature of the ferrimagnetism of magnetite, doping, even with a nonmagnetic species, can increase the magnetism. Other properties can be likewise affected such as the magnetoresistance (MR) of magnetite doped with zinc²⁷, improved MRI contrast agents and more effective hyperthermia treatment²⁸, and enhanced cathode stability during cycling²⁹. In the microwave application several properties can be affected

depending on the dopant introduced²⁶. This variation in properties is why spinels, in their many forms, have been the subject of so much investigation.

In functionalizing these applications, understanding how the materials might be affected by scaling down of the size of a crystal, becomes increasingly important, since nanoscaled materials exhibit interesting behaviors. Nanoparticles of the scale observed in this study are on the order of 10's of unit cells across and it is not unreasonable to conceive of crystal relaxations and surface effects that will become prominently important on the scale of these systems. This complication on the already complex spinel system is intrinsically interesting. In this work on nanoparticles, where there is the potential for crystal relaxations, the standard behavior can be at times negated due to behavior unique to the size of the particles in question.

In chapter 2, an overview of the spinel structure will provide an understanding of the crystal structure. A description of magnetite as the quintessential magnetic spinel will be reviewed, followed by an understanding of the magnetic coupling responsible for the ferromagnetic nature of spinels. An overview of some relevant spinel minerals will then be presented in order to better understand the expected bulk magnetic behavior that different elements will have as dopants. Next, a general description of how the dopant site preference has been developed so far in the literature will be reviewed. A simple calculation to predict the initial magnetic behavior will be introduced. This calculation will examine how the introduction of a dopant of varying ionizations and site occupations affects the moment of the material. Finally, a geometric argument for why a crystal relaxation for nanoparticles of the size covered in this work will be provided, in order to

give validity to the idea that a crystal relaxation could cause doping in spinel nanoparticles to behave differently than their bulk counterparts.

In chapter 3 the theoretical under-pinning of the measurements done in this work will be reviewed. A description of the characterization of the equipment used in doing these measurements and, when appropriate, a more thorough description of the method preparations will be discussed.

In chapters 4-9 the 6 papers that make up the breadth of research that forms this dissertation will be presented. Finally in chapter 10, there will be a discussion of the findings of these papers and how they relate to the understanding of how dopant preference in nanoparticles differs from that of the bulk spinel structure.

CHAPTER 2

UNDERSTANDING SPINELS

Magnetite, once known as lodestone, is thought to be the oldest known magnetic material³⁰. Because of this, magnetite introduced ancient humans to magnetism. Magnetite can be found in large quantities in some beach sand like the black sands found off the coast of California and the west coast of New Zealand³¹. Magnetite is also found in some bacteria as well as in the brains of bees, fish, some birds (for example pigeons) and humans; this is thought to be a key component of magnetoreception, which is the perception of the earth's magnetic field, thought to be involved in navigation in some species³¹. Magnetite along with maghemite has been used in magnetic recording media. Magnetic spinels, such as magnetite, have proved to be very useful for high frequency applications that require magnets, as they have considerably less eddy-current losses since they are not metallic³². It is also considered to be a half metal with the highest known Curie temperature at 858 K³⁰.

Overview of the Spinel Structure

The name Spinel comes from the naturally occurring mineral MgAl_2O_4 but now also refers to a crystal group with the same structure and the general formula PQ_2X_4 . For oxide spinels, the X refers to oxygen though there are other types of spinels, such as sulfide spinels. In this work, the X refers to oxygen unless otherwise stated. A standard unit cell for an oxide spinel has 32 oxygen anions and 24 cations (often transition metals). In this structure, as can be seen in figure 2.1, there are 2 distinct coordinations of the

cations: those which are surrounded by 4 oxygen atoms, having a tetrahedral coordination, which are known as the A-sites, and those surrounded by 6 oxygen atoms, the octahedral sites, which are known as the B-sites. If one looked at the oxygen atoms as a host matrix, there would be 64 possible tetrahedral cation sites and 32 possible octahedral cation sites; however, not all of these possible sites would be occupied³³. There are 8 atoms per unit cell in the tetrahedral A-sites and 16 atoms per unit cell in the octahedral B-sites, as seen in figure 2.1. So within one formula unit PQ_2O_4 there is one A-site and two B-sites. For charge neutrality with the O^{2-} anions, spinels can have $\frac{1}{3}$ of the cations 2+ and $\frac{2}{3}$ of the cations 3+ valence (which are referred to as 2-3 spinels) or $\frac{2}{3}$ 2+ and $\frac{1}{3}$ 4+ cations (which are called 4-2 spinels)³⁴. In this work we are only utilizing the 2-3 spinels, so this ionization will be assumed in further discussion.

Spinels can also be divided up into three categories: normal, inverse, or mixed,

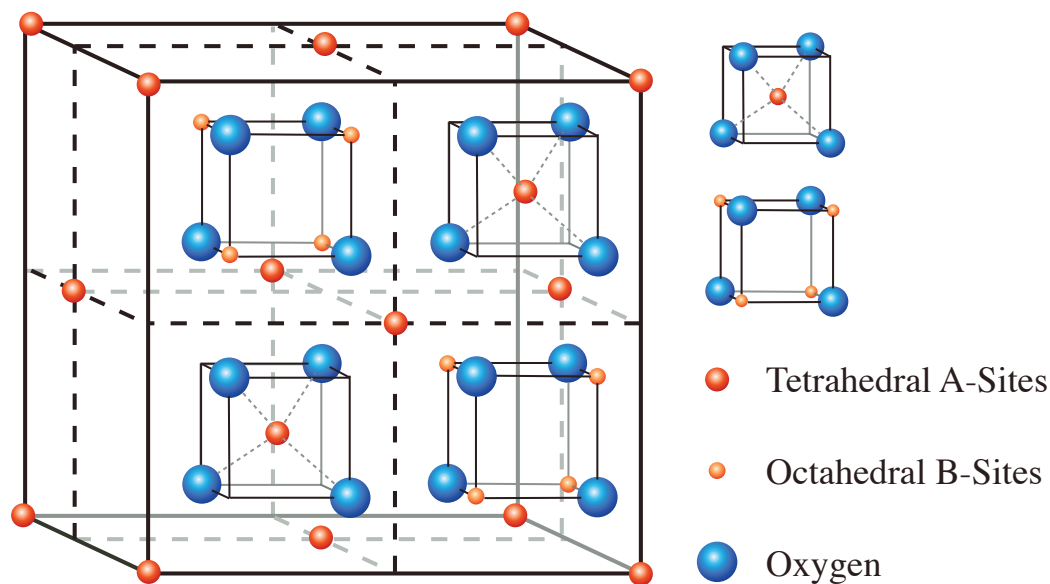


Figure 2.1: Spinel Structure

based on the arrangement of 2+ and 3+ cations in the tetrahedral and octahedral sites. If the 2+ cations occupy the tetrahedral sites and the 3+ cations occupy the octahedral sites, the material is classified as a normal spinel. If the tetrahedral sites are occupied by 3+ cations and the octahedral sites are occupied by an even split of 2+ and 3+ cations, the material is classified as an inverse spinel^{33, 35}. If the cations are not so well ordered and there is a mixture of 2+ and 3+ cations in the tetrahedral and octahedral sites, it is referred to as a mixed spinel. Spinel is often written in the form $P(Q_2)O_4$ for "normal" spinels or $Q(PQ)O_4$ for "inverse" spinels, where the elements in parentheses are understood to be in the octahedral site and the others in the tetrahedral site³⁵. For further specificity, the ionization of the cations can also be written as a superscript, for example $P^{3+}(P^{2+}Q^{3+})O_4$.

Overview of Magnetite

Magnetite will be used as the model of a magnetic spinel. In understanding the dopant's behavior it is useful to think of magnetite as the quintessential magnetic spinel: the standard from which other spinels are understood.

Magnetite, or Fe_3O_4 , is an inverse spinel and so in the notation mentioned previously it would be written $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$. Cubic in nature, Fe_3O_4 has a unit cell with $a = b = c = 8.391 \text{ \AA}$ where there are 24 iron atoms per unit cell, as shown in figure 2.1. For further information about the crystal characteristics, refer to Appendix A.1^{36, 37}, which contains additional information on a number of spinels. In magnetite, there are 32 oxygen ions and the oxygen is in the usual 2- ionization state, so for charge neutrality, the iron ionization is split $\frac{1}{3}$ with a 2+ ionization and $\frac{2}{3}$ with a 3+ ionization. The fact

that magnetite is an inverse spinel means that the 8 A-sites are all 3+ and the 16 B-sites are evenly split between 3+ and 2+^{33, 35}, as shown in figure 2.2. The ionization state is also important because of the valence dependence of the magnetic moment of the iron atom. Since most of the moment of an atom within a solid comes from the electron spin (as orbital quenching lessens the orbital moment contribution), a simple counting of unpaired electrons (each of which contributes $1 \mu_B$ to the total atomic moment) provides the moment of an individual iron atom of a given charge. By this reasoning, iron 2+ has a moment of $4 \mu_B$ and iron 3+ has a moment of $5 \mu_B$, as seen in figure 2.3. (A table outlining the number of d electrons for different ions is included in Appendix B.1a³⁸.) Given that there are 8 tetrahedral A-site atoms per unit cell all with 3+ ionization and 16 octahedral atoms per unit cell split evenly between 2+ and 3+ ionization, the A-sites contribute $40 \mu_B$ and the B-sites contribute $72 \mu_B$. For magnetite, the A-sites and B-sites are anti-aligned and the net moment per unit cell is $32 \mu_B$. With 24 iron atoms in a unit cell, the calculated moment per iron atom is $1.33 \mu_B$, though measured values are a bit higher at $1.36 \mu_B$ ³².

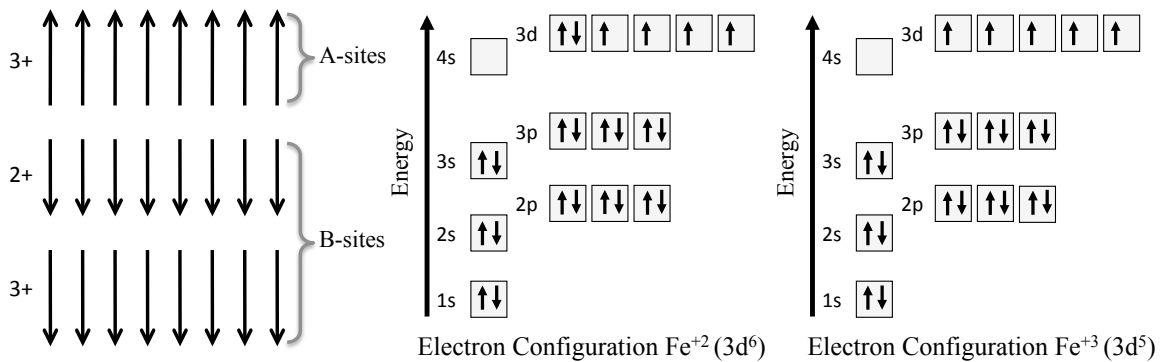


Figure 2.2: Spinel Arrangement Figure 2.3: Electron Configuration of Iron

The Spinel Structure: Magnetically Speaking

Now armed with an understanding of the generic crystalline structure of a spinel, the next step is to look at the magnetic structure of spinels that exhibit magnetism. Magnetite or Fe_3O_4 is not only the oldest magnet known, it is also an excellent example of a magnetic spinel, and it will be used as the generic magnetic spinel in this section.

Magnetic spinels are ferrimagnets, which can be thought of as a cross between a ferromagnet and an antiferromagnet. Ferrimagnets have an overall moment and, from a macroscopic perspective, behave like a ferromagnet. However, the magnetic ordering of a ferrimagnet has more in common with an antiferromagnet than a ferromagnet, as it is essentially an antiferromagnet whose opposing magnetic moments have different magnitudes and so do not fully cancel one another out. In this sense, it is really more like a subclass of antiferromagnetism, when thought of on an atomic scale.

The spinel structure is not the simplest ferrimagnet. In the simplest example of a ferrimagnet, you would have two different atom species in equal numbers, which are antiferromagnetically aligned but have different magnetic moments. In this case, the overall moment is simply the difference of the two moments. Magnetite has two different sublattices of the same element but with two different moments, as well as a two to one ratio of the number of atoms in each sublattice. In addition, the ordering that causes this sublattice antiferromagnetism in magnetite is, in fact, an example of two different indirect exchange interactions: superexchange and double exchange, that together produce its overall orientation and resulting magnetization. Before looking at

the spinel magnetic alignment any further, it is instructive to review the exchange mechanisms involved.

Direct Exchange Interaction

To understand indirect exchange perhaps we should first review direct exchange. Direct exchange results from the exchange interaction between two electrons in separate atoms. The Heisenberg Hamiltonian can be written in the form shown in equation (2.1). Here J_{ij} is the exchange integral for the two electrons and takes the form of equation (2.2),

$$(2.1) \quad \mathcal{H}_{\text{eff}} = - \sum_{i \neq j}^N J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j = -2 \sum_{i < j}^N J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j,$$

$$(2.2) \quad J_{ij} = \int \int \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \psi_i^*(\mathbf{r}_2) \psi_j^*(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2.$$

where ψ_i and ψ_j are the wave functions of the electron orbitals. If the spins are parallel, then $\mathcal{H}_{\text{eff}}$ is minimized for $J_{ij} > 0$, which is the ferromagnetic coupling case. If the spins are antiparallel, then $\mathcal{H}_{\text{eff}}$ is minimized for $J_{ij} < 0$, which is the antiferromagnetic coupling case.

Indirect Exchange Interaction

Indirect exchange interaction is an interaction that extends beyond the nearest neighbor interaction. This category of exchange interactions includes super-exchange (sometimes referred to as antiferromagnetic indirect exchange interaction), double exchange, and RKKY (which is applicable in metals and will not be covered here). Both superexchange and double exchange represent a coupling mechanism between two

magnetic atoms with relatively localized electron states through an intermediate, nonmagnetic atom, commonly oxygen.

Superexchange

Superexchange is an interaction that produces an antiferromagnetic coupling (usually) between two magnetic cations through an intermediate anion such as oxygen. The physical reason for superexchange is the same as for direct exchange: interaction of the electrons of the two adjacent atoms. Therefore it also depends on the strength of the overlap integral of these electrons. With superexchange, rather than just considering the electron states from two magnetic atoms, there is an intermediate oxygen atom. To look at it in a more intuitive light, let us consider the example of d_5 or d_6 configuration of iron, which has a 3d state with the characteristic 4 fold symmetry and an oxygen 2p state with the characteristic dumbbell shape as shown in figure 2.4. The oxygen atom, to be in its preferred $2-$ ionization, wants to accept 2 electrons from the iron cations. These additional electrons will fill the oxygen p-orbitals and so, by Pauli exclusion, the two

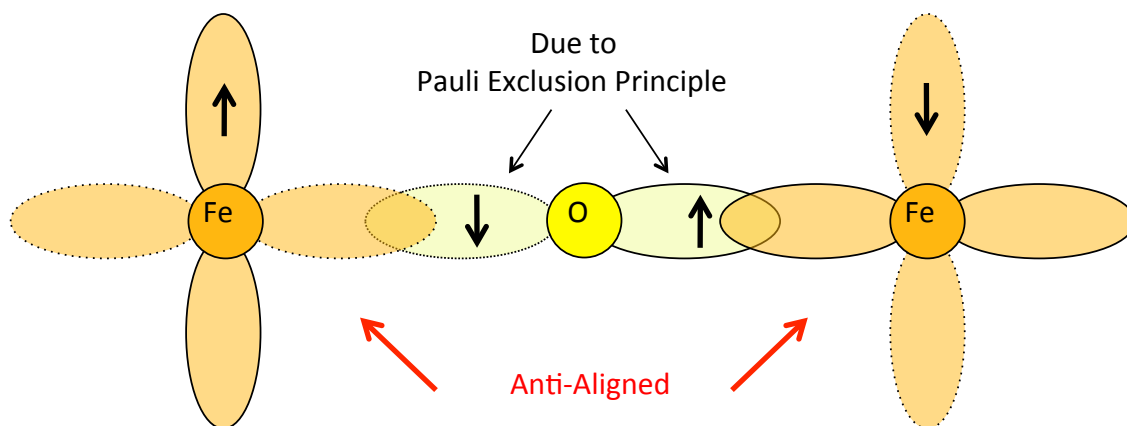


Figure 2.4: Superexchange for More than Half Filled Shells

electrons in the p-orbital must be anti-aligned. The oxygen's p-orbitals and the iron's d-orbitals will overlap. This overlap causes an energetic preference for the empty state of the iron to be of the same spin orientation as the spin of the oxygen atom, which in turn means that the filled states are pointing in the opposite direction (assuming only Fe^{2+} or Fe^{3+} are present). This can be thought of as sharing of the electron between the two states, and explains the energy preference; the electrons are less confined if they are allowed to occupy either state and so the configuration that allows this is the lower energy one. The oxygen p-orbital now has an electron in one of its two states, which is aligned opposite to the electrons in the nearest iron atom, since the 3d shell of the Fe ion is half or more than half-filled. Due to Pauli exclusion principle, the second electron in the p-orbital must be aligned opposite to the first. Since the energetic favorability will apply to the interaction between this second electron and the second iron atom's electrons, the result is that the two iron atoms are anti-aligned as seen in figure 2.4.

The alignment shown in figure 2.4 is for the case where the 3d electrons are half filled or more than half filled (the case for iron 2+ or 3+). If the figure were for the less than half filled case, then the electrons of the iron would be in the same direction as the direction of the overlapping oxygen atom's electron, still producing an antialigned configuration between the two iron atoms. In the case where one transition metal is less than half filled and the other is half or more filled, then superexchange produces a ferromagnetic interaction. This is because one oxygen p-electrons is aligned to the electrons in one of the transition metal ions, the other p-electron is anti-aligned to the other transition metal ion and the two p-electrons are anti-aligned to one another. The

interaction is essentially that of a direct interaction between the iron atom and the oxygen atom and then another from the oxygen atom to its other iron neighbor (in a collinear sense), hence it is bonding indirectly through the oxygen atom (indirect exchange interaction).

Since the indirect exchange interaction is mediated by the oxygen atom, the shape of the oxygen orbital is key, as it will determine the strength of the overlap integral. The dumbbell shape of the oxygen's p orbital, will produce a cosine dependence to the magnitude of the overlap integral and so the strength of this interaction is largest at 180° and zero at 90° . This dependence in the strength of the superexchange interaction on bond angle makes the angle between the various cations very important, as will be shown later when considering how superexchange produces the antiferromagnetic coupling of the A and B sublattices.

Double Exchange

Double exchange, like superexchange, is also mediated through the oxygen atom. However, double exchange requires cations with different ionizations, such as the Fe^{3+} and Fe^{2+} valence in the B-sites of an inverse spinel like magnetite. This kind of indirect exchange relies on the possibility of an electron from the Fe^{2+} to hop over to the Fe^{3+} atom, through the oxygen, effectively swapping their ionizations. This two-hop process is illustrated in figure 2.5. In double exchange, as in superexchange, the Pauli exclusion principle is key to the orientation of the two iron atoms. The Pauli exclusion principle requires that the two oxygen electrons have different spins. If Hund's rules are to be applied, then there is only one orientation of the moments of the two iron atoms that will

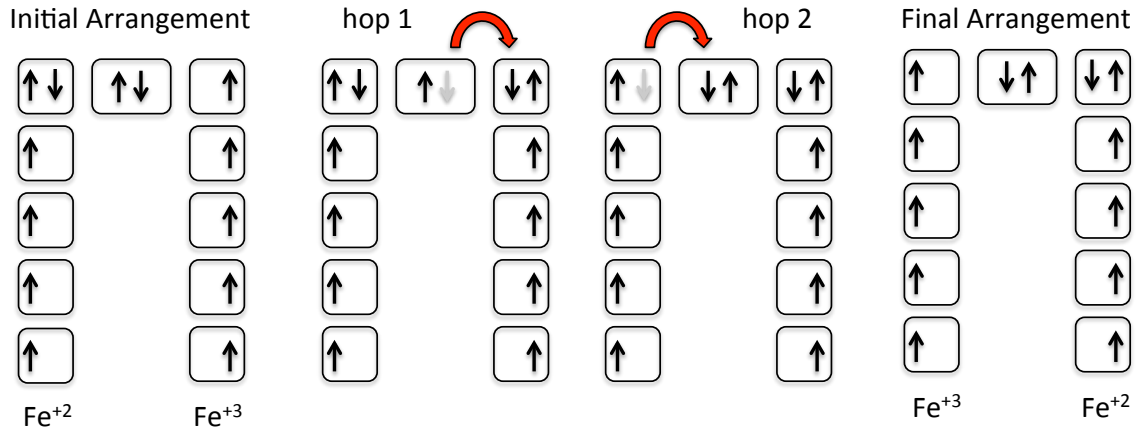


Figure 2.5: Double Exchange

allow for this hopping. If Hund's rule were ignored then the electron hopping could occur either way, but hopping into the anti-aligned configuration would be energetically unfavorable, so the energetically favored configuration is with the magnetic atoms aligned. If the two iron atoms are magnetically aligned, as shown in figure 2.5, then an electron from the intermediate oxygen atom can hop to the more ionized iron Fe^{+3} ion, creating a vacancy in the oxygen atom and changing the Fe^{+3} to Fe^{+2} . Subsequently, an electron from the Fe^{+2} can then hop into this vacancy, effectively swapping the ionization of the two iron atoms. The possibility of this hopping causes the magnetic alignment, as it is energetically favorable to have more electron configurations available (the higher entropy configuration)³⁹. Mathematically this is not reducible to the form of the indirect exchange in the way that superexchange was to direct exchange interaction.

Exchange Interactions in Magnetite

Magnetite is an interesting magnetic material as it exhibits both antiferromagnetic coupling between the A and B sublattices and ferromagnetic coupling within the B

sub-lattice, demonstrating both superexchange and double exchange. The mechanism for the antiferromagnetic alignment of the A-sites and B-sites is superexchange. As was discussed in the overview of superexchange, the strength of this interaction is correlated to the angle formed by the iron-oxygen-iron bond. These bond-angles are shown in figure 2.6³⁵ and it is clear that the bond-angles between the A-sites and B-sites are closest to 180° . It is as a consequence of the large bond-angle between the A-site and B-site atoms, as well as the large number of these bonds, that the A-B coupling dominates over the other coupling strengths. Since the overlap of the orbitals is what is important, it is not just the bond angles, but the bond lengths as well that determine the strength of the indirect exchange; this information has been included for convenience in Appendix A.2^{38, 40}.

This coupling alone could produce the observed antiferromagnetic alignment between the A and B sites. In magnetite however, this is not the only factor. The second form of indirect exchange, double exchange, comes into play and produces ferromagnetic coupling between the B-sites within the B sub-lattice. This is possible in magnetite because it is an inverse spinel and so the B sub-lattice is made up of 2+ and 3+ iron,

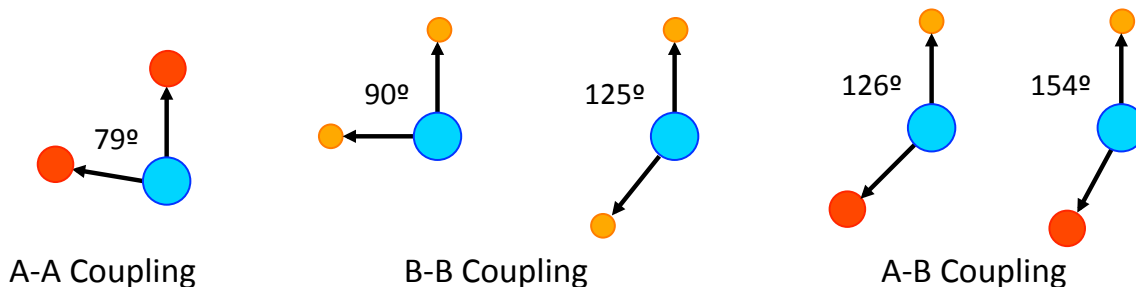


Figure 2.6: Spinel Bond-Angles

allowing for double exchange between the unlike ionized iron atoms.

With the B-sites all aligned, the A-site must also all be aligned for the A and B sites to all be anti-aligned. Additionally, double exchange would only have relevance for a spinel where there are both 2+ and 3+ species in the B-sites and so would not apply to the case of a normal spinel, where each sub-lattice has only one valence. In the case of a normal spinel, if the A-B coupling were to weaken, for example by the A-site being filled with a nonmagnetic atom, then the superexchange present between B-site atoms within the B sub-lattice become the dominant coupling mechanism and the entire material would become antiferromagnetic, as is the case for Franklinite ($\text{Zn(Fe}_2\text{)O}_4$). Once the magnetic ordering of the spinel is understood, it becomes clear how the placement of the dopant and its ionization has a dramatic effect on the magnetization of a magnetic spinel, making it a very interesting material to look at from a scientific perspective.

Other Relevant Minerals

Armed with a basic understanding of the crystalline and magnetic structure of spinels, we can consider magnetite (a defected spinel) and mixed element spinels. There are a great number of stable spinel structured crystals. This will not be an extensive list of them as most are not relevant; however, hopefully it will impart a general understanding of the magnetic behavior of spinels as it relates to this work. Since this is a study of doping into an iron-oxide spinel, it is instructive to review the atomic arrangement in naturally occurring spinel minerals and their bulk behavior. As spinel is only one of the structural possibilities for iron-oxide, a phase diagram for iron-oxide is included for reference in Appendix A.3³².

Maghemite

Magnetite is being used here as the representative magnetic spinel; however, it is not the only iron-oxide spinel. Maghemite, or $\gamma\text{-Fe}_2\text{O}_3$, has the same spinel structure, so it is very hard to distinguish between magnetite and maghemite in measurement, especially measurements relying only on lattice spacing. Maghemite differs from magnetite in that it is missing $2\frac{2}{3}$ iron atoms per unit cell, producing vacancies exclusively in the octahedral sites. For charge neutrality, this causes all the iron atoms in maghemite to be iron 3+ cations. Since all the vacancies are in the B sublattice, the contribution from the A-sites is still $40 \mu_B$. The B-sites now only have $13\frac{1}{3}$ atoms rather than 16; however, the fact that all the iron is now 3+ also means that the remaining atoms all have a moment of $5 \mu_B$ moments. This means that while the A-sites are still contributing $40 \mu_B$, the B-sites are now contributing $66.67 \mu_B$, rather than $72 \mu_B$, reducing the moment per unit cell to $26.66 \mu_B$, rather than $32 \mu_B$. Maghemite has a calculated moment of $1.25 \mu_B$ per iron atom, though the measured value is slightly lower at $1.2 \mu_B$ ³².

Hematite

Though not a spinel, hematite (written as $\alpha\text{-Fe}_2\text{O}_3$), is included here as it is a very common form of iron-oxide. Often found in locations with standing water, such as the hot springs of Yellowstone National Park, it produces the red color in many soils³¹. This mineral is stronger than metallic iron (though more brittle). Often referred to as an antiferromagnetic, it is technically a canted ferromagnet above its Morin transition at 250 K until its Néel temperature is reached at 948 K^{41, 42}. Its moment is extremely small

however, with only $0.002 \mu_B$ per iron atom, which is the result of canted spins. Hematite has a trigonal system with unit cell dimensions: $a = 5.04 \text{ \AA}$ $c = 13.44 \text{ \AA}$ ³⁶.

Franklinite

Franklinite or ZnFe_2O_4 is a nonmagnetic spinel where $\frac{1}{3}$ of the cation sites are now zinc rather than iron. In the bulk behavior for this spinel, zinc goes into the tetrahedral site as a $2+$ ^{35,43} valence cation. Zinc prefers the $2+$ ionization rather strongly forming ZnO as the predominant oxide. Zinc occupies the tetrahedral position in the bulk structure making franklinite a normal spinel. The lack of any magnetic atoms in the A-sites eliminates the A-B coupling and with all the B-site irons as $3+$ cations there is no potential for double exchange, so the B-sublattice is antiferromagnetic. In bulk studies of zinc doping into Fe_3O_4 , the moment increases with small incorporation of zinc before falling to zero³⁸. This trend is typical of a nonmagnetic dopant going into the tetrahedral site of an iron spinel. In low quantities the incorporation of the nonmagnetic atom into the A-site is insufficient to disrupt the A-B coupling. The A-sites magnetic contribution is reduced, causing the overall moment per unit cell to increase. For zinc this effect is compounded by the fact that the zinc substitutes for Fe^{3+} as a $2+$ ion, forcing the valence of some other Fe^{2+} atom in the B-site to become Fe^{3+} , producing a $5 \mu_B$ moment rather than $4 \mu_B$ moment, causing the moment per unit cell to be raised more than if the dopant substituted as a $3+$ ion. As the concentration of the non-magnetic atoms are increased, the number of antiferromagnetically interacting A-B bonds is reduced and the magnetic interaction between the A and B sublattice weakens. For zinc, the point where the total

moment reaches a maximum occurs at 15% incorporation of zinc in bulk studies⁴⁴, corresponding to a loss of A-B interaction.

Jacobsite

Jacobsite or MnFe_2O_4 is another example of a magnetic spinel and has an even larger moment per unit cell than magnetite. The larger moment is a result of manganese preferring the 2+ tetrahedral A-site positions in the bulk. As in the zinc case, this requires all the Fe B-sites to become 3+ ions for charge neutrality (with a respective moment of $5 \mu_B$). So far, this is the same as was seen for franklinite, but with one distinct difference: manganese has a moment. For manganese, Mn^{2+} has a moment of $5 \mu_B$ and Mn^{3+} has a moment of $4 \mu_B$. This means there is a contribution up $40 \mu_B$ per unit cell due to the manganese in the A-sites, while the iron contributes $80 \mu_B$ in opposition from the B-sites, producing an over all moment per unit cell of $40 \mu_B$ or $1.66 \mu_B$ on average per transition metal atom. Interestingly however, in this case the average moment per iron atom is $5 \mu_B$, whereas the average moment per iron atom of magnetite is $1.33 \mu_B$. This is pointed out because the magnetic information extracted using MCD in this research, which will be discussed later, is an element specific probe. This means that the moment extracted with Fe MCD for jacobsite would be $5 \mu_B$ rather than the $1.66 \mu_B$ moment associated with all transition metal atoms in the unit cell. Additionally, this material would show an elemental manganese MCD of $-5 \mu_B$. This is not demonstrated here, but is simply pointed out for the sake of clarity and completeness.

Iwakiite

Iwakiite or Mn_2FeO_4 or $\text{Mn}(\text{MnFe})\text{O}_4$ is not magnetic. For jacobsite $\frac{1}{3}$ of the iron was replaced with manganese, for iwakiite $\frac{2}{3}$ of the transition metal sites are manganese and it is antiferromagnetic. Manganese still occupies the tetrahedral sites as $2+$, but now also occupies half of the octahedral $3+$ sites as a $3+$ ion as well. With this larger incorporation of manganese, tetragonal distortions start to emerge; the unit cell is no longer cubic but instead has dimensions of $a=b=8.519 \text{ \AA}$ and $c=8.54 \text{ \AA}$.

Hausmannite

Hausmannite or Mn_3O_4 is a stable form of Mn-oxide with a spinel structure and it is antiferromagnetic. Hausmannite is a normal spinel, so all the $2+$ cations are in the tetrahedral coordination or A-sites and all the $3+$ cations are in the octahedral coordination or B-sites, leaving no possibility for double exchange in the B sublattice. Hausmannite has an even more pronounced tetragonal distortion than Iwakiite (not surprisingly), where $a \neq c$ to a very pronounced extent with $a=b=5.71 \text{ \AA}$ and $c=9.35 \text{ \AA}$ ⁴⁵. Though not magnetic, these higher concentrations of Mn have been included as the dopant study of Mn will also include up to 100% Mn incorporation.

Gallium Ferrite

I have found no mineral name for a gallium iron spinel, though it has been synthesized and there are references to Fe_2GaO_4 and FeGa_2O_4 structures. This may be because gallium is found in very few minerals in any quantity. There are a few minerals with a significant amount of gallium: gallite or CuGaS_2 where the gallium is tetragonally coordinated, a few hydroxides, such as tsumgallite or $\text{GaO}(\text{OH})$ and sohngeite or

$\text{Ga}(\text{OH})_3$. In general however, naturally occurring minerals only have trace amounts of gallium. This may be in part due to its extremely low melting point; while solid at room temperature, its melting temperature is 29.8 °C.

Gallium can be persuaded to form several oxides: Ga_2O , GaO and Ga_2O_3 , suggesting it can have 1+, 2+ or 3+ oxidation states, Ga_2O_3 being the most stable and forming several different crystal structures. Of the gallium (III) oxides, $\beta\text{-Ga}_2\text{O}_3$ is the most common and only thermodynamically stable phase in which the gallium occupies both tetrahedrally and octahedrally coordinated sites⁴⁶⁻⁴⁸. It also forms $\gamma\text{-Ga}_2\text{O}_3$, the vacancies occurring in the octahedral coordination sites. For this reason, and because it seems to be the consensus in the literature for Fe_2GaO_4 , gallium substituting into the tetrahedral site as a 3+ valence ion will be considered its bulk behavior^{43, 49}.

Coulsonite

Coulsonite or FeV_2O_4 is a named form of vanadium iron oxide mineral. Vanadium is an element of many ionizations 2+ to 5+ and forms VO , VO_2 , V_2O_3 , V_2O_5 , and V_3O_5 with an octahedral preference for V^{3+} ionization^{50, 51}. Furthermore, from these examples, vanadium prefers an octahedral coordination. In coulsonite, vanadium is found to substitute into the octahedral site with a 3+ valence⁵². There also seems to be some dispute over the unit cell lattice constant where values of 8.45 Å⁵³ and 8.28 Å⁵² are reported.

More Spinel Bulk Behavior

In the previous section, a number of spinel minerals were described in an effort to understand their bulk behavior and anticipate the dopant behavior in the nanoparticles. In

these cases, the spinels are empirical formula mixtures of iron with another element. With the substitution of $\frac{1}{3}$ of the iron with a non-iron element, the tetrahedral sublattice or half of the octahedral sublattice is filled. I have included the information about the minerals in an attempt to simplify the understanding of the dopant behavior; however, there is less agreement for the dopant site at low dopant concentrations. Hill, in a review of spinels, has compiled an extensive list of spinel work including some of these conflicting results⁴⁰. A table of a selection of these results is provided in Appendix A.4⁴⁰, but a shortened version, with only the materials appearing in this work is provided in table 2.1.

Table 2.1: Hill Table of Spinel

	a	A_{cat}	B_{cat}	Ref.★
Fe₃O₄	8.3940	Fe	FeFe	34
FeMn₂O₄	8.5280	Fe	Fe _{.1} Mn _{.19}	35
FeGa₂O₄	8.3600	Fe	GaGa	1
Fe₂VO₄	8.4210	V	FeFe	1
FeV₂O₄	8.4530	Fe	VV	26
Fe₂MnO₄	8.5110	Mn	FeFe	43
Mn₃O₄	8.6400	Mn	MnMn	29
Fe₂ZnO₄	8.4432	Zn	FeFe	43

★All Ref. Refer to the reference number cited by Hill

Research on vanadium iron-oxide spinels is not without discrepancies. Though the consensus favors the octahedral occupation, there are dissenting results. Some studies conclude that vanadium prefers the octahedral site exclusively⁵⁴⁻⁵⁸, while others find vanadium prefers the tetrahedral site⁵⁹. These inconsistencies may arise from concentration dependence, grain size issues or synthesis methods. In the references compiled by Hill, vanadium is found to be in the A-site for Fe₂VO₄⁵⁹, but in the B-site for FeV₂O₄^{60, 61}.

Gallium ferrites have been studied, though not as thoroughly as some other spinels, with most concluding that gallium prefers a 3+ ionization state. There are differing conclusions on the site preference: several studies suggest gallium prefers the tetrahedral site^{43, 62, 63} while others suggest it prefers the octahedral site⁶⁴, and yet others found that there was no preference⁶⁵. Wang⁶⁶ found that the occupancy was dependent on the gallium concentration, with gallium preferring the tetrahedral coordination at low concentrations, but with some octahedral occupancy at higher concentrations.

Site Preference in Spinel

There has been a plethora of work done to understand the site preference of atoms in the spinel structure. Initially, it was thought that the tetrahedral coordinated sites preferred the smaller ionization (M^{2+} cations over M^{3+} cations)^{35, 54}. This is why the valence configuration of franklinite is called "normal", because it was thought of as the normal arrangement of ions. This is clearly not sufficient as a complete description of site preference in spinels as magnetite is very abundant but has 3+ cations in the tetrahedral site and is an inverse spinel.

Another factor that is thought to contribute to site preference is ion size. This is in contradiction with the previous concept that an ion with a lower ionization will preferentially occupy the A-site, as M^{3+} is smaller than M^{2+} . A large compilation study was done by Hill⁴⁰, comparing not only different ion sizes amongst oxide spinels, but with sulfide spinels as well. This tetrahedral verses octahedral preference can be understood from a simple geometric argument, where the hard sphere approximation is used for the atoms. By calculating the size of the void created by a matrix of anions of a

given type, such as O^{2-} , and a given coordination, it is possible to calculate how well a hard sphere cation might fit in the void created by the anions. This is called the radius ratio rule⁶⁷.

With this, an ionic radii ratio can be established for a given geometry (this is worked out in Appendix B.2). This ratio is thought to dictate a preference for certain coordinations given the cation-to-anion ratio. The ratio is calculated by solving for the largest cation that can fit in the void of a given coordination created by touching oxygen anions (again see Appendix B.2 for more details). For the coordinations under consideration here, the ionic radii ratios are as follows: $R_c/R_{O_{Tet.}} = 0.225$, and $R_c/R_{O_{Oct.}} = 0.414$, where R_c is the cation radius and R_o is the oxygen radius. The radius ratio rule predicts that the atoms will arrange themselves tetrahedrally until they reach the octahedral ratio 0.414⁶⁷. A table of ion radii has been included with some elements in Appendix B.3⁶⁸ where the radii have been taken from Shannon's paper on ionic radii⁶⁸ and are given in pm. In Shannon's work there are two sets of data, the "crystal" ionic radii, which uses an anion radius of 126 pm for the oxygen radii denoted with a 'c', and the "effective" ionic radii, which uses a radius of 140 pm for the oxygen radii denoted with an 'e' (the effective radii was included for historic reasons, to be consistent with the definition of the Pauling radius⁶⁹).

A subset of the information from Appendix B.3 has been made into two graphs for convenience in figure 2.7. For these graphs the high spin configuration has been used as is appropriate (see Appendix B.3 for high spin low spin description). In figure 2.7 the

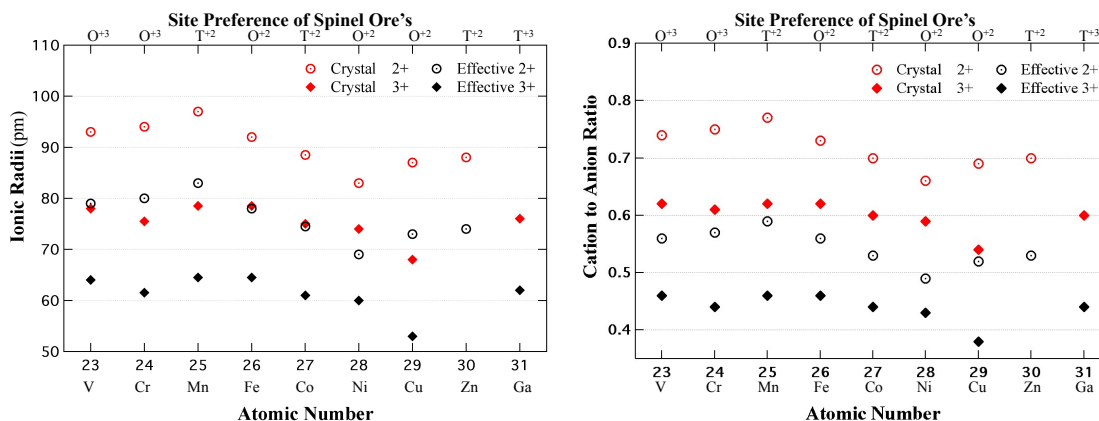


Figure 2.7: Ionic Radii and Ratios. Ionic Radii vs. atomic number (left), Cation to Anion Ratio vs. atomic number (right).

site preferences, as they can be understood from the bulk behavior, are included for context.

This model is clearly not sufficient to predict whether a dopant goes in tetrahedrally or octahedrally, as the cation to anion ratio would predict that none substitute tetrahedrally. Even an offset would not solve the problem, as the largest cation is manganese, which substitutes tetrahedrally in the bulk. This simplistic model may be better at predicting how two atoms might prefer to arrange themselves, rather than of which of two ions might end up in the A-site. It is clear looking at figure 2.7 that this model is insufficient to predict the site preference in a spinel. This may be due to the importance the shape of the cation orbitals plays in coordination preferences, which is ignored in a simple hard sphere approximation.

A more sophisticated approach to looking at site preference is to consider the shape of the filled electron orbitals and the relative coordination of the spinel atoms (see figure 2.8⁷⁰ for orbital shape). This approach, termed crystal field theory, involves

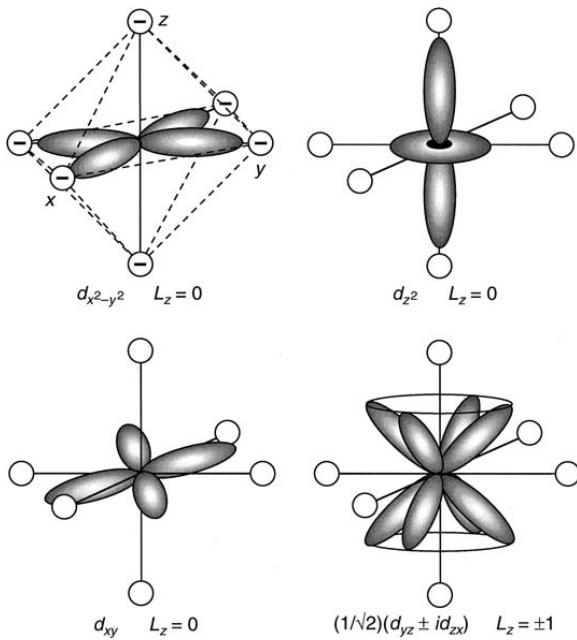


Figure 2.8: 3d Orbitals in Octahedral Coordination

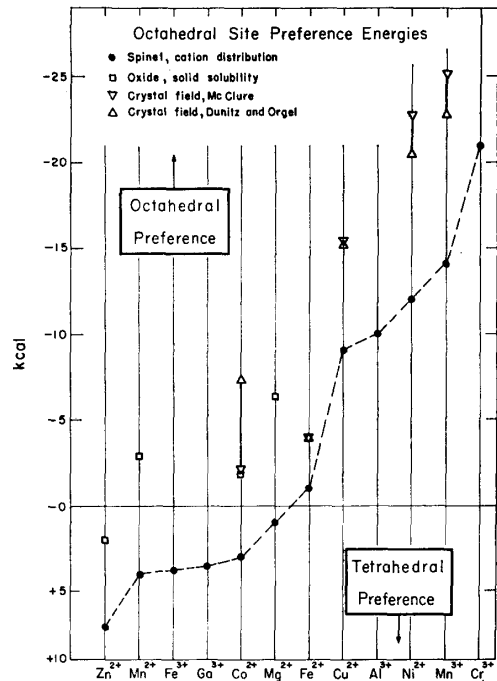


Figure 2.9: Spinel Site Preference

looking at how a central atom will respond to the electric fields of the surrounding atoms' electrons. Using the superposition of the fields of these electrons, the Stark effect of the central atom due to the surrounding atoms can be calculated and energy minimized. Since the lowest energy state is preferred, the favored configuration can be calculated in this way. Crystal field calculations for atoms have been performed for some time, where the ions are attributed a site preference and an energy associated with that preference. Navrotsky and Kleppa have included calculations of the energy associated with substituting different transition metal ions into the octahedral or tetrahedral site as well as measured values indicated with points connected by a dotted line (see figure 2.9⁶³). The measured values are attained by calculating the enthalpy from spinel synthesis reactions.

There is certainly better agreement with the trend for crystal field calculations than the radius ratio rule; however, there are still discrepancies, which indicates that an even more intricate approach is required. Crystal field theory, ligand field theory, and molecular orbital theory are all variants of this principle where increasing levels of sophistication and complexity are introduced. The details of ligand field theory and molecular field theory, however, are beyond the scope of this dissertation.

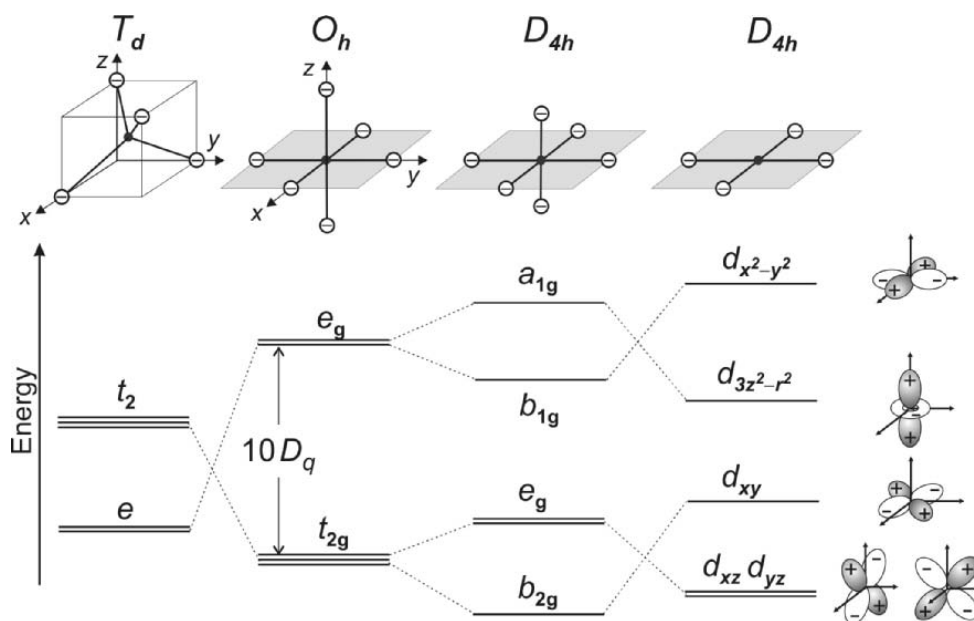


Figure 2.10: Energy Splitting of e_g and t_{2g} States

This preference causes an energy difference for the tetrahedral and octahedral configuration for a given electron orbital, which causes the e_g and t_{2g} energy splitting for the orbitals summarized in figure 2.10³⁰. This requires an understanding of the occupied electron orbitals for a given atom (see Appendix B.1b^{30, 61} 3d electron configurations).

Whichever of these factors dictates the site preference, it seems practical to look at the energy preference as a sliding scale. Some atoms have a mild preference for a given ionization, while others will only exist in one ionization, likewise, it seems that viewing the site preference in these terms is useful. A particular ionization of an atom may prefer one site over the other, but if it is in a spinel with an atom with a stronger preference, that preference will prevail. Additionally, it may be in these less preferential species that one should expect to see deviations from the expected bulk behavior when considering nanoparticles. Though the bulk behavior of spinels is mostly understood, the question arises how much of this applies to nanoparticles with diameters of the order of 10's of unit cells. It may be that in nanoparticles of such scales there are crystal relaxations that will alter the preference of a species in these environments. Investigating this question is the focus of this dissertation.

Magnetism as a Function of Dopant Incorporation

The variation of the total magnetic moment of a spinel with small dopant concentrations is a good indicator of the site preference. The net moment of the material often increases with a small incorporation of a dopant (even if the dopant is nonmagnetic). This is true even for dopants such as zinc, where at larger incorporation (for example $\frac{1}{3}$) the material has no net moment. Studies done by Gorter^{38, 71-73} detail this behavior for bulk spinels in replacing zinc within ZnFe_2O_4 with other transition metals; some of the results have been included in figure 2.11⁷¹. In this figure the values on the x-axis follow the formula $\text{Fe}_{1-x}\text{Zn}_x(\text{Me}^{\text{II}}_{1-x}\text{Fe}_{1+x})\text{O}_4$ and the dotted lines are prediction lines for $M_s = 10x + (1-x)gS_{\text{Me}^{++}}$, where M_s is the moment per formula unit (assuming the B-site

iron spins remain parallel), g is the g -factor for the transition metal ion ($g=2$ for orbitally quenched material) making $gS_{Me^{++}} = M_{Me^{++}}$, where $M_{Me^{++}}$ is the moment of the metal cation. For example, as zinc is doped into Fe_3O_4 the data for Me^{II} being Fe, the moment first increases (even though the dopant is not magnetic) and then at a higher concentration, is reduced, so that by $\frac{1}{3}$ incorporation of zinc (Fe_2ZnO_4) the moment has gone to zero. The rise of the moment can be understood by a very simple model of the spinels magnetic system.

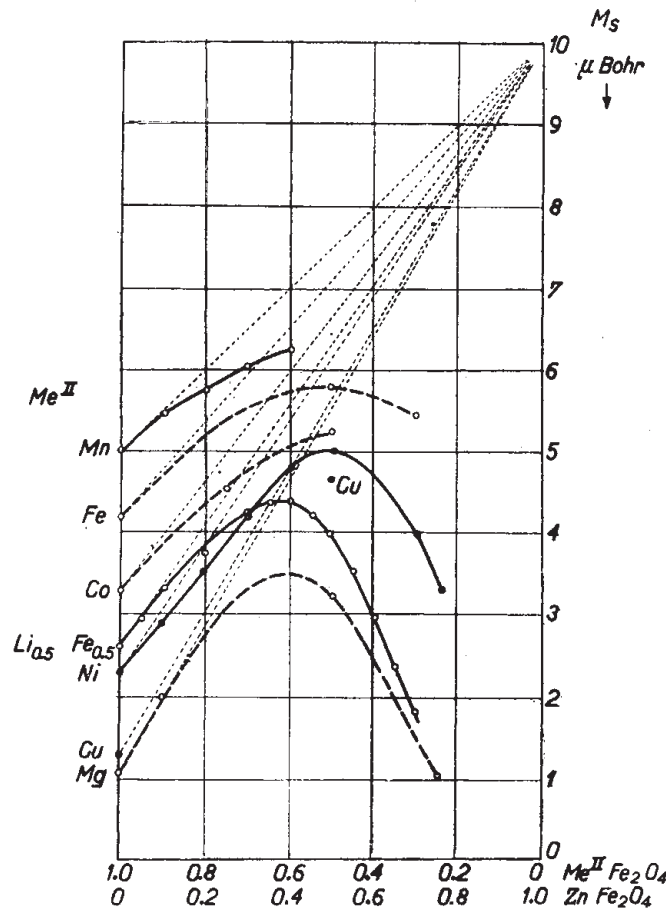


Figure 2.11: Magnetism of Doped Spinel

Modeling a nonspecific, nonmagnetic dopant and accounting only for the charge neutrality of the system (while ignoring any change in the interaction of the sublattices causing the magnetic alignment within the material), one can calculate the change in magnetic moment per unit cell as a non-magnetic dopant is incorporated into the host magnetite. The result of this calculation (shown in figure 2.12) shows that doping into the tetrahedral site causes the moment to increase. The largest increase occurs for doping of a 2+ ion into what was originally an Fe^{3+} site. As previously mentioned, charge neutrality requires the B-site Fe^{2+} ion to become an Fe^{3+} ion, with an increase in moment. Doping into the octahedral site causes the moment to decrease, with the most extreme reduction occurring for the 3+ dopant ion. Naturally, doping equally into both tetrahedral and octahedral sites causes the moment to be relatively unaffected, as the effect of the two dopant sites cancel each other out.

If these results are normalized by the number of remaining iron atoms, the moment per iron atom is obtained (shown in figure 2.13). This model, as simplistic as it is, is still useful as it predicts the behavior of low concentrations of nonmagnetic dopants. Furthermore, this not only models the behavior when nonmagnetic dopants are incorporated, but magnetic ones as well. This is because the material's magnetic behavior is measured with MCD, and MCD (as will be discussed in chapter 3) measures an elemental moment rather than averaging over the entire material. For this reason, figure 2.13 would predict the behavior of any 2+ or 3+ dopant, where the moment is normalized by the number of remaining iron atoms (since the moment per iron atom is proportional to the MCD spectra). When normalized by the number of remaining iron

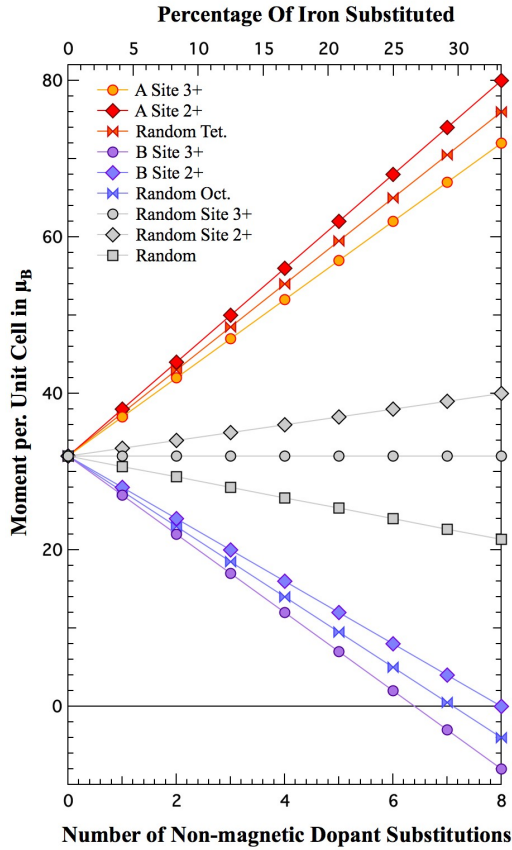


Figure 2.12: Moment per Unit Cell Calculation. Calculated variation of the moment per unit cell as a function of dopant substitution.

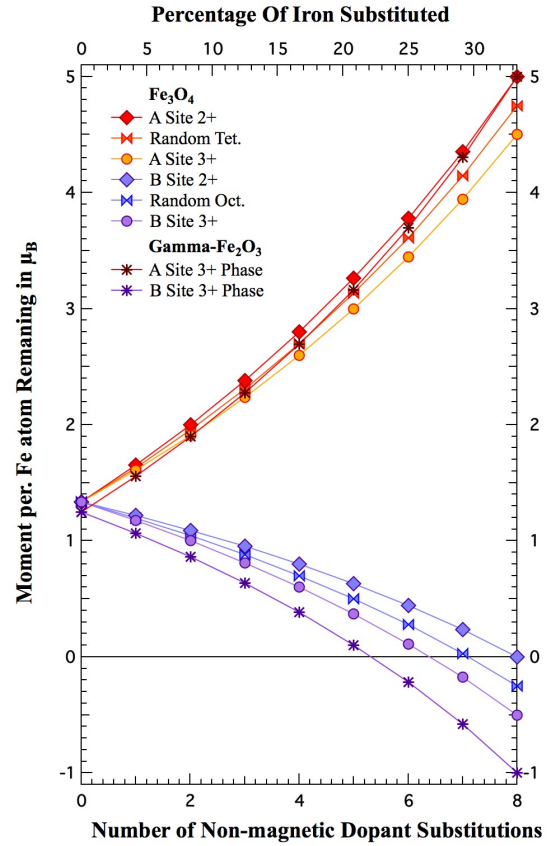


Figure 2.13: Moment per Iron Atom Calculation. Calculated variation of the moment per iron atom as a function of substitution.

atoms, the general behavior is the same, but the trend is no longer strictly linear. It should be noted that the negative moments denote the tetrahedral sublattice having a larger net moment than the octahedral sites in the ferrimagnetic ordering, not an actual negative moment, though this regime of the calculation is too high of a concentration to be realized. This model only works so long as the dopant does not significantly interfere with the magnetic ordering of the sublattices. If enough nonmagnetic material is incorporated, there will no longer be ordering between the two sublattices and the

material will lose its sublattice order. A similar calculation has been done for $\gamma\text{-Fe}_2\text{O}_3$ though as it has no Fe^{2+} , substituting as $2+$ has no meaning (see figure 2.13).

Geometric Nanoscale Effects

Part of what makes nanoparticles unique is that they have a high surface to volume ratio. As a consequence of this, surface effects, which in the bulk can be ignored, are significant in the case of nanoparticles. In this work, it is speculated that a crystal relaxation, made possible by the size of the nanoparticles, allows dopants to fit into sites that would not be energetically favorable in the bulk. In this section the question of whether this is a reasonable hypothesis will be explored.

To answer this question, let us consider what sort of cell distortion might be achieved by a simple radial distortion of a unit cell on a curved surface, where the curvature depends on, and can be parameterized by, the radius R . In the spirit of a back-of-the-envelope calculation, let us assume that a unit cell on the surface of the nanoparticle has its standard length for all sides, but the outermost side is allowed to expand by a small amount dx , to accommodate the larger circumference of the surface. This idea is illustrated in figure 2.14, where R is the radius of the nanoparticle and x is the length of the unit cell. This results in a simple geometric equation (2.2) for the change in length dx of a unit cell based on the variables R and x .

$$(2.2) \quad dx = (Rx/(R-x)) - x$$

Using this basic concept, a plot of the change in length (dx), as a function of the radius of the nanoparticle can be determined for the case where x is one unit cell for

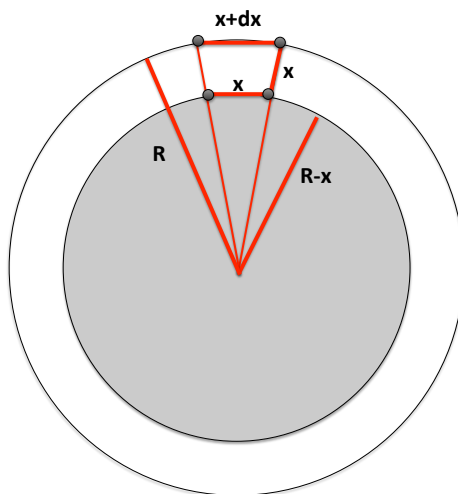


Figure 2.14: Geometric Distortion

magnetite $x=8.4 \text{ \AA}$, a half unit cell $x=4.2 \text{ \AA}$, and a quarter unit cell $x=2.1 \text{ \AA}$ (see figure 2.15 (top left)). Since in this model the distortion will not occur uniformly throughout the unit cell, the calculation of a unit cell, half a unit cell, and a quarter of a unit cell are informative. It is easy to see that in the range of radii appropriate for this work, the expansion of the outer length of the surface cells could be a significant percentage. With this much expansion of the cell, it is certainly plausible that the tetrahedral void would be larger than in a bulk cell, enough to allow for dopants that would otherwise be too tight a fit to accommodate the tetrahedral position comfortably. It is clear why this can create such an extreme effect when looking at the percentage of the nanoparticle that is taken up in this outer unit cell shell, again for the same three unit lengths (see figure 2.15 (top right)). A table of the results for nanoparticles of the three sizes considered in this work is compiled in table 2.2. The information has also been presented in a graph where the axes are ratios making them universal rather than specific.

Figure 2.15 bottom left shows the change in length vs. the radius of a particle normalized by x , and in figure 2.15 bottom right the outer volume is normalized by the volume and plotted against the normalized particle radius.

This model demonstrates that a significant expansion of the unit cell can be expected in these smaller nanoparticles. Additionally, since a large percentage of the volume of the nanoparticle is included in an outer shell one-unit cell deep, any changes to the structure in this zone will be a significant percentage of the makeup of the nanoparticle. These two factors together mean that a significant portion of the nanoparticle will be composed of a very relaxed crystal structure, which would allow for very different dopant occupation than in a standard crystal structure. From this it can be predicted that dopant site preference will be different in sufficiently small nanoparticles than in the bulk, due to crystal relaxation.

Table 2.2: Radial Expansion Values

Expiation in Å			
Nanoparticle	X		
	8.4Å	4.2Å	2.1Å
6.70nm	2.8	0.60	0.14
8.75nm	2.0	0.45	0.11
14.5nm	1.1	0.26	0.06

% of Nanoparticle in outer Shell			
Nanoparticle	X		
	8.4Å	4.2Å	2.1Å
6.70nm	58	33	18
8.75nm	47	26	14
14.5nm	31	16	8

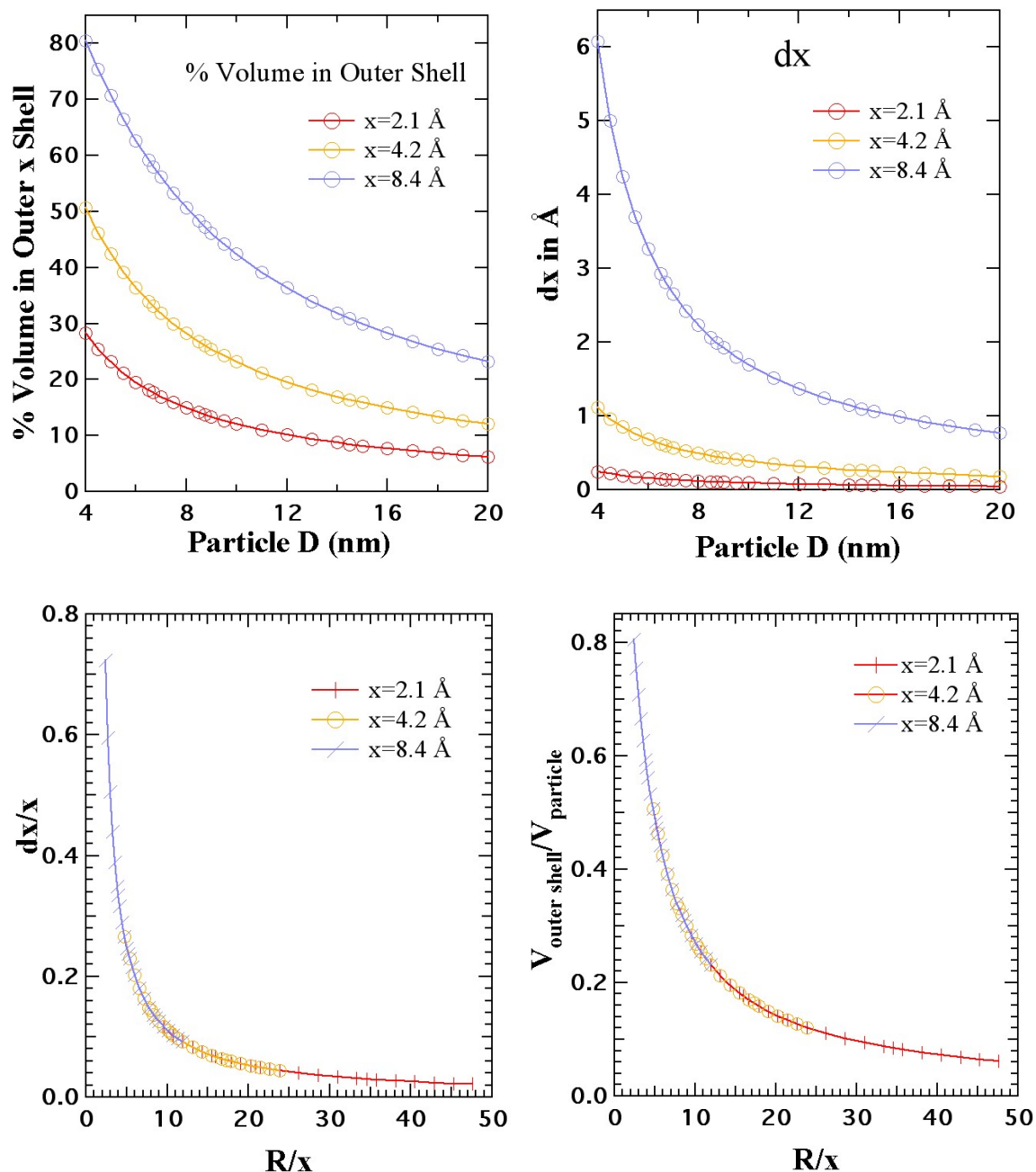


Figure 2.15: Geometric Distortion Calculation. The expansion of the unit cell in Å (top left), percentage of the volume that is in the shell one unit cell from the surface (top right), expansion of unit cell divided by unit cell vs. radius of nanoparticles divided by unit cell (bottom left), volume of outer unit cell shell divided by nanoparticle volume vs. radius of nanoparticles divided by unit cell (bottom right).

CHAPTER 3

EXPERIMENTAL TECHNIQUES

Theoretical Background of Experimental TechniquesX-ray Absorption Spectroscopy

X-rays were first discovered by Röntgen in 1895⁷⁴ and this immediately sparked a flurry of experimentation on the new form of radiation. Since then, the use of X-rays to understand the world has grown to include many techniques including X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD), and X-ray scattering (XRS).

X-ray absorption spectroscopy, or XAS, is characterized by a pronounced absorption of photons by electrons at an energy that is specific to the absorbing element, promoting a core electron to the states just above the Fermi energy. The spectrum is made up of several regions (see figure 3.1): the pre-edge, the X-ray absorption near edge (XANES), and the extended X-ray absorption fine structure (EXAFS). The pre-edge feature is caused by an excitation of a core electron to a virtual state below the Fermi energy, which is only realized if a second electron is scattered from the virtual state to the continuum. The extended x-ray absorption fine structure is caused by virtual scattering of electrons off of neighboring atoms, self-interfering with the absorption event. The near edge absorption, which is often just referred to as XAS, is the pertinent measurement here and the others will not be discussed further.

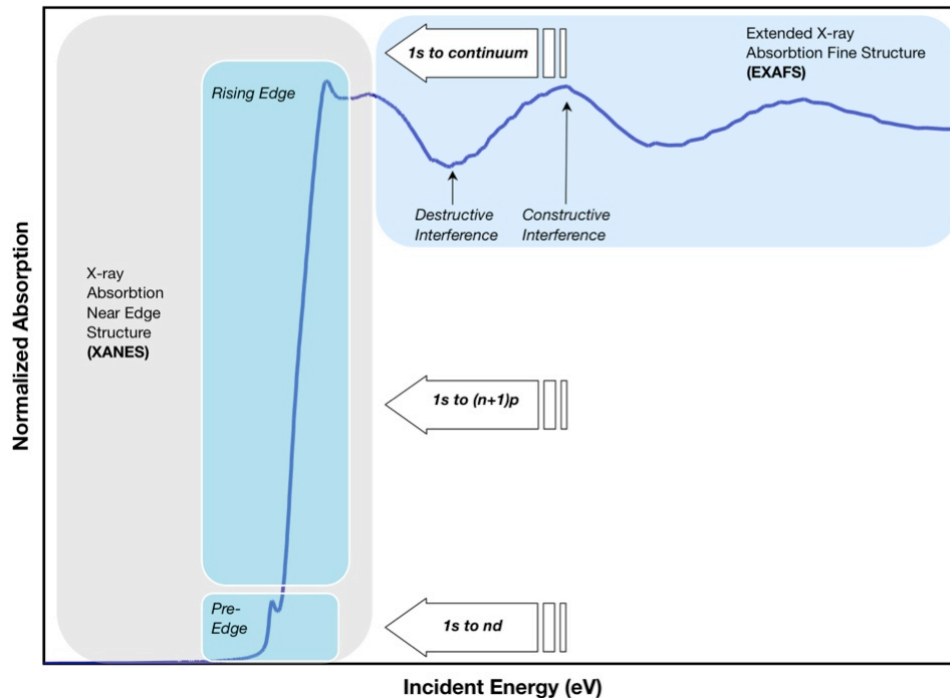


Figure 3.1: X-ray Absorption Edge Components

XAS is an element specific probe of the electronic structure using x-rays. In an XAS measurement, electrons are promoted from a core-state by absorbing an x-ray of the appropriate energy (see figure 3.2 (left)). Since the core-states have relatively well-defined energies, an understanding of the energy from a given core-state to the Fermi energy provides a rough estimate of at what X-ray energy, a strong absorption will occur for a given element. These absorption peaks are known as edges and are labeled based on the core-states the electron originates from. For example, the K-edge originates in the $n=1$ ($1s$) core-state and the L-edges originate from the $n=2$ ($2s$ and $2p$) core-states and so on, as shown in figure 3.2 (right). It is notable that while the energy of the core-state dictates the energy at which the edge is located, most of the structure of the edge is due to the final state into which the electron is being excited. The XAS is more a

measure of the unfilled density of states just above the Fermi energy, rather than the states originally occupied. For this work, the L-edges were singled out for investigation (rather than the K-edges), as they are the “active” states for the atoms and so are where “all the interesting physics happens”. Since the L-edges will be of the most interest to this work they will be used as the example as XAS is discussed further.

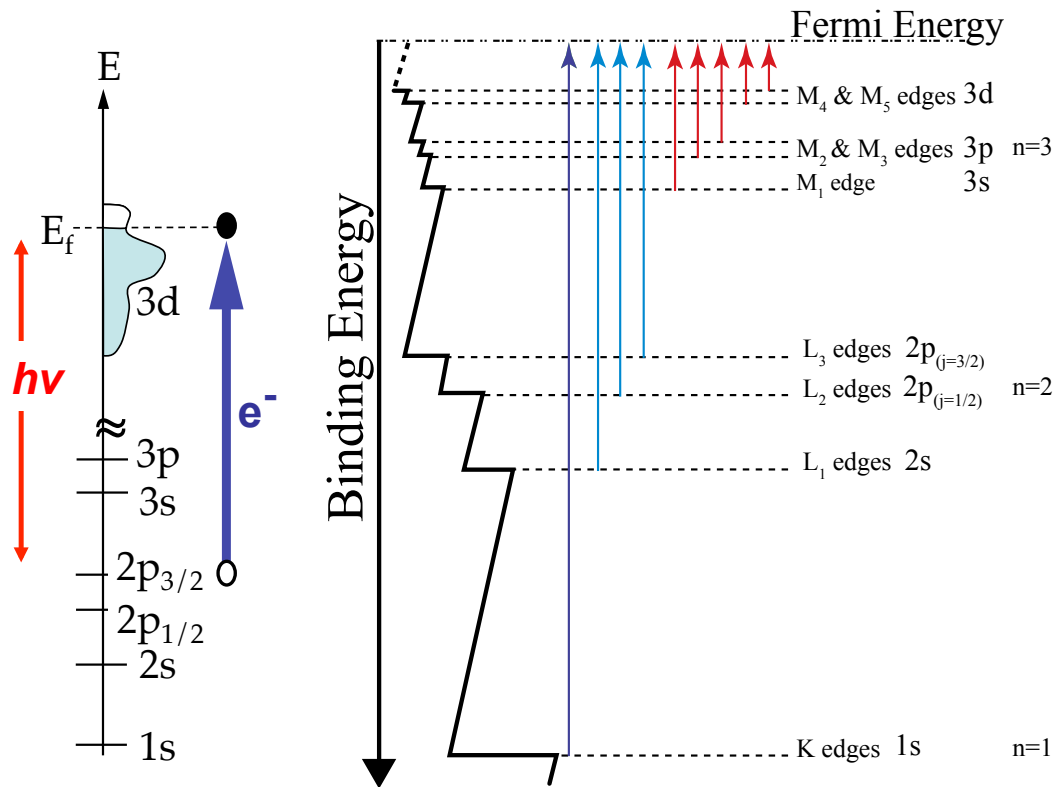


Figure 3.2: XAS

The L-edge is made up of three edges as can be seen in figure 3.2 (right). The L_1 -edge is usually ignored as the signal coming from the 2 electrons promoted from the 2s states to the 3p empty states produces a weak signal. The 2p to 3d transition constitutes the L_2 and L_3 edges. There are two edges rather than one, due to the split in

energy between the $2p_{3/2}$ and $2p_{1/2}$ core-states. This energy splitting is caused by the relativistic spin-orbit interaction between the electrons and the nucleus (where the 1/2 and 3/2 refers to the m_j value of the states).

Once the initial state is understood, the final states can be examined. By simply looking at the shape of the L_3 or L_2 edge it is easy to determine if an element is metallic or oxide in nature. In figure 3.3³⁰ a simplistic version of the band structure for metals and oxides is shown. This demonstrates the difference between the d-states of metals and oxides and so why their XAS spectra are different as well. For a metal, the electrons are not strictly associated with one atom, but are delocalized throughout the crystal (think of them as a sea of electrons); this is reflected in the band structure.

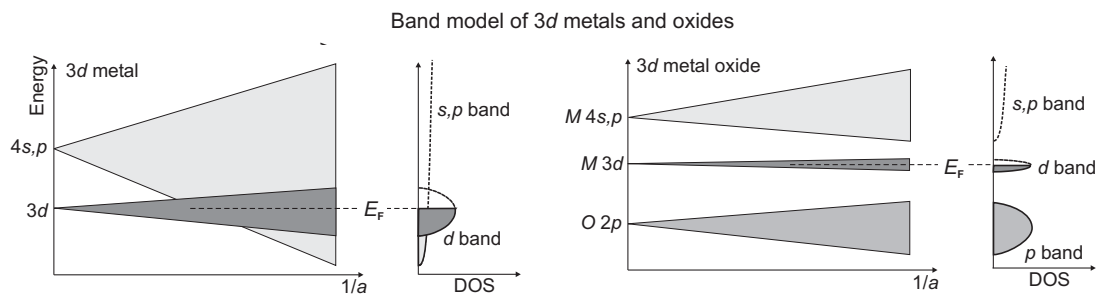


Figure 3.3: Simple Band Model. A simple band model is shown for a metal (left), and an oxide (right).

The differences between a metallic iron spectra and several iron-oxide spectra are compared in figure 3.4³⁰. The metallic iron edge has a broad peak for the L_3 and L_2 edges since there is a broad band of states into which the electrons could be excited. Transition metal oxides have much more structure to their peaks due to the more localized nature of the electron states. As seen in figure 3.3³⁰, the band structure does not have the broad

character of a metal, but rather a very tight band, which is reflected in the XAS of oxides by more sharply defined structures.

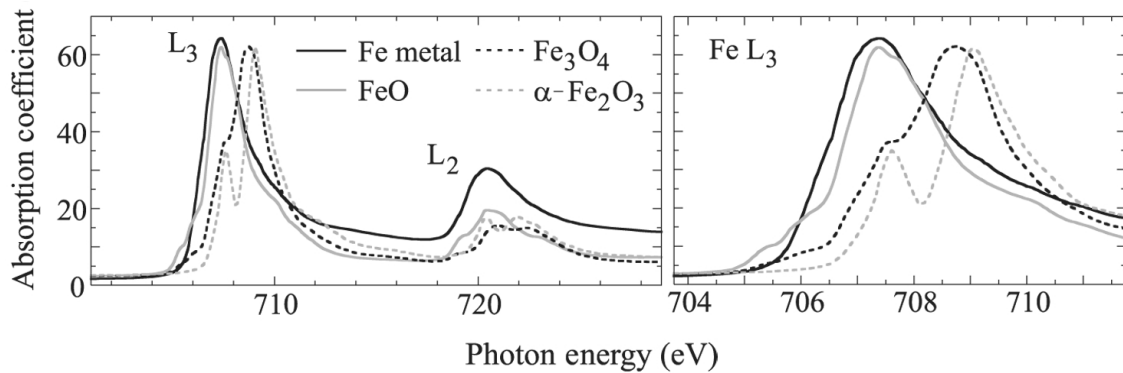


Figure 3.4: Iron XAS Spectra. Iron L23-edge XAS spectra of metallic iron and some iron-oxides.

One of the more prominent features that can be seen with XAS is the ionization threshold of the element being investigated. This is due to a shift in the energy of the empty 3d states with respects to the 2p ground states caused by the difference in how tightly bound the electron is. Due to shielding effects of the remaining electrons, the last electron would be easier to extract from the atom. One example of this shielding effect is the lower binding energy of the Fe^{2+} atom compared to an Fe^{3+} atom. The other feature that is of interest to this work is the oxygen coordination of the cation. As was covered in the previous chapter, which site is occupied by the dopant in a spinel is very important. XAS and its magnetic counterpart, magnetic circular dichroism (MCD), are used to help determine the ionization and coordination of the dopant.

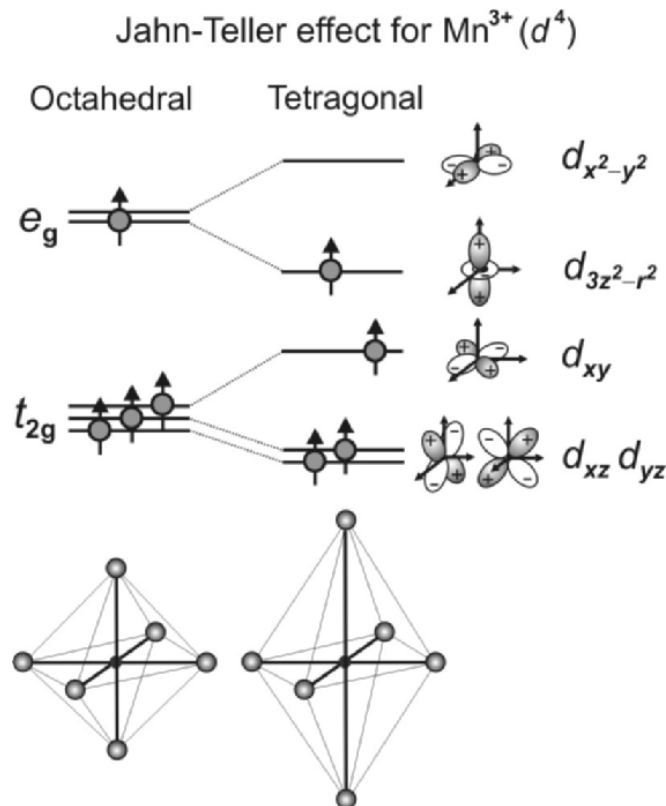


Figure 3.5: Tetragonal Distortion Energy Splittings

Crystal field theory is one of the simpler approaches to systems with fairly localized electrons. Crystal field theory has evolved into ligand field theory in which the exchange integral has the form of equation (2.2) given in chapter 2, where J_{ij} of the orbitals of the central atom and the neighboring atom are calculated. This is quite complex, as the orbitals will be affected by all the neighboring atoms, but in principal it can be calculated. In order to make the problem more tractable, approximations can be made and from this, molecular orbital calculations are derived. Molecular orbital calculations make it possible to predict how changes to the ionization and local environment of an atom will affect the XAS and XMCD spectra. Using molecular orbital

calculations it is possible to calculate what the difference should be between tetrahedral and octahedral states as well as more subtle changes such as differences in the energy of being in a t_{2g} state and e_g state. In figure 3.5³⁰, the energy shifts between an octahedrally coordinated Mn^{3+} atom and an octahedrally coordinated Mn^{3+} atom with a Jahn-Teller tetragonal distortion are illustrated. In this figure, energy levels and fillings of the undistorted configuration are depicted on the left, while the energy levels and fillings of the distorted configuration where some of the degeneracy found in the undistorted case is lifted, are depicted on the right. The changes in the energies of the states as a result of factors such as charge, coordination, or field application, are all represented in the XAS and MCD spectra.

In this work, spectra will be compared to molecular orbital calculations, done by other groups. Additionally, the older method of comparing spectra to known standards done by our group, or others, can also be insightful. As an experimentalist, there is a certain preference for actual measurements, as calculations are always only as good as the model being used to produce them. Calculations however, have their place, as there are not always measurements available with which to compare when working with novel materials. In this work, both are used where appropriate to understand the systems in question.

Once a measurement has been taken, it must be properly normalized and energy referenced in order to compare one spectrum to the next. This is done by using an area-normalization and setting the peak to a known peak value. The area under the peak is proportional to the number of d-holes, which causes the intensity of the L-edges to vary

as you go across the periodic table, as shown in figure 3.6³⁰. As you go across the transition metal series the number of filled 3d electrons increases, this means that the number of 3d holes decreases, which can be represented as the filling of the DOS in figure 3.6b. The more states that are available to be transitioned into, the greater the intensity of the L-peaks and so the intensity of the peaks goes down as you go across the periodic table as seen in figure 3.6a. The number of 3d holes and so the intensity of the XAS-edges are proportional as seen in figure 3.6c. This is why the iron spectra is so much more robust than the zinc spectra.

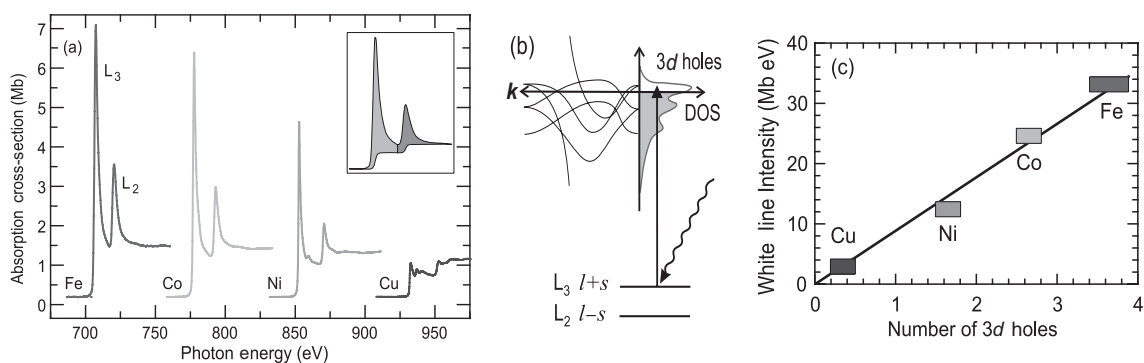


Figure 3.6: 3d-holes. Absorption cross-section vs. photon energy for Fe, Co, Ni and Cu (a), simple density of states picture of a transition metal (b), white line intensity vs. number of 3d holes for Cu, Ni, Co and Fe (c).

XAS and XMCD measurements require an energy tunable x-ray source; this means the use of a synchrotron. For the measurements discussed in this dissertation, the x-ray source was the Advanced Light Source (ALS) of Lawrence Berkeley National Labs in Berkeley, California. Work was done on beamlines 6.3.1 and 4.0.2, both run by Elke Arenholz. The details of the beamlines will be discussed more in the experimental set-up section of this chapter.

Understanding what is being measured is very important, but it is also important to understand how that measurement is being accomplished. The most conceptually straight forward method of measuring XAS is to measure the intensity of the light before and after it passes through the material, directly measuring how much of the light is absorbed for a given energy of x-ray. This is accomplished by measuring the incident flux with an 80% transmissive gold mesh and the transmitted flux with a photo-diode. This method is called transmission mode XAS (figure 3.7a³⁰). In this method, the absorption of electrons leads to a reduction in the transmitted signals and so the absorption appears as dips in the transmitted signal. Though conceptually

X-ray absorption spectroscopy techniques

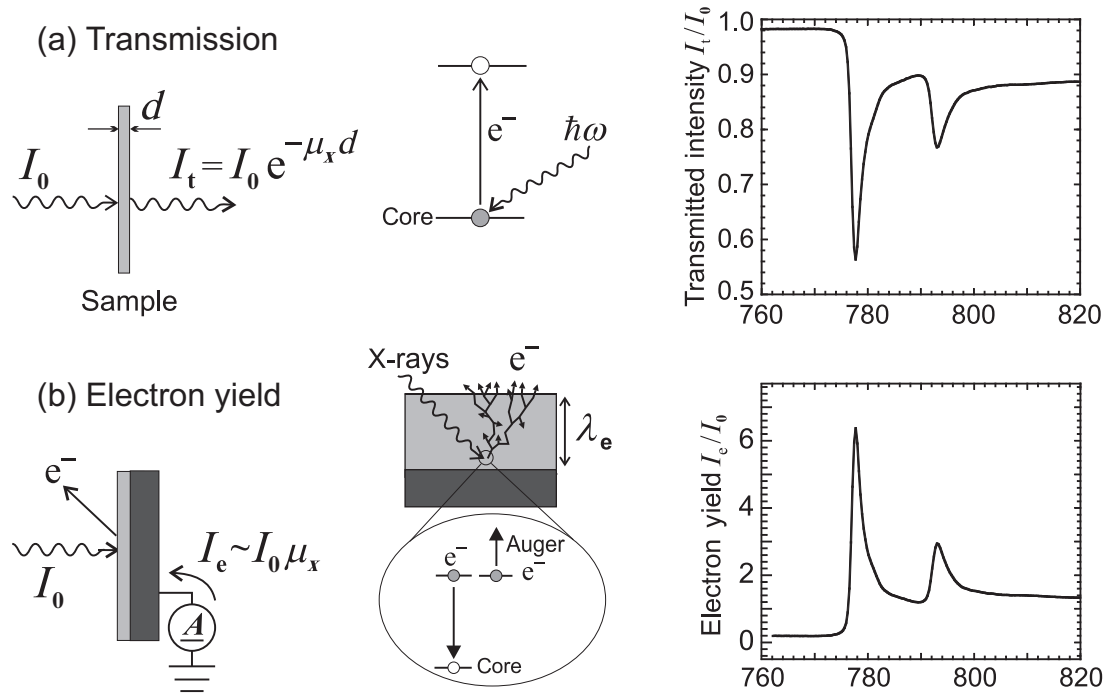


Figure 3.7: XAS Measurement Setups. Transmission yield (top), total electron yield (bottom).

straightforward this measurement is not always practical as it depends on a sample thin enough so that only 10% of the incident X-rays are absorbed which is not always an option. In addition, normalization is much more difficult for transmission yield if a supporting substrate, such as 10 μm thick Si_3N_4 , pyralene, or kaplon film, is used.

A more commonly utilized measurement technique is total electron yield (TEY). In total electron yield, x-rays are absorbed in the same manner as in transmission yield. However, rather than measuring this directly, TEY takes advantage of an electron cascade effect that is caused by the initial absorption. Absorption decay by-products lead to electrons being emitted by the material. As shown in figure 3.7b, an incident photon creates a core hole, which is subsequently filled, ejecting an Auger electron. This high energy Auger electron creates a cascade of secondary electrons. By allowing these ejected electrons to be replenished via a sample current (that is measured), the current of electrons being ejected is determined which is proportional to the absorption of x-rays. In this XAS measurement it is important that the material is reasonably conducting. In the case of oxides, such as the materials under investigation in this dissertation, poor conductivity can lead to artifacts caused by charging of the sample (though with careful sample preparation this can be kept at an acceptable level). In the electron yield set-up, the peaks are measured as an increase in the sample current and so an increase in the signal. It is important to note that it is not only the apparent inversion of the signal that is involved in comparing the transition and electron yield measurements. The electron yield measurement is equivalent to the negative natural log of the transmission yield⁷⁵. For this reason it is best to compare transmission spectra to other transmission spectra and

electron yield spectra to other electron yield spectra, avoiding problematic normalizations, as has been done in this work. For the samples measured here electron yield was used predominantly since the data analysis is more straightforward. Transmission data were used only in the cases where good electron yield spectra could not be acquired.

Fluorescence yield is another method of measuring XAS and MCD. Fluorescence yield measures photons emitted by the sample as a result of electrons falling from states just below the Fermi energy to fill the core hole states vacated by the excitation of the initial electron. This method does have the added advantage of not relying on a replenishment current, which makes it a good choice for insulators. It does, however, have other difficulties and is often noisier than electron yield. For these reasons this method was not used here.

X-ray Magnetic Circular Dichroism

Very soon after the discovery of X-rays by Rontgen⁷⁴, the idea of their potential polarization was investigated. Magnetism's potential influence on the interaction of x-rays in matter was conceived of as early as 1903 by Blondlt⁷⁴. However, it was not until 1987 that Schütz reported observing X-ray magnetic circular dichroism or XMCD (often just noted as MCD) on the Fe K-edge⁷⁶, at which point the field exploded. The advantages of using lower energy soft X-rays to probe 3d states was soon identified.⁷⁷⁻⁷⁹

MCD is similar to XAS with the marked difference that circularly polarized light is used in order to get at the magnetic information in magnetic materials. Like XAS, MCD measures in an element specific way, the transitions from core-states to states just above the Fermi energy. In the case of MCD however, the use of circularly polarized

x-rays allows for sensitivity to the magnetic structure of the material. This can be used to look at the average moment for a given element, such as iron shown in its metallic form (see figure 3.8).

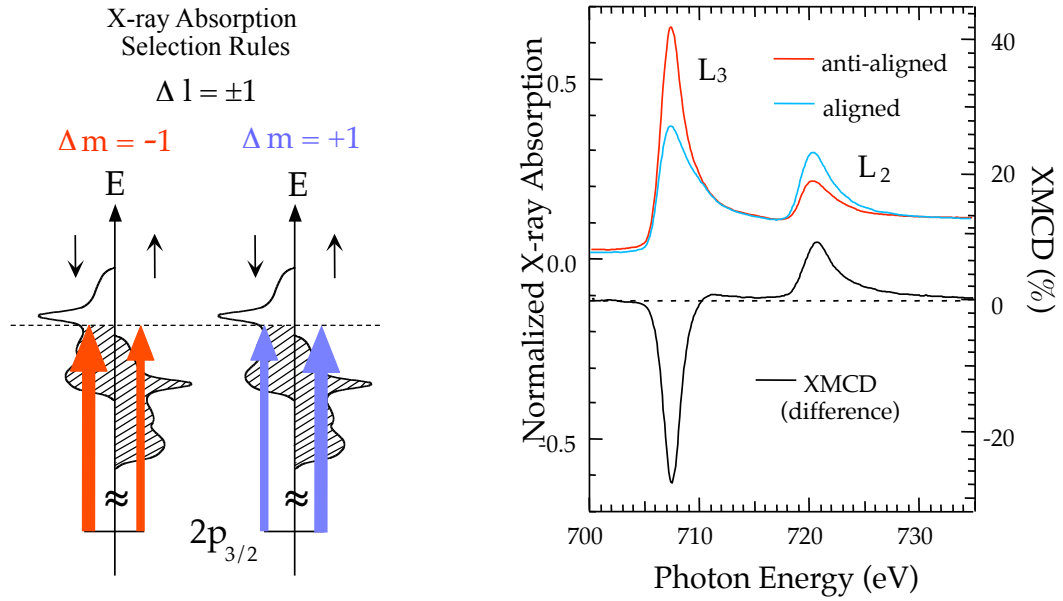


Figure 3.8: XMCD. Spin resolved DOS with l and m selection rules (left), iron L_{23} XAS for aligned and antialigned states and resulting MCD (right).

For magnetic materials with multiple magnetic elements, XAS can identify if the elements are aligned or anti-aligned. In the case of a complex oxide, such as a spinel, it can give details about the sites occupied by a given element. When a field is applied to a magnetic material, the spin-up and spin-down states become energetically separated. This, along with the selection rules associated with polarized x-rays, creates a preference for certain transitions depending on the respective orientation of the electron spin and photon helicity. The difference between the allowed transitions for the left and right

polarized light (or equivalently for these materials, the difference in the transition of specific magnetization orientations given a fixed polarization) gives the difference spectra of the MCD. The strength and selection of the states can be worked out in a simplified model with the Clebsch-Gordan coefficients (see Appendix B.4⁸⁰). The strength of the difference spectra as a percentage of the linear polarized (or averaged spectra), gives you the moment per atom of a specific element. Metallic iron being particularly robust and simple is a good example (though the iron spectra of oxidized iron is more complex as will be seen). The intensity of the MCD spectra is directly proportional to the moment per atom.

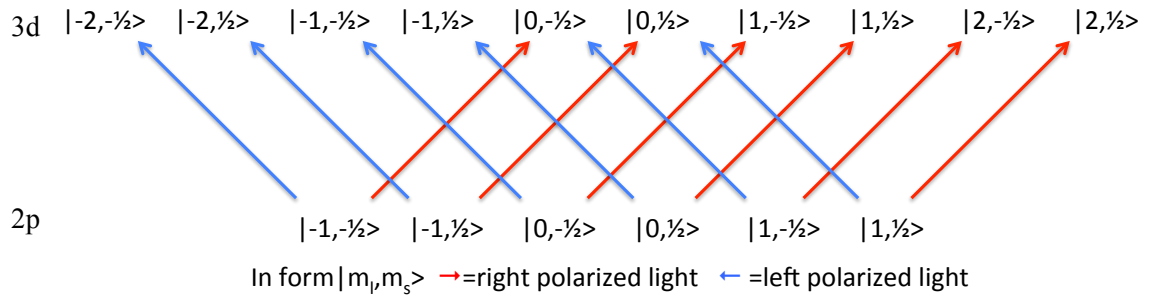


Figure 3.9: XMCD Selection Rules for the m_l Basis

The simplest way to look at the selection rules is by examining the states in terms of a basis where orbital moment and spin moment are good quantum numbers ($|m_l, m_s\rangle$). In this basis the rules are simplified to $\Delta m_l = \pm 1$ and, depending on polarization, $\Delta m_s = \pm 1$ (see figure 3.9). Allowed transitions are indicated by the arrows and are to the right for right circular polarized light and to the left for left circular polarized light. When including the probabilities of occupations and transitions, it is helpful to look at a subset,

such as in figure 3.10. The population of the states and the transition rates are given for $m_j \pm 1/2$ states and $\Delta m_l = +1$. It is useful to view the transition in terms of the m_j basis, since this is the basis appropriate to the spin-orbit splitting of the 2p's. This means a conversion from the m_l and m_s basis to the m_j basis, which is included in a table in Appendix B.4⁸¹. The basis conversion is calculated using equation (3.1):

$$(3.1) \quad |l, s, j, m_j\rangle = \sum_{m_l, m_s} C_{m_l, m_s; j, m_j} |l, s, m_l, m_s\rangle,$$

where $C_{m_l, m_s; j, m_j}$ represent the famous Clebsch-Gordon coefficients.

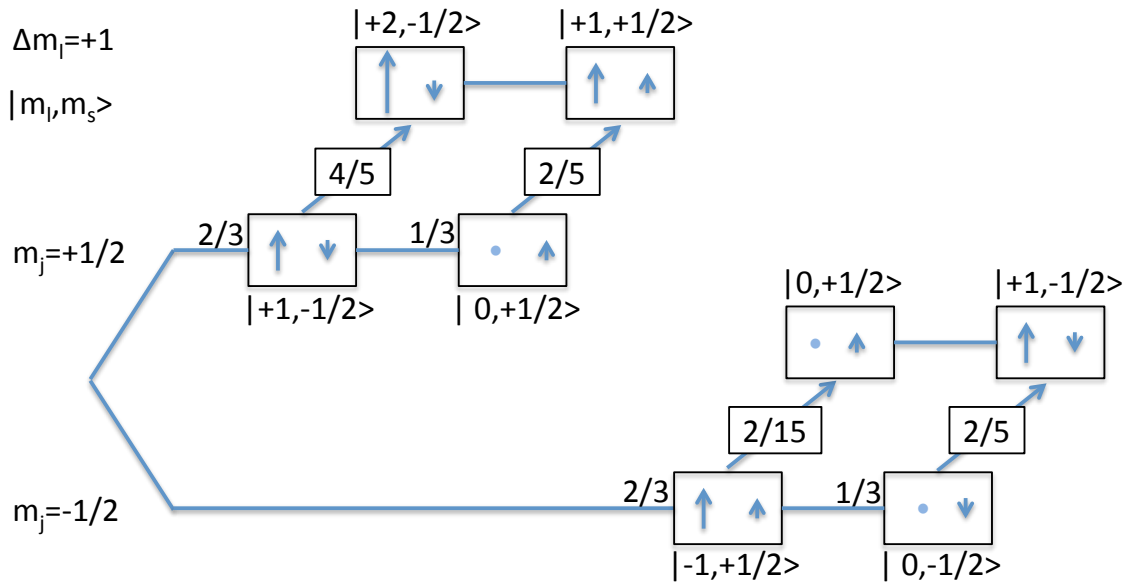


Figure 3.10: XMCD Selection Rules for the m_j Basis. Transition intensities given in fractional terms.

For oxidized iron, the MCD spectra gets a bit more complex, as the oxidized XAS spectra has more structure. In order to extract the coordination information about the iron, we used to calculations done by other groups⁸²⁻⁸⁴ as referenced in the papers with the

software developed by F.M.F. de Groot's group⁸⁵⁻⁸⁷. Here, one can clearly pick out the different positions in the spinel structure in figure 3.11. In the top left is a stick diagram

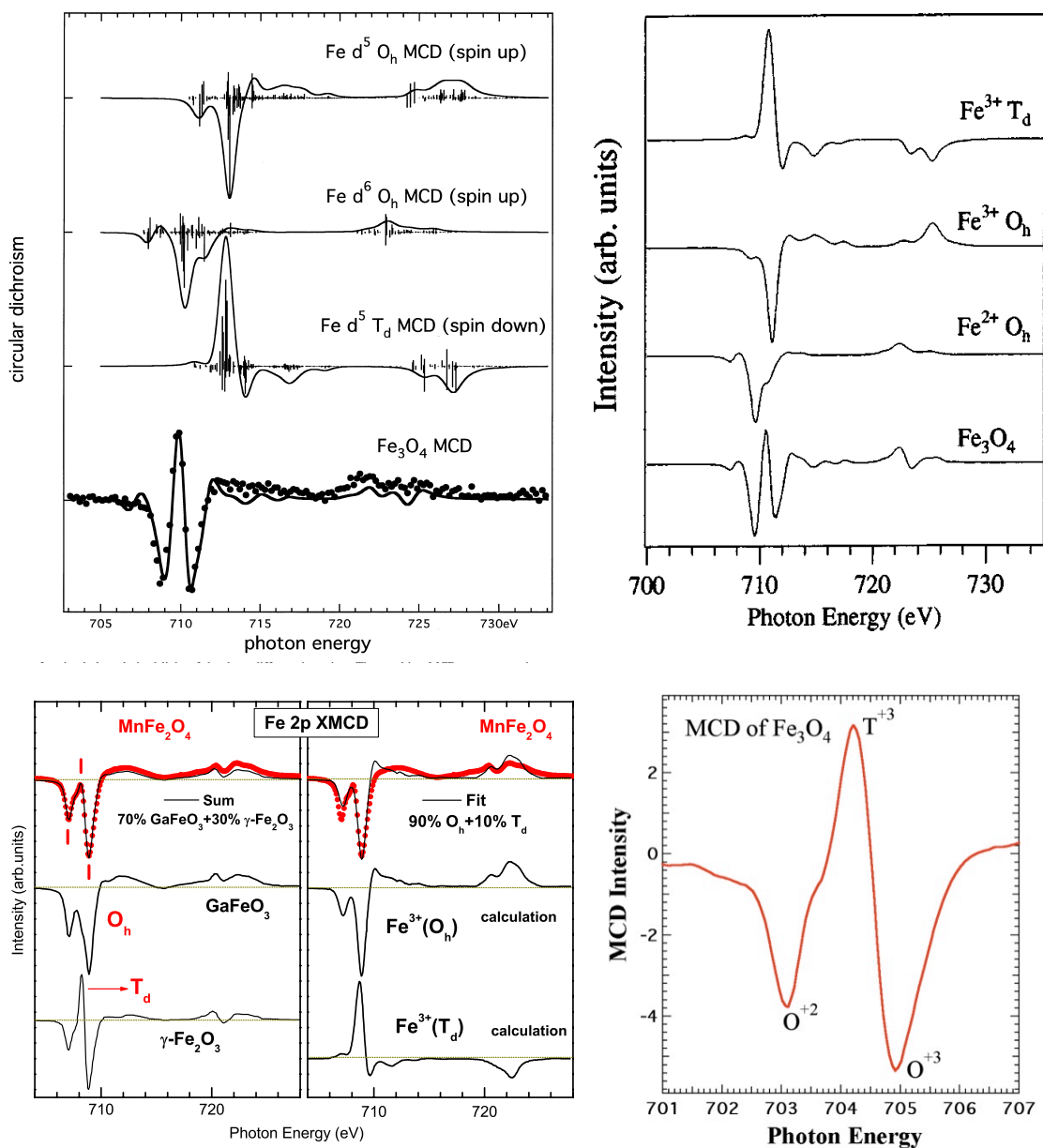


Figure 3.11: XMCD Calculations for Iron. Stick representation of iron MCD from Kuiper (upper left), molecular orbital calculation of iron MCD from Schedin (upper right) measured and calculated iron MCD from Kang (lower left), measurement taken by the Idzerda group on powdered Fe_3O_4 (lower right).

used to represent the iron MCD spectra calculations for the three spinel positions as well as the addition of the spectra compared to a measured spectra of Fe_3O_4 from a paper by Kuiper⁸². The stick diagram is the initial representation of the molecular orbital calculation before it is translated into the form of a spectrum. In the top right is a smoothed calculation of the iron MCD for the three positions and the combined calculated spectra for Fe_3O_4 from a paper by Schedin⁸³. In the bottom left, a figure from a paper by Kang⁸⁴ shows some calculations and some measured spectra for GaFe_2O_3 , MnFe_2O_3 and $\gamma\text{-Fe}_2\text{O}_4$. The Kang paper also includes calculations for manganese MCD and iron and manganese XAS which were helpful in understanding the manganese work presented in chapters 5-7. In the bottom right is a spectra measured from a powder sample of Fe_3O_4 with the peaks labeled. In this work the Iron MCD is used to determine which sites the dopant is substituting for by looking at which of the iron peaks diminishes, which in turn is the site the dopant is filling.

Extracting Orbital-Spin Moment Ratio

In the work on uncaged manganese doped iron oxide nanoparticles, covered in chapter 6, the measurements were cleaner than is usually the case for nanoparticles. As a result of this, additional information could be extracted from the data. In addition to the moment and coordination information, we were able to extract the orbital moment to spin moment ratio. The spin moment and orbital moment are separable quantities and are represented in different aspects of the MCD spectra. The orbital moment, given by equation (3.2), and spin moment, given by equation (3.3), are difficult to extract separately⁸⁸. They have a complex form and to extract them separately requires an exact

knowledge of the d-holes of the material that is hard to obtain. By solving for a ratio however, several of the more problematic terms cancel each other out or become negligible, and you are left with the much simpler equation (3.4)⁸⁹. In this case, a more straightforward measure of two quantities (P and Q as shown in figure 3.12⁸⁸) can be taken.

$$(3.2) \quad m_{\text{orb}} = -\frac{4 \int_{L_3+L_2} (\mu_+ - \mu_-) d\omega}{3 \int_{L_3+L_2} (\mu_+ + \mu_-) d\omega} (10 - n_{3d})$$

$$(3.3) \quad m_{\text{spin}} = -\frac{6 \int_{L_3} (\mu_+ - \mu_-) d\omega - 4 \int_{L_3+L_2} (\mu_+ - \mu_-) d\omega}{\int_{L_3+L_2} (\mu_+ + \mu_-) d\omega} \times (10 - n_{3d}) \left(1 + \frac{7\langle T_z \rangle}{2\langle S_z \rangle}\right)^{-1}$$

$$(3.4) \quad \mu_{\text{orb}}/\mu_{\text{spin}} = \frac{2q}{(9p - 6q)} \quad \text{where} \quad p = \int_{L_3+L_2} (\mu_+ - \mu_-) d\omega \quad q = \int_{L_3} (\mu_+ - \mu_-) d\omega$$

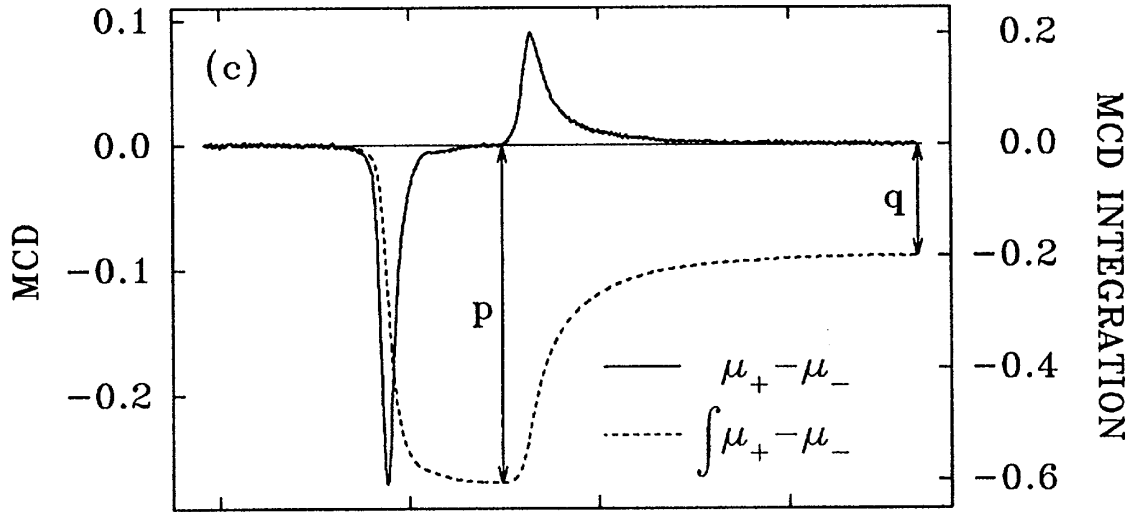


Figure 3.12: XMCD Orbital to Spin Ratio. Conceptualization of spin and orbital components (top), illustration of the physical meaning of p & q (bottom).

Alternating Current Magnetic Susceptibility

Frequency dependent alternating current magnetic susceptibility or ACMS has been used on several sets of nanoparticles in this study. ACMS is a measure of the magnetic susceptibility of a material in response to an alternating field as a function of the applied AC frequency and temperature. In order to understand this measurement as it relates to the materials in this study it might be useful to review a bit about nanoparticle properties.

Single domain particles like the ones investigated in this thesis are also known as Stoner-Wohlfarth particles⁹⁰. These particles can be thought of as macro spins, since in this description of a single domain nanoparticle, the particle has uniform magnetization and it is at saturation (M_S). If one were to measure a hysteresis loop on these nanoparticles, one would get an open loop, as one would expect of a ferromagnet. If we assume a uniaxial anisotropy, as is standard for nanoparticles, then the anisotropy energy density is given by equation (3.5), where K is the anisotropy constant (due to either shape or crystalline structure), θ is the angle between M_S and the easy-axis, and ϕ is the angle between the easy-axis and the applied field, H .

$$(3.5) \quad E = KV\sin^2\theta - MVH\cos(\phi - \theta)^{30}$$

This is a good description for large single crystal particles, where the energy barrier is much larger than the thermal energy kT , such that the thermal excitations are insignificant. However, if the particle is quite small, then the thermal excitations cannot be ignored, and the orientation of the nanoparticle is continually changing due to thermal energy. In this regime, the nanoparticles will not create an open hysteresis loop. Rather

than being like the small domains of a ferromagnet, the nanoparticles more closely resemble the behavior of a paramagnet. This behavior is known as superparamagnetism and is characterized by a particle that has a barrier to flipping that is less than the energy available due to thermal energy; this is illustrated in figure 3.13⁹¹. This superparamagnetic fluctuation can be expressed as $\tau = \tau_0 e^{\Delta E/kT}$ (though it should be noted that τ has units of time not frequency). Expressed in another way, this becomes $\Delta E = kT \ln(\tau/\tau_0)$, where ΔE is the energy difference between the extremes of the magnetization state. If the thermal energy were decreased to the point that it was no longer larger than the energy barrier, the superparamagnetic behavior would disappear; this critical temperature is known as the blocking temperature, T_B . Below this temperature the nanoparticles "freeze out", as the thermal energy is no longer larger than ΔE ⁹⁰. The nanoparticles measured with ACMS in this work fall into this category.

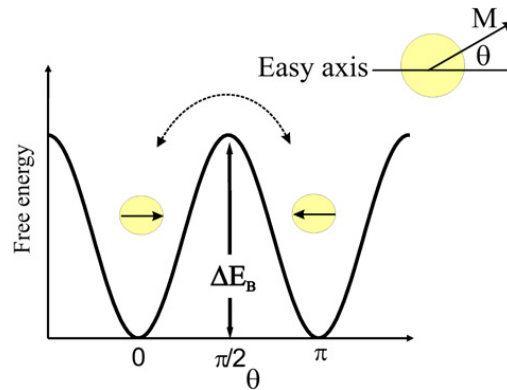


Figure 3.13: Superparamagnetism

With this understanding of the superparamagnetic behavior of the particles being studied, it is possible to see how to measure them with ACMS. For small AC fields at

low frequencies the moment of a frozen particle is given by equation (3.6):

$$(3.6) \quad M_{AC} = (dM/dH) \cdot H_{AC} \sin(\omega t) \quad ^{64, 92}$$

where M_{AC} is the induced moment, H_{AC} is the amplitude of the driving field, ω is the driving frequency, and the magnetic susceptibility χ is dM/dH . At higher frequencies (where the sample lags the driving field), a phase shift (relative to the driving frequency) is required to fully represent the phenomena. For low frequencies however, the real part of the magnetic susceptibility, labeled χ' (in phase with field), is described by the slope of $M(H)$ and the imaginary component, labeled χ'' (out of phase with field), is a measure of the dissipation within the material. This can also be thought of as a susceptibility that lags the field by a phase shift ϕ and can be written in the form seen in equation (3.7)⁹³.

$$(3.7) \quad \begin{aligned} \chi' &= \chi \cos \phi \\ \chi'' &= \chi \sin \phi \end{aligned} \Leftrightarrow \begin{aligned} \chi &= \sqrt{\chi'^2 + \chi''^2} \\ \phi &= \arctan(\chi''/\chi') \end{aligned}$$

Both components are sensitive thermodynamic phases and so can be used to measure freezing temperatures in spin-glasses. Here however, we have used ACMS to look at single domain ferromagnetic nanoparticles, which behave super-paramagnetically at room temperature. The nanoparticles susceptibility (the real part) increases in a Curie-like behavior ($\chi' \propto T^{-1}$) as the temperature decreases until it approaches the blocking temperature (T_B). The volume of the particle can be obtained by looking at the slope of $1/\chi'$ vs. T as long as the particles are monodispersed. Below the blocking temperature the nanoparticles are no longer super-paramagnetic.

$$(3.8) \quad \chi(T) = C/(T-T_C) \quad \text{Curie-Weiss law (well above } T_B)$$

The blocking temperature can be thought of as the point at which the nanoparticles can no longer respond quickly enough to track the field due to a lack of energy (as the thermal energy decreases). For non-interacting particles the Néel-Brown theory predicts that the blocking temperature behaves as in equation (3.9)⁶⁴.

$$(3.9) \quad T_B = \Delta E / (k_B \ln(\tau/\tau_0)) \quad \Leftrightarrow \quad \ln(\tau/\tau_0) = \Delta E / (k_B T_B)$$

Here ΔE is the energy barrier to reversal, τ is the measuring time, τ_0 is the attempt frequency (note: again this is in units of time not inverse time) and k_B is the Boltzmann constant. If this looks familiar, it is because it is the same equation that was given for the fluctuation period, only with T_B substituted in for T . This can be done for a number of different frequencies.

Once the blocking temperature as a function of frequency is extracted, a Néel-Arrhenius plot can be used to determine if the particles are interacting or non-interacting (at least to a reasonable degree). A Néel-Arrhenius plot is a plot of $\ln(1/\text{frequency})$ vs. $1/T_B$ plot. If the data is linear, and the intercept correlates to a τ_0 value of the order 10^{-9} - 10^{-12} , then the nanoparticles are considered to be non-interacting as they follow the behavior described in equation (3.9)⁶⁴.

If the behavior does not satisfy these criteria, the particles are interacting and the Vogel-Fulcher law⁹⁴ (4) is needed to evaluate the data. This includes a T_0 term, which is representative of the strength of the interaction $E_{\text{int}} = k_B T_0$.

$$(3.10) \quad T_B - T_0 = \Delta E / \ln(\tau/\tau_0) k_B \quad \Leftrightarrow \quad \ln(\tau/\tau_0) = \Delta E / k_B (T_B - T_0)$$

In equation 3.10 all the terms are as before, with the introduction of T_0 which is related to the interaction strength (where the interaction is assumed to be a weak dipolar interaction). From the Néel-Brown theory or the Vogel-Fulcher law, it is possible to extract the anisotropy energy and in the latter case an idea of the interaction strength. The analysis of the ACMS measurements is further outlined in Appendix C.1.

There are also other methods of looking at the data developed by work in spin glasses⁹⁵, and there has been some attempt to apply this to nanoparticles but that was found to be inappropriate in this case.

Transmission Electron Microscope

A transmission electron microscope or (TEM) was used to determine the size of some of the nanoparticles as well as to confirm their structure. TEMs, first conceived of in the early 1900's, are microscopes where the role of light in a visible light microscope or (VLM) is played by electrons, and rather than glass lenses, electromagnetic lenses are used to focus the electrons. Louis de Broglie was the first to theorize that electrons might have wave like properties in 1925⁹⁶. This was demonstrated in 1927 by two groups independently, Davisson & Germer, and Thomson & Read⁹⁶. The first paper proposing the electron microscope was published in 1932 by Knoll & Ruska⁹⁶ and the first electron microscope was developed 4 years later, though it was not until 1986 that Ruska won the Nobel prize for it⁹⁶. The electron microscope works because of the wave like character of electrons (or wave particle duality). Interestingly though, this was unknown to Ruska at the time; he apparently thought the wave limit simply did not apply. Luckily, this oversight did not hinder the conception of the TEM, since the idea that smaller features

could be imaged with the use of electrons was correct (though not perhaps for the reasons originally thought). A good VLM might be able to image something as small as 300 nm⁹⁶, however, to explore the nanoparticle regime one needs to probe structures that are on the order of 1 - 100 nm. With electrons this can be satisfied. The reason that electrons can be used to image such small features is of course that the wavelength associated with an electron is so much smaller than that of visible light. The wavelength associated with an electron additionally scales with its energy $\lambda = 1.22/E^{1/2}$, allowing the resolution to be increased with an increase in the kinetic energy of the electron. An approximation of the theoretical limit for resolution that can be achieved for an electron with 100 keV is around 4 pm⁹⁶. From a practical standpoint, some of the best TEMs today can resolve features on the order of (0.5 Å)⁹⁷. The TEM is an important advancement in our ability to probe the very small. For information on TEMs beyond the scope covered here, the reader is recommended "Transmission Electron Microscopy" by Williams and Carter, a book that has been used extensively as a reference here.

TEMs can be used in several different modes including: light field (LF)⁹⁸ and dark field (DF) imaging techniques, electron diffraction (ED), and energy-dispersive analysis of X-rays (EDX) (see figure 3.14⁹⁹). In this work, light field imaging and electron diffraction modes were used and they will simply be referred to as imaging and diffraction mode respectively, as DF and EDX will not be discussed further. A schematic of the difference in the optics of these two modes can be seen in figure 3.15⁹⁹.

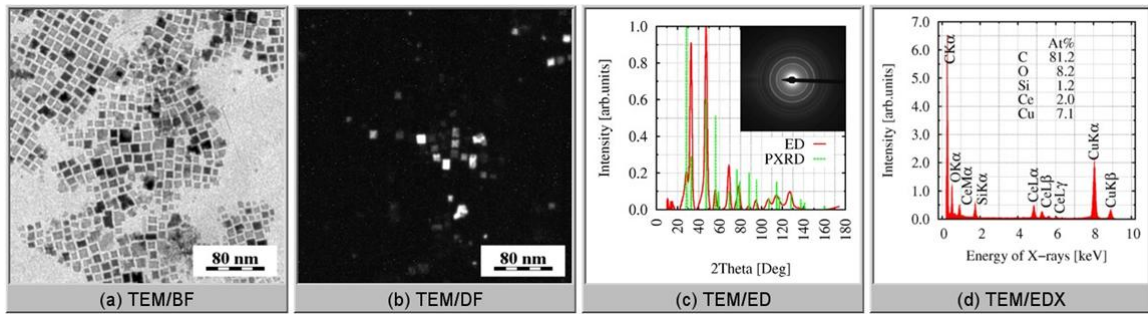


Figure 3.14: TEM Measurement Modes

With the imaging mode, the TEM is used like a microscope with the electrons made visible by a phosphorus screen (or simply with a detector). It was in imaging mode that the TEM was used to investigate the size of the nanoparticles in this work by simply measuring them. In the imaging mode, the entirety of the three dimensional image is flattened down into two dimensions, which can be deceptive. This is why very thin samples must be prepared. For nanoparticles of the size looked at in this work, the issue

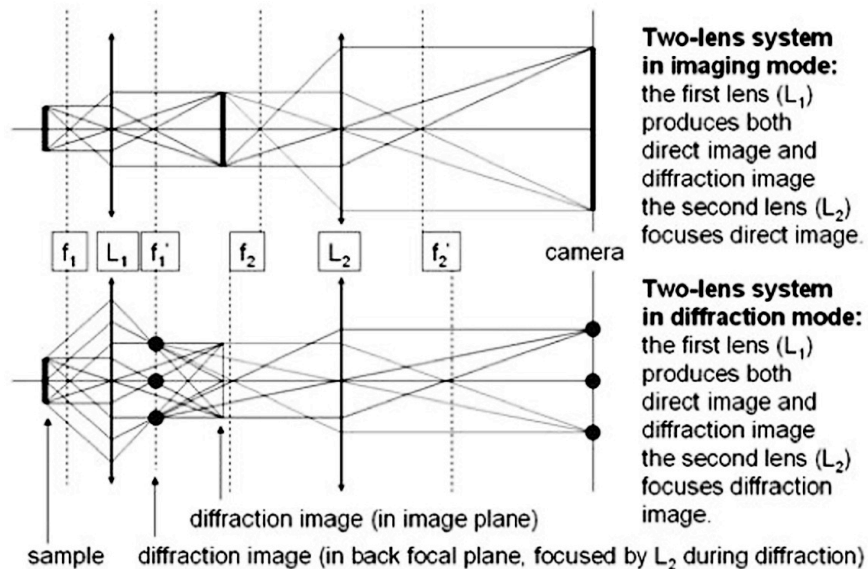


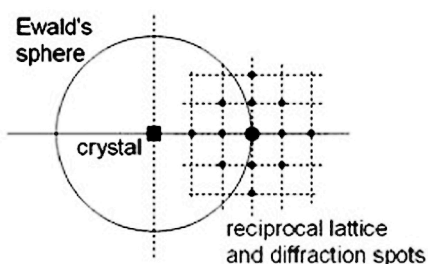
Figure 3.15: TEM Optics Schematics

results from nanoparticle pileups rather than sample thickness, but the danger is the same.

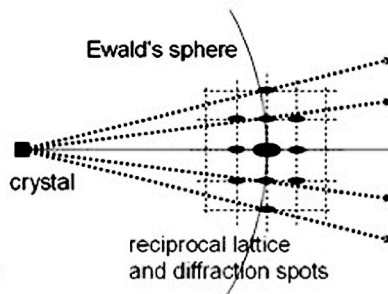
In addition to the imaging mode, TEMs can also be used in diffraction mode to take a diffraction pattern from a single nanoparticle, which can be then used to identify the structure. It was this method of measurement that was used in this work to verify the crystal structure of the nanoparticles investigated. In figure 3.16⁹⁹ the basic idea behind the electron diffraction measurement can be seen. The concept is the same as the more familiar X-ray diffraction technique. The X-rays, or in this case electrons, diffract off the atomic structure of the crystal and create a reciprocal lattice on the Ewald sphere. For this application of diffraction, the result looks like a set of concentric circles (as was seen in figure 1.16 inset) and the spacing of the circles reveals what the crystal's structure is. It should be noted, that as this method relies on lattice spacing for determining crystal structure, it is generally not good at determining whether the structure is $\gamma\text{-Fe}_2\text{O}_3$ or Fe_3O_4 ,

XRD and ED of a cubic monocrystal, one axis parallel with primary beam.

(1) XRD: no diffraction.



(2) ED: whole plane of reciprocal lattice.



Difference between XRD and ED:

- 1) Radius of Ewald's sphere = $1/\lambda$; for X-rays: $\lambda \approx 1\text{\AA}$, for electrons $\lambda \approx 0.03\text{\AA}$.
In ED, the radius of Ewald's sphere is very high due to extremely short wavelengths.
- 2) Width of diffraction spots (ϵ_{NM}) decreases with crystal thickness ($\epsilon_{\text{NM}} \approx 1/L_{\text{NM}}$):
In ED, the crystals must be very thin and, consequently, the spots are elongated.

Figure 3.16: TEM Diffraction

as they are both a spinel structure.

Pair Distribution Function

The pair distribution function (PDF) is a measure of the probability of finding the nearest atom a given radius away and is used in chapter 6 and 7. Originally used mostly for liquids and amorphous solids, it is now being used for nanoparticles and polycrystalline solids.

Since PDFs are in essence a measure of order, they can be used to probe the grain size in disordered crystals or to determine the size of nanoparticles. The PDF signal is obtained by taking the Fourier transformation of the normalized scattering intensity of a diffraction pattern. PDFs are still a form of crystallography, but rather than giving inter atomic vectors within a unit cell (as one gets for the Patterson function), the length scale of the bond beyond the unit cell is given. Additionally, by investigating different length scales, you can probe the lattice structure within a crystal grain or nanoparticle, as well as the size of the domain or particle (see figure 3.17¹⁰⁰).

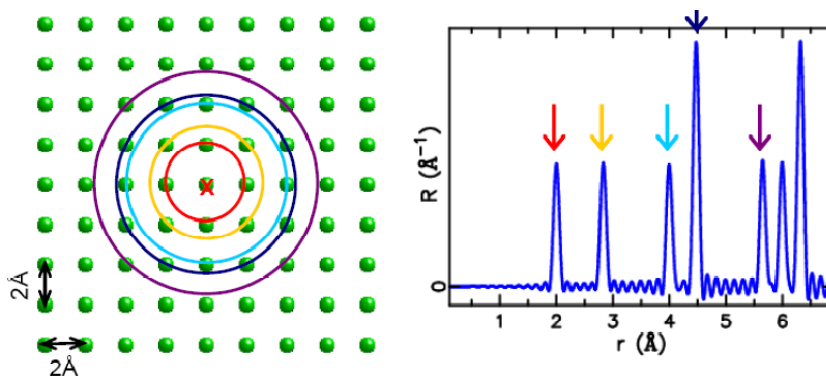


Figure 3.17: PDF. Illustration of PDF measurement (right), example PDF measurement (left).

To obtain a PDF, the Fourier transform is taken of the scattering intensity ($S(Q)$) of the powder diffraction data (see equation (3.11)).

$$(3.11) \quad G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^{\infty} Q[S(Q) - 1] \sin(Qr) dQ$$

$\rho(r)$ =microscopic pair density ρ_0 =average number density Q =|scattering vector|^{100, 101}

I will not discuss the PDF set up in the experimental section, as I have no experience with it, but for more details the reader is referred to the paper presented in chapter 7, and Jolley's paper on using PDF to establish crystal size¹⁰².

Experimental Set Up

Sample Descriptions

The nanoparticles discussed in this work were made by a number of different growers. In addition to being grown by different chemists, there are three different synthesis methods used. The first work on nanoparticles (discussed in chapters 4, 5 and 7) was done on nanoparticles grown inside a ferritin protein cage. Referred to simply as ferritin for convenience, there are different types of ferritin: horse spleen ferritin used in the work in chapters 4 and 5, and human ferritin used in the work done in chapter 7. (Work not included here used a form of ferritin extracted from bacteria from the hot springs in Yellowstone.) This difference is mentioned because it is hypothesized in the paper covered in chapter 7, that the different ferritin protein may affect the particle growth. This growth technique is well documented in a paper entitled "Biomimetic

magnetic nanoparticles"¹⁰³.

This type of growth is a relatively cool synthesis process with the temperature held at 65°C, since high temperatures would denature the protein. A pH of 8.5 was used in these growths. The ferritin protein cage the nanoparticles are grown in have an outer diameter of 12 nm, and an inner diameter of 8 nm. This has a number of effects on the particles' properties. Particles grown inside a protein are strictly confined in size on the upper end of the size limit, as the inner dimensions of the protein cage physically restrain the particle. While the lower limit is not as well constrained, this process produces nanoparticles that are rather homogeneous in size around 6.7 nm, varying by ± 1 nm. Additionally, the protein cage acts as a barrier to particle-particle interaction, as the nearest neighbor particle is at least 4 nm away.

The second synthesis process used in the work outlined in chapter 6 and 7, is to grow nanoparticles through the same method (pH, temperature and chemistry) as was used for the caged particles, but without the restraint of the protein. The particles are able to reach larger sizes without the protein to confine them, as was seen in the work done in this way. These particles are 14 nm - 15 nm, though as discussed in the paper in chapter 7, the size may vary with concentration.

Lastly, nanoparticles were made with no regard for protein compatibility, with a synthesis process reaching temperatures of 200°C, far exceeding temperatures that the proteins used can withstand. Particles made with this method were used in the work discussed in chapters 8 and 9. These particles were also not restrained by a cage and achieved sizes of 8.5 nm - 9 nm. While the obvious characteristics are caged verses

uncaged and size, the synthesis method must not be neglected, as this too can have an effect on how the nanoparticles grow, just as growth conditions do for thin films or bulk materials.

In addition to synthesis, our collaborators also used either PDF or TEM to determine that the particles grown were indeed spinels, and to acquire information as to their size. As I was not a part of these measurements, I will not go into detail as to the experimental setup. Once the nanoparticles were synthesized and characterized in this way by our collaborators, they would be given to us in one of two forms, dry or in solution. The dry samples were used for ACMS and the samples in solution were used for XAS and MCD. (For accuracy it is noteworthy that due to the chemistry of the high temperature uncaged particles, the samples were more like an ink when in solution and ranged from a paste to dried paint consistency when “dried”.)

Beamline Characteristics

Beamline 4.0.2 is an elliptically polarized undulator with a 5.0-cm period (EPU5). The energy range for this beamline is 100-2000 eV. Its monochromator is a variable-included-angle PGM. Its calculated flux (1.9 GeV, 400 mA) is 1×10^{13} photons/s/0.1%BW at 800 eV¹⁰⁴. The resolving power ($E/\Delta E$) is 5,000-10,000. Brightness Curves for these lines can be found in Appendix C.2¹⁰⁴.

The beamline 4.0.2's end station is equipped with an eight-pole electromagnet with a capability of a field up to 0.9 T (see figure 3.18³⁰). Measurements can be done in total electron yield, total fluorescence yield and transmission yield. The spot size is $100 \mu\text{m} \times 100 \mu\text{m}$ square (assuming an orientation with the sample perpendicular to the

x-ray beam). The pressure on the chamber is 10^{-6} - 10^{-9} Torr and the sample can be heated to 450 K or cooled to 15 K.

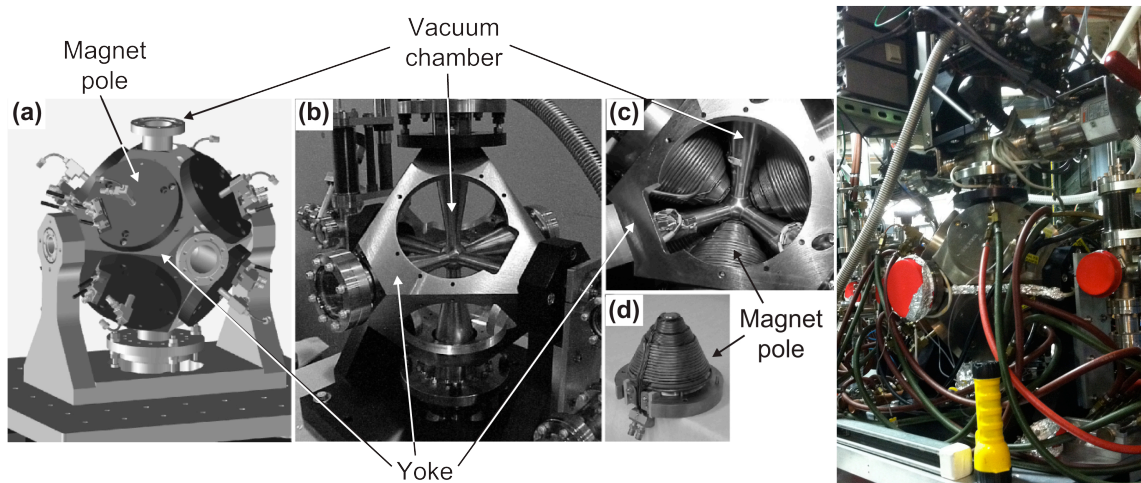


Figure 3.18: Beamline 4.0.2 End Station

Beamline 6.3.1 is a bend magnet. The energy range for this beamline is 300-2000 eV. It has a VLS-PGM monochromator with a fixed exit slit and refocusing mirror. Its calculated flux (1.9 GeV, 400 mA) 1×10^{11} photons/s/0.1%BW at 1000 eV. The resolving power ($E/\Delta E$) is 5,000.

The beamline 6.3.1's end station is equipped with an electromagnet capable of up to a 2 T field, which is collinear to the x-ray beam (see figure 3.19³⁰). Measurements can be done in total electron yield, fluorescence yield and transmission yield. The spot size is $500 \mu\text{m} \times 500 \mu\text{m}$ (assuming an orientation with the sample perpendicular to the x-ray beam). The pressure on the chamber is 10^{-6} - 10^{-9} Torr, and the sample can be heated to 800 K or cooled to 10 K. All of the technical specifications were taken from the beamline information posted on the ALS web site¹⁰⁴. As a side note, recently a new

program for doing XAS was set up on beamline 6.3.1, where a much faster measurement can be achieved, called a flying scan. This continuously moves the grating, rather than stopping and starting the motor on the grating for each measurement, achieving an equivalently accurate but much faster scan. In doing the scan in this manner, a much faster scan time can be achieved, which reduces the artifacts of charging mentioned earlier in the discussion of electron-yield measurements. This method of measurement was used in some of the later work and the charging effects were notably less.

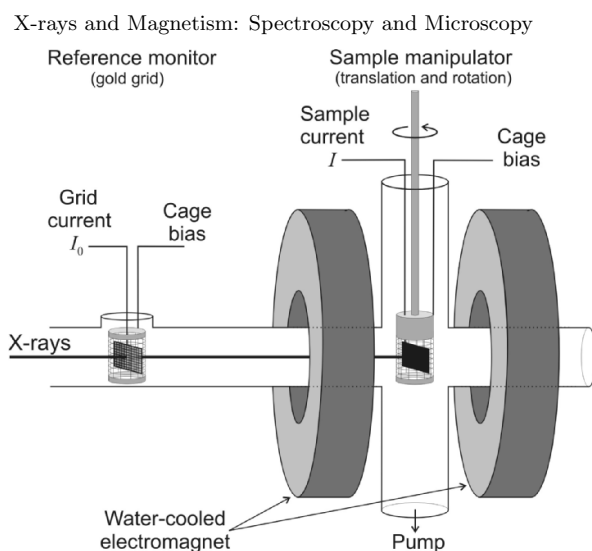
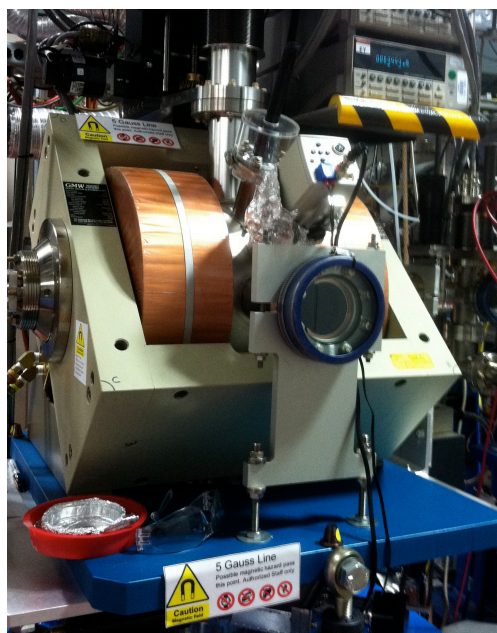


Figure 3.19: Beamline 6.3.1 End Station



Sample Preparation for XAS and XMCD

XAS and XMCD measurements were conducted at ALS in Berkeley, California. The specifications of the beamlines have been given. Some additional settings were changed depending on the edge being measured, and additionally to achieve a better flux

or resolution. When working on beam line 6.3.1, grating 600 lines/in or 1200 lines/in was used depending on the edge being measured. The aperture was set to 1 mm, and the slits were set to 20 by 20 microns (though for greater flux, they could be set to 40 by 40 microns without losing much resolution). Flying scans were done using a 0.1 eV increment and with a velocity 0.25 - 0.1 eV/sec. The magnet on beamline 6.3.1 was upgraded during the time the measurements for this thesis were collected. For this reason, the fields used are dependent in part on when the measurements were done; the values are specified in the papers. On beamline 4.0.2, the polarization was 90% during MCD measurements. Most of the measurements taken on beamline 4.0.2 used the 600 lines/in grating and the 3rd harmonic. The vanadium measurements however, were taken using the 1st harmonic rather than the 3rd harmonic, for better energy resolution over the energy range of the vanadium edge.

Samples were prepared for measurements by drying a liquid suspension of the nanoparticles onto Formvar coated TEM grids, which are 3 mm across (an image of a pristine TEM grid included as an inset in figure 3.27 in the TEM section). Pipettes are used to administer a small drop of the liquid suspension onto the grids. This is done in much the same manner as one would if preparing the samples for TEM with the exception that for XAS a much larger quantity of the sample is needed. To achieve a greater sample density, the drops were allowed to dry (the drying process aided by a lamp), and then a new drop was administered. This is repeated until the sample looks sufficiently dense, but is not too dense so that it begins to flake off. In some cases, the “dried” samples were not fully dry and more closely resembled a thick paste as

mentioned earlier. In these cases, the sample could be prepared from this more concentrated material. In this form, the samples could be smudged onto the formvar grids, rather than dried on, taking care to use nonmagnetic implements for smudging (such as wood). Once prepared on the TEM grids, the samples were mounted to a sample holder designed specifically for their dimensions with a cutout to allow for transmission yield measurements to be done in addition to electron yield measurements. The formvar grids were mounted to the sample paddle using carbon tape and a good contact was reinforced with a dab of silver paste at the edge of the sample or by an additional sandwiching layer of carbon tape as seen in figure 3.20. Though the transmission yield was not always analyzed, it provided a useful tool when aligning the sample.

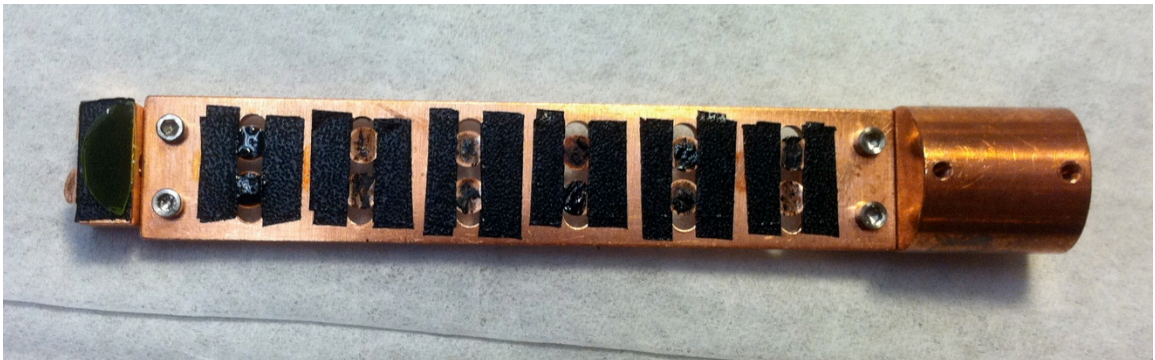


Figure 3.20: XAS and XMCD Sample Paddle

Quantum Design PPMS Measurements

A physical properties measurement system (PPMS) is designed such that by installing different attachments, a variety of measurements can be made with one piece of equipment, making it quite versatile. In this work, the Quantum Design PPMS 6000 was

used to measure vibrating sample magnetometry (VSM) and alternating current magnetic susceptibility (ACMS).

The ACMS attachment on this PPMS system has the capacity to measure in both an AC and a DC mode; here only AC has been used. The PPMS is rated to have a sensitivity of 2×10^{-8} emu or 2×10^{-11} Am² at 10 kHz and is capable of a temperature range of 1.9 K to 350 K. The temperature is reported to be accurate to $\pm 1\%$ and stable to $\pm 2\%$ for $T \leq 10$ K and $\pm 0.02\%$ for $T > 10$ K. In the measurements done in this work, the blocking temperature was always above 10 K, so the latter, more accurate stability is the applicable one. The allowed frequencies for the AC measurements are 10 Hz to 10 kHz. The strength of the applied AC field can be set from 2 Oe to 15 Oe as sited in the specs. Additionally an external DC field can be used if desired.

The ACMS attachment (model P500), seen in figure 3.21⁹³, is a sophisticated piece of equipment unto itself. The attachment has built in noise-reducing compensation coils. The ACMS attachment is able to separate the real and imaginary components of the AC signal with a high degree of accuracy due to an array of calibration coils. Low inductance calibration coils are at the center of the pickup coils in order to allow for true compensation of the instrumental phase shift. Calibrations are also done to eliminate the imbalance effects between the drive coils and sense coils. Together this allows for an accurate separation of real and imaginary parts of the susceptibility signal. Additionally, as can be deduced from the diagram of the ACMS head, the driving coils and detection coils are parallel, so the parallel component of the susceptibility is what is being measured. All the information about the specifications of the PPMS 6000 and ACMS

attachment model P500 were obtained from the information provided on the Quantum Design web site⁹³.

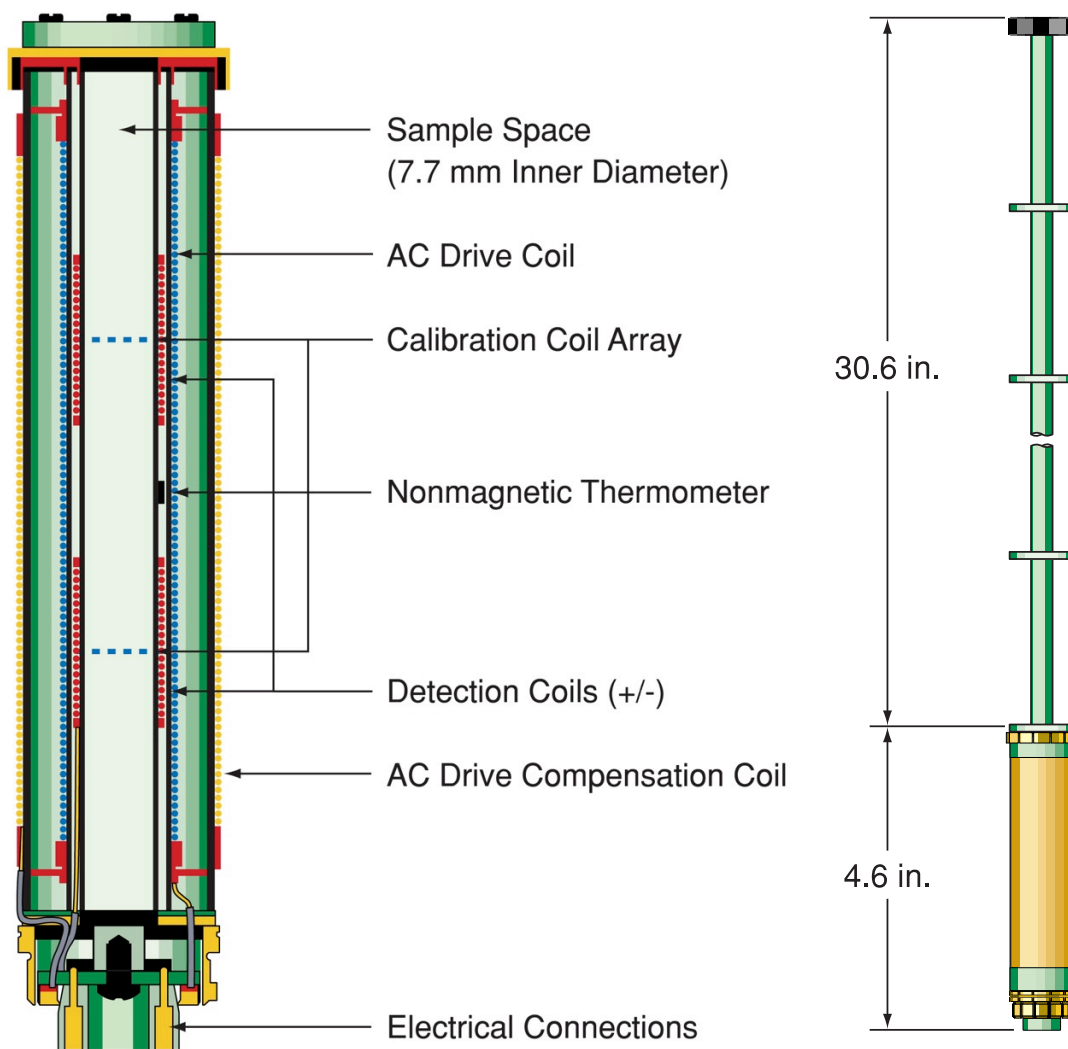


Figure 3.21: ACMS Schematic. ACMS head (left), full ACMS insert (right).

The samples were prepared for this measurement by encapsulating them in Duco Cement[®] glue (which has no ACMS signal). The Duco[®] nanoparticle pellet is then taped onto a small piece of plastic (cut from a clear plastic straw) and then taped around

securing it in a makeshift tape capsule. The capsule must be small enough that it can fit in the end of the clear plastic straw that is the sample holder, but it must be large enough that it is wedged in tightly so that it does not fall out. The straw should be perforated several inches away from the sample to allow for pressure equalization between the inside of the straw and its external pressure, when the chamber is pumped down. This straw is then fitted onto the end of the stick and inserted into the PPMS. Pictures of the sample preparation are included in figure 3.22.

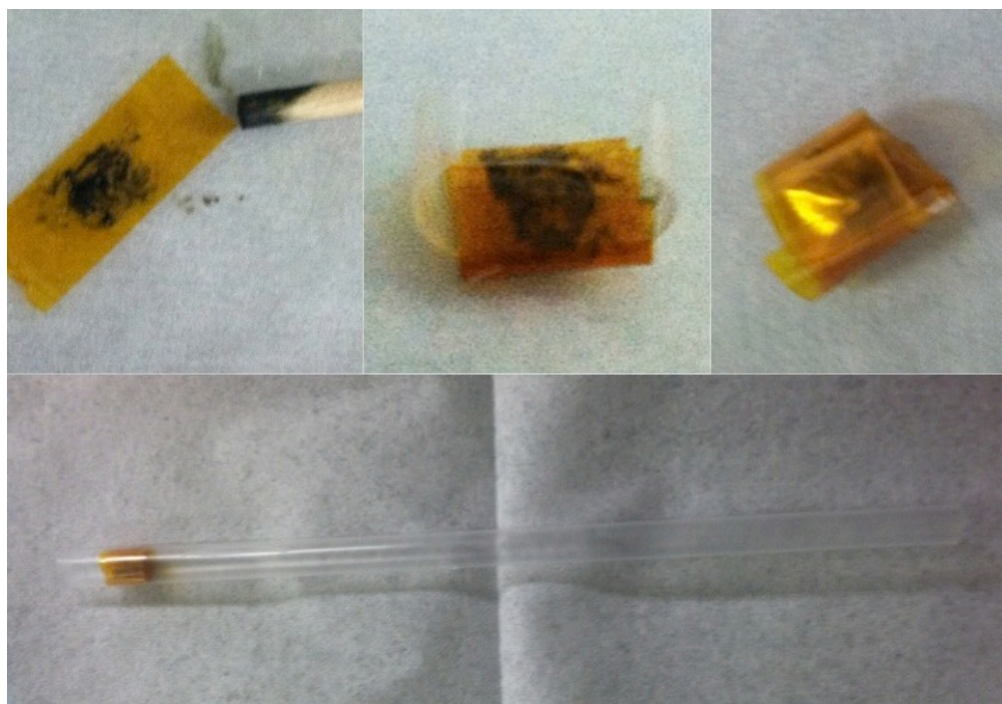


Figure 3.22: ACMS Sample Preparation

Once in the PPMS, the position of the sample is determined by using the AC extraction routine, which uses an alternating field (set to 10 Oe for this work) to find the sample. Most of the time the samples were located without the use of any external field

at room temperature. Some samples were of a sufficiently weak signal, that the ACMS software had a hard time locating them. In those cases, the temperature was lowered in order to facilitate the locating of the sample or in the worst-case scenario, the location was estimated and set manually.

The ACMS measurements presented in this dissertation were done over a temperature range starting at room temperature and going down to as low as 5 K (well within the specified “allowed range”). I chose to measure at 8 frequencies: 178 Hz, 356 Hz, 562 Hz, 1000 Hz, 1778 Hz, 3612 Hz, 5623 Hz and 10000 Hz. This provides a nice range, and when plotted as $\ln(1/\text{frequency})$ vs. $1/T_B$, gives a linear distribution. The strength of the applied AC Field used was 10 Oe. I did not add an external DC field in my measurements. This was all done using a program like the one listed in Appendix C.3.

Another attachment for the PPMS used in this work is the model P525 Vibrating Sample Magnetometer measurement system (see figure 3.23¹⁰⁵). VSM, though measured for some of the original sample sets (such as the zinc doped samples), was not found to be particularly illuminating. Originally, the hope was to measure the magnetic strength of the sample with VSM; this was abandoned as it became clear that the VSM measurements could not be mass normalized with any reliability due to several factors. VSM can give some information about the general character of the material (superparamagnetic or ferromagnetic) at a given temperature and whether there is an exchange bias due to, for example, a core-shell coupling. An example of a VSM loop done on one of the zinc samples is included (see figure 3.24). This measurement was done on a

10% zinc sample grown in ferritin at a temperature of 10 K. Though it was useful in a qualitative sense initially, it became clear that there was not much in the way of quantitative information to be gained from the measurement and it was discontinued. In light of this, VSM will only be discussed briefly.

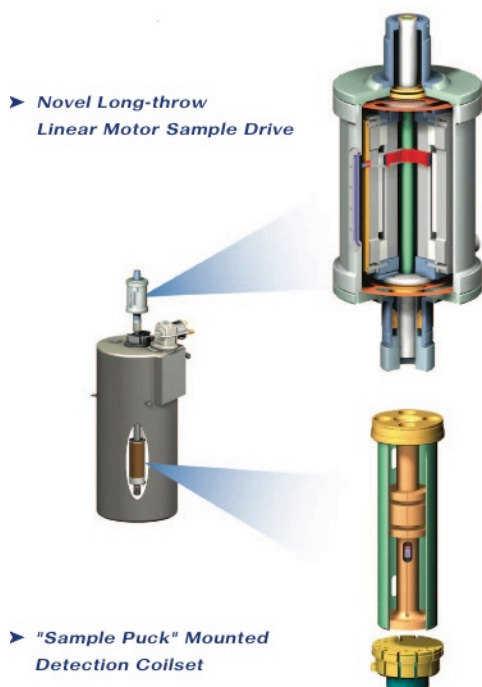


Figure 3.23: VSM Attachment

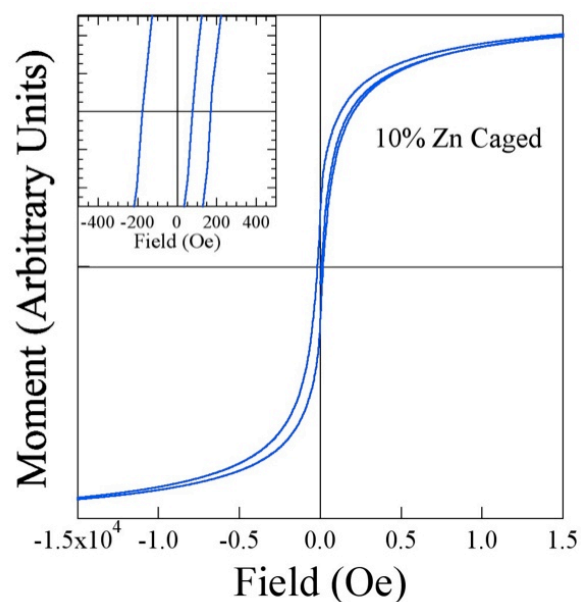


Figure 3.24: VSM Loop on Nanoparticles

The PPMS module used for these measurements is rated up to 8T^{105} . The measurement of the moment is acquired by sweeping through a range of fields, usually starting at zero field, increasing to the target field F_{max} (up to 8 T), then down to negative F_{max} , then again back up to F_{max} . The moment is measured at a set of points as specified by the user. Utilizing the nature of induction to isolate the sample moment from the

larger signal, the sample is oscillated through a set of pickup coils. In this way only the change is measured and the large DC field is not a factor. When measured with VSM, the sample was encapsulated into a pellet of sample duco slurry, much like as was done for VSM, with the exception that the sample size was more restrictive. The sample was then glued with more Duco[®] onto a quartz sample paddle, which is screwed onto the stick and inserted into the PPMS. The applied field was specific to the sample. The samples are superparamagnetic and so the saturation field is less obvious than with a ferromagnetic material, but the field was set high enough for the loops to close and to be satisfied that they were past their saturation field.

TEM Characteristics

TEM was used to characterize the nanoparticles discussed in chapters 4, 5, 8 and 9. A figure was never included for the TEM measurements due to space constraints, so a picture has been included here (figure 3.25); this is of one of the samples from the gallium series.

The TEM used for the measurements in this dissertation was the LEO 912, seen in figure 3.26, which claims a point-to-point resolution of 0.37 nm and a line resolution of 0.2 nm. The magnification range is listed as 80 - 500,000 $\times$ magnification, achieved using a 60 kV - 120 kV operating voltage range, with an accuracy in the accelerating voltage of 0.2 volts. The LEO 912 has a minimum beam size of 1.6 nm. Additionally it has the specimen tilt of $\pm 60^\circ$ ⁶⁴.

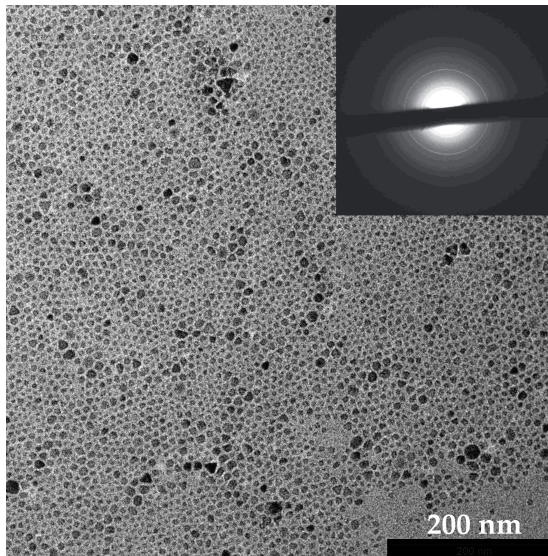


Figure 3.25: TEM of Nanoparticles. TEM of Gallium doped nanoparticles in imaging mode TEM and diffraction mode (inset).

Samples are mounted on a copper grid 3 mm (figure 3.27 inset) in diameter, coated with formvar in order to facilitate wetting. These are introduced via the specimen port into the TEM (figure 3.27). The TEM was used on a 80 keV setting with an Omega filter. Further explanation of the experimental set up is outlined in a paper by Michael Klem on cobalt iron oxide spinels^{106, 107}.

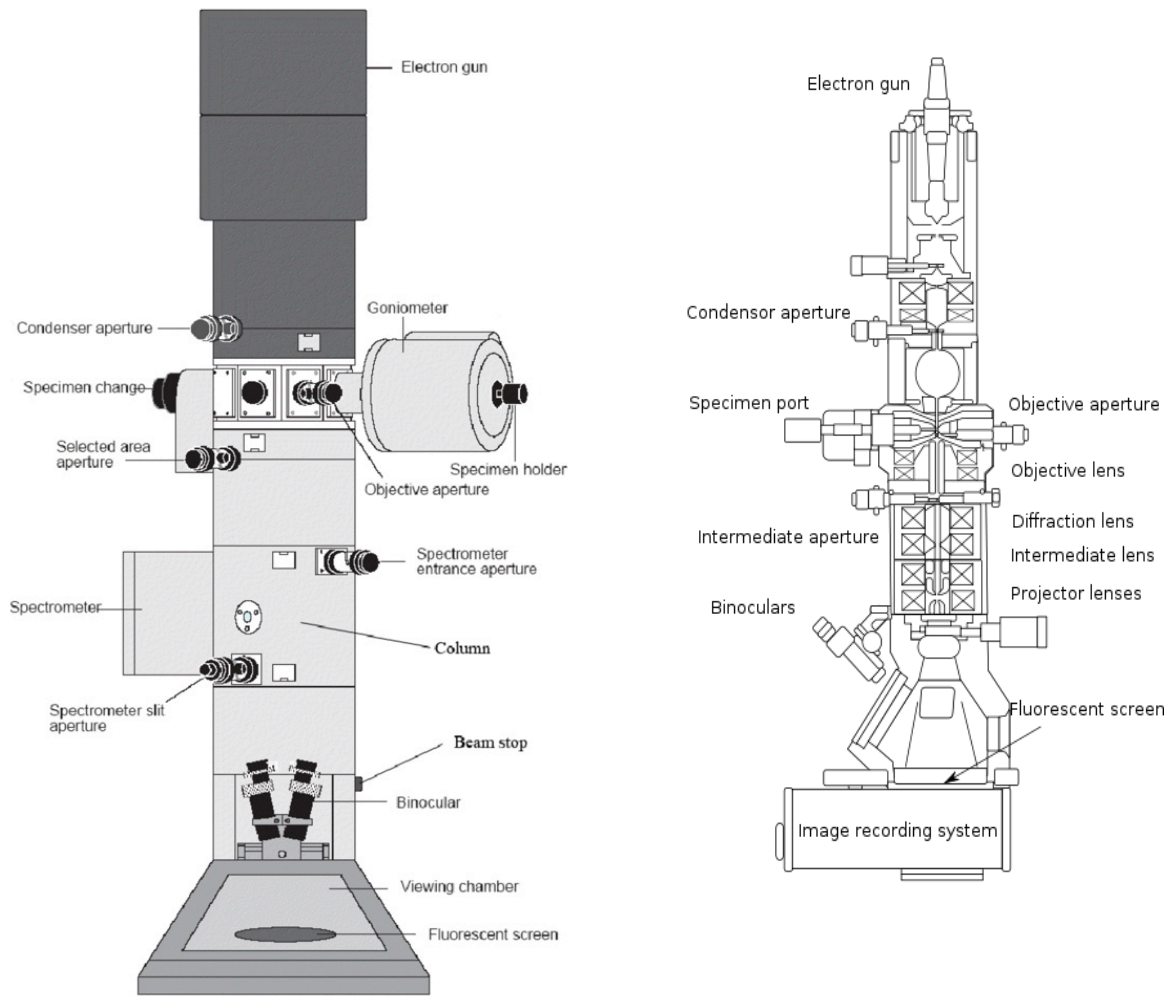


Figure 3.26: TEM Schematic. TEM Leo 9.12 model (left), Schematic of a generic TEM (right).

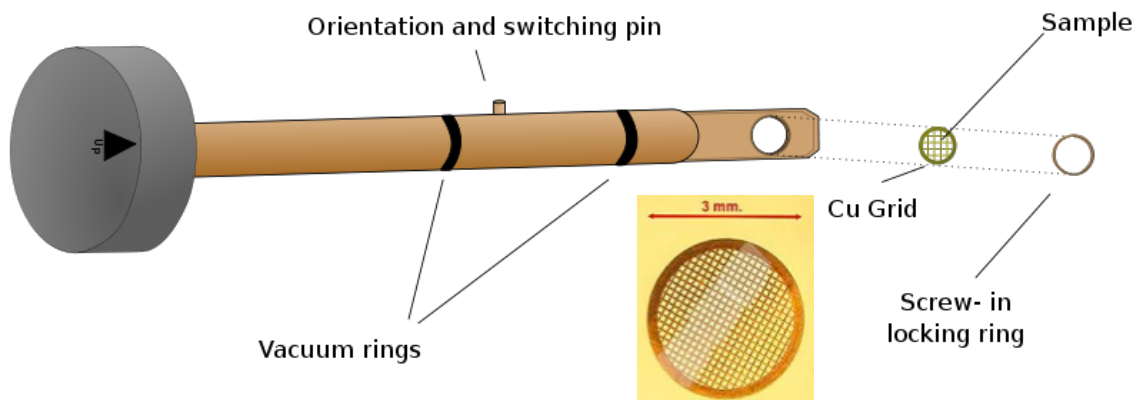


Figure 3.27: TEM Sample Arm Schematic

CHAPTER 4

ZINC DOPING OF IRON OXIDE NANOPARTICLES GROWN IN PROTEIN CAGES

Contribution of Authors and Co-Authors

Manuscripts in Chapters 4: Site Determination of Zn Doping in Protein Encapsulated $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ Nanoparticles

Author: Vanessa L. Pool

Contributions: I was responsible for taking the ACMS measurements and VSM data as well as modeling the moment per iron atom site.

Co-author: M.T. Klem

Contributions: M.T. Klem made the nanoparticles and he was also responsible for taking the TEM measurements used to identify crystal structure and size.

Co-author: J. Holroyd

Contributions: J. Holroyd was responsible for the XAS and XMCD.

Co-author: T. Harris

Contributions: T. Harris was involved in the conceptualization aspect of the paper.

Co-author: E.A. Arenholz

Contributions: E.A. Arenholz is the beamline scientist where XAS and XMCD measurements were done.

Co-author: M. Young

Contributions: M. Young was involved in the conceptualization aspect of the paper.

Co-author: T. Douglas

Contributions: T. Douglas was M.T. Klem's adviser and was involved in the conceptualization aspect of the paper.

Co-author: Y.U. Idzerda

Contributions: Y.U. Idzerda is my adviser, was involved in the conceptualization aspect of the paper and did the analysis on the XAS and XMCD for the paper.

Manuscript Information Page

Vanessa L. Pool, M. T. Klem, J. Holroyd , T. Harris E. A. Arenholz, M. Young, T. Douglas and Y. U. Idzerda

☐ Prepared for submission to a peer-reviewed journal

☐ Officially submitted to a peer-reviewed journal

☐ Accepted by a peer-reviewed journal

☒ Published in a peer-reviewed journal

Publisher Date of submission (10 October 2008) Date manuscript will appear (13 February 2009) Issue in which manuscript appears in (Journal of Applied Physics)

Zinc Paper Introduction

The investigation into growing nanoparticles inside ferritin protein cages had begun in the Idzerda research group prior to my participation. There had already been studies done on ferritin-grown nanoparticles of iron-oxide doped with cobalt¹⁰⁶ and nickel. In those early studies, methods were established to synthesize single-phase materials with reproducible magnetic properties. Zinc is an interesting choice of dopant, since unlike cobalt and nickel it is non-magnetic and, if it mimics the bulk behavior, will cause a marked increase in total moment of the nanoparticle. Zinc strongly prefers to substitute as a 2+ ion and, in the bulk, prefers the tetrahedral position rather avidly. This substitution results in an octahedrally coordinated iron atom that was initially a 2+ cation to become a 3+ cation (under the assumption that no oxygen vacancies are created). From what has already been discussed about the spinel structure, this substitution would increase the average iron moment in two ways. First, as the iron's ionization state changes from 2+ to 3+, its moment would increase from $4 \mu_B$ to $5 \mu_B$, increasing the total moment of the unit cell. Secondly, the zinc (being nonmagnetic) would displace an iron atom and eliminates an A-site iron moment that cancelled an iron moment from the B-sites, making the moment per unit cell increase further. Together with the previous effect, the total moment of the nanoparticle would increase by $6 \mu_B$ per unit cell after each Zn^{2+} substituted into a tetrahedral position. Unfortunately Zn substitution into the A-site also weakens the indirect exchange responsible for the antiferromagnetic ordering the A and B sublattice, limiting the moment increase. For this reason, zinc is a good

choice of dopant if a high moment is desired. This paper shows the result of doping zinc was not exactly as expected due to the effect of the protein cage.

Site determination of Zn doping in protein encapsulated $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ nanoparticles

V. L. Pool,^{1,2,a)} M. T. Klem,^{3,2} J. Holroyd,¹ T. Harris,^{3,2} E. Arenholz,⁴ M. Young,^{5,2} T. Douglas,^{3,2} and Y. U. Idzerda^{1,2}

¹Department of Physics, Montana State University, Bozeman, Montana 59715, USA

²Center for Bio-inspired Nanomaterials, Montana State University, Bozeman, Montana 59715, USA

³Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59715, USA

⁴Advanced Light Source, LBNL, Berkeley, California 94720, USA

⁵Department of Plant Sciences and Pathology, Montana State University, Bozeman, Montana 59715, USA

(Presented 13 November 2008; received 1 October 2008; accepted 10 October 2008; published online 13 February 2009)

The x-ray absorption spectra of the Fe and Zn L edges for 6.7 nm Fe_3O_4 nanoparticles grown inside 12 nm ferritin protein cages with 10%, 15%, 20%, and 33% zinc doping show that Zn is substitutional as Zn^{2+} within the iron oxide host structure. A Neel–Arrhenius plot of the blocking temperature in frequency dependent ac-susceptibility measurements shows that the particles are noninteracting and that the anisotropy energy barrier is reduced with Zn loading. X-ray magnetic circular dichroism of the Fe displays a linear decrease with Zn doping in sharp contrast to the initial increase present in the bulk system. The most plausible explanation for the decrease in moment is that Zn substitutes preferentially into the tetrahedral A site as a Zn^{2+} cation, generating a mixed spinel. © 2009 American Institute of Physics. [DOI: 10.1063/1.3055346]

I. INTRODUCTION

There are a number of applications for magnetic nanoparticles: biological detection, magnetic memory devices, cancer treatments, and magnetic resonance imaging contrast agents.^{1–3} For many applications, it would be beneficial to control the particle moment without size modification. The use of a biomimetic approach, including the synthesis of magnetic nanoparticles inside organic constructs, such as protein cages and capsids, adds additional functionality as well as constrains the encapsulated nanoparticle's volume, resulting in highly monodisperse size distributions.^{4–9}

The bulk iron oxide Fe_3O_4 has a mixed spinel structure with two structurally inequivalent Fe sites, the A site (eight Fe^{3+} ions with a $5 \mu_B/\text{atom}$ moment), which is tetrahedrally bonded to a nearby oxygen, and the B site (16 Fe atoms), which is octahedrally bonded. The B site occupation is further divided into Fe^{3+} valency (eight ions with a $5 \mu_B/\text{atom}$ moment) and Fe^{2+} valency (eight ions with a $4 \mu_B/\text{atom}$ moment). Indirect exchange coupling through the intervening oxygen atom couples these two sublattices antiferromagnetically to each other, resulting in a ferrimagnetic material with a net moment of $1.3 \mu_B/\text{atom}$.¹⁰ Doping Zn into Fe_3O_4 results in Zn^{2+} ions substituting for the tetrahedrally bonded A -site Fe^{3+} ion, initially increasing the net Fe atom moment followed by a subsequent rapid decrease.¹¹ The crystal ZnFe_2O_4 is the terminus (at 33% Zn doping) and is an antiferromagnet with no net moment.

In this study Zn doping has been used as a mechanism to alter the moment of Fe_3O_4 nanoparticles grown in ferritin protein cages. While it is straightforward to measure the magnetization density for bulk materials, it is extremely dif-

ficult for protein encapsulated nanoparticles since mass normalization becomes unreliable. To circumvent this difficulty, x-ray magnetic circular dichroism (XMCD) measurements are used to establish the variation of the Fe moment with composition.

EXPERIMENTAL PROCEDURE

For this study 6.7 ± 1.1 nm Fe_3O_4 nanoparticles were grown inside ferritin protein cages with an inner diameter of 8 nm and an outer diameter of 12 nm. Details of the synthesis process are provided elsewhere.¹² Dynamic light scattering of the ferritin reaction showed no apparent change in protein diameter. The lack of precipitation and the absence of any change in the exterior diameter of the protein cage suggest that the reaction occurred in a spatially selective manner within the ferritin cage. For this study, Zn doping concentrations of 33%, 20%, 15%, and 10% were used.

X-ray measurements were done at beamlines 4.0.2 and 6.3.1 at the Advanced Light Source of the Lawrence Berkeley National Laboratory. Both the x-ray absorption spectroscopy (XAS) and XMCD spectra of the Fe and Zn $L_{2,3}$ edges were performed at room temperature in transmission geometry, with the nanoparticles dried onto a Formvar coated transmission electron microscope grid. The XMCD spectra were acquired in the presence of a 0.5 T magnetic field, with the magnetic field directed along the photon propagation direction using 81% circular polarized light. For comparison, XAS and XMCD spectra for high purity standards of Fe_3O_4 powders (Aesar), $\gamma\text{-Fe}_2\text{O}_3$ powders (Aesar), ZnO powders (Aesar), ZnFe_2O_4 powders (Aesar), and ZnO nanoparticles (similarly synthesized in ferritin protein cages) were also acquired. Vibrating sample magnetometry (VSM) measurements and temperature dependent ac-magnetic susceptibility

^{a)}Electronic mail: Pool@physics.montana.edu.

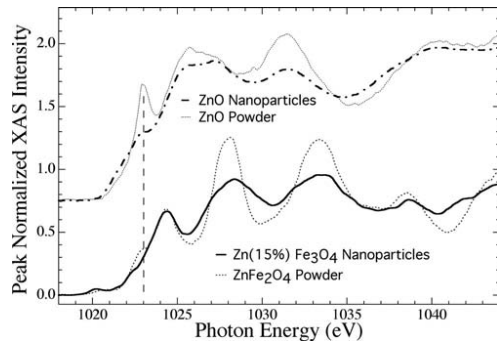


FIG. 1. The XAS of the $L_{2,3}$ edges of 15% Zn doping of the iron oxide nanoparticles along with a reference ZnFe_2O_4 powder and similarly synthesized ZnO nanoparticles and a reference ZnO powder (the latter two are offset for clarity).

(ACMS) measurements were performed at multiple frequencies using the Quantum Design physical property measurement system (PPMS).

III. RESULTS AND DISCUSSION

Figure 1 shows the Zn L edge of 15% Zn in Fe_3O_4 as well as the Zn L edge for several reference spectra of Zn oxide. (The XAS spectra for the other Zn loading factors that correspond to uniform doping levels of 10%, 20%, or 33% were identical to the 15% spectra in Fig. 1, the latter corresponding to the ZnFe_2O_4 stoichiometry.) It is clear that Zn is incorporated into the iron oxide nanoparticle rather than forming ZnO clusters within the Fe_3O_4 or distinct ZnO nanoparticles. Furthermore, the Zn spectrum agrees well with the Zn standards with tetrahedral oxygen bonding, suggesting Zn substitution into tetrahedral A site as a Zn^{2+} cation.

Fe $L_{2,3}$ -edge XAS spectra (not shown) for various Zn loading factors are nearly identical to that of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ standards. We can conclude that the Zn addition does not dramatically affect the nanoparticle formation.

The small Fe XMCD spectra for these nanoparticles are very similar to the spectra for Fe_3O_4 powders. The Fe L_{3} -edge XMCD intensity as a function of Zn loading is shown in Fig. 2. Also shown is the expected behavior of the nanoparticle net moment for three distinct models for Zn substitution and the experimentally determined behavior of the bulk moment. The Fe L_{3} -edge XMCD intensity displays a linear decline as the Zn concentration is increased.

In the bulk, as an increasing number of A sites are occupied by nonmagnetic Zn atoms, the A-B antiferromagnetic indirect exchange coupling weakens and a competing indirect exchange coupling within the B sublattice becomes dominant.¹⁰ As a result, the bulk material shows an initial rise in moment as Zn is substituted, then the moment falls as reported in Fig. 2.

Our samples show a distinctly different behavior. The simplest explanation of this behavior would be that the Zn is substituting into the octahedral B site as Zn^{2+} rather than the tetrahedral A site. The net Fe moment behavior of this sce-

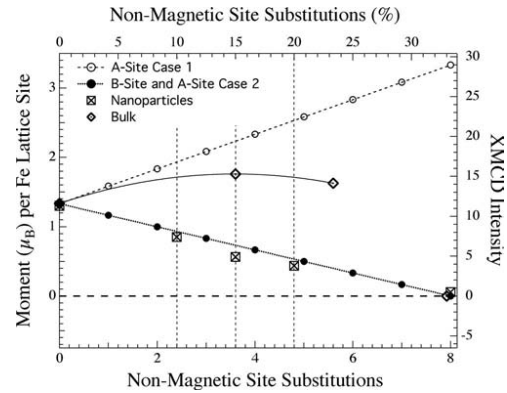


FIG. 2. The XMCD intensity of the L_3 edge of Fe and the extracted moment per Fe lattice site for various concentrations of Zn doped into Fe_3O_4 nanoparticles. Also shown are the experimental bulk values (Ref. 11) and the expected moment for three models described in the text.

nario is represented by the B-site curve in Fig. 2. Although there have been some works that suggest that Zn can substitute into the octahedral B site in significant amounts in the smaller nanoparticles,¹³ this seems highly unlikely given the agreement of the Zn XAS spectra with the spectra of tetrahedrally bonded Zn. Also, literature suggests that the octahedral occupation is accomplished under harsh synthesis conditions,¹⁴ and the conditions used here are the mildest reported.

The second model represents Zn substitution into the A site with the magnetic coupling remaining unchanged. Here, Zn^{2+} substitutes into the Fe^{3+} A site accompanied by a valence change in a nearby B site (from Fe^{2+} to Fe^{3+} with a corresponding moment increase from 4 to 5 μ_B/atom) to retain charge neutrality. The net result is an increase in Fe moment as displayed in the line labeled A-site Case 1 of Fig. 2.

A third model, which also generates a linear decline in the Fe moment (labeled A-site Case 2 in Fig. 2), can be explained in two ways. One picture is that the Zn substitution into the A site not only changes the valence (and so the moment) of the Fe B site but also reverses its magnetic orientation, although this seems unlikely given the strength of the other interactions. Alternatively, the B-B antiferromagnetic coupling could be dominant from the onset, with the A sublattice coupling antiferromagnetically to the Fe^{3+} ions in the B sublattice. This could be realized for a mixed phase of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ due to oxygen deficiencies¹⁵ causing coupling distinctly different than within the bulk Fe_3O_4 .

All these models assume uniform Zn distribution in the particles; an alternate explanation for the linear decline in the nanoparticle moment is that adding Zn to the synthesis process does not result in Zn-doped Fe_3O_4 but, rather, structurally homogeneous phases of mixed Fe_3O_4 and ZnFe_2O_4 composition. At 33% loading, all the particles are single phase ZnFe_2O_4 with zero net moment, while at intermediate loading values, the net moment would display a linear decrease

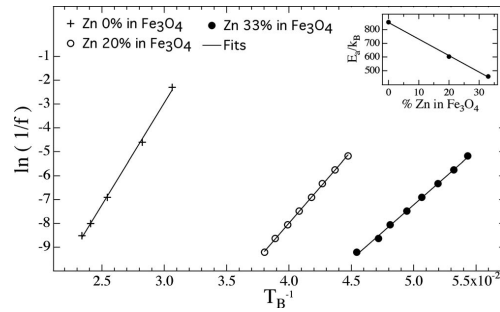


FIG. 3. The frequency dependence of the extracted blocking temperature of the real part of the ACMS of the Zn-doped iron oxide nanoparticles for 33%, 20%, and 0%. Inset: The least-squares-fit anisotropy energy values reported as E_a/k_B vs Zn doping.

with Zn concentration. This alternate explanation is consistent with the observation that the Fe and Zn XAS spectra for all Zn loading concentrations are identical.

To test this possibility, we have compared the magnetic hysteresis curves and the magnetic anisotropy energies as a function of composition. The observed variations of the hysteresis loops rule out a mixture of antiferromagnetic ZnFe_2O_4 and ferrimagnetic Fe_3O_4 nanoparticles, which would show nearly identical loops once normalized to their saturation moments. Also, the VSM loops do not show the exchange bias expected of a two-phase core-shell system between an antiferromagnet and a ferrimagnet as is observed in the $\text{Co}_3\text{O}_4\text{--Fe}_3\text{O}_4$ system.¹⁶

Determining the anisotropy energy density behavior with Zn composition may add insight into the resolution of this problem. The Neel–Arrhenius plot for the multi-frequency ACMS for the different Zn loadings is shown in Fig. 3. The linear fit demonstrates that the particles are noninteracting and allows for an extraction of the anisotropy energy in the standard way.^{17,18} The extracted anisotropy energy versus Zn loading (inset) shows a linear decrease in the anisotropy energy.

IV. CONCLUSIONS

The data suggest that Zn is substituting as Zn^{2+} into the tetrahedral A site of the spinel structure. Although this is in accordance to what is seen in the bulk material, the magnetic behavior is not the same as for the bulk. It seems most likely that the particles are forming a mixed phase of $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 particles, causing the A-B coupling to no longer dominate. To confirm this result and to understand the coupling in more detail, further work is needed.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation under Grant No. NIRT-DMR0210915 and the Office of Naval Research under Grant No. N00014-03-1 0692.

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CHAPTER 5

MAGNETISM DOPING OF IRON OXIDE NANOPARTICLES

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Contribution of Authors and Co-Authors

Manuscripts in Chapters 5: Site Determination and Magnetism of Doping in Protein Encapsulated Iron Oxide Nanoparticles

Author: Vanessa L. Pool

Contributions: I was responsible for the ACMS measurements as well as the XAS and XMCD.

Co-author: M.T. Klem

Contributions: M.T. Klem was responsible for making the nanoparticles and taking the TEM measurements used to identify crystal structure and size.

Co-author: C. Jolley

Contributions: C. Jolley added in making the nanoparticles.

Co-author: E.A. Arenholz

Contributions: E.A. Arenholz is the beamline scientist where XAS and XMCD measurements were done.

Co-author: T. Douglas

Contributions: T. Douglas was M.T. Klem's and C. Jolly's adviser, he was involved in the conceptualization aspect of the paper.

Co-author: M. Young

Contributions: M. Young was involved in the conceptualization aspect of the paper.

Co-author: Y.U. Idzerda

Contributions: Y.U. Idzerda is my adviser, was involved in the conceptualization aspect of the paper and did the analysis on the XAS and XMCD for the paper.

Manuscript Information Page

V.L. Pool, M.T. Klem, C. Jolly, E. A. Arenholz, T. Douglas, M. Young and Y.U. Idzerda

☐ Prepared for submission to a peer-reviewed journal

☐ Officially submitted to a peer-reviewed journal

☐ Accepted by a peer-reviewed journal

☒ Published in a peer-reviewed journal

Publisher Date of submission (30 October 2009) Date manuscript will appear (5 May 2010) Issue in which manuscript appears in (Journal of Applied Physics)

Manganese Paper Introduction (Caged Particles)

Manganese was chosen as a dopant for a number of reasons. It is an attractive dopant for a spinel, due to its flexibility to be ionized both as 2+ and as 3+. From bulk studies on doped Magnetite, manganese doping has shown a marked increase in moment with incorporation and is potentially magnetic even at 33%, which is stable in the bulk and known as Hausmannite as discussed in chapter 2. An additional cause of interest in this material came from a more application-oriented direction. Manganese-oxide had shown promise as an MRI contrast agent^{7, 8}. Nanoparticles grown in ferritin protein cages are far more difficult to produce than nanoparticles grown by other means; however, they have a major advantage in that they are extremely biocompatible. This quality is particularly valuable in applications such as MRI contrast agents and hyperthermia cancer treatments (a natural compliment for a material that could do both). These possible uses made manganese a natural choice of material as a dopant for this study.

Site determination and magnetism of Mn doping in protein encapsulated iron oxide nanoparticles

V. Pool,^{1,2,a)} M. Klem,^{2,3} C. Jolley,^{2,3} E. A. Arenholz,⁴ T. Douglas,^{2,3} M. Young,^{2,5} and Y. U. Idzerda^{1,2}

¹Department of Physics, Montana State University, Bozeman, Montana 59717, USA

²Center for Bio-inspired Nanomaterials, Montana State University, Bozeman, Montana 59717, USA

³Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717, USA

⁴Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, California 94720, USA

⁵Department of Plant Sciences and Pathology, Montana State University, Bozeman, Montana 59717, USA

(Presented 21 January 2010; received 30 October 2009; accepted 3 February 2010; published online 5 May 2010)

Soft x-ray absorption spectroscopy, soft x-ray magnetic circular dichroism, and alternating current magnetic susceptibility were performed on 6.7 nm iron oxide nanoparticles doped with (5%–33%) Mn grown inside the horse-spleen ferritin protein cages and compared to similarly protein encapsulated pure Fe-oxide and Mn-oxide nanoparticles to determine the site of the Mn dopant and to quantify the magnetic behavior with varying Mn concentration. The Mn dopant is shown to substitute preferentially as Mn⁺² and prefers the octahedral site in the defected spinel structure. The Mn multiplet structure for the nanoparticles is simpler than for the bulk standards, suggesting that the nanoparticle lattices are relaxed from the distortions present in the bulk. Addition of Mn is found to alter the host Fe-oxide lattice from a defected ferrimagnetic spinel structure similar to γ -Fe₂O₃ to a nonferromagnetic spinel structure with a local Fe environment similar to Fe₃O₄. © 2010 American Institute of Physics. [doi:10.1063/1.3359431]

I. INTRODUCTION

Protein encapsulated magnetic nanoparticles have generated interest for use in a number of applications including biological detection, cancer treatment, and as magnetic resonance imaging (MRI) contrast agents.^{1–3} In particular, Mn-doped iron oxides are being examined as a MRI contrast material where the protein cage is human ferritin, improving its biological compatibility, and the exterior of the protein cages can be genetically modified to bind to specific cell types. Separately controlling the properties of these nanoparticles without modifying their size is important for actualizing these unique applications envisioned for protein encapsulated magnetic nanoparticles.^{4–6} One important way to make these modifications is through doping iron oxides with other magnetic transition metals including transition metals that are ferromagnetic [e.g., Co (Ref. 7)], paramagnetic [e.g., Zn (Ref. 8)], and antiferromagnetic Mn in their bulk behavior.

The spinel structure AB₂O₄ is characterized by two structurally unequivalent sites, the tetrahedral A-site and the octahedral B-site. It is a mixed valence system with one third of the metallic cations in a +2 valence and two thirds in a +3 valence. The arrangement of these cations in the A and B sites determine whether it is a normal spinel, an inverted spinel, or a mixed spinel.⁹ Magnetite Fe₃O₄ is a ferrimagnet in the inverse spinel structure with an average measured moment of 1.37 μ_B per Fe atom.⁹ In addition to the possible variations within the ideal spinel structure, a defected spinel has the same basic structure but with vacancies. One ex-

ample, maghemite (γ -Fe₂O₃), has one in nine Fe sites vacant, since the vacant site would have been occupied by octahedral +2 iron ions, all Fe cations are in the +3 valence state for charge neutrality, and the average measured magnetic moment is reduced in this ferrimagnetic system to 1.2 μ_B per Fe atom.⁹ In general, a more complicated defect structure may be present and will be referred to as a Fe-oxide with a defected spinel structure.

II. EXPERIMENTAL PROCEDURE

In this study, Mn is doped (0%–33%) into 6.7 nm (+/-1 nm) Fe-oxide nanoparticles grown inside the hollow spherical shell horse-spleen ferritin (HSF) protein cages (exterior diameter 12 nm, interior void diameter 8 nm). For details of the synthesis process, refer to Ref. 10. Target atomic Mn concentrations (defined by the relative Fe and Mn concentrations in the aqueous solution) of 5%, 10%, 15%, 20%, 25%, and 33%, as well as pure Fe-oxide and Mn-oxide were all grown encapsulated inside the HSF protein. The solutions were all clear after synthesis indicating full incorporation into the protein cages. Elemental composition analysis in transmission electron microscopy (TEM) for a representative subset of these samples showed Fe and Mn incorporation into the protein shells, nominally at the target concentrations. As a check, the same synthesis procedure was carried out without the inclusion of the protein, resulting in a slightly orange-brown solution, indicative of bare Fe-oxide agglomerations.

To determine the composition and investigate the evolution of the electronic structure and the magnetic properties, x-ray measurements, both x-ray absorption spectroscopy

^{a)}Electronic mail: pool@physics.montana.edu.

(XAS) and x-ray magnetic circular dichroism (XMCD), were performed at the beamline 4.0.2 and 6.3.1 of the Advanced Light Source of the Lawrence Berkeley National Laboratory. Both the XAS and XMCD spectra of the Fe-edge and Mn $L_{2,3}$ -edge were performed in the transmission geometry and total electron yield configuration with the nanoparticles dried onto a formvar coated TEM grid. The XAS was performed primarily at room temperature, while the XMCD was performed both at room temperature and with the samples cooled to ~ 20 K in full saturation (in an applied field of 0.5–1 T) with the magnetic field directed along the photon propagation direction, using 90% circular polarized light. It should be noted that due to the difficulties in mass-normalization of protein encapsulated nanoparticles, all magnetization density measurements were obtained using XMCD measurements rather than vibrating sample magnetometry. By comparing the Fe-edge and Mn $L_{2,3}$ -edge XAS integrated peak areas, a precise but relative determination of the nanoparticle composition can be made. These relative peak area ratios can be related to the atomic concentration by comparing the Fe:Mn peak area ratios to that of the measured ratio for standard powders of Fe_3O_4 : Mn_3O_4 and Fe_2O_3 : Mn_2O_3 (99.99% purity from Aesar). Although the solution concentrations for the nanoparticles were targeted to be 0%, 5%, 10%, 15%, 20%, 25%, and 33%, the actual compositions were determined to be 0%, 6.1%, 10%, 15%, 23%, 26%, and 33%, respectively. This procedure can be in error if the electronic structure, in particular, the valence of the Mn, is found to change with concentration and cautious uncertainties (10%–20%, depending on the quality of the Mn XAS spectra at low concentrations) are employed here. (For these encapsulated nanoparticles, the determined Mn valence does not vary over this concentration range.)

For comparison, XAS and XMCD spectra were obtained of high purity powder standards from Aesar for a variety of Fe-oxide and Mn-oxide structures including powders of Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, Mn_2O_3 (Mn^{3+}), Mn_2O_4 (Mn^{4+}), Mn_2LiO_4 (Mn^{3+} and Mn^{4+}), and Mn_3O_4 (Mn^{2+} and Mn^{3+}), the final powder obtained from ESPI. The spectra from reference powders for MnO (Mn^{2+}) were not used because they were found to be contaminated with mixtures of higher Mn valence states both from the XAS measurement and x-ray powder diffraction. The theoretical spectrum from de Jong¹¹ is used for comparison as the Mn^{2+} reference spectra.

Temperature dependent, alternating current magnetic susceptibility (ACMS) measurements were performed at multiple frequencies on a Quantum Design Physical Property Measurement System to demonstrate that these particles were noninteracting and that to measure the anisotropy energy as a function of Mn concentration. In order to verify the size of the particles, size distributions from TEM were obtained and selected area TEM electron diffraction was used to acquire diffraction on the nanoparticles to verify a spinel structured oxide.

III. RESULTS AND DISCUSSION

Frequency dependent ACMS measurements were done on the nanoparticles with frequencies ranging from 178 to

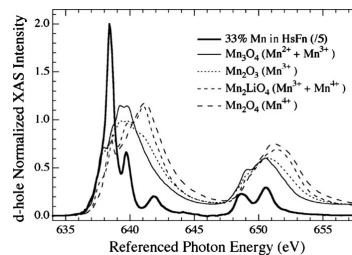


FIG. 1. Mn $L_{2,3}$ XAS spectra for Mn doped at 33% into 6.7 nm diameter iron oxide nanoparticles (heavy line) and various Mn-oxide reference powders.

10 000 Hz. The shape of the susceptibility curves does not show evidence of any secondary phases supporting the claim of a monodisperse size range and a single species of oxide. By constructing a Néel–Arrhenius plot (not shown) of the blocking temperatures as a function of the logarithm of the measurement frequencies, and examining the linearity of the fit (where the slope is proportional to the anisotropy energy) and the reasonable intercept values of the Néel–Arrhenius plot (equal to the attempt frequency), these particles are determined to be noninteracting. The anisotropy energy per particle is reduced from that of the pure iron oxide nanoparticle, and ranges from 8.56×10^{-21} to 13.1×10^{-21} J.

The measured Mn $L_{2,3}$ XAS spectra for all compositions are nearly identical to each other. The representative XAS spectrum for the 33% Mn doping into iron oxide (shown in Fig. 1) is compared to various Mn-oxide reference powders with different Mn valences. The reference spectra have been area normalized so that the integrated area of the Mn $L_{2,3}$ -edge is equal to the number of Mn d-holes anticipated for that Mn valence. The spectrum for the nanoparticle is reduced by a factor of 5 to fit on the same scale. The Mn L_3 XAS for the nanoparticle shows a simple three-peak structure with a very large and narrow peak at lower energy. Comparing the Mn XAS to these reference spectra and to published molecular orbit calculations^{11–13} indicates that the Mn is primarily in a Mn^{2+} valence state (the XAS peaks for higher Mn valence occur at higher energy). The simple nature of the Mn XAS structure also suggests that the nanoparticle is free of the tetragonal distortion present in bulk Mn_3O_4 .

In the bulk, the Mn substitutes primarily into the tetrahedral site as Mn^{2+} .⁹ As the Mn concentration increases to 33%, the material remains ferrimagnetic with an increasing total measured moment per formula unit to $4.6\mu_B$.⁹ By performing Fe $L_{2,3}$ -edge XMCD measurements in total electron yield at 20 K and in an applied field of 0.5 T on the particles, it is possible to obtain the average magnetic moment per iron lattice position and provide insight into the site occupation of the remaining Fe atoms. This result (shown as filled circles in Fig. 2) displays a rapid decline, not increase, in the average Fe moment, more rapid than a simple linear decrease would predict (dashed line). Moreover, both the Fe L_3 XMCD lineshape (inset of Fig. 2) and the Mn L_3 XAS lineshape show that as the Mn concentration increases, the oc-

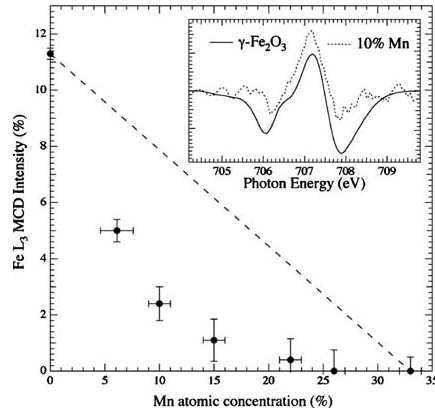


FIG. 2. Fe L_3 XMCD intensity as a function of Mn concentration (data: filled circles, model: dashed line). Inset: Normalized Fe L_3 XMCD spectra for 0% Mn doping and 10% Mn doping.

cupation by Fe of the Fe^{+3} octahedral site decreases while that of Mn in the octahedral site increases.¹³ This rapid decrease in moment must be indicative of a long-range variation in the magnetic properties of the nanoparticle, the most realistic being a change from ferrimagnetic behavior to antiferromagnetic or other nonferromagnetic behavior by 25% Mn incorporation. The Mn L_{23} -edge XMCD measurements acquired under the same conditions were inconclusive. No Mn XMCD signal was detected but considering the observed reduction in magnetism (Fe moment reduced by 80% at 10% Mn concentration) and the low Mn concentration it occurs at makes detection of the XMCD signal more problematic.

Further insight to the rapid loss in magnetism can be obtained from the evolution of the Fe L_{23} -edge XAS spectra with Mn concentration (shown in Fig. 3). At 0% Mn concentration the Fe XAS spectra of the nanoparticle is identical to $\gamma\text{-Fe}_2\text{O}_3$. As the Mn concentration rises, the L_2 feature (inset of Fig. 3) is seen to undergo a transformation, whereby spectral weight is shifted from the second peak to the first peak and a shoulder develops at lower energy. This is precisely the transformation observed as the local environment of the Fe changes from the defected spinel structure of $\gamma\text{-Fe}_2\text{O}_3$ to the undefected Fe_3O_4 structure.^{13,14}

IV. CONCLUSIONS

Valence determination of Mn dopant in a defected spinel Fe-oxide protein encapsulated nanoparticle system has been investigated for a range of Mn dopant concentrations. The nanoparticles, surrounded by a large protein cage, are found to be noninteracting with an anisotropy energy that is reduced from that of pure iron oxide nanoparticles. The XAS and XMCD measurements of the Fe and Mn L-edges indicated that the Mn prefers a +2 valence and initially occupies the octahedral site. As the Mn concentration increases beyond 10%, the Fe local environment changes to a Fe_3O_4

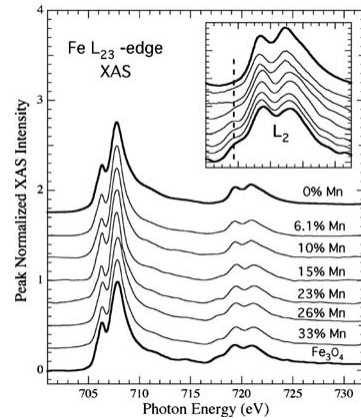


FIG. 3. Fe L_{23} -edge XAS as a function of Mn concentration. The heavier lines are the spectra for 0% Mn or $\gamma\text{-Fe}_2\text{O}_3$ in HFN (upper) and the reference Fe_3O_4 (lower). Inset: Fe L_2 -edge showing the growth of the shoulder and the redistribution of spectral weight between the two L_2 peaks.

spinel structure and the material becomes nonferromagnetic. In addition the relative simplicity of the Mn nanoparticles' spectrum, as compared to that of the bulk, is distinctly different suggesting that the tetragonal distortion characteristic of the bulk system may not be present in the 6.7 nm protein encapsulated nanoparticles.¹⁵

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation under Grant No. CBET-0709358 and through the Army Research Office under Grant No. W911NF-08-1-0325.

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CHAPTER 6

MAGNETISM DOPING OF IRON OXIDE NANOPARTICLES

Contribution of Authors and Co-Authors

Manuscripts in Chapters 6: Orbital Moment Determination in $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ Nanoparticles

Author: Vanessa L. Pool

Contributions: I was responsible for the ACMS measurements as well as the XAS and XMCD.

Co-author: C. Jolly

Contributions: C. Jolly was responsible for making the nanoparticles and the PDF measurements used to identify crystal structure and size.

Co-author: T. Douglas

Contributions: C. Jolly's adviser and was involved in the conceptualization aspect of the paper.

Co-author: E.A. Arenholz

Contributions: E.A. Arenholz is the beamline scientist where XAS and XMCD measurements were done.

Co-author: Y.U. Idzerda

Contributions: Y.U. Idzerda is my adviser, was involved in the conceptualization aspect of the paper and did the analysis on the XAS and XMCD for the paper.

Manuscript Information Page

Vanessa L. Pool, C. Jolly, T. Douglas, E.A. Arenholz and Y.U. Idzerda

☐ Prepared for submission to a peer-reviewed journal

☐ Officially submitted to a peer-reviewed journal

☐ Accepted by a peer-reviewed journal

☒ Published in a peer-reviewed journal

Publisher Date of submission (24 September 2010) Date manuscript will appear (7 April 2011) Issue in which manuscript appears in (Journal of Applied Physics)

Manganese Paper Introduction (Uncaged Particles)

Manganese nanoparticles were also grown out of the protein cage and in a slightly larger size. The increased nanoparticle size was initially of interest, as a relaxation of the bulk tetragonal distortion that is normally present for manganese-oxide spinels was seen in the smaller nanoparticles. Also, larger particles have better properties in regards to use in hyperthermia application. Finally, as previously mentioned, manganese is an attractive dopant for a spinel due to its ionic flexibility and, the concentration range of manganese dopant was expanded to include Mn_2FeO_4 and Mn_3O_4 . This allows us to monitor the evolution of the manganese XAS spectra and other nanoparticle properties with the increased dopant concentration.

In this paper an error was made in figure 3 of the paper and for this reason a correction to the figure has been included in Appendix D.

Orbital moment determination in $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ nanoparticles

V. L. Pool,^{1,2,a)} C. Jolley,^{3,4} T. Douglas,^{2,3} E. A. Arenholz,⁵ and Y. U. Idzerda^{1,2}

¹Department of Physics, Montana State University, Bozeman, Montana 59717, USA

²Center for Bio-inspired Nanomaterials, Montana State University, Bozeman, Montana 59717, USA

³Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717, USA

⁴Astrobiology Biogeochemistry Research Center, Montana State University, Bozeman, Montana 59717, USA

⁵Advanced Light Source, Lawrence Berkeley National Labs, Berkeley, California 94720, USA

(Presented 17 November 2010; received 24 September 2010; accepted 8 December 2010; published online 7 April 2011)

Nanoparticles of $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ with a concentration ranging from $x = 0$ to 1 and a crystallite size of 14–15 nm were measured using X-ray absorption spectroscopy and X-ray magnetic circular dichroism to determine the ratio of the orbital moment to the spin moment for Mn and Fe. At low Mn concentrations, the Mn substitutes into the host Fe_3O_4 spinel structure as Mn^{2+} in the tetrahedral A-site. The net Fe moment, as identified by the X-ray dichroism intensity, is found to increase at the lowest Mn concentrations then rapidly decrease until no dichroism is observed at 20% Mn. The average Fe orbit/spin moment ratio is determined to initially be negative and small for pure Fe_3O_4 nanoparticles and quickly go to 0 by 5%–10% Mn addition. The average Mn moment is anti-aligned to the Fe moment with an orbit/spin moment ratio of 0.12 which gradually decreases with Mn concentration. © 2011 American Institute of Physics. [doi:10.1063/1.3562905]

I. INTRODUCTION

The doping of spinel ferrite nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4) with magnetic and nonmagnetic substitutional transition metals has demonstrated good control of both moment and anisotropy,¹ with magnetic behavior and dopant occupancy sites often quite different from the bulk behavior. One example is for the biomineralization of $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ nanoparticles inside protein cage structures, where Mn initially substitutes as Mn^{2+} into the octahedral B-site causing the moment to decrease instead of as Mn^{2+} in the tetrahedral A-site,¹ creating an enhanced moment as occurs in the bulk.² It is unclear whether these differences are due to the gentle synthesis conditions of biomineralization, the presence of the protein encapsulation, or the reduced dimensionality of nanoparticles. A comparison of dopant occupation sites and anisotropy energies of similar nanoparticles synthesized under different conditions would be useful.

For noninteracting particles, frequency dependent ac-susceptibility measurements are a useful way to determine anisotropy energies.^{1,3} A related parameter to the magnetocrystalline anisotropy energy is the elemental orbital magnetic moment as determined from energy integration of the X-ray magnetic circular dichroism spectra (using the XMCD sum-rules).^{4–7} Used predominantly for single crystal thin film geometries, this unique method for separating the orbital moment and the spin moment of each element has utility for nanoparticles, especially those found to be interacting.

II. EXPERIMENTAL

Nanoparticles of $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ were synthesized with $x = 0$ to 1.0 by a chemical route identical to that used for pro-

tein encapsulated particles (the synthesis route used in ref #1 but without inclusion of the protein). Solutions of 12.5 mM $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 12.5 mM MnCl_2 were prepared using H_2O that had been sparged with N_2 to remove dissolved oxygen and mixed to obtain the desired $[\text{Fe}^{2+}]:[\text{Mn}^{2+}]$ ratio. The 12.5 mM metal mixture and a deaerated 4.17 mM H_2O_2 solution were added at a rate of 40 ml/h to a deaerated solution of 100 mM NaCl maintained at 65°C while the pH was maintained at 8.5 by addition of deaerated 100 mM NaOH using an autotitrator. Samples were centrifuged and triple washed with de-ionized water in order to remove NaCl and unreacted metal ions. Samples used for X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements were stored in an aqueous suspension and subsequently dried onto Formvar-coated TEM grids, while samples to be used for hard X-ray pair distribution function (PDF) analysis were immediately dried to powder using a vacuum lyophilizer.

The XAS and XMCD measurements were conducted at beamline 4.0.2 of the Advanced Light Source of Berkeley National Laboratories simultaneously in transmission yield (using a Ga photodetector) and total electron yield (in the sample current mode). Absorption measurements were made at room temperature with the photon polarization set at 90° and an alternating applied magnetic field of 0.5 T.

III. RESULTS

The Mn L_{23} -edge XAS spectra for a representative sampling of different Mn concentrations are shown in Fig. 1. The spectra have had a linear background removed, been normalized to the integrated peak area ($L_2 + L_3$), and were energy calibrated by comparing the peak position of a simultaneously collected Mn_3O_4 reference powder spectra (set to 640.05 eV). The evolution of the spectra show that as the Mn

^{a)}Author to whom correspondence should be addressed. Electronic mail: pool@physics.montana.edu.

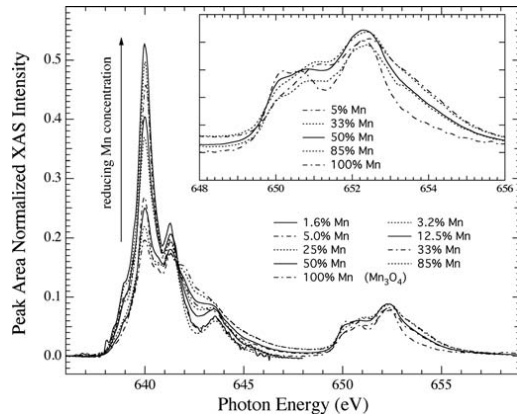


FIG. 1. The evolution of the peak normalized Mn L_{23} -edge XAS spectra as a function of Mn concentration. Inset: Evolution of Mn L_2 peak.

concentration is reduced, the Mn L_3 spectral weight shifts dramatically from a broad distribution of higher energy multiplet peaks to the single lower energy peak (the Mn L_2 peak evolves more gradually, see inset of Fig. 1). The final spectrum at 1.6% Mn is nearly identical to the theoretical spectrum for Mn^{2+} in a tetrahedral configuration.⁸ The spectra are quite similar for 1.6%–25% Mn concentrations, above which the Mn spectra continue to gradually evolve, but are all similar in shape. This is consistent with the evolution of the crystal structure determined from the hard X-ray scattering PDFs (not shown). From the X-ray scattering PDF, the local Mn structure at high Mn concentrations was identified to be a close match to the hausmannite (Mn_3O_4) structure with a crystalline domain size of 14–15 nm. At low Mn concentrations the PDFs, which are not element specific, closely resemble Fe_3O_4 with a slightly larger crystallite size of 16–18 nm. For all Mn concentrations, the crystalline domain size remains in the 16 ± 2 nm range.

Changes in the Fe XAS spectra have been used to differentiate between the various oxides of Fe.^{9,10} Unfortunately, distinguishing between the defective spinel structure of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and the inverse spinel structure of magnetite (Fe_3O_4) using the subtle variations in the XAS spectra is difficult. A more sensitive method for differentiating between these similar structural phases is the X-ray magnetic circular dichroism (XMCD) spectra of the L_{23} edge.^{9,10} Although the total electronic structure, as displayed in the XAS spectra, is rather similar, the spin-resolved electronic structure is better differentiated.

Figure 2 shows the evolution of the Fe XMCD as a function of Mn concentration. The spectra show that the peak-to-peak dichroism signal of Fe first dramatically increases with low Mn addition, then falls rapidly. This behavior, highlighted in the inset of Fig. 2, is well understood if the Mn initially substitutes into the A-site tetrahedral position for the Fe (a conclusion consistent with the subtle evolution of the Fe XAS spectra). In the spinel structure, due to indirect exchange coupling, the magnetic orientation of the Fe in the tetrahedral A-site is opposite the magnetic orientation of Fe

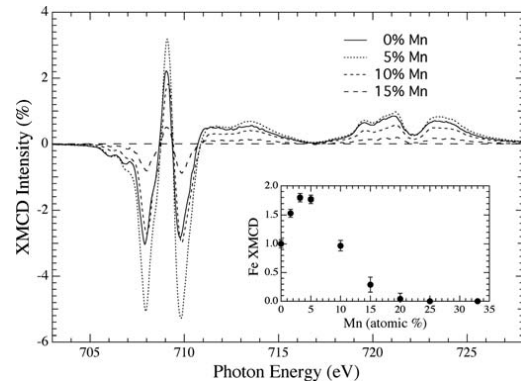


FIG. 2. The evolution of the Fe L_{23} -edge XMCD spectra as a function of Mn concentration. There is no discernable dichroism spectra above 20% Mn. Inset: Fe peak-to-peak XMCD intensity as a function of Mn concentration.

in the more numerous octahedral B-site, resulting in an overall reduction in the net Fe moment. Substitution of Mn into the A-site reduces the occupation of Fe in this site, effectively increasing the net Fe moment. This behavior is initially identical to the bulk behavior of $(Mn_xFe_{1-x})_3O_4$, but opposite the behavior recently determined for biomineralization of $(Mn_xFe_{1-x})_3O_4$ into protein cages, where Mn substitutes as Mn^{2+} into the octahedral B-site.¹ Although initially the structural and moment variation between these nonencapsulated nanoparticles and the bulk is similar, above 5% Mn the behavior is found to differ. Whereas the Fe moment in the bulk continues to increase, the moment in the nanoparticles drops rapidly to zero at 25% Mn concentration.

The XMCD spectra have utility beyond determining the relative net moment of an element. High-quality XMCD spectra can also be used to separately determine the elemental spin and orbit components of the moment.^{4,5} The orbital moment, μ_{orb} , and spin moment, μ_{spin} , can be obtained from the energy integration of the XMCD, rewritten in a more compact form as⁶

$$\mu_{orb}/\mu_{spin} = \frac{2q}{(9p - 6q)} \quad (1)$$

where μ_{orb} and μ_{spin} are in units of μ_B/atom , q represents the energy integral over the entire XMCD L_{23} edge, and p represents the integral of only the L_3 edge. Here the remaining difficulty is in the separation of the L_3 XMCD signal from the combined edges. When the L_3 XMCD intensity is zero over an extended energy region prior to the L_2 edge, the integrated spectra will have a well-defined plateau, allowing for a straightforward determination of the integral values (p and q).

In Fig. 3 is displayed the energy integral of the Fe L -edge XMCD for Mn concentrations of 0%–15%. The integrals are all well behaved, showing distinct plateau regions, and are quite robust to reasonable variations in the linear background subtraction. An inspection of Eq. (1) shows that if the final value of the integral (q) is zero then the ratio, and therefore the orbital moment, is also zero. We see that for the

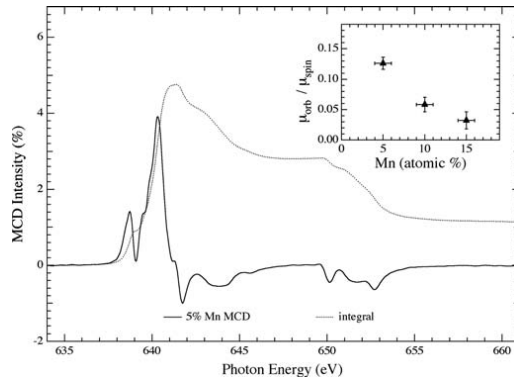


FIG. 3. The integrated Fe L_{23} -edge XMCD spectra for different Mn concentrations. Inset: Mn concentration dependence of the extracted orbital-to-spin magnetic moment ratio for Fe.

defected spinel Fe oxide nanoparticle, the net orbit-to-spin moment ratio for Fe is -0.12 . The net orbital moment is small and directed opposite the net spin moment. This can be understood, keeping in mind the multiple sites for the Fe atom. The tetrahedral Fe (A-site) is anti-aligned to the octahedral Fe (B-site). If the orbital moment of the lower symmetry tetrahedral Fe is significantly larger than the orbital moment of the octahedral Fe, then the average orbital moment can be directed opposite to the average spin moment, even though the spin moment and orbit moment of each individual Fe atom are aligned to each other. Significantly, even at the lowest measured Mn concentrations, the extracted net orbital moment for Fe is near zero.

The orbital moment information from the Mn can also be determined. Figure 4 displays the XAS XMCD spectra for the 5% Mn concentration, the energy integrated spectra, and the resulting p and q integral values. There is remarkable agreement between the Mn MCD spectra and the theoretical

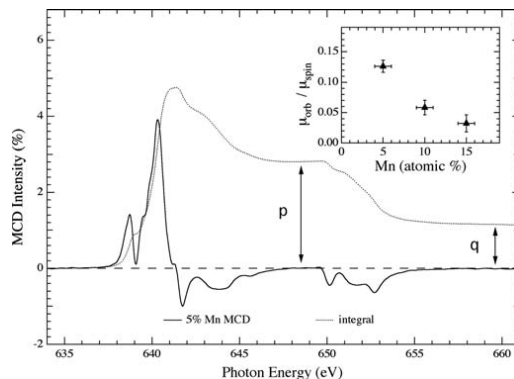


FIG. 4. The Mn L_{23} -edge XMCD spectra for 5% Mn concentration and its energy integral. Inset: Evolution of Mn spin-to-orbit moment ratio for Mn.

spectra,^{8,11,12} including the separation of the first shoulder of the XAS (first peak of the XMCD) and the subsequent peak, which has not been previously resolved. The evolution of the orbit/spin moment ratio shows a decline in moment to a small value at 15% Mn. Above this concentration, there is a small dichroism spectra, but the energy integrals are not as reliable (not robust to reasonable variations in the linear background subtraction). Below 5%, the XMCD integrals are also not reliable.

IV. CONCLUSIONS

Magnetic nanoparticles of $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ with a concentration ranging from $x=0$ to 1 and a crystallite size of 14–15 nm were measured using X-ray absorption spectroscopy and X-ray magnetic circular dichroism spectroscopy to determine the orbital moment to spin moment ratio for Mn and Fe. At low Mn concentrations, the Mn substitutes into the host Fe_3O_4 spinel structure as Mn^{2+} in the tetrahedral A-site, similar to the bulk behavior and not the protein encapsulated nanoparticle behavior, and the Mn XAS and XMCD spectra are in strong agreement with the theoretically predicted spectra. The net Fe moment as identified by the X-ray dichroism intensity is found to increase at the lowest Mn concentrations then rapidly decrease until no dichroism is observed at 20% Mn in contrast to the bulk behavior.

The elemental Fe orbit/spin moment ratio is determined to initially be small and negative (-0.12) for pure Fe_3O_4 nanoparticles and quickly go to 0 by 5%–10% Mn addition. The net Mn moment is anti-aligned to the Fe moment with a orbit/spin moment ratio of 0.12, which gradually decreases with Mn concentration.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation (NSF) under grant CBET-0709358 and by the Army Research Office (USARO) under grant W911NF-08-1-0325. The ALS is supported by DOE.

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CHAPTER 7

COMPARING MAGNETISM DOPING OF IRON OXIDE NANOPARTICLES

GROWN IN PROTEIN CAGES VERSES OUT OF CAGES

Contribution of Authors and Co-Authors

Manuscripts in Chapters 7: All in the Packaging: Structural and Electronic Effects of Nanoconfinement on Metal Oxide Nanoparticles

Author: C. Jolly

Contributions: C. Jolly was responsible for making the nanoparticles and taking the PDF measurements used to identify crystal structure and size.

Co-author: Vanessa L. Pool

Contributions: I was responsible for XAS as well as the XMCD.

Co-author: Y.U. Idzerda

Contributions: Y.U. Idzerda is my adviser, was involved in the conceptualization aspect of the paper and did the analysis on the XAS and XMCD for the paper.

Co-author: T. Douglas

Contributions: C. Jolly's adviser and was involved in the conceptualization aspect of the paper.

Manuscript Information Page

Vanessa L. Pool, C. Jolly, Y.U. Idzerda and T. Douglas

☐ Prepared for submission to a peer-reviewed journal

☐ Officially submitted to a peer-reviewed journal

☐ Accepted by a peer-reviewed journal

☒ Published in a peer-reviewed journal

Publisher Date of submission (6 may 2011) Date manuscript will appear (17 July 2011) Issue in which manuscript appears in (Chemistry of Materials)

Caged Verses Uncaged Manganese Doping Iron-Oxide Nanoparticles Paper Introduction

The purpose of this work was to compare the uncaged and caged manganese iron-oxide nanoparticles. A new set of caged manganese doped iron-oxide nanoparticles grown in cages was synthesized, with a larger range of manganese concentrations to better compare the evolution of the manganese dopant over the full concentration range. This paper, written by Craig Jolly¹⁰⁸ also highlights the X-ray scattering derived pair distribution functions (PDF) measurements, which were not discussed thoroughly in the previous papers. The PDF is sensitive to the nanoparticle structure in a different way than the diffraction methods used in the earlier work and so it is interesting to compare the caged and uncaged particles from this new perspective.

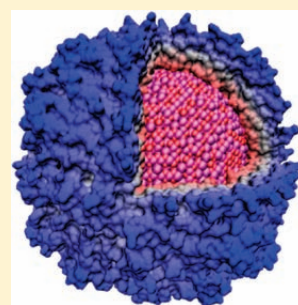
All in the Packaging: Structural and Electronic Effects of Nanoconfinement on Metal Oxide Nanoparticles

Craig Jolley,^{†,‡,||} Vanessa Pool,^{‡,§} Yves Idzerda,^{‡,§} and Trevor Douglas^{*,†,‡}

[†]Department of Chemistry & Biochemistry, [‡]Center for Bio-inspired Nanomaterials, and [§]Department of Physics, Montana State University, Bozeman, Montana 59717, United States

 Supporting Information

ABSTRACT: Encapsulation of inorganic nanoparticles within oligomeric protein cages can provide a multivalent approach for the synthesis of biocompatible nanomaterials by combining the nanoparticle-forming catalytic abilities of the cage interior with the biointeractive exterior surface of the cage. Protein cages provide more than simply a passive compartment for nanoparticle formation: protein-templated nanoparticles can exhibit structural and electronic properties that are dramatically different from materials synthesized without protein templating. Mixed Fe/Mn oxides formed under hydrothermal conditions form a structural series ranging from the γ -Fe₂O₃ (maghemite) to the Mn₃O₄ (hausmannite) spinel structure as the Mn fraction is increased from 0 to 100%, while similar materials formed inside of human ferritin transition instead from maghemite to a layered Mn oxide structure similar to chalcophanite. The electronic properties of the protein-templated nanoparticles, as determined from soft X-ray absorption spectroscopy, also differ from those of their protein-free counterparts, in agreement with the structural results. Protein-templated synthesis may provide the opportunity for powerful control over nanomaterial properties through nanoconfinement, but the ultimate physical basis for these effects remains to be determined.



KEYWORDS: composite materials, ferrites, X-ray spectroscopy, pair distribution functions, biomineralization

INTRODUCTION

The formation of hard biomaterials such as mollusk shell or vertebrate bone involves intimate interactions between biopolymers and nascent inorganic crystals.^{1–5} Soft materials such as proteins have shown a remarkable capacity to direct the growth and influence the final material properties of hard materials.⁶ A growing class of bioinspired nanomaterials^{7,8} mimics this formation process by using protein nanocages such as virus capsids^{9–12} or ferritins^{13–19} to encapsulate inorganic nanoparticles. This approach has a number of immediate advantages for nanotechnology applications: the protein shell can help to prevent aggregation of nanoparticles and can be chemically or genetically modified for in vivo targeting^{17,20} or in vitro assembly into hierarchical structures.^{21–23}

Another, more subtle effect of protein-confined nanoparticle synthesis is the potential for dramatic changes in the nanoparticle morphology. A simple example is the constraint on crystal-line domain size imposed not only by the size of the protein cage but possibly also by the arrangement of crystal nucleation sites on the cage interior.²⁴ More dramatic effects are also possible: ferritin forms a 24-meric protein cage with interior ferroxidase sites that can oxidize soluble Fe²⁺ to insoluble Fe³⁺, forming an Fe oxide nanoparticle in the cage interior. Under biologically relevant conditions (room temperature, near-neutral pH, ambient O₂), recombinant ferritin forms a ferrihydrite phase²⁵ similar to what is observed in native mineralized ferritin. If Fe²⁺ is exposed to the same conditions in the absence

of ferritin, however, it precipitates to form a lepidocrocite phase.²⁶ This can be understood in terms of a kinetic trap: ferritin stabilizes the metastable ferrihydrite phase that transforms into more-ordered Fe oxide structures under most conditions. In fact, such disorder–order transitions in ferritin-templated Fe oxides appear to be feasible only under elevated temperatures requiring the use of ferritins from hyperthermophilic organisms.¹⁹

Kinetic stabilization of amorphous phases is also relevant to the formation of structural biomaterials such as teeth and bones.^{3,27} In contrast to classical precipitation models in which growing crystals form directly from the addition of solution ions, calcium phosphate and carbonate have been shown to exist as stable nanometer-sized clusters in solution.²⁸ Amorphous phases form by aggregation of these nanoclusters, and macroscopically ordered crystals can arise through interaction with an ordered template that establishes crystal phase and orientation.²⁹ In the case of collagen biomineralization,³ the amorphous precursor phases are thought to be stabilized by noncollagenous proteins (NCPs), forming negatively charged clusters that are subsequently oriented on the positively charged collagen scaffold and reorganize into a larger-scale crystal. Similar solution-phase molecular clusters have been characterized for transition metals,³⁰ and ferritin (which also carries a significant

Received: May 6, 2011

Revised: July 17, 2011

Published: August 09, 2011

negative charge) may function similarly to NCPs by electrostatically stabilizing thermodynamically unfavorable amorphous phases. It should be noted, however, that Fe^{2+} ions must enter ferritin through narrow pores at the 3-fold symmetry axes,³¹ and it is unlikely that nanometer-scale Fe oxide clusters could pass into the ferritin cage intact: any solution-phase clusters that serve as a precursor to ferrihydrite formation must form inside the cage.

This study focuses on a more synthetically motivated model system: the formation of Mn ferrites (mixed spinels of Fe and Mn) both in a protein-free solution and inside of recombinant human ferritin (HFn). Ferrite spinel nanoparticles have been a subject of intense interest because of their superparamagnetic properties,^{32,33} which make them attractive targets for applications including ferrofluids, magnetocaloric refrigeration, and magnetic resonance imaging.³⁴ In addition, Mn oxides have been shown to form highly porous nanostructures with architectures reminiscent of biological materials,³⁵ which may be useful in sensing or catalytic applications that require high surface area. HFn has previously been shown to grow nanoparticles of $\gamma\text{-Fe}_2\text{O}_3$ under conditions of controlled oxidation at elevated pH and temperature; these particles show a strong magnetic response and are being investigated as potential contrast agents for magnetic resonance imaging.^{17,20,36} When HFn is incubated with Mn^{2+} under similar conditions, Mn oxide nanoparticles form instead; mixed Fe/Mn oxides grown in HFn have previously been studied using L_{23} -edge X-ray absorption spectroscopy (XAS).³⁷

When structural information obtained from X-ray pair distribution function (PDF) analysis is integrated with electronic information from L_{23} -edge XAS, it becomes clear that the protein template exerts a profound influence on the properties of the encapsulated metal oxide nanoparticle. The implications of this finding are both daunting and promising: daunting because the mechanistic details of a protein template's influence on nanoparticle formation are so poorly understood, and promising because the mere existence of such dramatic effects suggests that protein templates can be engineered for the formation of application-oriented materials with specific novel properties.

MATERIALS AND METHODS

Protein Expression and Purification. Recombinant HFn was obtained by overexpression in *Escherichia coli* BL21 cells as described previously.^{17,36} All protein-based samples were purified by size exclusion chromatography (SEC) and subsequent anion exchange chromatography before mineralization.

Synthesis. Mn ferrite samples were synthesized at doping levels ranging from 0 to 100% Mn. Solutions of 12.5 mM $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 12.5 mM MnCl_2 were prepared using H_2O that had been sparged with N_2 to remove dissolved oxygen and mixed to obtain the desired $[\text{Fe}^{2+}]/[\text{Mn}^{2+}]$ ratio. A syringe pump (KD Scientific) was used to simultaneously add the 12.5 mM metal mixture and a deaerated 4.17 mM H_2O_2 solution to a stirred reaction vessel. The reaction vessel temperature was maintained at 65 °C using a heated water bath (VWR) and the pH maintained at 8.5 by addition of deaerated 100 mM NaOH using an autotitrator (718 STAT Titrino, Metrohm). The reaction vessel initially contained a deaerated solution of 100 mM NaCl, to ensure proper functioning of the pH electrode. For protein-templated samples, purified HFn in unbuffered 100 mM NaCl was added to the reaction vessel at a concentration of ~0.3–0.5 mg/mL prior to mineralization. The metal ion and H_2O_2 solutions were added at a rate of 40 mL/h, and

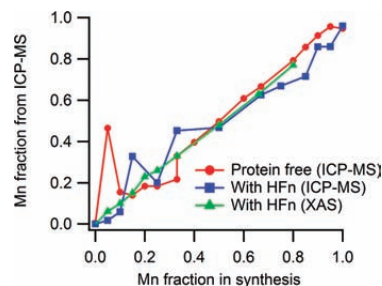


Figure 1. Mn doping levels determined by ICP-MS and by comparing the Mn and Fe XAS integrated intensities. Measured Mn fractions correlate well with the $\text{Mn}^{2+}/\text{Fe}^{2+}$ ratios used during synthesis, indicating a lack of systematic bias in Mn^{2+} uptake by HFn or incorporation into the growing nanoparticle relative to Fe^{2+} .

solutions were kept under a nitrogen atmosphere throughout synthesis. The same temperature and pH conditions were used in the protein-free and protein-templated reactions. Nanoparticle confinement inside the protein cages was confirmed using size-exclusion chromatography, dynamic light scattering, and transmission electron microscopy (TEM), as described elsewhere.^{17,24,36} The protein-free reaction solution was turbid and nearly black for 100% Fe, shading to a lighter brown for 100% Mn. For samples with <50% Mn, ferromagnetism was visually confirmed using a small magnet. When HFn was included, the reaction solutions showed similar color changes but were clear and lacked visible magnetic response.

Protein-free samples were centrifuged and washed 3× with deionized water to remove NaCl and unreacted metal ions. Protein-templated samples were purified by SEC with a running buffer of 50 mM PO_4^- , 100 mM NaCl, pH 7.5; samples intended for PDF analysis were then dialyzed for ~7 days against several changes of dd H_2O to remove unwanted electrolytes. Samples to be used for XAS measurements were stored in an aqueous suspension, while samples to be used for PDF analysis were dried to powder using a vacuum lyophilizer (FreeZone, Labconco).

Electronic Structure Determination. The Fe and Mn L_{23} -edge XAS and X-ray magnetic circular dichroism (XMCD) were measured at beamlines 6.3.1 and 4.0.2 of the Advanced Light Source at the Lawrence Berkeley National Laboratories. The samples were dried in air on Formvar-coated TEM grids prior to introduction into the ultrahigh vacuum chamber. The XAS measurements were made at room temperature using linearly polarized light in both total electron yield mode, in which the current required to replenish photoelectrons ejected from the sample is monitored, and in transmission mode using a Ga photodetector. Although both collection methodologies produced the same results, the electron yield had a lower noise level and is reported here. The incident photon flux was determined from an 80% transmission gold grid upstream from the sample. The XMCD measurements³⁸ were made in the presence of a ± 1.5 T magnetic field with 90% circular polarized light. All reported XMCD spectra are corrected for incomplete polarization. Energy referencing was accomplished using an internal reference powder mix (Fe_3O_4 and MnO) where the major peak in the Fe and Mn L_3 -edges have been set to be 704.70 and 637.75 eV, respectively.

Pair Distribution Function (PDF) Analysis. Pair distribution functions of the Mn ferrite samples were determined by high-energy total X-ray scattering. Powdered samples were placed in cylindrical Kapton capillaries with inner diameter 0.0575" (Cole-Parmer) and X-ray scattering was collected at a wavelength of 0.2128 Å on beamline 11-ID-B at the Advanced Photon Source at Argonne National Laboratories. Powder diffraction patterns were assembled by averaging 0.5 s

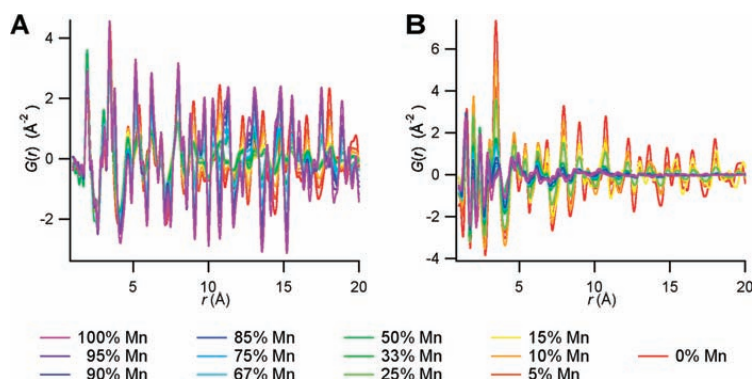


Figure 2. Experimentally determined PDFs for Mn doping series under protein-free (A) and protein-templated (B) conditions. Note the general agreement at short distances (especially <4 Å) and the larger divergence at longer distances (>8 Å), indicating the presence of two distinct structural types.

exposures, with a total collection time of 5 min for each sample; diffraction image processing used the Fit2D software package.³⁹ Diffraction patterns were radially integrated to obtain a one-dimensional trace of the total scattering; data up to $q = 19.2 \text{ Å}^{-1}$ for protein-templated samples and $q = 23.0 \text{ Å}^{-1}$ for protein-free samples were used to obtain the corrected X-ray structure factor $S(q)$. The radial pair distribution function $G(r)$ was obtained via a Fourier transform of $S(q)$; calculation of $S(q)$ and $G(r)$ used the PDFGetX2 software package.⁴⁰ Unit cell structures for bulk materials were obtained from the MINCRYST web server,⁴¹ and the PDFgui software package⁴² was used to fit crystal models to the experimental $G(r)$.

Compositional Analysis. Relative concentrations of Mn and Fe were measured for all samples using inductively coupled plasma mass spectrometry (ICP-MS) and by comparing peak edge jumps in the Fe and Mn XAS spectra after referencing to a Fe_2MnO_4 reference powder. Measured Mn/Fe ratios were roughly equal to the ratios used during synthesis (Figure 1) and do not indicate any systematic compositional bias in Mn ferrite mineralization, either in HFn or in protein-free solution.

RESULTS

Radial Pair Distribution Function $G(r)$ Shows Dramatic Structural Changes with Mn Doping. The experimentally determined $G(r)$ for Mn ferrites with and without protein are shown in Figure 2. For the protein-free samples, $G(r)$ shows a range of shapes with two end point structures represented by $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) and Mn_3O_4 (hausmannite). The plotted curves show general agreement at short distances ($r < 8$ Å), indicating that the spinel structure shared by both maghemite and hausmannite is present in all of the samples and that their local geometries are similar. At larger distances, the structures observed are dramatically out of register with each other (note the alternating peaks for $r > 9$ Å), suggesting that there is a change in unit cell spacing between the two structural types. The changes in the protein-templated samples are even more dramatic, with the high-Fe samples showing a spinel structure and the high-Mn samples appearing largely amorphous, with virtually no $G(r)$ features beyond ~ 7 Å.

Note that $G(r)$ tapers off with increasing r , and that this tapering effect is more pronounced in some samples than in others; this is a result of the finite size of crystalline domains.⁴³

The amplitude of $G(r)$ decreases once r becomes comparable to the crystalline domain size because fewer such long-range correlations can be found. In our data fitting protocol, this effect is modeled by assuming spherical domains and convoluting the modeled $G(r)$ by a spherical shape factor. The diameter of the assumed spherical domains is a parameter that can be fit to the data to obtain a typical domain size.

Fitting of Protein-Free Structures. To determine the nature of the structural changes that occur in the protein-free samples upon changing the Fe/Mn ratio in the synthesis, the doped samples were fit using the crystal structures of bulk maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hausmannite (Mn_3O_4). Maghemite and magnetite (Fe_3O_4) give virtually identical X-ray PDFs; usage of a Fe_3O_4 model rather than a $\gamma\text{-Fe}_2\text{O}_3$ model in the fitting procedures below produced negligibly different results. While Fe XAS spectra have been used to differentiate between various Fe oxides,⁴⁴ our XAS measurements (see below) also did not provide adequate information to distinguish $\gamma\text{-Fe}_2\text{O}_3$ from Fe_3O_4 . The structure will be referred to below as $\gamma\text{-Fe}_2\text{O}_3$ with the understanding that this designation is not entirely conclusive.

Three different fitting schemes were employed. The first assumes a simple mixture of phases: fits were performed for the $\gamma\text{-Fe}_2\text{O}_3$ and Mn_3O_4 phases, and the doped phases were assumed to be simple mixtures of these phases. The $\gamma\text{-Fe}_2\text{O}_3$ sample was well-described by maghemite with a crystalline domain size of 5.2 nm, while Mn_3O_4 was well-described by hausmannite with a somewhat larger domain size of 14.7 nm (Figure 3A,B). Mixtures of these two phases, however, did not provide an adequate description of the doped samples (Figure 3C); in general, the two-phase models gave higher amplitudes at large r than were observed experimentally, indicating that a model based on a simple two-phase mixture overestimates the crystallinity of the doped samples.

In the second fitting scheme attempted (Figure 4), the doped samples were assumed to consist of a mixture of the two bulk crystal phases, but the spherical domain diameter was treated as a free variable that was fit separately for each doped sample. Two things are immediately apparent from this fitting procedure. The first is that, while the pure $\gamma\text{-Fe}_2\text{O}_3$ and Mn_3O_4 samples are well-described by the bulk crystal structures, the fraction of Mn_3O_4 used to fit the experimental $G(r)$ is a monotonically increasing function of Mn concentration, as would be expected. Second, one

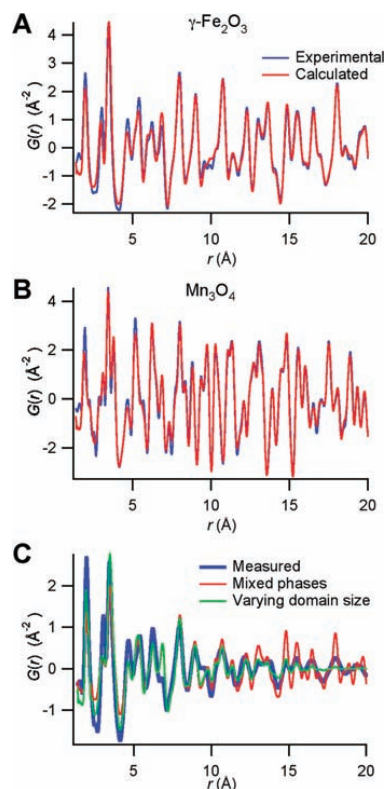


Figure 3. Experimental $G(r)$ and model fits for protein-free $\gamma\text{-Fe}_2\text{O}_3$ (A), Mn_3O_4 (B). $\gamma\text{-Fe}_2\text{O}_3$ doped with 25% Mn (C) was fit using the fitting schemes described in the text. Note that a simple mixture of the $\gamma\text{-Fe}_2\text{O}_3$ and Mn_3O_4 phases without a reduction in the crystalline domain size (red trace, see Figure 4A) results in an overestimation of the $G(r)$ amplitude at high r . Allowing the domain size to fluctuate along with the $\gamma\text{-Fe}_2\text{O}_3/\text{Mn}_3\text{O}_4$ composition (green trace) results in an improved fit. Several differences still persist, notably the dramatic overestimation of a peak height at ~ 7 $\text{\AA}$; these may result from defects or other deviations from the idealized spinel model.

can see the reason for the failure to fit the correct particle size in the two-phase approach; there is a dramatic loss of crystallinity at intermediate doping levels, with the crystalline domain size shrinking to as little as 2 nm in the case of 25% Mn.

The final fitting approach made use of the fact that the $\gamma\text{-Fe}_2\text{O}_3$ data can be fit reasonably well with the bulk hausmannite model, as long as the unit cell parameters are allowed to vary. The opposite approach was not as successful, probably because the cubic structure of $\gamma\text{-Fe}_2\text{O}_3$ does not allow for the anisotropic lattice distortions required to fit Mn_3O_4 properly. All samples could be fit with a single crystal phase, and the free parameters that varied from one sample to another were the crystalline domain size and the axis lengths a and c of the orthorhombic unit cell. (Figure 4). As Mn content increases from 0 to 33%, there is a slow increase in c . Between 33% and 50% Mn, c increases dramatically, and then settles into another slow increase in the region from 50% to 100% Mn. Between 0 and 100% Mn, c undergoes an overall increase of about 1 $\text{\AA}$. At the same time, we see a much smaller decrease in a which appears to lack the

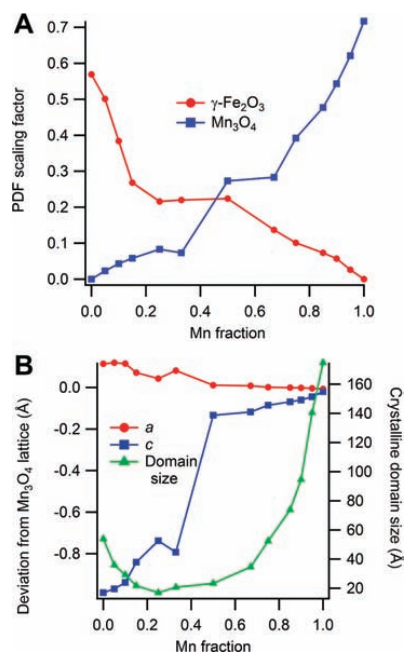


Figure 4. (A) Relative ratios of Fe_3O_4 and Mn_3O_4 as a function of Mn doping, in the two-phase fit model. (B) Crystalline domain size and lattice parameter changes as a function of Mn doping. The pure Fe_3O_4 and Mn_3O_4 samples are more crystalline (i.e., have larger domain sizes), while the domain size shrinks dramatically in the samples with intermediate doping levels. As Mn concentrations increase, the unit cell elongates along the c axis and contracts slightly along the two perpendicular ($a = b$) axes.

same type of sudden change. Comparison of Figures 4A and 4B shows that the sharp increase in c happens at the same Mn fraction as a similar, but less distinct, increase in the Mn_3O_4 contribution to the mixed model. This point, somewhere between 33% and 50% Mn, can be identified as the doping level at which a transition between a maghemite-like lattice and a hausmannite-like lattice takes place.

Two major conclusions can be drawn from these model-fitting results. The first is that a major structural change occurs at a Mn doping level of between 33 and 50%. The clearest way to interpret this is using Figure 4B, which shows a dramatic increase in the length of the unit cell c axis, corresponding to a sudden change from a $\gamma\text{-Fe}_2\text{O}_3$ -like lattice to a Mn_3O_4 -like lattice (Figure 4A). The other major result is that both end points of the doping series show comparatively high crystallinity (Figure 4B), while intermediate doping values are far less crystalline. The minimum crystalline domain size is reached at doping levels fairly close to the abrupt increase in the unit cell c axis, possibly indicating that local compositional heterogeneities lead to structural defects which inhibit the formation of large crystalline domains.

Fitting of Protein-Templated Structures. HF N -templated $\gamma\text{-Fe}_2\text{O}_3$ samples have previously been characterized by PDF analysis²⁴ and show excellent fits to maghemite (or, equivalently, magnetite) structures. This spinel-like structure was present without any major changes from 0 to 25% Mn (Figure 2). After

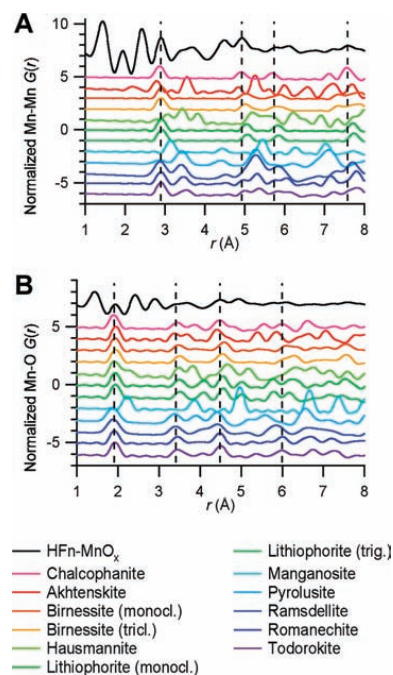


Figure 5. Comparison of HFN-templated 100% Mn oxide with calculated PDFs of known Mn oxide phases. When only Mn–Mn correlations are plotted (A), it is clear that the edge-sharing MnO_6 peak at 2.9 Å is clearly present in the experimental data, while the vertex-sharing MnO_6 peak at 3.5 Å that is present in many Mn oxide phases is lacking in the experimental data. The peak at around 4.9 Å agrees well with an Mn–Mn correlation in chalcophanite; the corresponding distances in the other phases are all too long. Plotting the Mn–O correlations (B), allows us to clearly identify the Mn–O bond correlation at 1.9 Å, along with features at 3.4 and 4.4 Å arising from edge-sharing MnO_6 octahedra.

this point, however, things change dramatically. The measured PDFs for high-Mn samples did not provide a satisfactory fit to hausmannite, or to other pure Mn-oxide phases (akhtenskite, manganosite, pyrolusite, ramsdellite). Taking a cue from PDF studies of biogenic Mn oxides formed by bacteria and fungi,⁴⁵ we attempted to fit to a variety of weakly ordered Mn oxide phases (lithiophorite, birnessite, romanechite, todorokite, and chalcophanite), which often contain H_2O and well-ordered counterions (mostly Group 1 and 2 ions, along with Al^{3+} in lithiophorite and Zn^{2+} in chalcophanite) in the crystal structure.

The 100% Mn oxide sample in HFN shows several clear features at low r that can aid in phase identification (Figure 5). First, there are the clear peaks at 1.5 Å and 2.5 Å that are observed in all protein-templated nanoparticle PDFs^{12,24} and arise from correlations between bonded carbon and nitrogen atoms (1.5 Å) and second-nearest neighbors (2.5 Å) in protein. Other low- r peaks are diagnostic for Mn oxide phases; a peak at about 1.9 Å has decreased amplitude because of its position in the valley between the major protein peaks, but agrees well with distances measured for Mn–O bonds. A correlation at 2.9 Å arises from Mn–Mn correlations in edge-sharing MnO_6 octahedra; the asymmetric feature at 3.7 Å is somewhat longer than Mn–Mn correlations in vertex-sharing MnO_6 octahedra but matches well

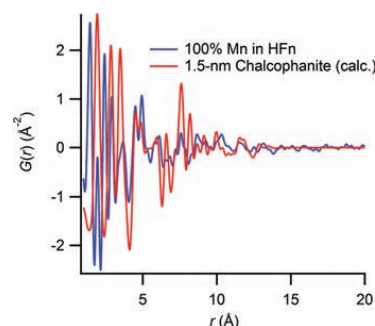


Figure 6. Measured PDF for 100% Mn oxide in HFN, compared with a calculated PDF for chalcophanite with a 1.5 nm spherical domain size. The protein peaks at ~ 1.5 and ~ 2.5 Å are absent in the calculated structure, and several of the peaks are lower-amplitude in the protein structure, reflecting the presence of defects. The prominent set of peaks at 7–8 Å in the calculated PDF results from correlations between planes of MnO_6 octahedra; their lower amplitude in the measured PDF reflects interplane stacking faults that render the idealized model of spherical crystal domains unreliable.

with a Mn–O peak for second-nearest neighbors. Many structures with edge-sharing MnO_6 show a Mn–O correlation near 4.5 Å that agrees well with the experimental peak observed at 4.4 Å; beyond this distance the differences between different phases begin to look more dramatic. Most significantly, many phases show a significant Mn–Mn correlation near 5.3 Å; most of these are longer than the 4.9 Å peak observed experimentally, but the peak for chalcophanite is quite close. An overlay of the experimental PDF and a calculated PDF for chalcophanite with a domain size of 15 Å is shown in Figure 6; note that the double peak at around 6 Å is also fairly well duplicated.

The calculated chalcophanite structure contains features at ~ 7.5 Å which arise from interlayer Mn–Mn correlations; these are largely absent in the measured PDFs and indicate that interlayer stacking faults are present in the protein-templated samples, leading to weak overall order. The crystal-line domain model used for PDF calculations in PDFgui assumes spherical domains which are unlikely to be an accurate approximation in such an anisotropic structure. Interestingly, biogenic Mn oxides produced by bacteria fit to a birnessite-like layered structure that is similar to chalcophanite, in contrast to fungal Mn oxides which fit to a tunnel-like todorokite structure; it remains unclear whether the mechanistic details of bacterial chalcophanite formation might be similar to what was observed in our experiments.

Previous work²⁴ has identified the Mn oxide phase synthesized in HFN under the reaction conditions described as a hausmannite structure, similar to what was observed in the protein-free case. While the synthesis conditions described in this study are essentially identical to those in these previous studies, the postsynthesis size-exclusion chromatography (SEC) purification step was absent. Given the largely amorphous structure of protein-templated Mn oxides and the highly crystalline structure of the protein-free samples, it is possible that a small amount of bulk crystallization (which would be removed by SEC) could give a spurious hausmannite diffraction pattern. The fact that nearly identical PDFs were obtained for a variety of high-Mn

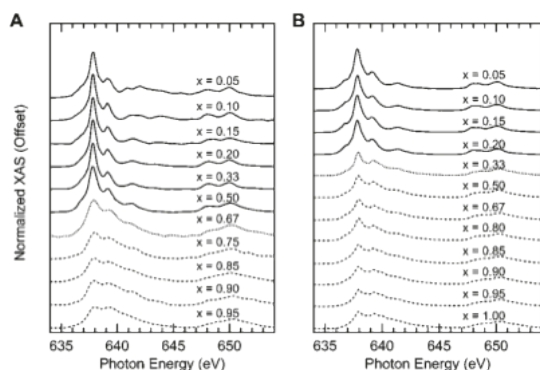


Figure 7. Area normalized Mn L_{23} -edge XAS spectra for particles with protein (left panel) and without protein (right panel). Line types indicate similar phases (solid line is low Mn concentration phase, dashed line is high Mn concentration, and dotted line is transition region).

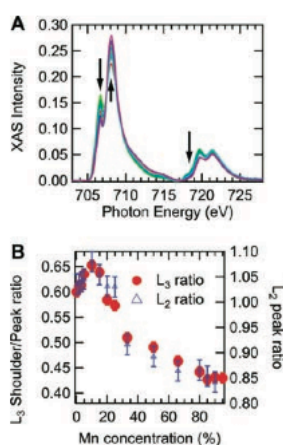


Figure 8. (A) Area normalized Fe L_{23} -edge XAS spectra for particles without protein. The color range for Mn doping levels is the same as in Figure 1. Arrows indicate the evolution trend of various features as the Mn concentration is increased. (B) Ratio of the intensities of the L_3 shoulder feature (706.5 eV) and main L_3 peak (708 eV) displayed as solid circle using left axis and the intensity ratio of the first L_2 peak (719.5 eV) and second L_2 peak (721.5 eV) displayed as open triangles using right axis.

doping levels suggests that the results presented here probably do not stem from an error in synthesis or characterization, but that the structure of protein-templated Mn oxide nanoparticles (which have been rigorously purified) is not highly crystalline.

Electronic Properties. The Mn L_{23} -edge XAS spectra for a representative sampling of different Mn concentrations with and without protein are shown in Figure 7. The spectra have been normalized to the integrated peak area ($L_2 + L_3$) and energy calibrated by comparing the peak position of a reference powder that is simultaneously collected with each sample spectra. The evolution of the spectra for the protein-free particles (right panel) shows that as the Mn concentration is reduced, the Mn L_{23} spectral weight shifts dramatically from the higher-energy peaks to the lower-energy peak. The spectra are quite similar for

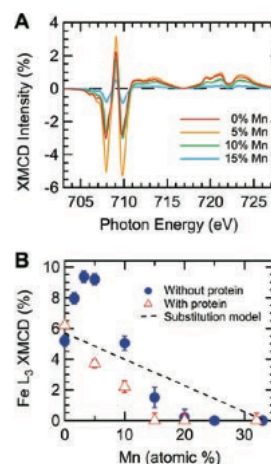


Figure 9. (A) Fe L_{23} -edge XMCD spectra for particles without protein for different Mn concentrations. (B) The Fe peak-to-peak MCD variation with Mn concentration without protein (solid circles), with protein (open triangles), and a calculated linear moment reduction for Mn displacement of Fe in the octahedral site (dashed line).

5%–25% Mn concentrations, changing rapidly at 33% Mn. Above this concentration, the Mn spectra evolve gradually, but are all quite similar. The range of Mn concentrations over which the electronic structure evolves rapidly is the same range at which dramatic structural changes were observed (see above).

While the overall trend in the Mn L_{23} -edge XAS of the protein-templated particles (left panel) is fairly similar to the protein-free particles, important differences exist. In particular, the highly structured peaks seen at low Mn concentrations persist to higher Mn doping levels in the protein-templated samples, changing suddenly after 67% Mn instead of 33% Mn. Above 75% Mn, the electronic structure remains fixed. There are also subtle differences in the shapes of both the high-Mn and low-Mn spectra.

Confirmation of this varied evolution of the structure of Mn ferrite nanoparticles can be found in the Fe XAS spectra. Figure 8A displays the area normalized Fe L_{23} -edge XAS spectra for protein-free nanoparticles. The slight change in the local electronic structure of Fe is conveyed in the changing shoulder intensity of the L_3 peak in comparison to the main peak and in the redistribution of spectral weight between the first and second peak of the L_2 edge (along with the development of a small shoulder at lower binding energy). These variations are qualitatively clear from the spectra themselves, but the trend can be quantitatively understood by displaying these two intensity ratios (Figure 8B). Once again we see a gradual evolution of the Fe electronic spectra from 0%–33% Mn, with a transition around 50% Mn. These changing ratios have been attributed to increased occupation of Fe in the octahedral site of the spinel structure, consistent with the Mn displacing Fe in the tetrahedral site. The corresponding Fe L_{23} -edge spectra for the protein-templated particles are very similar to those published previously and are included in the Supporting Information accompanying this article.

Additional structural information can be obtained from the XMCD spectra of the L_{23} edge.⁴⁶ Figure 9 shows the evolution of the Fe XMCD as a function of Mn concentration for protein-free

particles. The spectra show that the dichroism signal of Fe first dramatically increases at low Mn addition, then falls rapidly. This behavior, highlighted by the solid circles in Figure 9B, is well understood if the Mn initially substitutes for Fe in the A-site (tetrahedral) position. In the spinel structure, because of indirect exchange coupling, the magnetic orientation of the Fe in the A-site is opposite the magnetic orientation of Fe in the more numerous octahedral B-sites, resulting in a reduction of the net Fe moment. Substitution of Mn into the A-site reduces the occupation of Fe in this site, thus increasing the net Fe moment. Also shown in the Figure 9B (dashed line) is the calculated Fe MCD signal if the Mn were to merely displace the Fe atoms from the octahedral site. In contrast, for Mn addition with protein encapsulation, the Fe MCD signal is observed to drop rapidly to zero and is consistent with Mn substituting as Mn^{2+} in the octahedral B-site, displacing the Fe and reducing the overall moment.³⁷ Moreover, both the Fe L_3 XMCD line shape and the Mn L_3 XAS line shape show that as the Mn concentration increases, the fraction of Fe atoms with an Fe^{3+} valence in the octahedral site decreases while the occupation of the octahedral site by Mn increases.⁴⁷ For both the protein-free (solid circles) and protein-templated samples (open triangles), the eventual decrease in the net Fe moment is significantly faster than the hypothetical linear decrease. This suggests that Mn does more than simply dilute the magnetism of the Fe atoms; significant levels of Mn disrupt the magnetic coupling, effectively abolishing ferromagnetic behavior by 25% Mn incorporation.

DISCUSSION

Agreement of PDF and XAS Methods. The results obtained by PDF analysis and L-edge XAS studies of these materials are in broad agreement, and the data obtained by these two methods are largely complementary. As a diffraction method, PDF analysis is highly sensitive to small shifts in the unit cell geometry. For example, the Mn ferrites shown in Figure 2A look extremely similar at very short distances ($<4 \text{ \AA}$); it is only at higher values of r that the changes in the lattice geometry resulting from the substitution of Mn for Fe become apparent. For these oxide materials, the XAS is a much more local method, revealing information only about the immediate coordination environment of the element whose absorption edge is being measured. Comparison of Figure 2 with Figure 7, for example, indicates that, although the protein-templated and protein-free Mn oxide nanoparticles show dramatically different crystal structures (chalcophanite-like and hausmannite-like, respectively), the coordination environments of the Mn atoms are fairly similar. In both cases, the Mn X-ray absorption signal is dominated by distorted MnO_6 octahedra, in contrast to the less-distorted structures that prevail when Mn is doped into a lattice dominated by Fe oxide. PDF analysis struggles to extract information from very weakly ordered materials (such as the protein-templated Mn oxides), while XAS spectra are less sensitive to the degree of larger-scale order.

Valence and Site Occupation of Mn Atoms. This combined PDF/XAS approach is particularly fruitful in determining the incorporation of Mn into the $\gamma\text{-Fe}_2\text{O}_3$ lattice at low Mn concentrations. Figure 7 shows that the two types of samples undergo roughly similar changes, from well-defined spectra indicative of relatively undistorted Mn geometries to broader spectra that suggest the distorted geometries present in many bulk Mn oxides. These changes happen, however, at rather

different concentrations: around 33% Mn in the protein-free samples and around 67% in the protein-templated samples. If Mn were incorporating preferentially into the tetrahedral A-sites of the spinel lattice, one would expect a transition at about 33% doping, when all of these sites became occupied. Conversely, a transition at around 67% occupancy would suggest incorporation into the octahedral B-sites. Further evidence can be gleaned from the shape of the XAS spectra themselves; the low-concentration (5% Mn) spectrum of the protein-free nanoparticles is nearly identical to the theoretical spectrum of Mn^{2+} in a tetrahedral configuration,⁴⁸ consistent with incorporation into the A-sites. In the Fe XMCD results (Figure 9), the initial substitution of Mn into the ferromagnetic A-sites serves to increase the net Fe moment, at least until Mn concentrations become high enough to interfere with the long-range magnetic coupling of the Fe sites. In contrast, the protein-templated nanoparticles show no such increase, suggesting that they do not prefer the A-sites at low doping levels.

The PDF results paint a similar picture for the protein-free nanoparticles; Figure 4 shows a dramatic change in the spinel lattice parameters at around 33% Mn, consistent with the XAS results indicating initial doping into the tetrahedral sites. The protein-templated particles are somewhat different; close examination of Figure 2 suggests that the spinel structure has largely broken down by 33% Mn, being replaced by the layered chalcophanite-like structure, in which all metal sites are octahedral. Because of the overall weak ordering of this phase, it is impossible to determine what subtle structural shifts may be taking place at higher Mn doping levels. The XAS spectra reported in Figure 7 suggest that, in the 33–67% Mn range, the character of this weakly ordered lattice is still sufficiently determined by Fe as to create largely undistorted local environments for the Mn ions. It is only at doping levels above about 67% that the distorted Mn octahedral geometries become clearly apparent.

Loss of Crystallinity at Intermediate Doping in Samples. As an increasing number of Mn atoms are inserted into the $\gamma\text{-Fe}_2\text{O}_3$ lattice (or conversely, Fe atoms into Mn_3O_4), they will introduce defects that will tend to decrease the crystalline domain size in the material. A simple calculation indicates, however, that the spinel lattices are fairly tolerant of Fe/Mn substitutions. For example, $\gamma\text{-Fe}_2\text{O}_3$ has a molar volume of $43.71 \text{ cm}^3/\text{mol}$; this corresponds to about $2.8 \times 10^{22} \text{ Fe}/\text{cm}^3$, or a characteristic inter-Fe spacing of roughly $3.3 \text{ \AA}$. If 5% of these Fe atoms are replaced with Mn and each Mn substitution is a defect site, then the Mn density will be $1.4 \times 10^{21} \text{ Mn}/\text{cm}^3$, for an inter-Mn spacing of about $9 \text{ \AA}$. The crystalline domain size at 95% Fe is nearly $36 \text{ \AA}$, meaning that (in this rough approximation) a defect is introduced at 0.08% of Fe lattice sites, or 1.6% of Mn substitution sites. It is more likely that isolated Mn atoms can be incorporated into the Fe oxide lattice fairly easily (and vice versa) while a cluster of several nearby Mn atoms will be sufficient to introduce a defect.

Spinel-Chalcophanite Transition. In the high-Mn protein-templated samples, crystallinity loss likely involves a different mechanism, as the nanoparticle adopts a chalcophanite-type lattice that is dramatically different from the spinel lattice present in the high-Fe samples; the reasons for this structural change are less clear. In the protein-free synthesis, the 100% Mn samples showed larger domain sizes than the 100% Fe samples (Figure 4); it is possible that the tightly bonded hausmannite structure is only stable in fairly large, well-ordered crystalline

domains, while the layered chalcophanite structure can easily be disrupted by defects and is more amenable to a nanoconfined environment. By analogy with the protein-directed formation of calcium phosphate biominerals,³ it is possible that ferritin affects the crystal phase of Mn-dominated oxide phases either through electrostatic stabilization of thermodynamically unfavorable amorphous phases or by limiting nucleation precursors to individual ions which can successfully enter the protein cage, rather than nanometer-scale metal oxide clusters. The possible role of cage entry is highlighted by the fact that Fe oxide phases can easily be formed within both human ferritin (used in this study) and ferritin from the hyperthermophilic Archaeon *Pyrococcus furiosus*,⁴⁹ while attempts to form Mn oxide nanoparticles within *Pyrococcus* ferritin were unsuccessful. This suggests that the kinetics of cage entry may be affected by subtle details of the protein cage structure, leading to a significant impact on nanoparticle formation.

CONCLUSION

Protein cages used for inorganic nanoparticle encapsulation are far more than just passive containers; they exert a significant influence on the structural and electronic properties of the composite nanomaterials. Pair distribution function analysis from total X-ray scattering clearly shows that the structural changes experienced by Mn ferrite nanoparticles as a function of increasing Mn doping is qualitatively different in HFn-templated and protein-free nanoparticles. The reasons for this difference are not as clear: possibilities include changes in lattice stability because of the small crystalline domain size enforced by protein cage confinement and multiple nucleation sites or kinetic effects on crystal growth resulting from the limited rate of ion diffusion into the cage. A more thorough understanding of the physical underpinnings of these cage-induced material effects will be essential to realize the full potential of protein-mediated inorganic nanomaterials synthesis.

ASSOCIATED CONTENT

S Supporting Information. Further details are given in Figures S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tdouglas@chemistry.montana.edu.

Present Addresses

[†]Laboratory for Systems Biology, RIKEN Center for Developmental Biology, Kobe, Japan.

ACKNOWLEDGMENT

This research was supported in part by grants from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering DE-FG02-07ER46477, the National Science Foundation under Grant CBET-0709358, and the NASA Astrobiology Institute (NNA08CN85A). Compositional analysis by ICP-MS was carried out by Energy Laboratories, Inc., Billings, MT. X-ray scattering was obtained at beamline 11-ID-B at the APS with the assistance of Karena Chapman, Peter Chupas, and Evan Maxey. The Advanced

Photon Source is supported by the U.S. Department of Energy under Contract No. DE-AC02-06CH11357. The Advanced Light Source is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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CHAPTER 8

GALLIUM DOPING OF IRON OXIDE NANOPARTICLES

Contribution of Authors and Co-Authors

Manuscripts in Chapters 8: Enhanced Magnetism of Fe_3O_4 Nanoparticles with Ga doping

Author: Vanessa L. Pool

Contributions: I was responsible for the ACMS measurements as well as the XAS and XMCD.

Co-author: M.T. Klem

Contributions: M.T. Klem is C.L. Chorney's adviser, was responsible for the TEM used to identify crystal structure and size and was involved in the conceptualization aspect of the paper.

Co-author: C.L. Chorney

Contributions: C.L. Chorney was responsible for making the nanoparticles.

Co-author: E.A. Arenholz

Contributions: E.A. Arenholz is the beamline scientist where XAS and XMCD measurements were done.

Co-author: Y.U. Idzerda

Contributions: Y.U. Idzerda is my adviser, was involved in the conceptualization aspect of the paper and did the analysis on the XAS and XMCD for the paper.

Manuscript Information Page

Vanessa L. Pool, M.T. Klem, C.L. Chorney, E.A. Arenholz, Y.U. Idzerda

☐ Prepared for submission to a peer-reviewed journal

☐ Officially submitted to a peer-reviewed journal

☐ Accepted by a peer-reviewed journal

☒ Published in a peer-reviewed journal

Publisher Date of submission (22 October 2010) Date manuscript will appear (5 April 2011) Issue in which manuscript appears in (Journal of Applied Physics)

Gallium Paper Introduction

Gallium was a good choice of dopant if a high potential moment is desirable. Out of the elements examined in this dissertation, gallium has the smallest ionic radius of the group and substitutes into the tetrahedral position in the bulk and in the nanoparticles. From a practical standpoint, gallium iron oxides have shown interesting properties in regard to energy absorption as a function of gallium concentration¹⁰⁹, suggesting other potentially interesting applications. Additionally, gallium-oxides have demonstrated promising catalytic behaviors¹¹⁰, and nanoparticles are superior catalysts due to their high surface to volume ratio. Since the nanoparticles grown here are not grown in cages, an emphasis on biocompatibility was not a consideration, though gallium also shows promise as an MRI contrast agent¹¹.

Enhanced magnetism of Fe_3O_4 nanoparticles with Ga doping

V. L. Pool,^{1,a)} M. T. Klem,^{2,3} C. L. Chorney,^{2,3} E. A. Arenholz,⁴ and Y. U. Idzerda¹

¹Department of Physics, Montana State University, Bozeman, Montana 59715, USA

²Department of Chemistry and Geochemistry, Montana Tech, Butte, Montana 59701, USA

³Center for Advanced Supramolecular and Nano Systems, Montana Tech, Butte, Montana 59715, USA

⁴Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

(Presented 18 November 2010; received 22 October 2010; accepted 1 December 2010; published online 5 April 2011)

Magnetic $(\text{Ga}_x\text{Fe}_{1-x})_3\text{O}_4$ nanoparticles with 5%–33% gallium doping ($x=0.05$ – 0.33) were measured using x-ray absorption spectroscopy and x-ray magnetic circular dichroism to determine that the Ga dopant is substituting for Fe^{3+} as Ga^{3+} in the tetrahedral A-site of the spinel structure, resulting in an overall increase in the total moment of the material. Frequency-dependent alternating-current magnetic susceptibility measurements showed these particles to be weakly interacting with a reduction of the cubic anisotropy energy term with Ga concentration. The element-specific dichroism spectra show that the average Fe moment is observed to increase with Ga concentration, a result consistent with the replacement of A-site Fe by Ga. © 2011 American Institute of Physics. [doi:10.1063/1.3562196]

I. INTRODUCTION

Gallium doped iron oxide, $(\text{Ga}_x\text{Fe}_{1-x})_3\text{O}_4$, is interesting as it exhibits an energy-dependent photoabsorption as a function of Ga concentration in bulk samples.¹ This property could be advantageous in nanoparticles providing utility for applications. Additionally, Ga-based mixed oxides have shown interesting catalytic behavior, an application that nanoparticles are known to be exceptional for due to their large surface-to-volume ratio.^{2–4} Furthermore, the doping of magnetic nanoparticles can have behaviors distinct from bulk alloys, including changes in dopant site occupation and different variations of moment and anisotropy with doping concentration, making them interesting from a purely scientific standpoint.

Bulk $(\text{Ga}_x\text{Fe}_{1-x})_3\text{O}_4$ magnetic trends have not been fully studied, but Ga is typically present as a 3+ valence ion so it is likely to be present as a 3+ valence ion given the two options in the spinel structure.¹ The effect on the magnetic properties of doping Fe_3O_4 with other nonmagnetic transition metals of similar ionic radii, such as Zn, show that Zn preferentially substitutes for Fe^{3+} as Zn^{2+} in the tetrahedral coordination. For bulk Zn doped Fe_3O_4 the total moment per unit cell increases as the tetrahedral sites become occupied by the nonmagnetic transition metal.⁵ These substitutional atoms no longer partially cancel the Fe moment in the octahedral coordination. For Zn doping the average moment of the octahedral Fe sites also slightly increases as charge neutrality requires that some of the octahedral Fe^{2+} convert to Fe^{3+} . If Ga substitutes into the tetrahedral coordination as a Ga^{3+} ion (rather than Zn^{2+}), it should produce a similar, though slightly reduced effect.

Nanoparticles do not always follow the same trends as the bulk. Properties are often size dependent where surface effects and the relaxation of crystal lattice distortions can

cause nanoparticles to have distinctly different magnetic properties.^{6,7} In addition, nanoparticles are notoriously synthesis dependent, while a chemically gentle nanoparticle synthesis process like protein encapsulation may generate one behavior, a harsher chemical process may show an entirely different behavior.⁸ In particular, encapsulation of Zn nanoparticles in protein structures does result in substitution of Zn to the tetrahedral A-site, but generates a distinctly different magnetic behavior, characterized by a steep reduction in nanoparticle moment with Zn concentration, opposite the bulk behavior.⁹ From simple crystal filling arguments, the reduced ion radius of Ga^{3+} in comparison to Zn^{2+} suggests that the Ga dopant should more strongly prefer the tetrahedral coordinated site than Zn, allowing for a further investigation of the peculiar moment behavior.

II. EXPERIMENTAL PROCEDURES

In this study, magnetic $(\text{Ga}_x\text{Fe}_{1-x})_3\text{O}_4$ nanoparticles with 5%–33% gallium doping ($x=0.05$ – 0.33) were synthesized by mixing $\text{Fe}(\text{acac})_3$, 1,2-hexadecanediol, benzyl ether, oleic acid, and oleylamine under evacuated conditions. The Fe_3O_4 (magnetite) nanoparticles were synthesized by combining $\text{Fe}(\text{acac})_3$ (0.5 mmol), oleic acid (1.5 mmol), oleylamine (1.5 mmol), 1,2-hexadecanediol (2.5 mmol), and benzyl ether (5 mL) in a 50 mL roundbottom flask under vacuum. The mixture was gradually heated to 200 °C and allowed to anneal for 24 h. The reaction mixture was then cooled to room temperature, and the particles were precipitated in ethanol, centrifuged, and dried. Gallium doped magnetite nanoparticles, $(\text{Ga}_x\text{Fe}_{1-x})_3\text{O}_4$ were synthesized by substitution of $\text{Ga}(\text{acac})_3$ for the $\text{Fe}(\text{acac})_3$. TEM measurements determined their size to be 8.5–9 nm.

Investigation of the composition, electronic structure, and magnetic properties were accomplished using x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD). These measurements, performed on beamline 4.0.2

^{a)}Author to whom correspondence should be addressed. Electronic mail: pool@physics.montana.edu.

and 6.3.1 of the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratories, give element-specific information with high sensitivity and strong magnetic contrast and have been used to identify doping positions and electronic valence of doped magnetic nanoparticles in the past.^{9–11}

For these nanoparticles, samples were dried onto Formvar coated TEM grids and measured primarily in the electron yield configuration, though supplemental measurements were done in the transmission geometry. XAS was performed on the Fe and Ga $L_{2,3}$ edges to determine the valence of the elements and the substitutional site of Ga. XMCD was performed on the Fe L_3 edge to determine the moment per iron atom. XMCD measurements were done both at room temperature and at approximately 20 K with applied fields ranging from 0.5 to 1 T using 90% polarized light. For comparison, measurements were done on β -phase Ga_2O_3 acquired as a powder standard from Alfa Aesar.

To determine if the particles are interacting with one another, temperature-dependent, alternating-current magnetic susceptibility (ACMS) measurements were performed over a range of frequencies from 178 to 10,000 Hz using a Quantum Design Physical Property Measurement System (PPMS).

III. RESULTS AND DISCUSSION

A standard Neel–Arrhenius plot of the frequency-dependent ACMS data was created for various Ga concentrations (not shown). The negative natural log of the frequency was plotted as a function of the inverse of the blocking temperature (the peak in the real part of the susceptibility curve) over a range of frequencies from 178 to 10,000 Hz. A straight-line fit of the data was found to be unsatisfactory, suggesting that these bare nanoparticles are slightly interacting. The interaction is significant enough that it is not possible to reliably extract the quantitative anisotropy energies and the attempt frequencies from the ACMS data, although

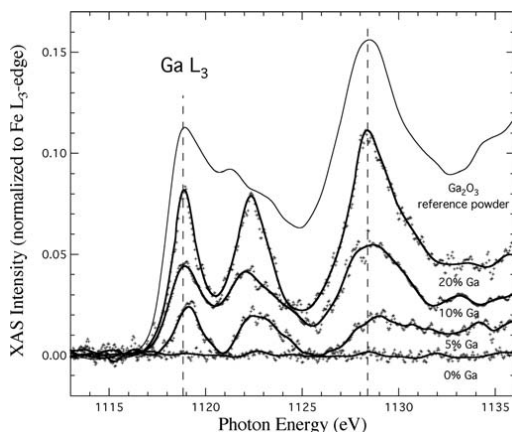


FIG. 1. The Ga L_3 -edge XAS spectra for $(\text{Ga}_x\text{Fe}_{1-x})_3\text{O}_4$ with $x=0, 0.05, 0.1$, and 0.2 . The points are single scans and the solid lines are the average of multiple scans. The spectra are normalized to the Fe L_3 -edge XAS peak intensity for each scan. Also shown is an arbitrarily normalized single scan of the Ga L_3 -edge spectrum for β -phase Ga_2O_3 reference powder.

the trend of the ACMS data is toward reduced anisotropy with increasing Ga content.

By comparing the evolution of the Ga L_3 XAS spectra to that of a β -phase Ga_2O_3 reference powder (shown in Fig. 1), the L_3 peak energies (dashed line at 1118.9 eV) are found to correspond nearly exactly, suggesting that the Ga is substituting into the host lattice as a $3+$ cation. The Ga XAS of the $(\text{Ga}_x\text{Fe}_{1-x})_3\text{O}_4$ are normalized to the Fe L_3 XAS intensity of each scan so that the relative intensities can be used to confirm the target Ga concentration percentages. The β - Ga_2O_3 reference spectrum is arbitrarily normalized to aid in the comparison. Although good agreement in peak position of a high energy peak occurs (dashed line at 1128.2 eV in Fig. 1) differences of the Ga XAS of $(\text{Ga}_x\text{Fe}_{1-x})_3\text{O}_4$ suggest that the actual local Ga bonding is not identical to the β - Ga_2O_3 structure, but more likely a substitution into Fe sites in the host Fe_3O_4 spinel structure, similar to that determined in coprecipitation studies.¹ A definitive determination of the site occupancy of the Ga cannot be made from the Ga XAS spectra alone.

Indirect evidence for preference of the A-site or B-site substitution for the Ga dopant can be found in the Fe L_3 XAS and XMCD. In the top panel of Fig. 2, the spectra for 0% gallium looks as expected for pure Fe_3O_4 .¹² The primary peak at 709.25 dominates and the pre-edge is appropriately small. As

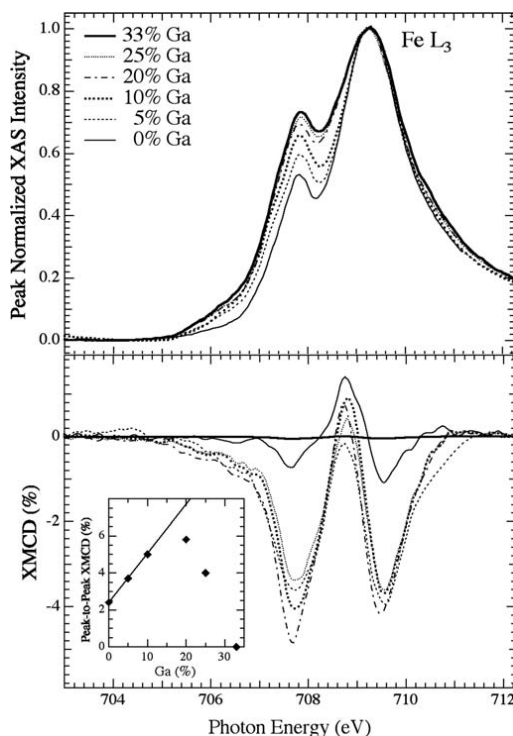


FIG. 2. XAS (top panel) and XMCD (bottom panel) of the Fe L_3 edge for 0% (pure iron-oxide), 5%, 10%, and 20% Ga in Fe_3O_4 . Bottom inset: The extracted peak-to-peak Fe XMCD intensity as a function of Ga concentration with a straight-line guide to the eye.

the amount of gallium increases the shoulder peak at 707.8 grows with respect to the primary peak. The growth of the shoulder peak at 707.8 is similar, indicative of an increase in the Fe^{+2} state in the octahedral coordination (B-site).^{12,13} This means that as the Ga substitutes into the spinel structure, it is not displacing the Fe^{2+} in the octahedral configuration so that the relative percentage of iron in this configuration is increasing. Given that the Ga XAS spectra is consistent with Ga in a 3+ valence (and in a tetrahedral coordination) and the Fe XAS data evidence that the iron is not removed from the octahedral 2+ coordination, the gallium appears to preferentially substitute into the tetrahedral Fe^{3+} A-site.

Dichroism spectroscopy (XMCD) is not only an excellent method of obtaining element-specific magnetic information but it also can be insightful in determining bonding configurations.^{13–15} Examining the Fe L_3 XMCD spectra for these nanoparticles (shown in the bottom panel of Fig. 2), the shape of the Fe XMCD spectra initially starts out with a mix of tetrahedral and octahedral coordination as one would expect of Fe_3O_4 .^{13–15} As the Ga percentage increases the central peak quickly reduces in prominence. As has been noted,^{13–15} the intensity of this central peak is representative of the tetrahedral coordination, so the reduction of this peak is evidence of increasing octahedral coordination of Fe as opposed to the 1/3 tetrahedral to 2/3 octahedral mix of Fe_3O_4 . In addition, comparing the relative intensities of the two downward peaks in the XMCD spectra, the lower energy peak is becoming more prominent as the concentration increases from 5% Ga to 25% gallium, which also indicates that the octahedral Fe^{2+} is becoming more dominant in the spectra at higher concentrations.

The observed increase in the Fe XMCD intensity is consistent with this picture. If the Ga is preferentially substituting into the tetrahedral A-site, then given the ferrimagnetic nature of the Fe_3O_4 structure, substituting into the down spin site with a nonmagnetic dopant atom results in an overall increase in the moment per unit cell (as observed in the bulk for Zn doping). This is in fact observed as shown in the inset to Fig. 2. As the Ga is introduced the peak-to-peak dichroism signal increases up to 20% Ga. Due to the interplay between the three features present in the Fe L_3 XMCD spectra, a quantitative extraction of the moment per Fe atom must be performed carefully with modeled spectra.

IV. CONCLUSIONS

Gallium doped iron oxide spinel nanoparticles of average size 8.75 nm have been synthesized and demonstrate weak interparticle interactions expected of such particles. The Ga is found to preferentially substitute into the tetrahedral A-site of the Fe_3O_4 spinel structure as a 3+ ion. This can be seen clearly in the Fe L_3 XAS and XMCD spectra and is supported by the observed magnetization trend. The doping of Ga as 3+ in the tetrahedral configuration causes the moment per iron atom of the particles to increase with increasing Ga concentration until 20% Ga, after which the nonmagnetic nature of Ga causes the moment to quickly fall to 0 in a manner similar to other dopant materials in bulk Fe_3O_4 .

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation under Grant No. CBET-0709358. The ALS is supported by DOE.

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CHAPTER 9

VANADIUM DOPING OF IRON OXIDE NANOPARTICLES

Contribution of Authors and Co-Authors

Manuscripts in Chapters 9: V paper Title

Author: Vanessa L. Pool

Contributions: I was responsible for the ACMS measurements as well as the XAS and XMCD.

Co-author: M.T. Klem

Contributions: M.T. Klem is C.L. Chorney's adviser, was responsible for the TEM used to identify crystal structure and size and was involved in the conceptualization aspect of the paper.

Co-author: C.L. Chorney

Contributions: C.L. Chorney was responsible for making the nanoparticles.

Co-author: E.A. Arenholz

Contributions: E.A. Arenholz is the beamline scientist where XAS and XMCD measurements were done.

Co-author: Y.U. Idzerda

Contributions: Y.U. Idzerda is my adviser, was involved in the conceptualization aspect of the paper and did the analysis on the XAS and XMCD for the paper.

Manuscript Information Page

Vanessa L. Pool, M. T. Klem, C.L. Chorney, E. A. Arenholz and Y. U. Idzerda

☒ Prepared for submission to a peer-reviewed journal

☐ Officially submitted to a peer-reviewed journal

☐ Accepted by a peer-reviewed journal

☐ Published in a peer-reviewed journal

Publisher Date of submission (for submitted manuscript) Date manuscript will appear
(for accepted work) Issue in which manuscript appears in (for published works)

Vanadium Paper Introduction

Vanadium has a very wide range of potential ionizations from V^{1+} to V^{5+} , making it inherently interesting in a spinel structure. It also substitutes into the octahedral site in the bulk, unlike the other dopants investigated here. Vanadium dopes into the octahedral site preferentially but as it is only slightly larger than gallium which prefers the tetrahedral site, if the cell relaxation theory is correct, then vanadium may substitute tetrahedrally in the nanoparticle case.

Vanadium-oxides have been of interest as cathodes^{51, 111, 112} and catalysts¹¹³⁻¹¹⁷, again suggesting other interesting physical properties. As it turned out, they did have a very interesting dependence of the blocking temperature as a function of vanadium concentration.

Enhanced Magnetization in $V_xFe_{3-x}O_4$ Nanoparticles

V. L. Pool¹, M. T. Klem², C. L. Chorney², E.A. Arenholz³, and Y.U. Idzerda¹

¹*Dept. of Physics; Montana State University; Bozeman, MT 59715*

²*Dept. of Chemistry; Montana Tech; Butte, MT 59701*

³*Advanced Light Source; Lawrence Berkeley Nat. Labs; Berkeley, CA 94720*

The V-dopant site and magnetic behavior of 9 nm diameter nanoparticles of $V_xFe_{3-x}O_4$ with 5% to 33% vanadium doping ($x=.15$ to 1) are determined. The Fe and V L_{23} -edge X-ray absorption and X-ray magnetic circular dichroism spectra are used to identify that vanadium initially substitutes into the tetrahedral Fe site as V^{3+} and that the average Fe moment is observed to increase with V concentration up to 10% ($x=.3$) vanadium incorporation, followed by a rapid decrease to zero average moment at 33% ($x=1$). The frequency-dependent alternating-current magnetic susceptibility (ACMS) displayed a substantial increase in blocking temperature with V concentration and indicated substantial control in the strength of inter-particle interactions.

Introduction

Doping into a magnetic spinel structure can have a dramatic impact on the properties of the host material. Vanadium atoms in oxide form can be present in a variety of oxidation states making it promising as a cathode material for lithium ion rechargeable batteries¹, a useful catalyst², and for application in optical switches and detectors³. This multi-valence makes vanadium a promising dopant in spinels, and particularly in nanoparticles.

Spinel has 24 transition metal sites per unit cell. For Fe_3O_4 there are 8 tetrahedral Fe^{3+} sites with $5 \mu_B$ moment per iron atom and 16 octahedral sites split evenly between $4 \mu_B Fe^{2+}$ and $5 \mu_B Fe^{3+}$ atoms. The indirect exchange interaction between tetrahedral and octahedral sublattices dominates the magnetic behavior and the resulting anti-aligned sublattices generate a net moment that comes from the 8 Fe^{2+} octahedral iron atoms each with a moment of $4 \mu_B$. If a nonmagnetic dopant substitutes into the octahedral position, the moment decreases linearly, however if it takes the place of the tetrahedral iron atom the moment would initially increase. If the dopant is nonmagnetic or prefers an antiferromagnetic alignment the ferrimagnetic ordering of the material will eventually break down with sufficient dopant incorporation^{4,5}. For these reasons doping into a magnetic spinel structure can have a dramatic impact on the properties of a host material, especially if the material is a nanoparticle where the dopant may substitute differently than for the bulk case.

Experimental Procedure

Nanoparticles of $V_xFe_{3-x}O_4$ with 3% to 33% vanadium doping ($x=.09$ to 1) were synthesized by mixing appropriate ratios of solutions of 0.5 mmol $V(acac)_3$ and $Fe(acac)_3$, 1,2-hexadecanediol with benzyl ether, oleic acid (1.5 mmol), and oleylamine (1.5 mmol) under evacuated conditions. The mixture was gradually heated to 200°C and allowed to anneal for 24 hours. The reaction mixture was then cooled to room temperature, and the particles were precipitated in ethanol, centrifuged, and dried. Transmission electron micrographs (TEM) showed that these nanoparticles had a size distribution of 9 ± 2 nm.

X-ray absorption spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) measurements were performed in electron yield mode at beamline 6.3.1 of the Advanced Light Source of the Lawrence Berkeley National Laboratories. Nanoparticles were prepared by drying the liquid suspension of the particles on formvar coated TEM grids. The XMCD measurements were made with an alternating 0.5 T magnetic field at every energy point, sufficient to align the magnetic moment of the nanoparticles with the propagation direction of the circular polarized soft x-rays. The V and Fe L_{23} -edge and O K-edge XAS and Fe L_3 -edge XMCD spectra were compared to reference standards and molecular-orbital calculations. The V L_3 -edge peak energies are referenced to 515.9 eV by comparing the XAS of a subsequently measured TiO_2 powder standard with the literature value for Ti from de

Groot *et al.*⁶ This energy calibration automatically references the nearby O K-edge, which is collected along with the V-edge spectra.

Frequency-dependent alternating-current magnetic susceptibility (ACMS) measurements from a Quantum Design Physical Properties Measurement System (PPMS) were performed on dried samples of the nanoparticles with a distribution of frequencies ranging from 178 Hz-10,000 Hz to determine the frequency dependence of the blocking temperature of the nanoparticles.

Results and Discussion

To determine the valence of the substituting vanadium, area normalized XAS of the V L_{23} -edge were measured. The results (displayed in Figure 1) can be compared to the variation in the vanadium spectra in reference powders and with reference materials reported in the literature⁷⁻⁹ to associate various peaks in the spectra with vanadium valence. In the L_3 peak, the higher energy peak at 515.9 eV is strictly associated with the V^{3+} valence and the lower energy shoulder is associated with V^{2+} . This peak association with vanadium valence is used to determine that the vanadium initially substitutes as V^{3+} up to 12.5% ($x=0.375$) but as the concentration rises to 15% ($x=0.45$), the additional vanadium substitutes as V^{2+} , as evidenced by the growth of the lower binding energy peak in the vanadium structure and the shift in energy of a lower energy peak in the oxygen spectra. Peak fitting of the vanadium spectra allows for a quantitative determination

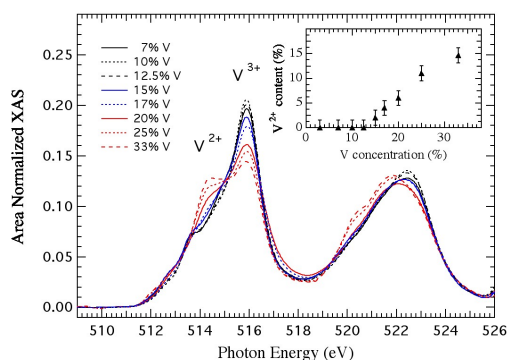


FIGURE 1: XAS of the O K-edge (top panel) and XAS of V L_{23} -edge (bottom panel) for V doped iron oxide in 5%, 10%, 20% and 33% concentrations. Bottom insert: the % V^{2+} to %V.

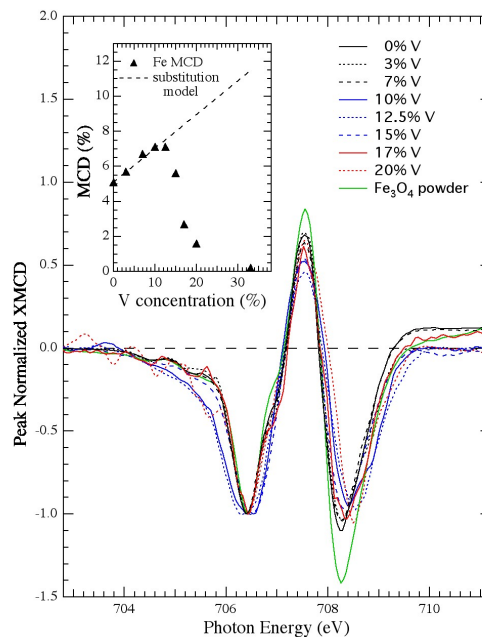


FIGURE 2: Iron XMCD for L_3 edge for V 0%, 5%, 10%, 20% and 33%. Insert: XMCD % versus V concentration.

of the V^{2+} compositional content (shown as an inset in Figure 1b). At 33% vanadium doping levels, only 15% of the vanadium resides in the V^{2+} state.

As vanadium is substituted into the Fe-oxide spinel structure, the average moment of the iron atom, as determined by the Fe L_3 XMCD intensity, is observed to initially increase over the same range as the V^{3+} substitution (inset of Figure 2). Furthermore, the evolution of the Fe L_3 XMCD spectra with vanadium concentration (Figure 2 displays the Fe L_3 XMCD after peak normalization for comparative purposes) indicates a predominantly A-site substitution of the vanadium as evidenced by the reduction in relative intensity of the middle peak of the XMCD which is associated with iron being in the tetrahedral position¹⁰. The reduction in Fe occupation of the tetrahedral site and the overall increase in XMCD strength is strong evidence that the vanadium initially substitutes into the tetrahedral site of the spinel structure.

As the concentration of vanadium increases beyond 12.5% to the 15% range (where the vanadium begins to

substitute as V^{2+}), the average Fe moment falls. The relative strength of the first dip in the Fe XMCD spectra is also reduced for this doping level, indicating that the average moment of the Fe^{2+} ion in the octahedral position is smaller which would occur if the additional vanadium now substitutes into the octahedral position (thereby reducing the overall iron moment).

The XAS and XMCD spectra are useful for determining elemental electronic and magnetic structure but, as local probes, are not useful for determining inter-particle interactions that can modify the macroscopic magnetic behavior. Frequency dependent ACMS is often used to determine anisotropy energies and demonstrate that nanoparticles are weakly interacting by showing they obey a linear Neel-Arrhenius behavior that extrapolates to a reasonable attempt frequency^{11,12}. The ACMS data for the

V-doped nanoparticles revealed an increasing blocking temperature with increasing vanadium concentration (see Figure 3a). This increase is quite dramatic, for the 5% sample the blocking temperatures were around $80K \pm 5K$, but for nanoparticles with a 33% concentration the blocking temperatures were above room temperature and so were not measurable. For those concentrations that had measurable blocking temperatures, a standard Néel-Arrhenius plot was derived and the anisotropy energies were determined and displayed in Figure 3b. While the data fits a straight-line fairly well, suggesting a good match to the Arrhenius law (see Eq.(1)), for all non-zero vanadium concentrations, the extrapolated attempt frequencies were far from realistic suggesting that the particles become strongly interacting.

$$\tau = \tau_0 \exp \{E_a/k_B(T_B)\} \quad (1)$$

The fact that the particles are interacting is not surprising for this synthesis method and has been seen previously in our study of Ga-doped iron oxide particles¹³ but is not observed for an alternate synthesis processes in which nanoparticles are encapsulated in protein shells¹⁴.

For interacting nanoparticles, a more appropriate treatment is to analyze the frequency dependent ACMS data using the Volger-Fulcher law (see Eq.(2)) where the interactions are represented by a critical temperature T_0 which serves to correct the measured blocking temperature^{15,16}.

$$\tau = \tau_0 \exp \{E_a/k_B(T_B - T_0)\} \quad (2)$$

Additional measurements at much higher frequencies like Mossbauer experiments (GHz) would illustrate this non-linearity and allow for a simultaneous fitting of the effective interaction temperature and the anisotropy energy. In the absence of an independent determination of this effective interaction temperature, pre-selecting the attempt frequency allows for a determination of both the anisotropy energy and T_0 . Employing a reasonable set of attempt frequencies ranging from 10^{-9} - 10^{-12} sec, the resulting anisotropy energies determined from the Volger-Fulcher treatment are displayed in Figure 3c using an expanded scale. The trend is an increasing anisotropy with vanadium concentration. Extracting the effective interaction temperature and normalizing it by the measured blocking temperature generates a figure-of-merit for the

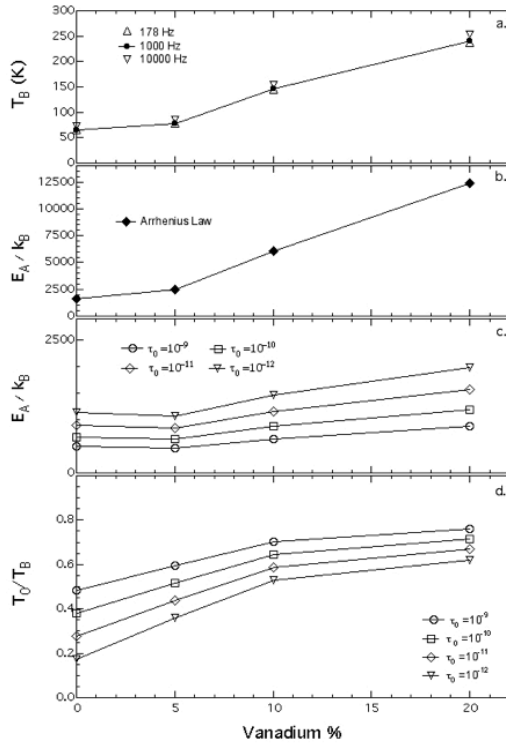


FIGURE 3: Blocking temperature vs. V % (a.), extracted slope using Arrhenius law vs. V% (b.), extracted slopes using Volger Folchr law with different set τ_0 (c.), τ_0 to τ_B ratios vs. V%(d.)

strength of the inter-particle interaction for each concentration for the different preselected attempt frequencies and is displayed in Figure 3d. The inter-particle interaction is similarly observed to increase with vanadium concentration, even in the region where the net Fe moment is small.

While at first glance this appears to provide more reasonable values with more believable anisotropy energies, the T_0 values extracted from this method were quite high in comparison to the blocking temperatures as seen in Figure 3d. In strict terms, the Volger-Fulcher law is valid for small interactions where the smallness criteria is $T_0 \ll T_B$ ¹⁶. Attempts to extend this treatment to larger interactions through the generalization of either the Arrhenius treatment¹⁷ or the Volger-Fulcher treatment¹⁸, have been employed with limited successes. These more involved treatments raises additional questions while maintaining the trend of increasing anisotropy energy with vanadium concentration.

Conclusions

Vanadium doped into iron oxide nanoparticles of average size 9 nm were found to preferentially substitute into the tetrahedral site as V^{3+} up to 12.5% vanadium incorporation, corresponding with an increase in the net Fe moment. By 15% however, vanadium appears start going in as V^{2+} oxidation in the octahedral configuration and correspondingly the Fe moment drops of as would be expected from the A-B sublattice interactions. The ACMS results identify a strong correlation between the vanadium concentration and the blocking temperature and anisotropy energy per particle. Furthermore, the interaction strength of

these nanoparticles is determined to be strongly dependent on vanadium concentration identifying them as dramatically tunable in this regard.

Acknowledgements

This work is supported by the National Science Foundation (CBET-0709358).

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CHAPTER 10

CONCLUSIONS

In this work it has been demonstrated for sufficiently small nanoparticles, a crystal relaxation occurs. The crystal relaxation is demonstrated in the manganese XAS spectra, which shows a relaxation of the tetragonal distortion seen in hausmannite and to a lesser extent iwakiite. This crystal relaxation in turn allows for a change in the site preference of the dopants allowing for dopants to incorporate differently than as seen for the bulk where structural constraints prevent dopant substitution into the preferred site. The demonstration of this comes from the vanadium substituting tetrahedrally in nanoparticles, rather than octahedrally as it is found to in coulsonite and other bulk vanadium iron oxide studies.

In this dissertation a variety of different nanoparticles have been investigated. This investigation has examined zinc, manganese, gallium, and vanadium doped into an iron-oxide spinel. The major conclusion is that crystal relaxations created by nanoparticles allow some dopant ions to substitute into sites not observed in the bulk. The synthesis has also varied from nanoparticles that were grown in ferritin, where the size of the nanoparticles was constrained by the proteins, giving an average of around 6.7 nm, to particles grown with the same synthesis processes but without the protein cage confinement, resulting in an average size of 14.5 nm, to the harsher chemical synthesis used for the gallium and vanadium doped samples with a size of about 9 nm. Since part of this investigation is to look at what role the size of the nanoparticles might have on

how the dopant substitutes into the spinel structure, the size for resultant nanoparticles could be considered the characteristic of merit.

In the book by Gleitzer and Goodenough⁵⁴, both manganese and gallium are considered to be non-exclusive in their dopant preference. Additionally in the Hill⁴⁰ paper, some of the findings are in contradiction with those in the Gleitzer and Goodenough work. The specifics of a growth are always important, but this lack of agreement may indicate that these materials are more particular than most. The potential for the chemistry of the nanoparticles' synthesis to affect the outcome in ways beyond the effects that size alone would have, should not be underestimated. All the synthesis methods here are among the mildest reported.

Before it is possible to draw conclusions from the papers presented in the last 6 chapters, I believe that it would be instructive to review the findings as they relate to the argument at hand. Additionally, some data that was not included as figures in the original papers due to space constraints has been added in Appendix D.

The first paper, presented in chapter 4, concerned zinc doped iron-oxide nanoparticles, which were grown in protein cages. In this paper, it is found that the trend of the magnetic moment, as a function of concentration, more strongly resembles a nonmagnetic dopant going into the octahedral site than the tetrahedral site. This was not stated as the conclusion in the papers for two reasons. First, it seemed unlikely that zinc was substituting into the octahedral site, since it prefers a tetrahedral configuration exclusively in its oxide forms and is considered to strongly prefer the tetrahedral coordination according to sources such as Goodenough⁴³. This is not to say that it is

impossible, but extraordinary claims require extraordinary proof, and the moment reduction did not seem like enough evidence to conclude that an atom was substituting octahedrally, that so obviously prefers a tetrahedral coordination in its many other forms. Second, there are other possible explanations for a diminishing MCD signal. In such small nanoparticles, there could be a general disruption of the superexchange ordering of the moments due to changes in the bond lengths or angles, or as was suggested in the paper, defects in the crystal such as oxygen vacancies or iron vacancies like the ones in $\gamma\text{-Fe}_2\text{O}_3$, or a combination of the two.

In the case of the protein-caged nanoparticles, the iron XAS and MCD signal are particularly weak (weaker than any other nanoparticle studied here). MCD is already an order of magnitude smaller than XAS, so the MCD data is just not as reliable. Not only are the spectra noisy, but the iron MCD is harder to interpret when the dopant is going into the tetrahedral site as $2+$ rather than as $3+$. This is because addition of zinc in the tetrahedral configuration not only lowers the amount of iron in the tetrahedral configuration, but in the octahedral $2+$ configurations as well. This means that not only is the tetrahedral peak varying in strength, but the ratio of one octahedral peak to the other is varying as well. In light of this, the MCD has been normalized such that the vertical distance between the O^{2+} and T^{3+} peak is 1 (see Appendix D.1); this makes it easier to see the shape of the MCD as it changes with changing concentrations. Examining the MCD spectra with this normalization, it appears as though the zinc is substituting into the tetrahedral site. The tetrahedral peak is not diminishing as dramatically as it would be expected to for a pure tetrahedral substitution, which suggests

that there may be some octahedral substitution as well. This is not entirely without precedent, as a previous work found that for smaller nanoparticles zinc substituted in the B-sites to some extent¹¹⁸. In summary, the conclusions in regard to zinc doping are the most uncertain. Fortunately, they do not impact the major conclusions of this thesis.

In the paper presented in chapter 5, manganese doped iron-oxide nanoparticles were grown in protein cages, with a size of 6.7 nm. In this case, we found that the manganese substitutes into the 2+ octahedral site, which was verified by both the shape of the iron MCD and by the decline in moment upon increase in manganese concentration. The decrease however, was even faster than would be predicted from the simple substitution model introduced in chapter 2. In addition, the iron spectra looked increasingly Fe₃O₄ like, rather than γ -Fe₂O₃ like. This led to the conclusion that there were oxygen vacancies being introduced, as one would otherwise expect a γ -Fe₂O₃ like spectra (as the Oct²⁺ sites became occupied by manganese). The fact that this set of nanoparticles and the zinc set previously mentioned, seem to be rather defected, and the fact that these are both the smallest of the nanoparticles at 6.7 nm (and nanoparticles grown in cages), is probably not a coincidence.

This work is also where the first demonstration of the potential for size effects was seen. The manganese spectra have a decidedly less broadened character than bulk measurements of manganese, even in the case of Mn₃O₄ (see Appendix D.2), and this is attributed here to a lessening of the tetragonal distortion that appears with larger quantities of manganese in the bulk manganese iron oxide spinels.

The next chapter in this dissertation focused on the manganese doped iron oxide nanoparticles not grown in cages, but still grown with the same synthesis process that was used for the caged particles. These nanoparticles were larger than their caged counterparts, with an average size around 14.5 nm. For these nanoparticles, the total particle moment initially increases with incorporation of manganese, which would be consistent with the initial incorporation into the tetrahedral site, as is verified by the iron L_3 -edge MCD spectra. It also substitutes as a $2+$ cation, and similar to the bulk behavior. However, as concentrations become larger than 5%, the moment begins to reduce. This is not consistent with the bulk, as even at $\frac{1}{3}$ incorporation of manganese (as is the case for Jacobsite), there is still a rather robust moment in the bulk material. The moment per iron atom should increase even more when measured with MCD, since MCD only measures the moments of the iron atoms. At 33% manganese doping, the bulk behavior would have all the iron in the B-sublattice and all the iron moments aligned in the same direction. These manganese doped nanoparticles do still have very sharp XAS features, but by 66.7% incorporation the XAS peaks broaden. It is only in Iwakiite (the $\frac{2}{3}$ manganese spinel) and Hausmannite (the all manganese-oxide spinel) that you find that the tetragonal distortion cause the unit cell to no longer be cubic. Jacobsite (the $\frac{1}{3}$ manganese case) is still cubic, though that does not rule out magnetic frustration within the unit cell. It should be noted that some of the apparent broadening of the spectra is from the occupation of other oxidation states.

The comparison of the bare nanoparticles and the nanoparticles grown in protein cages is brought under investigation in chapter 7. In this work the particles from

chapter 6 grown out of a cage are compared to particles grown in cages by Craig Jolly. (The nanoparticles grown by Craig Jolly were very similar to the ones grown by Michael Klem and all the same conclusions can be applied to them that were applied to the earlier work; however, they were not quite identical, so where both sets of data are shown, they will be denoted as Klem and Jolly particles.) For these nanoparticles, there were transitions in the lattice parameters, a and c , at varying points in the growth as a function of manganese concentration. The work outlines two different transition points in the growths for the different nanoparticles: the nanoparticles grown in cages had a transition point closer to 66% incorporation of manganese, while the uncaged particles have a transition around 33%. It is pointed out that these transitions happen at critical fillings of the tetrahedral and octahedral sites measured with PDF. If the manganese were going into the octahedral sites, in the case of the caged particles, the octahedral sites would be all full at $\frac{2}{3}$ incorporation of manganese. Likewise in the case of the uncaged particles, if the manganese were going into the tetrahedral sites, the sublattice would be filled at $\frac{1}{3}$ manganese incorporation. This may not be the only contributing factor. The relaxation of strain may also be accounting for some of the differences. The XAS from the Mn-edge show less peak broadening (associated with a relaxed crystal structure) than the larger encaged particles at the same incorporation of manganese (see Appendix D.3). This same conclusion was drawn in the work done in chapter 5.

Since PDF is so sensitive to interatomic spacing, it was susceptible to disorder in a way that the XAS and MCD, or for that matter TEM crystallography, was not. In this work the nanoparticles grown in cages were found to not be highly crystalline. This is

not surprising considering that in the previous work on the caged nanoparticles it seemed that the spinels were potentially defected in some manner, so this measurement adds credence to this thought. Additionally, the differences in the nanoparticle behavior may not just be due to the size differences. In the paper¹⁰⁸, Jolly comments on the possibility that the protein cages themselves may play a role in the particle formation that could affect the resulting particles' structure evolution.

“By analogy with the protein-directed formation of calcium phosphate biominerals, it is possible that ferritin affects the crystal phase of Mn-dominated oxide phases either through electrostatic stabilization of thermodynamically unfavorable amorphous phases or by limiting nucleation precursors to individual ions which can successfully enter the protein cage, rather than nanometer-scale metal oxide clusters.”

Jolly et al. go on to mention that the results varied slightly with different strains of ferritin.

The first of the protein incompatible growths was done on gallium doped into iron oxide in the work outlined in chapter 8. This growth procedure produced nanoparticles that are $9\text{ nm} \pm 2\text{ nm}$ in size. Gallium in the literature for the bulk material is known to substitute into the tetrahedral site as a 3+ cation, and it did so in this nanoparticle synthesis study. This is seen from the iron XAS spectra becoming more 2+ like with increasing gallium, as it would if the dopant was displacing 3+ valence iron ions, and from the reduction of the tetrahedral peak in the iron MCD spectra with gallium concentration. This study was a clear demonstration of the nanoparticle acting in a manner similar to its bulk behavior. The moment increased by 50%, showing reasonably good agreement with the prediction outlined in chapter 2 for a 3+ valence nonmagnetic species substituting into the tetrahedral site of a spinel. The moment increases close to

the prediction line until 10%, after this point the moment breaks from the prediction line, but continues to rise through 20%, before finally falling off to zero by 33%.

One of the more interesting materials from the standpoint of anisotropy energy, the work done for chapter 9 is on vanadium doped iron oxide nanoparticles grown in the same manner as the gallium work. Vanadium in the bulk substitutes into the octahedral site as 3+ (or in some spinels 4+). In this work, we found that vanadium substitutes tetrahedrally as V^{3+} , with an increasing moment up to 12.5% vanadium incorporation. Starting around 15%, the vanadium XAS shows that it begins going in as 2+, additionally, it appears that the tetrahedral component of the MCD starts regaining prominence, suggesting that the V^{2+} substitutes octahedrally. The moment increasing initially and then dropping off more rapidly than anticipated for a T^{3+} substitution can be explained by this change over from tetrahedral 3+ to octahedral 2+. Unlike gallium, which behaves as would be expected from the bulk behavior, vanadium doping in nanoparticles does not behave as it does in the bulk. In the nanoparticles, the vanadium initially substitutes tetrahedrally rather than octahedrally as it does in the bulk, and in the range above 12.5% vanadium, where there is some octahedral occupation, there are indications that the vanadium substitutes octahedrally as a 2+ cation rather than a 3+ cation as it does in the bulk. The ionization change could encourage the site change, as a 2+ ion is larger, and the octahedral coordination will more easily fit a larger ion.

This behavior on the part of the vanadium dopant is strong evidence that the nanoparticles ability to relax its crystal structure allows for the accommodation of the V^{3+} in the tetrahedral site. The size of a Ga^{3+} ion is less than that of a V^{3+} ion. In the bulk,

the Ga^{3+} is able to fit in the tetrahedral site better than the V^{3+} , but with the nanoparticles' slightly expanded cell, now it too can fit (though perhaps not quite as well as the gallium). I am not claiming that a simple comparison of radii is enough to determine which ion will occupy the tetrahedral position. The only claim I make is that a crystal relaxation allows ions that might be excluded on the basis of physical constraint, to no longer be excluded.

Preliminary work that has not been published was done on uncaged zinc doped nanoparticles grown with the same process as the caged nanoparticles, but without the cage (as in chapter 6). These nanoparticles were also grown by Craig Jolly. For this series we found that the moment increased, consistent with zinc substituting into the tetrahedral site (see figure 10.1). By normalizing the Fe MCD spectra so that the difference between the octahedral $2+$ and tetrahedral $2+$ is 1, the tetrahedral peak is observed to diminish with zinc concentration, while the octahedral peaks increase, indicating that zinc substitutes for the tetrahedral iron.

Unexpectedly, the iron signal does not reduce to zero by 33% zinc incorporation. This could occur if the zinc substitutes into the octahedral site in the 15% - 33% region, allowing for the A-B sublattice coupling to remain active at this high concentration. Alternatively, if the spinel was defected with enough oxygen vacancies, a significant amount of iron could remain $2+$ in the B-sublattice for the double exchange to remain active, which would likewise allow for a magnetic moment at this concentration of zinc. The effect would be the same as if the zinc substituted as a $3+$ ion rather than a $2+$ ion.

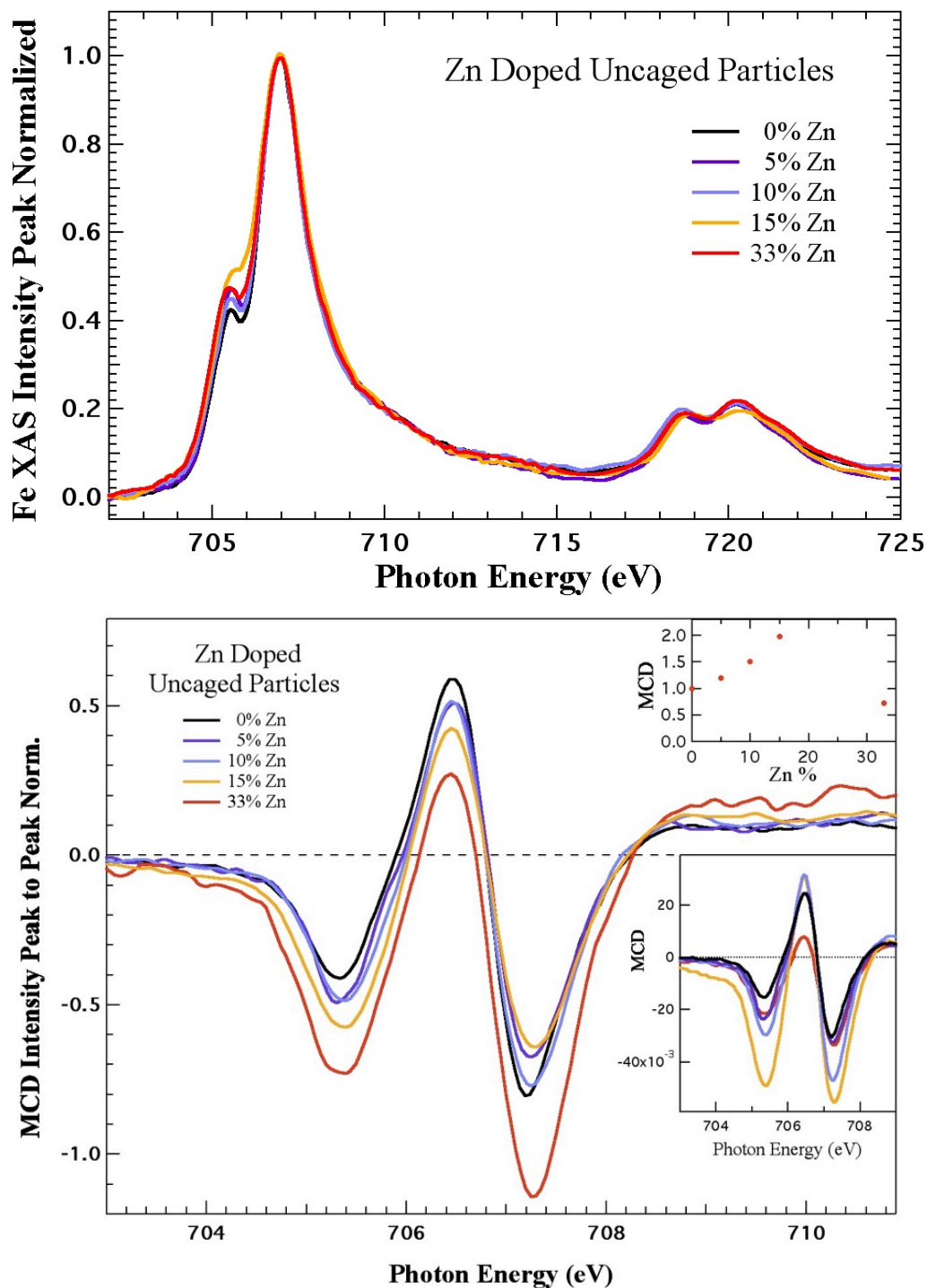


Figure 10.1: Uncaged Zinc Doped Iron-Oxide Particles. Iron XAS of nanoparticles (top), an inset with the extracted MCD normalized to a 0% incorporation value of 1 (upper inset), iron MCD with the Oct.²⁺ to Tet.³⁺ jump normalized to 1 (bottom), and the MCD un-normalized (lower inset).

Summary and Outlook

To put all this work into perspective, figure 10.2 reproduces the iron MCD variation for all the nanoparticles measured. The tetrahedral and octahedral models introduced in chapter 2, have been included for comparison. The nanoparticles MCD values, and the prediction models have all been scaled to 1 for the pure iron-oxide case.

In this work the dopants that were grown in cages and whose bulk behavior would predict an increased moment with concentration, all display greatly diminished moments for the nanoparticles. The most straightforward explanation of the data sets where zinc or manganese were doped into iron-oxide nanoparticles in ferritin cages is that the dopant atoms substituted into the octahedral B-site reducing the moment. In these materials the effects of growing the particles in the protein cages cannot be ignored either, as the cages could have a myriad of effects, from altering the crystal formation based on how the crystal is nucleated within the protein, to altering the chemistry of the environment the nanoparticles were grown in as a result of the gating capacity of the protein itself. So from the caged nanoparticles we can still conclude that the particle behavior was different than the bulk, likely due to size effects, though other factors may have contributed.

In the case of the uncaged nanoparticles, the data is also clear. Both the zinc and manganese initially dope into the tetrahedral site as 2+ unequivocally, yet they still act differently than expected. The iron MCD intensity for the manganese doped samples increases very rapidly initially, and then abruptly diminishes. While the zinc doped particles show an increase as expected.

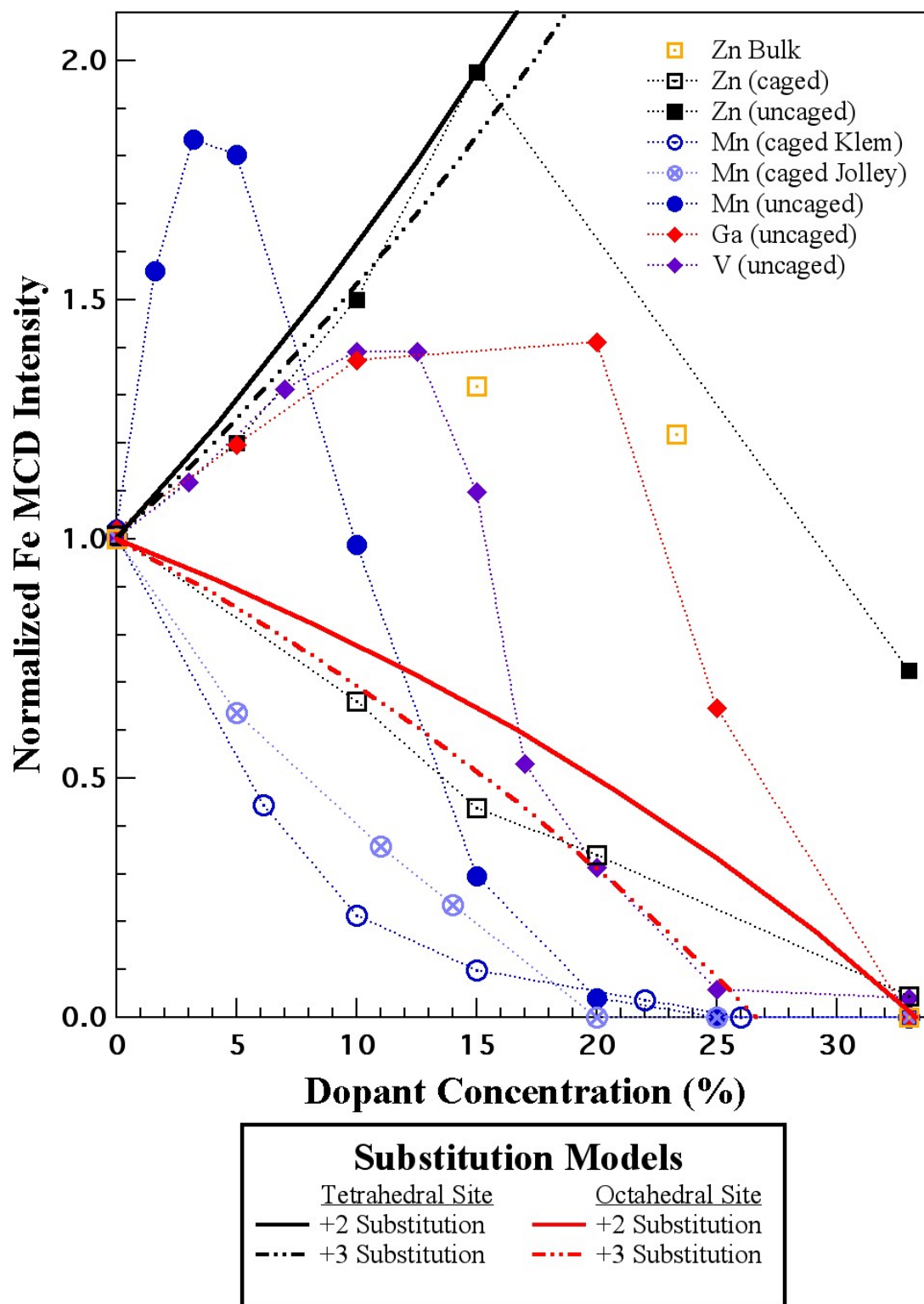


Figure 10.2: MCD vs. Dopant Concentration

The gallium and vanadium doped iron-oxide nanoparticles, are essentially proof of concept in regards to my thesis. Gallium is found to substitute into the tetrahedral coordination as $3+$, as would be predicted by its bulk behavior. The total nanoparticle moment initially increases, then is reduced, again as would be predicted from its bulk behavior. Vanadium doping into iron oxide nanoparticles behaves identically to the gallium, substituting into the tetrahedral site as a $3+$ cation. But vanadium, with its larger ionic radius does not behave this way in the bulk where it is found to substitute into the octahedral site. In this case, an ion with a somewhat larger ion radius is able to substitute into the tetrahedral site. Vanadium proves to be a good example of a larger ion, which would normally be “sized out” of the A-site, occupying a tetrahedral coordination, thus confirming my thesis.

This crystal relaxation likely has a nanoparticle size range over which it optimally occurs. It is possible that if the nanoparticles are too small, they are prone to defects, starting with the sort of defects we see in the 6.7 nm caged particles, but which would likely get worse as the particles got smaller. If the particles are large enough they will simply act bulk like. The nanoparticles’ size may have to be in a Goldilocks zone of sorts to see this crystal relaxation effect, where (for a given crystal structure) the nanoparticles are small enough to allow for relaxation, but not so small as to be heavily defected and so being an optimal size for the relaxation effect to be realized. The 8.75 nm nanoparticles, which are about 10 unit cells across, may be just the right size to see a relaxation of the crystal structure.

What can be concluded? First of all, it has been demonstrated beyond a shadow of a doubt that the behavior in the bulk may not be represented by behavior in the nanoparticle version of the same material. This is not surprising, as the nanoparticles are on the order of 10 unit cells. The argument has been made that with a simple model of the unit cell expansion, as a result of geometric curvature of the nanoparticle surface that a significant expansion occurs. Though a simplistic model, this along with the observed sharpening of manganese XAS (attributed to cell relaxation) makes it reasonable to conclude that some manner of cell distortion (in the form of relaxation) is occurring. The evidence of less relaxation in the larger nanoparticles than in the smaller nanoparticles produced with the same synthesis process, but with the smaller nanoparticles grown in protein cages, is further proof of concept.

If we grant that there is some cell expansion in nanoparticles, then the next question is: does this affect the dopant site preference? First, it is important to note that since ionic size is not the only factor in determining dopant site preference, it is not my intent to claim that all dopants will, if given the option, go into the tetrahedral configuration. It is merely my conjecture that if the unit cell is expanded, as the data would suggest, then the dopants may be able to occupy positions that they may otherwise not be able to. In this dissertation, the main example of this is the vanadium doped nanoparticles. In this study we found that up to 12.5% incorporation of vanadium, the vanadium went into the tetrahedral site rather than the octahedral site as V^{3+} , contrary to its bulk counterpart.

The obvious selection of the dopant to use in future work examining the thesis of this dissertation would be chromium. Chromium like vanadium, goes into the spinel iron-oxide system as O^{3+} in the bulk. It also has an orthorhombic distortion at higher concentrations, which could make for some interesting XAS studies (if it is anything like manganese with its tetragonal distortion). Additionally, its ionic radius is only 1 pm larger than vanadium, so it could be an interesting test.

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APPENDICES

APPENDIX A

SPINELS

Name [†]	Formula [†]	μ_B c/ μ_B	System ^{‡§}	Class, ^{‡§}	Space Group ^{‡§}	Axes of Symmetry ^{‡§}					a(A) ^{‡§}	c(A) ^{‡§}	Dns. ^{‡§} g/cm ³	
						2-f	3-f	4-f	Pl	Ct				
Magnetite	Fe(Fe) ₂ O ₄	4/4.1	Isometric	Hexoctahedral	4/m $\bar{3}$ 2/m	Fd3m	6	4	3	9	1	8.39	NA	5.21
Maghemite	γ -Fe ₂ O ₃	3.3/3.2	Isometric	Tetartoidal	2 3	P 2 ₁ 3	3	4	0	0	0	8.34	NA	5.49
Hausmannite	Mn ₂ O ₄	-	Tetragonal	Ditragonal-Dipyramidal	4/m2/m2/m	<i>I</i> 4 ₁ /omd	4	0	1	5	1	5.76	9.46	4.85
Iwakiite	FeMn ₂ O ₄	-	Tetragonal	Ditragonal-Dipyramidal	4/m2/m2/m	P 4 ₁ /mmm	4	0	1	5	1	8.52	8.54	4.93
Jacobsite	MnFe ₂ O ₄	5/4.6	Isometric	Hexoctahedral	4/m $\bar{3}$ 2/m	F d3m	6	4	3	9	1	8.46	NA	4.92
Franklinite	ZnFe ₂ O ₄	-	Isometric	Hexoctahedral	4/m $\bar{3}$ 2/m	F d3m	6	4	3	9	1	8.42	NA	5.26
Coulsonite	FeV ₂ O ₄	-	Isometric	Hexoctahedral	4/m $\bar{3}$ 2/m	F d3m	6	4	3	9	1	8.3	NA	5.16
Hercynite	FeAl ₂ O ₄	-	Isometric	Hexoctahedral	4/m $\bar{3}$ 2/m	Fd3m	6	4	3	9	1	8.12	NA	4.39
Xieite	FeCr ₂ O ₄	-	Orthorhombic	Dipyramidal	2/m 2/m 2/m	Bbmm	3	0	0	3	1	9.46 b=9.56	2.92	5.63
Cupropinel	CuFe ₂ O ₄	1/1.3	Isometric	Hexoctahedral	4/m $\bar{3}$ 2/m	Fd3m	6	4	3	9	1	8.37	NA	5.19
Magnesiiferriite	MgFe ₂ O ₄	1/1.1	Isometric	Hexoctahedral	4/m $\bar{3}$ 2/m	Fd3m	6	4	3	9	1	8.39	NA	4.51
Trevorite	NiFe ₂ O ₄	2/2.3	Isometric	Hexoctahedral	4/m $\bar{3}$ 2/m	Fd3m	6	4	3	9	1	8.41	NA	5.2
Ulvöspinel	Fe ₂ TiO ₄	-	Isometric	Hexoctahedral	4/m $\bar{3}$ 2/m	Fd3m	6	4	3	9	1	8.46	NA	4.91

mm (2/m 2/m 2/m) 4-mm = (4/m $\bar{3}$ 2/m) = (4/m $\bar{3}$ 2/m)

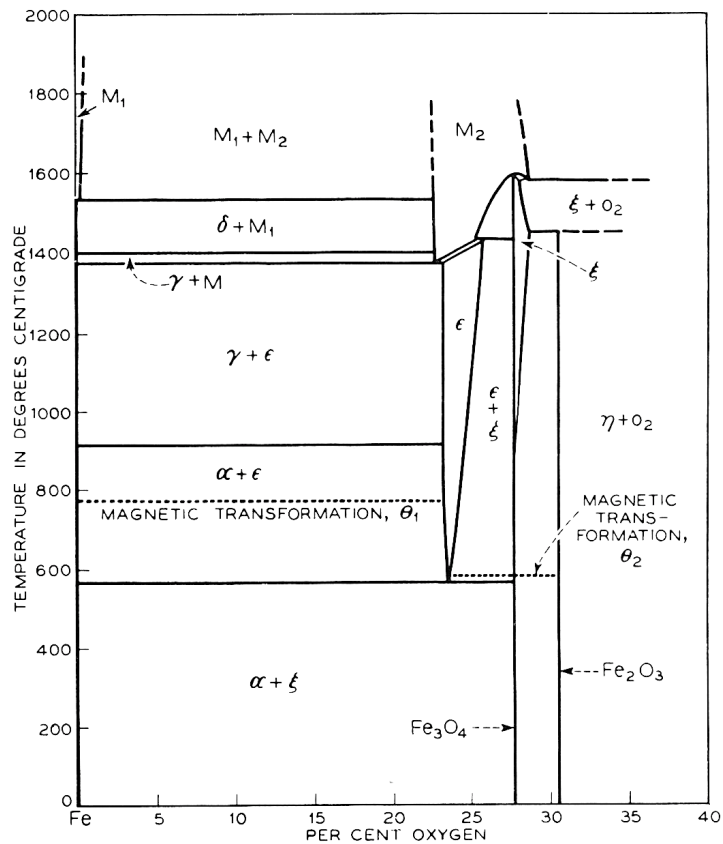
<http://www.mindat.org/>
<http://webmineral.com/crystal.shtml>
 §Morrish

A.2: Spinel Bond Length

The distances given here are for a spinel written as $A(B)_2X_4$, where X represents oxygen and A and B represent the tetrahedral and octahedral coordinated cations respectively, as they normally do. The value a as usual is the length of the side of the unit cell and u is the anion position parameter.

Atom pair	Distance	Comments
$A \dots A$	$a\sqrt{3}/4$	tet-tet cation separation
$A \dots B$	$a\sqrt{11}/8$	tet-oct cation separation
$B \dots B$	$a\sqrt{2}/4$	oct-oct cation separation
$A-X$	$a\sqrt{3}(u-0.125)$	tet bond
$B-X$	$a(3u^2-2u+0.375)^{1/2}$	oct bond
$X \dots X$	$a\sqrt{2}(2u-0.25)$	tet edge
$X \dots X$	$a\sqrt{2}(0.75-2u)$	shared oct edge
$X \dots X$	$a(4u^2-2u+0.375)^{1/2}$	unshared oct edge

A.3: Iron Oxide Phase Diagram



Appendix A.4: Hill Study

In this table select spinels have been taken from the extensive table in Hill's paper.

In this table a is the unit cell length, u is the anion coordination and x is the inversion parameter. The ionic ratios R_{tet} and R_{oct} are taken from Shannon's 1976 paper. The values u_{calc} , a_{calc1} are the anion coordinate and cell edge calculated from expression (1) and a_{calc2} is the cell edge obtained from expression (2) both from Hill's work. A_{cat} and B_{cat} are the standard from the formula AB_2X_4 and ref is the reference number as cited in the paper.

Spinel	a	u	x	R_{tet}	R_{oct}	X_{tet}	X_{oct}	U_{calc}	A_{calc1}	A_{calc2}	A_{cat}	B_{cat}	Ref.*
Fe_3O_4	8.3940	.2548	1.000	.490	.713	1.830	1.830	.2526	8.4598	8.4604	Fe	FeFe	34
FeMn_2O_4	8.5280	-	-	-	-	-	-	-	-	-	Fe	$\text{Fe}_1\text{Mn}_{19}$	35
FeGa_2O_4	8.3600	-	1.000	.470	.700	1.810	1.820	.2522	8.3945	8.3949	Fe	GaGa	1
FeVO_4	8.4210	-	1.000	-	-	1.830	1.730	-	-	-	V	FeFe	1
FeV_2O_4	8.4530	.2610	0.000	.630	.640	1.830	1.630	.2621	8.4675	8.4813	Fe	VV	26
Fe_2MnO_4	8.5110	.2615	.150	-	-	1.592	1.809	-	-	-	Mn	FeFe	43
Mn_3O_4	8.6400	-	-	-	-	1.550	1.550	-	-	-	Mn	MnMn	29
Fe_2ZnO_4	8.4432	.2615	0.000	.600	.645	1.650	1.830	.2605	8.4381	8.4484	Zn	FeFe	43
MgFe_2O_4	8.3600	.2612	.900	.488	.679	1.778	1.596	.2539	8.3652	8.3666	Mg	FeFe	1,45
FeAl_2O_4	8.1490	.2650	.000	.630	.535	1.830	1.610	.2670	8.1744	8.2013	Fe	AlAl	31,32
Fe_2SiO_4	8.2340	.2409	.024	.269	.775	1.898	1.831	.2400	8.2770	8.2855	Si	FeFe	52
Fe_2TiO_4	8.5300	.2650	1.000	-	-	1.830	1.685	-	-	-	Ti	FeFe	1
FeTi_2O_4	8.5000	-	1.000	.420	.820	1.540	1.685	2.453	8.6360	8.6379	Fe	TiTi	31
FeCr_2O_4	8.3920	-	.000	.630	.615	1.830	1.660	.2632	8.3982	8.4146	Fe	CrCr	33
Fe_2CoO_4	8.3500	.2560	1.000	-	-	1.830	1.855	-	-	-	Co	FeFe	1
FeCo_2O_4	8.2540	-	1.000	-	-	1.880	1.855	-	-	-	Fe	CoCo	1
NiFe_2O_4	8.3250	.2573	1.000	-	-	1.830	1.870	-	-	-	Ni	FeFe	37
$\text{Fe}_{2.5}\text{Cu}_{0.5}\text{O}_4$	8.4130	-	.000	-	-	1.865	1.830	-	-	-	Cu_3Fe_3	FeFe	1,2
Fe_2CuO_4	8.3690	.2550	1.000	-	-	1.830	1.865	-	-	-	Cu	FeFe	2,30
Fe_2GeO_4	8.4110	.2500	.000	.390	.780	2.012	1.830	.2455	8.4833	8.4851	Ge	FeFe	1
Fe_2CdO_4	8.7050	-	.000	.780	.645	1.690	1.830	.2685	8.6914	8.7255	Cd	FeFe	2
Fe_2MoO_4	8.5010	.2500	.500	-	.748	1.995	1.913	-	-	-	Mo	FeFe	2

★ All Ref. #'s refer to the reference numbers cited in the 1979 Hill paper the table's contents were taken from.

APPENDIX B

ELECTRON HABITS

B.1: 3d Electrons

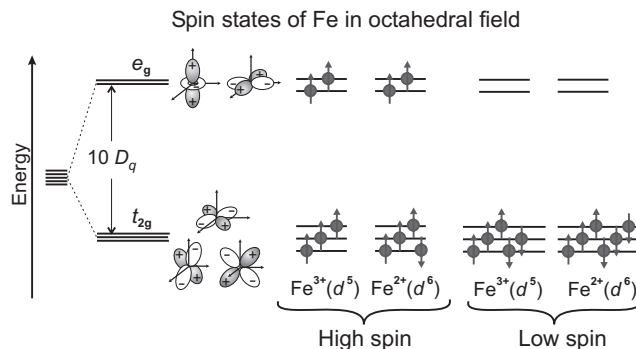
B.1a: Unpaired 3d electrons (From Gorter's Phillips Report)

ions										# of 3d electrons	# of unpaired 3d electrons (2s)
Sc ³⁺	Ti ⁴⁺	V ⁵⁺	Cr ⁶⁺	Mn ⁷⁺						0	0
	Ti ³⁺	V ⁴⁺	Cr ⁵⁺	Mn ⁶⁺						1	1
	Ti ²⁺	V ³⁺	Cr ⁴⁺	Mn ⁵⁺	Fe ⁶⁺					2	2
		V ²⁺	Cr ³⁺	Mn ⁴⁺						3	3
		V ⁺	Cr ²⁺	Mn ³⁺	Fe ⁴⁺					4	4
				Mn ²⁺	Fe ³⁺	Co ⁴⁺				5	5
					Fe ²⁺	Co ³⁺	Ni ⁴⁺			6	4
						Co ²⁺	Ni ³⁺			7	3
							Ni ²⁺			8	2
								Cu ²⁺		9	1
								Cu ⁺	Zn ²⁺	10	0

B.1b: 3d Electron Configurations (left from McClure right from Stohr)

Number of d-electrons	Ion	Free ion ground state	Octahedral field ground state	Tetrahedral field ground state	state	free ion term(s)	octahedral ground state	configuration
1	Ti ³⁺	² D	² T _{2g}	² E _g	high spin			
2	*V ³⁺	³ F	³ T _{1g}	³ A _{2g}	3d ¹	² D	² T ₂	(t _{2g} [↑]) ¹
	V ²⁺	⁴ F	⁴ A _{1g}	⁴ T _{1g}	3d ²	³ F	³ T ₁	(t _{2g} [↑]) ²
3	Cr ³⁺	⁴ F	⁴ A _{1g}	⁴ T _{1g}	3d ³	⁴ F	⁴ A ₂	(t _{2g} [↑]) ³
	Cr ²⁺	³ D	³ E _g	³ T _{2g}	3d ⁴	⁵ D	⁵ E	(t _{2g} [↑]) ³ (e _g [↑]) ¹
4	Mn ³⁺	⁵ D	⁵ E _g	⁵ T _{2g}	3d ⁵	⁶ S	⁶ A ₁	(t _{2g} [↑]) ³ (e _g [↑]) ²
	Mn ²⁺	⁶ S	⁶ A _{1g}	⁶ A _{1g}	3d ⁶	⁵ D	⁵ T ₂	(t _{2g} [↑]) ³ (e _g [↑]) ² (t _{2g} [↑]) ¹
5	Fe ³⁺	⁴ S	⁴ A _{1g}	⁴ A _{1g}	3d ⁷	⁴ F	⁴ T ₁	(t _{2g} [↑]) ³ (e _g [↑]) ² (t _{2g} [↑]) ²
	Fe ²⁺	⁵ D	⁵ T _{2g}	⁵ E _g	3d ⁸	³ F	³ A ₂	(t _{2g} [↑]) ³ (e _g [↑]) ² (t _{2g} [↑]) ³
6	*Co ³⁺	⁴ D	⁴ A _{1g}	⁴ E _g	3d ⁹	² D	² E	(t _{2g} [↑]) ³ (e _g [↑]) ² (t _{2g} [↑]) ³ (e _g [↑]) ¹
	Co ²⁺	⁴ F	⁴ T _{1g}	⁴ A _{1g}	3d ¹⁰	¹ S	¹ A ₁	(t _{2g} [↑]) ³ (e _g [↑]) ² (t _{2g} [↑]) ³ (e _g [↑]) ²
7	Ni ³⁺	³ F	³ T _{1g}	³ A _{1g}	low spin			
	Ni ²⁺	³ F	³ T _{1g}	³ A _{1g}	3d ⁴	³ (P, H)	³ T ₁	(t _{2g} [↑]) ³ (t _{2g} [↑]) ¹
8	Cu ³⁺	² D	² E _g	² T _{2g}	3d ⁵	² (I)	² T ₂	(t _{2g} [↑]) ³ (t _{2g} [↑]) ²
	Cu ²⁺	² D	² E _g	² T _{2g}	3d ⁶	¹ (G, I)	¹ A ₁	(t _{2g} [↑]) ³ (t _{2g} [↑]) ³
10	Zn ²⁺	¹ S	¹ A _{1g}	¹ A _{1g}	3d ⁷	² (G)	² E	(t _{2g} [↑]) ³ (t _{2g} [↑]) ³ (e _g [↑]) ¹

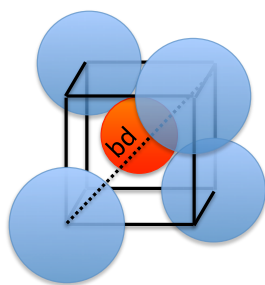
B.1c: In this figure spin states for iron in an octahedral crystal field in the high spin and low spin configurations are shown, where the high spin configuration is the configuration that produces the higher net spin for the atom.



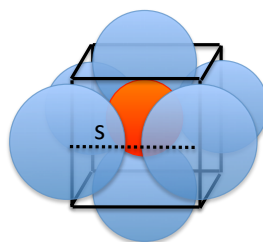
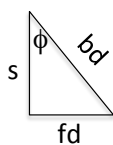
B.2: Hard Sphere Model

The radius ratio rule is derived here for the tetrahedral, octahedral, and cubic coordinations. The ratio is calculated by solving for the largest cation that can fit in the void of a given coordination created by touching oxygen anions. In the following equations: R_c represents the radius of the cation, R_o represents the radius of the oxygen anion, fd stand for the face diagonal, bd stands for body diagonal, and s stands for side length. This rule is outlined on dr. S.J. Heyes's class web site for further reference.

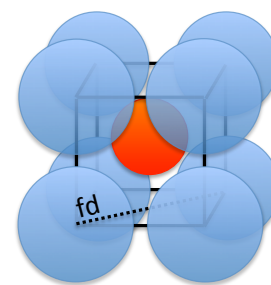
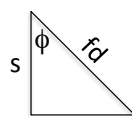
http://www.chem.ox.ac.uk/icl/heyas/structure_of_solids/strucsol.html



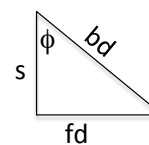
$$\begin{aligned} fd &= 2R_o \\ bd &= 2(R_o + R_c) \\ s &= 2R_o \cos(45^\circ) \\ \phi &= 35.26^\circ \\ \tan \phi &= s/fd = \cos(45^\circ) \end{aligned}$$



$$\begin{aligned} s &= 2R_o \\ fd &= 2(R_o + R_c) \\ \phi &= 45^\circ \\ R_c/R_o &= 1/\cos \phi - 1 \\ R_c/R_o &= .414 \end{aligned}$$



$$\begin{aligned} s &= 2R_o \\ fd &= 2R_o / \cos(45^\circ) \\ bd &= 2(R_o + R_c) \\ \phi &= 54.74^\circ \\ \tan \phi &= fd/s = 1/\cos(45^\circ) \end{aligned}$$



Rc/Ro	.225	between	.414	between	.732	<
Coordination	T	tetrahedral	O	octahedral	C	cubic

B.3: Ionic Radii

Elements	Mg	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Cd	In
Atomic Number	12	13	23	24	25	26	27	28	29	30	31	48	49
Shannon_c (2+) O=126	86	-	93	LS:87 HS:94	LS:81 HS:97	LS:75 HS:92	LS:79 HS:88.5	83	87	88	-	109	-
Shannon_c (3+) O=126	-	67.5	78	75.5	LS:72 HS:78.5	LS:69 HS:78.5	LS:68.5 HS:75	70 HS:74	68	-	76	-	94
Shannon_e (2+) O=140	72	-	79	LS:73 HS:80	LS:67 HS:83	LS:61 HS:78	LS:65 HS:74.5	69	73	74	-	95	-
Shannon_e (3+) O=140	-	53.5	64	61.5	LS:58 HS:64.5	LS:55 HS:64.5	LS:54.5 HS:61	LS:56 HS:60	53	-	62	-	80
Rc/Ro (2+) O=126	.68	-	.74	.75	.77	.73	.70	.66	.69	.70	-	.87	-
Rc/Ro (3+) O=126	-	.54	.62	.61	.62	.62	.60	.59	.54	-	.60	-	.75
Rc/Ro (2+) O=140	.68	-	.56	.57	.59	.56	.53	.49	.52	.53	-	.68	-
Rc/Ro (3+) O=140	-	.48	.46	.44	.46	.46	.44	.43	.38	-	.44	-	.57
Site Pref. Bulk	* [†] T ²⁺	*O ³⁺	*O ³⁺	*O ³⁺	* [†] T ²⁺	* [†] T ³⁺	* [†] T ²⁺	*O ²⁺	* [†] T ⁺	* [†] T ²⁺	* [†] T ³⁺	* [†] T ²⁺	* [†] T ³⁺
(ionic radii in pm) from Shannon : (Site Preference) *Gleitner&Goodenough 1985 [†] Not Exclusive													
Other dopant Preferences: *Li=B ⁺ *Si=T ⁺⁴ *Ti=O ⁺⁴ * [†] Ge=T ⁺⁴ *Sn=O ⁺⁴ *Mo=O ⁺⁴													
*V can go in as O ⁴⁺ and say V ³⁺ /V ²⁺ not highly unlikely though they give no examples													
All Shannon Calc. From Oct. Crystals And HS Cases Used When Available	Shannon_c (O=126)	Shannon_c (O=126)	Shannon_e (O=140)	Rc=Cation Radius (O=140)	Rc=Oxygen Radius	Rc/Ro _{ref} = .225	Rc/Ro _{ref} = .414	Rc/Ro _{ref} = .732					

B.4: Clebsch-Gordan Coefficients

A table of some of the Clebsch-Gordan coefficients is included along with the equation used for basis conversions and a table of 2p states converted from the m_j to m_l basis.

$$|(j_1 j_2) j m\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 m_1 j_2 m_2\rangle \langle j_1 j_2; m_1 m_2 | j_1 j_2; j m\rangle$$

Table B.4: 2p m_l to m_j Conversions

2p state	$ j, m_j\rangle$	$ m_l, m_s\rangle$
$2p_{3/2}$	$ 3/2, 3/2\rangle$	$ 1, 1/2\rangle$
$2p_{3/2}$	$ 3/2, 1/2\rangle$	$1/\sqrt{3}(\sqrt{2} 0, 1/2\rangle + 1, -1/2\rangle)$
$2p_{3/2}$	$ 3/2, -1/2\rangle$	$1/\sqrt{3}(-1, 1/2\rangle + \sqrt{2} 0, -1/2\rangle)$
$2p_{3/2}$	$ 3/2, -3/2\rangle$	$ -1, -1/2\rangle$
$2p_{1/2}$	$ 1/2, 1/2\rangle$	$1/\sqrt{3}(\sqrt{2} 1, -1/2\rangle - 0, 1/2\rangle)$
$2p_{1/2}$	$ 1/2, -1/2\rangle$	$1/\sqrt{3}(0, -1/2\rangle - \sqrt{2} -1, 1/2\rangle)$

APPENDIX C

EXPERIMENTAL MATERIALS

C.1: ACMS Data Analysis

Once the data is collected, a set of frequency dependent scans can be generated as seen in figure C.1, where there are clearly peaks that shift in temperature as a function of the frequency at which the measurements are taken. This is the raw data for a small temperature range (from the 4 K - 300 K data set) of real chi intensity scan over the range of frequencies from 178 Hz -10,000 Hz. These frequency values are selected to give a uniform spacing in the $\log(f)$ Néel-Arrhenius plots.

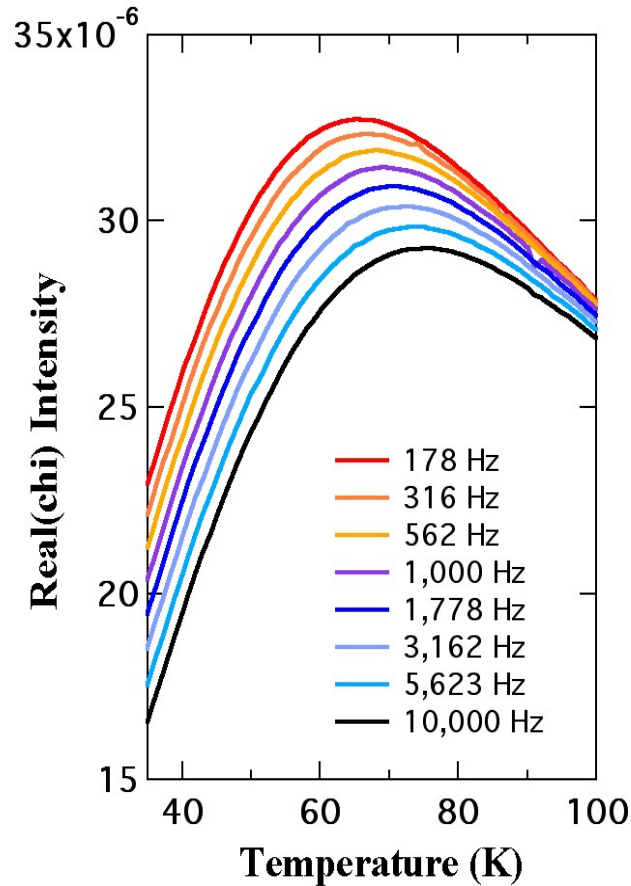


Figure C.1: ACMS Curve

To extract the blocking temperature, the Gaussian fit that is standard in the Igor software was used. Though the peak is clearly not Gaussian in shape, peaks can be

approximated as Gaussian when sufficiently close to the peak (approximately 10 pts are used in the fit and here that is exploited. A Gaussian fit does a good job of approximating the peak as can be seen in the figure C.2. In this figure the results of the fit are shown where x_0 is T_B .

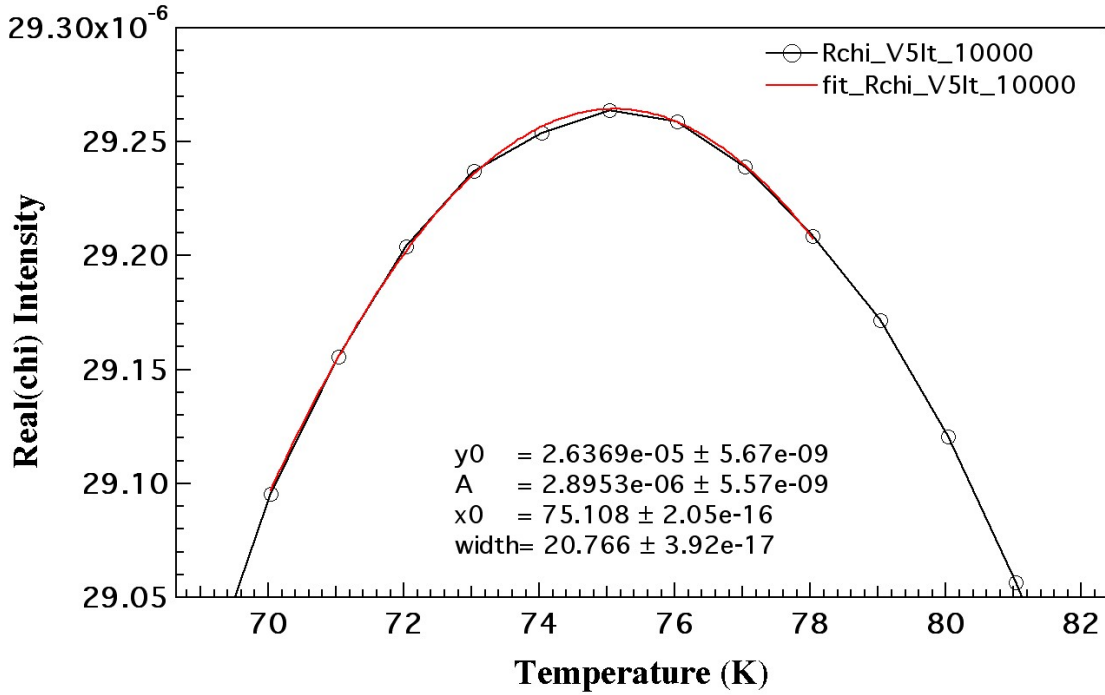


Figure C.2: ACMS Peak Fitting

Once the blocking temperature is extracted in this manner for all eight frequencies, the Néel-Arrhenius plot can be produced by plotting the inverse of the blocking temperature against the negative of the natural log of the inverse frequency as demonstrated in figure C.3. A linear fit to the data is done where the fit line is shown in red, 'a' is the intercept of the fit, and 'b' is the slope.

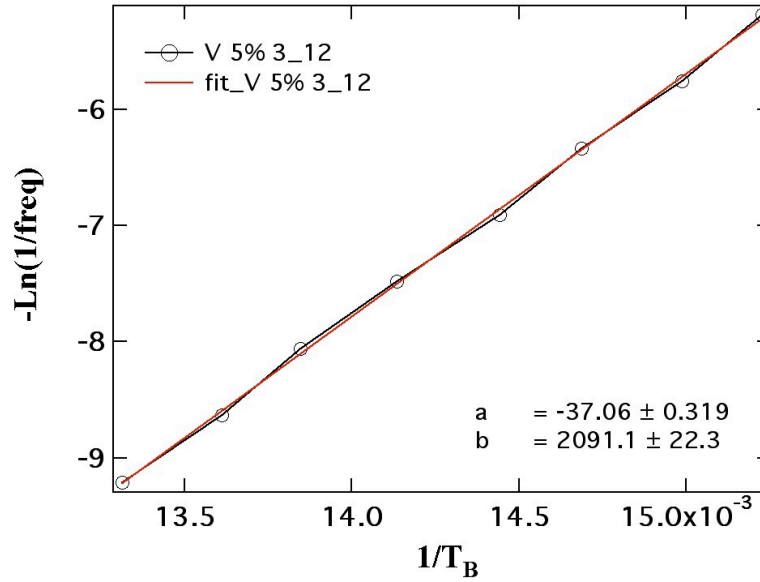
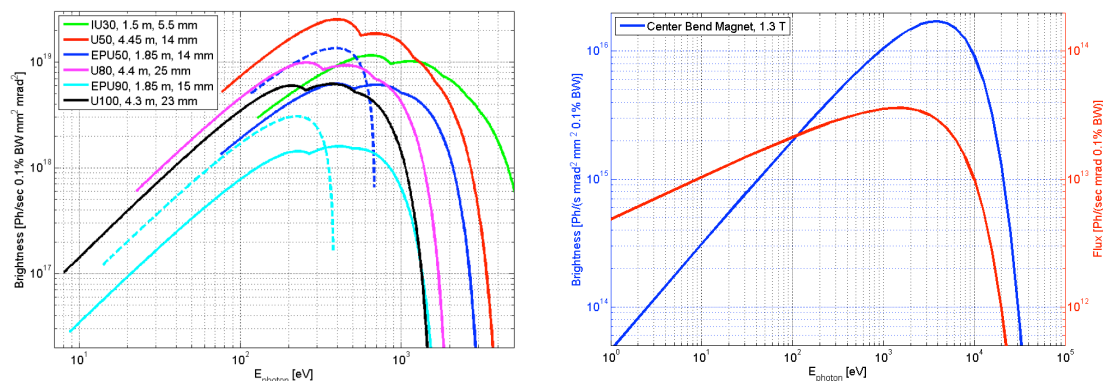


Figure C.3: Néel Arrhenius Plot

The slope is related to the anisotropy energy and the intercept is related to the attempt frequency, $\text{intercepted} = \ln(1/\tau_0)$, and the slope $= \Delta E / k_B$, where the anisotropy energy is the energy per nanoparticle rather than being normalized by unit volume as would be done for bulk materials. An intercept of negative 37 corresponds to an attempt frequency of the order 10^{-17}_{sec} (remember despite the name attempt frequency is in units of time), which is not a physically valid result. This indicates that even though the straight line fits the data well (usually an indication of non-interacting particles) the particles are weakly interacting and the Vogel-Fulcher law must be used. The fit using the Vogel-Fulcher law includes a T_0 term (indicative of the strength of the interaction), which is subtracted from the T_B before it is inverted making the x-axis $1/(T_B - T_0)$. In the work done on vanadium doped iron-oxide nanoparticles, when the Vogel-Fulcher law was applied, the T_0 value is the value which gives an attempt frequency of the desired value (between 10^{-9} and 10^{-12}).

C.2: Beamline Brightness Curves

These figures pulled of the ALS website are brightness curves for beamline 4.0.2 an undulator (left) and beamline 6.3.1 a bend magnet (right)



C.3: ACMS Scan File

This is a sample scan file used to running an ACMS measurement on the PPMS.

ACMS New Datafile

"C:\QDPPMS\Data\ldzerda\Vanessa\ACMS\V_Work\V_5_acmsscan.DAT"

Set Temperature 150K at 20K/min. Fast Settle

Scan Temp from 150K to 30K at 15K/min, in 91 steps, Uniform, Fast

AC Mag 178,316,562,1000,1778,3162,5623,10000 Hz 10 Oe 10 Sec

Stickyrange Flags=33554439

End Scan

Set Temperature 50K at 20K/min. Fast Settle

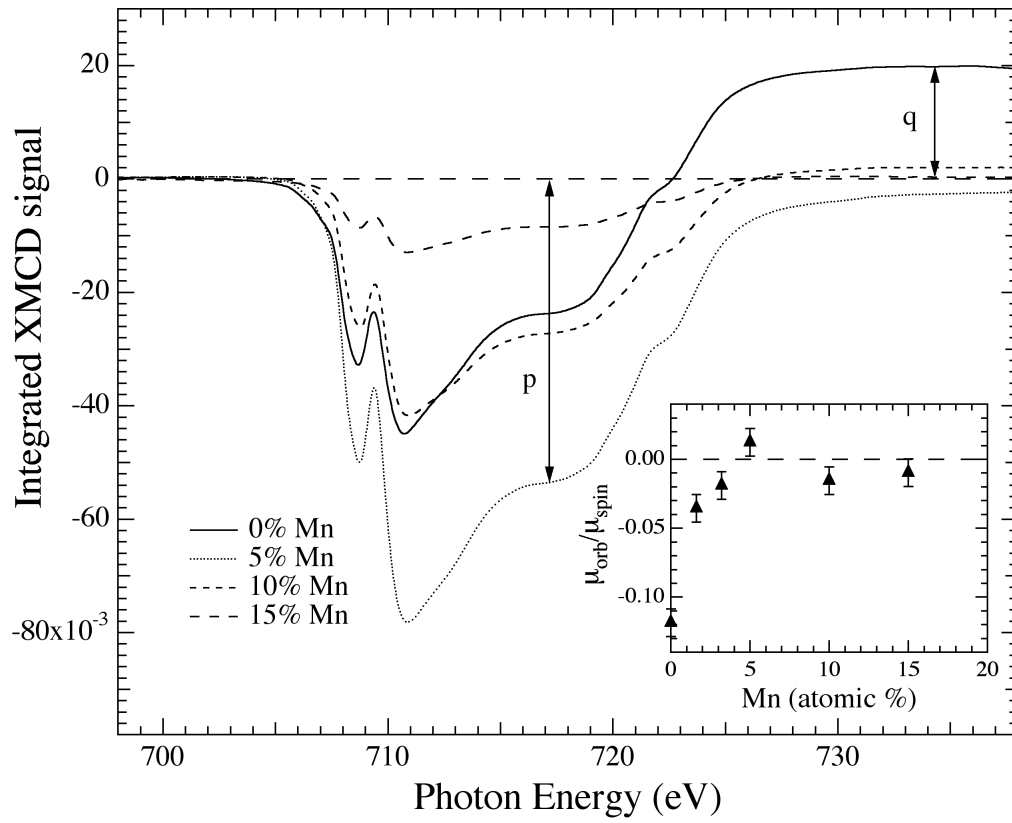
Shutdown Temperature Controller

APPENDIX D

ADDITIONAL DATA

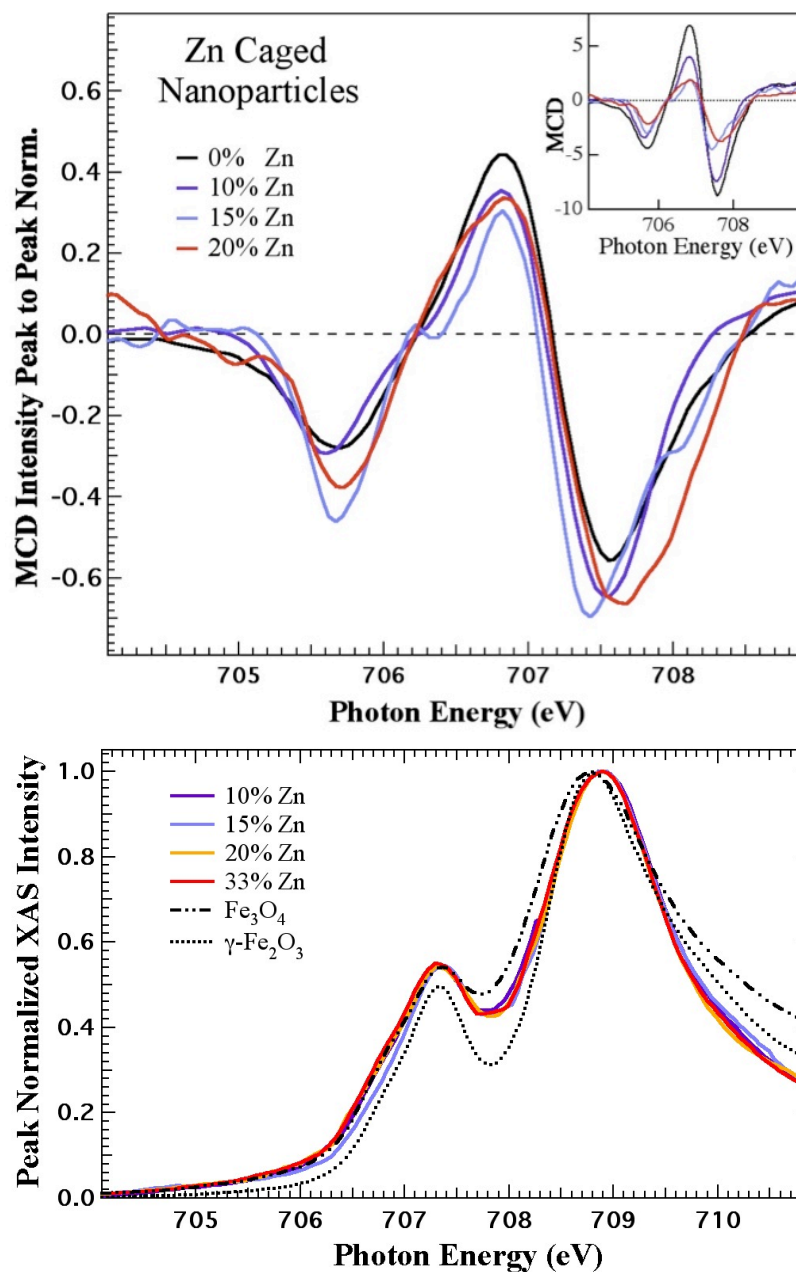
Appendix D.1: Integrated Iron L-edge XMCD

In the paper entitled "Orbital moment determination in $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ nanoparticles" the wrong figure was included as figure 3 in the paper. For Clarification the correct graph is included here.



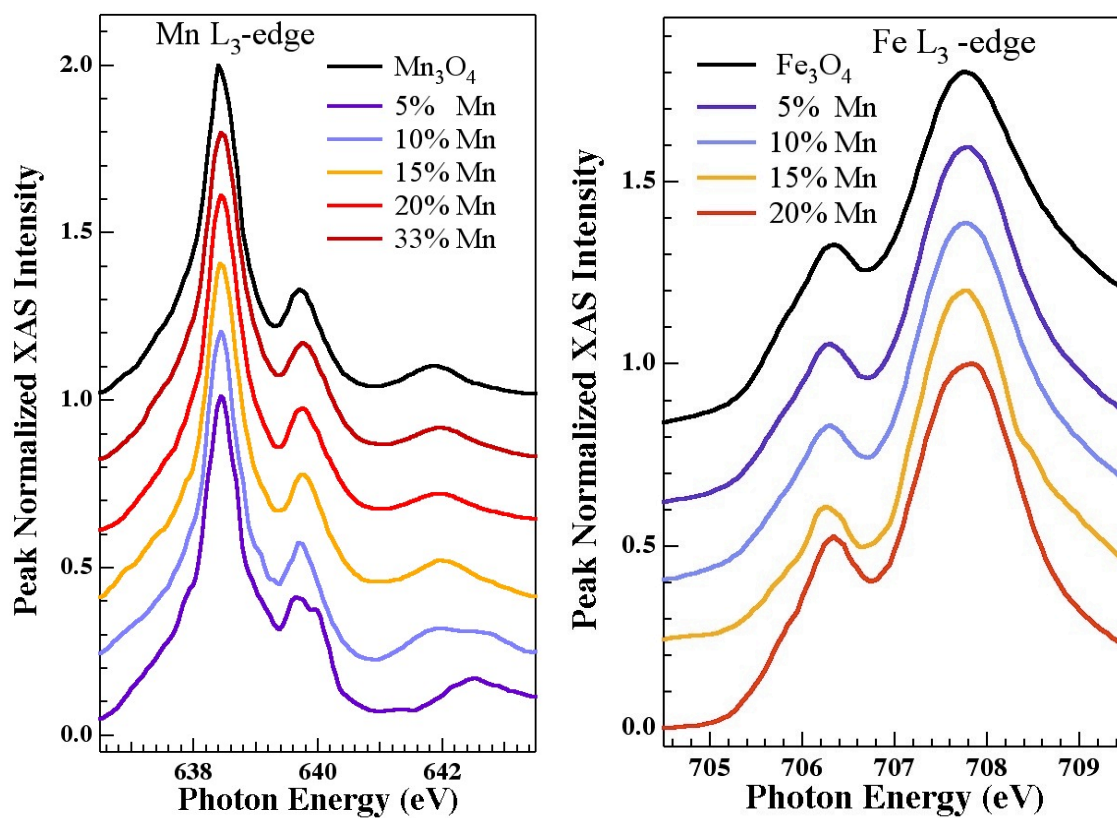
Appendix D.1: Caged Zinc Doped Iron Oxide Nanoparticles

XMCD of caged zinc doped nanoparticles normalized so that the octahedral 2+ to tetrahedral 3+ peak-to-peak height is 1. The inset shows the XMCD normalized as a percentage of the XAS spectra.



Appendix D.2: Caged Manganese Doped Iron Oxide Spinels

Here the XAS spectra for the iron L_3 -edge and the manganese L_3 -edge are shown for the caged particles made by Michael Klem and were not included in the paper.



Appendix D.3: Caged Vs. Uncaged Manganese Doped Iron Oxide Particles

The data presented here is from the work presented in chapter 6 and 7. The data is included here, even though it was included in the original papers in some form, because the figures were quite small, making their contents hard to discern.

