

SIZE DEPENDENCE OF THE MAGNETIC PROPERTIES OF COBALT OXIDE  
NANOPARTICLES MINERALIZED IN PROTEIN CAGES

by

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

of

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in

Physics

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Damon Aaron Resnick

November 2005

To my mother Nina,  
Wish you were here

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## ABSTRACT

A major question in the physics of magnetic nanoparticles is how the size affects the magnetic properties in magnetic nanoparticle systems. In particular, the magnetic properties can be affected by finite-size effects or surface effects. It is this author's belief that surface effects and not finite-size effects play the dominate role. This study is a specific example of how to try to answer this question by looking at different sizes of  $\text{Co}_3\text{O}_4$  nanoparticles.

In order to answer this question as well as better understand this system, different antiferromagnetic  $\text{Co}_3\text{O}_4$  nanoparticles of 4.35 nm and 6.3 nm in diameter were synthesized. These particles were determined to be relatively uniform and monodispersed. In this study, Transmission Electron Microscopy (TEM), electron diffraction (ED) and X-ray Absorption Spectroscopy (XAS) were used to study the physical and electronic structure of the nanoparticles.

Alternating Current Magnetic Susceptibility (ACMS) was used to measure the magnetic anisotropy energy density of the different size nanoparticles. It was found that the anisotropy energy density increases with decreasing size, from  $1.09 \times 10^4 \text{ J/m}^3$  for the 6.3 nm particles to  $7.53 \times 10^4 \text{ J/m}^3$  for the 4.35 nm particles, consistent with the importance of surface anisotropy with decreasing particle size. Vibrating Sample Magnetometry (VSM) was used to measure the Néel temperature and coercive field of the different particles. It was found that the Néel temperature decreases with decreasing size, from 40 K to 15 K, consistent with a simple surface approximation of the finite-size scaling theory, while the coercive field increased with decreasing particle size consistent with a surface model.

The main conclusion of this work is that surface effects and not finite-size effects play a major role in the change of the magnetic properties with size in  $\text{Co}_3\text{O}_4$  nanoparticles. The evidence also suggests that the increase in the anisotropy energy density is due to the creation of a surface anisotropy component normal to the surface of the particles.

## CHAPTER 1

## INTRODUCTION

With the continual miniaturization of technology, the world is quickly moving towards an age where nanotechnology will make an impact on everyday life. Nanotechnology can be defined as the fabrication of devices on the atomic or molecular scale,  $<100$  nm. This nano scale marks the nebulous boundary between the classical and quantum worlds, and the merging of these boundaries brings the promise of revolutionary capabilities. This dissertation focuses on this nano region and specifically explores what happens to the magnetic properties of  $\text{Co}_3\text{O}_4$  nanoparticles at small nanoscale sizes.

In an almost radical lecture titled *There's Plenty of Room at the Bottom*, in 1959, Richard P. Feynman expounded on how the amount of space available to us for information storage is enormous. He talked about how there is nothing besides our clumsy size that keeps us from using this space. He described how the laws of physics do not limit our ability to manipulate matter at the atomic and molecular scale. It is only that the tools and methods did not exist yet. Feynman thought of atomic scale fabrication as a *bottom-up*, rather than a *top-down* approach. In the macroscopic world, we are very familiar with making things smaller, but in order to build nanoscale devices we will have to start from the basic building blocks; atoms and molecules. Instead of taking away bits to make things smaller, starting with tiny bits to make larger devices more efficient brings the hope of giving devices more complexity and creating them with a more specific usefulness.

We are now in a time where the construction of nano-size devices is becoming a reality. This forces us to try to not only understand how to construct such devices but to try understanding their basic building blocks. This may sound strange, but if you think about it, physics is built around either understanding the macroscopic world or the atomic world. In fact the nebulous region, between the two, sees a meeting between the atomic and macroscopic worlds where the physics of many atoms overlap with the physics of a few atoms. In this region a plethora of new emerging properties come about that are not seen in either the atomic or the macro-scale worlds.

This dissertation explores one of the building blocks of future nano-scale devices, nanoparticles. Just as bricks are the building blocks of macroscopic structures, so nano-scale devices must be made of nano-size materials. One of those materials will almost certainly be nanoparticles. In general, the term nanoparticle can refer to any small particle on the nanometer scale. In this dissertation the term nanoparticle refers to a roughly spherical inorganic particle with a diameter below 50 nm and above 1 nm.

### Historical Perspective

Magnetic nanoparticles have been of extreme interest ever since they could be hypothesized and synthesized. As an example, superparamagnetism is an extremely interesting and simple solution to the effects of thermal disorder on small magnetically ordered particles. In fact, the theory of superparamagnetism goes back to the days of L. Néel,<sup>1</sup> E. C. Stoner and E. P. Wohlfarth,<sup>2</sup> as well as W. F. Brown<sup>3</sup> from the late 1940's through the 1960's when so much postulation and experimentation was being done to

figure out the nature of different types of magnetism. Néel<sup>1, 4</sup> was the first to derive the equation for what was termed superparamagnetism and is now called the Néel-Brown<sup>1, 3</sup> expression.

Nanoparticles provide a rare look at the low dimensional behavior of magnetically ordered materials. They inherently have a significant surface to volume ratio. These types of systems exhibit properties that can differ greatly from the bulk materials. As an example, superparamagnetism itself is a very extraordinary change in magnetically ordered materials. This behavior is only seen because of the low dimensional nature of these types of systems. Also, in some systems the surface of a nanoparticle was found to be an entirely different compound. For example, the earliest examples of exchange biased systems were found in Co nanoparticles with CoO shells.<sup>5-7</sup> In these systems the shell is antiferromagnetic and couples to the ferromagnetic core. This coupling produces a uni-directional shift in the hysteresis of the Co core called exchange bias. This behavior has since been theorized, seen, and characterized for magnetic thin-films.<sup>8-10</sup>

The surface can also affect the particles even if the surface is the same material as the core. Spins on the surface of nanoparticles can have different preferred axes of magnetization as well as having different anisotropy energies associated with these axes. These types of effects have a tendency to change the overall magnetic properties of nanoparticles. It has been postulated that the spins on a surface of a magnetic nanoparticle can have an additional magnetic anisotropy.<sup>11</sup> This surface anisotropy is a complex phenomenon and is still being studied and explored in order to understand its effects on nanoparticles. In this dissertation surface anisotropy will be used to explain

some of the changes in the magnetic anisotropy for these nanoparticles.

Finite-size effects have also been shown to play a significant role. Finite-size effects originate from the cut off of some characteristic length in the system due to the purely physical constraint of finite volume. In other words, if this characteristic length, or correlation length, becomes of the order of the length of the sample, the overall properties that this interaction produces can be affected. These effects can have a profound influence on the magnetic properties of nanoparticles. Finite-size effects find themselves competing with surface effects governing the change in the magnetic properties of nanoparticles. The investigation of both surface and finite-size effects on  $\text{Co}_3\text{O}_4$  is a primary concern in this study.

This dissertation explores how the magnetic properties of a specific antiferromagnetic material,  $\text{Co}_3\text{O}_4$ , change as the size is further reduced in this nanoscale region. The specific experiments performed to help increase understanding center around the magnetic measurements of different sized spherical nanoparticles of 4.35 and 6.3 nm diameter as well as different size particles from the literature. The two nanoparticles made for this study were synthesized inside spherical protein cages.

Recently many studies have been done on magnetic nanoparticles,<sup>12-15</sup> particularly, studies on antiferromagnetic nanoparticles have shown a stunning array of emergent properties reminiscent to the case of magnetic thin films compared to bulk materials.<sup>12, 16</sup> In the case of magnetic thin films, low dimensionality, surface and interface effects play a significant role. For magnetic nanoparticles, when the number of atoms that make up the surface become of the order of the number that make up the

remaining volume, the surface spins compete with the core, resulting in unusual magnetic properties. Magnetic nanoparticles have been intensely studied recently because of these interesting emergent properties, including their uses in a multiple assortment of technological applications, specifically certain bio-medical and hard drive densifying technologies.<sup>17-19</sup>

In this study biological containers as well as biological protein like structures were used as constraining vessels for the synthesis of  $\text{Co}_3\text{O}_4$  nanoparticles. With the help of organic synthesis these nanoparticles can be manufactured to be very uniform and monodisperse. Also the biological components naturally separate the magnetic particles creating a buffer between them that help to inhibit interparticle magnetic interactions. One of the biological containers used in this study is horse-spleen ferritin (HsFn), an iron-storage protein which is ubiquitous in nature. It has been found that the ferritin proteins and other similar protein cages can be emptied of their contents and mineralized with a multitude of different materials, forming monodisperse and highly uniform nanoparticles.<sup>20-22</sup> Studies of native ferritin and  $\gamma\text{-Fe}_2\text{O}_3$  mineralized ferritin have previously been reported.<sup>23-25</sup>

The mineralization of the nanoparticles inside biological containers is worthy of particular importance. Since the particles are inside biological containers they can now be manipulated with biological means. In fact, these biological containers like to arrange and assemble themselves without manipulation in a process called self-assembly. Additionally, the exterior of the proteins can be functionalized to favor a linkage with other biological entities. This could help in the construction of nano-size structures, or be

helpful with drug delivery.<sup>21, 26</sup> Also, the particle-protein system can be very useful in things like hyperthermia,<sup>27</sup> where the containers are functionalized to link to certain cells and then a high frequency magnetic field is set to oscillate. The increase in temperature of the particles causes the surrounding tissue to heat up and be destroyed. These types of applications are currently being explored as a means for cancer treatment. The details of the synthesis are outlined in chapter two.

### Co<sub>3</sub>O<sub>4</sub>

Co<sub>3</sub>O<sub>4</sub> is a traditional precursor of the anode material in Li-ion rechargeable batteries<sup>28</sup> and is an effective catalyst in the reduction of SO<sub>2</sub> by CO.<sup>29</sup> Further, Co<sub>3</sub>O<sub>4</sub> is helpful in the reduction of NO by methane<sup>30</sup> and in ammonia oxidation.<sup>31</sup> These properties make it a very useful material in environmental protection and chemical engineering.

Co<sub>3</sub>O<sub>4</sub> makes an interesting magnetic nanoparticle system. It is antiferromagnetic in the bulk and has a very complex structure with a low bulk Néel temperature. This low Néel temperature provides a small range of temperatures in which to study changing properties. Since it is antiferromagnetic its uncompensated spins can become a large fraction of the total number of spins for small particle sizes. This produces only a very small moment which makes the effects of interparticle dipole interactions negligible.

Co<sub>3</sub>O<sub>4</sub> is known to have a normal cubic spinel structure, displayed in Figure 1.1., and is antiferromagnetic in the bulk with a Néel temperature, T<sub>N</sub>, between 30 – 40 K.<sup>32-34</sup> The typical Co<sub>3</sub>O<sub>4</sub> unit cell has a lattice constant of 8.08 Å and contains 8 Co<sup>2+</sup> ions in

tetrahedral sites and 16  $\text{Co}^{3+}$  ions in octahedral sites. The  $\text{Co}^{2+}$  ions are ordered antiferromagnetically with magnetic moments of roughly  $3\mu_B$ , while the  $\text{Co}^{3+}$  ions behave diamagnetically and are in a low spin state.<sup>34</sup> The tetrahedral sites have four bonds to oxygen and the octahedral sites have six.

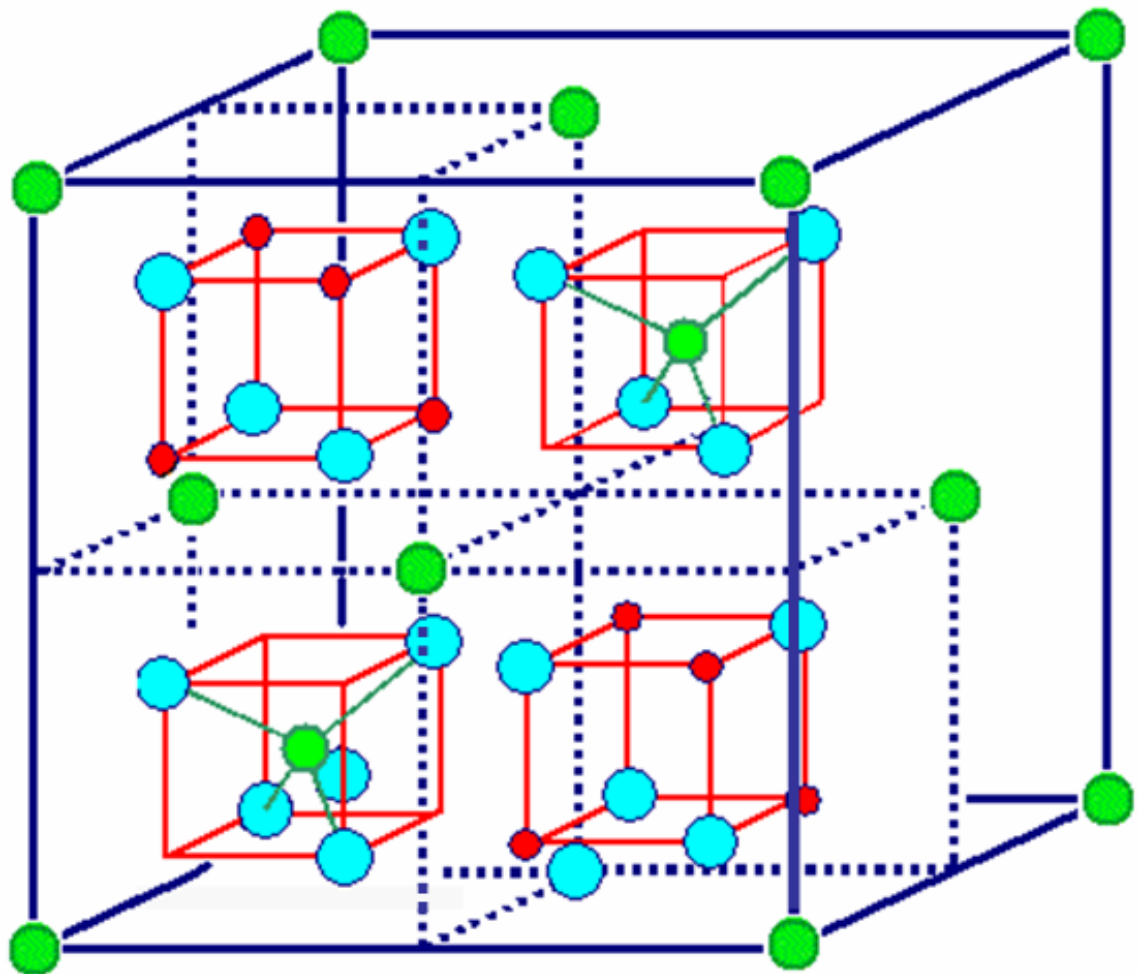


Figure 1.1: A typical normal spinel structure. The green circles represent the tetrahedral sites, the red circles represent the octahedral sites, and the blue circles represent the oxygen atoms.<sup>35</sup>

$\text{Co}_3\text{O}_4$  is known to have a normal cubic spinel structure, displayed in Figure 1.1., and is antiferromagnetic in the bulk with a Néel temperature,  $T_N$ , between 30 – 40 K.<sup>32-34</sup> The typical  $\text{Co}_3\text{O}_4$  unit cell has a lattice constant of 8.08 Å and contains 8  $\text{Co}^{2+}$  ions in tetrahedral sites and 16  $\text{Co}^{3+}$  ions in octahedral sites. The  $\text{Co}^{2+}$  ions are ordered antiferromagnetically with magnetic moments of roughly  $3\mu_B$ , while the  $\text{Co}^{3+}$  ions behave diamagnetically and are in a low spin state.<sup>34</sup> The tetrahedral sites have four bonds to oxygen and the octahedral sites have six.

Figures 1.2a and 1.2b show a blow up of typical tetrahedral and octahedral sites. Both sites overlap in the same unit cell and share oxygen atoms. The oxygen atoms surround the cobalt atoms, their wavefunctions overlap, hence the crystal field splitting of these different arrangements of oxygen atoms surrounding the cobalt atoms influence the magnetic nature of the cobalt ions creating different magnetic states for the two cobalt ions.

### Background

It is useful to note that a few other studies have been done on the size dependent effects on magnetic nanoparticles and similar systems. Some very interesting studies have been done in the Mørup group with the help of Bødker and Frandsen and others.<sup>36-38</sup> These papers are mainly focused on the behavior of  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles. Like  $\text{Co}_3\text{O}_4$ ,  $\alpha\text{-Fe}_2\text{O}_3$  is an antiferromagnetic material but with a much higher Néel temperature. These papers outline trends, similar to those presented in this study, for the dependence of the magnetic anisotropy energy density on the size of the particles. Another paper by

Tang *et al.*<sup>39</sup> on  $\text{MnFe}_2\text{O}_4$  nanoparticles, explores the effects of finite-size on the Curie temperature of these particles. The behavior and extracted parameters they found follow a model for finite-size scaling. In the case of their  $\text{MnFe}_2\text{O}_4$  particles, the Curie temperature was perceived to increase with smaller particle sizes instead of decrease. In a paper by Ambrose and Chien,<sup>40</sup> the finite-size effects on CoO thin-films were studied. They found a decrease of the Néel temperature with thin-film thickness in antiferromagnetic CoO thin-films similar to what is seen in this dissertation for  $\text{Co}_3\text{O}_4$  with decreasing diameters. Another study of antiferromagnetic CuO nanoparticles and nano-rods by Zheng *et al.*<sup>41</sup> found a decrease in the Néel temperature.

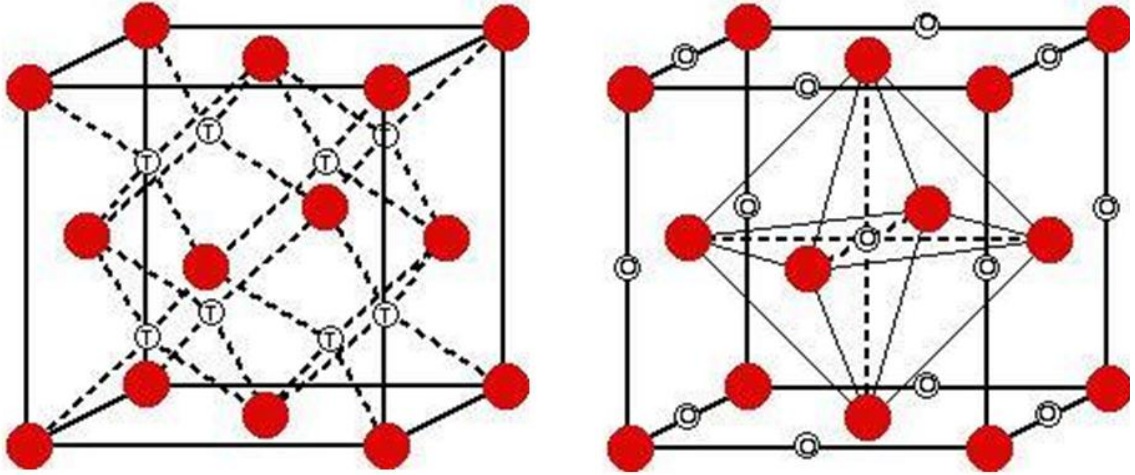


Figure 1.2: a) Tetrahedral sites in a normal spinel structure. The tetrahedral sites are labeled, T, and are associated with the position of the antiferromagnetic  $\text{Co}^{2+}$  ions. The red circles are the oxygen atoms. b) Octahedral sites in a normal spinel structure. The octahedral sites are labeled, O, and are associated with the position of the diamagnetic  $\text{Co}^{3+}$  ions. The red circles are the oxygen atoms.

Other studies of  $\text{Co}_3\text{O}_4$  nanoparticles have been undertaken by a few other groups. Some of the first studies performed on so called fine particles of  $\text{Co}_3\text{O}_4$  were conducted by Kundig *et al.*<sup>42</sup> in the late 1960's. Using Mössbauer spectroscopy they determined the basic magnetic properties of  $\text{Co}_3\text{O}_4$ . More recently in a paper by Takada *et al.*<sup>43</sup> in 2001, in which 3 nm  $\text{Co}_3\text{O}_4$  particles were studied, very similar behavior to the particles used in this study was seen. They did ac-susceptibility and dc-magnetometry and measured the anisotropy energy density, magnetic moment, and hysteresis of 3 nm  $\text{Co}_3\text{O}_4$  particles. Another paper in which 20 nm  $\text{Co}_3\text{O}_4$  particles were studied by Makloun *et al.*<sup>44</sup> in 2002, outlined some of its basic properties. They found exchange bias in their particles. There are also a few papers from Li *et al.*<sup>45, 46</sup> in 2004, which study 15 nm  $\text{Co}_3\text{O}_4$  particles outlining some peculiar properties. Throughout this dissertation these papers will be referred back to as references to the determined nature of similar  $\text{Co}_3\text{O}_4$  nanoparticles.

### Outline

This dissertation explores how the size affects the magnetic properties of nano-sized spherical particles of  $\text{Co}_3\text{O}_4$ . In particular different sizes of  $\text{Co}_3\text{O}_4$  nanoparticles are studied and compared. The diameter of the particles synthesized for this study is 4.35 and 6.3 nm. These two particles were synthesized inside biological protein cages and were then electronically and magnetically characterized.

This study explores how different sized particles from this study, and others, have slightly different properties and how this behavior can be modeled in order to understand

why these particles behave the way they do. Specifically, the change in the magnetic anisotropy energy density, Néel temperature, particle moment, and coercive field are modeled with particle size. The insight gained from the change in these different properties is used to form a physical model. This model is then used to gain a better understanding of how the spins in the material behave, interact, and arrange themselves at these low dimensions.

The first chapter is the introduction, which introduces, motivates, and gives a background to the topic. Chapter two outlines the basics of the synthesis and preparation of the samples as well as details the experimental techniques for determining and characterizing the structural, chemical, and magnetic nature of the samples.

Chapter three introduces the theory of antiferromagnetism and superparamagnetism. It outlines the best ways of determining the anisotropy energy and Néel temperature and provides a framework for the understanding of the basic physical concepts underlying this body of work.

In chapter four the theories behind the origin of the Néel temperature and the anisotropy energy are discussed as well as previous work done with their dependence on size. This is presented to compare these results and use these models in order to better understand the phenomena explored in this dissertation.

Chapter five explores the new data collected and attempts to answer the question of how and why the anisotropy energy density of  $\text{Co}_3\text{O}_4$  nanoparticles changes with size. To tackle the problem the anisotropy energy density of the nanoparticles is measured with the help of the ACMS. Next the particles are modeled and compared to similar

systems in an attempt to better understand these data and answer the questions posed. This chapter outlines a model for the change in anisotropy with particle size that differs from previous models.

Chapter six tries to answer the question of how and why the Néel temperature and coercive field for these  $\text{Co}_3\text{O}_4$  nanoparticles changes with size. In order to tackle this problem a way must be found to measure the Néel temperatures of each nanoparticle. This turns out not to be a trivial matter, due to the superparamagnetic nature of the particles and their low blocking temperatures. The Néel temperature and coercive field for the different nanoparticles are modeled in order to understand how and why they change. To do this, the VSM data is analyzed and the magnetic properties, such as the saturation moment, are also studied and discussed. The magnetic moment is also measured and its size dependence is studied.

Chapter seven is the summary and conclusions. The last chapter finalizes this study by discussing and remarking on the conclusions so far presented. It summarizes the dissertation and remarks about the future of this work and the implications of the conclusions.

## CHAPTER 2

## EXPERIMENT

Introduction

The study of magnetic nanoparticles can be a very intricate and complicated task. Many different issues come up during such an undertaking and a careful and scientific approach used. This study is broken up into several experiments which first includes the synthesis of the nanoparticles. The particles are synthesized with the help of biological components, in a chemistry lab. After the synthesis several techniques for determining the quality of the synthesis must be undertaken. Then the particles themselves are examined for uniformity and size, and the quality of the crystal structure is then examined. Finally, characterizations of the magnetic properties of the nanoparticles are undertaken and experiments are performed in order to better understand their magnetic properties.

This chapter focuses on the details of the experiments performed in this study. The different experiments are outlined in chronological order. Whenever possible the relevant information is presented in a detailed and specific way and referenced. If presenting the details for a specific part of an experiment is too involved then the information is presented in a more general way and the details are referenced and shown at the end of this dissertation. In some cases even this is difficult to do and so the relevant information is only referenced.

### Synthesis

The protein cage samples used in this study were made by either Dr. Michael Klem or Mark Allen in the Trevor Douglas group in the Montana State University Department of Chemistry and Biochemistry. Protein cages were either purchased or supplied from the Mark Young group in the Montana State University Department of Plant Sciences.

The particles synthesized for this study were made with the help of small biological protein containers. Some of the motivations for this work and the work of collaborators come from the amazing nano-sized structures that nature all by itself can create. Being inspired by these tiny incredible creations we have tried to emulate what nature has already done and tailor specific creations for our own uses. In this effort we have undertaken to emulate what native ferritin and other similar proteins can do naturally,<sup>47</sup> mineralize iron into a spherical particle, and create spherical particles of the composition and mineral phase of our choosing. In the end there could be a multitude of advantages to this. First, since the particles would be inside biological entities the particles would then go where the protein went. The proteins could be manipulated using biological and chemical process to bond specifically to other proteins or materials. This sets the stage for the construction of nano-sized structures. Also these proteins naturally like to assemble themselves into patterned arrays. With particles inside these proteins two dimensional arrays of particles can then be constructed. Besides these uses the mineralization of the nanoparticles with the help of biological containers creates an

environment for the growth of spherical particles separated by protein which prevent the particles from growing together to form larger and asymmetric particles. This also helps by being a buffer that inhibits magnetic and electrostatic interactions that could affect the properties of the magnetic nanoparticles by separating the particles physically with a non-magnetic matrix.

The synthesis of the smaller particles used in this study was accomplished by the mineralization of  $\text{Co}_3\text{O}_4$  inside two different protein cages. The smallest cage used is the *Listeria innocua* Dps, or LDps for short. This sample was made by Mark Allen in the Trevor Douglas lab at MSU. LDps was expressed and purified to homogeneity from an *E. coli* expression system outlined in a paper by Allen *et al.*<sup>48</sup> It is composed of 12 identical 18 kDa subunits, which self-assemble into an empty cage having 23 symmetry, (Figure 2.1),<sup>49-52</sup> and has an outer diameter of 8.5 nm and an inner diameter of 5 nm with 0.8 nm pores at subunit interfaces allowing molecular access to the interior. These pores or ion channels allow  $\text{Co}^{2+}$  ions to penetrate into the interior for the size constrained synthesis of  $\text{Co}_3\text{O}_4$ .

Native horse-spleen ferritin was also used as the growth vessel for  $\text{Co}_3\text{O}_4$  nanoparticles. (Figure 2.2) Native horse-spleen ferritin, or HsFn, is an iron-storage protein found ubiquitously in nature. It has a spherical shell with an external diameter of 12 nm and an inner cavity diameter of 8 nm.<sup>47</sup> A fully loaded, naturally occurring mammalian ferritin protein possesses an antiferromagnetic 8 nm iron oxyhydroxide core,  $(\text{Fe}(\text{O})\text{OH})$ , with roughly 4500 Fe atoms.<sup>53</sup> HsFn can be emptied of its contents and then mineralized with  $\text{Co}_3\text{O}_4$  nanoparticles.

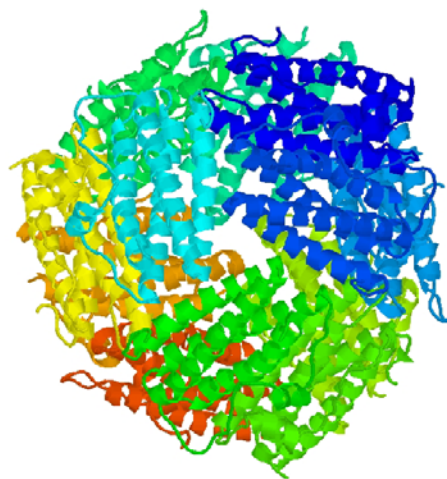


Figure 2.1: A ribbon diagram of LDps looking down the 3-fold channel.

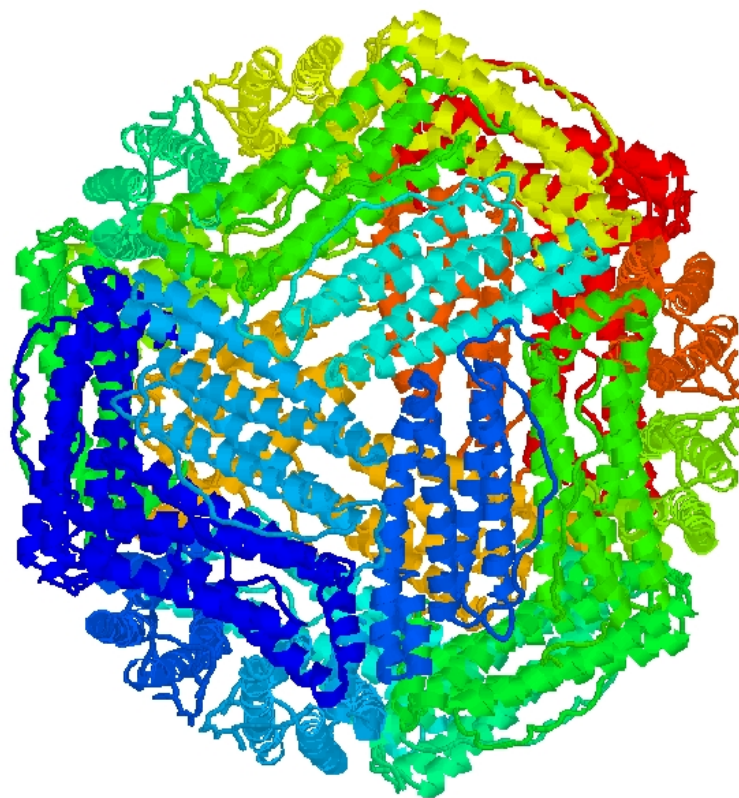


Figure 2.2: A ribbon diagram of HsFn.

Mineralization of the HsFn is accomplished, similar to LDps, utilizing the fact that the interior of the empty cages have a negative electromagnetic charge. The empty cages were suspended in a salt solution and brought to a temperature of 65 °C and a pH of 8.5.  $\text{Co}^{2+}$  ions were then loaded into the solution slowly as well as de-aerated solutions of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and the oxidant  $\text{H}_2\text{O}_2$  constantly over a 15 minute period. Slowly the  $\text{Co}^{2+}$  ions entered into the interior of the protein cages and oxidized into the  $\text{Co}_3\text{O}_4$  crystal phase. Since the growth was both size and shape constrained the resulting crystals were generally spherical nanoparticles with diameters smaller than the interior of HsFn or LDps in that case.

An attempt to make larger particles of  $\text{Co}_3\text{O}_4$  failed with two different methods. Both these particles, particles mineralized inside the Cowpea Chlorotic Mottle Virus (CCMV) and particles made using carboxyl-terminated dendrimers (generation 4.5, Dendritech), were found to be mixtures of the different cobalt oxide phases and were therefore unsuited to this study.

Because of the difficulties of synthesizing the larger particles, particles from Sigma-Aldrich were used. These purchased particles came in the form of  $\text{Co}_3\text{O}_4$  powders. The powders were characterized with X-ray Diffraction (XRD) and were determined to have the same structure as bulk  $\text{Co}_3\text{O}_4$ . The nano meter sized particles from Sigma-Aldrich have diameters between 20 – 30 nm. For this study the diameter of these particles is taken to be  $25 \pm 5$  nm. The micron sized particles from Sigma-Aldrich have diameters less than 10  $\mu\text{m}$ . The diameter of these particles is taken to be 5  $\mu\text{m}$  or  $5000 \pm 3000$  nm.

## TEM

Transmission Electron Microscopy (TEM) was used to determine the size and characterize the mineral phase of the cobalt oxide particles mineralized inside the protein cages. The data was collected on a Leo 912, with  $\Omega$  filter, operating at 80 keV. The mineralized samples were concentrated onto carbon coated copper grids and were imaged both stained with uranyl acetate and unstained.

The  $\text{Co}_3\text{O}_4$  nanoparticles in LDps were imaged by Allen *et al.*<sup>52</sup> They were found to be spherical and monodispersed with an average diameter of  $4.35 \pm 0.55$  nm, consistent with the maximum 5 nm interior of the LDps cage. Figure 2.3 shows TEM images and electron diffraction (ED) measurements of the LDps sample taken from Allen *et al.*<sup>52</sup> with the permission of the author. The electron diffraction measurements in the TEM have shown the nanoparticles to have the structure and d-spacings of  $\text{Co}_3\text{O}_4$ . (Figure 2.3, Table 2.1)

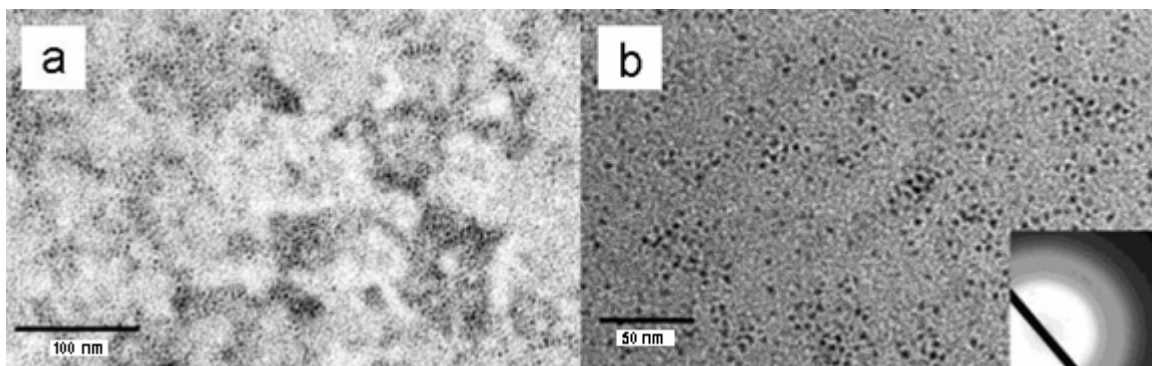


Figure 2.3: a) TEM image of the  $\text{Co}_3\text{O}_4$  in LDps in uranyl acetate. b) TEM image of the  $\text{Co}_3\text{O}_4$  in LDps unstained. The inset is the electron diffraction of the  $\text{Co}_3\text{O}_4$  in LDps.<sup>52</sup>

| Measured d-spacing | d-spacing for Co <sub>3</sub> O <sub>4</sub> | Miller Indices |
|--------------------|----------------------------------------------|----------------|
| 2.4 Å              | 2.432 Å                                      | 311            |
| 2.0 Å              | 2.016 Å                                      | 400            |
| ---                | 1.55 Å                                       | 333            |
| 1.4 Å              | 1.426 Å                                      | 044            |

Table 2.1: The measured d-spacings of the LDps mineralized particles determined from electron diffraction pattern compared to the known spacing of bulk Co<sub>3</sub>O<sub>4</sub>. From comparison of these spacings we conclude that the particles are Co<sub>3</sub>O<sub>4</sub>.

TEM done by Eric Smith on the HsFn particles showed monodispersed spherical nanoparticles with an average diameter of  $6.3 \pm 0.5$  nm, consistent with the maximum 8 nm interior of the HsFn cage. Electron diffraction measurements in the TEM showed the nanoparticles to be consistent with the structure and d-spacings of Co<sub>3</sub>O<sub>4</sub> (Table 2.2, Figure 2.4). It should also be noted that high resolution transmission electron microscopy (HRTEM) of similar particles show that particles made in these fashions are mostly single crystal and single domain.

| Measured d-spacing | d-spacing for Co <sub>3</sub> O <sub>4</sub> | Miller Indices |
|--------------------|----------------------------------------------|----------------|
| 2.494 Å            | 2.432 Å                                      | 311            |
| 2.078 Å            | 2.016 Å                                      | 400            |
| 1.594 Å            | 1.552 Å                                      | 333            |
| 1.468 Å            | 1.426 Å                                      | 044            |

Table 2.2: The measured d-spacings of the HsFn mineralized particles determined from electron diffraction pattern compared to the know spacing of bulk Co<sub>3</sub>O<sub>4</sub>. From comparison of these spacings we conclude that the particles are Co<sub>3</sub>O<sub>4</sub>.

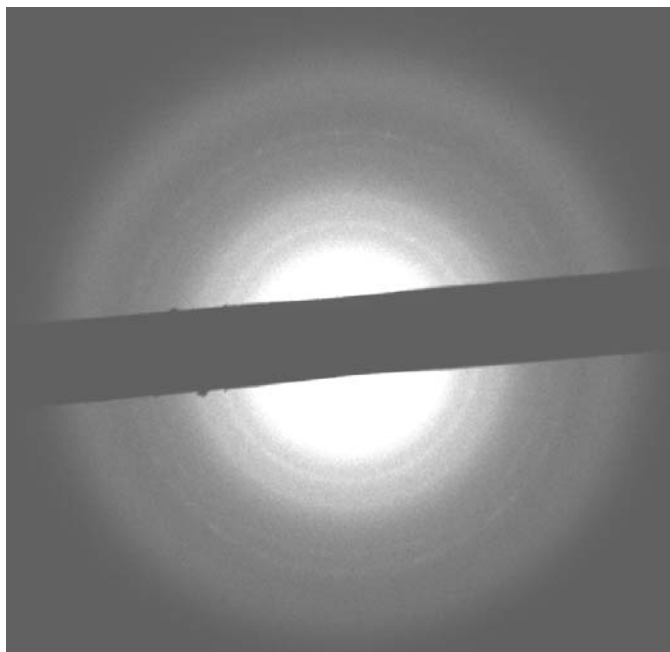


Figure 2.4: Electron diffraction image of the  $\text{Co}_3\text{O}_4$  in HsFn used to get the d-spacings in the table below.

### XAS

X-ray Absorption Spectroscopy, XAS, is a very useful synchrotron technique. Like most synchrotron techniques the energy of the photon stream bombarding the sample is changed. While the energy is being scanned the electron yield current or the transmission of the light through the sample is measured to get the proportion of light absorbed at discrete energies. Each material has a unique absorption spectra that is related to its chemical structure and conduction bands. This technique is a way to probe the electronic structure of a material. For more in-depth information about this technique see the useful books on the subject or excellent papers on using the XAS technique.<sup>54-56</sup>

All XAS spectra were taken at either the Brookhaven National Lab Beam-line U4-B at the National Synchrotron Light Source, or the Advanced Light Source beam-line 4.02 at Lawrence Berkeley National Lab. XAS spectra of the protein cage samples presented in this dissertation were taken in transmission while the spectra of the powder samples were taken using the electron yield technique.

In order to obtain good quality XAS spectra the protein cage encased nanoparticles, in solution, were dried out on formvar coated copper TEM grids and placed in the beam in front of a CCD camera. The transmitted light was then measured by the CCD camera as the photon energy was scanned through the  $L_3$  and  $L_2$  edges of cobalt, roughly from 770 – 800 eV. The spectra are then compared to the XAS spectra of bulk  $\text{Co}_3\text{O}_4$  powder,  $\text{CoO}$  powder, and large nanoparticle powders of  $\text{Co}_3\text{O}_4$  purchased from Sigma-Aldrich, whose structure was verified using XRD. Spectra of  $\text{CoO}$   $\text{Co}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  thin films can be found in the literature.<sup>57, 58</sup> The XAS for the powders were taken by Joseph Dvorak at NSLS with the electron yield technique in which the electrons freed from the samples during absorption are measured. XAS for the particles were taken with the help of Keith Gilmore and Joe Dvorak at the NSLS and Elke Arenholz and Marco Liberati at the ALS.

Data for the LDps and HsFn samples as well as the larger particle powders used in this study are shown in Figure 2.5. The  $\text{Co}_3\text{O}_4$  nanoparticles synthesized for this study match up well with the bulk spectra of  $\text{Co}_3\text{O}_4$  as well as the larger nanoparticles. The LDps shows a slightly different peak ratio in the first  $L_3$  peak while the HsFn sample shows a slightly raised bump between 773 and 774 eV corresponding to what could be an

extra contribution of  $\text{Co}^{2+}$ . Since nanoparticles have such a large surface to volume ratio the finite-size and termination of the lattice on the surface leaves uncoordinated cobalt atoms. This can slightly change the XAS spectra of the nanoparticles creating slightly different spectra that resemble the different cobalt oxide spectra but are not linear combinations of them. Also since these particles are superparamagnetic the uncompensated spins must be a significant fraction of the bulk material. These uncompensated cobalt spins could contribute to a slight difference between bulk and nanoparticle spectrums. These types of effects are just a few of the changes that finite size can bring about in the XAS spectra of nanoparticles.

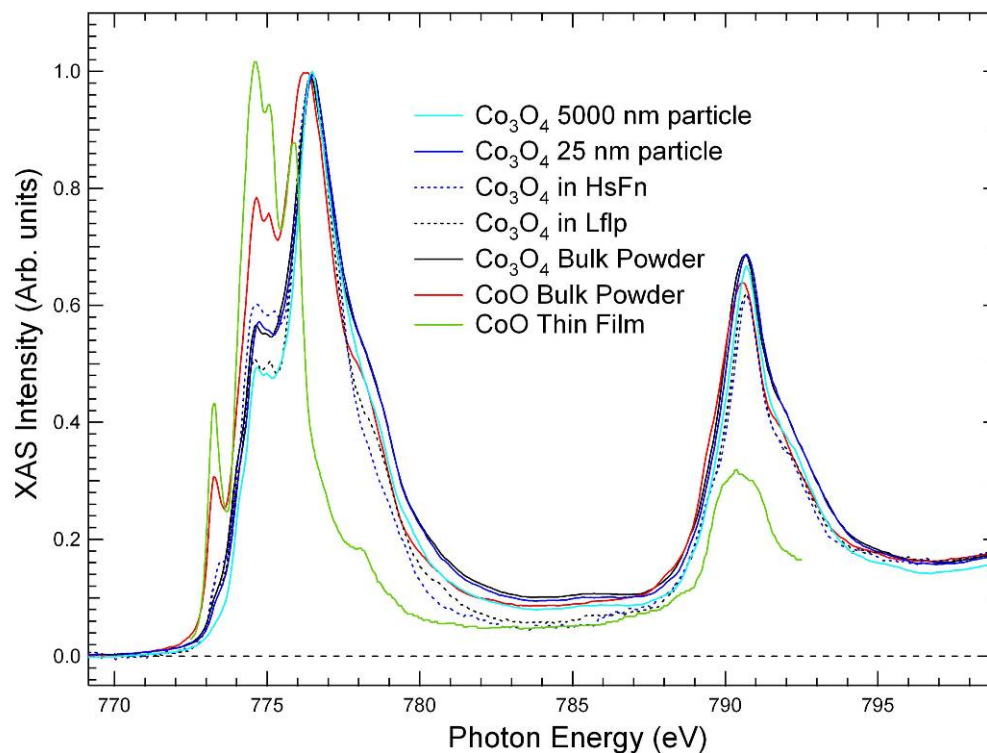


Figure 2.5: XAS of  $\text{Co}_3\text{O}_4$  nanoparticles compared to bulk  $\text{Co}_3\text{O}_4$  and bulk CoO.

It should be noted that a CoO thin film spectra taken from, Regan *et al.*<sup>58</sup>, is also shown in this figure. Evidently the CoO powder used as a baseline for the XAS data is likely to be composed of a contribution of CoO and Co<sub>3</sub>O<sub>4</sub>. This is noticeable in a few different respects. One is the slight shift of the main peak of the CoO powder from the Co<sub>3</sub>O<sub>4</sub>'s peak energy to the lower energy of the CoO thin film main peak. Also the double peaked feature at 774 eV is below the thin film feature at that energy and the ratio of the first peak at 773 eV is now larger than the 774 eV peak, just like CoO and not like Co<sub>3</sub>O<sub>4</sub>. It should also be mentioned again that X-ray Diffraction was done on all the powder samples in this study. All the powders corresponded well to the bulk XRD patterns associated with their respective materials, including the CoO powder. Since XRD can not detect below 5% composition very well, and the electron yield technique used in XAS probes mostly the first 100 Å of a sample, then the most likely conclusion is that the CoO powder has a significant contribution of Co<sub>3</sub>O<sub>4</sub> that is mainly on the surface of the big CoO powder particles.

### ACMS

Alternating Current Magnetic Susceptibility (ACMS) is a very useful technique for looking at superparamagnetic materials. In this study the ACMS option for the Quantum Design Physical Property Measurement System (PPMS) was used to study the samples. The standard PPMS 6000 was used to control the magnet, temperature and other relevant variables while the Model 6500 PPMS Option Controller was used to control the ACMS itself. The PPMS has a liquid helium dewar and can take

measurements with the ACMS down to a limit of 2 K.



Figure 2.6: The PPMS control system along with the helium dewar where the superconducting magnet and magnetic probes measure the magnetic properties.

The ACMS measures the magnetic moment and susceptibility of a sample by measuring the induction in two counter-wound coils while an ac-field is being applied. Voltage induction in the coils is directly related to the magnetic moment in the sample. This device has a range of 10 – 10000 Hz and a maximum amplitude of 20 Oe. Measurements presented in this dissertation were all taken with a 10 Oe amplitude.

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Figure 2.7: The ACMS option head.

Ac-magnetometry can be understood in terms of dc-magnetometry with a small ac-field. In this case the magnetic moment of the sample follows the  $M(H)$  curve that would be measured in a dc measurement. However, if the ac-field is small, the induced ac moment is given by

$$M_{AC} = \left(\frac{dM}{dH}\right) \cdot H_{AC} \sin(\omega t), \quad (2.1)$$

where  $H_{AC}$  is the amplitude of the driving field,  $\omega$  is the driving frequency, and  $\chi = dM/dH$  is called the susceptibility and is just the slope of the  $M(H)$  curve. For different applied dc fields, the different portions of the  $M(H)$  curve are measured, and so different susceptibilities are measured. The ac measurement is sensitive to small changes in  $M(H)$ , because it measures the slope of the  $M(H)$  curve. Hence small magnetic shifts can be detected even if there is a large moment. Going to higher frequencies the ac moment does not necessarily follow the dc magnetization curve due to dynamic effects in the sample. In fact, the ac-susceptibility may lag behind the drive field. This lag is measured by the ACMS and so the susceptibility is reported as two quantities, an in-phase, or real, component,  $\chi'$  and an out-of-phase, or imaginary, component,  $\chi''$ .

$$\begin{aligned} \chi' &= \chi \cos(\varphi) \\ \chi'' &= \chi \sin(\varphi) \end{aligned} \quad (2.2)$$

In this study all of the frequency dependent ac magnetometry measurements were taken at 100, 200, 300, 500, 1000, 2000, 3000, 5000, and 10000 Hz with an oscillation amplitude of 10 Oe, while being cooled in a zero dc field down to 2 K. Samples for the ACMS were prepared by drying out  $\text{Co}_3\text{O}_4$  mineralized cages, immobilizing them with epoxy into a small pellet form, and then placing them in plastic straws that fit on the end of the ACMS sample rod which goes into the ACMS option probe sitting down inside the

helium dewar. (Figure 2.6) The ACMS is primarily used in this study to find the blocking temperatures of the particles as well as to determine the anisotropy energy densities and attempt times.

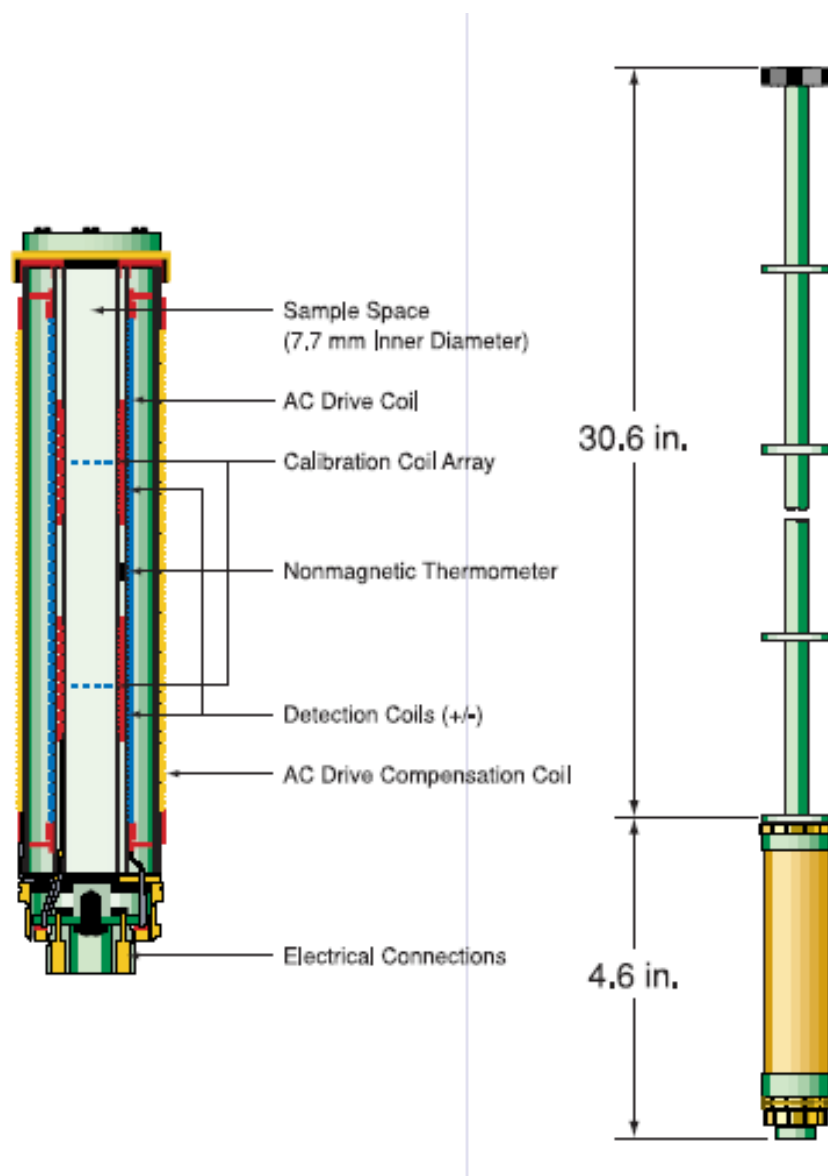


Figure 2.8: ACMS coil-set and dewar probe.

VSM

Similar to the ACMS the Vibrating Sample Magnetometer (VSM) is an option for the Quantum Design PPMS and is controlled with the Model 6000 and 6500. Samples are prepared in a similar way as for the ACMS. Particles are dried out and pressed into a pellet and glued to a VSM quartz sample paddle with Devcon Duco cement. Also like the ACMS, the VSM has two counter wound coils where a sample can sit deep down in the dewar at the center of the magnet where the field is homogenous. The sample is held inside the coil-set with a long rod that is driven by a linear motor. The motor drives the rod, and hence the sample, up and down in a sinusoidal manner with an amplitude of 1-3 mm at a frequency of 40 Hz. By moving the samples in this manner the PPMS can measure the magnetic moment of the sample

The basics of the theory of operation of the VSM are presented below. If the sample is magnetized, the oscillating sample produces a changing magnetic flux,  $\Phi$ , that the two coils pickup by the generation of a current. This potential difference generated,  $V_{coil}$ , is then equal to the change in flux per unit time,  $t$ , given by

$$V_{coil} = \frac{d\Phi}{dt} = \left( \frac{d\Phi}{dz} \right) \left( \frac{dz}{dt} \right), \quad (2.3)$$

where  $z$  is the position of the sample.

The potential difference measured is then related to the change in time of the position of the sample by

$$V_{coil} = 2\pi f C m A \sin(2\pi f t), \quad (2.4)$$

where  $f$  is the frequency of oscillation, 40 Hz,  $A$  is the amplitude of oscillation, 1-3 mm,  $C$  is a coupling constant, and  $m$  is the magnetic moment that we want to measure.

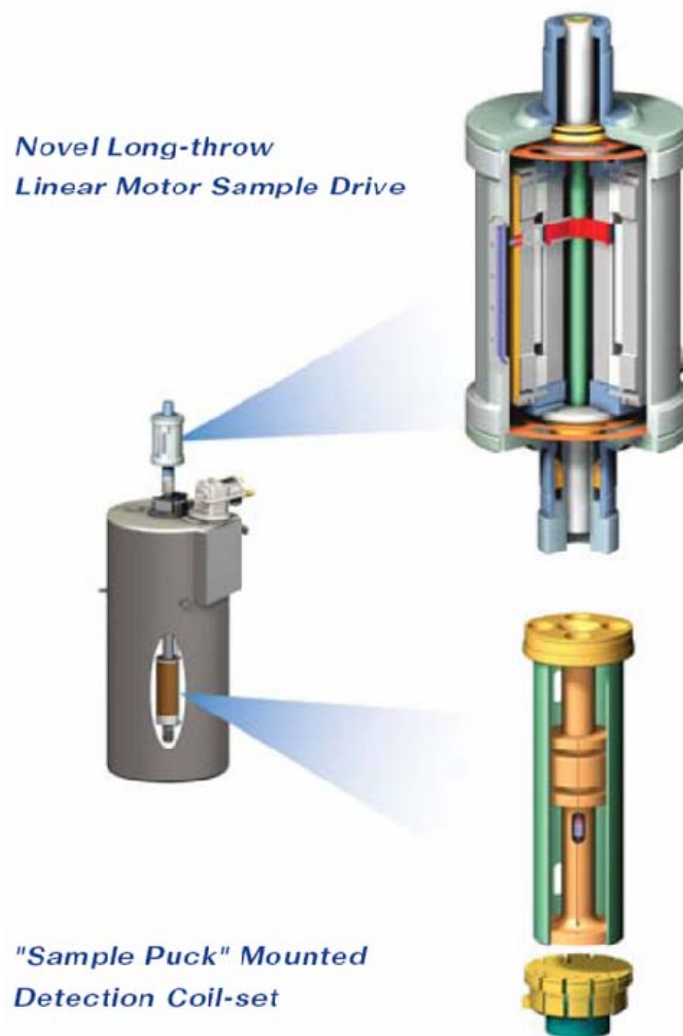


Figure 2.9: The VSM head, which houses the linear motor, as well as the VSM coil-set and probe.

The magnetic moment of the sample is generated because of the applied field of the superconducting magnet inside of the dewar. This field induces a different magnetic moment as the field changes and so the magnetic moment is measured versus the magnetic field applied to the sample.

For this study VSM measurements are typically made by measuring the magnetic moment of the samples at different temperatures as the applied field is being changed from 0 – 8 T. These scans are called initial magnetization curves. They simply show how the samples respond to an increasing applied magnetic field at different temperatures. These measurements help to pinpoint primarily the Néel temperature of the particles as well as helping to quantify the magnetic moment of an individual particle. Other standard hysteresis measurements are also made from  $\pm 8$  T in order to measure the coercive field and determine if any exchange bias is evident.

The experiments that are done in this study are all standard measurements that can be found throughout the literature. It should be pointed out that the synthesis is the most atypical part of this study. More extensive details on the synthesis of these nanoparticles can be found in the referenced articles.

## CHAPTER 3

## ANTIFERROMAGNETISM AND SUPERPARAMAGNETISM

Introduction

In order to further explore the physical nature of these different cobalt oxide nanoparticles we have to first understand the origin of the basic physical properties that these particles possess.  $\text{Co}_3\text{O}_4$  is known to have a normal cubic spinel structure and is antiferromagnetic in the bulk with a Néel temperature,  $T_N$ , between 30 – 40 K.<sup>33, 34</sup>

For this study, its most important properties are its magnetic properties, including its low Néel temperature and low blocking temperature. These properties can be seen as either a blessing or a curse since these low temperatures provide a small range to study different physical phenomena, and hence changes in these properties can be studied without going to high temperatures. It should be mentioned that these low temperatures can also make it more difficult to model these phenomena, since the blocking temperatures of these materials are very close to their respective Néel temperatures.

Antiferromagnetism

Antiferromagnetism was first postulated by Louis Néel in 1932.<sup>59</sup> At the time ferromagnetism was well understood by taking into account a quantum mechanical exchange coupling that favors parallel alignment of atomic spins. Under exchange of electron coordinates, space and spin, the wavefunction must be antisymmetric. This is a

way of taking into account the Pauli Exclusion Principle stating that two fermions, electrons, can not occupy the same state. This exchange favors a parallel orientation of two nearby electron spins and thus ferromagnetism. However, Néel postulated that there could also be an anti-parallel exchange coupling that would lead to another form of magnetic order he called antiferromagnetic exchange coupling. Just like ferromagnetic exchange coupling, antiferromagnetic exchange coupling is mediated by an exchange energy  $J$ . The Heisenberg Hamiltonian for the interaction can be written with  $J$  positive for ferromagnets and negative for antiferromagnets, which falls off rapidly with increasing distance between two atoms with total spin angular momentum  $\mathbf{S}$ .<sup>60</sup>

$$H = - \sum_i \sum_{j \neq i} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (3.1)$$

With a negative exchange energy,  $J$ , between the nearest neighbors giving rise to antiparallel spins, the total moment of an antiferromagnetic material should be zero. Like ferromagnets, antiferromagnets have a critical temperature below which there is magnetic ordering and above which the material behaves paramagnetically. The critical ordering temperature is termed the Néel temperature.

Antiferromagnetism can be thought of as two ferromagnetic lattices pointed in opposite directions. This configuration obviously has a total moment of zero. An equivalent way to think about an antiferromagnet for thin films is to think about each monolayer of atoms having spins that point in the opposite way to the next monolayer. Figure 3.1 shows an antiferromagnetic alignment with an extra layer that is

uncompensated. This last layer has spins that don't have neighbors that are anti-aligned. This arrangement of spins would have a total moment. These spins are called uncompensated spins and are easy to detect in an antiferromagnet system of extremely reduced dimensions, such as films of less than 100 monolayers or particles with diameters of less than 10 nm. In these cases the uncompensated spins make up a significant fraction of the material and so their effect is not negligible. For antiferromagnetic particles the moment comes exclusively from uncompensated spins.

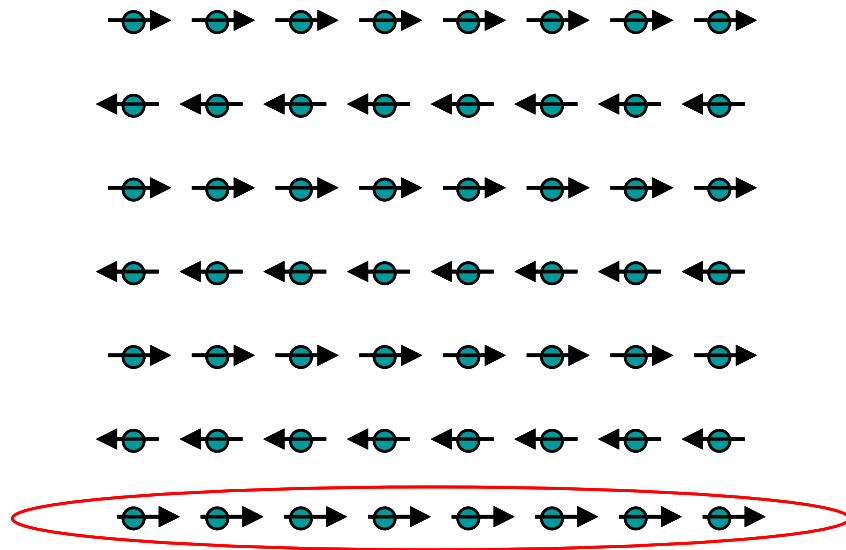


Figure 3.1: Antiferromagnetic arrangement of atomic spins. The bottom layer is not compensated with any other layer and so this arrangement has a total magnetic moment.

### Uncompensated Spins and the Origin of the Magnetic Moment

First proposed by Néel, uncompensated spins are thus the main origin of the magnetic moments of small antiferromagnetic particles.<sup>61</sup> In particles they can arise from

the large surface to volume ratio. Similar to the illustration above the antiferromagnetic matrix can be terminated in such a way that some of the spins on the surface of a small antiferromagnetic particle are uncompensated. Also defects within the crystal lattice of an antiferromagnetic material can create uncompensated spins. If there are defects in a crystal lattice, a missing Co atom in every 5 unit cells for example, then some of the spins in that material would be uncompensated and thus contribute to a total moment.

Another way an antiferromagnetic material could have a moment is if the spins were canted by an external magnetic field. Now the typical exchange energy between atoms is very large and a gigantic external field of the order of 100 Tesla would be needed in most cases to totally overcome this exchange energy and flip the spins. However, the spins don't have to flip completely. Since there is no moment to begin with, a small canting of the spins in the direction of the magnetic field can produce a moment. The spins simply point slightly along the external field direction producing a magnetic moment in that direction. In the case of particles, this small contribution was proposed by Néel to be directly proportional to the applied field.<sup>61, 62</sup>

One other way an antiferromagnetic material could have a moment is a phenomena suggested by Mørup et al. to account for some discrepancies of antiferromagnetic nanoparticle moments in the literature.<sup>14</sup> In this case the moment would arise via thermo-activation. Two compensated spins can precess about their easy axis in an unequal fashion. If one spin precesses away from the easy direction more than another, because of the thermal excitation being exerted on spins with slightly different coupling to the crystal structure, the result is a total magnetic moment associated with

compensated spins! This effect is thought to produce a linear increase in the magnetic moment of antiferromagnetic nanoparticles with increasing temperature and has been proposed to explain large linear increases in the magnetic moments of ferrihydrite particles.

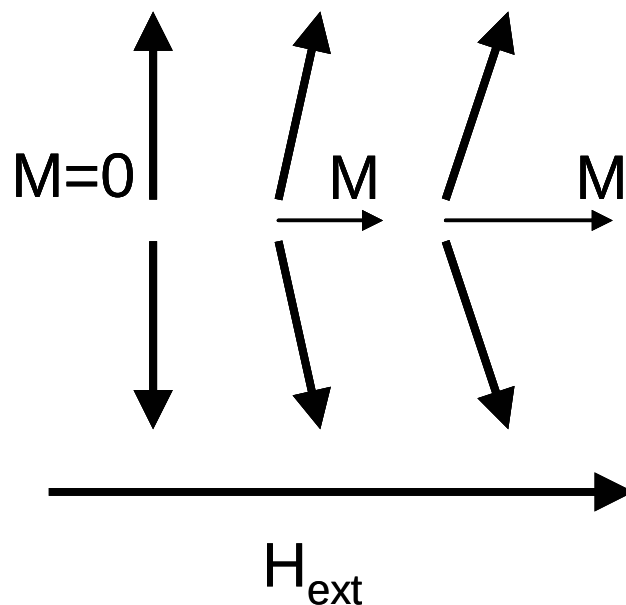


Figure 3.2: Antiferromagnetic spins respond to a larger and larger applied field. A magnetic moment is created perpendicular to the spin axis. The stronger the applied field the larger the induced magnetic moment in the sample. (The amount of canting shown above is exaggerated in order to better illustrate the example.)

### Exchange Bias

Another interaction dealing with antiferromagnet materials is called exchange bias. Exchange bias is the exchange coupling of an antiferromagnetic material with a

ferromagnetic material as first studied at by C.P. Bean<sup>63</sup> and W.H. Meiklejohn<sup>6</sup>. It is easy to understand exchange bias in a basic way by thinking about it with a simple example detailed in Figure 3.3.<sup>10</sup> Magnetic spins normally interact via exchange coupling. The coupling is either parallel or antiparallel. If one spin is flipped then the other spin, which is coupled to it, will feel a torque to flip as well. In order to keep the coupled spin from flipping, the exchange coupling energy must be overcome. This is the essence of exchange bias. In the specific case of a ferromagnetic thin film with an antiferromagnetic thin film grown on top, this coupling can become important. Above the Néel temperature of the antiferromagnetic thin film the hysteresis loop will be unchanged. However, if the films are cooled in the presence of an external field larger than the saturation field of the ferromagnetic film, then the hysteresis, at temperatures below the antiferromagnetic Néel temperature, can be shifted and enhanced. The origin of this shift can be thought to arise due to the coupling of the two materials at the interface. The antiferromagnetic layer acts to pin the spins of the ferromagnetic layer to point in a preferred direction. This effects the coercive field of the ferromagnetic by enhancing it and making it more favorable, taking less energy ( $\mathbf{M} \cdot \mathbf{H}$ ), to point one direction and less favorable, taking more energy, to point along another direction.

Exchange bias has been seen in other systems besides a pure antiferromagnetic thin film on top of a pure ferromagnetic thin film. In fact, small antiferromagnetic particles have been shown to also produce exchange bias; it was first observed in tiny particles cobalt oxide particles.<sup>5, 7</sup> It is thought that the uncompensated spins, below the blocking temperature of the superparamagnetic state, could act like a ferromagnetic

component and thus any hysteresis of these blocked uncompensated spins could be coupled to the antiferromagnetic bulk and demonstrate exchange bias.

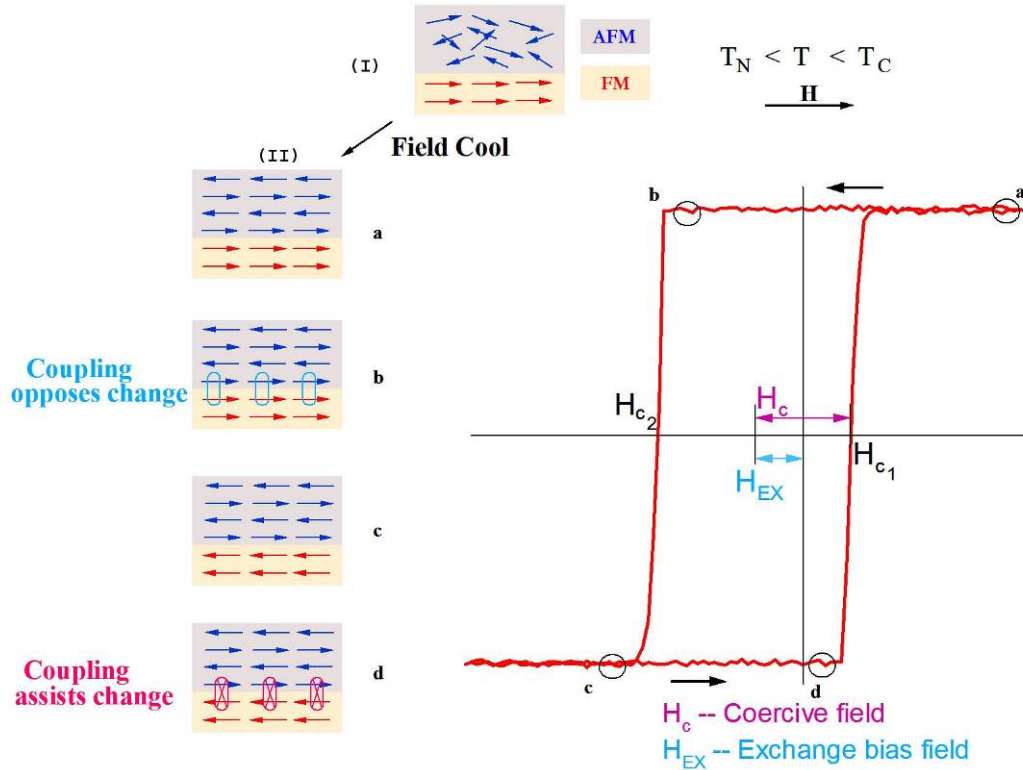


Figure 3.3: The effect of exchange bias on ferromagnetic hysteresis. In part I the sample is above the Néel temperature of the antiferromagnetic but below the Curie temperature of the ferromagnet. II a) The sample is frozen below the Néel temperature of the antiferromagnet in a high applied field. This freezes the spins into the arrangement shown. II b) The exchange coupling between the ferro and antiferromagnetic systems opposes the change and so the magnetization flips at a higher applied field. II c) The magnetization is now flipped. II d) The coupling now assists the change in magnetization causing the magnetization to flip at a lower field applied in the opposite direction. This effect of shifting the coercive field is known as exchange bias.<sup>10</sup> (Data provided by Ezana Negusse.)

### Superparamagnetism

In a discussion of uncompensated spins, especially in small particles, it is useful to talk about superparamagnetism and the large role it plays in the magnetic behavior of small magnetic particles. The term superparamagnetism comes from the fact that it describes large, or “super”, particle moments behaving paramagnetically instead of just regular paramagnetism, which describes the behavior of atomic spin moments behaving paramagnetically. Paramagnetism simply refers to the tendency of spins, which do not interact magnetically and therefore point in random directions due to thermal energy, to line up and point in the same direction in the presence of a magnetic field. At low fields, paramagnetism exhibits a linear relationship between the induced magnetic moment and the field,  $\mathbf{M} \approx \chi \times \mathbf{H}$ .  $\mathbf{M}$  is the induced magnetization of the material in the same direction as the applied external field  $\mathbf{H}$ .  $\chi$  is called the susceptibility and is thought of as how susceptible a paramagnetic material is to being magnetized. Other materials called diamagnets can be negatively magnetized by a field, and so have a negative susceptibility.

Physically and mathematically, superparamagnetism can be described by the introduction of uniaxial anisotropy as an energy barrier for a magnetic moment to overcome in order to flip directions, or change states. The total magnetic energy of the particle is given by<sup>64</sup>

$$E_{tot} = E_a \sin^2 \phi - \mu H \cos \phi, \quad (3.2)$$

where  $E_{tot}$  is the total magnetic energy,  $E_a$  is the anisotropy energy barrier, and  $\phi$  is the angle between the magnetic moment of the particle,  $\mu$ , and the applied field along the easy axis direction,  $H$ . Figure 3.4 shows equation 3.2 graphically. If thermal fluctuations are of the order of the maximum magnetic energy minus the ground state,  $E_M - E_1$ , then the particle can flip direction.

Thermal fluctuations can then flip the moment back and forth with a relaxation time,  $\tau$  given by

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_b T}\right), \quad (3.3)$$

where  $\tau_0$  is the attempt time of the material,  $E_a$  is still the anisotropy energy,  $k_b$  is Boltzmann's constant, and  $T$  is the temperature of the particle.<sup>64</sup> There is typically a broad peak in the ac-susceptibility, which is associated with the blocking temperature,  $T_B$  and taking the natural log of equation 3.3, the Néel–Arrhenius relation results. This equation has worked well to describe the behavior of protein-encapsulated nanoparticles, and is given by<sup>24</sup>

$$\ln\left(\frac{1}{f}\right) = \ln\left(\frac{1}{\Gamma_0}\right) + \left(\frac{E_a}{k_b}\right)\left(\frac{1}{T_B}\right), \quad (3.4)$$

where  $f$  is the measurement frequency of a small oscillating ac-field,  $\Gamma_0 = \tau_0^{-1}$  is the attempt frequency, and  $E_a$  is the anisotropy energy barrier that the magnetic moment of the particle must overcome to flip its spin.

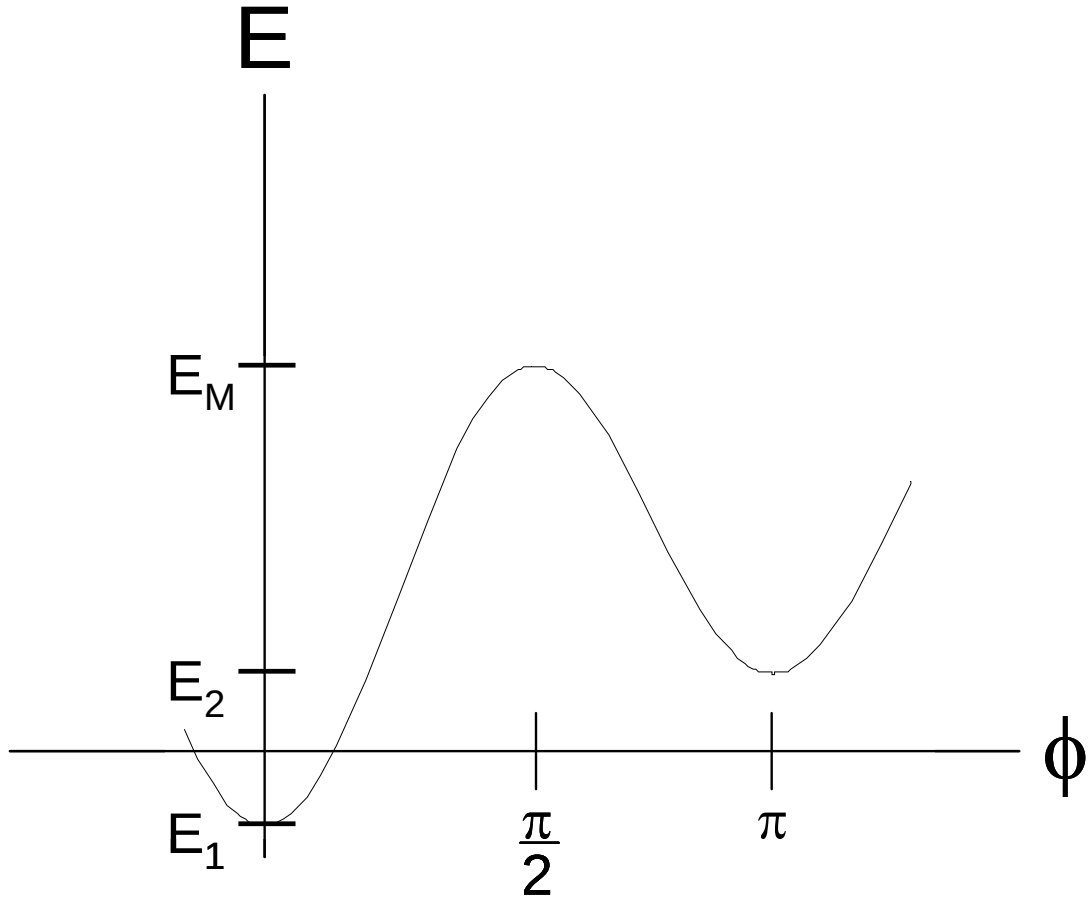


Figure 3.4: The energy barrier that a magnetic nanoparticle has to overcome in order to flip its spin. For superparamagnetic particles above the blocking temperature, this barrier is overcome by thermal excitation.

The Néel–Arrhenius relation is a very powerful way of thinking about superparamagnetism. It turns out that the peaks in an ac-susceptibility measurement correspond to the blocking temperature  $T_B$ . The frequency dependence of the ac-susceptibility measurement can give the anisotropy energy and the attempt time for a particle. This is accomplished by making a Néel–Arrhenius plot of the frequency dependence of the blocking temperature. Plotting  $\ln(1/f)$  versus  $1/T_B$ , the attempt time

can then be extracted from the intercept of the y axis and the slope can then give you the anisotropy energy. This method is used to extract these parameters and is shown in detail with the data collected for the particles of interest in this study in chapter 5.

### Langevin Model

The Langevin function corresponds to a general treatment of paramagnetism. This model describes how non-interacting spins in the presence of an external magnetic field will respond to that field collectively. Superparamagnetic materials behave in this same way, only on a larger scale. This behavior can occur for ferromagnetic or antiferromagnetic materials when the collective anisotropy energy of a magnetic particle is of the order of the total thermal energy of the particle. For small sizes, the neighboring spins in a superparamagnetic material are still exchange coupled, but their collective spin, the magnetic moment of the entire particle, is flipped with the help of the thermal energy in overcoming the anisotropy energy barrier. These particle moments then act as “super” spins and in the presence of a magnetic field they are forced into a state that aligns them with the field and so the overall effect is similar to paramagnetism. The difference is that the spins in a superparamagnet are much larger; the effect of an external field has a greater response to the magnetization. Well above the blocking temperature, superparamagnetism can be thought of as just paramagnetism on a larger scale.

The particles used in this study are superparamagnetic because the uncompensated spins contribute to give a total overall moment to the particles. These particle moments do not interact and behave collectively like a superparamagnetic

material. Below the blocking temperature, in the case of an antiferromagnetic superparamagnet, the uncompensated spins are “blocked”, forced to hold their alignment, and produce a hysteretic ferromagnetic behavior

In this view, for large external fields the magnetization of paramagnetic materials can be described using a simple semi-classical treatment, which corresponds to treating the total angular moment of the spins as  $J = \infty$ , not to be confused with  $J$  the exchange energy. A true quantum mechanical treatment where  $J$  can take any integer or half-integer value is not necessary and would not describe the magnetic response of a superparamagnetic system. The Langevin function, not the Brillouin function, is the best function suited to describing a collection of randomly oriented superparamagnetic nanoparticle spins.

### Langevin Function

Assuming the magnetic moments are at angles  $\theta$  and  $\theta + d\theta$  to the applied field  $H$ , which is along the  $z$  direction, the energy of the moments are then  $-\mu H \cos\theta$ . With a random orientation of the moments, the probability that a moment will be between  $\theta$  and  $\theta + d\theta$  at temperature  $T$ , is proportional to the product of the statistical factor,  $\frac{1}{2}\sin\theta d\theta$ , and the Boltzmann factor  $\exp(\mu H/k_b T)$ . The average moment along  $H$  is then<sup>65</sup>

$$\langle \mu_z \rangle = \frac{\int_0^\pi \mu \cos \theta \exp\left(\frac{\mu H \cos \theta}{k_b T}\right) \frac{1}{2} \sin \theta d\theta}{\int_0^\pi \cos \theta \exp\left(\frac{\mu H \cos \theta}{k_b T}\right) \frac{1}{2} \sin \theta d\theta}, \quad (3.5)$$

and

$$\frac{\langle \mu_z \rangle}{\mu} = \coth \frac{\mu H}{k_b T} - \frac{k_b T}{\mu H} \equiv L(x), \quad (3.6)$$

where  $L(x)$  is the Langevin function with  $x = \mu H/k_b T$ . The Langevin function describes a paramagnetic response to a field. (Figure 3.5)

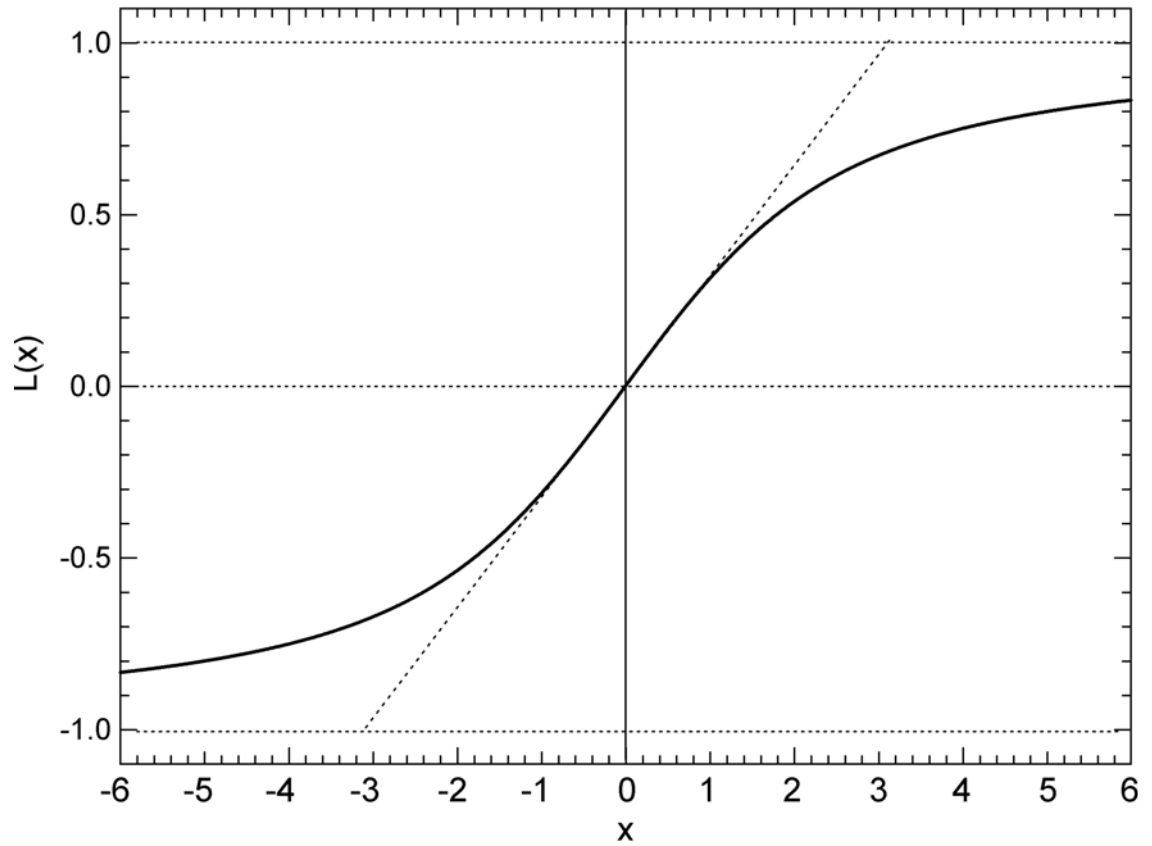


Figure 3.5: A Langevin curve. The curve saturates at 1. At low fields the magnetic moment approximately changes in a linear fashion.

In the limit of small  $x$ , the Langevin function reduces to  $L(x) \approx x/3$  which gives the low field linear approximation, discussed above, for paramagnetism. The magnetization is then directly proportional to  $x$  resulting in Curie's law, in which the susceptibility is proportional to  $1/T$ , or  $M/H \propto 1/T$  and

$$m = m_s L(x) + \chi H, \quad (3.7)$$

where  $M$  is the magnetization and  $M_s$  the saturation magnetization.

#### Add Linear Term — Get Langevin Model

In this study we use the so called Langevin model that sets the magnetic moment measured,  $m$ , equal to the saturation moment,  $m_s$  times the Langevin function plus a linear susceptibility term,  $\chi H$ .

$$\frac{M}{M_s} = \frac{\langle \mu_z \rangle}{\mu} = \frac{\mu H}{3k_b T}, \quad (3.8)$$

This function is used throughout this dissertation to model  $m$  vs.  $H$  data collected by the VSM.

The linear term is added to the model in order to account for the antiferromagnetic susceptibility, spin canting of the bulk of the particles, and any other paramagnetic effect in the samples. This term is added to this model because the particles are composed of the antiferromagnetic material  $\text{Co}_3\text{O}_4$ , organic proteins, as well as left over salt from the

solution in which the particles were synthesized.

The Langevin model has worked well to model the behavior of superparamagnetic particles. Throughout the literature this model is used to extract the magnetic moment and saturation moment of superparamagnetic particles.<sup>16, 24, 25, 66</sup> It should be noted that this model does not take into account anisotropy. This means that the Langevin model is a good model for describing the magnetic response of superparamagnetic particles above the blocking temperature. Above the superparamagnetic blocking temperature the anisotropy energy is overshadowed by the thermal energy in the system. Near or below the blocking temperature the Langevin function is a poorer model to describe the response of the magnetization. However a full model that takes anisotropy into account is a difficult numerical calculation to perform. If the Langevin model is used at temperatures below  $T_B$ , the parameters that are extracted would have a much larger error. In this study the only parameter extracted below the blocking temperature that is used for modeling is the saturation moment. Out of all the parameters the saturation moment is the least sensitive to the model and can be extracted independent of the model, as long as this error is understood. One of the ways that will be used to try and overcome this is to add a constant magnetic remnant term to this model. This is done in chapter six in order to determine the Néel temperature more precisely.

## CHAPTER 4

## MAGNETIC PROPERTIES

Introduction

In this dissertation the effects of particle size on the magnetic properties of small antiferromagnetic particles are investigated. A deeper reason behind this study is to obtain a better understanding of the why the particles behave the way they do. The properties that are studied give information and clues to what the smallest parts of the particles are doing. The questions that need answering are: What are the individual spins doing and why? Where are the spins located? How does their arrangement affect the properties of the particles? How do they interact? How do the answers to these questions change when the particles get smaller? Some of the properties that can be measured include the individual magnetic moments of the particles, the Néel temperature and the magnetic anisotropy energy density. The study of how these properties change with particle size will help to answer some of these questions.

Néel Temperature

As discussed in the previous chapter the Néel temperature,  $T_N$ , is the temperature of an antiferromagnet above which the long range order ceases to be important. In other words the spins associated with the atoms are randomized by thermal fluctuations and the material loses its antiferromagnetic order and becomes paramagnetic. One can think

about the Néel temperature as the critical ordering temperature of an antiferromagnet. Close to this temperature the thermal fluctuations become critical fluctuations and the susceptibility diverges or undergoes critical behavior. Below the Néel temperature antiferromagnetic spins order antiparallel, and above the Néel temperature they behave paramagnetically.

The Néel temperature is a very important property of an antiferromagnetic. Structural positioning of atoms, wavefunction overlap, anisotropy, and other factors can all contribute to the temperature at which magnetic order disappears. So in studying changes in the Néel temperature the different factors that contribute to and change it can be indirectly studied.

In the divergence of the susceptibility a Néel temperature can be defined. Many text books discuss the Néel and Curie temperatures and loosely define it in the case of the Curie-Weiss function. The Curie-Weiss function adds to the useful result of the Curie law which, as stated in the previous chapter, states that the susceptibility for a paramagnetic system is inversely proportional to the temperature, with  $C$  as the Curie constant and  $T$  the temperature.

$$\chi = \frac{C}{T} \quad (4.1)$$

A simple derivation of the Curie law is shown following the derivation of the Langevin function at the end of chapter 3. In the limit of small external fields the Langevin function, which describes paramagnetic behavior, shows that the susceptibility is proportional to  $1/T$ .

Taking a molecular field approach, Weiss was able to approximate the susceptibility of a ferromagnet. Later Néel modified it for an antiferromagnetic material.<sup>60, 65, 67</sup> The susceptibility above the critical ordering temperature is then proportional to the inverse of the temperature minus the critical temperature and is called the Curie-Weiss law.

$$\chi \propto \frac{C}{T - \theta} \quad (4.2)$$

For ferromagnetic materials  $\theta$  is the Curie temperature and for antiferromagnets  $-\theta$  is the Néel temperature. Although observed ferromagnetic behavior fits this behavior well, antiferromagnetic behavior does not. In fact the assumption that the magnetization of one sublattice depends only on the magnetization of the other sublattice, which Néel made in the molecular field theory, is inherently not physical. A more realistic calculation taking into account the contribution of the same sublattice produces a correction to the Curie-Weiss law that reduces to equation 4.2.<sup>65</sup>

Since it is difficult to determine the Néel temperature above it, one must take a different approach. One thing that can be done, in the case of antiferromagnetic thin films, is to measure the susceptibility at many temperatures through  $T_N$  as a small field is applied. The susceptibility peaks through the phase changing region, thereby giving the Néel temperature. One thing peculiar about antiferromagnetic materials is that at zero Kelvin the perpendicular and parallel susceptibilities are not equal.

The perpendicular susceptibility is defined as the susceptibility of the antiferromagnetic material when a small field is applied perpendicular to the sublattice

spin orientations. The parallel susceptibility is defined as the susceptibility when the field is applied parallel to the sublattice spin orientations. When the field is perpendicular to the sublattice spins, the spins tend to bend slightly in the direction of the field creating a large susceptibility at zero Kelvin. However, when the field is applied parallel to the sublattice spins at zero Kelvin no magnetization is induced; the susceptibility is zero. As the temperature is increased, the spins are slightly randomized and the parallel susceptibility becomes positive and increases with temperature approaching the peak at the Néel temperature. (Figure 4.1)

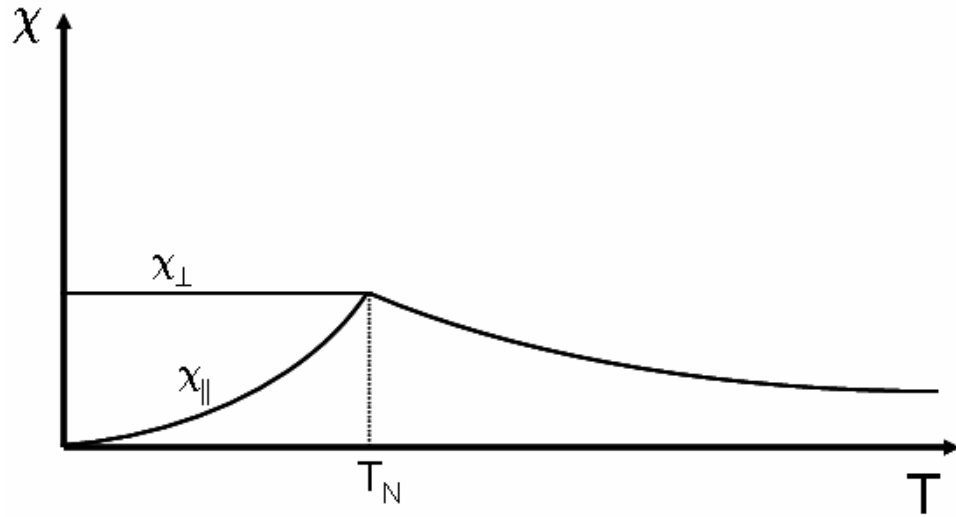


Figure 4.1: The difference in the perpendicular and parallel susceptibilities for antiferromagnetic materials.

The perpendicular susceptibility does not change much with temperature; it remains relatively constant until the temperature reaches the Néel temperature, in which case the parallel susceptibility is now the same as the perpendicular susceptibility. In this

case, it would be expected that the susceptibility would peak at the Néel temperature and that all that would need to be done would be to measure the susceptibility as a function of temperature and find the peak. Ideally this can be done. In the case of antiferromagnetic thin films,<sup>40</sup> you can measure the susceptibility at many temperatures through this region thereby measuring the Néel temperature. However since the nanoparticles used in this study are superparamagnetic, this feature is washed out in favor of the superparamagnetic susceptibility whose peak corresponds to the blocking temperature. The Néel temperature can be difficult to determine in a superparamagnetic particle.

One way used to determine the Néel temperature, in the case for antiferromagnetic nanoparticles, is by measuring the magnetic saturation of particles below the Néel temperature. It was found by D. Mills<sup>68</sup> and well demonstrated experimentally by Makloulf *et al.*<sup>16</sup>, that the saturation magnetization decreases in a linear way as the temperature increases towards the Néel temperature. In fact Punnoose *et al.*<sup>66</sup> showed that the saturation magnetization follows a very simple behavior given by

$$M_S = M^* \left[ 1 - \frac{T}{T_N} \right], \quad (4.3)$$

where  $M_S$  is the saturation magnetization at some temperature  $T$ ,  $M^*$  is the extrapolated saturation magnetization at  $T = 0$  and  $T_N$  is again the Néel temperature. Plotting out the saturation magnetization versus temperature will then give a straight line that points to the Néel temperature where  $M_S$  should equal zero. This behavior is attributed to a surface exchange effect worked out by D. Mills.

By determining the Néel temperature with this last method, it has been shown in this study that the Néel temperature decreases with smaller and smaller sizes. This behavior is similar to the change in the Néel temperature for antiferromagnetic thin films as the film thickness is decreased.<sup>40</sup> This change in the Néel temperature for thin films is attributed to finite-size scaling.

### Finite-Size Scaling

One method for modeling the change in Néel temperature with size is a theory known as finite-size scaling. Finite-size scaling is a way of modeling how critical temperatures shift with the reduction of dimensions. In one case, it has been used to model how the Néel temperature of CoO thin films shift to temperature lower than the bulk Néel temperature.<sup>40</sup> M. Fisher and M. Barber wrote a land mark paper in which they outline how this critical temperature should shift.<sup>69</sup> More details were published by Barber in 1983.<sup>70</sup>

In order to model this behavior, the fractional shift  $\varepsilon(d)$  must be set to equal a constant that depends on the correlation length exponent,  $\nu$ , and some characteristic microscopic dimension of the system,  $d_0$  given by

$$\varepsilon(d) = \left[ \frac{T_C(\infty) - T_C(d)}{T_C(\infty)} \right] \approx \left( \frac{d}{d_0} \right)^{-1/\nu}, \quad (4.4)$$

where  $d$  is the diameter of a nanoparticle,  $T_C(\infty)$  is the bulk critical temperature and  $T_C(d)$  is the reduced critical temperature. This equation is only strictly valid for small changes in the critical temperature but has been found to work for values much lower than the

bulk critical temperature.<sup>40</sup> Later in this dissertation equation 4.4 will be used to model the observed reductions in the Néel temperature for the reduced size nanoparticles. The behavior of the reduction of the Néel temperature and extraction of the correlation length and shift exponent may help to give a better understanding of the  $\text{Co}_3\text{O}_4$  nanoparticle system.

### Anisotropy

Magnetic anisotropy is as fundamental to magnetism as the spin-orbit interaction. In a simple Heisenberg description of ferromagnetism, the Hamiltonian is totally isotropic with exchange. However, if the spin-orbit coupling term is added to the Hamiltonian, an anisotropic coupling term with the nearest neighbors is a result to 1<sup>st</sup> order. Essentially, the spins have a preferred orientation because of their coupling with orbit and the symmetry of the charge density of their atoms. This preferred direction depends on the alignment of these orbitals and hence on the crystal and lattice structure of the particular material as well as on the arrangement of these spins in a structure. The dependence of the spins' energy on absolute orientation is known as the magnetic anisotropy energy and is usually quite weak for individual spins. However, it does contribute a fixed energy per spin to the energy of a line of deviant spins, for example, and that is why it can eventually outweigh the exchange energy. This is the origin of the thickness of domain walls, which arises from the balance of the exchange and anisotropy energies.

For the purposes of the particles in this study, the anisotropy was defined, in

equation 3.2, as an energy barrier for the particle moments to overcome in superparamagnetism. This equation assumes a uniaxial energy barrier for a particle corresponding to up and down states. The magnetic anisotropy energy density is determined in the ACMS experiments by measuring how the susceptibility changes as a function of temperature and frequency. Equation 3.3 is used as well as the frequency dependence of the Néel-Arrhenius equation 3.4. Equating the peak in the susceptibility with the blocking temperature, the anisotropy energy barrier to the spins can be extracted. This number is then divided by the average volume of a particle and the magnetic anisotropy energy density,  $K$  of particle is determined.

It should be noted that the anisotropy energy density has been found to change with temperature. Specifically the bulk anisotropy energy density of  $\text{CoFe}_2\text{O}_4$ , for example, varies from  $10^6 \text{ J/m}^3$  at 4 K to  $2.6 \times 10^5 \text{ J/m}^3$  at room temperature.<sup>19</sup> Presumably this type of affect is also present in  $\text{Co}_3\text{O}_4$  systems. This slight temperature dependence is noted here because superparamagnetic particles of different sizes typically have different blocking temperatures. This effect may have to be taken into account when comparing the anisotropies measured at different temperatures. However in this dissertation, the blocking temperatures are all within 1.7 K of each other, and it is assumed that the anisotropy energy density does not change significantly over this temperature range.

Nanoparticles have a high surface to volume ratio. In fact, many experimental results for metallic and metal oxide particles<sup>11, 71-75</sup> indicate that the anisotropy of nanoparticles increases as the volume is reduced because of the contribution of an

additional anisotropy on the surface.

### Surface Anisotropy

Magnetic surface anisotropy has been suggested to have a major contribution to the effective magnetic anisotropy energy density of magnetic nanoparticles.<sup>76</sup> Increases in anisotropy energy density as much as an order of magnitude more than the bulk have been measured for Co particles.<sup>73</sup> Also, Co particles embedded in a Cu matrix were seen to have anisotropy energy densities even two orders of magnitude greater than the bulk.<sup>75</sup>

Surface anisotropy is thought to have a crystal-field origin and comes from the breaking of symmetry on the boundaries of small particles. This symmetry breaking can cause structural relaxation leading to the contraction of surface layers. Combined with the existence of atomic disorder and vacancies, local crystal fields can be induced with mostly axial character normal to the surface, which can produce easy-axis or easy-plane anisotropies.<sup>77</sup> This can be understood by thinking about the axis of the local crystal field,  $\mathbf{n}_i$ , as the combination of the dipole moment of the nearest-neighbor atomic position with respect to the position of a given surface atom described by

$$\mathbf{n}_i \propto \sum_j^{nn} (\mathbf{P}_j - \mathbf{P}_i), \quad (4.5)$$

where  $\mathbf{P}_i$  is the position of the  $i^{\text{th}}$  atom and the sum extends to the nearest neighbors. Since there are some missing neighbors, a crystal field exists with an axis that should point perpendicular to the surface.<sup>78</sup> This effect can be modeled by adding a term to the Hamiltonian of the form<sup>79</sup>  $K \cdot S_s^2$ , where  $K$  is the magnetic anisotropy energy density and

$S_s$  is the component of the spin along a vector normal to the surface with  $K < 0$  corresponding to the easy-axis case and  $K > 0$  to the easy-plane case. When  $|K|$  is comparable to the exchange energies, the perpendicular and tangential spin configurations result. (Figure 4.2) This can be thought of as a competition between the surface anisotropy and exchange energies. Generally, the surface anisotropy makes the surface magnetically harder than the core of the particle.

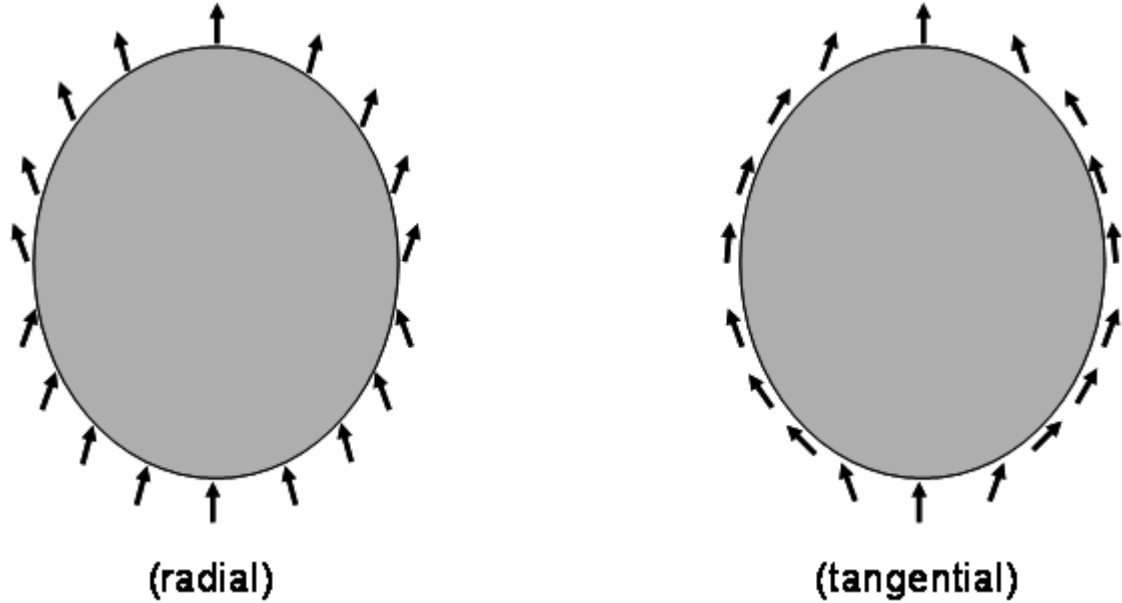


Figure 4.2: A radial and tangential arrangement of surface spins for spherical like particles.

Another anisotropy that should be mentioned is strain anisotropy. Mostly found in thin films, strain anisotropy is usually induced by a lattice mismatch between a film and its substrate at the interface. Strain anisotropy could yield perpendicular anisotropy

as has been seen in different films,<sup>80-82</sup> but for the majority of nanoparticles systems the strain energy is weak. In fact, in most free particles it is negligible.

### Phenomenological Models for the Effective Anisotropy

In an effort to further understand why smaller sized nanoparticles have larger magnetic anisotropy energy densities than the bulk, efforts to quantify surface anisotropy have been undertaken.<sup>11, 83</sup> The effective anisotropy energy density of a particle,  $K_{eff}$ , is assumed to be made up of a bulk term,  $K_b$ , and a surface term,  $K_s$ . By writing the energy barrier as a function of these terms, the average volume of the particles  $V$ , and the area of the surface of the particles  $A$ :

$$\Delta E_a = K_{eff}V = K_bV + K_sA \quad (4.6)$$

the effective anisotropy energy density for a spherical particle can then be described by the phenomenological expression<sup>11</sup>

$$K_{eff}(d) = K_b + \frac{6}{d}K_s, \quad (4.7)$$

where  $d$  is the diameter of the particle. This equation has worked well to model the increase of the anisotropy energy density as a function of reduced size for ferromagnetic and ferrimagnetic particles.<sup>11, 83</sup> The second term in equation 4.7 falls directly out of equation 4.6 and can be thought of by assuming that the anisotropy would scale with the surface. The ratio of the area to the volume is  $6/d$  therefore this term is simply  $(6/d)K_s$ .

A modification of this equation was proposed by Gilmore *et al.*<sup>83</sup> in order to model a slight perceived deviation from this behavior. It should be noted that the particles used in the Gilmore *et al.* study were synthesized in the exact same way as the particles used for this dissertation. The only difference is that Gilmore *et al.* used iron instead of cobalt, consequently  $\gamma\text{-Fe}_2\text{O}_3$  particles were synthesized and not  $\text{Co}_3\text{O}_4$  particles. It was proposed in this paper that a more realistic model for the increase in the surface anisotropy should be one that increases asymptotically as the diameter of particle got smaller and smaller. The function above, equation 4.7, was modified to include a hyperbolic tangent function given by

$$K_{eff}(d) = K_b + \frac{6}{d} K_s^0 \tanh(d / \lambda), \quad (4.8)$$

and,

$$K_s \equiv K_s(d) = K_s^0 \tanh(d / \lambda) \quad (4.9)$$

where  $\lambda$  is a scaling factor.

Symmetry arguments for a spherical particle dictate that the surface anisotropy (normal to the surface) should average out to be zero. However, for a particle with a few atomic layers this is not true and it has been shown, in particular cases, that the dependence of equation 4.7 or 4.9 does hold true.<sup>11, 83</sup> These simply illustrate the large role surface anisotropy can play in the effective anisotropy of a particle as well as gives a way to model and understand the role of surface anisotropy and the axis of the spins.

In this dissertation, it has been found that this type of treatment of the effective anisotropy does not work well to model the measured anisotropy energy densities. It is found that the smaller size particles have larger effective anisotropy energy densities than the model predicts. The increase and trend the  $\text{Co}_3\text{O}_4$  particles follow is much more striking than what has previously been studied and modeled with equation 4.7. The trend is not proportional to  $d^{-1}$ .

### Other Properties

Besides the Néel temperature and magnetic anisotropy, nanoparticles have other properties that can change with size. Some of these properties can also be measured to give clues to understanding these systems. In fact, some of these properties, most notably the coercive field, are very interesting in terms of applications. After all, if you cannot flip a magnetic material very easily, it is not very useful as a bit in a hard drive. Likewise, if it is too easy to flip, it is also not very useful as a bit because small magnet fluctuations can erase the memory.

In principle, the coercive field can tell us a great deal about a magnetic system. For nanoparticles it becomes very interesting to look at the coercive field. Finite-size effects are thought to effectively reduce the coercive field of a nanoparticle.<sup>84</sup> In a study by Iglesias and Labarta,<sup>84, 85</sup> spherical maghemite particles are modeled in a Monte-Carlo simulation with Ising spins. They found that finite-size effects should reduce the coercive field. However, in real samples the decreasing of the coercive field by finite-size effects is overshadowed by the role surface anisotropy can play. It has been clearly

illustrated that the coercive fields increase in real particles and that this is due to surface anisotropy.<sup>84</sup> These works demonstrated that uniaxial anisotropy normal to the surface can yield an enhancement of the coercive field. The model is a simple core-shell model in which the surface shell has a higher anisotropy than the core. This means that the core spins would flip at lower fields than the surface spins. The effective coercive field would then be elevated. Kodama and Berkowitz<sup>78</sup> also modeled a similar enhancement by using an atomic-scale model for ferrimagnetic nanoparticles that included a surface anisotropy and surface disorder terms.

Other things, like special coatings and surface treatments have also been shown to increase the coercive field of a nanoparticle.<sup>86-88</sup> Diluted samples of nanoparticles are also seen to have enhanced coercive fields.<sup>89-91</sup> It is thought that inter-particle interaction between particles can decrease the coercive field.

An increase of the coercive field is observed for the two smallest particles used in this study. The largest particles did not have any measurable hysteresis since their blocking temperatures were below 2 K. Other properties like magneto-resistance and heat capacity while interesting are very difficult to measure in these bio-particle systems and so can't give us any additional information.

## CHAPTER 5

## HOW SIZE AFFECTS THE ANISOTROPY ENERGY DENSITY

Introduction

Alternating Current Magnetic Susceptibility (ACMS) measurements have been a useful way of measuring the magnetic anisotropy energy density for the superparamagnetic nanoparticles used in this study. The experimental details and basics of operation of the ACMS have been explained in chapter 2. In this chapter, the results of the ACMS studies in determining the magnetic anisotropy energy density are presented and discussed.

In this chapter the main question pursued is: How does size affect the magnetic anisotropy energy density and attempt time of  $\text{Co}_3\text{O}_4$  nanoparticles? We are interested in gaining a better understanding of  $\text{Co}_3\text{O}_4$  nanoparticles and similar systems as well as trying to determine how big a role the surface plays in the changing of the anisotropy. Specifically, the understanding of how the uncompensated spins arrange themselves in the particles, how the spins interact, and how these lead to an enhancement of the effective anisotropy energy density is of particular interest. Is this effect predominantly due to the surface or the finite size of the system? Answering these questions satisfactorily can help to gain a better understanding of this system and other antiferromagnetic systems.

LDps

The LDps sample, which contains nanoparticles of roughly 4.35 nm with a mass of roughly 3.5 mg, was studied with the ACMS. The in-phase and out-of-phase susceptibilities were measured for these nanoparticles from 2 to 12 K. The peak in the susceptibility graphs is taken to represent the change in phase of these superparamagnetic particles from a blocked phase at low temperatures to an un-blocked phase at higher temperatures, and is called the blocking temperature ( $T_B$ ). The blocked phase of superparamagnetic particles is characterized by ferromagnetic like hysteretic behavior while the un-blocked phase is characteristic of large, “super”, moments with a collective paramagnetic behavior. The frequency dependence of the real-part of the susceptibility is seen in Figure 5.1. Peaks of different frequency shift down and to the right, from a larger signal at lower temperatures and smaller frequencies to a weaker signal at higher temperatures and larger frequencies. This  $T_B$  shift with frequency is due to the fact that  $T_B$  is dependent on the sampling time and must be larger for higher frequencies. This type of behavior is typical of that found in the ACMS of superparamagnetic particle systems throughout the literature.<sup>43, 92-96</sup> The only feature that may be considered atypical in these scans is the fact that these peaks are very symmetrical. This means that the peaks are narrower than one might expect for superparamagnetic systems. However, previous results in the literature with ACMS on  $\text{Co}_3\text{O}_4$  3 nm nanoparticles<sup>43</sup> show very similar behavior. This behavior may be typical for such low blocking temperature systems or be specific to  $\text{Co}_3\text{O}_4$  nanoparticles.

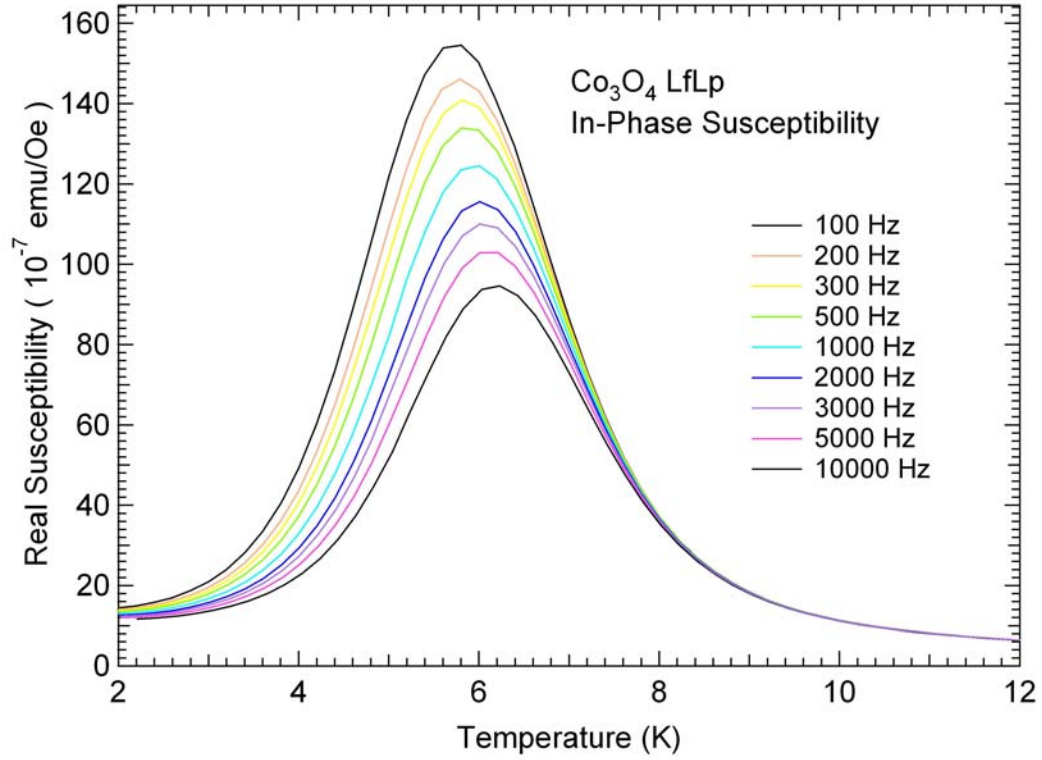


Figure 5.1: Multiple frequency scans of the in-phase component of the ac-susceptibility for LDps.

The superparamagnetic blocking temperature,  $T_B$ , is taken to be 5.4 K, corresponding to the 1000 Hz peak of the out-of-phase susceptibility. (Figure 5.2) The imaginary susceptibility shifts like the real susceptibility and shows the same type of symmetry. The differences between the in and out-of-phase components are striking. For the in-phase, all the peaks are right on top of each other and do not cross. However, they all come together above 8 K showing that the frequency dependence is only prevalent close to the blocking temperature. One would expect that the zero field cooled magnetization would have a peak around the blocking temperature, like that shown. On

the other hand, if the sample were field cooled the dc-magnetization would diverge at the blocking temperature. The in-phase, in a way, shows this divergence with lower frequency, as the field goes from being rapidly oscillating to slowly oscillating, more like a constant field. The out-of-phase however, shows some more peculiar properties. First off, like the in-phase, the out-of-phase peaks do get higher with lower temperature and lower frequency, however these peaks cross one another. A similar property of the two is that they both seem to meet up around the same temperature, a bit above 8 K. Both show the same lack of frequency dependence above 8 K showing the lack of out-of-phase components to the susceptibility well above the blocking temperature which would be expected for superparamagnetic particles.

The peaks of the imaginary components are extracted from the data. The imaginary components can be normalized to 1 and graphed versus a temperature scale normalized by the blocking temperature. (Figure 5.3) The data is normalized in this way to determine the prevalence of interparticle interactions. For the LDps sample the different frequency curves overlap very well. This type of behavior is consistent with the absence of frequency dependent interparticle interactions. Interparticle interactions can have a large effect on the susceptibility of superparamagnetic materials.<sup>13, 97-99</sup> Interparticle interactions have a tendency to lower the blocking temperature.<sup>98</sup> They can have a slightly different effect on different frequencies therefore plotting them in this way, frequency dependent interparticle interactions can be excluded. It should be mentioned, that if the interactions produced a very small frequency dependence in this range the curves would still overlap but not as well.

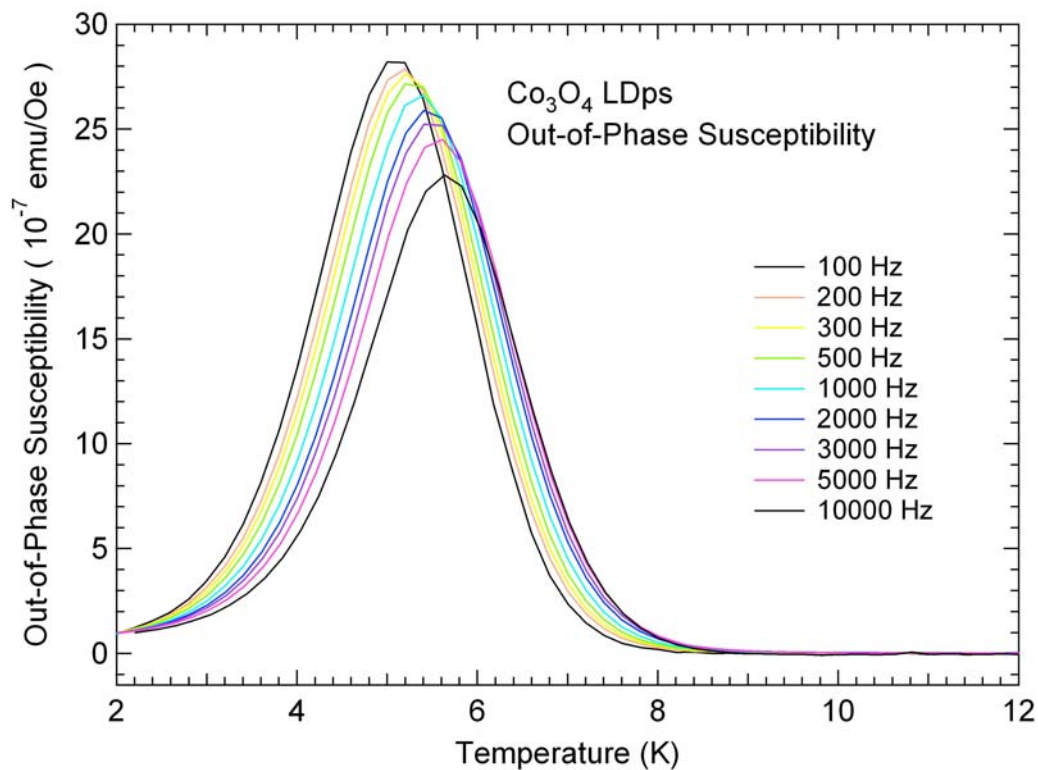


Figure 5.2: Multiple frequency scans of the out-of-phase component of the ac-susceptibility for LDps.

The peaks of the imaginary components are extracted from the data. The imaginary components can be normalized to 1 and graphed versus a temperature scale normalized by the blocking temperature. (Figure 5.3) The data is normalized in this way to determine the prevalence of interparticle interactions. For the LDps sample the different frequency curves overlap very well. This type of behavior is consistent with the absence of frequency dependent interparticle interactions. Interparticle interactions can have a large effect on the susceptibility of superparamagnetic materials.<sup>13, 97-99</sup> Interparticle interactions have a tendency to lower the blocking temperature.<sup>98</sup> They can

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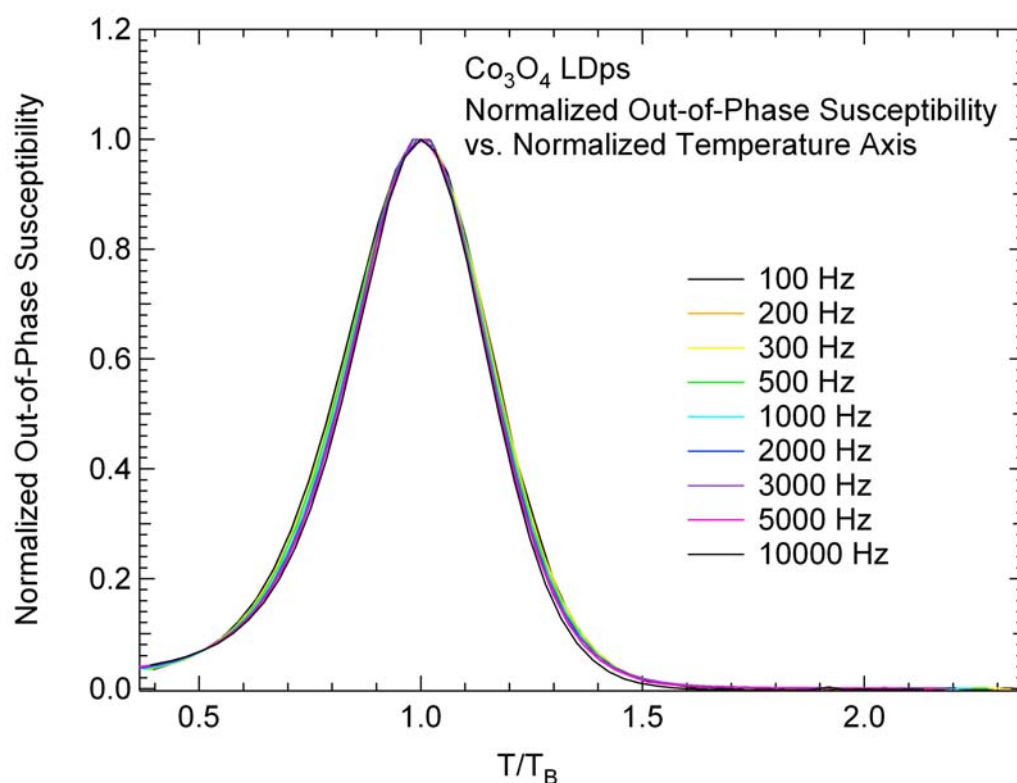


Figure 5.3: Multiple frequency scans of the normalized out-of-phase component of the ac-susceptibility for LDps vs. a temperature axis that has been normalized to the blocking temperature of each frequency.

Another way to verify that interparticle interactions are not having an effect on a system is to plot what is called a Néel-Arrhenius plot. As stated in chapter 3 the Néel-

Arrhenius relation is another way of rewriting the Néel-Brown relation for superparamagnetism. The natural log of the Néel-Brown relation is taken for the blocking temperature at a given frequency. The blocking temperatures for each frequency are then plotted on a graph of  $\ln(1/f)$  vs.  $1/T$ . (Figure 5.4) If there were frequency dependent interactions between the particles, plotting them in this manner would produce a deviation from a straight line. In fact the line should curve up at lower inverse temperatures. If there are no interactions or other factors that might affect the relaxation between states, the intercept of this line gives the attempt time,  $\tau_0$ , of the material. The slope of this line gives the magnetic anisotropy energy,  $E_A$ , of the particles. When this number is normalized to the volume, the magnetic anisotropy energy density,  $K$ , for the particles can be extracted.

In this case, the Néel-Arrhenius plot of the LDps encased 4.35 nm nanoparticles gives an extracted attempt time of  $(1.87 \pm 1.50) \times 10^{-29}$  sec for the in-phase component of the susceptibility and  $(8.15 \pm 1.50) \times 10^{-23}$  sec for the out-of-phase component of the susceptibility. The magnetic anisotropy energy of the in-phase extracted is  $(4.86 \pm 1.00) \times 10^{-21}$  J and the out-of-phase is  $(3.24 \pm 1.00) \times 10^{-21}$  J. The volume of a 4.35 nm diameter particle is  $4.31 \times 10^{-26}$  m<sup>3</sup>. Taking this as the average volume for these particles the average magnetic anisotropy energy density,  $K$ , for the in-phase component of the susceptibility must be  $(1.13 \pm 0.80) \times 10^5$  J/m<sup>3</sup> with the out-of-phase being  $(7.53 \pm 5.00) \times 10^4$  J/m<sup>3</sup>. These values of the anisotropy energy density are comparable to values in the literature for magnetic nanoparticles.

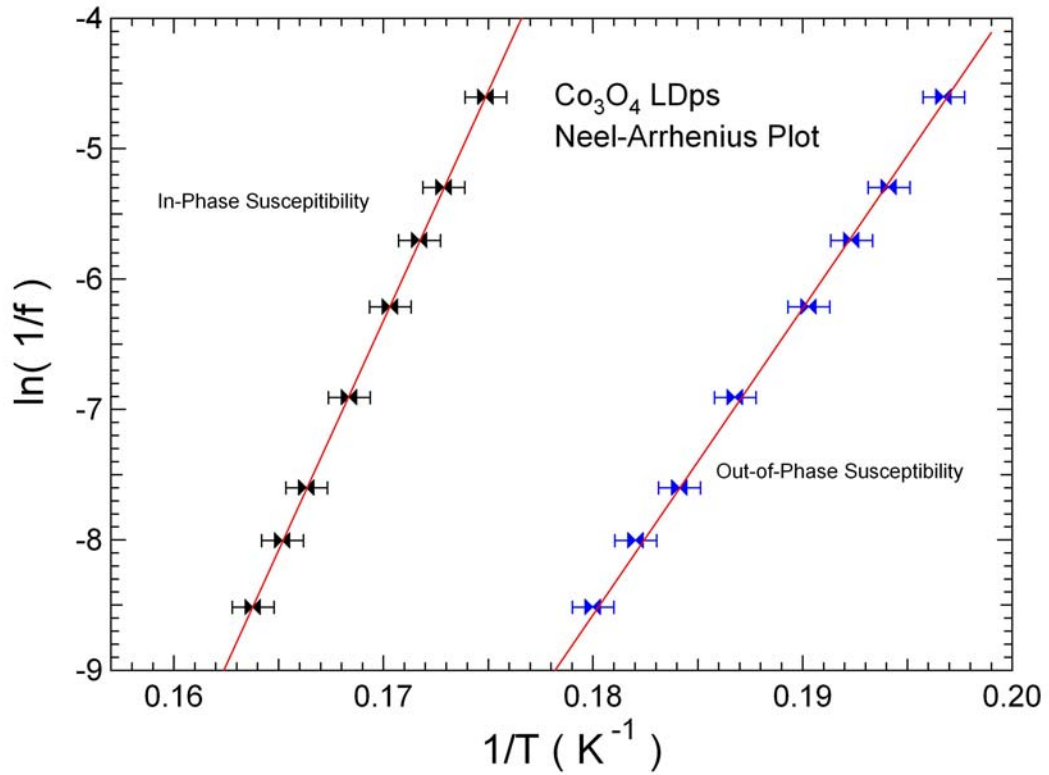


Figure 5.4: Néel-Arrhenius plots of the in-phase and out-of-phase components of the ac-susceptibility for LDps. The intercept of these data give you the attempt time while the slope gives you the magnetic anisotropy energy.

The attempt time values extracted are much higher than would be expected for the bulk. The difference is most likely due to an additional energy added to the bulk anisotropy energy. This additional energy is most likely a surface anisotropy. Also the values for the anisotropy energy density correspond to values slightly below those previously determined for 3 nm  $\text{Co}_3\text{O}_4$  nanoparticles with a superconducting quantum interference device (SQUID).<sup>43</sup> This difference in the anisotropy energy for different size particles could be due to the effect of an increased surface anisotropy. At the end of this chapter, and in chapter 7 these differences will be discussed and remarked on in detail.

HsFn

The horse-spleen ferritin protein sample, HsFn, with a mass of roughly 4.3 mg was also studied with the ACMS. HsFn contain nanoparticles of roughly 6.3 nm diameters inside their protein shells. The in-phase and out-of-phase susceptibilities were measured for these nanoparticles from 2 to 12 K. The peak in the susceptibility graph is taken to represent the change in phase of these superparamagnetic nanoparticles from the blocked phase at low temperatures to the un-blocked phase at higher temperatures. The peak for a given scan is taken to represent the blocking temperature for that particular frequency. The typical frequency dependence of the real-part of the susceptibility is shown in Figure 5.5. The peaks shift down and to the right, just like in the LDps sample, demonstrating a typical superparamagnetic signature. Like the LDps mineralized nanoparticles' susceptibility the Gaussian like shape of the peaks are slightly different from higher temperature superparamagnetic materials but similar to other  $\text{Co}_3\text{O}_4$  samples found in the literature.

The superparamagnetic blocking temperature,  $T_B$ , is 4.1 K, for the 1000 Hz peak of the out-of-phase susceptibility. (Figure 5.6) This value is taken as a reference to compare to other values and should not be construed as the “true” blocking temperature. The imaginary susceptibility shifts like the real susceptibility and shows the same type of symmetry. The peaks of the imaginary components are extracted from the data. The imaginary components are then normalized to one and graphed versus a temperature scale normalized by the blocking temperature. (Figure 5.7)

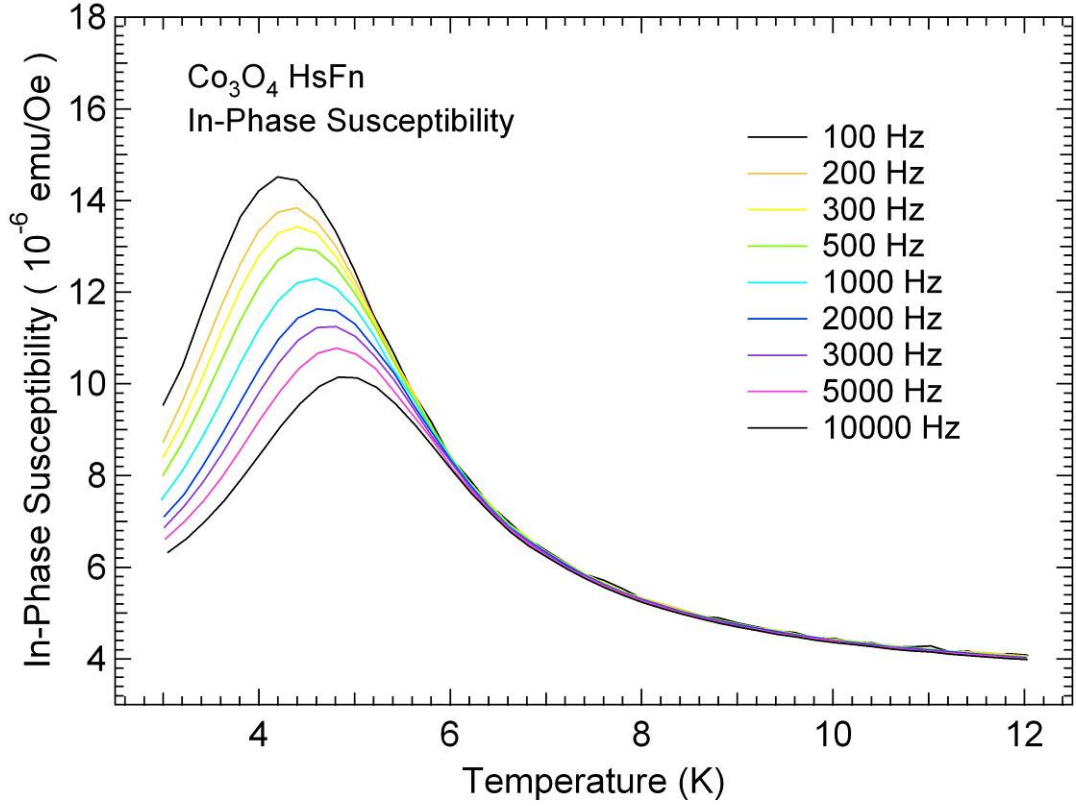


Figure 5.5: Multiple frequency scans of the in-phase component of the ac-susceptibility for HsFn.

Both the susceptibility graphs of the in and out-of-phase susceptibilities for the HsFn sample have the same type of characteristics as the LDps graphs. The in-phase ACMS multiple frequency curves lie on top of each and do not cross while the out-of-phase curves lie on top of each other but do cross. Like the LDps sample curves both phases for the HsFn also seem to lose frequency dependence above the same temperature, in this case 6.5 K.

The peaks of the imaginary components are extracted from the HsFn data. The imaginary components can also be normalized to 1 and graphed versus a temperature

scale normalized by the blocking temperature. (Figure 5.7) The data is normalized in this way to determine the prevalence of interparticle interactions. Any additional interaction, like a dipole interaction between different particles, would have a different frequency dependence and hence would change the shape of the curves. For the HsFn sample the different frequency curves overlap well. This type of behavior is consistent with the absence of frequency dependent interparticle interactions and is one way of verifying that claim.

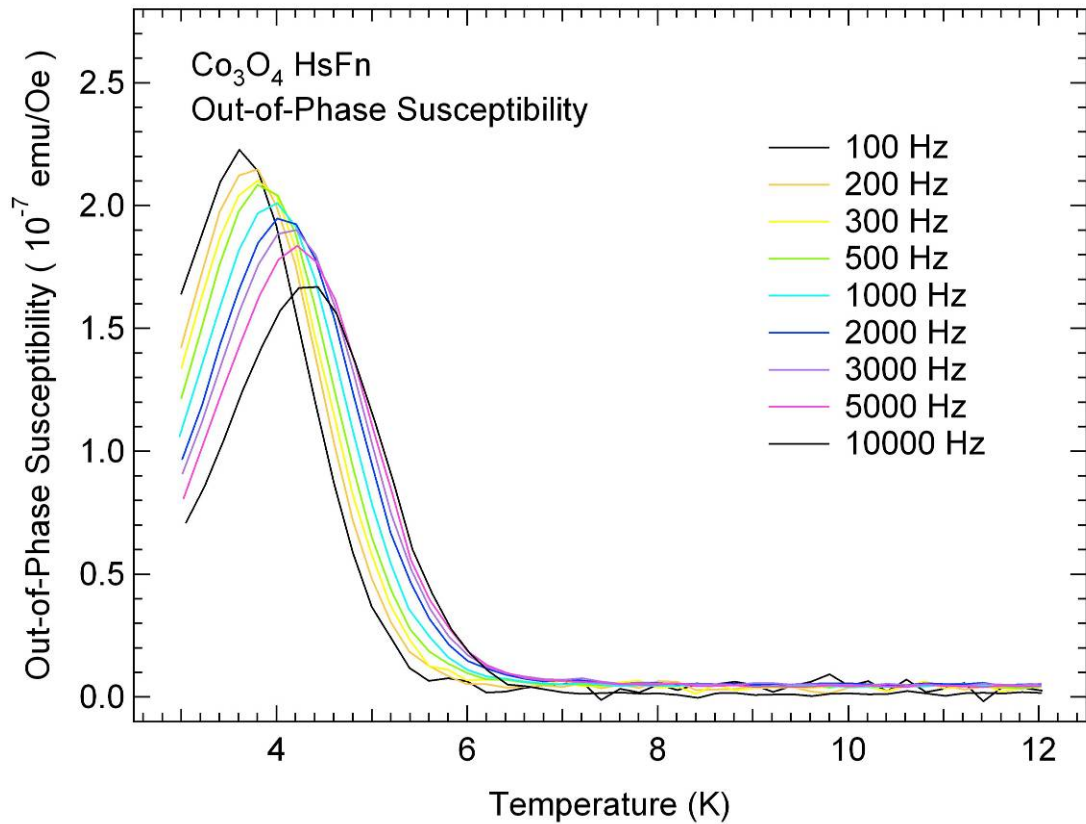


Figure 5.6: Multiple frequency scans of the out-of-phase component of the ac-susceptibility for HsFn.

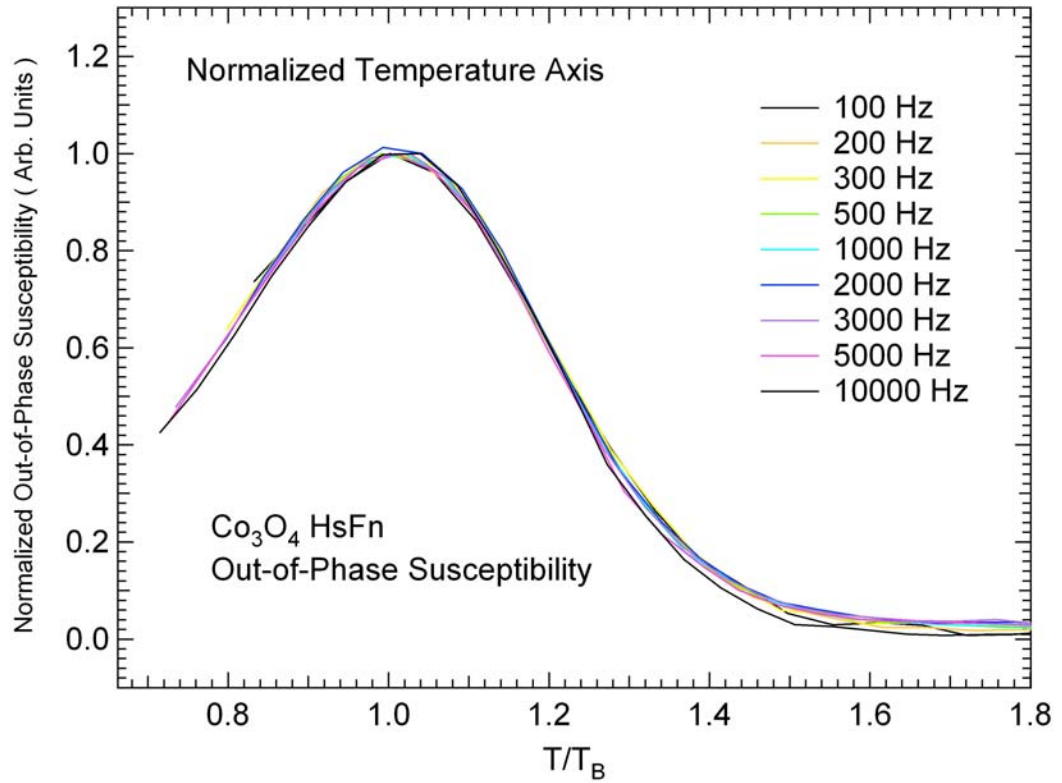


Figure 5.7: Multiple frequency scans of the normalized out-of-phase component of the ac-susceptibility for HsFn vs. a temperature axis that has been normalized to the blocking temperature of each frequency.

The HsFn data can also be plotted to look for interparticle interactions through a Néel-Arrhenius plot. The natural log of the Néel-Brown relation is taken for the blocking temperature at a given frequency. The blocking temperature for each frequency is then plotted on a graph of  $\ln(1/f)$  vs.  $1/T$ . (Figure 5.8) If there were frequency dependent interactions between the particles, plotting them in this manner would produce a deviation from a straight line. If there are no interactions the intercept of this line gives you the attempt time,  $\tau_0$ , of the material and the slope of this line gives you the magnetic

anisotropy energy,  $E_A$ , of the particles. When this number is normalized to the volume, the magnetic anisotropy energy density,  $K$ , for the particles can be extracted.

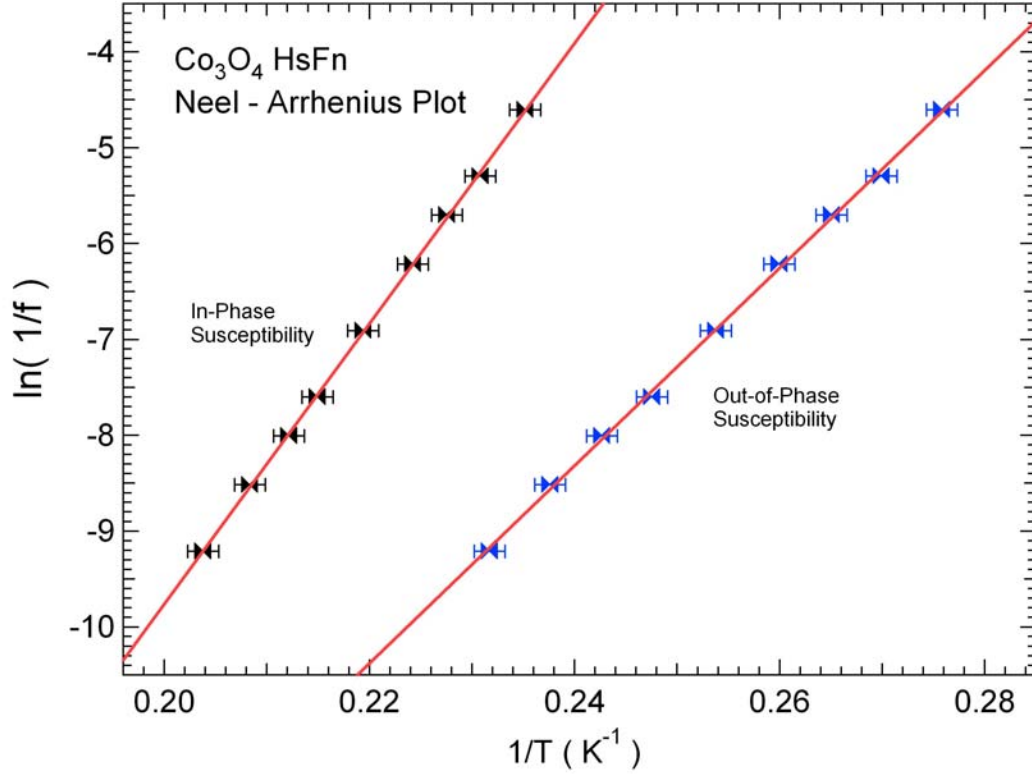


Figure 5.8: Néel-Arrhenius plots of the in-phase and out-of-phase components of the ac-susceptibility for HsFn. The intercept of these data give you the attempt time while the slope gives you the magnetic anisotropy energy.

In this case the Néel-Arrhenius plot of the HsFn encased 6.3 nm nanoparticles gives us an extracted attempt time of  $(1.15 \pm 0.25) \times 10^{-17}$  sec for the in-phase component of the susceptibility and  $(4.37 \pm 1.50) \times 10^{-15}$  sec for the out-of-phase component. The magnetic anisotropy energy of the in-phase extracted is  $(2.02 \pm 1.00) \times 10^{-21}$  J and the out-

of-phase is  $(1.42 \pm 1.00) \times 10^{-21}$  J. The volume of a 6.3 nm diameter particle is  $1.31 \times 10^{-25}$  m<sup>3</sup>. Taking this as the average volume for these particles the average magnetic anisotropy energy density,  $K$ , for the in-phase component of the susceptibility must be  $(1.54 \pm 1.00) \times 10^4$  J/m<sup>3</sup> and the out-of-phase  $(1.09 \pm 0.80) \times 10^4$  J/m<sup>3</sup>.

It should be noted that the LDps ac-susceptibility peaks are all at higher temperature than the HsFn peaks. At first glance this seems odd. For typical superparamagnetic materials larger particles should have larger blocking temperatures since the blocking temperature scales with the total anisotropy energy of a particle. This means that the smaller LDps particles must have a larger total anisotropy energy, which is a product of the anisotropy energy density and the volume. HsFn has a much larger volume, more that 3 times the volume of LDps, so the anisotropy energy density of the LDps particles must be at least 3 times as large. In fact, we find that they have an anisotropy energy density of almost an order of magnitude larger! This is a very large difference that points to an incredible size effect on the effective anisotropy energy density for the Co<sub>3</sub>O<sub>4</sub> nanoparticles.

### Discussion

The values extracted for the LDps and HsFn samples seem reasonable when compared to each other as well as compared to values found in the literature.<sup>34, 42, 43</sup> Since there was trouble synthesizing reliable larger particles, other values from the literature have been used in an attempt to determine the nature of this particle system.

The anisotropy energy densities in these two particles were found using two

different methods. The first was done on 10 nm  $\text{Co}_3\text{O}_4$  particles by Kundig *et al.*<sup>42</sup> using Mössbauer spectroscopy. They found that the  $\text{Co}^{2+}$  site spectrum broadening at a certain temperature corresponded to the antiferromagnetic to superparamagnetic transition. The anisotropy constant they estimated for this transition was  $4 \times 10^3 \text{ J/m}^3$ . The most recent measurement of the anisotropy energy density of  $\text{Co}_3\text{O}_4$  was found in a paper by Takada *et al.*<sup>43</sup> in which they study 3 nm  $\text{Co}_3\text{O}_4$  particles. These measurements were done in an almost identical way to the measurements performed in this study. ACMS measurements were done for these 3 nm  $\text{Co}_3\text{O}_4$  particles. The anisotropy energy density was determined to be  $1.9 \times 10^5 \text{ J/m}^3$ .

It is useful to note once again that the anisotropy energy that is being measured in the frequency dependence of the superparamagnetic phase transition, is the energy barrier that the total magnetic moment of a particle experiences. Since the particle moment in this case must be made up of the uncompensated spins, the anisotropy energy can then be thought of as the energy barrier that all the uncompensated spins must overcome in order to move between the up and down states. Therefore, the arrangement of these spins within the particle could have an effect on the size of this energy barrier. In fact, if a majority of spins were simply scattered throughout the bulk of the particle, there would only be a small change in the total effective anisotropy energy density due to the few number of uncompensated spins on the surface. However, if the spins were mostly concentrated on the surface of the particle the arrangement of these spins on the surface could have a large effect on the energy barrier. As stated in the previous chapter, surface arrangements of spins tend to give rise to surface anisotropy and hence produce an

increase in the effective anisotropy energy of a system. In the case of a particle with uncompensated spins predominately on the surface, the technique used to measure the anisotropy energy density would be more sensitive to the surface. Moreover, if the surface spins became weakly coupled to the core spins the energy barrier measured would be almost exclusively due to the surface anisotropy.

It may be useful to point out that the only reported values of the anisotropy energy density of  $\text{Co}_3\text{O}_4$ , found by this author, were for small particles of  $\text{Co}_3\text{O}_4$ <sup>34, 43</sup> and none for bulk  $\text{Co}_3\text{O}_4$ . Apparently this system has not been of enough interest to measure the bulk anisotropy energy density more closely.

The technique used, ACMS, measures the energy barrier that the uncompensated spins have to overcome in order to flip. If the spins that make up the moment are mainly on the surface, then this technique is predominately measuring the surface anisotropy. However, there should be some coupling between the surface spins with some of the bulk spins, so any exchange energy would contribute, unless of course the coupling was very weak. If the coupling were weak, then the anisotropy energy that is being measured would be just the anisotropy energy density of the uncompensated spins. In view of these facts, and taking into account that the uncompensated spins should mainly be on the surface, the anisotropy energy for these spins should be greatly affected by surface effects.

Adding the values from the literature to the anisotropy energy densities determined for the particles synthesized in this study puts the values in a better perspective and helps to answer the question of how the anisotropy energy density of

$\text{Co}_3\text{O}_4$  particles varies with size. In Figure 5.9, the anisotropy energy densities for the four different particle sizes are plotted. This is a meaningful way to plot this data because it shows the dependence of the anisotropy energy density with diameter.

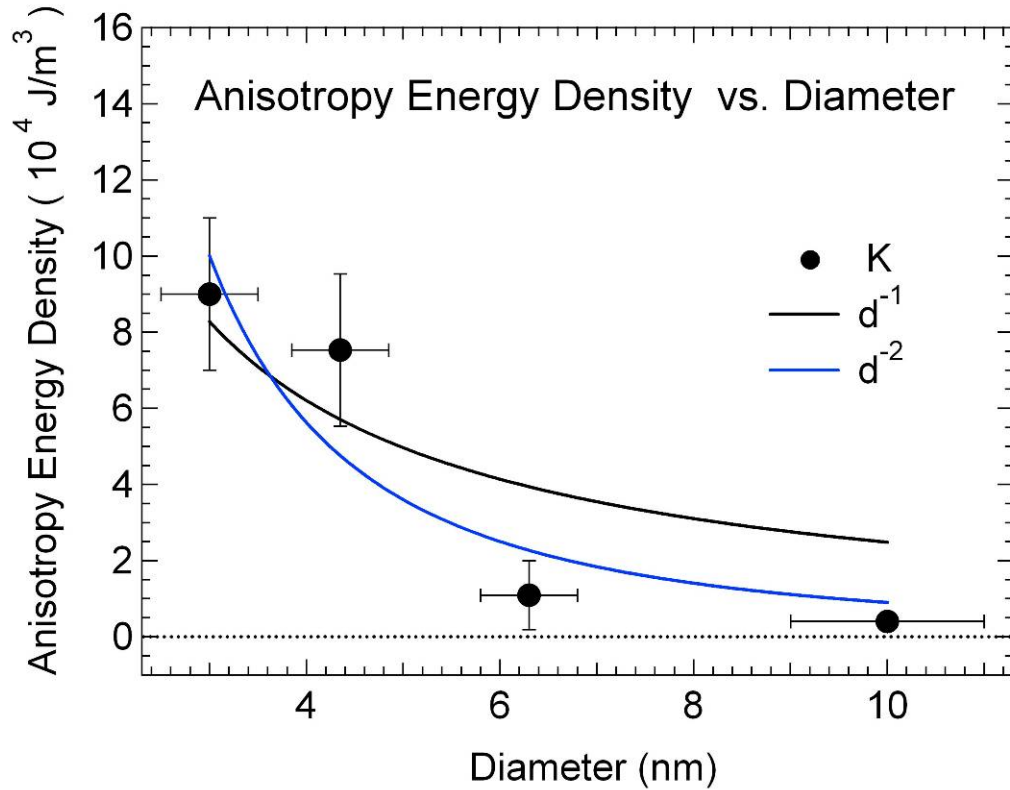


Figure 5.9: Magnetic anisotropy energy density versus particle size. The black circles represent  $K$  for the four different particles. The different colored lines represent the different models used. The phenomenological model using  $d^{-2}$  corresponds to a better fit to the data than a  $d^{-1}$  fit.

It is also useful to note, that these anisotropy energy densities are measured at similar low temperatures so there should not be a significant difference due to temperature variations. The general trend of the data is an increase of the anisotropy

energy density as the particle size is reduced.

An increase of the anisotropy energy density as the particle size is reduced is expected to correlate with the increase of the effect of the surface on the anisotropy, which was described in the previous chapter. Simply put, the curvature of a particle's surface becomes more pronounced as a particle is further reduced in size. This increase in curvature causes an increase in the anisotropy energy density for the spins on the surface of a particle, creating a greater effective anisotropy energy density for the entire particle. However, looking at the data collected in this study and comparing it with data from similar systems, the degree of increase of the effective anisotropy energy density is much greater, for the nanoparticles studied in this dissertation, than would be expected for a simple surface model. This degree of increase has only been seen in one other similar system. In fact, some very interesting studies have been done in the Mørup group with the help of Bødker and Frandsen and others.<sup>36-38</sup> These papers describe how the behavior of  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles change with size. Like  $\text{Co}_3\text{O}_4$ ,  $\alpha\text{-Fe}_2\text{O}_3$  is an antiferromagnetic material but with a much higher Néel temperature. These papers outline trends, similar to those presented in this study, for the dependence of the magnetic anisotropy energy density on the size of the particles. What was found is that the anisotropy energy density for their  $\alpha\text{-Fe}_2\text{O}_3$  particles also increases with reduced particle size. The  $\alpha\text{-Fe}_2\text{O}_3$  anisotropy energy density does not follow the surface model discussed in chapter 5 but follows a different phenomenological model. They found that a simple phenomenological model given by

$$K_{eff}(d) = \frac{A}{d} + \frac{B}{d^2}, \quad (5.1)$$

described the trend well. Here  $d$  is the diameter of the particles and  $A$  and  $B$  are phenomenological constants of the material, similar to the bulk and surface terms used in equations 4.7 and 4.9.

Figure 5.13 shows a large increase in the anisotropy energy density as the particles get smaller. Like the  $\alpha\text{-Fe}_2\text{O}_3$  particles, these  $\text{Co}_3\text{O}_4$  nanoparticles do not follow the standard surface model but instead increase more dramatically with decreasing size. These two different phenomenological models are fit to the data. The Bødker model discussed above corresponds well to the  $d^2$  curve while the standard surface model, which corresponds well to the  $d^1$  curve, does not fit as well. This  $d^2$  curve is a phenomenological description of the anisotropy energy density's dependence on the diameter. This behavior may be due to isolated spins on the surface with a large anisotropy energy density normal to the surface

This model is a modification of the models used to represent a surface effect to anisotropy. Starting with the model described in Mørup *et al.*<sup>11</sup> and later changed in Gilmore *et al.*<sup>94</sup>, equations 4.7 and 4.9, the bulk and simple surface anisotropy energy terms are ignored and a simple model is used given by

$$K_{eff}(d) = \frac{K_P}{d^2}, \quad (5.2)$$

where  $d$  is the diameter of a particle, and  $K_P$  is a phenomenological constant with units of

energy. The best fit to the data for this model gives  $K_p = (9.0 \pm 2.0) \times 10^{-13}$  J/m.

It is pertinent to note that the simple treatment of surface anisotropy, given in previous works with equation 4.7, would average out to be zero for spherical particles using symmetry arguments. However it has been shown with ferro and ferrimagnetic particles to be valid.<sup>11, 83</sup> Now the Mørup group with the help of Bødker and Frandsen and others<sup>36-38</sup> helped to demonstrate that this simple model does not adequately describe the behavior of small antiferromagnetic particles. This indeed seems true for the particles in this study and leads to the conclusion that the surface can play an unexpectedly large role in the total effective anisotropy of, at the very least, antiferromagnetic particles.

## CHAPTER 6

## HOW SIZE AFFECTS THE NÉEL TEMPERATURE AND COERCIVE FIELD

Introduction

Vibrating Sample Magnetometry (VSM) measurements have been a useful way of determining the Néel temperature and coercive field for these superparamagnetic nanoparticles. A size dependence of the Néel temperature, particle moment, and coercive field are modeled and analyzed. In this chapter, the results of the VSM studies in determining the Néel temperature for the different particle sizes are presented and discussed. The methods used are explained and supported. The permanent magnetic moments of the individual particles for each size particle is determined and the arrangement of spins that make up these moments are discussed. Also, hysteresis loops of the samples cooled with and without an applied field, below the Néel and blocking temperatures, are presented and discussed.

LDps

The LDps sample, which contains nanoparticles of roughly 4.35 nm and has a mass of roughly 3.5 mg, was studied with the VSM at various applied fields. Initial magnetization scans were done on these nanoparticles at several different temperatures. From these scans the magnetic saturation, magnetic moment and dc-susceptibility at each temperature were extracted with the help of two different modified Langevin models.

The Langevin model was discussed earlier in chapter 4. Hysteresis scans were also done on these nanoparticles at 2 K in order to measure the coercive field of the two different particles.

### Initial Magnetization Scans

Initial magnetizations scans for the LDps samples from 300 – 2 K are shown in Figure 6.1 below. As the applied magnetic field is increased the magnetization of the samples increases and starts to roll over before in saturates. The shape of these curves demonstrates the magnetic properties of the particles, thus the Langevin model was fit to all these different initial magnetizations curves. One thing to note is that at high temperatures the curves are very linear and do not fit well to a Langevin model. Another thing to note is that as the Néel temperature is approached from high temperatures Langevin behavior is observed. The fits are very good in the temperature range of 15 – 100 K. Below the reported blocking temperature of 5 K, the fits become increasingly worse. This is due to the magnetic anisotropy playing a more dominant role in the magnetization response rather than the thermal energy. It must be mentioned that since the Langevin model does not include an anisotropy term, the extracted parameters for the fits below 5 K, as well as the extracted Néel temperatures, have substantial errors associated with them. In order to try and over come the lack of anisotropy in the model, a term is added to the Langevin model incorporating the remnant magnetization. It is shown that the susceptibility extracted using this extra term for fits to the data above 5 kOe determine a similar Néel temperature.

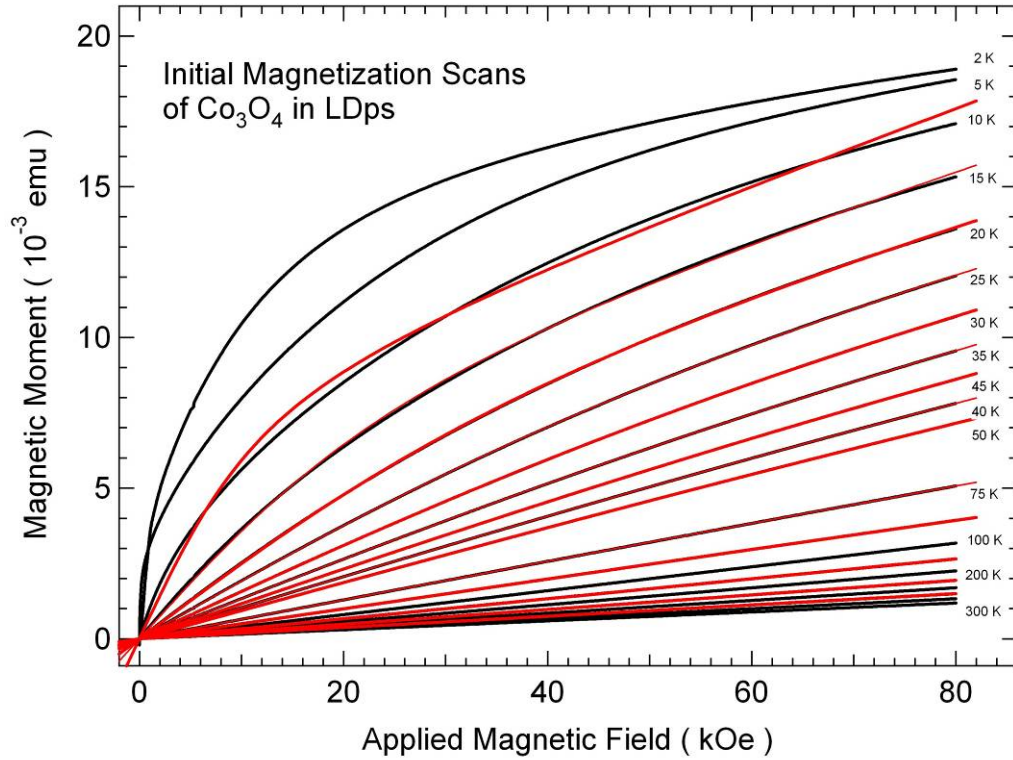


Figure 6.1: Initial magnetization scans of the LDps samples at temperatures from 2 - 300 K. The red curves are Langevin fits to the data that are then used to extract out the magnetic properties.

Because of the linear behavior at high temperatures, the slope of the curves at high field was used instead of the Langevin susceptibility term. In Figure 6.2 the high field susceptibility for the different temperature curves is plotted versus temperature. The peak of this graph around 20 K shows that there is indeed a change in the behavior of these particles, and corresponds roughly to the Néel temperature.

Because of the difficulty of resolving the Néel temperature more initial magnetization scans were taken at low temperature. Scans from 2 – 15 K were taken at 1

K intervals. Figure 6.3 shows these initial magnetization scans. The curves were fitted with the Langevin model and the saturation moments at each temperature were extracted from those fits.

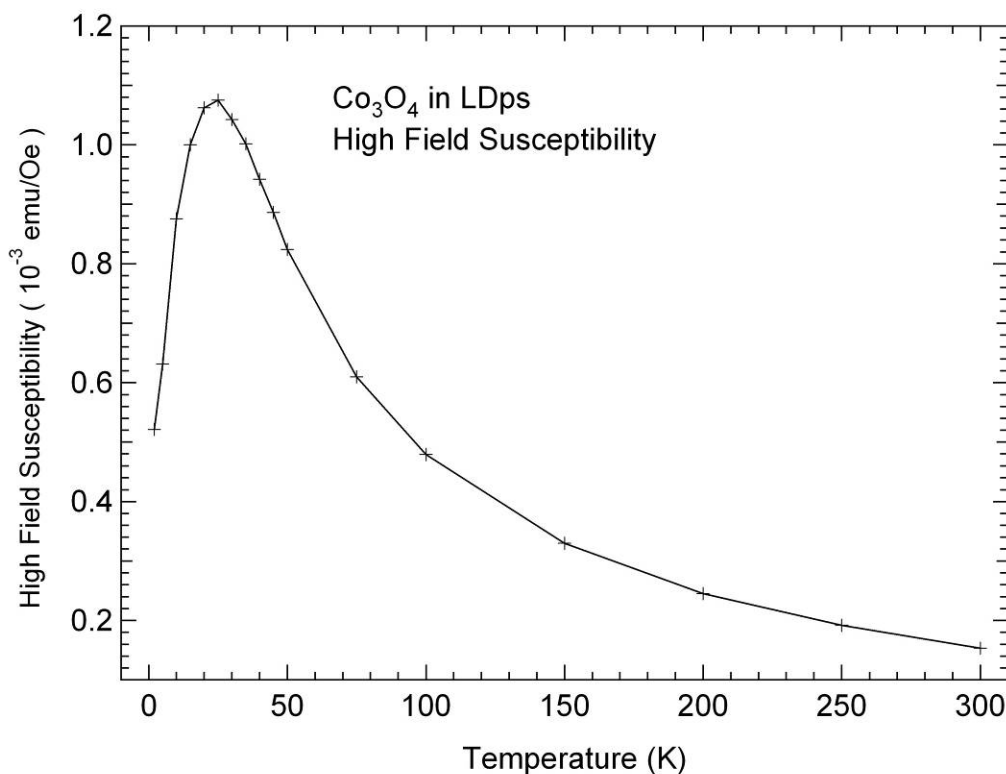


Figure 6.2: Susceptibility at high field in the LDps sample. The peak separates the blocked and unblocked phase of the superparamagnetic nanoparticles.

Shown in Figure 6.4 are the extracted saturation moments versus temperature. Starting at 2 K the saturation moments decrease in a linear fashion until the saturation moment starts to level off around 10 K. A straight line fit to the first four data points intersects the temperature axis at 15 K. Extrapolating that trend down to zero is a way of

determining the Néel temperature for antiferromagnetic nanoparticles.<sup>16, 66</sup> The Néel temperature for these 4.35 nm nanoparticles mineralized in LDps is then taken to be  $15 \pm 6$  K. This critical ordering temperature is significantly smaller than the purported bulk Néel temperature for  $\text{Co}_3\text{O}_4$  of 30 - 40 K. The change in the Néel temperature for different particles size is a main point of study in this dissertation and will be further discussed later in this chapter.

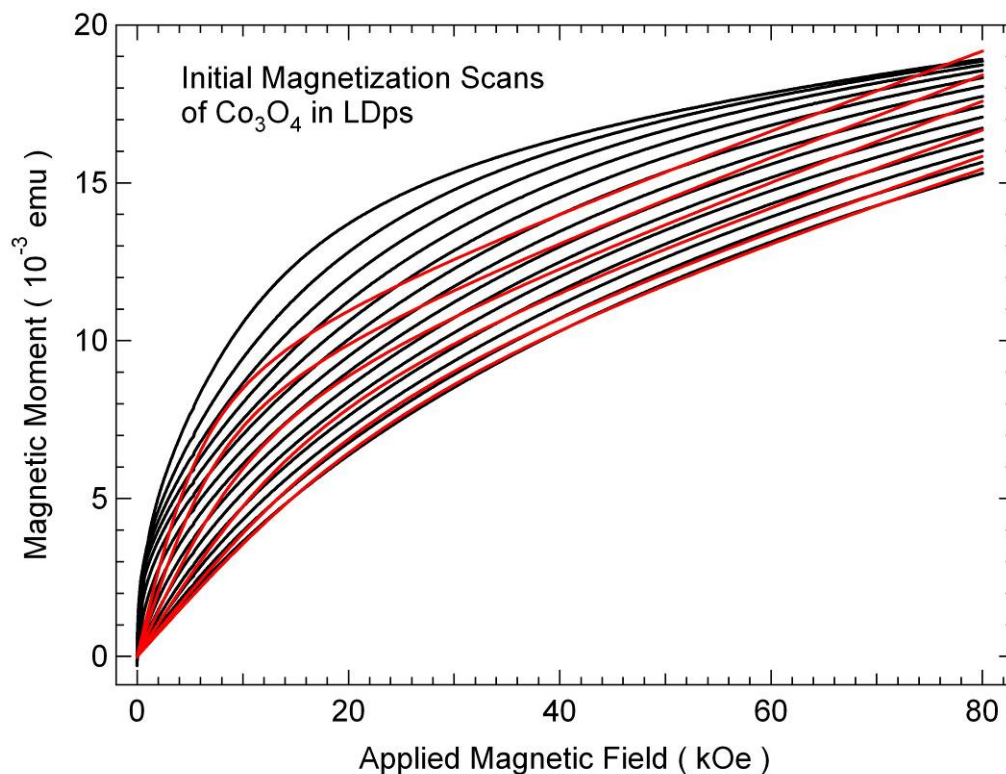


Figure 6.3: Initial magnetization scans of the LDps sample at temperatures from 2 - 15 K. The red curves are Langevin fits to the data that are then used to extract out the magnetic properties. Only the fits for 15, 14, 12, 10, 8, and 6 K are show. The fits get worse at temperatures close to and below the blocking temperature.

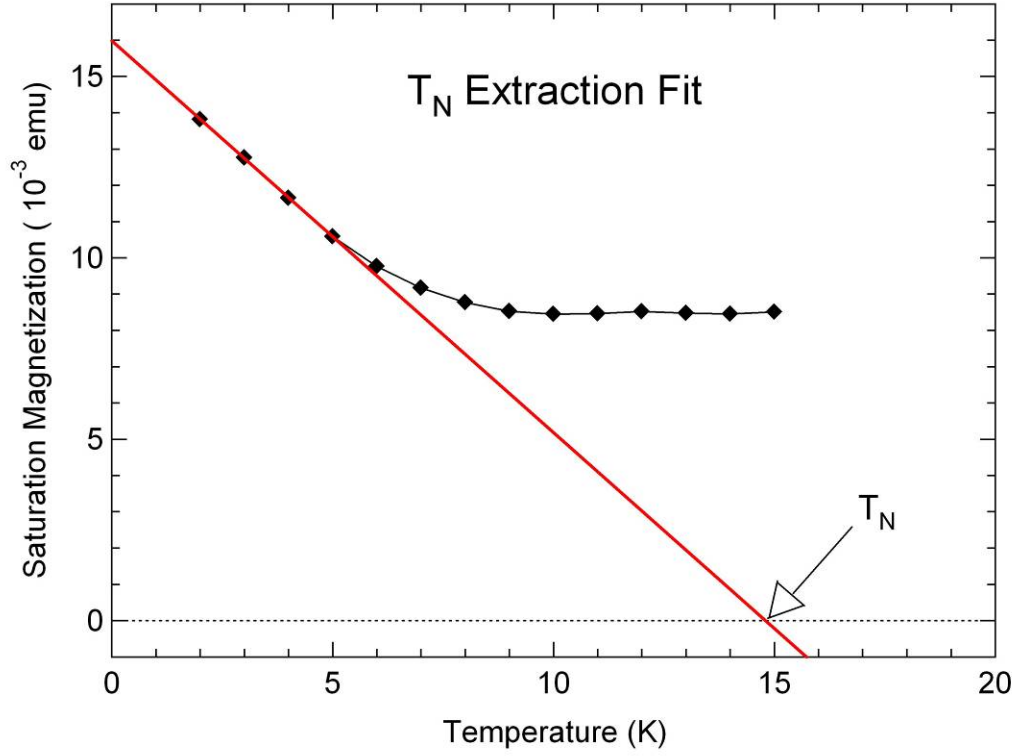


Figure 6.4: Saturation moments extracted from the Langevin fits from Figure 6.3 versus temperature. A linear fit to the data below 6 K determines a Néel temperature for the LDps sample of 15 K.

Because of the poorness of the fits of the Langevin model to the low temperature initial magnetizations curves for the LDps sample, an additional term trying to account for the anisotropy was added. This additional term tries to account for the remnant magnetization that such a sample with a high anisotropy close to the blocking temperature would produce. The new fit function is then equal to the previous Langevin model plus this remnant term and is given by

$$m = m_r + m_s L(x) + \chi H, \quad (6.1)$$

where now  $m_r$  represents the remnant moment. Figure 6.5 shows the fits to this new Langevin model. The fits were taken over the data above 5 kOe. In all cases the fits are extremely good.

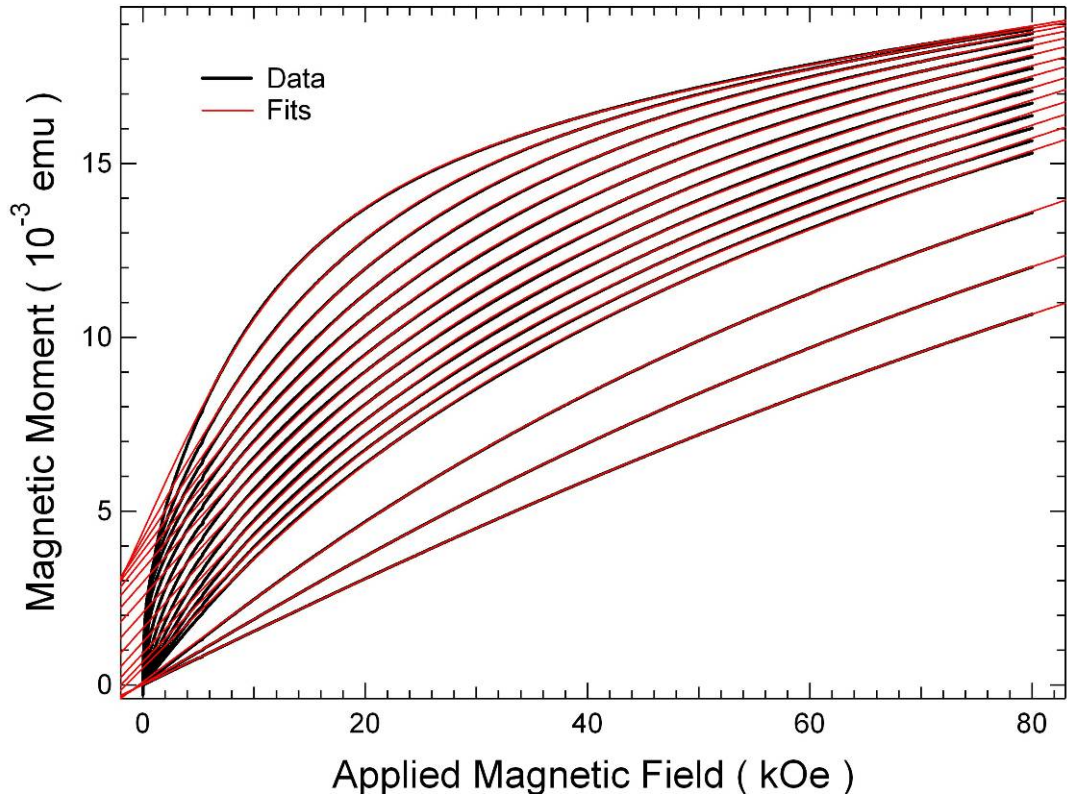


Figure 6.5: Fits to the LDps low temperature initial magnetization curves to the Langevin model plus a remnant moment term. The data from 2 - 30 K was well fit above 5 kOe.

The susceptibility was then extracted from these new fits in order to better resolve the Néel temperature. Figure 6.6 shows the extracted susceptibility of this new model plotted versus the temperature. The peak in the susceptibility was determined to be 15.4 K when the data from 5 – 30 K was fit with a polynomial function. The Néel temperature

is then taken to be  $15.4 \pm 2.0$  K.

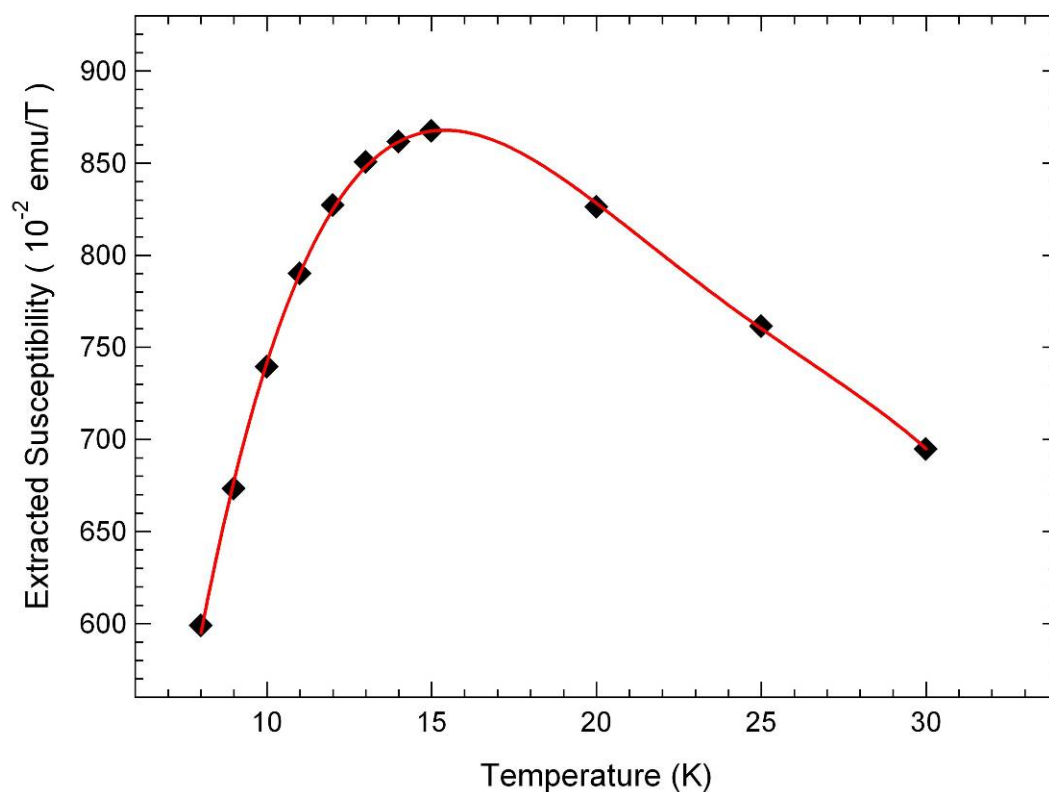


Figure 6.6: Extracted susceptibility from the fits to the Langevin model plus a remnant moment term. The data was fit with a 5<sup>th</sup> order polynomial in order to extrapolate a peak of 15.4 K.

The magnetic moment for these nanoparticles was also extracted. Instead of simply using the Langevin model, another method was used. This other method was used in this case because at these temperatures the Langevin model does a poor job of modeling the magnetic moments of the particles. In fact, the low field curve of the initial magnetizations curves are highly susceptible to the magnitude of the individual particle

moments. The larger the moment, the more pronounced the curve. However, because the temperature region between the Néel temperature and blocking temperature is so small, from 5 – 15 K in this case, anisotropy energy plays a large role. This makes the extracted magnetic moment from the Langevin model different than the real value. It should be noted that this effect close to, and below, the blocking temperature also effects the saturation moments.

The method used to extract out the magnetic moment uses a low field approximation of the Langevin function. This is a method adopted by Harris *et al.*<sup>100</sup> Assuming that the anisotropy plays a large role at higher fields, the low field approximation to the Langevin function, equation 3.7, is used. First, the paramagnetic background is first subtracted from an initial magnetization curve between the blocking temperature and the Néel temperature, in this case 10 K. (Figure 6.7) Then the curve is normalized to 1 and the low field curve is fit to a line. It is seen that this region is very linear and a line fits very well below 500 Oe. Using equation 3.7 the slope of the line should be,  $\mu/(3k_B T)$ . The slope is then multiplied by  $3k_B T$  to get the magnetic moment,  $\mu$ .

The magnetic moment extracted with this method for the 4.35 nm LDps nanoparticles is  $44 \pm 10 \mu_B$ . This corresponds to roughly 14 uncompensated  $\text{Co}^{2+}$  spins, with  $3 \mu_B$  per atom. Looking at this from a geometrical standpoint, 14 uncompensated  $\text{Co}^{2+}$  spins correspond to roughly 1/82 of the total  $\text{Co}^{2+}$  spins in this 4.35 nm size particle. This is calculated by taking into account the volume of one unit cell of  $\text{Co}_3\text{O}_4$  and using the knowledge that one unit cell has 8  $\text{Co}^{2+}$  spins. With a lattice constant of 8.08 Å, the volume of a unit cell of  $\text{Co}_3\text{O}_4$  is  $5.28 \times 10^{-28} \text{ m}^3$ . This volume corresponds to 8  $\text{Co}^{2+}$

spins, so the volume of a 4.35 nm particle is  $4.31 \times 10^{-26} \text{ m}^3$ . Therefore there are roughly 81.7 unit cells in the LDps nanoparticles. Since there are 8  $\text{Co}^{2+}$  spins per unit cell that means that the average number of  $\text{Co}^{2+}$  spins in an LDps particle is roughly 654.

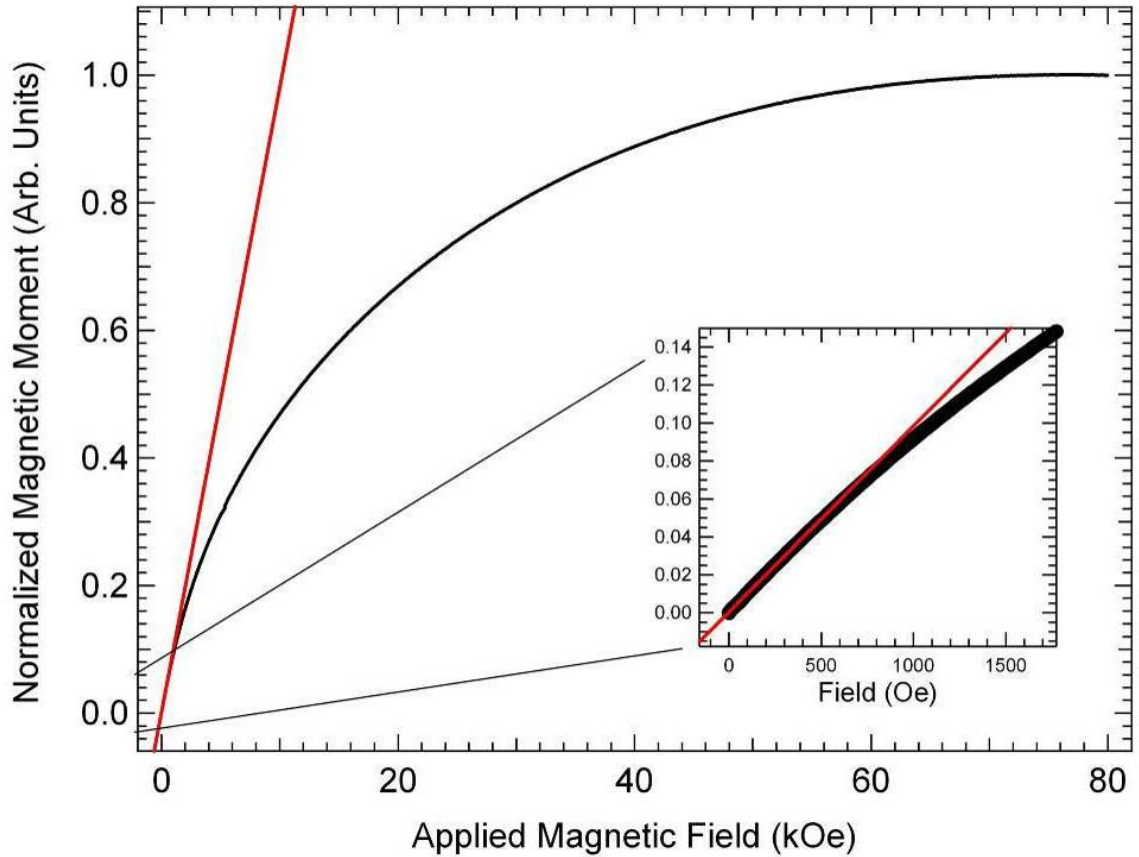


Figure 6.7: This figure demonstrates the method used to extract out the average magnetic moment of the nanoparticles. The black line represents the initial magnetization of the LDps sample at 10 K with the linear component subtracted and the end point normalized to one. The red line is a fit to the data at below 500 Oe, in order to extract out the magnetic moment of the sample above the blocking temperature but below the Néel temperature. The inset is a blow up of the low field linear region.

Néel proposed a model for the distribution of uncompensated spins in antiferromagnetic particles.<sup>101</sup> Néel proposed that the total number of uncompensated spins,  $N_{uc}$ , would be related to the total number of spins,  $N$ , in a particle. For randomly distributed uncompensated spins, he proposed that  $N_{uc} \approx N^{1/2}$ , where as for surface restricted spins it was suggested<sup>102</sup> that  $N_{uc} \approx N^{1/3}$ . This last relation relating the total number of spins to the number of uncompensated spins on the surface come straight out of the volume relation. With the total number of spins on the surface as roughly  $N^{2/3}$  then the total of number of uncompensated spins on the surface is  $(N^{2/3})^{1/2}$ . Therefore if  $N_{uc} \approx N^{1/2}$  then  $N_{uc} \approx 26$  and if  $N_{uc} \approx N^{1/3}$  then  $N_{uc} \approx 9$ . Based on these models the best conclusion is that most of the uncompensated spins are on the surface of the particle and not scattered throughout the entire volume of the nanoparticles. In fact, there may be a couple of uncompensated spins that are not on the surface but the majority should be on the surface. It should also be mentioned, that the magnetic moment measured for the particles could be slightly elevated if there was a contribution to this moment from thermal energy. As discussed in chapter 3, Mørup *et al.*<sup>14</sup> suggested that a thermoinduced moment could be produced in antiferromagnetic materials and that in a nanoparticle system this moment could be a large fraction of the total moment. If this is true, then the true number of uncompensated moments per particle may be smaller than with this previous argument and would unambiguously imply a surface distribution of the uncompensated spins.

Another thing that should be mentioned is that some previous studies on  $\text{Co}_3\text{O}_4$  nanoparticle systems have seen much larger permanent magnetic moments, up to  $625\mu_B$

for 20 nm<sup>44</sup> and even as much as 826-1439  $\mu_B$  for 12 nm.<sup>45, 46</sup> However another study by Takada et al.<sup>43</sup> found the magnetic moment of 3 nm particles to be roughly 15  $\mu_B$ . In the Takada paper, it was clearly shown that the nanoparticles were very clean and definitely Co<sub>3</sub>O<sub>4</sub>. The 3 nm nanoparticles behaved very similar to the particles synthesized for this work.

### Hysteresis

Hysteresis was also seen in these LDps particles. In this measurement the sample was cooled down to 2 K in a zero applied magnetic field and then the field was ramped between  $\pm 8$  T. Figure 6.8 shows the hysteresis loop of the LDps sample with a coercive field of roughly  $398 \pm 10$  Oe. The presence of an open hysteresis loop corresponds well to the superparamagnetic nature of the particles and ferromagnetic like blocking of the uncompensated spins.

A hysteresis loop was also measured after being cooled down to 2 K in the presence of an 8 T applied magnetic field. No exchange bias was seen, within the  $\pm 10$  Oe error of the measurement and is essentially identical to the zero field cooled hysteresis shown in figure 6.8. This is a slightly surprising result since in other studies of Co<sub>3</sub>O<sub>4</sub> nanoparticles found that there was exchange bias in these types of systems.<sup>44-46</sup> However, the Co<sub>3</sub>O<sub>4</sub> nanoparticles in those studies either had the particles in a conglomeration where the individual particles could touch and interact physically<sup>44-46</sup> or else they were coated with a biological material.<sup>45, 46</sup> The difference between the samples used here and the ones used in other studies could account for the lack of exchange bias.

It could very well be possible that the method used for synthesizing the  $\text{Co}_3\text{O}_4$  nanoparticles in this study are inherently more suited to the creation of good quality  $\text{Co}_3\text{O}_4$  nanoparticles, and that the uniformity, monodispersity, tight size distributions, and non-magnetic buffer provide an environment that is ideal for studying the properties of small antiferromagnetic particles. The much lower moment found in these particles, as just discussed, could also be a contribution to the lack of exchange bias as well as evidence for the high quality of the nanoparticles used in this study.

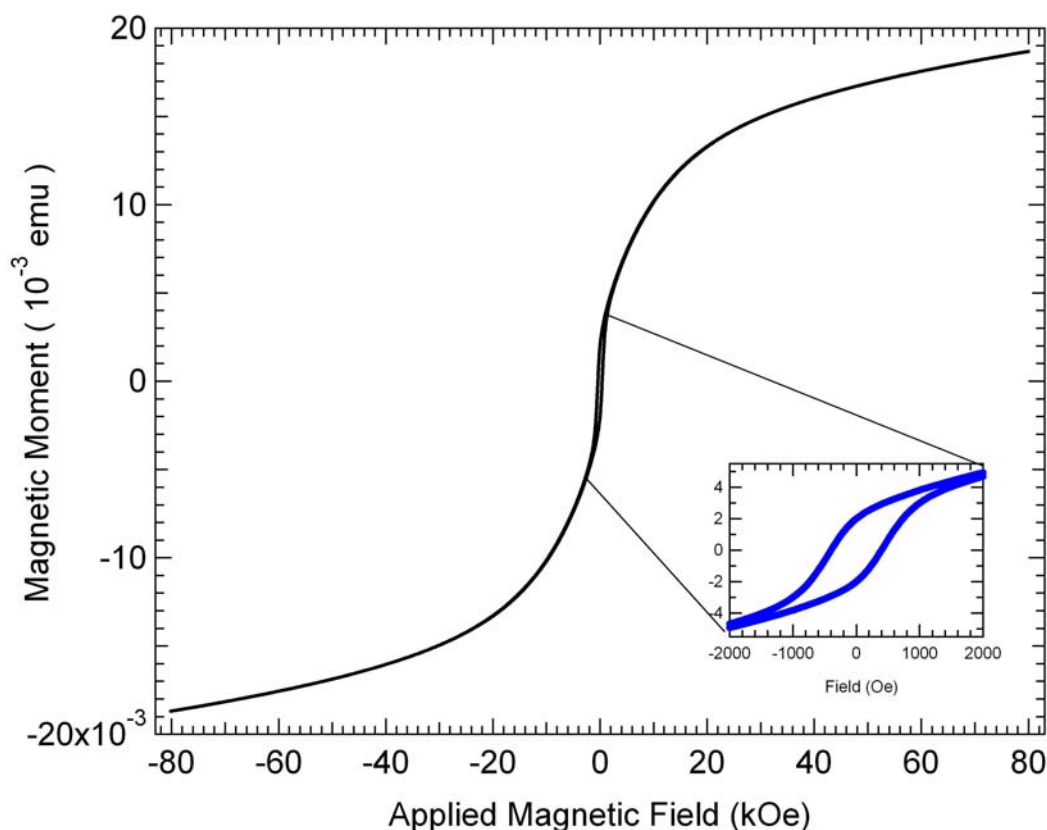


Figure 6.8: Hysteresis of the LDps sample at 2 K. The inset is a blow up of the low field region.

This lack of exchange bias could also suggest that the coupling between the uncompensated and core spins is weak. This demonstration of weak coupling between the surface and core spins as well as the surface distribution of spins would lead to the supposition that the ACMS measurements of the anisotropy energy density were almost entirely due to the surface.

### HsFn

The HsFn sample, which contains nanoparticles of roughly 6.3 nm, and has a mass of roughly 4.3 mg was also studied with the VSM. The same measurements were done for the HsFn samples as for the LDps sample.

### Initial Magnetization Scans

Initial magnetizations scans for the LDps samples from 200 – 2 K are shown in Figure 6.9 below. As the applied magnetic field is increased the magnetization of the samples increases. The Langevin model was fit to all these different initial magnetizations curves. One thing a little different is that at high temperatures the curves are not as linear as the LDps but do fit very well to the Langevin model. Langevin behavior is observed as the Néel temperature is approached. The fits are very good in the temperature range of 10 – 100 K and are overall better fits to the data are obtain for the HsFn sample due to the decrease in the magnitude in the anisotropy energy density determined with the ACMS. Below the reported blocking temperature, around 4 K the fits become increasingly worse. In this temperature region the magnetic anisotropy plays

a more dominant role in the magnetization response.

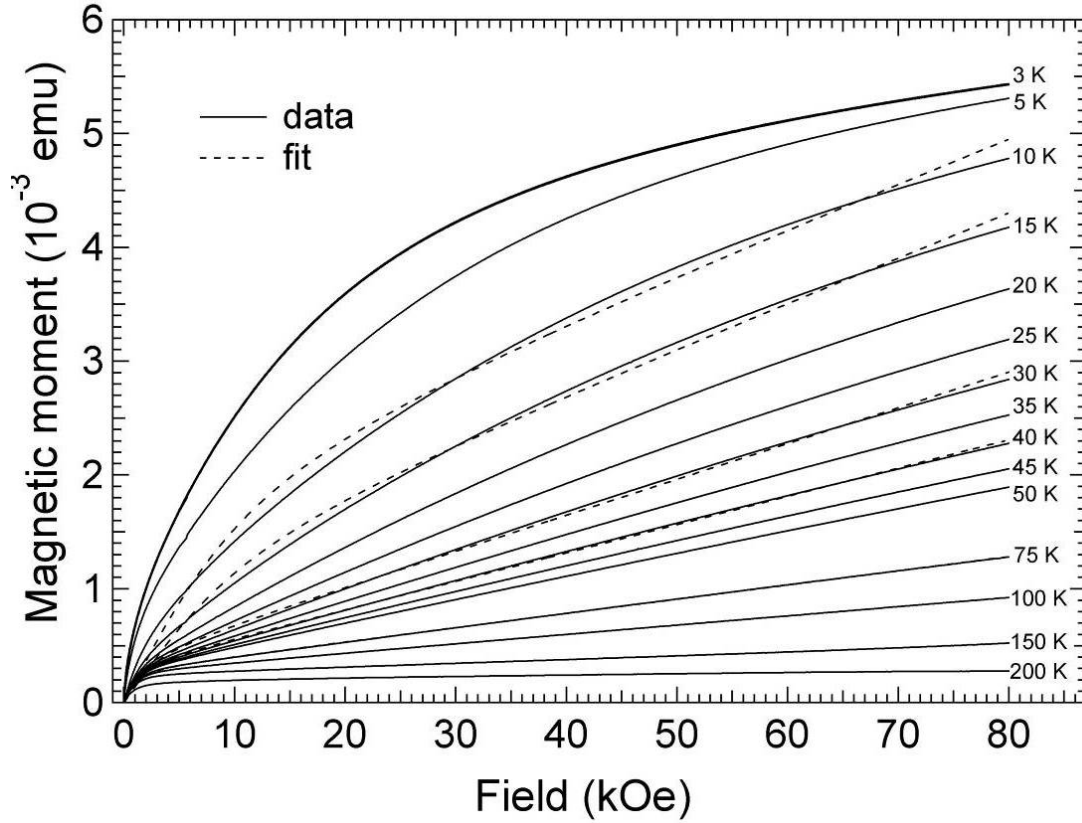


Figure 6.9: Initial magnetization scans of the HsFn sample at temperatures from 2 -200 K. The dashed curves are Langevin fits to the data that are then used to extract out the magnetic properties.

Figure 6.10 shows the saturation moment extracted from the initial magnetizations curves fitted by the Langevin model. There is a clear trend in the data showing the change in phase of the  $\text{Co}_3\text{O}_4$  nanoparticles as the temperature is increased. A straight line fit to the points below 20 K intersects the temperature axis at 21 K. As

discussed in the LDps section and chapter 4 the intersection is taken to be the Néel temperature for these HsFn mineralized nanoparticles. The Néel temperature in this case is taken to be  $21 \pm 6$  K. As discussed for the LDps sample, this determined Néel temperature is lower than the reported bulk value of  $\text{Co}_3\text{O}_4$  of 30 - 40 K. These differences will be explored in more detail as well as the fits to finite-size scaling models later in this chapter.

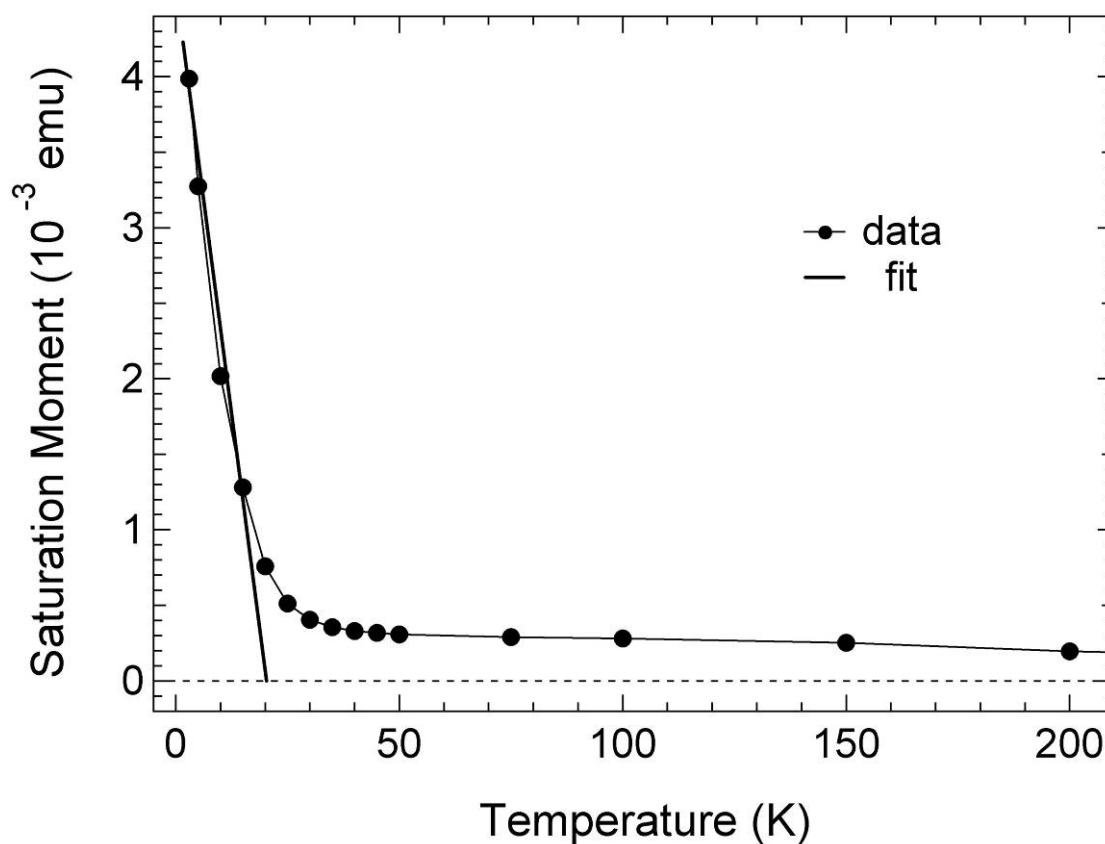


Figure 6.10: Saturation moments extracted from the Langevin fits from Figure 6.8 versus temperature. A linear fit to the data below 15 K determines a Néel temperature for the HsFn sample at 21 K.

The linear susceptibility term was also extracted from the initial magnetization curves for the HsFn sample. In Figure 6.11 the extracted susceptibility versus temperature curve is shown. The peak in the susceptibility represents a change in the behavior of this magnetic material. In fact, the peak separates the paramagnetic and antiferromagnetic phases of these  $\text{Co}_3\text{O}_4$  nanoparticles. A Curie-Weiss curve was fit to the points above 40 K. The Curie-Weiss parameter extracted from this data was roughly -20 K.

The Curie-Weiss parameter gives a rough estimation for the critical ordering temperature of a magnetic material. If the sign in front of the parameter is positive the material is exhibiting a ferromagnetic coupling of the spins, but if the sign in front of the parameter is negative the material exhibits antiferromagnetic coupling between the spins. Since the parameter measured for this material is negative, the phase transition must be antiferromagnetic. The fact that this number is so close to the determined Néel temperature is telling. For most antiferromagnetic materials the Curie-Weiss parameter is much larger than the determined Néel temperature. However, it has been experimentally shown that in general the smaller the Néel temperature the closer the Curie-Weiss parameter is to the determined Néel temperature.<sup>65</sup>

The poorness of the fits below the Néel temperature makes the error in the Néel temperature significant. In order to reduce this error a remnant magnetization term is added to the Langevin function. Figure 6.12 shows the fits to the data above 5 kOe using the model from equation 6.1. The fits are much better than the regular Langevin model providing another way of determining the Néel temperature.

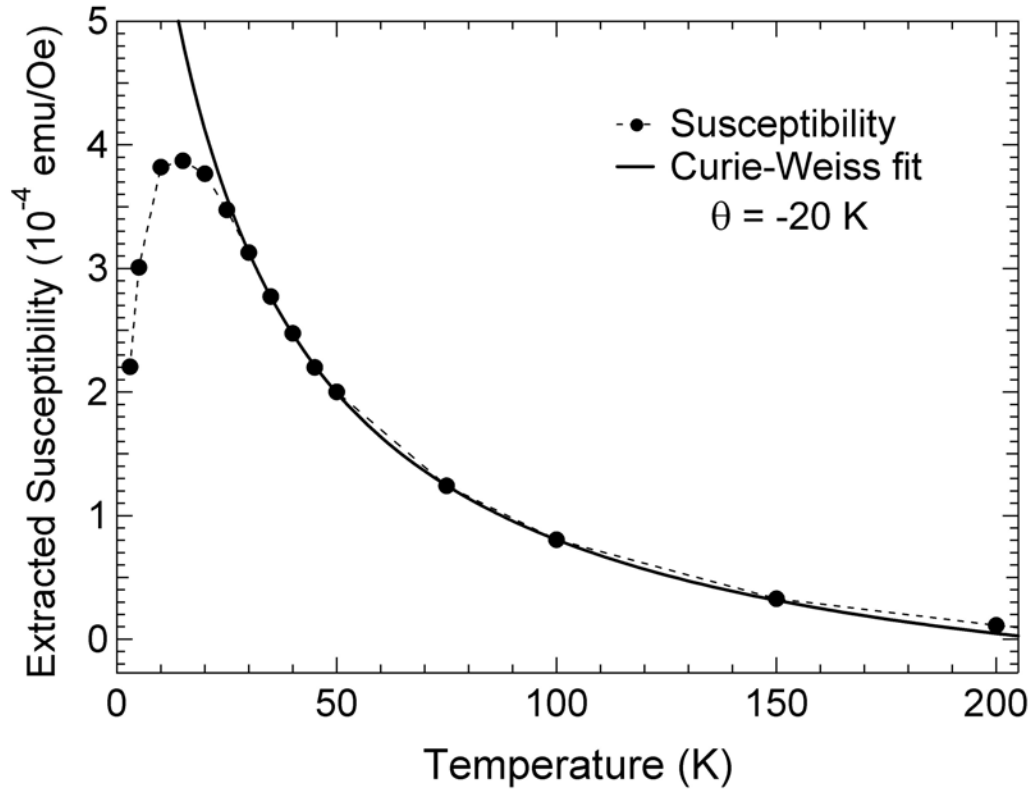


Figure 6.11: Susceptibility extracted from the Langevin fits from Figure 6.10 for the HsFn sample. The peak separates the blocked and unblocked phase of the superparamagnetic nanoparticles.

The susceptibility was then extracted from these new fits in order to better resolve the Néel temperature. Figure 6.13 shows the extracted susceptibility plotted versus the temperature. The peak in the susceptibility is roughly 17.6 K when the data from 5 – 30 K was fit with a lognormal function. For this method the Néel temperature is taken to be about  $17.6 \pm 3.0$  K, very close to the value extracted using the other method. This other method does not only provide another way of determining the Néel temperature but is a way of verifying the other method.

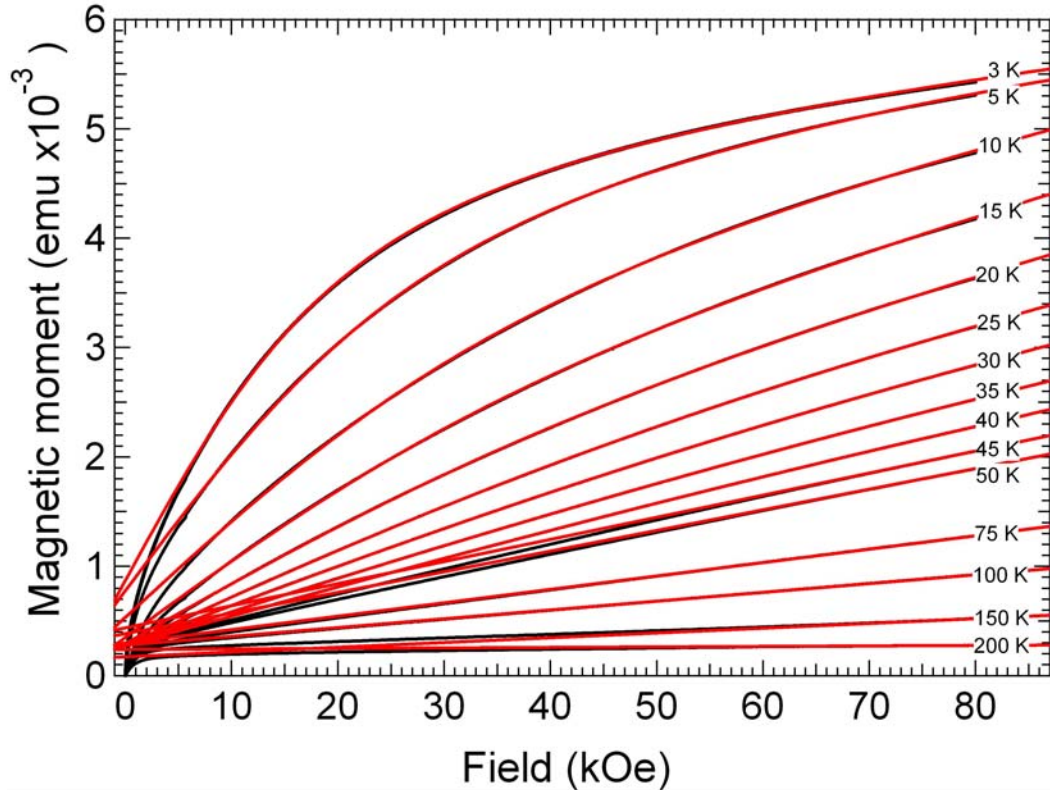


Figure 6.12: Fits to the HsFn initial magnetization curves to the Langevin model plus a remnant moment term are shown in red. The data, black, was well fit above 5 kOe.

The moment was also extracted for these nanoparticles. From 10 K to 15 K, the average extracted magnetic moment,  $\mu$ , for the particles was found to be roughly  $55 \pm 15 \mu_B$  corresponding to about  $18 \pm 5$  uncompensated  $\text{Co}^{2+}$  atoms with  $3\mu_B$  per atom. The moment was extracted from the fits with a method used by Harris *et al.*<sup>100</sup> in which the low field slope, after a linear background subtraction and normalization, was set equal to  $\mu/(3k_B T)$ . This was described for the LDps nanoparticles in the previous section. The large uncertainty in the magnetic moment is due to uncertainties in the measurement and the nature of the extraction.

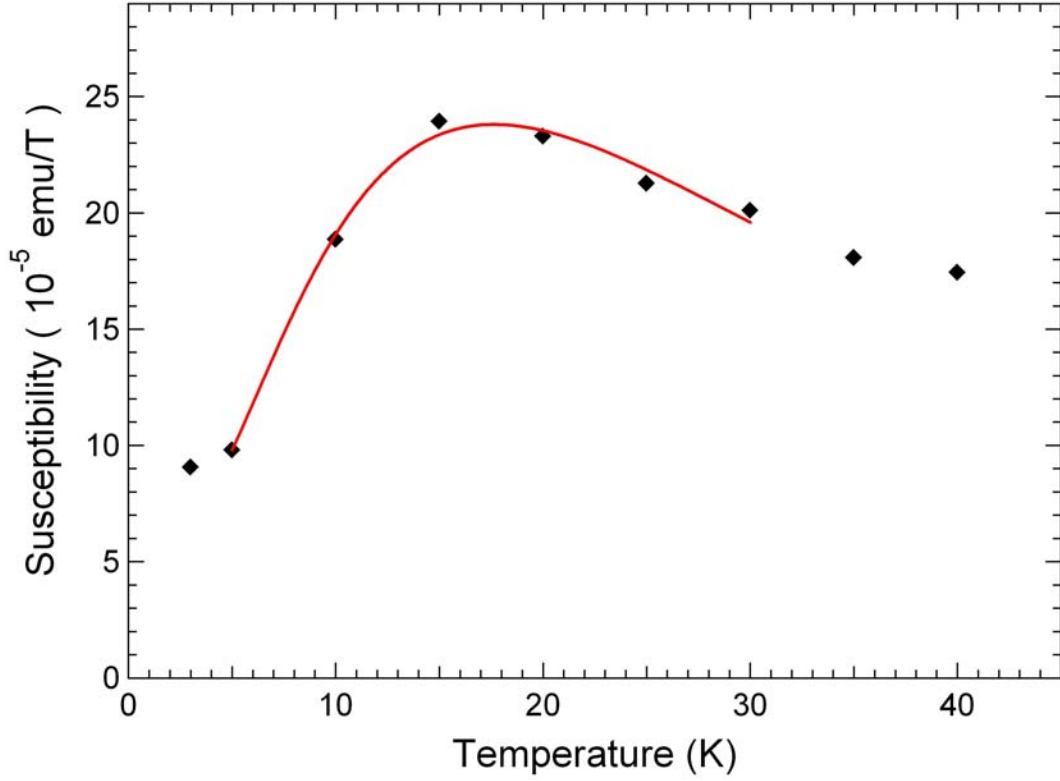


Figure 6.13: Extracted susceptibility from the fits to the Langevin model plus a remnant moment term. The data was fit with a log normal function in order to extrapolate a peak of 17.6 K.

The moment was also extracted for these HsFn nanoparticles. From 10 K to 15 K, the average extracted magnetic moment,  $\mu$ , for the nanoparticles was found to be roughly  $55 \pm 15 \mu_B$  corresponding to about  $18 \pm 5$  uncompensated  $\text{Co}^{2+}$  atoms with  $3\mu_B$  per atom. The moment was extracted from the fits with a method used by Harris *et al.*<sup>100</sup> in which the low field slope, after a linear background subtraction and normalization were performed, was set equal to  $\mu/(3k_B T)$ . This was described for the LDps nanoparticles in the previous section and is being used again here. The large uncertainty

in the magnetic moment is due to uncertainties in the measurement and the nature of the extraction.

Similar to the LDps nanoparticles, this value for the magnetic moment would be expected if the uncompensated spins were on the surfaces of the particles. Based on the average volume of the particles, and the volume of a unit cell of  $\text{Co}_3\text{O}_4$ , the total number of Co atoms in each particle should be roughly  $\sim 6000$ . The magnetic  $\text{Co}^{2+}$  ions make up only  $1/3$  of the total Co atoms, so the total number of spins in an average particle is distributed over  $\sim 2000$   $\text{Co}^{2+}$  ions. In this case  $N \approx 2000$  and so for surface spins only  $N_{\text{uc}} \approx 13$ , with  $N_{\text{uc}} \sim N^{1/3}$ , which corresponds, within the error, to the number extracted. The true number of uncompensated moments per particle may be smaller than this if a fraction of the net moment is thermo-induced as suggested by this picture that Mørup and Frandsen have detailed.<sup>14</sup>

### Hysteresis

Hysteresis was also seen in these HsFn particles. In this measurement the sample was cooled down to 2 K in a zero applied magnetic field and then the field was ramped between  $\pm 8$  T. A typical hysteresis loop was performed. Figure 6.14 shows the hysteresis loop of the HsFn sample. The magnetic moment crosses zero at different fields in the down and up sweeps. This coercive field was roughly  $140 \pm 10$  Oe. The presence of an open hysteresis loop corresponds well to the superparamagnetic nature and blocking of the particles at low temperatures. Hysteretic behavior below the blocking temperature is observed in all superparamagnetic systems.

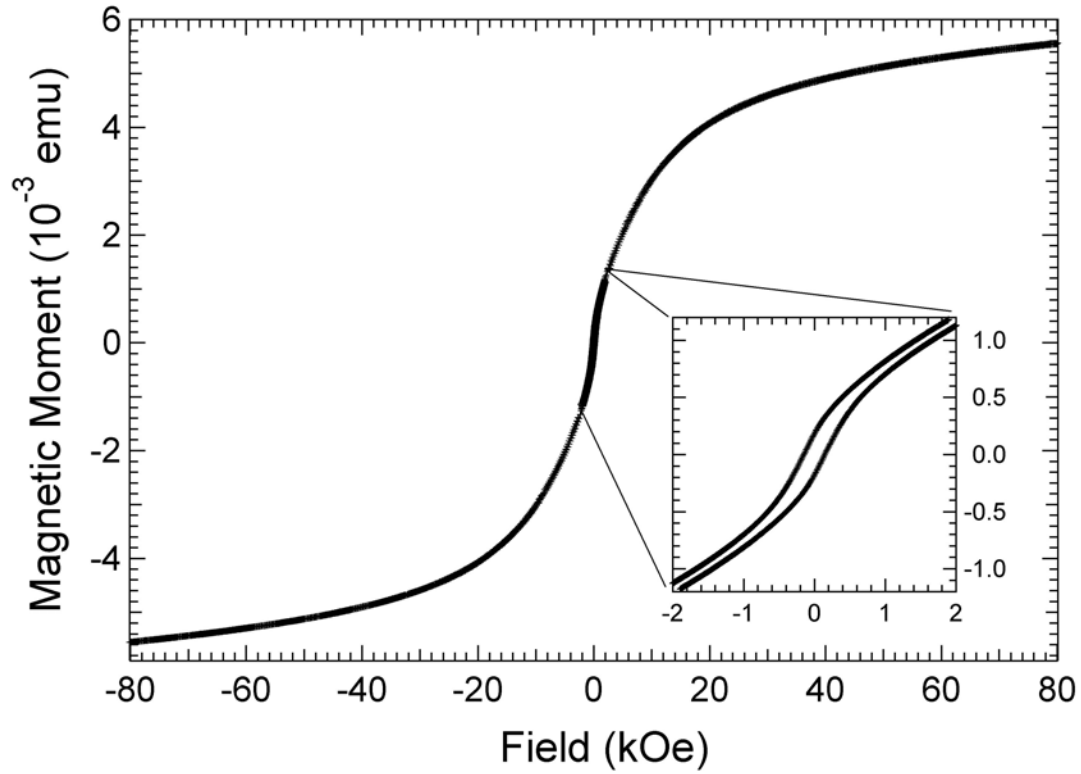


Figure 6.14: Hysteresis of the HsFn sample at 2 K. The inset is a blow up of the low field region.

The coercive field for this sample is smaller than the observed coercive field for the LDps sample. At first glance this may be due to a few different effects. First the coercive field for HsFn is measured closer to its blocking temperature than LDps. Because LDps has a slightly higher blocking temperature, measuring the coercive field at 2 K in both cases means that the LDps sample is farther below its blocking temperature, so the coercive field should naturally be larger. Also, size has been shown to affect the coercive field of small particles.<sup>78, 84</sup> An even more simple reason could be that since the LDps sample has a much higher anisotropy, born out by the ACMS, the coercive field is

naturally larger. This will be discussed in greater detail and compared to the other particles later in this chapter.

A hysteresis loop was also performed after being cooled down to 2 K in the presence of an 8 T applied magnetic field. Like the LDps sample, no exchange bias was seen within the  $\pm 10$  Oe error of the measurement, so the hysteresis loop was essentially identical to the zero field cooled measurement. This slightly surprising result further supports the interpretation that the methods used in synthesizing these particles have created high quality  $\text{Co}_3\text{O}_4$  nanoparticles. As stated before, other studies on  $\text{Co}_3\text{O}_4$  nanoparticles found that there was exchange bias in these types of systems.<sup>44-46</sup> This result also suggests a weak coupling between the surface and core spins.

### Larger Particles

Using the biological methods available for the synthesis of the  $\text{Co}_3\text{O}_4$  we were only able to synthesize the particles in LDps and HsFn. Hence, we were limited in the number of different particle sizes to use in this study. Consequently, some commercial  $\text{Co}_3\text{O}_4$  particles were purchased from Sigma-Aldrich as described in the experiment section. Two different particle sizes were available.

The smallest commercial particles used in this study were nanometer sized particles in a powder form. These particles were roughly 25 nm in diameter with a sample mass of roughly 8.0 mg. The Néel temperature of these particles was measured using the ACMS. Figure 6.15 shows the ac-susceptibility versus temperature for these 25 nm particles. It should be pointed out that both powder particles exhibited little

superparamagnetic behavior. The in-phase components of the ac-susceptibility were enough in both these samples because the peaks were not frequency dependent. The peak, at 39 K for the 25 nm particle, is taken to be the Néel temperature. This technique is similar to what is typically used to determine the Néel temperature in antiferromagnetic systems.<sup>40</sup>

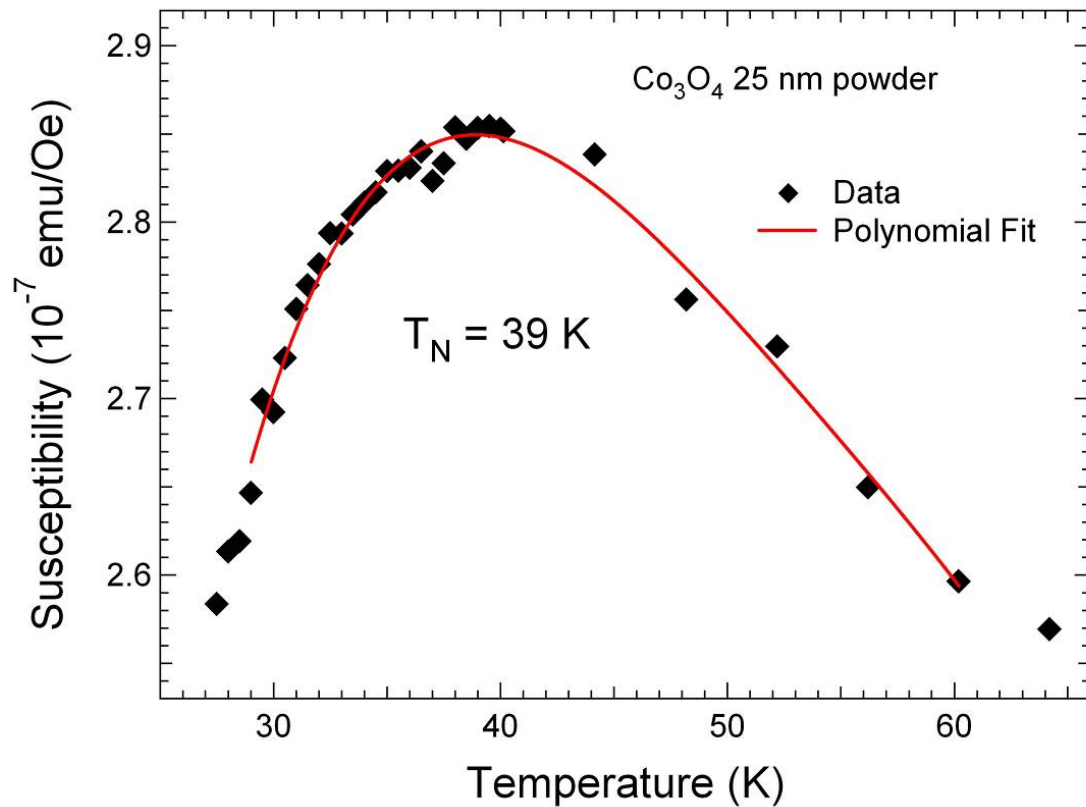


Figure 6.15: Susceptibility of the 25 nm  $\text{Co}_3\text{O}_4$  powder. The peak at 39 K is taken to be the Néel temperature. The red curve is the polynomial fit to the data in order to determine the best value for the peak.

The largest particles used in this study are micron sized particles purchase from

Sigma-Aldrich. These particles, with roughly 5  $\mu\text{m}$  diameters and a sample mass of roughly 15.0 mg, were also obtained and used in a powder form. Like the 25 nm powdered particles the susceptibility of these particles was also measured with the ACMS. (Figure 6.16 For these particles, the Néel temperature was determined to be 40 K identical to the bulk value reported.<sup>34</sup> This is not unexpected since micron sized particles essentially correspond to the bulk.

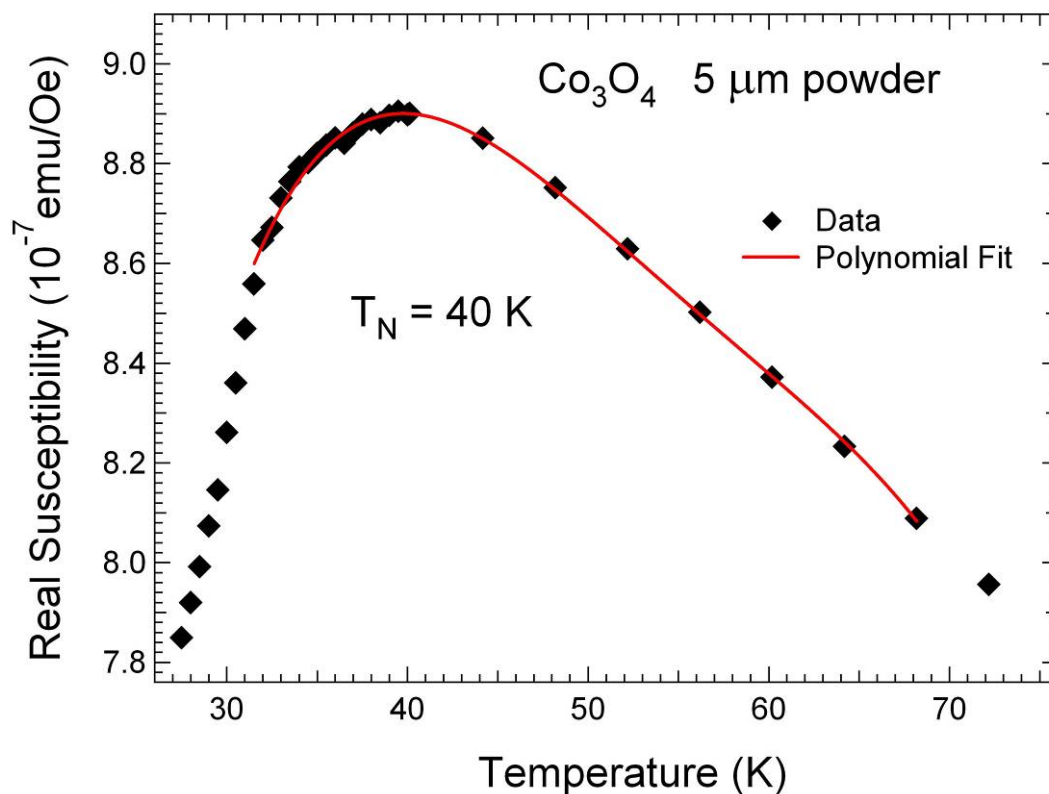


Figure 6.16: Susceptibility of the 5  $\mu\text{m}$  Co<sub>3</sub>O<sub>4</sub> powder. The peak at 40 K is taken to be the Néel temperature. The red curve is the polynomial fit to the data in order to determine the best value for the peak.

### Discussion

Before more detail about the size effects on the Néel temperature is given, it would be prudent to point out a few of the other properties, determined with the VSM, which support the ACMS data and conclusions drawn from that data. The lack of interactions between particles is born out by the VSM data. Low individual magnetic moments, determined with the VSM, as well as the minimum spacing between particles rule out any possibility of interactions between particles in a sample. Also, these low moments support the conclusion that most of the uncompensated spins must be on the surface and not scattered throughout the bulk.

Weak coupling between the surface and core spins are supported by the VSM data. The lack of exchange bias in the two particles demonstrates that the coupling between the antiferromagnetic core and any uncompensated spins on the surface is very weak. This supports the speculation that the ac-susceptibility measured is almost entirely due to the surface.

### Size Effects on the Néel Temperature

The four different sized  $\text{Co}_3\text{O}_4$  nanoparticles have different determined Néel temperatures. Size effects on the critical ordering temperatures of magnetic materials have been theorized<sup>69, 70</sup> and measured for both magnetic nanoparticles<sup>39</sup> and magnetic thin films<sup>40</sup>. Finite-size effects were determined to play a major role in this change and it is thought that it may have an effect in the reduction of the Néel temperature for  $\text{Co}_3\text{O}_4$

particles. Some of the theory of finite-size effects was discussed in chapter 4.

Néel temperatures determined with the VSM and ACMS measurements show a dependence on size. (Figure 6.17, Figure 6.18) The different values make sense compared to each other and when thought to be caused by the reduced size of the system. In the two figures below the different Néel temperatures for the four different size particles are plotted versus their diameters. The two different sets of data represent the Néel temperatures extracted with the Langevin model and the Langevin model with the added remnant moment term.

In both cases the finite-size scaling model was used to fit the decrease in the Néel temperature,  $T_C(d)$ , with decreasing particle size,  $d$  given by

$$T_C(d) = T_C(\infty) - T_C(\infty) \left( \frac{d}{d_0} \right)^{-1/\nu}, \quad (6.2)$$

where  $T_C(\infty)$ , is the bulk Néel temperature set to equal 40 K,  $\nu$  is the correlation length exponent, and  $d_0$  is some characteristic microscopic dimension of the system. The correlation length exponent determines how steeply the curve decreases, or the shape of the curve, and  $d_0$  determines at what diameter the Néel temperature goes to zero. More precisely, since it is unlikely that the material will entirely lose its magnetism,  $d_0$  corresponds to a critical diameter where other factors affect the Néel temperature and the finite-size model is no longer an appropriate model. In the case of  $\nu = 1$ , which corresponds to a surface model,  $d_0$  does in fact represent the exact diameter in which the Néel temperature would go to zero.

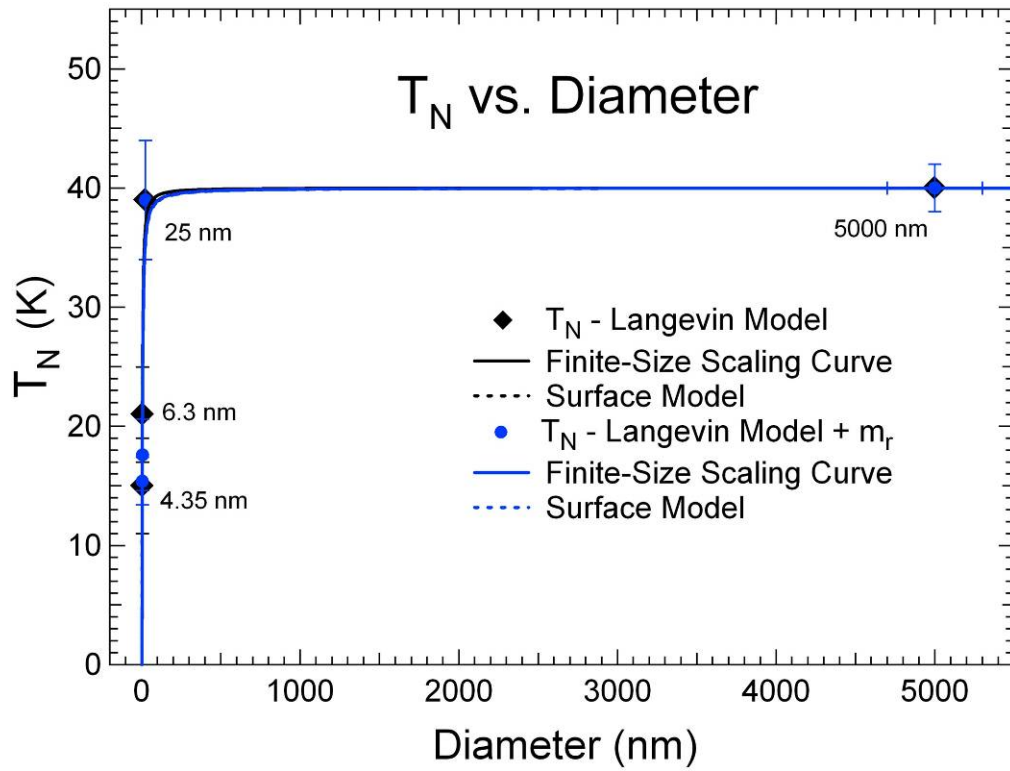


Figure 6.17: Extracted Néel temperature for the four different particles versus their particle sizes. The black curve is a fit to the data, extracted with the simple Langevin model, with a model for finite-size scaling, while the dashed black curve is a fit to the data, extracted with the simple Langevin model, with a surface model. The blue curve is a fit to the data, extracted with the Langevin model plus a remnant moment term, with a model for finite-size scaling. There is a sharp decrease in the Néel temperature of the  $\text{Co}_3\text{O}_4$  particles in the nanometer regime. Figure 6.18 is a blow up of the nanometer region in this graph so that the differences in the models can be seen more clearly and a comparison can be made.

With the bulk Néel temperature set to equal 40 K, the best fit to the data was for the Langevin model's extracted  $T_N$ 's which gave  $d_0 = 3.03 \pm 0.44$  nm and  $\nu = 0.85 \pm 0.23$ . Values extracted from the Langevin model with the remnant term are  $d_0 = 2.94 \pm$

0.78 nm and  $\nu = 0.98 \pm 0.43$ . The surface model is a model in which  $\nu = 1$ , assuming that a surface dependence would be proportional to  $d^l$ , which is a likely assumption since many purely surface effects are proportional to  $d^l$ , coming from surface/volume  $\sim d^l$ .<sup>39</sup> With  $\nu = 1$ ,  $d_0 = 2.76 \pm 0.19$  nm for the Langevin model and  $d_0 = 2.90 \pm 0.30$  nm for the Langevin model with the remnant term. The uncertainty of  $d_0$  for this last model is smaller not because this number gives a better fit but because  $\nu$  was specified, therefore there are fewer parameters, and so the uncertainty is less.

The value of about 3 nm for the  $d_0$  found is a bit less than four times the lattice spacing of  $\text{Co}_3\text{O}_4$  and hence fulfills its identification as a microscopic length scale and termination length scale for the collective magnetism. This number is also close to that found for  $\text{MnFe}_2\text{O}_4$  particles.<sup>39</sup> The value of  $\nu = 0.85$  is very similar to the values found in  $\text{CoO}$  thin films and the  $\text{MnFe}_2\text{O}_4$  systems.

It was found that the best fit to the data for the finite size scaling model to the simple Langevin determined  $T_N$ 's can be obtained if the bulk Néel temperature is set to 41.0 K. The best fit to the data for the Langevin model's extracted  $T_N$ 's was then  $d_0 = 2.98 \pm 0.41$  nm and  $\nu = 0.91 \pm 0.22$ . For the surface model, the best fit was with the bulk Néel temperature set to equal 41.4 K. The values extracted from the Langevin model for  $\nu = 1$  gave  $d_0 = 2.85 \pm 0.16$  nm. With the bulk Néel temperature set to equal 41.4 K the values extracted from the Langevin model with the remnant term are  $d_0 = 2.88 \pm 0.74$  nm and  $\nu = 1.07 \pm 0.42$ . For the surface model, the best fit was with the bulk Néel temperature held at 41.1 K, and with  $\nu = 1$ ,  $d_0 = 2.87 \pm 0.28$  nm.

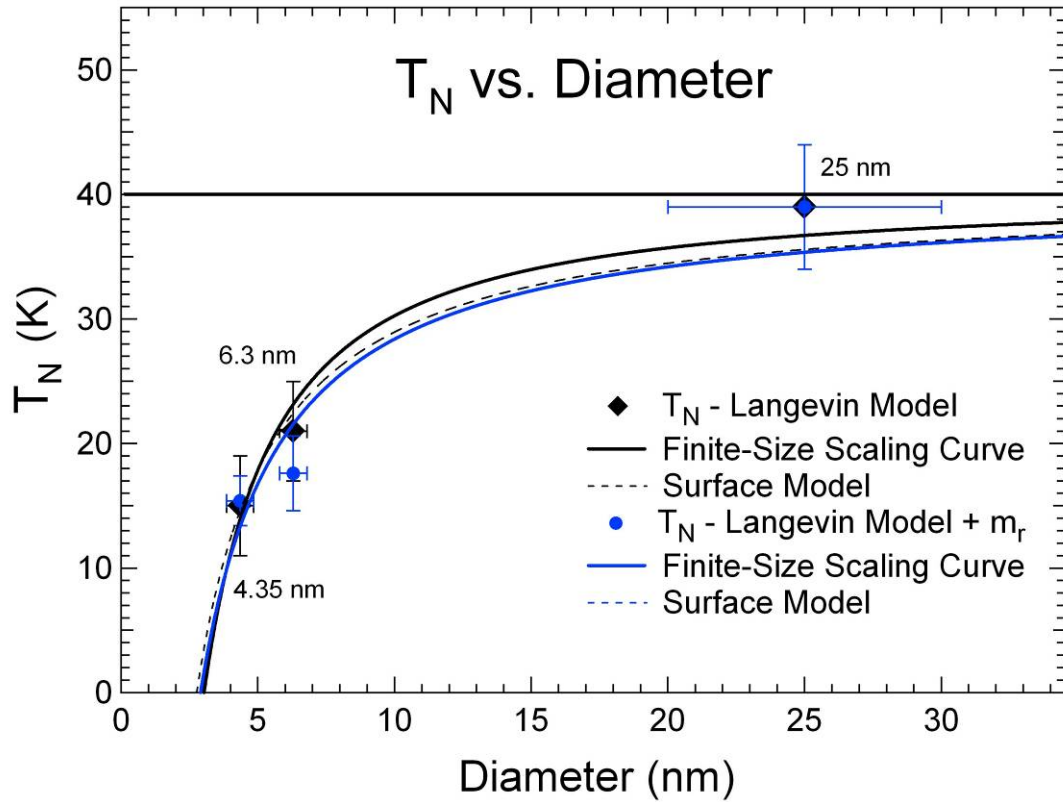


Figure 6.18: A blow up of the extracted  $T_N$  for the four different particle sizes in Figure 6.20. The black curve is a fit to the data, using the simple Langevin model, with a model for finite-size scaling. The dashed black curve is a fit to the data, using the simple Langevin model, with a surface model, while the blue curve is a fit to the data, using the Langevin model plus a remnant moment term, with a model for finite-size scaling. The dashed blue curve, which is a fit to the data, extracted with the simple Langevin model, with a surface model is not visible because it fits right over the solid blue curve. This graph resolves the different models used so that the difference can be seen graphically.

In this study only four different particle sizes were used. Because of this, it is difficult to tell whether finite-size scaling can account for the reduction of the Néel temperature. Also, the purely surface approximation fits even better. In fact, looking at

these different fits, the surface model approximation with  $\nu = 1$  gives extracted parameters within the error of the finite-size scaling models. Taking this into perspective, it should be pointed out that the finite-size scaling model has one more parameter than the surface model. It is then surprising that it does not fit even better. In fact, looking at the reduced chi squared,  $\chi^2_{\text{red}}$ , for these fits, shows that the surface model actually does a better job. In this case,  $\chi^2_{\text{red}} = \chi^2/(N-P)$ , where  $\chi^2$  is the chi squared of the fit,  $N$  is the number of data points and  $P$  the number free parameters,  $\chi^2_{\text{red}}$  for the finite-size scaling fit was found to be 5.58 and  $\chi^2_{\text{red}}$  for the surface model fit was found to be 4.66. The surface model gives a better fit. This reinforces the previous conclusions that the surface plays a dominant role in the magnetic properties of this system.

#### How Size Affects the Magnetic Moment

As presented above the magnetic moment of the particles reduces with smaller particle size. This is not unexpected since the total number of uncompensated spins must diminish as the total number of spins diminishes. However, is the spin reduction proportional to the surface or the volume? Already, the case has been made for the uncompensated spins to be mainly on the surface, based on the total number of uncompensated spins expected in the two different cases. However, a difficulty arises when trying to make this determination that depends on the method used to determine the total magnetic moment of the particles: the error that results in the magnetic moment is simply too large to make very strong conclusions. Also, in determining the ratio of moment reduction this error prevents a conclusive comparison and determination of

whether the spins are on the surface or throughout the volume. However the data does show a trend better following the surface.

Below is Figure 6.19 which plots the magnetic moments of the particles as a function of particle diameter. The smallest particle comes from the data of Takada *et al.*<sup>43</sup> In that paper, the particle moment of 3 nm Co<sub>3</sub>O<sub>4</sub> nanoparticles was measured and found to be 15  $\mu_B$ , which corresponds to a surface arrangement of spins using the model described above. Figure 6.19 also shows two curves fit to the data that are proportional to  $d^2$  and  $d^3$ . The  $d^2$  curve gives a better fit than the  $d^3$  curve, suggesting that the reduction is due to the spins being on the surface rather than scattered throughout the volume. However, the errors for the magnetic moments of the two particles synthesized in this study clearly overlap. These errors are too large to say conclusively whether the reduction of the moment is proportional to the reduction of the surface or the volume. Part of this difficulty may arise from the fact that a small fraction of the uncompensated spins could be scattered throughout the bulk. This could be more of a random phenomenon and be extremely sample dependent. In order to check this many samples would have to be made under strictly identical conditions. Then a careful study of the sample size and composition would need to be done. After this, the magnetic measurements would have to be performed on the different samples to see if the differences in the magnetic properties were measurable. On this point, it should be mentioned that several samples of the two particle sizes synthesized in this study were looked at and showed qualitatively similar behavior.

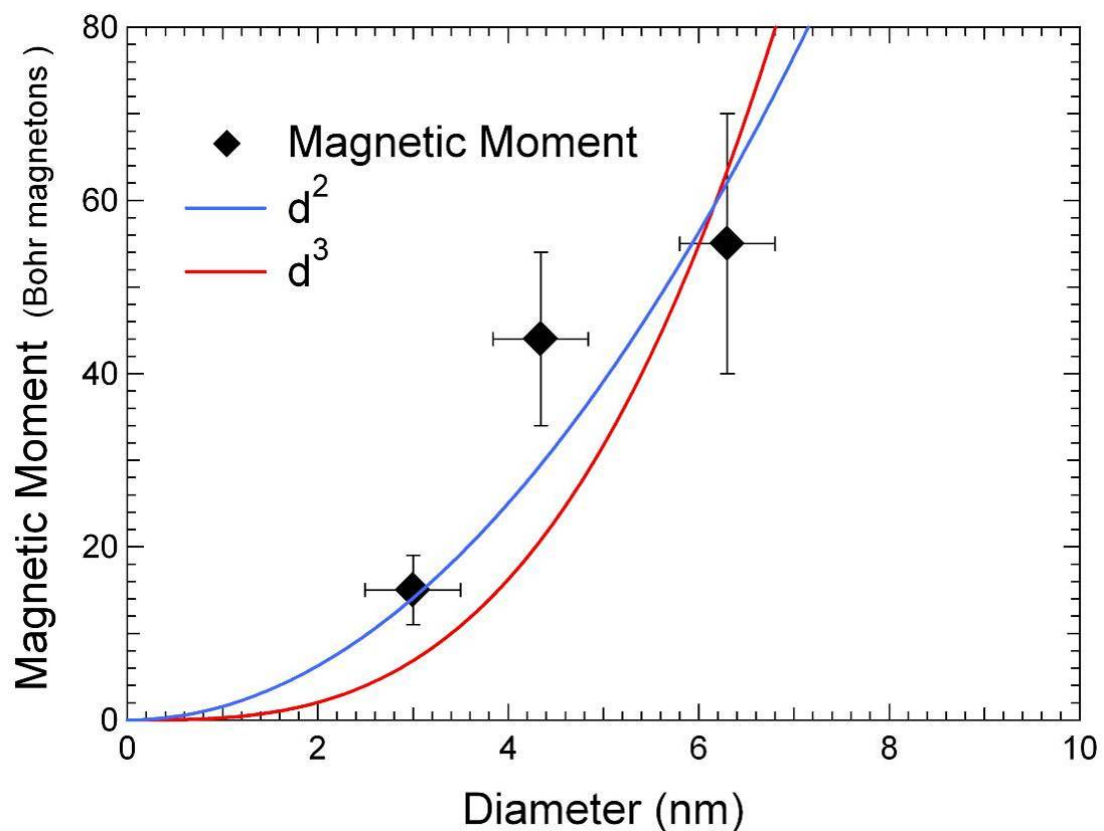


Figure 6.19: Magnetic moment per particle of the different particle sizes versus their diameters. The blue curve is a fit to the data proportional to  $d^2$  while the red curve is a fit to the data proportional to  $d^3$ . The magnetic moment per particle reduction ratio can not be shown conclusively to be proportional to the area or volume. It does however correspond to be proportional to the area more than to the volume supporting the conclusion that the uncompensated spins are mainly on the surface of the particles and not scattered throughout the entire volume.

#### How Size Affects the Coercive Field

Another property of this system that changes with size is the coercive field. As presented above, the coercive field increases in magnitude as the size of the particles is reduced. This is further born out in Takada *et al.*<sup>43</sup> in which they determined that the

hysteresis of 3 nm  $\text{Co}_3\text{O}_4$  particles, with blocking temperatures of 5.2 K at 100 Hz in the real-part of the susceptibility, was roughly  $500 \pm 30$  Oe. Figure 6.20 shows the data for the 4.35 nm and 6.3 nm particles presented here as well as the 3 nm Takada value.

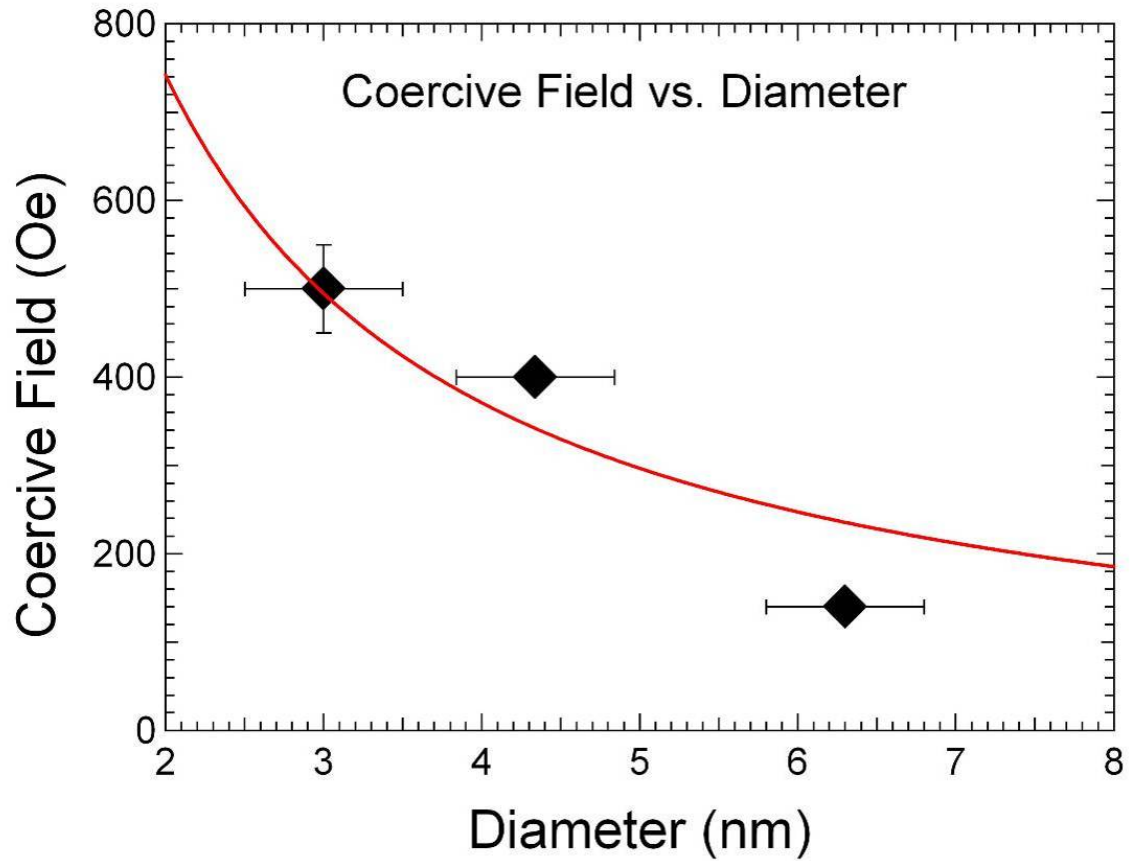


Figure 6.20: Coercive fields for the different particle sizes of  $\text{Co}_3\text{O}_4$  all measured at 2 K. Since the blocking temperatures of the three particles only vary by as much as 1.6 K, the general trend in the data is real. The red curve is a  $d^{-1}$  fit to the data.

The coercive field can be affected by both the finite-size and surface effects. Finite-size effects tend to reduce the coercive field<sup>84</sup> with smaller particle size while

surface effects tend to increase it.<sup>103</sup> In the case of the particles used in this study, there is a definite increase in the coercive field as the particle size is reduced.

It should be noted that the 3 nm particle value is needed to put this in perspective. First of all, the hysteresis loops were all taken at 2 K. The blocking temperature of the 4.35 nm particles is slightly higher than the 6.3 nm particles. Also, the general trend for the coercive field in superparamagnetic systems is a large increase in the coercive field below the blocking temperature.<sup>16</sup> In this case, it would be difficult to determine if the increased coercive field of a smaller particle was due to a surface effect. Therefore the coercive fields of each particle should be normalized to their zero temperature values. This can be accomplished by using a formula worked out by Kneller and Luborsky<sup>104</sup> to account for the increase in the coercive field below the blocking temperature. The equation they used is given by

$$H_c(T) = H_c(0) \left( 1 - \sqrt{\frac{T}{T_B}} \right), \quad (6.3)$$

where  $H_c(T)$  is the measured coercive field at a given temperature  $T$ ,  $H_c(0)$  is the coercive field at zero temperature, and  $T_B$  is the blocking temperature. Using these zero temperature coercive field values gives a slightly different trend. (Figure 6.21)

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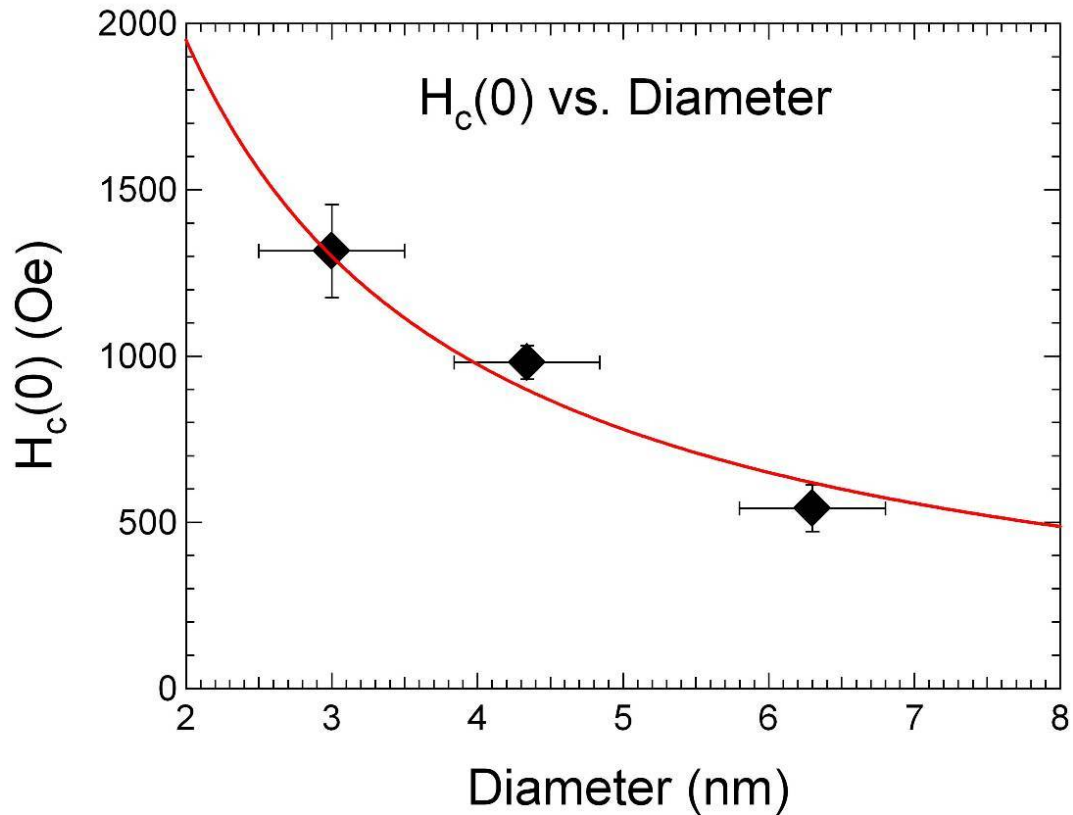


Figure 6.21: Coercive fields normalized to their zero temperature values for the different particle sizes of  $\text{Co}_3\text{O}_4$  all measured at 2 K. The proportionality of  $d^{-1}$  fit is more believable.

It should also be pointed out that the blocking temperature of the 4.35 nm particle is above that of the 3 nm particle. This effect can not be due to being below the blocking temperature. In fact, the conclusion that can be drawn is that the increase in the coercive field is due to a surface effect. This change could have its root in the increased anisotropy of these particles with reduced particle size but could also be due to a surface normal component to the anisotropy. In fact, it has been shown by Dimitrov and Wysin<sup>103, 105</sup> that a uniaxial surface anisotropy normal to the surface yields an enhancement of the coercive field. Dimitrov and Wysin also showed that this normal surface anisotropy would be proportional to  $d^{-1}$ . It is hard to say if the coercive fields in this study follow a  $d^{-1}$  trend, due to having only three different sizes, however a strictly  $d^{-1}$  trend may not what to expect in this case anyways. More than one thing is affecting the coercive field. One is finite size effects which tend to reduce. Another is surface anisotropy which would increase it following a  $d^{-1}$  trend. Lastly it should be noted that the anisotropy energy density is also increasing. It is known that the coercive field is proportional to the anisotropy energy density so this would also make the coercive field increase.

It is useful to note that the HsFn sample has a blocking temperature less than a few K above 2 K. This could mean, even with the relatively tight distribution of particle sizes, that a percentage of the particles in this sample may not be totally blocked and hence have a much reduced coercive field. If this were true then the actually value would be slightly higher and fit the  $d^{-1}$  curve much better.

The fit to a  $d^{-1}$  curve is good so attributing this to a uniaxial component to the anisotropy normal to the surface in these particles is reasonable. With the large increase of the effective anisotropy energy density and a coercive field that increases with reduced particle size, the conclusion that the increase in the effective anisotropy of the particles is due to a uniaxial surface anisotropy normal to the surface seems likely. As discussed previously this type of argument leads to a surface term addition to the effective anisotropy energy density for magnetic systems.

## CHAPTER 7

## SUMMARY AND CONCLUSIONS

One of the goals of this work was to determine how large a role surface effects play in the changing of the magnetic properties in the  $\text{Co}_3\text{O}_4$  nanoparticle system. Towards this, different particle sizes of  $\text{Co}_3\text{O}_4$  were synthesized and examined. It was found that the majority of magnetic properties used to characterize the magnetism in this system were largely affected by the surface.

First the anisotropy energy density was examined. The size effects on the anisotropy energy density for ferro and ferrimagnetic nanoparticles were shown, by Bødker *et al.*<sup>11</sup> to increase  $K$  with decreasing particle size according to a simple phenomenological expression, equation 4.7. Those efforts to quantify surface anisotropy met with success in those systems but seem to not be sufficient to describe the larger increases of  $K$  in antiferromagnetic nanoparticles of  $\alpha\text{-Fe}_2\text{O}_3$  and the  $\text{Co}_3\text{O}_4$  antiferromagnetic nanoparticles in this study.<sup>37</sup>

It was found in chapter 5 that the anisotropy energy density increased with smaller particle size in a dramatic way similar to that of the  $\alpha\text{-Fe}_2\text{O}_3$  system. This large increase with decreasing particle size shows the importance of surface effects in this system. In fact, this substantial effect may be due to isolated surface spins, large amounts of surface frustration, atomic disorder, uncoordinated surface spins, vacancies, and a break in the symmetry of the structure on the surface. It is known that some of these factors can bring about a large anisotropy component normal to the surface.<sup>76</sup>

The Néel temperatures of the different particles were also examined. A clear reduction of  $T_N$  was seen with reduced particle size. This reduction was found to best fit a simple surface model approximation of finite-size scaling theory. However, finite-size effects can not be ruled out completely due to the error in the  $T_N$  extraction and the lack of additional data points. This does not conclusively point to surface effects but together with the other measurements it is compelling.

Along with  $T_N$ , the magnetic moment and coercive field for different particle sizes were determined. While the reduction of the moments did not provide unambiguous evidence for surface spins, the proportional of this reduction to the reduction of the area of the surface seems much more likely than a reduction due to the volume. Also, the relative sizes of the particle magnetic moments pointed to the likelihood that a large fraction of the uncompensated spins were on the surface. These different factors, combined with the increase in the coercive field with reduced particle size, all point to a large surface anisotropy energy density that has a component normal to the surface. In fact, this increase in the coercive field could also be due to the large increase of the effective anisotropy energy density with reduced particle size.

This combination of factors leads to the conclusion that surface effects dominate the magnetic properties of  $\text{Co}_3\text{O}_4$  nanoparticles. In almost every case where the magnetic properties were measured, surface effects provide the best solution. This work, combined with those done on  $\alpha\text{-Fe}_2\text{O}_3$ , give strong evidence that there is a substantial difference in how antiferromagnetic particles are affected by the surface compared to ferro and ferrimagnetic particles. The large increase of the anisotropy energy density in both cases

is phenomenologically different than ferro or ferrimagnetic particles. More work on the theory using more advanced techniques is needed to better understand this difference.

### Perspective

To be complete in this treatment, it would be prudent to present some of the difficulties and shortcomings that came about during this study in order to put this work into perspective. First of all, a lack of particles sizes is difficult to overcome. A study like this normally requires a few more particles to make the conclusions more concrete. The errors inherent in the measurements performed make this especially important. This author would have been more comfortable with three or four more particles. Naturally, the conclusions would have been stronger with additional data. Also, more theoretical analysis would have been easier to accomplish with more particles. There are only so many parameters that can be added to a functional model, when there are only three or four data points to fit. If the number of parameters is the same to the number of data points the fits give ambiguous results.

Attempts were made to better analyze both the ACMS and VSM data in order to extract out a better understanding of the system. Theoretical calculations using Mathematica were used in these attempts. This proved to be a difficult challenge. The ACMS curves were especially difficult to model. Why this was difficult is still unclear, however the Néel-Arrhenius treatment is sufficient for the conclusions presented. It is also worth noting that the initial magnetization measurement fits did not improve by adding a size distribution. This demonstrates the quality of the synthesis and the tight

size distribution of the particles. Yet incorporating the anisotropy energy density into these fits would have made a big difference in the errors of the extracted parameters. For instance, by adding anisotropy to the Langevin model the error in the extraction of the magnetic moment and Néel temperatures could have been reduced. This was not done mainly because of the complexity of this sort of treatment.

Coupled into all this is a lack of a concrete physical explanation of the phenomenological  $d^2$  trend of the anisotropy energy density. The importance of the phenomenological description of Bødker *et al.*<sup>11</sup> in equation 4.7, is best described by the intuitive picture that adding an extra term to the energy barrier proportional to the area of the surface gives. In this dissertation, this type of picture is difficult to use. However, it is clear that  $K$  is increasing more than the simple surface treatment predicts. This would seem to require a deeper fundamental model with a quantum mechanical and first principles approach to this problem in order to better understand this effect.

### Future Projects of Worth

This study has been an experimental attempt to understand the Co<sub>3</sub>O<sub>4</sub> nanoparticle system as well as draw conclusions for antiferromagnetic systems in general. It has also been an attempt to better understand the nature and affect of surface anisotropy in antiferromagnetic nanoparticles systems. In this endeavor, this dissertation has only scratched the surface in pursuing these objectives. Because of this, suggestions for future work on these problems are presented.

As stated previously, more particles with different particle sizes would further add

to those taken here. Adding more data points would make the modeling easier and the results more concrete. Future work studying these particles with Mössbauer spectroscopy would also provide more information. Mössbauer could supply an additional way of measuring the anisotropy energy density as well the Néel temperature. Another project of future worth would be the use of a High Resolution TEM (HRTEM). Using HRTEM to study the particles would be a great way of looking at the difference between the surface and core. This type of instrument is able to resolve the relative size and distribution of the surface as well as composition differences. This type of measurement would be very useful.

It would also be worthwhile to study individual particles. If single particles could be isolated and probed, many difficulties could be overcome. It is much cleaner to examine one particle and a lot of the guess work could be avoided. By doing this type of measurement, the easy and hard axes could be identified, directional measurements could be performed, and the anisotropy could be examined in different directions, providing a larger picture.

It should be mentioned that although the mineralization inside of protein cages provides many benefits, it also limits the number of different particle sizes available. There are not enough protein cages with differing inner diameters. In order to synthesize a number of different size nanoparticles in this way, a different size protein cage would need to be genetically engineered for each particle size. Because of this difficulty, a worthy future experiment would involve using a different synthesis technique able to produce similarly high quality particles with many different diameters. Most especially,

particles below 4 nm would be a great benefit. Perhaps an adaptation of the methods used in Takada *et al.*<sup>43</sup> could be used to make several different Co<sub>3</sub>O<sub>4</sub> nanoparticle sizes.

The last and perhaps most important future pursuit would be the addition of other antiferromagnetic nanoparticles systems. Systems such as CoO, NiO, CuO, FeO, MnO, MnF<sub>2</sub>, and Cr<sub>2</sub>O<sub>3</sub> would all be worthy candidates for future research. Certainly, other materials should be looked at in an attempt to further understand surface anisotropy and the effects of the surface on the magnetic properties of antiferromagnetic nanoparticle systems.

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