

A Study of the Oxidation of $\text{Fe}_{1-x}\text{Co}_x$ Alloys and their Resulting Magnetic Properties

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Abstract

Iron-cobalt (FeCo) and its various alloys have many applications where soft magnetic materials are needed, especially in high temperature applications. Recent research has looked into the nanocrystallization of amorphous alloys of FeCo and very briefly into the oxidation of FeCo nanoparticles and bulk materials. Attempts will be made to more carefully investigate the oxidation of FeCo and its alloys utilizing nanoparticles, and thin films with (100), (110), and (211) texture to observe the kinetics of oxidation. Thin film epitaxial relationships between the substrate and thin films have been determined, and this will be extended to the oxide and thin film. The role of alloying has been discussed, especially in the context of oxidation of FeCo. The composition of the oxide at different oxidizing temperatures is also proposed.

FeCo-based nanoparticles have been analyzed to understand their change in magnetization and oxide phase as a function of temperature. The oxide thickness has been measured at various temperatures, along with the observation of a voided core. This research has been coupled with thin film work to show that the core gets richer in cobalt as oxidation progresses, with Fe acting as the mobile species. Oxygen may diffuse early in the oxidation, but only until a certain oxide thickness has been established. The oxidation kinetics seen in the nanoparticles is slower than that seen in thin films, and it has currently been analyzed to follow a logarithmic rate law at lower temperatures.

To understand the formation of faceted nanoparticles, nucleation and growth has been modeled for both BCC and FCC systems showing the surface energy ratios necessary to produce different faceting of nanoparticles. It has been shown that the critical nuclei are the same as the growth shapes.

To extend the basic science research into the applications field, thin film work on CoCrPt has been performed to achieve out-of-plane anisotropy in thicker films for use in a portable AGFM. While this has been achieved, further study is necessary to improve the remnant magnetization and make it more comparable to SmCo, which is the current standard. The magnetic properties have been measured as a function of temperature and film thickness to begin understanding the system better to produce the desired thin film properties for a biomedical sensor.

Prologue

In writing this thesis, I thought of many ways to make it more exciting or enjoyable. First, I thought of turning it into a musical, but the ease with which one can recreate a TEM and other doctoral “toys” on stage proved non-trivial. A choose-your-own-adventure style thesis also came to mind, allowing the reader to decide what he wants to learn about next, for example “If you’d like to oxidize nanoparticles isothermally, turn to page XX. If you’d like to oxidize them isochronally, however, turn to page YY.” While promising, this technique would not allow the author to build on prior sections or assume a certain knowledge based upon the text, since the path taken by the reader is not predetermined. While I don’t mean to suggest that you *have* to read the text in sequential order, I will have to assume that you did. Otherwise, the repetition will get a little too overwhelming (while my father has told me that “Repetition is the mother of learning!”, I will forgo that advice for this instance). Instead, I have decided to include below a novelized form of reporting research which I find very catchy, and I expect many theses in the future to adopt this style. As with any new “radical” change in distributing information, I will only briefly introduce it here both to posit the idea and in hopes that I do not scandalize the reader.

Nicholas Jones
November, 2011

As the grad student approached the furnace, he laughed “Oh nanoparticles, you’ll never make it out alive this time!” The nanoparticles fiercely replied, “You may take our smallest members, but you won’t take all of us! Nanoparticles, clump together!” They entered the 350 °C furnace bravely, initially aggregating due to their magnetic attraction, with some sintering together due to the heat. While the cores of some remained, some were lost to the world, being overcome by the overwhelming presence of the tyrant Oxygen molecules...

That day will be remembered for many years to come. The Co atoms yielded a strong preference to pursue one direction of magnetization, and with the addition of Pt to the Co ranks, this preference only got stronger. But, yet the atoms seemed to be under the sway of their geometrical overlord, since the crystallography would not win over the overwhelming pressure of their geometrical shape. But, we...we wanted them to pursue their original direction, without the overbearing shape energy deciding the shots...a 90° turn from what they were pursuing, and normal to their current skewed preference. In the evening, we sent Cr atoms to begin to infiltrate their front lines, decreasing the magnetization, and slowly changing their course to our preference. But, at times, the effort was too much for the Cr. Rather than retreat, our side enlisted some help to enforce our decisions and pursue the course of action we had decided. We couldn’t just rely on crystallography and the decrease in magnetization anymore...we had to start stressing the geometry. By bringing Magnetoelastic energy to the forefront, we began to overturn the effect of shape...but the battle...it was not won yet...there was much more that needed to be done....

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List of Publications

N. J. Jones, R. Swaminathan, M. E. McHenry, D. E. Laughlin, "Nucleation and Growth Model for {110}- and {111}-truncated Nanoparticles", *Acta Materialia*, In Preparation.

N. J. Jones, H. Ucar, J. J. Ipus, M. E. McHenry, D. E. Laughlin, "The Effect of Distributed Exchange Parameters on Magnetocaloric Refrigeration Capacity in Amorphous and Nanocomposite Materials", *J. Appl. Phys.*, Submitted.

N. J. Jones, Cassandra L. Ondeck, Vincent Sokalski, Michael E. McHenry, and David E. Laughlin, "The Effect of Interfacial Stresses on the out-of-plane anisotropy of continuous CoCrPt Thin Films", *J. Appl. Phys.*, Submitted.

N. J. Jones, J. B. Restorff, M. Wun-Fogle, A. E. Clark, "Optimization of the Processing Parameters for building in uniaxial magnetic anisotropy in Tension Annealed $\text{Fe}_{82}\text{Ga}_{18}$ Rods", *J. Appl. Phys.* **109**, 07A935 (2011).

N. J. Jones, K. L. McNerny, V. Sokalski, M. Diaz-Michelena, D. E. Laughlin, and M. E. McHenry, "Fabrication of thin films for a small alternating gradient field magnetometer for biomedical magnetic sensing applications", *J. Appl. Phys.* **109**, 07E512 (2011).

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Chapter 1

Introduction

This thesis investigates synthesis $\rightarrow$ structure $\rightarrow$ properties $\rightarrow$ performance relationships in the oxidation of FeCo magnetic nanoparticles. The major motivation for this work is the need to understand the change in the properties of nanoparticles due to their oxide layer, whether native or grown at elevated temperatures. This entails the understanding of the faceting of nanoparticles through different synthesis techniques (here looking primarily at BCC plasma-torch synthesized nanoparticles), and then the observation of the oxides that form on the various facets. The structure and properties of the oxide and how it effects the metallic nanoparticle core are based on epitaxial relationships and kinetics of growth. Of great importance is the understanding of the passivation shell that was observed to protect the FeCo nanoparticles of interest in this thesis. Besides studying the synthesis of these particles and their oxide, and the structure of the two and how they relate, this thesis has also intended to look at the effect of the oxide on the magnetic properties of the FeCo core. The core has soft magnetic properties and a high magnetization, which is desirable for many applications, but for biomedical purposes and other purposes needing a polar and/or non-toxic surface, these nanoparticles need an oxide layer. This oxide layer, especially at increasing thicknesses, can change the magnetic properties. This thesis intends to look at these effects as a function of oxide chemistry and interfacial structure as they pertain to different FeCo facets, and how the different layers effect each other. In particular, the effect of exchange coupling, interfacial anisotropy, and superexchange interactions between the oxide and metal layers is important in many of the motivating applications.

By determining the two-dimensional properties of this system and relating it to three-dimensional nanoparticles, we can understand how these nanoparticles will perform in biomagnetic applications, specifically cancer therapy and the tagging of tissue scaffolds. Rather than actually pursuing these applications, however, the focus was shifted toward sensing the nanoparticles in the body to know where they are located and their general concentration. This sensing technology is also applicable to other fields such as space

exploration, geomagnetic analysis, and the manufacturing of electromagnetic interference absorption or reflection polymer-shielding (again looking at nanoparticle distribution, throughout the polymer this time). A portable sensor is needed, so modern thin film technologies were relied upon to begin designing a magnetic film for sensitive, yet non-stationary, applications.

Chapter 2

Objectives

This Thesis has as its major focus the oxidation of FeCo alloys, specifically when present as nanoparticles. In order to distinguish the properties of the various facets seen on these nanoparticles, three dimensional shapes have been reduced to effectively two dimensions by employing textured thin films grown on single crystal substrates. Some bulk studies have also been performed to make further comments on oxidation.

Given the presence of facets in these nanoparticles, it is essential to understand their nucleation and growth in order to tailor their shape based on the properties desired. This has been accomplished through a nucleation and growth model for BCC and FCC materials, taking into account particle shape and the appropriate surface energies.

Assuming, however, that we have the desired nanoparticles with the correct shape and we understand their properties, it is essential to determine their spatial uniformity in the desired application, which necessitates a small, sensitive, yet rugged and portable magnetometer.

To accomplish these objectives, FeCo nanoparticles have been oxidized and observed throughout the oxidation process using Transmission Electron Microscopy (TEM), X-Ray Diffractometry (XRD), Vibrating Sample Magnetometry (VSM), Mössbauer Spectroscopy, and Thermogravimetric Analysis (TGA). Thin films have been fabricated on the correct substrate to get the desired texture, and then analyzed similar to the nanoparticles, taking into account the surface orientation, adding Alternating Gradient Field Magnetometry (AGFM) and Vector-VSM (VVSM, for Torque Magnetometry) to the magnetometry equipment, and X-ray Photoelectron Spectroscopy (XPS). Nucleation and growth models have been tailored specifically to deal with the desired facets of the system under inspection. And, finally CoCrPt thin films have been grown at varying thicknesses to determine their usability in portable AGFM sensors, and to best understand the energetic factors that are important in attaining out-of-plane magnetic anisotropy.

2.1 Thesis Outline

Chapter 1 introduces the topics to be discussed in this thesis and how they intersect the materials paradigm. This chapter also serves to unite all aspects of this thesis and show how they connect.

Chapter 2, the current chapter, briefly discusses the main goals of the project and how they have been accomplished, and outlines the rest of the document.

Chapter 3 discusses most of the background necessary for understanding the results and discussion. This chapter mostly delves into generic background, and any more specific background necessary to explain a particular result will be mentioned in the appropriate section.

Chapter 4 discusses the motivating applications behind the research, and what has mainly fueled the decisions on research path or the techniques used for analysis. It is these motivating applications that have outlined the Results and Discussion section.

Chapters 5, 6, and 7 are the bulk of this document, looking primarily at and analyzing the results of four research sections: Oxidation of Nanoparticles, Oxidation of Thin Films, Modeling of Nucleation and Growth, and Fabrication of an AGFM-type Sensor. Each individual section has its own summary as needed, although a more overarching summary will be provided in the next chapter.

Chapter 8, the final chapter, briefly summarizes all the work done, connecting the topics together in a cohesive fashion, and recommends future work in the different areas studied.

Chapter 3

Background

Iron (Fe) and Cobalt (Co) are well known elements in the world of magnetic materials. They are both near the peak of the Slater-Pauling curve (see Figure 3.1), and when combined they can form a soft magnetic material with the highest room temperature saturation magnetization of any known material (for $\text{Fe}_{70}\text{Co}_{30}$) [17]. Due to their high Curie temperatures, FeCo alloys have also gained widespread use in high-temperature applications. In more recent times, FeCo alloys have become of interest due to the properties of their amorphous phase (which is attainable through melt-spinning and planar flow casting) and their nanocrystalline phase (annealing amorphous ribbons to initiate nanocrystallization).

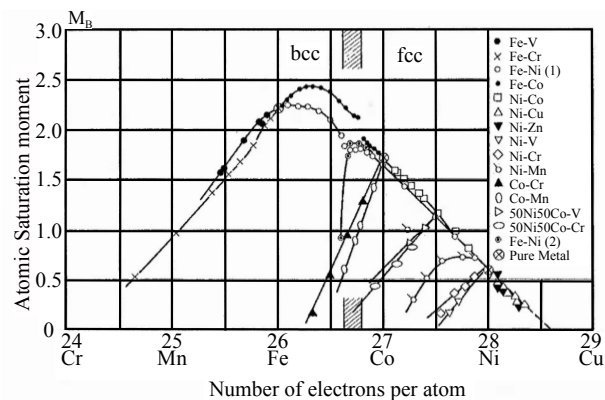


Figure 3.1: The Slater-Pauling curve (adapted from [14]).

In developing alloys for applications at elevated temperatures, it is also necessary to understand their oxidation properties and its effect on the magnetic properties of the alloy. While the oxidation of Fe has been studied in depth, FeCo and its alloys have not been as closely researched (this research is especially important in biomedical applications where Fe and Fe-oxides are preferred of Co and its oxides). With

the burgeoning field of nanomaterials, new types of oxidation studies need to be devised to understand the faceting of nanoparticles and their subsequent oxidation. It is also necessary to understand the oxidation sequence in order to understand the oxide's effect on the material's magnetic properties, and any interfacial anisotropies that result from the oxidation.

3.1 Oxidation

Oxidation is an important field of study that has not been done in depth for FeCo [85]. The oxides that form on nanoparticles and thin films are key to the materials performing in the way they are intended. This oxidation depends on the surface orientation and composition, along with oxidizing conditions and diffusion paths in the material's microstructure.

3.1.1 Thermodynamics

In oxidizing FeCo with no other alloying elements, we can get many different oxides to form depending upon oxidizing temperature and atmosphere. Since iron and cobalt are very similar, their oxides are also very similar. Cobalt can form CoO, Co₂O₃ (synthetically), and Co₃O₄ and iron can form FeO (wustite), Fe₃O₄ (magnetite), α -Fe₂O₃ (hematite), and γ -Fe₂O₃ (maghemite). In order to assess the stability of these various oxides, we must look to the Ellingham diagram to compare the changes in Gibbs free energy of the different reactions. Figure 3.2 is an Ellingham diagram for Fe, Co, Nb, and V. Niobium and Vanadium were added due to their use in Permendur and Hiperco alloys for grain size refinement, and added resistivity and strength, respectively. In looking at Figure 3.2, we can see that Nb and V have the most negative Gibbs free energy for their oxidation reactions, so their oxides are most stable and they will form first if the elements are present. Next in stability are the iron-oxides, followed by cobalt oxides. We can also see from the Ellingham diagram that magnetite is favored over wustite at temperatures below 570 °C, which can be verified by the Fe-O phase diagram. There are many other reactions that could take place, transforming one oxide into another (for example, $2\text{Fe}_3\text{O}_4 + 1/2\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3$); these reactions become important as the oxide layer grows and the ratio of available reactants changes (favoring compounds with more oxygen due to diffusional constraints on the metal cations). For clarity, they were not included in Figure 3.2.

3.1.2 Kinetics

In discussing oxidation, there are many other factors that can determine the preferred oxidation reaction and its rapidity. Initially we have to look at the mobility of the different elements involved and the defect

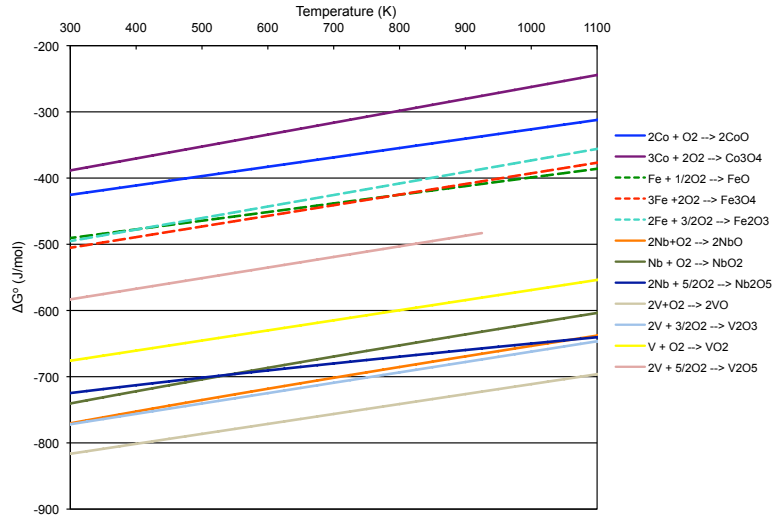


Figure 3.2: An Ellingham diagram depicting the various oxides of Fe, Co, Nb, and V, formed from their base elements (plotted using data from [45]).

reaction governing that diffusional motion. While oxygen atoms can move throughout the material, they are generally bigger, and therefore slower, than cations (i.e., Fe^{3+} or Fe^{2+}).

As oxygen adsorbs onto the iron surface, an initial oxide layer is formed which passivates the surface. If the sample is left at room temperature, it is estimated that the largest oxide layer will be 3 nm (growing over 40 weeks in air; a 4 nm layer would take 600 years) [92]. This growth will take place, through cation diffusion, at the atmosphere-oxide interface, with metal vacancies replacing the Fe atoms. It is possible that, while the oxide layer is still thin, oxygen ions can also diffuse through the oxide layer, causing the oxide/metal interface to move into the thickness of the metal. However, the oxygen diffusion rate will generally slow down as the oxide thickness increases, eventually being much more strongly dominated by cation diffusion (see Figure 3.3).

While single crystal materials will have diffusion rates limited by the mobility of the ionic species, polycrystalline materials have other paths for increased rates of oxidation. In particular, grain boundaries can dramatically increase the rate of oxidation, as all mobile species will move more easily through the grain boundaries.

The kinetics of oxidation may also depend on the surface orientation of the metal layers and the epitaxy between the oxide and metal layers. This will be discussed in Section 3.1.7.

There are three major rate laws that describe the rate of oxidation of metals, and these have different environmental conditions in which they are favored. By integrating these rate laws with respect to time,

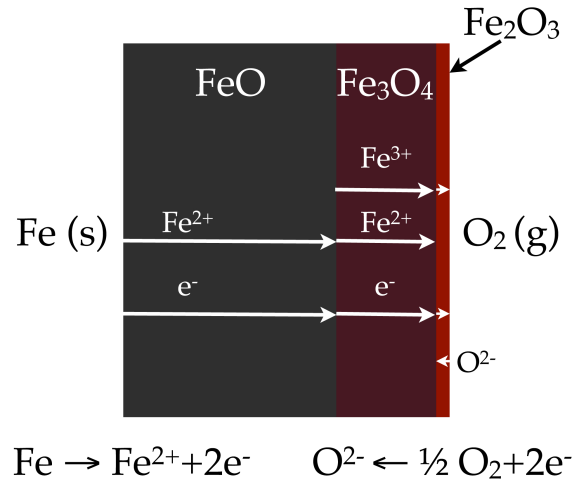


Figure 3.3: Diagram showing the oxidation of Iron above 570 °C

we can get an equation to describe the thickness of the oxide layer as a function of time:

$$x = k_1 t \quad (\text{Linear Rate Law}) \quad (3.1a)$$

$$x^2 = k' t \quad (\text{Parabolic Rate Law}) \quad (3.1b)$$

$$x = k_{\log} \log(t + t_o) + A \quad (\text{Direct Logarithmic Law}) \quad (3.1c)$$

$$1/x = B - k_{\text{il}} \log t \quad (\text{Inverse Logarithmic Law}) \quad (3.1d)$$

Here, x is the thickness of the oxide layer, k_1 , k' , $k_{\log}$, and k_{il} are the linear, parabolic, logarithmic, and inverse logarithmic rate constants, t is time, and A , B , and t_o are constants. By introducing magnetic data of the growing oxides and remaining metal, magnetization as a function of time can also be produced (since the material's magnetization will depend upon the amount of oxide present). The first law is the linear law (Equation 3.1a), where the rate of oxidation does not change over time. This type of rate does not depend upon the concentration of reactants in the metal and their diffusivity, but is normally limited by a surface reaction, or the rate of oxygen transport to the oxidizing surface. In other words, there is a constant supply of oxidizing material at the surface which does not depend on oxide thickness; since the oxidation rate is constant, it is either determined by the reaction rate, or the ability of oxygen to reach the surface (assuming a constant partial pressure of oxygen, p_{O_2}). The parabolic rate law (Equation 3.1b) is limited by the diffusion of cations or anions through the growing oxide scale, and the rate varies inversely with the square-root of time. The logarithmic laws (Equations 3.1c and 3.1d) are the final laws that we will consider here, although they are not well understood. The oxidation rate is a function of the logarithm of time. It is often not

considered, because it only applies to low temperatures (below 400 °C) and very thin oxide layers ($\sim 2 - 4$ nm, but up to a maximum of 100 nm), yet this is precisely where the nanoparticles and thin films, discussed herein, lie. The logarithmic-type growth is characterized by a very quick initial growth, which dies off quickly to a slow rate. The logarithmic rate law is thought to be determined by electric field gradients in the growing oxide layer due to ion mobility; an electrical potential is set-up through the thickness of the oxide as the cations diffuse to the gas-oxide interface and the anions diffuse to the metal-oxide interface. While oxides are normally highly resistive materials, it has been seen that their high resistance does not hold at very low thicknesses due to quantum mechanical tunneling [6].

3.1.3 Types of Iron Oxides and their Properties

There are four oxide phases of iron which vary based upon oxygen content, and their stable temperature range. They are Magnetite (Fe_3O_4), Hematite ($\alpha\text{-Fe}_2\text{O}_3$), Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and Wüstite (Fe_{1-x}O).

Magnetite is the most common of all these oxides, and adopts the spinel crystal structure (Space Group No. 227, $\text{Fd}\bar{3}\text{m}$; lattice parameter, $a_o = 8.3941 \text{ \AA}$) with Fe cations filling a fraction of the tetrahedral and octahedral interstices of an O^{2-} FCC cell [19]. The composition of spinels is normally written as AB_2O_4 , where the A and B sites correspond to the tetrahedral and octahedral interstices, respectively. Iron occupies both the A and B sites in pure magnetite, forming $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$, with a mixed valency of Fe^{2+} and Fe^{3+} ions; while the stoichiometry here is correct, the more accurate way to write the composition is $\text{Fe}^{3+}(\text{Fe}^{3+}\text{Fe}^{2+})\text{O}_4^{2-}$, since Magnetite is an inverse spinel, with the 3+ and 2+ cations sharing the octahedral sites [78]. Magnetite is a ferrimagnet, with oppositely pointing moments on each Fe cation, but these moments are not equal, and therefore do not cancel, yielding a specific magnetization, σ of 84 emu/g (Fe_3O_4 has a mass density, ρ of 5.206 g/cm³) [63].

Maghemite adopts the same crystal structure as Magnetite ($a_o = 8.352 \text{ \AA}$), but there are no divalent Fe cations [47]. Therefore, the composition becomes $\square_{1/3}\text{Fe}_{8/3}\text{O}_4$ to balance out the Oxygen anions, where $\square$ corresponds to an Fe vacancy; this reduces to Fe_2O_3 , hence why it is referred to as $\gamma\text{-Fe}_2\text{O}_3$. There are trivalent Fe cations on both A and B sites and it adopts the inverse spinel structure, $\text{Fe}^{3+}(\square_{1/3}\text{Fe}_{5/3}^{3+})\text{O}_4$. Maghemite is also ferrimagnetic and is often the magnetic oxide used for magnetic recording tapes ($\sigma = 74$ emu/g). [63,79]

Hematite only has divalent Iron cations, and adopts the hexagonal corundum crystal structure (Space Group No. 167, $\text{R}\bar{3}\text{c}$; $a_o = 5.427 \text{ \AA}$, $\alpha = 55.27^\circ$) [52]. The moments of the Fe^{2+} cations lie parallel in the (001) plane, but are antiparallel in alternating (001) planes (along the c-axis); therefore Hematite is antiferromagnetic. [14,63,79]

Wüstite is antiferromagnetic, adopts the NaCl crystal structure ($Fm\bar{3}m$), and is only stable above 570 °C. [14,63,79]

In this thesis, since we will be dealing primarily with FeCo alloys, it is possibly that Co could enter the structure of any of the above-mentioned oxides. Fe and Co are so similar that it is often hard to distinguish between the two, and they share many similar oxides, both in oxygen composition and structure.

Co forms three oxides: CoO, Co₂O₃, and Co₃O₄. CoO adopts the NaCl crystal structure ($Fm\bar{3}m$; $a_o = 4.261 \text{ \AA}$), and is antiferromagnetic below 291 K, although it is not the stable room temperature phase. [35,69] Co₂O₃ adopts a Rhombohedral structure, and has not been studied too intensively; it is normally synthetically fabricated under high pressures. The Co ions prefer the 2+ state, and therefore favor the other two oxides. [11] Co₃O₄ is a Normal Spinel ($Fd\bar{3}m$; $a_o = 8.065 \text{ \AA}$) which is paramagnetic at Room temperature, with an antiferromagnetic transition (Néel Temperature) at 40 K. [70]

3.1.4 Oxide Composition

Both Thermodynamics and Kinetics are essential for determining the actual oxide that forms, and the subsequent properties of the material. Depending upon the mobility of Fe^{3+/2+} and Co²⁺ ions/vacancies, the properties can change. From initial experimentation with Fe and FeCo nanoparticles and bulk alloys, we know that below 570 °C it is possible to get hematite to grow first [6,41], although the predominant oxide layer that forms is magnetite or iron-deficient magnetite (i.e., maghemite) [6,16,20,91,92]. While it is possible to form a Co-Ferrite oxide (CoFe₂O₃) by substitutional replacement of the Fe²⁺ ions with Co²⁺ ions [78], given initial results from the oxidation of FeCo bulk alloys [85] and Mössbauer spectroscopy done on oxidized FeCo nanoparticles (see Section 5.2.5), it appears that this is not the case for FeCo; the cobalt seems to oxidize separately from the iron. The nature of the oxide separation can become especially important if the cobalt forms a layer of CoO, which has the possibility of increasing anisotropies due to exchange coupling (see Section 3.1.8) [60,61].

The nature of the oxide is especially important when considering the magnetic properties. Opposite to the change in magnetocrystalline anisotropy of Fe with the addition of Co, where K_1 decreases with a zero crossing slightly above 40% Co (going negative thereafter) [25], as we add Co to Fe₃O₄, the magnetocrystalline anisotropy constant switches from negative to very positive (from $\sim -10^3$ to $\sim +10^6 \text{ erg/cm}^3$) [7]. We also see a sign reversal in the saturation magnetostriction (positive to negative) with the addition of Co. While stoichiometric Cobalt-Ferrite has a high coercivity ($\sim 4 \text{ kOe}$) [63], Co has also been added in small quantities to other ferrites to decrease high frequency losses [21].

As noted by Birks et al. [6], grown oxides may often have multiple layers of different composition. This of course depends on the concentration of the diffusing species at the surface. So it is possible to have a

layer varying in composition as we move through the thickness of the oxide. Due to the many variations in properties due to the addition of cobalt into iron films and nanoparticles, it is important to understand the nature of the oxidation in order to predict and understand the properties of the resulting material given the concentration of Co in the metal and resulting oxide.

3.1.5 Fe, Co, O Phase Diagrams

When predicting equilibrium products in a certain environment, it is essential to look to the phase diagrams which include the base elements to see what materials should be expected, and what type of phase field they are in.

The Fe-O phase diagram is fairly well known, and has been studied intensively (and is reproduced in Figure 3.4). We can see that below 570 °C, pure Fe cannot dissolve oxygen, but with the introduction of O₂ we immediately enter a two-phase region of α -Fe (BCC) with magnetite until 57.14 at.% O. Therefore, when oxidizing below this temperature, we can expect magnetite to grow first, since the amount of Fe (and Co) available for reaction at the beginning of oxidation is highest and decreases as the oxide grows and cation diffusion decreases through the scale. Once the ratio of available metal reactants decreases so that the oxygen content is above 57.14 at.% O and below 60 at.% O, we have another two-phase region but this does not include any pure Fe phase, but is now between magnetite and α -hematite, with the percentage of each being calculated by the tie line between the two pure phases. In most of the temperatures considered, the magnetite and hematite phases can be approximated as line compounds, with only one composition where they are found as pure phases (rather than in a solution).

Above 570 °C, not only does wüstite become an applicable phase, but the “line-compounds” of magnetite and hematite begin to split into single-phase regions. Therefore, at low oxygen concentrations (i.e., when the available Fe and Co is high), we would expect the equilibrium phase to be wüstite, with a two-phase region between α -Fe and wüstite until $\sim 55.26 - 51.38$ at.% O, depending upon temperature, where the single-phase wüstite region begins. The single-phase region breaks up into a two-phase region between wüstite and magnetite, then a single-phase region of magnetite, then a two-phase region between magnetite and α -hematite. In many of the experiments below, wüstite was never seen, even though the temperature range was above 570 °C. This may be due to other factors affecting the oxidation scenario presented here. In particular, the oxide-shell that grows at room temperature will be magnetite. This already provides a “template” for the rest of the oxidation, and could set the Fe:O ratio at the Oxide-Gas surface before any high temperature experiments begin, removing wüstite from the possible oxide phases present. Another possibility could be temperature lag, where the initial oxidation temperature drops due to the opening of

a furnace or insertion of a RT sample into a tube furnace, which would again allow oxidation to initially proceed below the wüstite stability temperature.

The Co-O phase diagram has hardly any data present in it, and it only shows temperatures above 1400 °C, which is beyond the scope of this thesis, and below 3.5 at.% O.

The Fe-Co-O ternary phase diagram will help us gain a better understanding of the oxidation of Fe and Co when they are in a solid solution, providing helpful information that could not be gathered from the Co-O phase diagram, even though the temperatures in the ternary phase diagram being analyzed in Figure 3.5 are primarily above those being studied below. Because our initial nanoparticle composition is around 50 at.% Co, we can initially follow a vertical line beginning at 50 at.% Co on the bottom (horizontal) axis. We again see that the first phase to precipitate out is wüstite, since we are at 700 °C. As we increase oxygen content (by proceeding vertically) while keeping the Fe:Co ratio the same, we hit a three-phase field, with a magnetite rich spinel; there may be some Co dissolved in the spinel, but it is primarily Fe-rich. The spinel phase has been introduced here with a much lower oxygen content than for pure Fe (less than 30 at.% O, here). As will be discussed in Section 3.1.6, this decrease in necessary oxygen content for Fe-rich spinel stability is due to the lower activity of Fe when in solution with Cobalt. [4] This decreases the activity gradient of Fe through the growing oxide, decreasing the diffusion rate and the overall metal amount available. With increasing oxygen content, we eventually move out of the region of wüstite stability, where the Fe-rich spinel is in equilibrium with the α , $\alpha + \gamma$, and γ -phases of iron. At 700 °C, we eventually CoO as a stable phase, and only until the oxygen content is more than 50% do we see a Co-rich spinel as stable, right before hematite becomes stable. The lack of presence of the Co-rich spinel is probably since that compound is less energetically favorable, as seen from the Ellingham diagram (Figure 3.2).

Two things must when utilizing the ternary phase, however. The composition of the core of FeCo in these nanoparticles is not fixed since we do not have an infinite supply, and certain cations will diffuse faster than others. Therefore, as the phase diagram showed us, Fe will oxidize first in nanoparticles of 50:50 composition, assuming equilibrium. Therefore, the core will become richer in Co changing the composition of our alloy in equilibrium. We will also have an oxide layer growing on top of the core which will change kinetics and equilibrium phases even further. So, while the oxide grows, the core gets richer in Co. This might lead one to think that the outer oxide layers should be cobalt-rich. However, the Co ions now have a much thicker scale to travel through, and the true Co-rich area is close to the metal-oxide interface which is not where the large amount of oxygen is present; the ratio of oxygen (or its partial pressure) at this interface will in fact be fixed (following Yurek et al. [98]), which will preclude the equilibrium formation of any Co-rich spinel. The entire oxide seems like it will be “stuck” in the Fe-rich regions due to kinetics and scale development. The second consideration is the decreased temperature of most of the oxidation conditions

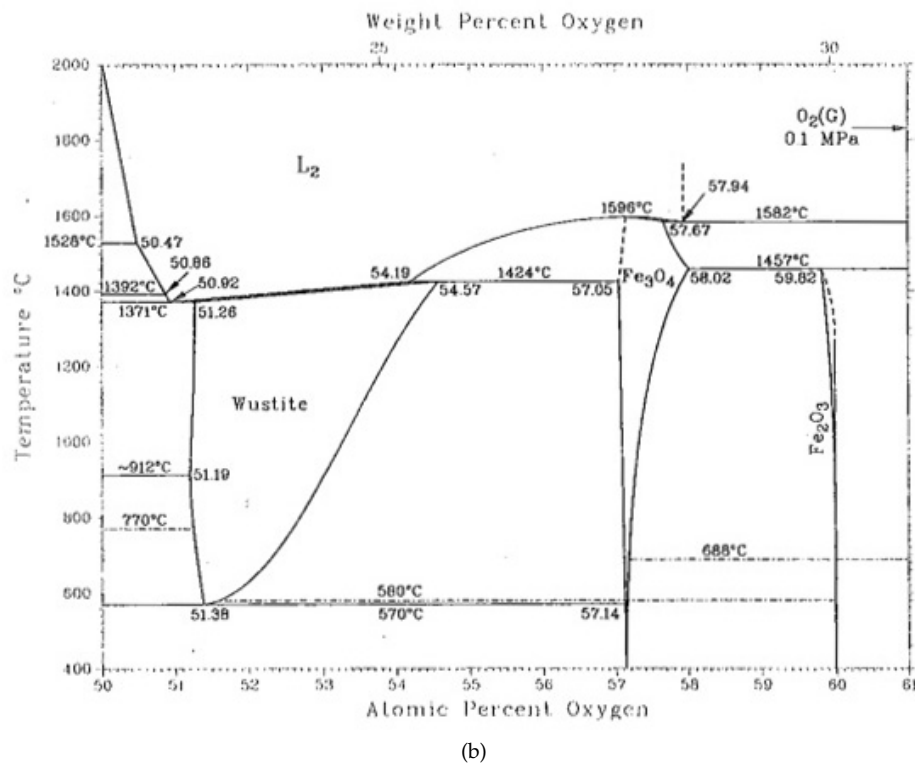
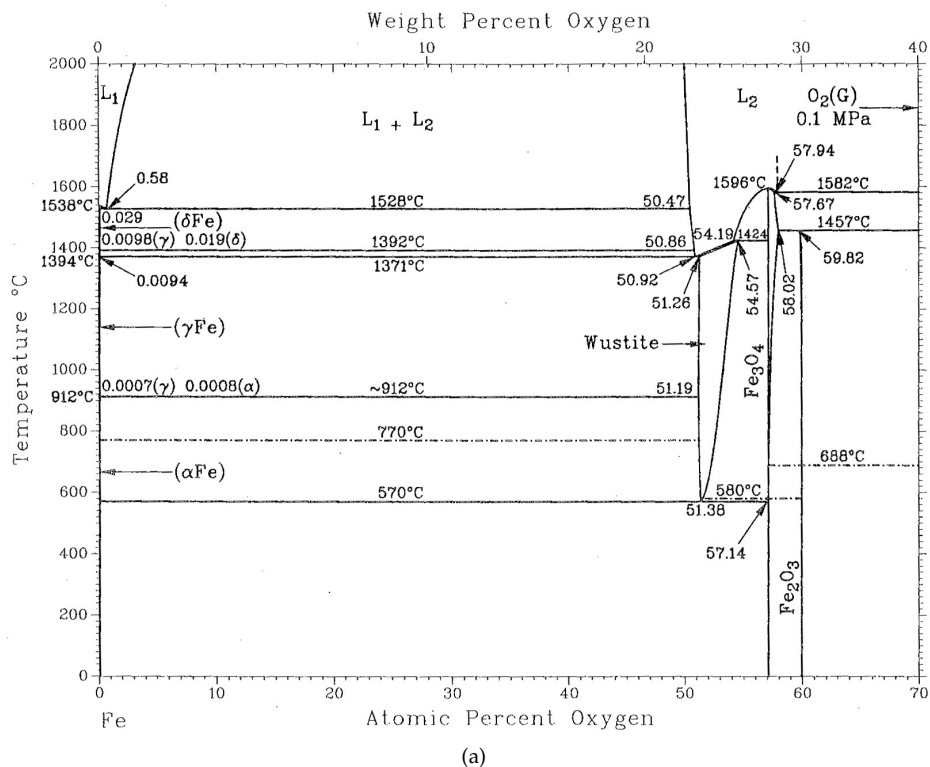


Figure 3.4: The Fe-O Phase Diagram showing (a) the full diagram from 0 °C to 2000 °C and from 0 to 70 at.% O, with (b) showing a detailed view of the transition region between Oxide types and Wüstite stability (reproduced from [55]).

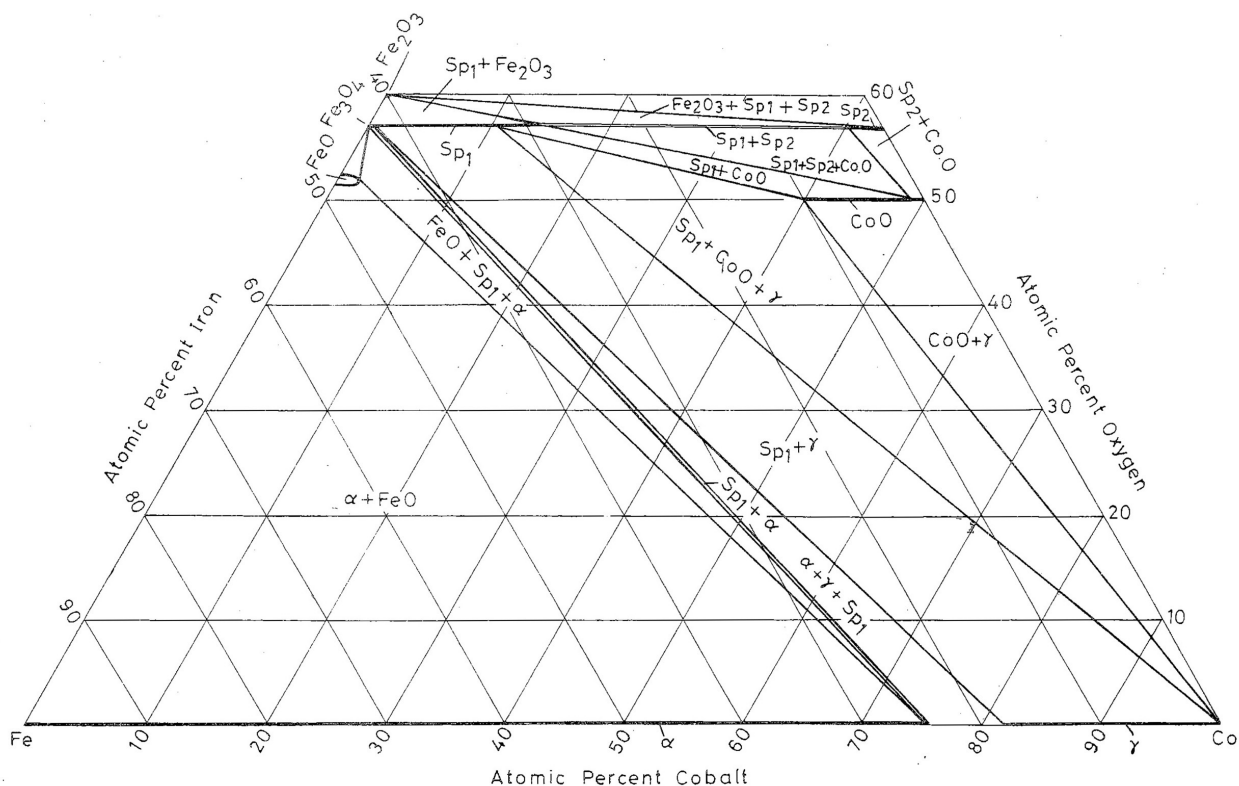


Figure 3.5: Isothermal Fe-Co-O Ternary Phase Diagram at 700 °C, where Sp_1 is an Fe_3O_4 -rich spinel, and Sp_2 is a Co_3O_4 -rich spinel.

studied here. By comparison with the binary Fe-O phase diagram discussed above, a decrease in temperature would mainly extend the spinel phase field into the wüstite region, giving it a larger compositional range of stability.

3.1.6 Activities of Fe and Co with O

As was discussed above, the activity gradients are an important property which can determine the oxidation products and their rate, especially as the different components change composition and the oxide increases in thickness.

The migration of ions is primarily determined by the electric field gradient set-up throughout the oxide, and the chemical potential of all the reacting species. Since our materials are normally not found in their pure state but in some sort of solution, they have an activity less than one; this activity defines the difference in partial molar Gibbs free-energy of a material in solution and a pure material ($RT \ln a_i$). By knowing the activities of our materials in their appropriate states during oxidation, we can understand more about their mobilities and their tendency to oxidize. Figure 3.6 shows the activities of Fe and Co in solution with each

other. These are not Raoultian solutions, so it is helpful to have actual data when comparing oxidation materials with different starting compositions. The nanoparticles and thin films, discussed below, have different starting compositions (50 at.% and 30 at.% Co), and may therefore display different oxidation rates and compositions based purely on the activities of the different components in solution.

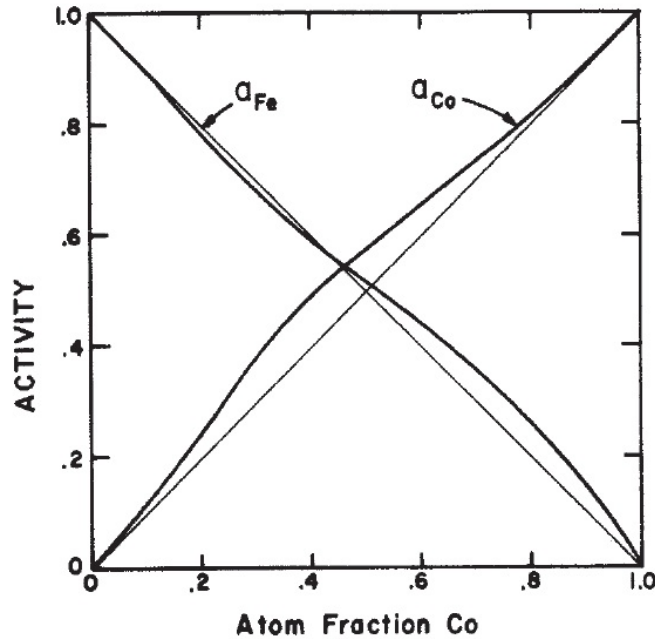


Figure 3.6: FeCo activities at 1590 °C, from [4].

Throughout oxidation, we have two major interfaces: Metal-Oxide and Oxide-Gas. This assumes that we only get one oxide product, which may not always apply. At each of these interfaces, we can assume our species are in thermodynamic equilibrium, which then sets our activity coefficients at these interfaces. Since our activities are set, we now have an activity gradient across the oxide layer, which will direct the migration of ions through the scale, and determine their diffusion rate. As the oxide grows, eventually our metal ions become diffusion limited (assuming we don't have an infinite supply and they can't travel infinitely fast). Once the oxide composition is set at the Oxide-Gas interface, we have set our final cation activity there (in the oxide solution), and, assuming no change in phase, as the oxide grows, the gradient through the oxide will decrease, thus slowing our diffusion rate due to the reduced gradient. [6]

3.1.7 Surface Orientation

Initial oxidation studies of FeCo nanoparticles have been done by Collier et al. [16], and on Fe nanoparticles by C. M. Wang et al. [91]. It was shown that the surfaces of plasma torch synthesized nanoparticles (and

those of other techniques as well) end on $\{100\}$ and $\{110\}$ facets. These two orientations, however, oxidize in a different fashion due to the crystallographic orientation of the surface with respect to the oxide layer. For FeCo, the oxide layer was assumed to be a Co-Ferrite shell, with an inverse spinel crystal structure. As is shown in Figure 3.7a, the $\{100\}$ FeCo surface has good epitaxy with the oxide (only 5.65% contraction of the oxide) and has the orientation relationship of:

$$(100) \text{ FeCo} \parallel (100) \text{ Oxide}$$

$$[010] \text{ FeCo} \parallel [110] \text{ Oxide}$$

The $\{110\}$ surface was not shown to have any good orientation with the oxide. Figure 3.7b is plotted with a proposed orientation of $(110)\text{FeCo} \parallel (111)\text{Oxide}$ and $[001]\text{FeCo} \parallel [\bar{1}\bar{1}0]\text{Oxide}$, although this orientation produces a strain of 3.77% in the $[1\bar{1}0]$ direction and 20.3% in the $[\bar{1}\bar{1}1]$ direction. These orientations determine the adherence of the oxide to the metallic layer and any future spallation of the oxide layer as oxidation progresses. Table 3.1 shows the orientation relationships between different FeCo surface facets and a grown oxide layer. While FeO has fairly good epitaxy for both metal orientations ($\sim 5.95\%$ oxide contraction), it is not seen unless above 570°C . Magnetite has been described above. And, hematite has a rhombohedral structure, for which it is hard to determine the relationships; although, one can assume that the close packed planes of FeCo and hematite will be parallel to one another.

FeCo	FeO	Fe ₃ O ₄	Fe ₂ O ₃
(100)	(100)	(100)	?
[010]	[110]	[110]	?
(110)	(110)	(111)?	(104)?
[001]	$[\bar{1}\bar{1}0]$	$[1\bar{1}0]$?	?

Table 3.1: The possible orientation relationships of FeCo and the Iron Oxides

Another factor that has to be taken into account when determining orientation relationships is the composition of the oxide layers being grown, as they may change depending upon the plane of oxidation. As can be shown through polyhedral models of magnetite, the (100) planes have the correct composition of the oxide in each plane, and all that changes from layer to layer is the angle of the tetrahedral and octahedral sites (they rotate 90° as we change layers, due to the screw axis along the $\{100\}$ directions). The (111) planes of magnetite, however, do not retain the correct composition of tetrahedral and octahedral sites. One layer has a composition of A_2B while the next layer has a composition of B_3 (where A = tetrahedral site and B = octahedral site). Therefore, it seems reasonable to assume that the (100) planes will grow more favorably, since they always retain the correct ratio of A- and B-sites during growth.

These orientation relationships can also affect the oxidation kinetics of the system if the oxide layer is not a dense layer (as is often assumed by models such as Cabrera and Mott [3] and Wagner [89]), and may introduce other diffusional paths. These relationships can also affect the overall oxidation of nanoparticles with multiple surface facets.

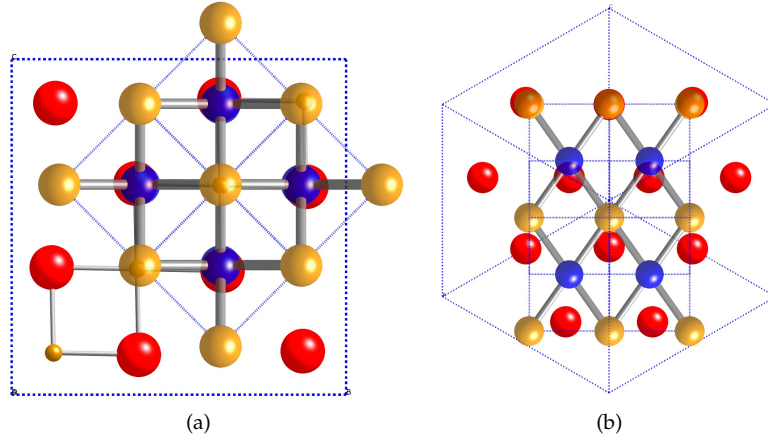


Figure 3.7: The epitaxial relationships between FeCo and Magnetite showing (a) a single layer of (100) Magnetite in the background with (100) FeCo in the foreground (Red is Oxygen, Gold is Fe, and Blue is Co), and (b) a single layer of (111) Magnetite in the background and (110) FeCo in the foreground (same color scheme).

3.1.8 Interfacial/Exchange Bias Anisotropy

In growing an oxide layer on top of a surface, we introduce an anisotropy due to the created interface. This interface will have some effect on the anisotropy of the thin film, possibly altering the easy magnetization direction (EMD) or the soft magnetic properties in high frequency applications (see Section 4.2). Both Interfacial and Exchange Coupling anisotropy depend upon the interaction energy between the configuration of a ferromagnetic layer with a “stiffer” magnetic layer. For Exchange Bias, this “stiffer” layer is an Antiferromagnetic layer; a material with a high magnetocrystalline anisotropy may produce a similar effect through interfacial anisotropy. With only interfacial anisotropy, we may get an increase in coercivity due to the preferential alignment of moments, but with exchange bias, a unidirectional anisotropy can be achieved that causes a shift in the hysteresis loop, an increase in coercivity, and destroys the time-reversal symmetry of the material. This was initially proposed by Meiklejohn and Bean, and has been studied in depth although different understandings have developed [5,40,44,54,56,60,61,66,72].

In general, though, these anisotropies become important in materials after oxidation. While these effects might depend strongly on the presence of antiferromagnetic CoO (due to possible separate oxidation

of Fe and Co, forming two different oxides), exchange effects have also been seen in oxygen-passivated Fe nanoparticles [66], and the possibility of a Co-Ferrite shell around nanoparticles introduces a high anisotropy to the material due to its high magnetocrystalline anisotropy and the oxide-metal epitaxial relationships.

3.2 Analysis Techniques

Many analysis techniques were used throughout this thesis. Some of the major techniques will be described below, focusing on the techniques that are less common, or techniques that seem similar to each other. An emphasis has been placed on those techniques that do not have entire books written about them.

3.2.1 X-Ray Diffractometry

X-Ray Diffractometry (XRD) has been used to verify the crystal structure of both nanoparticles and thin films, although it has also been used to evaluate the texture and orientation of the thin film layers. In order to perform XRD scans other than θ - 2θ , parallel optics are needed. Traditionally, the X-ray source is a fixed point source and detector, with slits and focusing optics; the x-rays incident on the surface will reconverge at the detector, assuming the sample surface is aligned correctly. However, once the surface is tilted in ϕ , ψ , or Ω , the surface is no longer in alignment, and the optics are no longer focused correctly, requiring the sample or the detector to be moved to correct the point of convergence. By aligning the X-ray source so all the rays run parallel, the sample can be tilted in any orientation and the X-rays will still make it to the detector, since there is no requirement for them to converge at the detector; all of the x-rays will diffract off of the appropriate planes, and stay parallel.

There are two major techniques to establish parallel radiation. Fiberoptic bundles can be used to capture the spreading light, bending the rays so they are all parallel. The other technique is to use parallel plates (made of a heavier element) to absorb any radiation that is not aligned parallel, with the remaining x-ray radiation being parallel. The fiberoptic technique retains much of the initial intensity from the point source, while the parallel plates drastically reduces the intensity. Therefore, since the radiation incident on the sample should have the highest intensity, the beam is normally made parallel using fiberoptics, and then it is refined at the detector using parallel plates, in case any diffracted radiation has come out of parallel alignment; assuming the incident radiation was fairly well aligned, there should not be much reduction due to the detector.

Given that parallel optics are available, there are three rotation axes that can be utilized: ϕ , ψ , or Ω . The traditional θ - 2θ scan is defined by the source angle and the planes of diffraction, where 2θ is the angle

between the transmitted beam and the diffracted X-rays (which should also be at the same location as the detector). We can fix 2θ to ensure that we are always looking at the same sets of planes, but we can tilt the sample in the plane of the incident and diffracted radiation; this is termed an omega tilt (see Figure 3.8a). When mounting samples, it is often necessary to align the sample surface as well. By tilting the sample we can align the fixed substrate peaks, and then perform a 2θ - Ω scan, which keeps the sample tilt correct. If we just do an Ω -scan, we are tilting the sample while keeping 2θ constant; this is termed a “rocking” curve, since we are rocking the sample back and forth. This allows us to look at the orientation of crystallites in the sample, and determine the quality of texture present in oriented samples. A rotation in ψ is a rotation about the axis in the plane of the film (and in the plane of the radiation path). By rotating ψ close to 90° ($\sim 88^\circ$), we are able to perform an in-plane scan, looking at the planes perpendicular to the surface. A rotation in ϕ is a rotation about the film normal. This type of rotation is primarily useful in conjunction with ψ scans, allowing us to probe the crystallography of the sample (especially highly textured samples), looking at epitaxial relationships between layers, and doing pole figures if necessary.

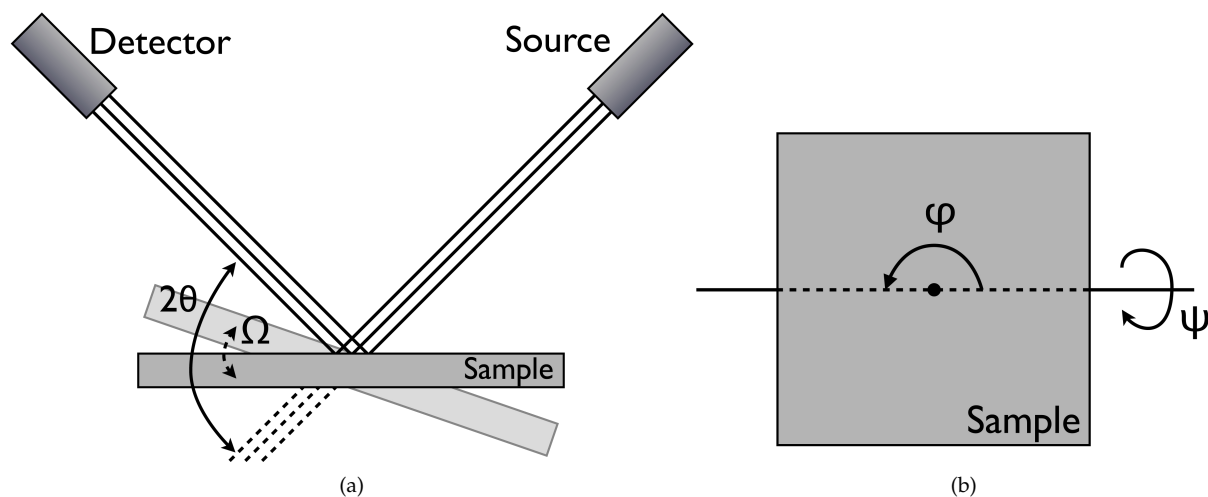


Figure 3.8: XRD schematic showing (a) parallel optics with an Ω -tilt, and (b) a sample with a ϕ and ψ rotations.

High temperature XRD scans have also been used to observe the change in phases (and crystallography) isothermally over time. This was accomplished by attaching a furnace to the XRD stage, and heating the sample in a flowing reactant gas. Air was used for the tests below.

3.2.2 X-Ray Photoelectron Spectroscopy

XPS is a surface sensitive technique looking at the top 1 - 10 nm of a film. X-rays are focused on the surface, similar to XRD, although it is different from XRD in that the analysis utilizes the electrons released from

the surface, rather than any diffracted X-rays. The electron detector measures the number and energy of electrons released from the surface. Because these electrons are expelled due to X-rays, they are called photoelectrons; the electron binding affinity can be calculated from the measured kinetic energy of the expelled electrons assuming a known energy of the incident radiation. By etching away surface layers and repeating scans, a compositional depth profile can be determined; this depth profile is measured with respect to etch time, which can be changed to depth (in nm) after using a standard of known thickness.

3.2.3 Vibrating Sample Magnetometry

The vibrating sample magnetometer (VSM) was used to measure the magnetic moments of many of the samples in this document, especially nanoparticles. The VSM works by vibrating the sample which has been attached to a non-magnetic rod (quartz or fiberglass) at a known frequency in an applied field, normally applied by an electromagnet and focused uniformly using pole faces (Figure 3.9). The applied field induces a magnetization in the sample, which will then produce its own stray field. The stray field can be measured independently of the applied field, by application of Faraday's law (Equation 3.2), where an oscillating magnetic field will induce an electromotive force (EMF), which will generate a current in coils affected by that oscillating magnetic field; similarly, this can be understood using the Lorentz Force (Equation 3.3), which determines the force on a point charge, also yielding a current. The current measured by the sensing coils is proportional to the magnetization of the sample, assuming the system has been calibrated with a standard that is preferably of a similar shape to the sample being measured.

$$\text{EMF} = \oint \left(\vec{E} + \vec{v} \times \vec{B} \right) d\vec{l} \quad (3.2)$$

$$\vec{F} = q \left[\vec{E} + \left(\vec{v} \times \vec{B} \right) \right] \quad (3.3)$$

In order to remove some instrumental error from the system, a permanent magnet is often attached to the top of the sample rod, or to the speaker head, and used to measure the frequency of oscillation of the sample, correcting for any variation in the frequency. Multiple sensing coils are also used to remove any variation in magnetization due to inhomogeneity in the applied field. The current measured by the system is normally small and needs to be amplified by a lock-in amplifier that is set to amplify signals only oscillating at the frequency of the system. [17]

One advantage of the VSM is its versatility in measuring different types of samples and measuring their magnetization in different environments. Thin films can be attached to the rod using Silicon grease (taking note of the diamagnetic moment of the Si), yielding in-plane or out-of-plane measurements by rotation of

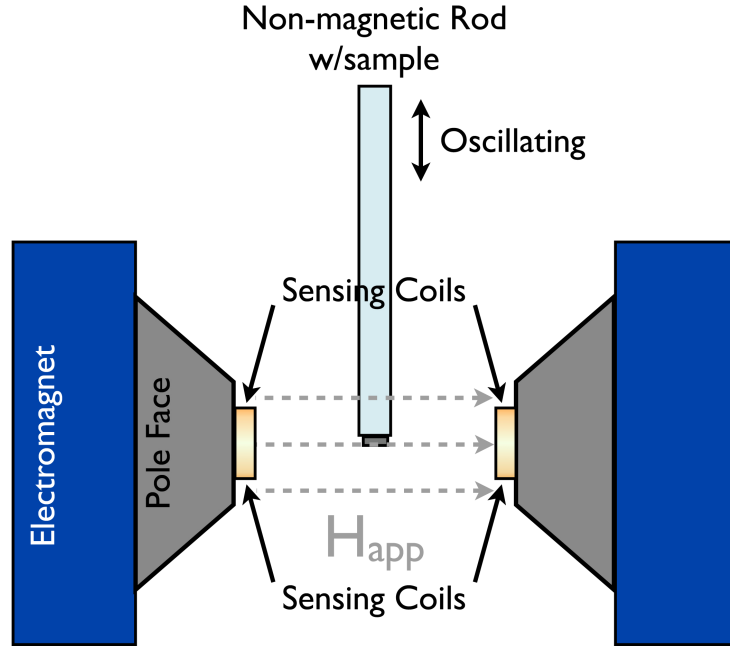


Figure 3.9: Schematic of a VSM, showing the basic system components.

the magnetic rod. Powder samples can be packed into a cup and screwed onto the sample rod; there are different sized cups for different amounts of sample or liquid samples, and quartz wool can also be used as a filler to prevent the powder from bouncing around during the test. The temperature of the sample can also be elevated by attaching a furnace in which the sample rod can be inserted. This allows magnetization versus temperature measurements and isothermal magnetization measurements when using argon flowing through the furnace, and can also provide oxidation measurements by allowing air to fill the furnace (although this is only allowed up to 350 °C due to oxidation of the furnace heating elements). Low-temperature measurements can also be accomplished, although our VSM did not have this attachment; for low temperature measurements, a liquid Helium cooled Physical Properties Measurement System (PPMS) with a VSM head was used. Since the VSM can rotate the sample rod, torque magnetometry can be performed by attaching another set of sensing coils. The traditional sensing coils measure the magnetization in the x -direction; the new coils are attached at a 90° rotation to measure the magnetization in the y -direction. This system doesn't measure torque, but torque can be calculated using Equation 3.4, by multiplying the magnetization component perpendicular to the applied field by the field magnitude; if the magnetization component in the z -direction is close to zero due to sample geometry, then the perpendicular component is just M_y [64]. This 2D torque set-up is called vector-VSM (VVSM), since the two sets of coils allow for the magnetization to be described by a planar vector, rather than just a magnitude. By calibrating the rotation

alignment (to minimize mechanical precession) and the new set of coils (using a permanent magnet), magnetocrystalline anisotropy, moment rotation, and domain wall motion can be monitored, depending upon the field strength. It is difficult, however, to minimize the mechanical precession during rotation to ensure that the sample stays at the same location, and the torque can be difficult to calculate at low applied fields, due to the restraints of the equation and the sensitivity of the system.

$$|\tau| = |M_{\perp H} H_{\text{app}}| = |M_y H_{\text{app}}| \quad (3.4)$$

3.2.4 Alternating Field/Force Gradient Magnetometry

The Alternating Field/Force Gradient Magnetometer (AGFM or AGM) can do similar measurements to the VSM, and, although it is not as versatile, it is often more sensitive, and much quicker. The system operates much differently than the VSM. The sample is placed at the end of a non-magnetic fiber (in this case, quartz), and placed in a DC magnetic field. An alternating field gradient is applied by coils on the pole faces that imposes an alternating force upon the sample. The alternating force cause the sample to oscillate, and by tuning the vibrational frequency imposed by the alternating field gradient to be the resonance frequency of the system, the signal amplitude can be multiplied. The sample fiber is attached to a piezoelectric crystal which produces a voltage proportional to the vibrational amplitude of the sample oscillation; the measured current, induced by that voltage, is proportional to the sample moment. The vibration in this system, rather than being vertical like the VSM, is horizontal (in the direction of the electromagnet pole faces). Due to the vibrational constraints of the system, sample mass is limited, and sample size is limited by the sample platform. This technique is primarily useful for thin film samples. There is no rotational function of this system, either, but in-plane and out-of-plane hysteresis loops can be measured by changing the sample holder, which will have a different fiber orientation. [17]

Chapter 4

Motivating Applications

4.1 Biomedical Therapies

Biomedical cancer therapies using nanoparticles are very dependent on the oxide grown on the nanoparticles. These therapies rely on the power-loss of magnetic nanoparticles during the application of an AC magnetic field to heat up the nanoparticles and the surrounding cancerous cells in order to kill them. This technique is a form of thermoablative cancer therapy. While iron oxide particles are normally used, it is more efficient to use a high moment material, like FeCo, because we can get a higher power-loss, but using less material (see Figure 4.1a). When injected into the body, though, they need to be coated with a surfactant, for both biological reasons and in order to form a stable ferrofluid. Establishing an oxide shell around the magnetic nanoparticles helps in the adherence of the surfactant due to the polar surface created by the oxide, and it also helps in decreasing the particle size necessary for the desired heating rates (see Figure 4.1b). In growing an oxide shell on the particles, we introduce new anisotropies into the system, such as increased magnetocrystalline anisotropy and interfacial anisotropies due to the addition of the oxide. This increases the total anisotropy of the particle, allowing smaller particle sizes to achieve the same heating rates as larger, purely metallic, nanoparticles; the smaller particle sizes are also helpful for the safe incorporation of nanoparticles into the body and for developing a stable ferrofluid.

4.2 Electromagnetic Interference Absorption

In Electromagnetic Interference (EMI) absorption, it is necessary to understand all of the losses in a material and where they come from in order to tune the desired absorption frequency. For most modern applications, the band of interest is in the GHz frequency range.

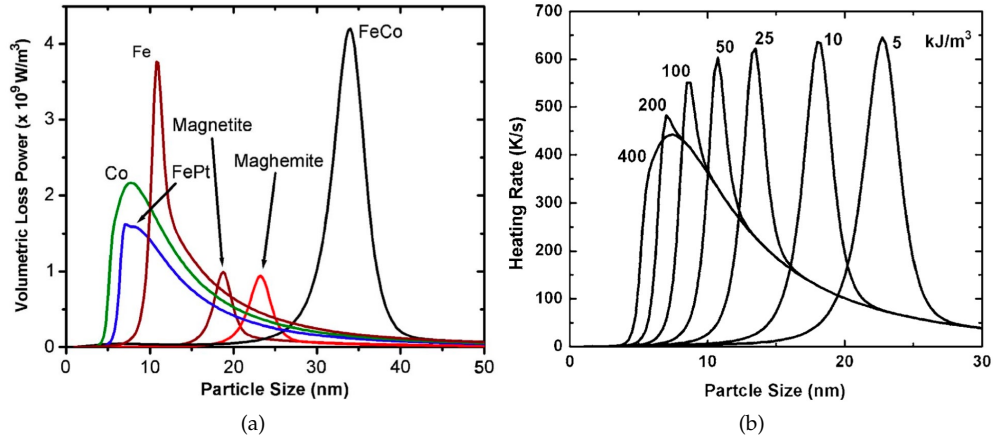


Figure 4.1: (a) Volumetric Power Loss versus Particle size for various magnetic materials; (b) Heating Rate as a function of Magnetic Anisotropy showing a decrease in the particle size necessary for peak heating rates (both plots from [23]).

There are many paths of energy loss in magnetic materials. As shown in Equation 4.1 there are three components to the power loss in a magnetic material: Hysteretic (hys), Eddy Current (ec), and anomalous losses (an).

$$P_{tot} = P_{hys} + P_{ec} + P_{an} \quad (4.1)$$

The hysteretic losses are linear with frequency, while the eddy current losses increase with the square of frequency and the anomalous losses increase with a power greater than one. Due to these relationships, the hysteretic losses will dominate at lower frequencies. These losses are primarily due to domain wall motion during the cycling of a magnetic material in an AC field. Since the focus is on high frequency absorption, it is necessary to stop domain wall motion and allow only moment rotation, in order to control the losses occurring in the material. The pinning of domain wall motion can be accomplished through the introduction of increased anisotropies in the material. These anisotropies can occur in the form of magnetocrystalline, shape, magnetoelastic, interfacial, and induced anisotropies, although magnetoelastic and interfacial anisotropies can be more difficult to control.

The eddy current losses dominate at higher frequencies, but they also need to be removed in order to allow the anomalous losses to dominate (the anomalous losses are primarily losses at the Ferromagnetic Resonance Frequency). Eddy current losses can be removed through an increase in the resistivity of the material and/or a decrease in particle size (see Equation 4.2). The increase in resistivity prevents the currents from flowing through the material, and is the reason for the predominance of ferrite materials in high frequency applications. A decrease in size will limit the path of currents through the material, thus

diminishing their effect.

$$P_{ec} = C \cdot B_m^2 f^2 \frac{d^2}{\rho}, \quad (4.2)$$

where C is a geometric constant of the material, B_m is the maximum induction in Gauss, f is the frequency in hertz, d is the smallest dimension of the material transverse to the flux, and ρ is the resistivity of the material [21].

While ferrite nanoparticles may seem to accomplish both of these goals (i.e., highly resistive, small particles), high moments are necessary to push the limits of high frequency applications. These moments are only available through metallic magnetic materials and the tuning of Ferromagnetic resonance (FMR) losses. We can see in Equation 4.3 for a specimen in a plane geometry that the Larmor frequency (ω_o) is a function of the field perpendicular to the plane (H_z) and the magnetic induction in the specimen (B_z), where γ is the gyromagnetic ratio [42, 43, 96]. This can lead to Equation 4.4 for the FMR frequency, in the extreme case where H_z becomes the anisotropy field, H_k , and B_z becomes the saturation induction, B_s [57]:

$$\omega_o = \gamma \sqrt{B_z H_z} \quad (4.3)$$

$$f_r \sim \sqrt{B_s H_k} \sim \sqrt{K_u} \quad (4.4)$$

We can see, then, that to push the limits of high frequency EMI absorption we need a magnetic material with a high magnetic induction with large anisotropies. And, from Snoek's relationship, $\mu' f_r \sim M_s$, we can see that high permeabilities are not compatible with high frequency losses (μ' is the real part of the complex permeability). So, we need a material with small dimensions (on the order of the skin depth of the EMI frequency), high resistivity, high saturation induction, a large anisotropy field, and lower permeabilities (produced through induced anisotropies and pinned domain wall motion). Our group has decided that FeCo alloyed materials fit this description, but only with the addition of an oxide layer. The oxidation properties, then, become important.

Current applications being researched using FeCo have looked at FeCo nanoparticles embedded in an epoxy, and nanocrystals in an amorphous matrix, possibly using an oxide layer to make a laminated thin film. The nanoparticles are small enough to decrease the eddy currents, but they still need an oxide layer to increase the resistivity and the anisotropy (possibly through magnetocrystalline and interfacial/exchange bias anisotropies, depending upon the oxide layer). For the FeCo nanocomposites (i.e., nanocrystals embedded in an amorphous matrix), the nanocrystals are small enough that the eddy current don't have much space to flow, and the amorphous matrix acts as a high resistivity medium. It is also possible to induce

anisotropies (through field and stress annealing) in ribbons of materials, although this has not been investigated in thin films. A layered structure of Nanocomposite-Oxide-nanocomposite may even improve the EMI properties, again depending on the properties of the oxide.

4.3 Other Applications

Hiperco alloys ($\sim\text{Fe}_{50}\text{Co}_{50} + \text{V, Nb}$) are used for high temperature, high stress applications in aircraft power generation, specifically in rotor and stator laminations in motors and generators. While these materials were designed to operate at high temperatures, oxidation is still a concern, but it is not well understood. For safer aircraft operations, it is essential to understand the modes and kinetics of oxidation.

Chapter 5

Oxidation: Nanoparticles, Thin Films, Bulk

5.1 Introduction

Nanoparticles of a nominally Hipercó alloy ($(\text{Fe}_{50}\text{Co}_{50})_{97}\text{V}_2\text{Nb}_1$) were synthesized using a Plasma torch, yielding polydisperse powders. These particles were oxidized in air at temperatures between Room Temperature (RT) and 900 °C for various durations of time. Multiple techniques were used to understand the kinetics of oxidation, and the changes in phase as oxidation progresses. To further understand this oxidation, thin films were sputtered on single-crystal Si and MgO substrates to understand oxidation on certain surfaces, and to elucidate any differences between single crystal and polycrystalline FeCo. These thin films had a nominal composition of $\text{Fe}_{70}\text{Co}_{30}$, due to the available sputtering target. Bulk samples will also be analyzed, with compositions close to 50% Fe: 50% Co, with Nb or Nb/V additions.

5.2 Oxidation: Nanoparticles

5.2.1 Transmission Electron Microscopy - Nanoparticles

Transmission Electron Microscopy (TEM) was used to image nanoparticles which were oxidized from room temperature to 900 °C for 2 hours in air in a tube furnace. Of particular interest were the nanoparticles' preferred facets, particle size, and oxide thickness as a function of oxidation temperature. Diffraction was also done to verify some assumptions about the oxide layer. These images and diffractions are correlated below with other techniques used to analyze these particles.

Figure 5.1 shows four sets of nanoparticles oxidized at room temperature (RT), 200 °C, 350 °C, and 900 °C for 2 hours in air. At room temperature (Figure 5.1a), we can see that the nanoparticles have a highly faceted core with a thin, passivating oxide shell that prevents the nanoparticle from oxidizing further. This shell has an average thickness of 3 nm, and is relatively independent of the size of the nanoparticle, with the shell thickness ranging from about 2.5 – 4 nm. The shell, while continuous in certain cases, has the morphology of islands of oxide nuclei that have grown together; at higher temperatures the oxide thickness becomes more even. The average RT core diameter is around 42 nm, with a size distribution from 25 – 60 nm; the thin oxide shell is completely adherent to the core. The facets correspond to the (100) and (110) low energy truncations for a BCC crystal, in agreement with Collier et al., and the mass-thickness contrast is attributed to the underlying particle faceting [16].

After 2 hours at 200 °C, the nanoparticle cores are still highly faceted, but display a growing oxide layer (Figure 5.1b). The oxide layer is practically doubled in size, about 6 nm (with only 1 nm variance), and still follows the core facets. The smallest particles are oxidized through, and show a light center, indicating a voided or less dense region, which will be discussed further in Section 5.2.4 and later in this section. This change in core contrast implies that the cations are the mobile species, diffusing out of the core and moving to the gas-oxide interface to be oxidized, leaving vacancies behind in their place, in agreement with the Kirkendall effect. Ignoring the fully oxidized particles, the average core diameter is 36 nm. The core has decreased by 6 nm in diameter, yet the overall oxide thickness has only increased by 3 nm; the oxide is less dense and should take up more volume than the metal core.

The nanoparticles oxidized at 350 °C for 2 hours (Figure 5.1c) have cores with less contrast, similar to the smallest particles seen at 200 °C, again indicating a possible voided region in accordance with many similar nanoparticle studies [12, 13, 67, 90, 92, 97]. The oxide layer has begun to round, and is no longer adapting the underlying faceting of the core (although the core still resembles the correct faceting); this is similar to what was seen for Fe nanoparticles by Wang et al. [91]. It is still the metal cations that are the mobile oxidizing species, diffusing out of the core. The core diameter has decreased even further to about 25 nm, while the oxide has tripled from its room temperature thickness to about 9 nm. It seems that we are getting some oxide diffusion, due to the decreasing core diameter, but the particles may also be collapsing upon the voided interior.

After being at 900 °C for 2 hours (Figure 5.1d), the nanoparticles are now fully oxidized and now oval in shape. The central void is no longer visible, because the oxide particles have sintered together, removing the central void and increasing the particle size tremendously (the scale bar is a factor of 5 to 10 larger than the previous images). There is no FeCo core remaining, and the oxide particles are approximately 127 nm in diameter.

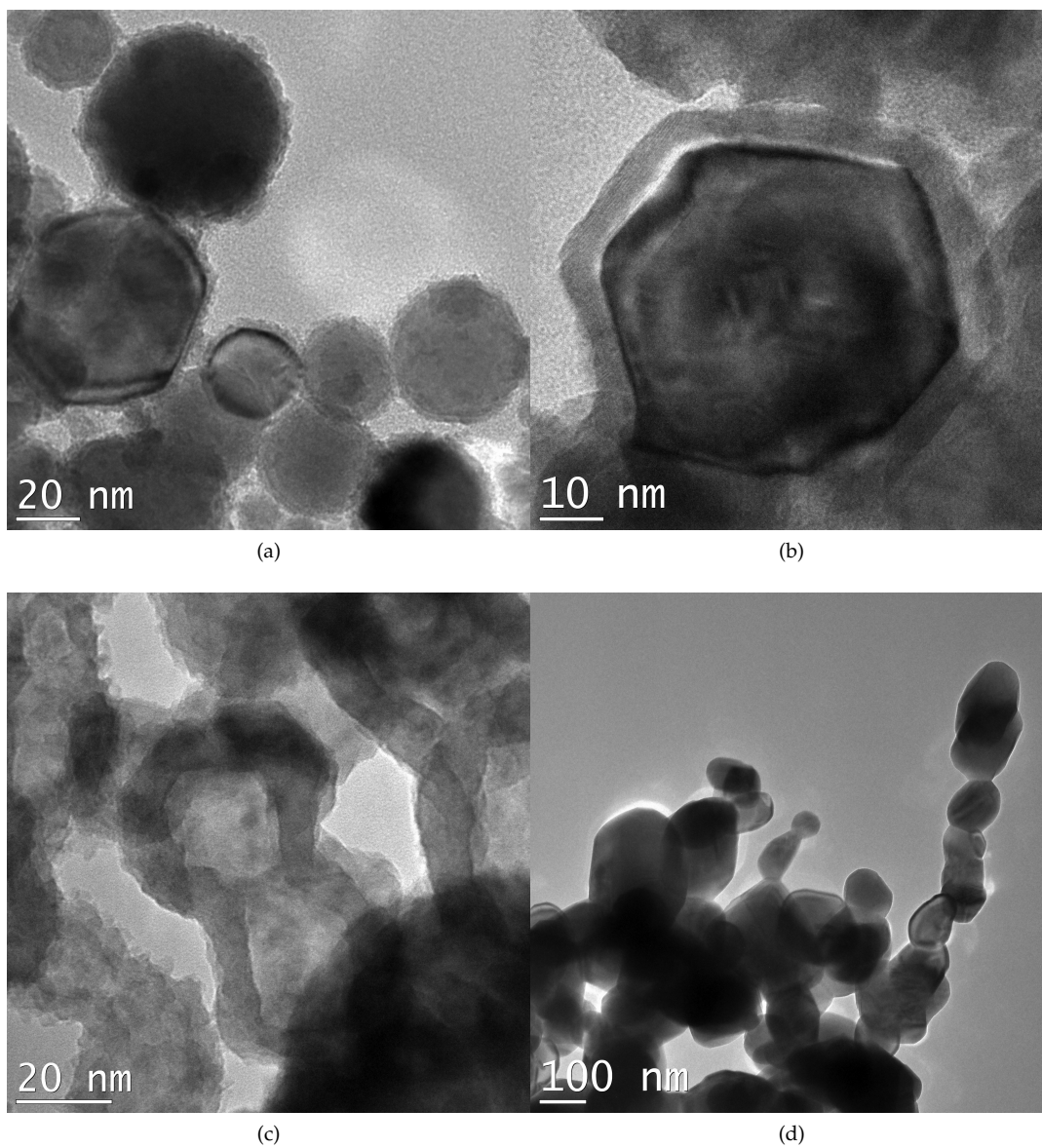


Figure 5.1: TEM bright field micrographs of FeCo nanoparticles oxidized for 2 hours at (a) RT, (b) 200 °C, (c) 350 °C, and (d) 900 °C.

There has been much speculation as to whether the central volume of the nanoparticle is truly a void, due to Kirkendall diffusion, or if it just looks like a void due to the imaging techniques used. High resolution TEM (HRTEM) was used to further probe this problem. Figure 5.2 shows two micrographs of nanoparticles at low-resolution, to initially show the difference in appearance between those nanoparticles oxidized at 200 °C and those oxidized at 350 °C for 2 hours. The lower temperature shows no large particles with light center, whereas the higher oxidation temperature shows most of the particles with a light center. There is also a big clump of particles in each image. This clumping may prevent oxidation of the entire sample, leaving some of the particles untouched and FeCo-rich, affecting the resulting magnetic properties and XRD pattern, since they are bulk techniques (while TEM is not).

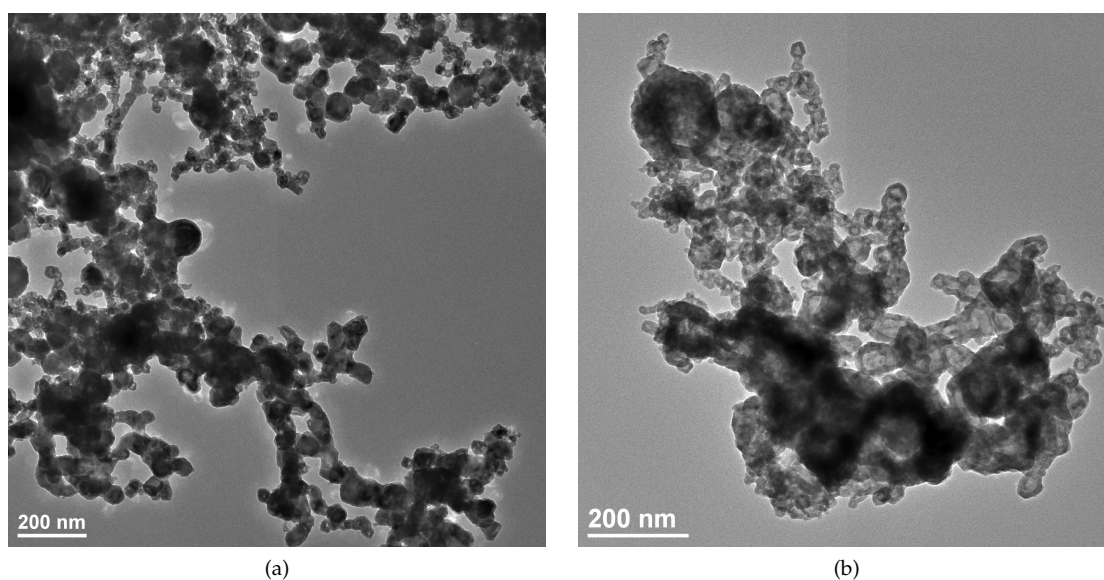


Figure 5.2: Low-resolution TEM phase-contrast micrographs of FeCo nanoparticles oxidized for 2 hours at (a) 200 °C, and (b) 350 °C.

By examining the HRTEM images, one can ascertain that the void is truly empty in the middle of the 350 °C particles, in accordance with Ref. [12, 13, 67, 90, 92, 97] (see Figure 5.3a and b); the void often has the same contrast as the background. In certain cases the particles connect and form a tube-like structure. These tubes may form if the nanoparticles chain up along their magnetic easy axes, due to magnetostatic interactions; oxidation of these chains will be preferential along the outside and the ends of the chain, allowing for void coalescence along the magnetic easy axis, creating a hollow tube. Some of these voids are nicely faceted with (110)-facets, while others look like cubes (see Figure 5.3b). Further comparison has been made with simulation work by C. M. Wang et al. for a high resolution TEM image of a voided nanoparticle (see Figure 5.3c).

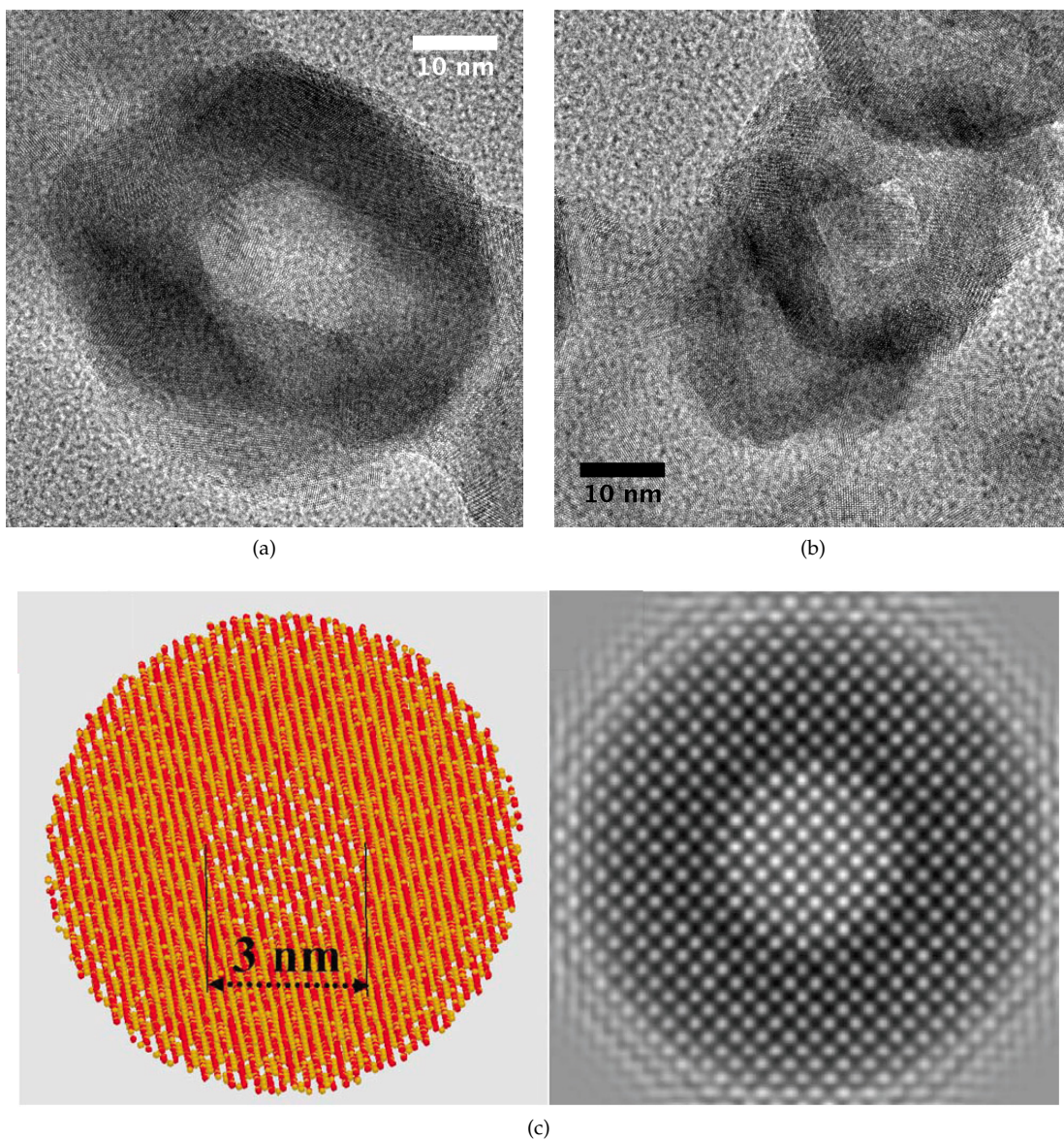


Figure 5.3: High-resolution TEM bright field micrographs of FeCo nanoparticles oxidized for 2 hours at 350 °C, showing (a) a voided core and (b) a voided core with (100) facets; (c) shows an atomic model and HRTEM simulation by C. M. Wang et al. for an 8 nm Fe nanoparticle with a 3 nm diameter void [92].

Analytical HRTEM has helped identify the composition of the nanoparticles through Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive X-ray Spectroscopy (EDX). The EELS compositional maps are shown in Figure 5.4. The oxide is rich in both Fe and O, although Co is nowhere to be found, indicating that Co is oxidizing separately, and the oxide being formed is primarily Fe-rich. EDX has not corroborated the EELS analysis completely, however. EDX, for the particles analyzed, has shown that the particles have Fe and O, but they also have Co. By focusing on the Oxide and comparing it with the Core, it appears that the core is richer in Fe than the outside layers, although all sections have a large percentage of oxygen, and are most likely oxide. It may be difficult to find the smallest particles through EDX, which uses STEM mode, rather than HRTEM, which is used by EELS, which would give us different compositional distributions, but further analysis with more particles would give a better statistical distribution.

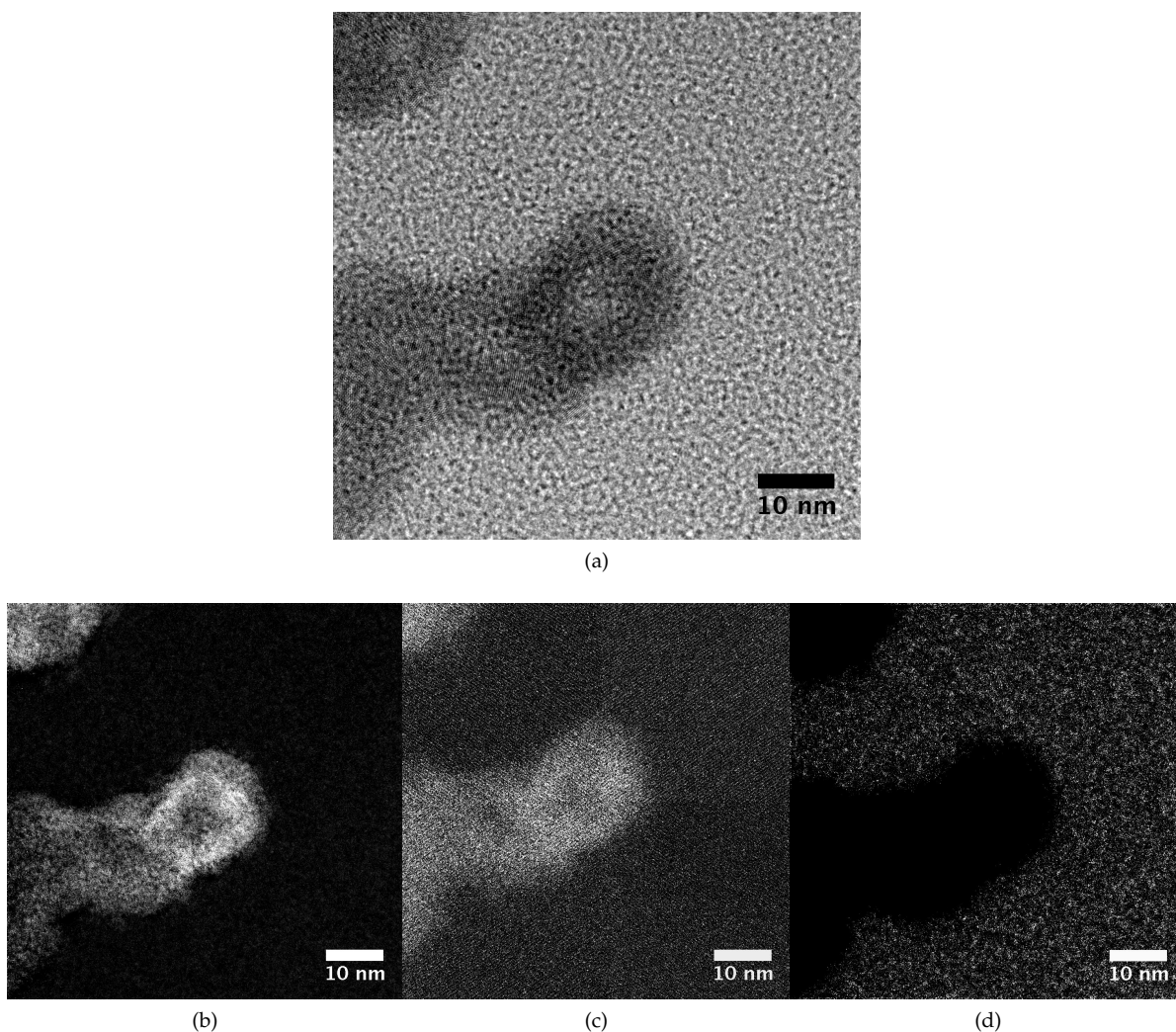


Figure 5.4: Compositional analysis of an FeCo nanoparticle using EELS, showing (a) a High-resolution TEM bright field image, (b) an Fe map, (c), an O map, and (d) a Co map.

5.2.2 Vibrating Sample Magnetometry

Vibrating Sample Magnetometry (VSM) was performed on the isochronally oxidized nanoparticles to further extend the TEM study above. The FeCo nanoparticles were packed into cups to measure hysteresis loops and saturation magnetization. At each temperature, the saturation magnetization was averaged over three different powder sets since the polydispersity of the sample set requires a larger number of particles to be averaged for an accurate measurement. Figure 5.5 shows the room temperature magnetization of the FeCo nanoparticles oxidized in air for two hours at various temperatures; to ensure even oxidation through the powder sets, the particles were spread out in alumina boats inside the tube furnace, to ensure that oxygen transport to the particle surface was not a rate limiting factor. The passivated nanoparticles have a saturation magnetization of about 173 emu/g, with a coercivity of about 50 Oe. This value is below what is expected for $\text{Fe}_{50}\text{Co}_{50}$, which should have a magnetization around 235 emu/g. While we saw through TEM that there is a 3 nm oxide shell present at RT, this decrease in magnetization would correspond to a particle with 42 wt.%-magnetite ($M_{\text{s,Fe}_3\text{O}_4} \approx 90$ emu/g); the particles are only an average of 24 wt.%-magnetite according to TEM, though. The magnetization curve, however, was averaged over a greater particle distribution, and may therefore have many more small particles which are more fully oxidized than the representative TEM images. This will bring down the RT saturation magnetization due to the larger percentage of magnetite [39].

Even at 200 °C, the oxidation hasn't progressed to bring down the magnetization any further. It is only at 350 – 400 °C that oxidation actually begins to progress. Before this, the oxide thickness is limited by diffusion through the passivation shell, which is slow at these temperatures. For low temperature applications this oxide shell means that other passivating coatings, like C, are unnecessary [86].

As oxidation progresses after 2 hours at 350 °C, we see the magnetization decrease to 152 emu/g with a coercivity increase to 125 Oe. The magnetization here drops off and approaches an inflection point around 600 °C. Only after two hours at 600 °C do we see the M_{s} drop to values closer to magnetite ($M_{\text{s}} \approx 97$ emu/g) with coercivity values of 400 Oe. The inflection point signifies a change in the mode of oxidation, whether that be a change in the oxide phase (which will be discussed below in Section 5.2.4, or a change in the diffusion rate due to the build-up of the oxide layer.

As the isochronal oxidation temperature increases from 600 ° to 900 °C, the saturation magnetization curve flattens, indicating the completion of oxidation. This is in agreement with the TEM images from the same 900 °C sample set, where there is no FeCo core remaining, and the particles are completely oxidized. It is interesting to note that the final magnetization of the nanoparticles after complete oxidation ($M_{\text{s}} \approx 50$ emu/g) is well below that of magnetite ($M_{\text{s,Fe}_3\text{O}_4} \approx 90$ emu/g). Therefore other oxide phases must be

present, to reduce the final M_s below that of magnetite.

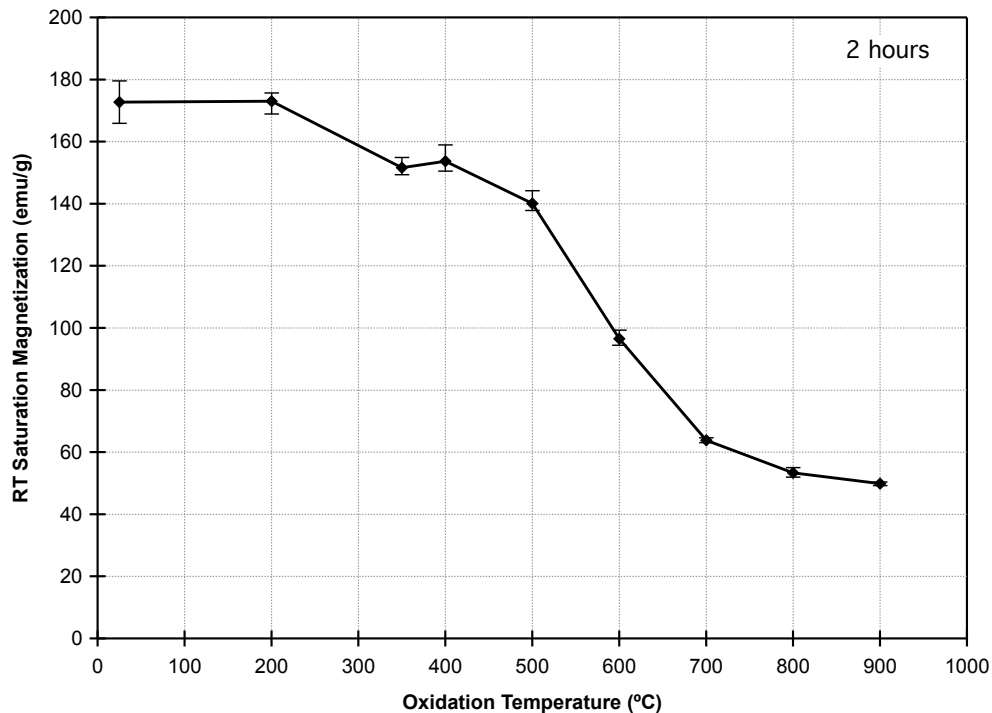


Figure 5.5: RT nanoparticle saturation magnetization as a function of 2 hour oxidation temperature.

Besides the actual data trend of Figure 5.5, it is interesting to note that the error bars change their height as the oxidation temperature increases. The data spread shown by the error bars at low temperatures is due to the particle size dispersion, and while all the nanoparticles have a 3 nm passivating oxide layer, this oxide layer takes up varying percentages of the nanoparticles depending upon their size. So, at room temperature, we have a large particle dispersion and a finite oxide layer. As the temperature increases, the error bars decrease, and finally by 900 °C they are virtually non-existent. This is because the oxide layer continuously grows and consumes the entire particle. At the lower temperatures, there is a great amount of variance in the amount of core left, so the sample taken for each VSM measurement will vary a good bit. At the higher temperatures, however, the core has been completely oxidized, and it is the phase of the oxide and shape of the particle that is changing, along with sintering of particles. Therefore, there will be much more uniformity in the particle magnetization, since it is not determined by their starting size and core dimension, but rather all are oxide, and the phase would only be dependent upon the temperature of oxidation.

To understand the progression of the nanoparticle magnetization before and after the isochronal measurements shown in Figure 5.5, new samples were oxidized isothermally for 5 hours. The measurements

shown below are in-situ isothermal measurements in the VSM. The argon jacket around the VSM furnace could be left open to air up to 350 °C, so we could measure the instantaneous saturation magnetization as oxidation progressed. The as-received nanoparticles were placed in a boron nitride cup and screwed to the sample rod, then placed in the VSM when the furnace was at temperature. The magnetization was measured for 5 hours. Due to data variance in equipment over time, the measured data was normalized so that the magnetization at 0 hours corresponded to the average saturation magnetization of the room temperature nanoparticles from the isochronal measurements above.

At 200 °C, oxidation is minimal (from 173 to 172 emu/g after 5 hours), although it proceeds very quickly at short times. The magnetization stabilizes within 30 minutes, and any further oxide growth (or magnetization decrease) is diffusion limited and slow due to temperature. This data point at two hours agrees fairly well with the isochronal data discussed above. From the TEM analysis above, an average particle at 200 °C is 47 wt.%-oxide (which would give $\sigma_s \approx 167$ emu/g). From the magnetic data after oxidation ($\sigma_s = 172$ emu/g, and assuming $\text{Fe}_{50}\text{Co}_{50}$ and Fe_3O_4), rule of mixtures calculations show a nanoparticle to be 43.4 wt.%-oxide; this is close to the TEM calculation and can be accounted for by the powder polydispersity, although if the core happens to decrease in Co concentration, the weight percent of oxide could increase to 45.3, which is even closer to the image analysis.

At 350 °C, oxidation proceeds more substantially, and is still fairly quick at short times; after five hours, the magnetization has stabilized. The stabilized magnetization is still fairly high, though, which points that the nanoparticles are not fully oxidized but a magnetite shell with an FeCo core. The magnetization at two hours is close to that seen above, but is slightly higher (161 emu/g compared to 152 emu/g above). This will be discussed below, but may be due to both oxygen transport in the sample cup and an increase in mass during oxidation.

These magnetization curves have both been fit with a direct logarithmic rate law (Equation 5.1), and the agreement seems fairly good; $k_{\log}$, A , C , and t_0 are all constants at constant temperature. The logarithmic rate law is applicable at low temperatures, normally below 400 °C, and thin oxide layers, normally below 100 nm, both of which are applicable in this case; here, the law has been extended to predict magnetization, rather than oxide thickness, as a function of time [6].

$$M_s(t) = k_{\log} \cdot \log (At + t_0) + C \quad (5.1)$$

While the logarithmic rate law seems to fit these curves quite well, it is not yet known if a different model would describe the oxidation process in nanoparticles. In particular, as temperatures increase and the oxide layer gets larger, a more parabolic rate law may be necessary. At the moment, it is also difficult

to take anything away from this analysis, since many factors affect the change in magnetization. Not only does the magnetization change depending upon the oxide formed and the composition of that oxide, but the mass of the sample also changes. Since magnetization here was measured per gram, the actual mass of the sample should have increased as oxidation progressed, but due to the measurement technique this was not possible. In actuality, the magnetization curves shown in Figure 5.6 should decrease a little more quickly, and have a final saturation magnetization lower than what is shown. This may account for the discrepancy between Figure 5.5 at 350 °C and Figure 5.6 at 2 hours, as mentioned above. Further analysis of this weight change using a TGA will be described below, in Section 5.2.3.

Two more considerations need to be mentioned while interpreting this data. While the sample was inserted when the oven was at temperature, there will nevertheless be a sample temperature lag, allowing the sample to reach temperature and the hot air to enter the sample cup; the local environment may also initially decrease in temperature due to the insertion of a room temperature quartz rod sample holder. There is also a question of oxygen transport to the sample and throughout the packed powder sample. A small space at the top of the sample cup was left empty for oxygen, although this may not have been enough for the entire sample, and there is still a question of oxygen transport through the packed powder. This will be discussed further below with the help of a TGA.

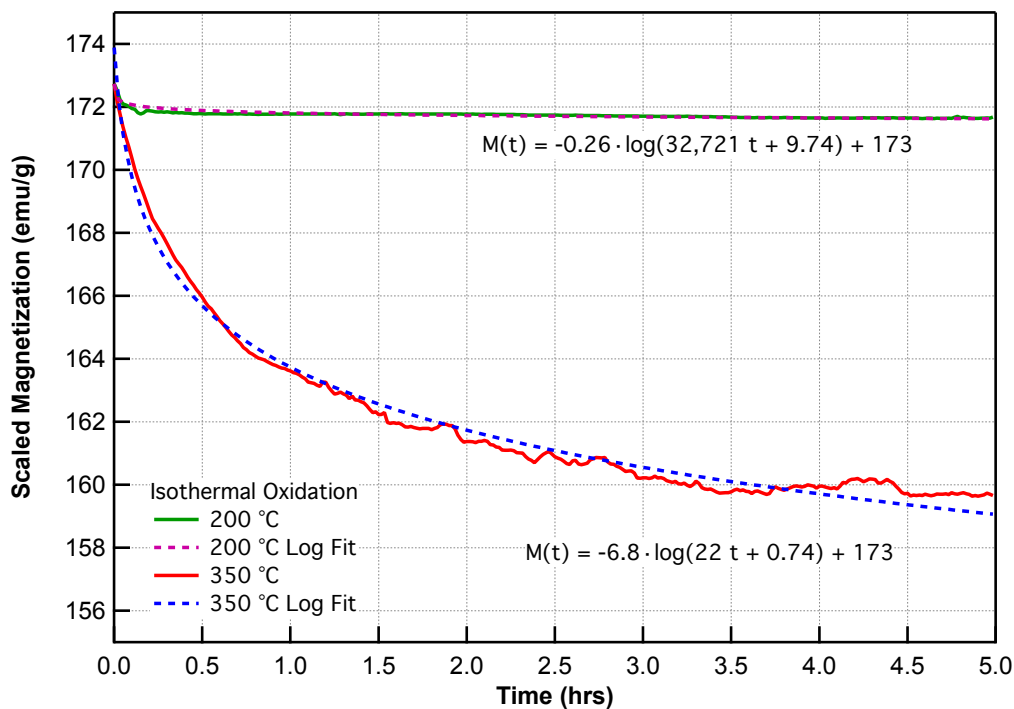


Figure 5.6: Scaled saturation magnetization of isothermally oxidized FeCo Nanoparticles, measured in-situ in the VSM in air.

5.2.3 Thermogravimetric Analysis

Since questions remained from the isothermal VSM oxidation analysis above, thermogravimetric analysis (TGA) was also used, rather than just oxidation in-situ in the VSM. This is a system that measures the sample mass change over time while in an oxidizing atmosphere. The sample is spread out into an alumina crucible, and loaded into the system. The weight change was measured by a calibrated laser system, sensitive to mass changes of 10^{-5} g, with a maximum mass change of 30-35 mg. In the current test, the sample was heated to the desired temperature in an atmosphere of ultra high purity (UHP) argon, and then air was let into the chamber as the reactant gas. Because the reacting air was at room temperature, the system temperature initially drops, stabilizing after a few minutes. After stabilizing, the isothermal hold is performed in air.

Figure 5.7 shows a TGA for as-received FeCo nanoparticles, isothermally oxidized at 350 °C. There are 3 major sections to the TGA curve (signified by the cross lines at the 350 °C line in the temperature profile). The first section is where the preparation for the isothermal test took place. The temperature was ramped to the set temperature in flowing UHP Argon (190 mL/min), and once it reached temperature the flow was switched to air (90 mL/min). During the switch in gases, it will take some time for the chamber to fill up with air, rather than UHP argon, and the temperature will drop due to the introduction of room temperature air. After 300s, the air flow rate was increased to 100 mL/min, and the isothermal timing was begun; this is the second section (after the first line). There is still some temperature fluctuation during the initial section, so another line has been added where most of the temperature fluctuations have diminished and the temperature is approaching the set-point (this line was put at 15 minutes after the initial flow of air). The third line shows the end of the 8 hour period, where the furnace was shut off.

The oxidation proceeds very rapidly, characteristic of logarithmic growth, and then slows down, never fully plateauing (the direct logarithmic fit was constrained to $t_i = 0.17$ h and $t_f = 8.17$ h). After 8 hours, the oxidation is still progressing, albeit very slowly. This is a slightly different picture than what was seen with the VSM, where the initial oxidation was not as quick, and after 5 hours all oxidation progress stopped. This can be understood through the limiting reactions in the different systems. In the VSM, the oxidation process is slowed down by gas phase mass transfer through the packed powder, and into the sample cup; the air was also not flowing, but stationary. In the TGA, the powder was not spatially packed in to a cup, but poured into an Alumina crucible. Along with flowing air, this ensured that gas-phase mass transfer is not a rate limiting step. The final tapering of the oxidation rate is therefore due to diffusion through the oxide shell. This taper may also be affected by a limited supply of reactant as nanoparticle cores are consumed. Some of the smaller particles will not be able to oxidize further, besides changing the phase of the already

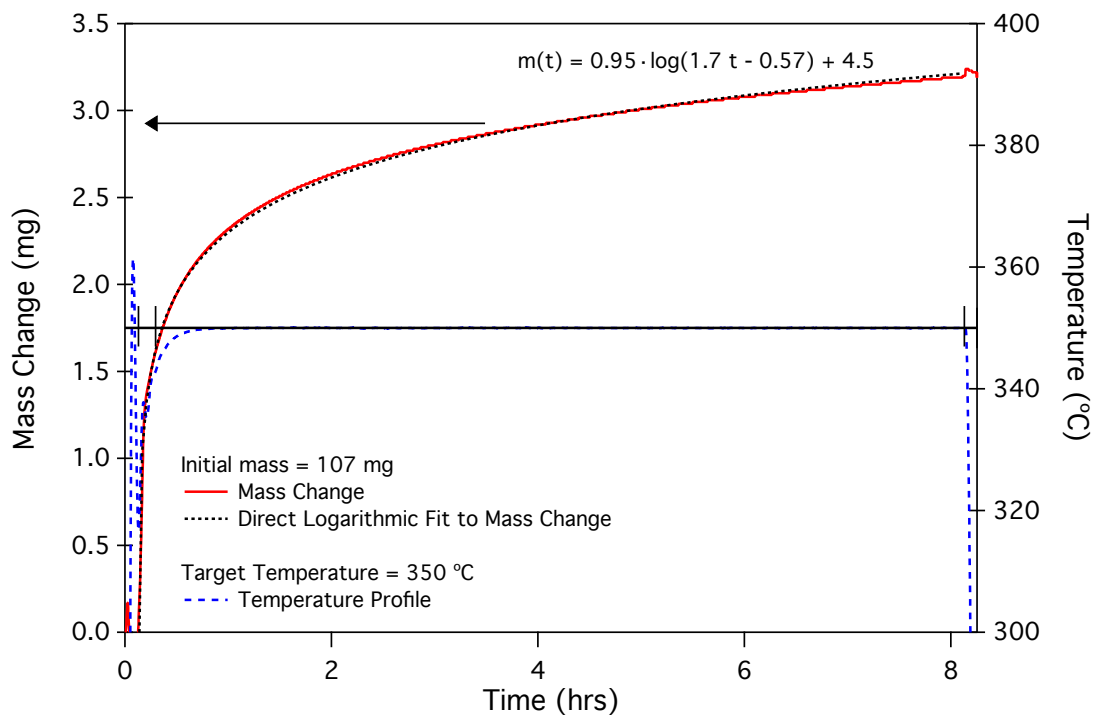


Figure 5.7: TGA of as-recieved FeCo Nanoparticles oxidized at 350 °C in flowing air for 8 hours(the first line is where the 8 hours began, with an air flow rate of 100 mL/min; the second line is where temperature fluctuations became minimized; the third line is where the furnace was turned off).

produced oxide. Since XRD, below, does not show such phase changes, it must be a combination of fewer particles available for oxidation, and the size of the shell on those particles.

The differences between VSM and TGA become more readily apparent when plotted next to each other. While we have no mass change data for the VSM, we can convert the TGA data into magnetic data by assuming the mass change is entirely due to the addition of Oxygen atoms into a magnetite lattice. For every gram of Oxygen added to the nanoparticle system, we lose ~ 2.6 g of metal from the core. By starting from 173 emu/g, and calculating the new magnetization by decreasing the FeCo percentage ($\sigma_s = 235$ emu/g) and increasing the Fe₃O₄ percentage ($\sigma_s = 90$ emu/g) appropriately, we can get Figure 5.8. As can be seen, the TGA measurements proceed more quickly than the VSM, but the TGA reaction rate drops rapidly. It is encouraging to note that the calculated TGA final magnetization is in good agreement with that measured by VSM. While it is slightly lower, and would continue to decrease, this makes sense because the reaction is not limited by the imposed environment, but will continue so long as diffusion can proceed and reactants are available.

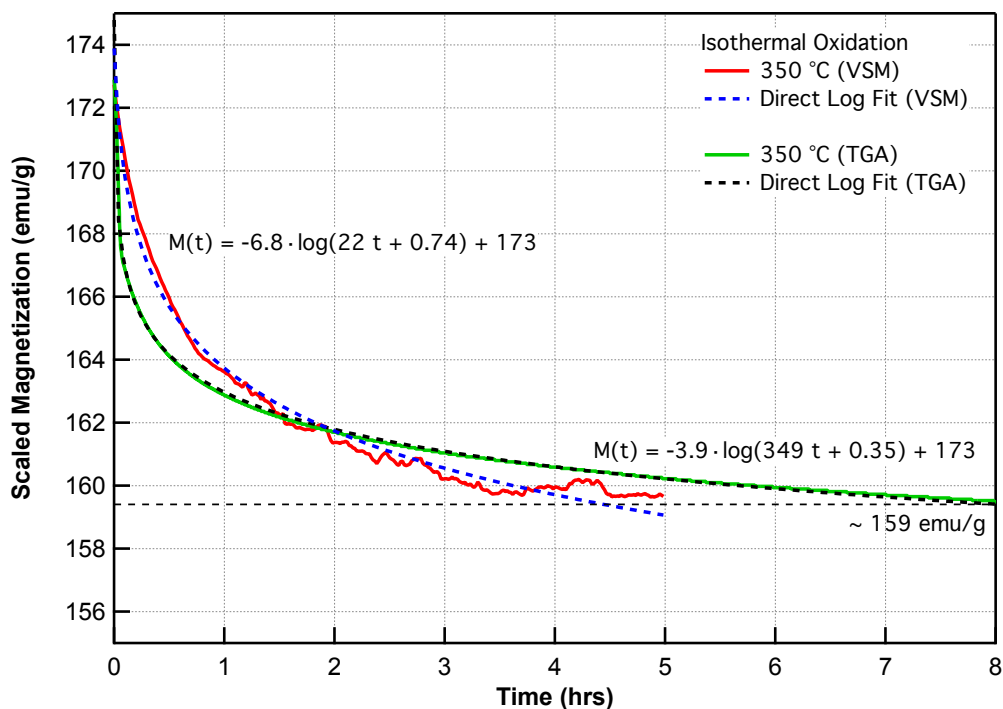


Figure 5.8: Change in magnetization versus time for nanoparticles oxidized isothermally at 350 °C, using the measured, normalized VSM results from Figure 5.6 and calculated TGA results from Figure 5.7.

5.2.4 X-Ray Diffractometry

As has been stated previously, XRD is an invaluable technique that can reveal the crystal structure and phases of a material by non-destructive means. Samples were initially oxidized in air at low temperatures (250 - 350 °C) to monitor the development of the oxide, and then the samples were oxidized at higher temperatures (up to 900 °C) for 2 hours to see the final oxide structures present (the same powders used for Figure 5.5). The analysis below will help clarify some of the questions remaining from the above techniques.

Initial X-ray diffraction of FeCo nanoparticles oxidized at low temperatures, between 200 and 350 °C, shows qualitatively that the oxide peaks begin to appear after only 15 minutes, and they can all be attributed to magnetite. The peaks continue to grow as the FeCo peaks decrease in intensity. We can also see a sharpening of the oxide peaks as they grow, and a slight broadening of the FeCo peaks as they are consumed, indicating, through a Scherrer analysis, the growth of the oxide and decreasing size of the FeCo core.

While such qualitative remarks seem obvious, the trend changes as time and temperature increase. The major difficulty with the FeCo–Oxide system is the ability to resolve the different oxide peaks, which is necessary in order to understand what phases are growing and how they are changing. Figure 5.9 shows

calculated intensities for FeCo and its four Fe-Oxide types (described above in Section 3.1.3). It can easily be noticed that many of these oxide peaks overlap or are close together, and resolving the actual phase present can be difficult, especially without any higher angle peaks present or any unique peak found for a specific phase. Therefore, it is necessary to perform the XRD with a standard, to make sure to align all of the peaks before analysis. This will ensure that any change in peak position is truly due to a change in lattice parameter due to stress or oxide composition.

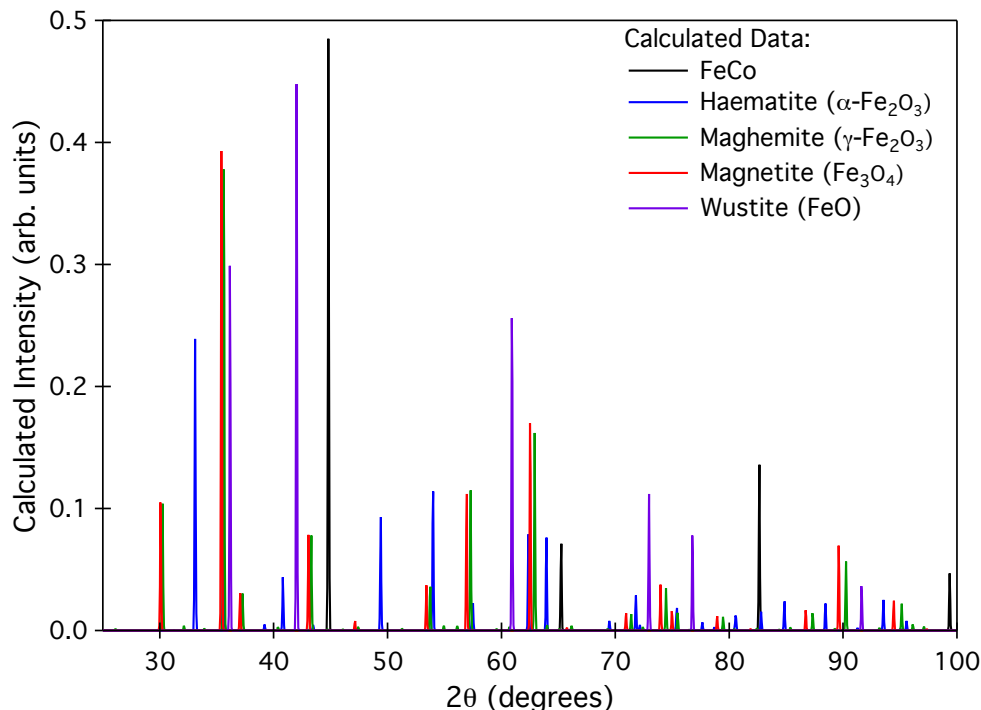


Figure 5.9: Calculated X-Ray Diffraction Intensities (from CrystalDiffract™, Version 5.1.6, using Cu-K_α Radiation, with a 1 μm particle size, and 0.1° 2θ instrumental broadening).

To extend the initial low temperature oxidation studies, isochronal studies were performed from room temperature to 900 °C in a tube furnace in air for 2 hours, in a fashion similar to Collier et al. [16]. In this case, however, the nanoparticles were then mixed with Si powder to align the corresponding XRD patterns (see Figure 5.10). At RT, there were practically no oxide peaks present, since the passivated shell is so thin. As the temperature increases, the oxide peaks grow in intensity, and sharpen, since their thickness is increasing. At 350 °C, the magnetite (311) oxide peak is already well defined, and by 700 °C the FeCo peaks have disappeared. As the temperature increased, the magnetite peaks shifted to the right indicating a decrease in d-spacing, which here is ascribed to increased vacancies in the oxide structure. The increase in vacancies is probably due to a lack of remaining iron to participate in the oxidation reaction, either due to a depleted core, or diffusion through the thick oxide layer; with less iron present, maghemite can form,

continuing the preferred spinel crystal structure seen at shorter times and lower temperatures, but with more and more vacancies added as the structure grows. None of these peaks ever reached the full $\gamma\text{-Fe}_2\text{O}_3$ structure, possibly due to sintering and densification at higher temperatures, competing with the oxidation, as seen through TEM. The oxide peaks seen for all temperatures are therefore all magnetite and maghemite, except for one isolated peak in two scans. No wustite was seen, contrary to that reported by Collier et al. It is the presence of maghemite that is therefore responsible for the low magnetizations seen after oxidation at high temperatures in Figure 5.5.

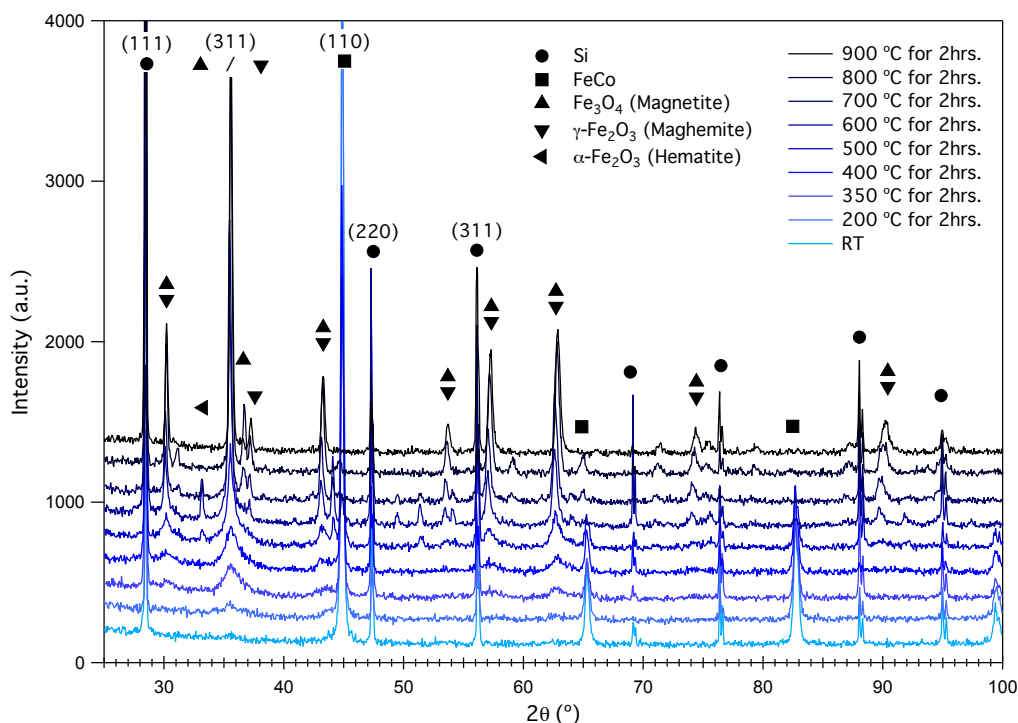


Figure 5.10: X-ray Diffraction pattern of FeCo powders oxidized isochronally for 2 hours at temperatures from RT to 900 °C in air in a tube furnace; Si powder was used as a standard.

5.2.5 Mössbauer Spectroscopy

While the techniques used thus far can tell us many things about the oxide and its formation at various temperatures, it is difficult to resolve what happens to Fe or what happens to Co. Through Mössbauer Spectroscopy we can look a little more deeply into the oxide formation, since it is an Fe sensitive technique. The sextets seen in the Mössbauer spectra and the hyperfine field from those spectra are very sensitive to the elements present, especially iron. As can be seen in Figure 5.11a for RT FeCo nanoparticles, we get a characteristic single sextet which corresponds to the splitting of the incident gamma ray by the hyperfine

field at the nucleus of the atoms being analyzed. In fitting the sextet, we get a hyperfine field (BHF) value of 35.5 T, which corresponds to that of FeCo nanoparticles (α -Fe particles have a BHF of 33.1 T).

After two hours of oxidation at 350 °C, we can see that the nanoparticles have oxidized, but not fully, in agreement with VSM and XRD results seen above. We now see an octet in the spectrum (Figure 5.11b) which can be fit by three sextets. The initial analysis of this data pointed towards one sextet corresponding to α -Fe, and the other two corresponding to the octahedral and tetrahedral sites of magnetite. It must be noted, however, that Mössbauer Spectroscopy is not an absolute technique in and of itself, but provides data that must be interpreted in the context of other data. By looking at X-ray Photoelectron Spectroscopy (XPS) data from polycrystalline thin films (see Section 5.3.1), it does not make sense that the core would be pure Fe, since Fe is the mobile oxidizing species, much more so than Co; this is why the other two sextets correspond to the octahedral and tetrahedral sites of magnetite, and not Co-ferrite. The core should be getting more rich in Co, since Fe is diffusing out of the core to the Core-Oxide interface, or Oxide-gas interface. The core BHF decreased to 33.1 T, however, which was said above to be pure α -Fe. However, while the addition of cobalt initially increases the BHF to 35.5 T, the BHF goes back down with increasing amounts of Co, and crosses through 33.1 T, in a similar trend to the Slater-Pauling curve with magnetic moment (see Figure 3.1) [26]. Therefore, we have one sextet for Co-rich FeCo (BHF = 33.1 T) and two sextets for the octahedral and tetrahedral sites of the oxide (BHF = 46.5/ 49.5 T), respectively. The magnetite BHF values calculated here are different from those seen for cobalt-ferrite (BHF = 47.5/ 50.5 T), so cobalt does not enter the structure of magnetite [39,78]. Fe is therefore the mobile species being oxidized, leaving vacancies in the Co-enriched core; this may also be why the core in the above TEM images was getting lighter.

Finally, in Figure 5.11c, after two hours at 900 °C, the nanoparticles are completely oxidized. We again see a sextet, although this can be fit by the two spectra for octahedral and tetrahedral sites occupied by Fe in magnetite. The hyperfine field values are again those of magnetite, and not of Co-Ferrite. So, all the Fe is oxidized and we have completely oxidized nanoparticles, although the fate of the cobalt is still unknown.

5.3 Oxidation: Thin Films

Both polycrystalline and single crystal thin films have been sputtered with an Fe₇₀Co₃₀ target. The polycrystalline films have been primarily used to study different oxidation mechanisms and rates in polycrystalline FeCo when compared to single crystal FeCo films.

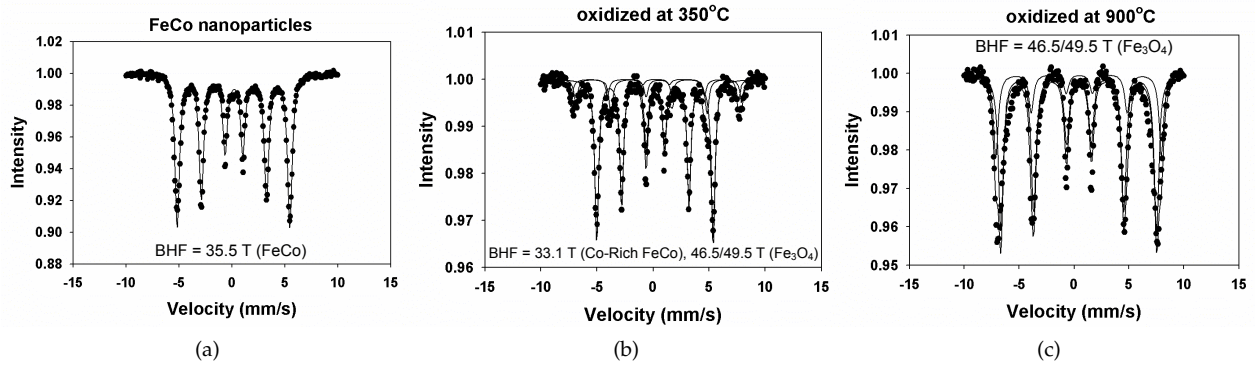


Figure 5.11: The Mössbauer Spectra and Hyperfine Field (BHF) values for nanoparticles oxidized in air at (a) Room Temperature, (b) 350 °C for two hours, and (c) 900 °C for two hours.

5.3.1 Polycrystalline Thin Films

Polycrystalline thin-films of Fe₇₀Co₃₀ have been sputtered on Si substrates with (110) and some (200) texture. A predominantly (110) film has been oxidized in air at 350 °C for 30, 60, and 90 minutes. After oxidation, the samples were analyzed by various methods to quantify the progression of the oxide layer.

X-Ray Diffractometry

The sample initially analyzed had good (110) texture, although a (200) peak could be seen. The FeCo layer had a BCC-derivative structure, as shown through in-plane and out-of-plane XRD scans; the out-of-plane scans were performed to ensure that the addition of Cobalt did not change the crystal structure to FCC or HCP. The FeCo peaks decreased as the oxidation time increased, although no oxide peaks ever appear even as the sample seems to approach complete oxidation. It is apparent that the nanoparticles (discussed above) oxidized slower than the thin films, even though they have an increased amount of surface area.

Vibrating Sample Magnetometry

Vibrating Sample Magnetometry (VSM) was done to monitor the magnetization of the thin film as oxidation progressed. Hysteresis loops were measured for an unoxidized sample and a sample oxidized at 350 °C for 90 minutes. The unoxidized sample was very soft, with an in-plane saturation magnetization of about 205 emu/g, coercivity of about 15 Oe, and an anisotropy field of 24.7 kOe; the anisotropy field can be accounted for with magnetocrystalline and shape anisotropies. The oxidized sample showed a dramatic increase in coercivity and a decrease in magnetization; the sample is almost completely oxidized after only 90 minutes.

Transmission Electron Microscopy

At room temperature (Figure 5.12a), there was no oxidation except for a 3 nm passivated layer, as calculated by C. M. Wang et al. [92]. The FeCo layer is about 100nm, and is polycrystalline. After oxidizing in air at 350 °C for 30 minutes, the oxide layer has grown significantly, and is crystalline in nature (Figure 5.12e). Figure 5.12c and 5.12d are different sections from the same sample, but both show different characteristics of the oxidation process. Both have a darker oxide layer with a white layer, followed by the remaining unoxidized FeCo. The white layer is the voided region created by the accumulation of cation vacancies during oxidation. In Figure 5.12c, the oxide layer is very uniform, whereas in Figure 5.12d, the oxide has peaks and valleys. While one might initially think that Figure 5.12d is oxidizing differently because of grain boundaries in the original FeCo layer, we can see that in both oxidized figures the grains of the oxide are much larger than those of the underlying FeCo layer, so the correlation is lost. In trying to understand the reasoning for this difference, though, we can surely bring in surface energy, showing that the oxide in Figure 5.12d has started to become more hemispherical, attempting to decrease its surface to volume ratio and reduce its energy. Eventually, after increased oxidation, this may lead to spallation of the oxide layer.

In looking at the amount of FeCo left in the oxidized samples, we see that one sample only has 36 nm remaining while the other sample has 78 nm remaining. While as of yet this cannot be explained, of interest is the summation of the FeCo layer plus the white voided layer. In Figure 5.12d, they add together to form approximately 100nm, the initial starting thickness of FeCo. From this we can say that the oxide-metal interface never moved, but that the metal sites traded places with cation vacancies. Therefore, there was primarily cation diffusion taking place. In Figure 5.12c, on the other hand, the FeCo layer plus the voided layer is very much less than 100 nm (similar to what was seen with nanoparticles in section 5.2.1). This implies that the interface has moved, and therefore we must have more than one mobile species. We can infer that the anions were very mobile at the onset of oxidation, with cation diffusion eventually taking over (as symbolized by the presence of the Kirkendall voids). While we do see some anion mobility here, it is not yet clear when this stopped, and why this was not seen in the other sample.

Finally, it is beneficial to compute how much oxide should be present given the amount of FeCo remaining. Assuming the oxide is magnetite, for Figure 5.12c we can calculate that the oxide layer should be 136 nm thick, which is very close to the observed oxide thickness. Figure 5.12d is not as close, as we should expect the oxide layer to be only 46 nm thick. While this discrepancy might be due to the hilly nature of the oxide, it does not seem like it can account for over 50 nm extra oxide.

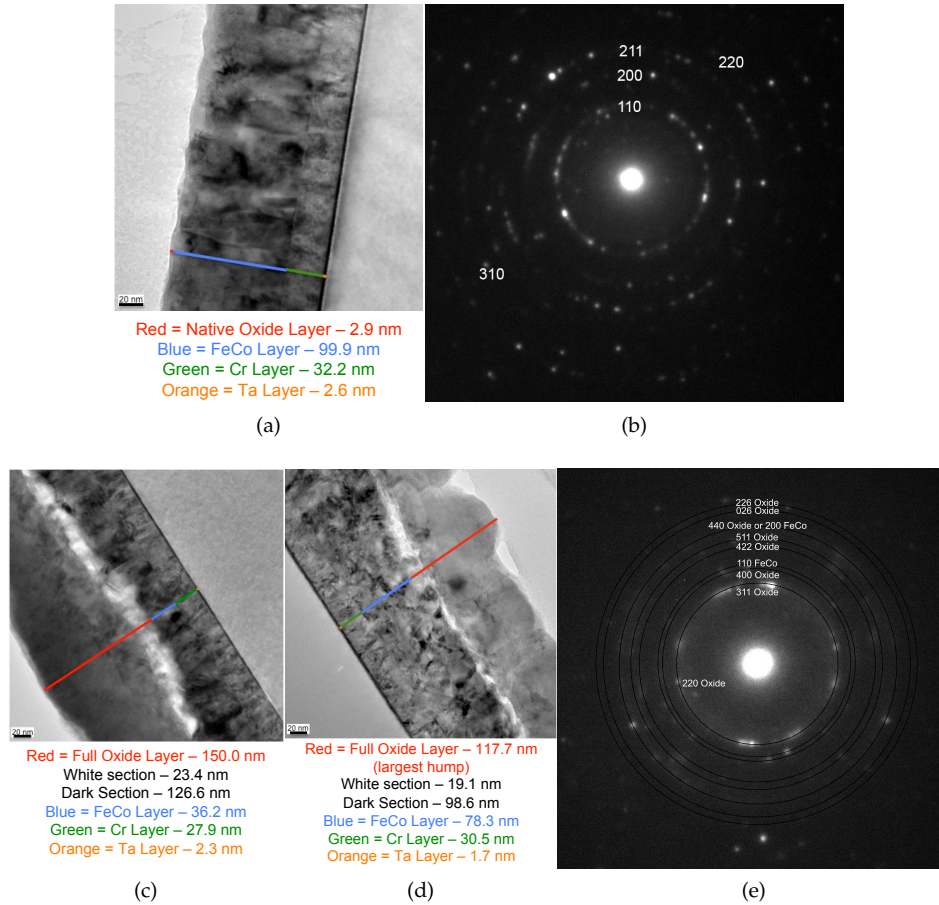


Figure 5.12: Cross-sectional images from the TEM showing samples oxidized at (a) Room Temperature (RT) (Phase Contrast), (b) RT (Diffraction), (c,d) 350 °C for 30min. (Phase Contrast), (e) 350 °C for 30min. (Diffraction).

X-Ray Photoelectron Spectroscopy

Through X-ray Photoelectron Spectroscopy (XPS) we were able to initially analyze the composition of the thin films observed by TEM in Section 5.3.1. By analyzing a polycrystalline thin film oxidized at 350 °C for 30 minutes, we can see that at the free surface there is a cobalt depleted oxide, with Fe and O in the correct ratio for magnetite (3:4); this agrees with the nanoparticle Mössbauer data discussed in section 5.2.5. As we move towards the Silicon substrate we see an increase in Si, implying that Si was able to diffuse through the sample at the oxidizing temperatures. At the same position that cobalt begins to increase, oxygen begins to decrease, so there appears to be a relationship between them, such that we may get a region of Co-rich oxide, possibly CoO in nature (which we can see at 600 seconds of etch time); it seems plausible that a small Co-ferrite region would exist, insofar as the Co cations could diffuse into the oxide structure, although Mössbauer spectroscopy says differently. Finally, the oxygen concentration continues to

decrease, and we have a layer of FeCo, slightly depleted in Fe (the initial composition was 70%Fe-30%Co). This further validates the assumption of the increased mobility of the Fe atoms, such that it is the dominant cation in the oxide layer and has left the film richer in cobalt.

To combine XPS and TEM (Figure 5.13b), the compositional profile has been overlayed on the TEM image from Figure 5.12c (the same sample, just a different region). The various compositional regions that were discussed above roughly correspond to regions of different contrast throughout the sample. We first have a darker magnetite oxide, followed by a lighter oxide, when the oxygen composition drops off. Then there is a white region which would correspond with the voided nanoparticle cores; there is still a composition here since XPS is averaged over a much larger surface area than TEM can show through cross-section. After the voided region, we have the remaining metal layer (now Co-rich), followed by the Cr underlayer, Ta layer, and Si substrate.

These compositions will need to be further analyzed by integrating over the entire thickness to determine the total amount of each element in the sample, to help understand the sample before oxidation and in its current state. One factor that must be kept in mind when analyzing these profiles, however, is the angle at which the sample is being etched. This angle is not known for the current sample, however, this should be documented for future samples. If the sample is etched at an angle, rather than normal to the surface, this may produce a compositional profile that is not comparable with TEM; this could also explain why we see so much Si throughout the rest of the sample. A comparison with analytical TEM compositional analyses will help round out the understanding displayed here through XPS.

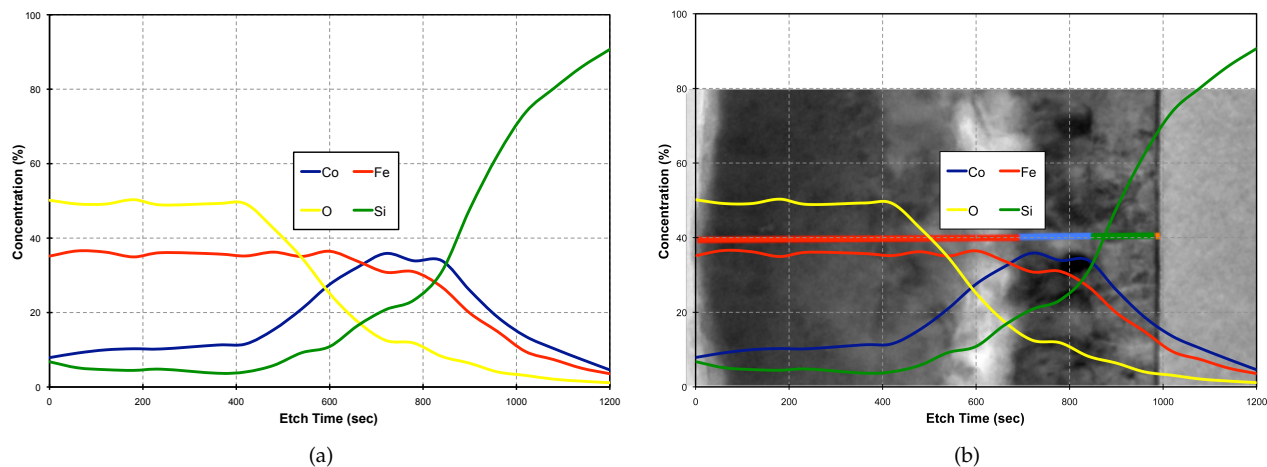


Figure 5.13: XPS curves showing (a) the concentration profile and (b) the concentration profile overlayed on Figure 5.12c of a polycrystalline FeCo thin film oxidized at 350 °C for 30 minutes (on the right of each is the silicon substrate, and the left is the free surface).

5.3.2 Orientational Variants on MgO

Before pursuing single crystal work using MgO substrates, it is essential to understand and verify the epitaxial relationships between FeCo and the MgO substrate to produce the correct “2D-simulated” facets in thin film form. Single Crystal MgO substrates come in three orientations: (100), (110), and (111). These can be used to alter the preferred growth of the FeCo layer during sputtering. This preferred growth is based upon the lattice mismatch of the two layers and the sputtering conditions, producing either an equilibrium or non-equilibrium orientation. MgO takes on the structure of NaCl, forming an FCC superlattice structure with the Mg cations sitting on the Na sites, and the O anions sitting on the Cl sites. The FeCo layer, however, has a BCC-derivative structure.

While crystals normally prefer to align themselves along their close-packed plane in order to reduce the number of broken bonds and the resulting surface energy, strain energies must also be factored into the nucleation and growth model when we are concerned with sputtering on a substrate. If the strain energy is too large due to the lattice mismatch between substrate and film planes, that orientation may not grow preferentially (normally this condition is below 5% mismatch, although there are exceptions).

(001) MgO with FeCo

A single crystal (001) substrate of MgO was sputtered with FeCo at room temperature. MgO has a lattice parameter of 4.2112 Å, while FeCo has a lattice parameter of 2.8571 Å. There is a factor of 1.474 between the two parameters, which is fairly close to the square root of two (1.414), which means that we can have fairly low strains by rotation of the (001) FeCo plane 45° about the (001) MgO plane, thus aligning the [110] FeCo and [100] MgO directions. This yields a lattice strain of 4.33%, which is below the preferred limit for epitaxial growth.

XRD A regular out-of-plane θ -2 θ XRD scan with Cu-K α radiation, confirmed that the (001) planes of MgO and FeCo are parallel (see Figure 5.14a); while the intense MgO peak has been removed from the scan, the MgO Cu-K β peak is still visible. By tilting the sample 45° off of the plane normal ($\psi = 45^\circ$) and adjusting 2 θ for MgO and FeCo, we can bring the {110} planes into Bragg orientation; by rotating the sample at this satisfied Bragg condition ($\phi = 0 - 360^\circ$), we can find their orientation with respect to each other (see Figure 5.14b). From these two sets of scans, we get a good picture of the orientation relationship between the FeCo and MgO layers.

To assist in viewing these orientations however, it seemed helpful to take the scans, and represent them in a 2D plot, similar to a contour plot from a pole figure; Figure 5.15 is the 2D projection of the FeCo and

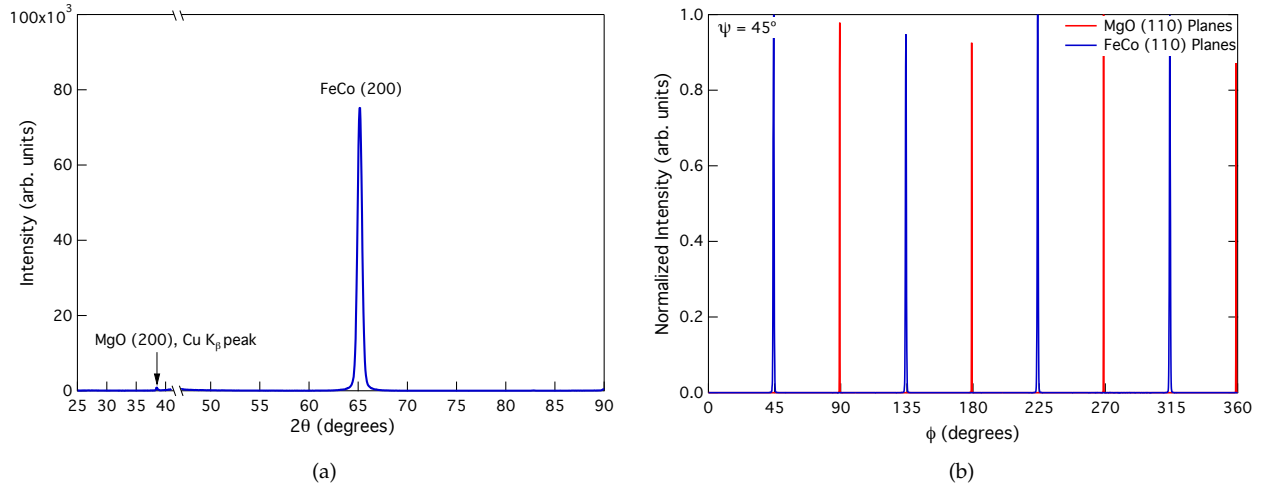


Figure 5.14: XRD patterns of FeCo on a (100) MgO substrate using Cu-K α radiation, showing (a) a $\theta - 2\theta$ scan (the intense (002) MgO peak has been removed), and (b) a ϕ -scan at a 45° tilt to bring out the (110) planes.

MgO orientations. The orientation relationship is therefore:

$$(001) \text{ FeCo} \parallel (001) \text{ MgO}$$

$$[110] \text{ FeCo} \parallel [010] \text{ MgO}$$

This is in agreement with what had been assumed, and with what was reported by Shikada et al. for ultrahigh vacuum Molecular Beam Epitaxy [73].

TEM These relationships can be further verified through TEM analysis, using both plan-view and cross-section samples. We can also see the initial oxide thickness due to passivation. As can be seen through the bright field image in Figure 5.16, the FeCo formed an adherent layer with the MgO substrate, with a clear transition between the two layers and no apparent voids at the interface. There is a 3 nm passivating oxide layer on the surface of the FeCo layer. The FeCo layer is 37 nm thick. While the 3 nm oxide layer is normal for FeCo, it is interesting that the thickness of this initial oxide seems invariant with the underlying microstructure of FeCo (i.e., single crystal, polycrystal, nanoparticles, etc.).

By varying the position of the Selected Area Diffraction (SAD) aperture, we can get diffraction patterns with varying contributions from the different layers. This allows for the separation of diffraction spots due to each layer, through the comparison of the different diffraction patterns. Figure 5.17 shows two such diffraction patterns. Figure 5.17a is the diffraction pattern taken only from the MgO along a $\{100\}$ Zone-axis. By moving the SAD aperture over the FeCo layer, we get a mixed diffraction pattern, as seen in Figure

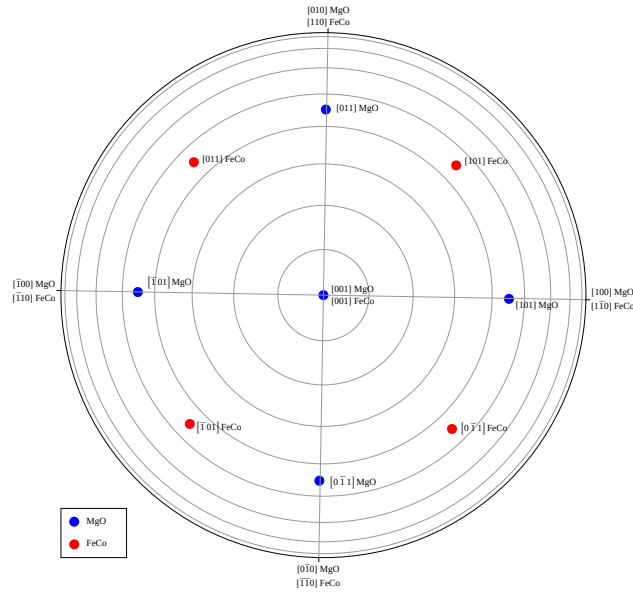


Figure 5.15: A 2D projection of the ϕ -scans from Figure 5.14, showing the orientation relationships of FeCo on an (001) MgO substrate.

5.17b. The FeCo spots correspond to a $\{110\}$ Zone-axis. Some of the spots that appear to be indexed by both MgO and FeCo are actually a combination spot (or a distorted spot) due to the overlapping patterns in Figure 5.17b. For example, the $(1\bar{1}0)$ FeCo spot is elongated compared to the (020) MgO, and the $(2\bar{2}0)$ FeCo spot is actually separate from the (040) MgO spot, although it can be difficult to see in the figures. These two patterns indicate that we have a $\{100\}$ MgO Zone-axis parallel to a $\{110\}$ FeCo Zone-axis, giving us a parallel direction in the two crystal systems. To get a parallel plane in this system, we have to know which direction corresponds to the surface of the layers. Comparing Figures 5.16 and 5.17 is misleading, however, due to the rotation of the Orius (regular imaging) and Coolsnap (diffraction) TEM CCD cameras with respect to each other. By comparing the Silicon diffraction pattern (from the cross-section stack; not shown) with the MgO and FeCo patterns, the surfaces in the diffraction patterns are rotated by approximately 90 degrees from the image in Figure 5.16. So, the surface in Figure 5.16 gives rise to the (002) and (004) MgO spots in Figure 5.17a, which are in the same direction as the $(00\bar{2})$ and (002) FeCo spots, indicating that the (001) FeCo and MgO planes are parallel. This leaves us with an orientation relationship of (001) MgO $\parallel$ (001) FeCo and $[010]$ MgO $\parallel$ $[110]$ FeCo, as seen above.

The plan view diffraction patterns (Figure 5.18) show splitting of diffraction spots due to the stacked layers of MgO, FeCo, and Oxide. Figure 5.18a was taken at a thicker region, where most of the diffraction spots would come from the MgO substrate. This has a cubic (001) zone-axis diffraction pattern similar to

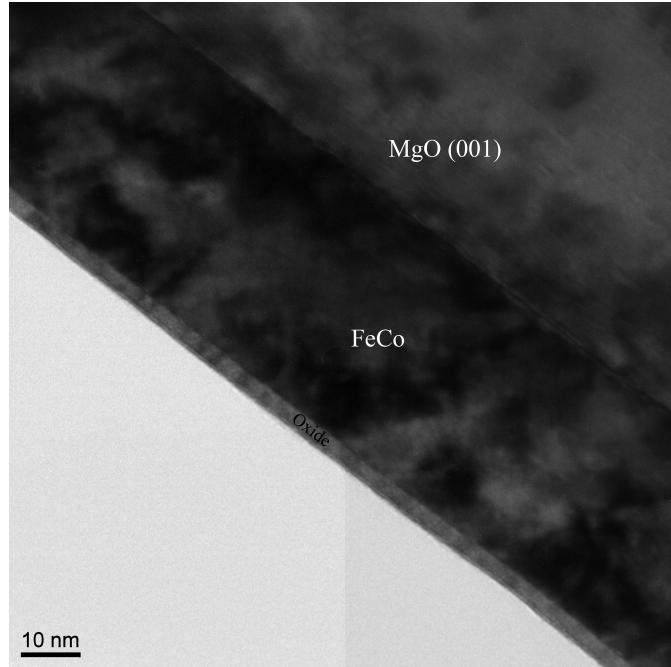


Figure 5.16: Cross-section Bright Field image of FeCo sputtered on (001) MgO.

that seen in Figure 5.17a. A key difference here is the splitting of peaks at the higher index spots (circled in red), which was not seen in cross-section. As the SAD aperture moves towards the thinner area of the sample, more pronounced splitting of diffraction points can be seen (Figure 5.18b). This splitting has been indexed in Figure 5.18b, showing the alignment of the (110) FeCo diffraction spots with the (200) MgO spots. Both of the diffraction patterns correspond to (001) zone-axes, but they are rotated 45° from each other. There are some other diffraction spots seen in the image (two have been circled in red), although these have not been indexed. They may correspond to the thin oxide layer present, although they do not agree entirely with what is predicted. This may be due to the strains in the oxide due to the FeCo layer or just poor signal due to low thickness. As we finally reach the thinnest section of the sample (Figure 5.18c), we see more spots come out, and a ring pattern seems to be forming inside the lowest index FeCo and MgO spots. This is most likely due to the oxide layer, and may indicate a polycrystalline oxide. There may also be more spots due to the curvature of this thin portion of the sample.

VSM and AGFM Some of the FeCo thin films on MgO (001) substrates have been capped with a Ta layer to prevent oxidation. While no in-depth analysis has been done yet, VSM and AGFM hysteresis loops show a decrease in coercivity by a factor of 3.5 (from 230 Oe to 65 Oe) with the addition of a capping layer. While more analysis is needed, especially TEM to quantify any layer of oxide underneath the Ta capping layer, it seems that the thin magnetite oxide layer is still thick enough to pin the FeCo magnetization, thus

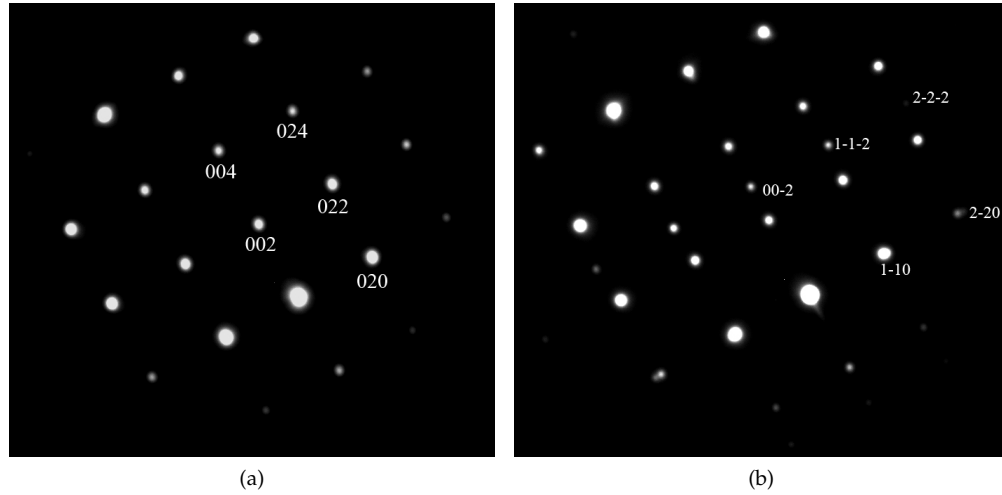


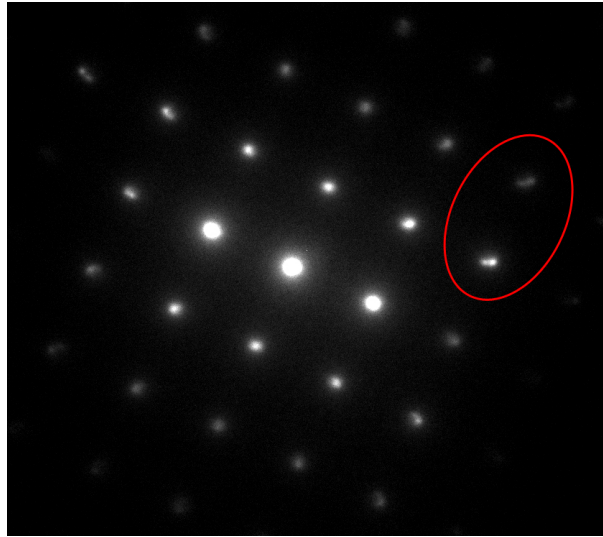
Figure 5.17: Cross-section diffraction patterns of a thin film of FeCo on (001) MgO taken from (a) just the MgO substrate and (b) both the FeCo layer and the MgO substrate. In (b), only the FeCo spots are indexed.

increasing the coercivity. This is due to exchange coupling between the layers and interfacial anisotropy resulting from the magnetocrystalline anisotropy of the magnetite layer; the diffusivity of the Co into the oxide layer will therefore become very important, since the magnetocrystalline anisotropy of Co-ferrite is two orders of magnitude larger than magnetite.

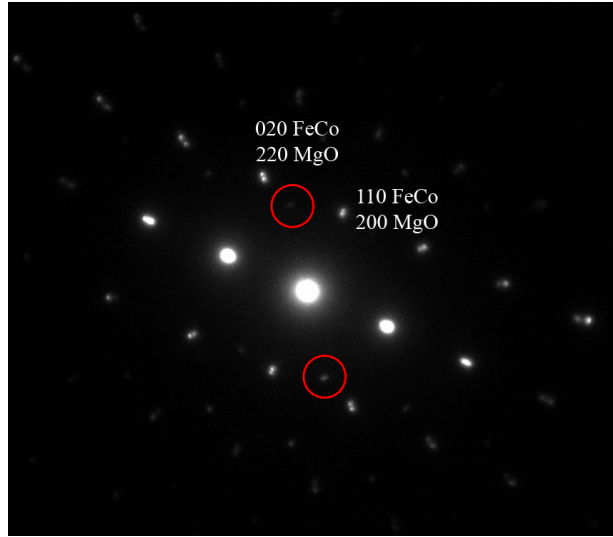
(110) MgO with FeCo

By sputtering FeCo onto (110) MgO substrates, it seems initially obvious by a look at crystallography and epitaxial relationships that (110) FeCo could come down on top, with the [001] MgO direction parallel to $[\bar{1}10]$. The strain is about the same as above (about 4.33% in both crystallographic directions). This, however, is not the case.

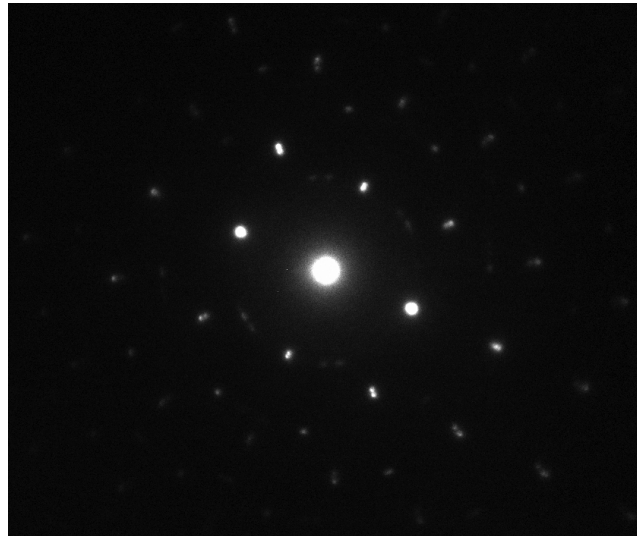
As can be seen in Figure 5.19a, the (211) FeCo plane grows on top of the (110) MgO substrate; the additional aluminum peaks are artifacts from the sputtering system. From the ϕ -scans in Figure 5.19b, we can see that there are also two variants of the FeCo epitaxy; this is even more clear in Figure 5.20, where the peaks are separated from one another. The (211) surface is assymetric, and should therefore have only two red dots (from $\psi = 30^\circ$), and one green dot (from $\psi = 54.7^\circ$). There is a second green dot, however, which has been labeled “variant”. There are two distinct orientations of FeCo, but rotated 180° from each other. So, in Figure 5.20, all the FeCo labels are for one variant, except for the repeated label of [011] FeCo. The labels of the red dots, [101] and [110] should be switched for this second variant; for simplicity, it has been labeled with only one direction per dot. While this FeCo orientation has a large mismatch with the MgO



(a)



(b)



(c)

Figure 5.18: Plan-view diffraction patterns of a thin film of FeCo on (001) MgO taken in a (a) thick, (b) thin, and (c) edge region of the sample. The red circles indicate (a) splitting of diffraction spots and (b) possible oxide diffraction spots.

substrate, the epitaxial relationships are in agreement with Shikada et al. [73]:

$$(211) \text{ FeCo} \parallel (110) \text{ MgO}$$

$$[0\bar{1}1] \text{ FeCo} \parallel [001] \text{ MgO}$$

and

$$[01\bar{1}] \text{ FeCo} \parallel [001] \text{ MgO}$$

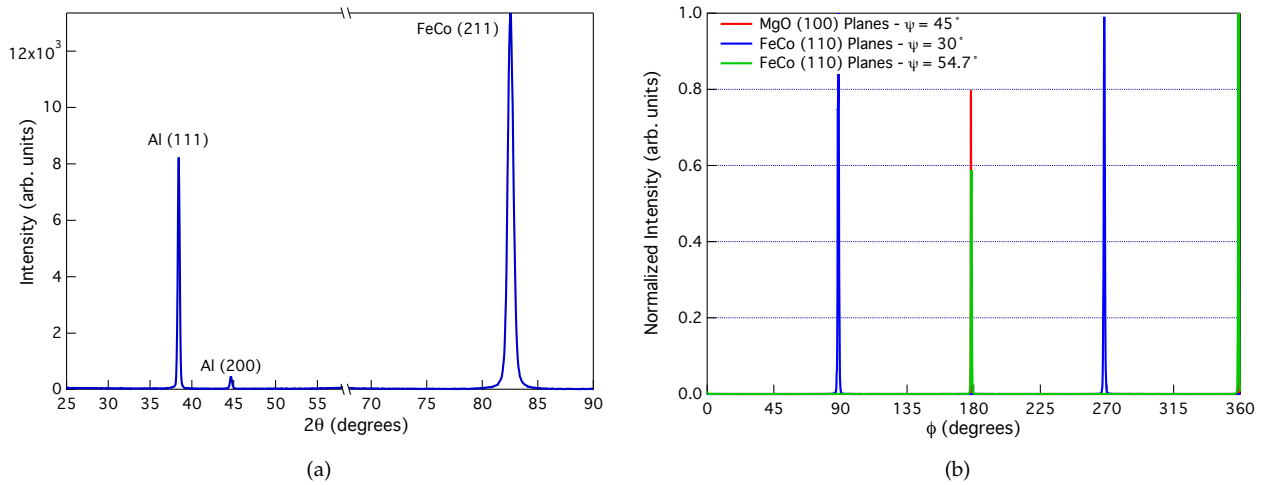


Figure 5.19: XRD patterns of FeCo on a (110) MgO substrate using Cu- K_{α} radiation, showing (a) a θ - 2θ scan (the intense (220) MgO peak has been removed), and (b) a ϕ -scan at multiple tilt angles to bring out the (110) and (100) planes.

TEM Plan-view TEM work shows results in agreement with the XRD data above. The two variants are not visible by plan-view diffraction, since they will produce the same line of dots, just with the negative names associated with each dot. Figure 5.21a is a diffraction pattern from a thicker region of the sample, showing only the diffraction pattern for the FeCo and MgO layers, which shows the same orientation relationships seen above; the splitting of the diffraction spots is confirmed by a simulated overlaid pattern, shown in Figure 5.21c. Figure 5.21b is a diffraction pattern taken closer to the sample edge, and has been colored and drawn on for clarity. The colored spots are those corresponding to different plane families, and the circles correspond to the specific distance calculated for FeCo spots in a $[211]$ zone axis; these circles are just beyond the MgO spots, further elucidating the splitting. Since this is a thinner region, we also begin to see other spots, which could be indexed to magnetite.

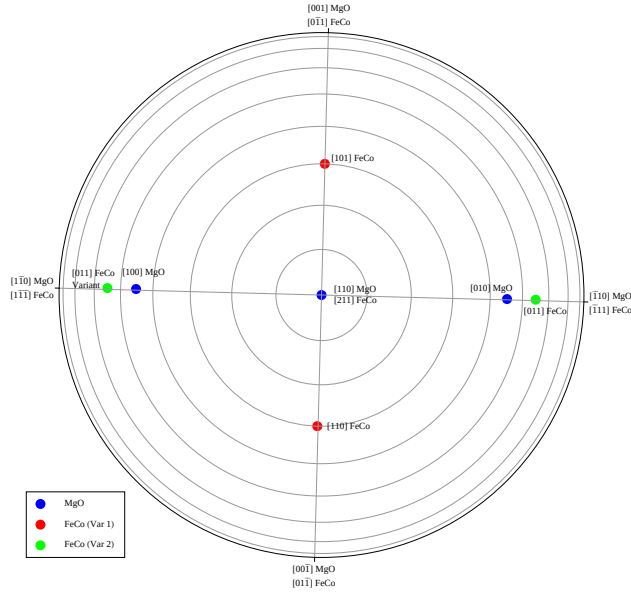


Figure 5.20: A 2D projection of the ϕ -scans from Figure 5.19, showing the orientation relationships of FeCo on a (110) MgO substrate.

(111) MgO with FeCo

By sputtering FeCo on (111), we observe the Nishiyama-Wasserman (N-W) relationship where FCC and BCC crystals let their close-packed planes lie parallel to each other, even though the crystallographic sites don't match up [65]. Figure 5.22a shows that (110) FeCo grows on top of (111) MgO, and through Figure 5.22b and 5.23, we can see that the relationship is:

$$(110) \text{ FeCo} \parallel (111) \text{ MgO}$$

$$[\bar{1}10] \text{ FeCo} \parallel [\bar{1}2\bar{1}] \text{ MgO}$$

or

$$[001] \text{ FeCo} \parallel [\bar{1}01] \text{ MgO}$$

This is again in agreement with Shikada et al., and here we have three variants, rotated 60° with respect to each other [73].

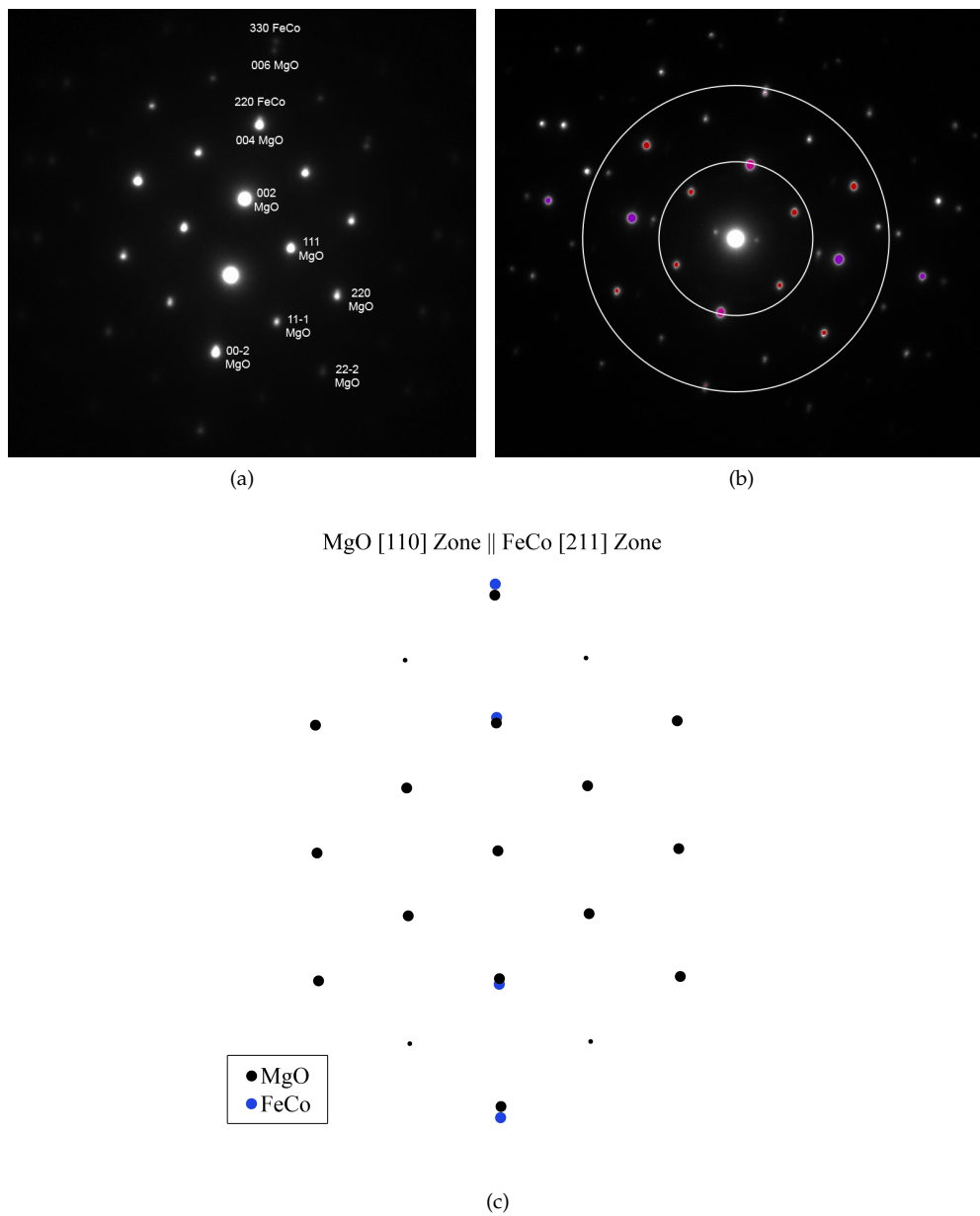


Figure 5.21: Plan-view diffraction patterns of FeCo on (110) MgO for (a) a thicker region (indexed for FeCo and MgO), (b) a thinner region with drawn rings for FeCo, magenta for {002} MgO dots, red for {111} MgO dots, and purple for {220} MgO dots, and (c) a simulated overlaid pattern using SingleCrystal™.

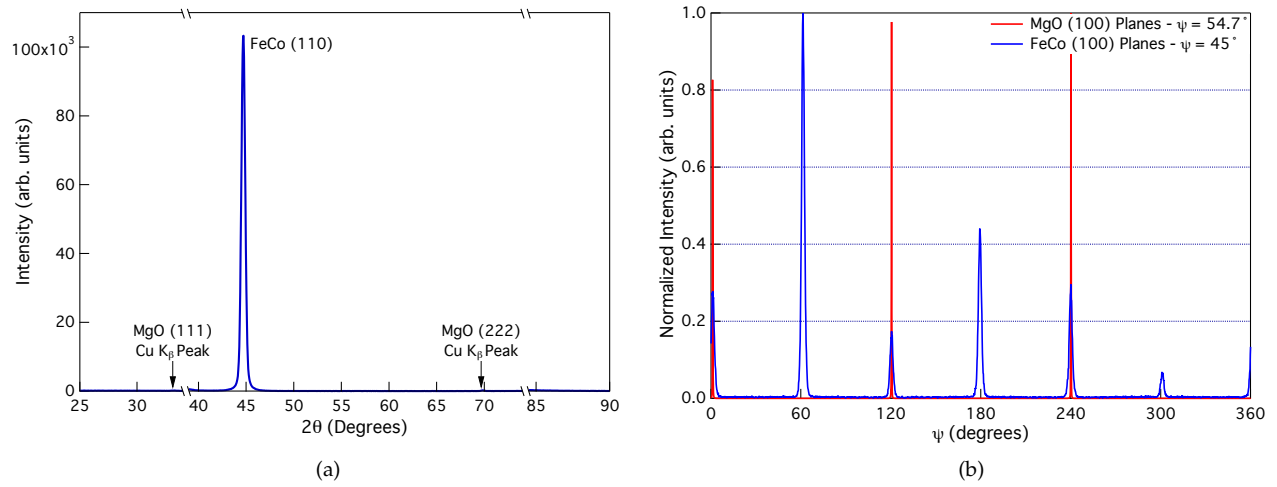


Figure 5.22: XRD patterns of FeCo on a (111) MgO substrate using Cu- K_{α} radiation, showing (a) a θ - 2θ scan (the intense (111) and (222) MgO peaks have been removed), and (b) a ϕ -scan at multiple tilt angles to bring out the (100) planes.

5.4 FeCo Bulk Samples

Since the role of Nb and V in the nanoparticles is difficult to discern, even in thin films, some bulk samples were analyzed, in a similar fashion to Turgut et al. [85]. Samples of weight percent $\text{Fe}_{49.35}\text{Co}_{48.75}\text{V}_{1.9}$ and $\text{Fe}_{49.05}\text{Co}_{48.75}\text{V}_{1.9}\text{Nb}_{0.3}$ were oxidized in air at 500 °C for 5000 hours. Figures 5.24 and 5.25 show images from the SEM using secondary electrons and energy dispersive X-ray spectroscopy. It is fairly evident that the oxidation rate of the Nb containing sample was much greater than with just V additions. Fe is again the mobile species, with a build up of Cobalt near the surface of the metal, due to both diffusion of Fe out of the metal, and diffusion of Co to the surface. Where the Co is most concentrated, it seems that in both samples there is a voided region, similar to what was seen in the nanoparticles and polycrystalline thin films. The V in both samples is most concentrated right at the sample-oxide interface, where the Co is also enriched. The Nb in general seems evenly dispersed throughout the sample. There may be a little island growth of oxide, especially in Figure 5.25, due to Oxygen diffusion into the metal, especially at short times when the oxide is thinnest.

5.5 Summary

The oxidation of FeCo and FeCo alloys is integral to their integration into modern-day devices. Many applications utilizing FeCo rely on the oxide layer for certain desirable properties. Therefore, it is necessary for the oxidation and the oxide properties to be understood. There are many factors affecting the oxidation of

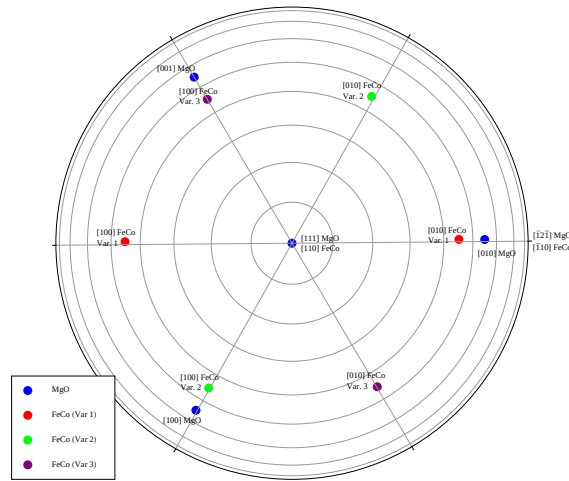


Figure 5.23: A 2D projection of the ϕ -scans from Figure 5.22, showing the orientation relationships of FeCo on a (111) MgO substrate.

FeCo, especially in the use of nanoparticles. These factors have been analyzed through many different techniques in hopes of truly isolating the different effects on the oxidation kinetics and epitaxial relationships of FeCo.

Nanoparticles oxidize rather slowly, beginning with a 3 nm passivated oxide shell. This shell is invariably 3 nm at RT, irrespective of the FeCo microstructure or geometry that preceded the oxidation. Oxidation doesn't progress more quickly until at least 350 - 400 °C. Even at these temperatures, however, the oxidation does not progress to completion, and by 5 hours oxidation has almost ceased. The oxide formed was initially Magnetite, but eventually a more voided structure began to appear, although this never fully reached maghemite; this change is due to the overabundance of Oxygen, and the limited amount of Iron available for oxidation. During oxidation, Fe is the mobile species, although Oxygen cations may have some mobility when the oxide is thin. Low temperature oxidation is governed by a logarithmic rate law. Cobalt doesn't appear to enter the oxide structure, as determined from multiple techniques, although the EDX analysis from HRTEM has provided opposing information. It is possible that some of the comparisons made between thin films and nanoparticles, concerning Co, are not entirely viable, since the activity of Co will decrease in the thin films (since their beginning composition is Fe-rich); this reduces the Co activity gradient through the oxide, reducing the diffusion speed. Nevertheless, as the nanoparticles oxidize, a voided region is left in the middle, and either the metal-oxide barrier physically moves due to diffusion or the oxide begins collapsing inward due to the voided core.

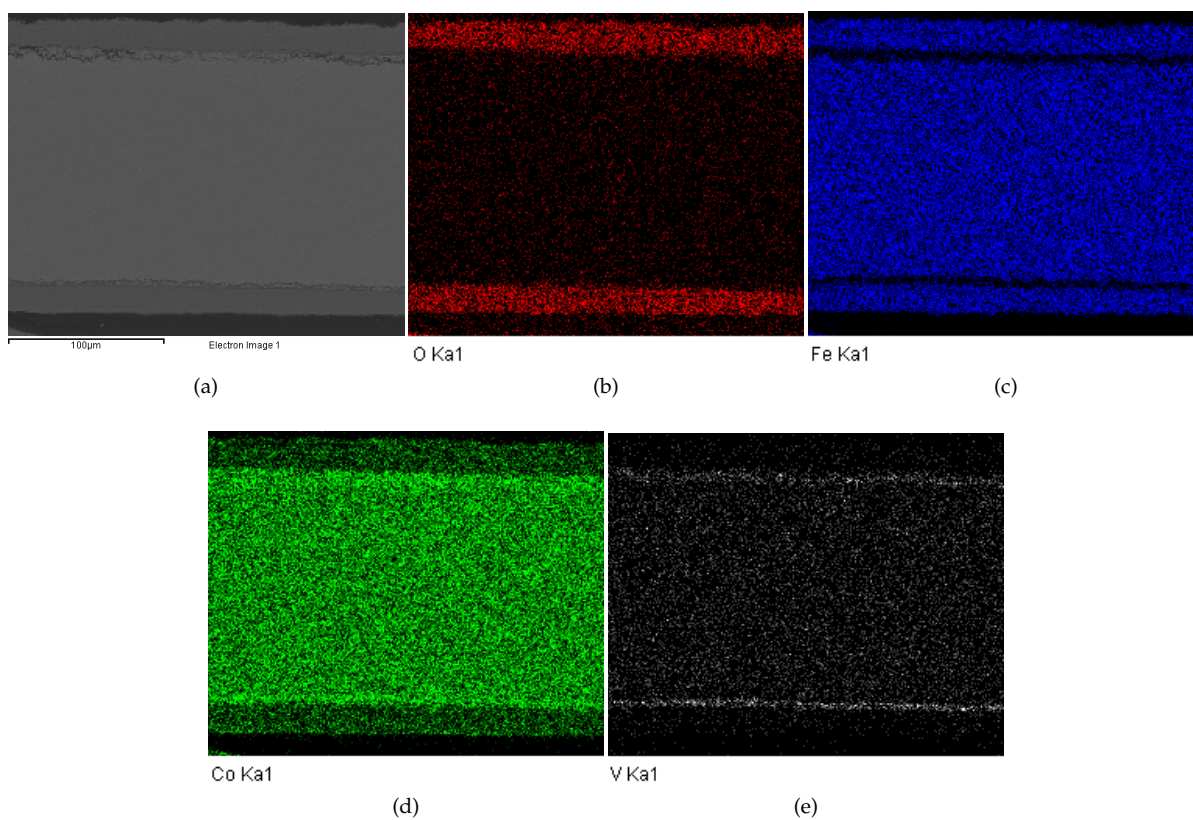


Figure 5.24: SEM analysis of a bulk $\text{Fe}_{49.35}\text{Co}_{48.75}\text{V}_{1.9}$ alloy oxidized in air at 500 °C for 5000 hours, showing (a) the sample cross-section using Secondary Electrons, and the EDX compositional analysis for (b) Oxygen, (c) Iron, (d) Cobalt, and (e) Vanadium.

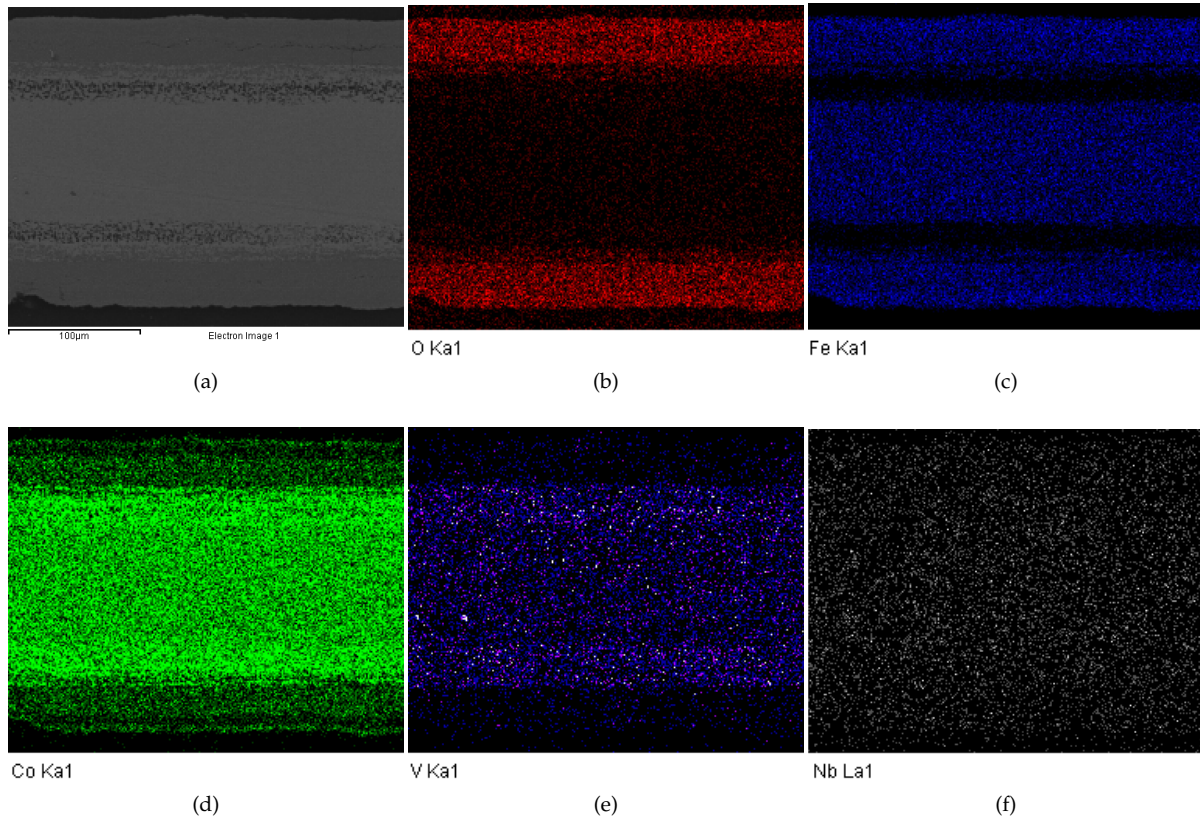


Figure 5.25: SEM analysis of a bulk $\text{Fe}_{49.05}\text{Co}_{48.75}\text{V}_{1.9}\text{Nb}_{0.3}$ alloy oxidized in air at 500 °C for 5000 hours, showing (a) the sample cross-section using Secondary Electrons, and the EDX compositional analysis for (b) Oxygen, (c) Iron, (d) Cobalt, (e) Vanadium, and (f) Niobium.

FeCo thin films oxidize more quickly than the nanoparticles. This was originally thought to be due to the selective oxidation of Nb and V in the nanoparticles (both of which were not in the thin films). But, bulk films of a similar composition to the nanoparticles showed that they do not act as sacrificial oxidation elements, although there was a large change in oxidation between only Vanadium additions, versus Vanadium and Niobium. Both oxygen and iron can be mobile species during initial stages of oxidation, although iron will dominate as a thicker oxide layer develops. Cobalt seems to oxidize separately from iron, although when and where the Co oxidizes and the composition of the resulting Cobalt-oxide are not yet known. The orientation relationships of FeCo on different single crystal MgO Substrates have been verified by XRD, and some by TEM. TEM cross-section samples show that single crystal samples also have a 3 nm passivating oxide layer, similar to the nanoparticles and polycrystalline thin films.

Chapter 6

Nanoparticle Nucleation and Growth

6.1 Introduction

Since the nanoparticles are very surface sensitive and their oxidation depends upon the faceting present, it is essential to understand how they nucleate and grow, and under what conditions different facets are predicted. Nucleation and growth is important in understanding nanoparticles and controlling/tailoring their properties.

The faceting of nanoparticles depends upon the underlying crystal structure. FCC-derivative ferrite nanoparticles are faceted with preferred crystallographic orientations, specifically the (111) and (100) planes, and these crystallographic orientations have distinct magnetic properties [76, 81, 82]. BCC-FeCo/ferrite core-shell nanoparticles have facets on the (110) and (100) planes, with oxide orientation relationships determined by Collier et al. [16, 39]. Control of the core facets, and oxide orientation based on epitaxial relationships is important in many applications, and is critical for the usability of these nanoparticle systems [16, 23, 24, 59, 62].

While an indepth study of FCC ferrite-based systems has already been done by Swaminathan et al., a re-analysis of the previous data is provided below (Section 6.4.2), although the bulk of this section will be concerned with the (100)–(110) system for BCC materials [83]. To understand nucleation and growth in BCC systems, it is necessary to first calculate both the critical nucleus and growth form shapes of BCC nanoparticles with (100) and/or (110) terminating surfaces. This is done by developing equations for the cube and rhombic dodecahedron which are applicable to all the shapes in between using volume and surface energy terms. Critical nuclei are found by maximizing these curves in one dimension (truncation parameter or volume), and finding the minimum amongst those maxima. Growth form shapes are obtained by minimizing the total surface energy associated with (100) and (110) surfaces while constraining

the volume to a constant size.

6.2 Requirements for Nucleation Growth Shapes

In order for a material to nucleate, there is a surface energy barrier that must be overcome. The creation of surfaces, which always cost energy, can be considered an introduction of two-dimensional defects. It is for this reason that heterogeneous nucleation is often preferred over homogeneous nucleation, because in heterogeneous nucleation there is already a surface present which can assist in reducing the energy barrier to nucleate new surfaces. Irrespective of the mode of nucleation, the shape of the critical nuclei can be determined to be the nuclei shape that has the lowest free energy of formation. While this has often been thought to be the same as the growth shape (often termed "self-similar growth"), this has not been proven analytically for three dimensional objects [15].

Beginning very simply, we can look at the general equations for traditional nucleation and growth shown below (Equations 6.1 and 6.2).

$$\text{Nucleation} \quad -V\Delta f_v + \sum_i \sigma_i A_i \quad (6.1)$$

$$\text{Growth} \quad \sum_i \sigma_i A_i \quad (6.2)$$

The nucleation equation has both a volume energy term and a surface energy term, while the growth shape only has a surface energy term. The nucleation equation has a 3rd power volume term, and a 2nd power surface area term, so we get a traditional nucleation curve, for which the critical nuclei can be found by setting the first derivative equal to zero (finding the critical points), and solving for when the curvature (or second derivative) is less than zero. While we use the maximum in the nucleation equation to give us the critical nuclei and nucleation energy barrier, we instead find the minimum in energy for the growth shape, minimizing the total surface energy. Since we are maximizing in one case and minimizing in another, both with two different equations, it seems reasonable to assume that the shape of the critical nuclei and growth shapes will be different, which is contrary to what has been previously stated by Christian and Aaronson [1,15]. This assumption is based upon the traditional arguments using a dimension of the shape, whether that be the radius of a sphere or the edge length of a polyhedra. It is inadequate, however, to compare edge lengths when dealing with the possibility of different shapes. This will be expanded upon below, with a three dimensional analysis for both {110} and {111} faceting of cubes, but Figure 6.1 shows this graphically for FCC based structures. When plotting the Helmholtz free energy versus the equivalent edge length of multiple polyhedra, it seems that there is one shape with a minimum nucleation energy

barrier (the Cube), and another which will provide the minimum energy growth shape at a certain edge length. While this is surely easier to plot, this is misleading and incorrect.

In order to compare different shapes, we need to compare equivalent volumes, otherwise the energies we are comparing are due to different amounts of atoms attaching to the nucleus, which will alter the energies being compared. By comparing volumes, we change the traditional shape of the nucleation curves (Figure 6.1b), but we can do both nucleation and growth analyses at the same time. The minimum energy barrier for nucleation will not change, since we are only altering the x -axis dimensions; we don't change the maxima in energy, but only their lateral position with respect to each other. By comparing volumes, however, we can set a constant volume and compare the energies for the different shapes, which is a Wulff Construction, in essence (rather than removing the volume term from the equation, we are just making it a constant) [36,95]. We can now see that the critical nucleus is not different from the growth shape but will be the same, since the curve with the minimum nucleation energy barrier will always be less than any other curve.

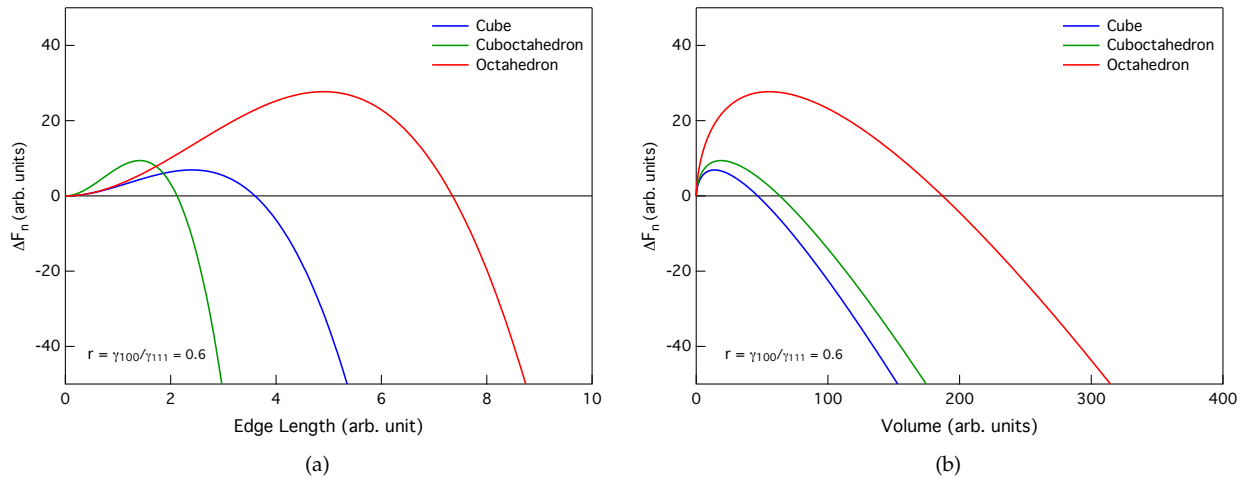


Figure 6.1: Helmholtz free energy plots for a cube, cuboctahedron, and octahedron when the FCC surface energy ratio, r , is 0.6, plotted against (a) equivalent edge lengths and (b) equivalent volumes.

Instead of choosing three different polyhedra and comparing them, it is better to allow any degree of truncation in a given system (BCC and FCC, in the current paper), and then calculate critical nuclei and growth shapes. This is done analytically below, but it is essential to briefly discuss the analysis before continuing. When considering the nucleation of spheres, surface energy is made isotropic, and the calculations only consider critical points in one dimension (the radius). It is therefore only necessary to find the maximum in the nucleation curve. When expanding the two-dimensional graph of *energy* and *shape dimension* to a three-dimensional *energy*, *volume*, and *truncation amount* graph, the surface maximum is no longer of

interest. The *volume* axis takes the place of the previous *dimension* axis, and the *truncation* axis allows us to plot all the possible shapes and their energies at one time, starting from no truncation to full truncation (for BCC, Cube to Rhombic Dodecahedron; for FCC, Cube to Octahedron). We still need to find the maxima along the volume axis, finding the critical nucleus at a specific truncation ratio. But, while we find the maximum in energy with increasing particle size, we must find the minimum in energy with changing truncation parameter. This is illustrated in Figure 6.2, where the two directions of interest are labeled; *edge length* is used for this schematic, rather than *volume* to demonstrate the concept more easily through graphical means, and to preserve the shape of the traditional nucleation curves, but in three-dimensions. While it is not traditionally considered a critical point, this analysis needs to look at saddle points as the true minimum in energy and the true critical nucleus for a given surface energy ratio between faceting faces [68].

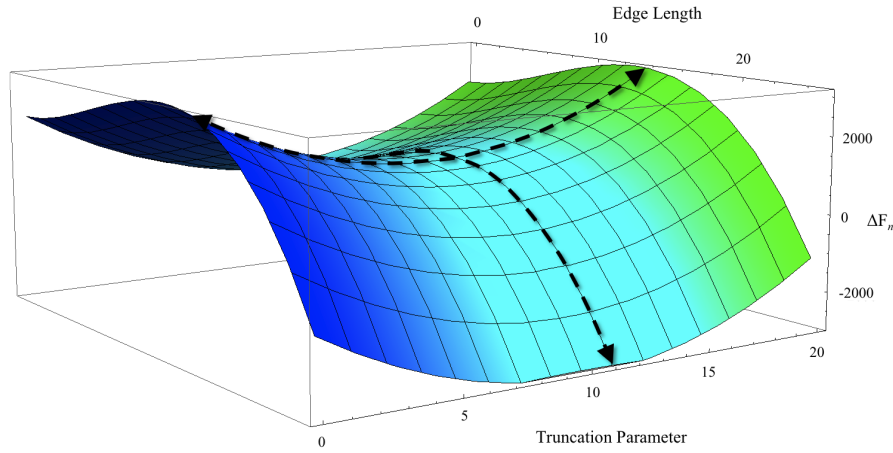


Figure 6.2: Schematic of a saddle point, illustrating their necessity in Free Energy critical point analyses.

The saddle figure shown will not always be the shape of the energy surface, due to constraints on the system; the saddle point may occur at the edges of the plot (i.e., full truncation in either direction). And, in fact, none of the three-dimensional energy surfaces discussed below will look like Figure 6.2, completely, since the truncation parameter needs to be plotted logarithmically in order to show the features accurately in three-dimensions.

6.3 Two-Dimensional Models

Before considering three-dimensional growth, we motivate these ideas by consideration of two-dimensional growth to see the similarities and differences. We can initially assume a shape with $\{10\}$ -type faces, which would form a square, or a shape with $\{11\}$ -type faces, which would form a diamond (see Figure 6.3). These

two shapes are analogous to the cube and octahedron/rhombic dodecahedron in three-dimensional space, respectively. The more complicated cases of mixed faceting will be looked at later.

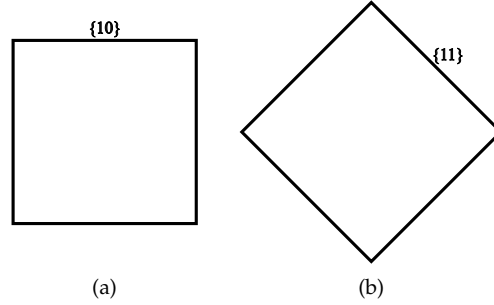


Figure 6.3: The two-dimensional representations of a cube and octahedron/rhombic dodecahedron with (a) $\{10\}$ -type and (b) $\{11\}$ -type faceting.

Considering a square with an edge length, a_1 , and a diamond with an edge length, a_2 , the areas and perimeters of each can be expressed as (the subscript s means square; d means diamond; A_i is the area of i , and P_i is the perimeter of i):

$$A_s = a_1^2$$

$$A_d = a_2^2$$

$$P_s = 4a_1$$

$$P_d = 4a_2$$

An expression for the free energy of formation of a nucleus uses these values. The free energy difference in forming the nucleus from the parent phase, Δg_{area} , is multiplied by the area of the forming nucleus, and the surface (perimeter) energy, γ_{facet} , is multiplied by the perimeter length, with the two terms summed to yield:

$$\Delta G_{form} = -A_{shape} \cdot \Delta g_{area} + P_{facet} \cdot \gamma_{facet} \quad (6.3)$$

We then need to substitute in the appropriate areas and perimeters, and differentiate the equations to find the critical dimension for nucleation. All the equations should also be constrained to equal area since the chosen dimensions are not always comparable (initially, however, this is trivial), and the area free energy of formation for both the square and the diamond are the same since this is a bulk term and not affected by the shape ($\Delta g_{a_1} = \Delta g_{a_2}$); it should be noted, however, that, similar to surface energies, the perimeter

energies are not always the same. The energy equations are then:

$$\Delta G_s = -a_1^2 \Delta g_{a_1} + 4a_1 \gamma_{10}$$

$$\Delta G_d = -a_2^2 \Delta g_{a_2} + 4a_2 \gamma_{11}$$

Differentiating the first with respect to a_1 and setting this equal to zero, we get:

$$\frac{\partial \Delta G_s}{\partial a_1} = -2a_1 \Delta g_{a_1} + 4\gamma_{10} = 0$$

$$a_1^* = 2 \frac{\gamma_{10}}{\Delta g_{a_1}}$$

And similarly with respect to a_2 :

$$\frac{\partial \Delta G_d}{\partial a_2} = -2a_2 \Delta g_{a_2} + 4\gamma_{11} = 0$$

$$a_2^* = 2 \frac{\gamma_{11}}{\Delta g_{a_2}}$$

Substituting back in for a_1^* and a_2^* , we get ΔG_s^* and ΔG_d^* :

$$\begin{aligned} \Delta G_s^* &= - \left(2 \frac{\gamma_{10}}{\Delta g_{a_1}} \right)^2 \Delta g_{a_1} + 4 \left(2 \frac{\gamma_{10}}{\Delta g_{a_1}} \right) \gamma_{10} \\ &= 4 \frac{\gamma_{10}^2}{\Delta g_{a_1}} \\ \Delta G_d^* &= 4 \frac{\gamma_{11}^2}{\Delta g_{a_2}} \end{aligned}$$

Since $\Delta g_{a_1} = \Delta g_{a_2}$ as described above, ΔG_s^* and ΔG_d^* are only dependent upon the energy of the {10} and {11} surfaces. Ignoring kinetic arguments [18], if $\gamma_{10} < \gamma_{11}$, then the critical nuclei will be a square since it's nucleation energy barrier is lower, and if $\gamma_{10} > \gamma_{11}$, then the critical nuclei will be a diamond. Calculating the equilibrium growth shapes in a similar fashion, area is constrained, $a_1^2 = a_2^2$ and $a_1 = a_2$, therefore ΔG_s and ΔG_d are only a function of {10} and {11} surfaces, respectively. So, if the square is the critical nucleus, then the square will also be the equilibrium growth shape, and the same for the diamond.

If we introduce varied faceting amounts, we can see a similar trend. First, the equations become:

$$A_s = (a_1 + 2b_1)^2 - 2b_1^2$$

$$P_s = 4a_1 + 4\sqrt{2}b_1$$

$$A_d = (a_2 + 2b_2)^2 - 2b_2^2$$

$$P_d = 4a_2 + 4\sqrt{2}b_2$$

where b_1 and b_2 are the amount of faceting of the square and diamond, respectively, measured parallel to their regular dimension, a_1 and a_2 (see Figure 6.4). The final energy equations become:

$$\Delta G_s = -\Delta g_A \left[(a_1 + 2b_1)^2 - 2b_1^2 \right] + \gamma_{10} (4a_1) + \gamma_{11} (4\sqrt{2}b_1)$$

$$\Delta G_d = -\Delta g_A \left[(a_2 + 2b_2)^2 - 2b_2^2 \right] + \gamma_{11} (4a_2) + \gamma_{10} (4\sqrt{2}b_2)$$

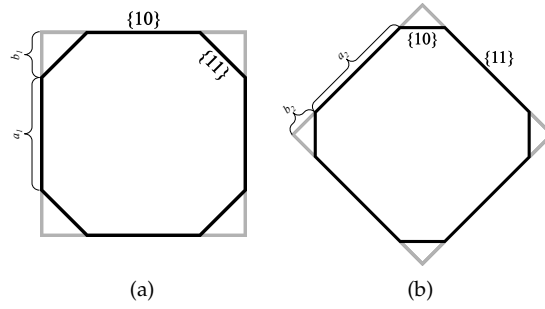


Figure 6.4: The two-dimensional truncated representations of a cube and octahedron/rhombic dodecahedron with (a) $\{10\}$ -type and (b) $\{11\}$ -type faceting.

But, to simplify the equations and make them more easily analyzable, they will be normalized by γ_{11} , and since Δg_A is the same for both equations (as will be $\Delta g_A/\gamma_{11}$), this term can be set constant for the analysis.

$$\Delta G'_s = -\frac{\Delta g_A}{\gamma_{11}} \left[(a_1 + 2b_1)^2 - 2b_1^2 \right] + \frac{\gamma_{10}}{\gamma_{11}} (4a_1) + (4\sqrt{2}b_1) \quad (6.4)$$

$$\Delta G'_d = -\frac{\Delta g_A}{\gamma_{11}} \left[(a_2 + 2b_2)^2 - 2b_2^2 \right] + (4a_2) + \frac{\gamma_{10}}{\gamma_{11}} (4\sqrt{2}b_2) \quad (6.5)$$

For the rest of the analysis, $\Delta g_A/\gamma_{11}$ will be reduced to 1, and γ_{10}/γ_{11} will be replaced by r . By differen-

tiating ΔG_s by a_1 and b_1 , and setting the new equations equal to zero,

$$\begin{aligned}\frac{\partial \Delta G'_s}{\partial a_1} &= -2(a_1 + 2b_1) + 4r = 0 \\ \frac{\partial \Delta G'_s}{\partial b_1} &= -4(a_1 + 2b_1) + 4b_1 + 4\sqrt{2} = 0\end{aligned}$$

we find can find the critical parameters, a_1^* and b_1^* , to be:

$$\begin{aligned}a_1^* &= 2\sqrt{2} - 2r, \quad r \leq \sqrt{2} \\ b_1^* &= 2r - \sqrt{2}, \quad r \geq \sqrt{2}/2\end{aligned}$$

These critical parameters are only applicable when they are non-negative, therefore r has boundary conditions for these solutions, such that $\sqrt{2}/2 \leq r \leq \sqrt{2}$, and if r is above or below this perimeter energy ratio, the solution will yield a pure shape with no truncation. To more easily define the critical nucleus shape at a certain perimeter energy, we can rewrite the critical parameters as a ratio of edge lengths:

$$\frac{a_1^*}{\sqrt{2}b_1^*} = \frac{\sqrt{2} - r}{\sqrt{2}r - 1}, \quad \frac{\sqrt{2}}{2} \leq r \leq \sqrt{2} \quad (6.6)$$

To understand the nature of these critical points, we need to inspect the curvature around them through the use of the second derivative. All of the second derivatives, mixed and pure, are no longer a function of r , and we can create a hessian matrix of their values:

$$H = \begin{bmatrix} \frac{\partial^2 \Delta G'_s}{\partial a_1^2} & \frac{\partial^2 \Delta G'_s}{\partial a_1 \partial b_1} \\ \frac{\partial^2 \Delta G'_s}{\partial b_1 \partial a_1} & \frac{\partial^2 \Delta G'_s}{\partial b_1^2} \end{bmatrix} = \begin{bmatrix} -2 & -4 \\ -4 & -4 \end{bmatrix}$$

By taking the determinant, we find that $\det(H) = -8 < 0$, which means that the critical points are all saddle points. This is exactly what we are looking for here, since we want the minimum of all the energy barrier maxima. While it is hard to think of the saddle point conceptually given these second derivatives, this is because the system is not conceptually defined using cartesian coordinates, but rather using polar coordinates. This however makes the analysis difficult, due to the inclusion of trigonometric functions and their inverses. Therefore, the mathematical analysis, while more conceptually difficult, is much more feasible analytically.

To compare the growth shapes with the critical nuclei, we must set the area constant, here $A = 1$. By setting the area, we can now substitute in values for a_1 in terms of b_1 into the energy equation (Eq. 6.4),

ignoring the areal energy terms (which are constant):

$$a_1 = \sqrt{2b_1^2 + 1} - 2b_1 \quad (6.7)$$

$$\Delta G'_{s,Wulff} = 4r\sqrt{2b_1^2 + 1} - 8rb_1 + 4\sqrt{2}b_1 \quad (6.8)$$

By performing a first and second derivative analysis, we can get a critical growth shape parameter by setting the first derivative equal to zero:

$$b_{1,Wulff}^* = \pm \frac{1}{2} (2r - \sqrt{2}) \sqrt{\frac{-1}{r^2 - 2\sqrt{2}r + 1}} \quad \text{and} \quad \frac{(2r - \sqrt{2})^2}{r^2 - 2\sqrt{2}r + 1} \leq 0 \quad (6.9)$$

The second term constrains our Wulff solution for b_1^* to $\sqrt{2} - 1 \leq r \leq \sqrt{2} + 1$, and since the sign of b_1^* has to be positive, the coefficient for its solution (the first term) is positive for $r > \sqrt{2}/2$ and negative when $r < \sqrt{2}/2$; since below $r = \sqrt{2}/2$, $b_{1,Wulff}^*$ would again be increasing while its perimeter energy is becoming much larger than that for $a_{1,Wulff}^*$, the equation no longer applies when $r < \sqrt{2}/2$, and therefore $b_{1,Wulff}^* = 0$. And, since we have constrained our volume to equal 1, the maximum value of $b_{1,Wulff}^*$ is $\sqrt{2}$ (when $a_{1,Wulff}^* = 0$). By solving for the boundaries of r , our solution for $b_{1,Wulff}^*$ now only applies when $\sqrt{2}/2 \leq r \leq \sqrt{2}$.

To verify that the critical points from the Wulff construction minimize the surface energy of the two-dimensional system, we evaluate the second derivative:

$$\frac{\partial^2 \Delta G'_{s,Wulff}}{\partial b_1^2} = \frac{8r}{(2b_1^2 + 1)^{3/2}} \quad (6.10)$$

This should be greater than zero to verify that the critical points give a minimum in energy, and since r and b_1 are always non-negative, Equation 6.10 is always positive (except for the limit where $r = 0$), therefore our critical points define the shape with the minimum energy when compared at a constant volume.

Given that we have found the critical points for the 2D Wulff construction where we minimize the surface energy at constant volume, we can define the shape by a ratio of edge lengths as a function of r by substituting Equation 6.9 in for b_1 :

$$\frac{a_1^*}{\sqrt{2}b_1^*} = \frac{\sqrt{2(b_1^*)^2 + 1} - 2b_1^*}{\sqrt{2}b_1^*} = \frac{\sqrt{2} - r}{\sqrt{2}r - 1}, \quad \frac{\sqrt{2}}{2} \leq r \leq \sqrt{2} \quad (6.11)$$

As can be seen, Equations 6.6 and 6.11 are the same, and prove that in two dimensions the critical nucleus and growth shape will always be the same, proving self-similar growth to be the equilibrium condition for 2D particles.

6.4 Three-dimensional Models

6.4.1 $\{110\}$ Truncations

Moving into three dimensions, we have to specify the faceting planes more precisely. An in-depth study on the faceting of $\{100\}$ - and $\{111\}$ -type faces has already been published, looking at ferrite nanoparticles [83]. FeCo nanoparticles, however, are not based on an FCC crystal structure but rather on a BCC or BCC-derivative structure. Therefore, the faceting planes will be of $\{100\}$ - and $\{110\}$ -types, since the $\{110\}$ planes have the fewest broken bonds; this has been shown for FeCo polydispersed nanoparticles [16,51]. The two basic polyhedra are the cube and the rhombic dodecahedron, formed by only $\{100\}$ or $\{110\}$ facets on a cube, respectively. The truncated cube and truncated rhombic dodecahedron occupy all shapes in between (see Figure 6.5). Similar to the $\{111\}$ -faceting, there is a polyhedron in the middle of the truncation for which all the edge lengths are equal. This is termed the truncated rhombic dodecahedron (not to be confused with the rest of the truncated shapes leading up to the rhombic dodecahedron). There is no special name for this polyhedron, though, since the faces are all equilateral, but not regular; the angles of the hexagons are not 120° . This polyhedron, while similar to a truncated octahedron, has only two-fold symmetry for the hexagonal $\{110\}$ faces.

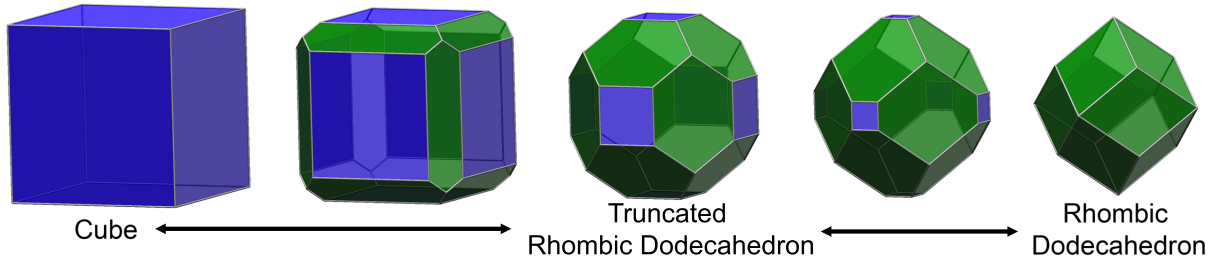


Figure 6.5: Three-dimensional polyhedra progression formed from the $\{110\}$ -truncation of a cube.

To begin to quantitatively describe these polyhedra, we need to define dimensions which can describe the area of the $\{100\}$ and $\{110\}$ faces, and the volume of the polyhedra. Figure 6.6 shows the convention used in this paper. By projecting the shapes in 2-dimensions, we can define x as the edge length of the square, $\{100\}$ faces, and y as the distance from the end of a $\{100\}$ face to the next $\{100\}$ face, projected parallel to the original face ($y\sqrt{2}$ would be the actual distance along the $\{110\}$ face). In Figure 6.6b, we see the relationship between lengths a , b , and x , where a is the major length of the rhombic dodecahedron, and b is the truncation parameter parallel to a ; x is the edge length of the emerging $\{100\}$ faces. Cubic parameters, x and y , can be defined for the the rhombic dodecahedron, and vice versa, as $x = 2b/\sqrt{3}$ and $y = 2a/\sqrt{3}$.

By combining these different edge-length and truncation parameters, we can get the areas of the $\{100\}$

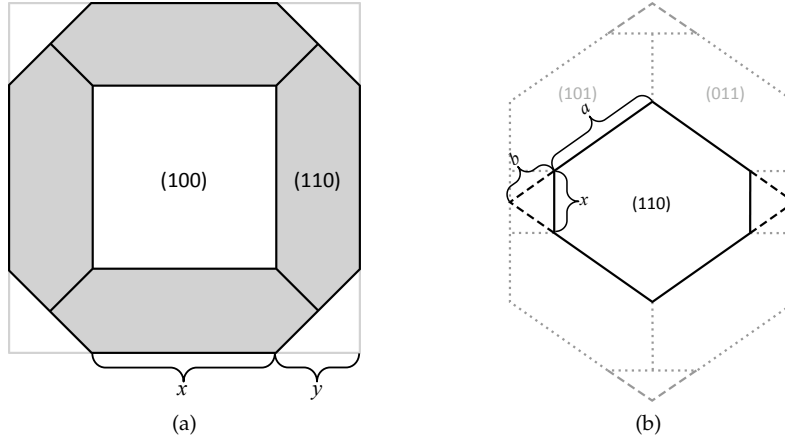


Figure 6.6: Projections of the three-dimensional polyhedra formed from the (a) $\{110\}$ -faceting of a cube and the (b) $\{100\}$ -faceting of a rhombic dodecahedron, indicating the appropriate measurement lengths for the model.

and $\{110\}$ faces and the volumes of the truncated polyhedra, as shown in Table 6.1. As the different polyhedra are truncated, we will have 6 $\{100\}$ faces and 12 $\{110\}$ faces that contribute to the overall surface energy. Because the energy of each face can be different for different materials, the critical nuclei for a certain surface energy ratio can be found by varying the truncation parameters, and the middle equilateral shape can be found when all edge lengths are equal (i.e., $x = a$). This middle shape, however, is not necessarily an equilibrium shape, since that will depend on the ratio of surface energies. Each of these faces has a different surface energy which we will call γ_{100} and γ_{110} . The bulk energy (free energy of formation of a solid), Δf_v , is independent of shape, and is therefore a constant that can be ignored when comparing the different shape energies. The appropriate equation for calculating the critical nuclei is the Helmholtz free energy of nucleation, given below:

$$\Delta F_n = -V\Delta f_v + 6\gamma_{100}A_{100} + 12\gamma_{110}A_{110}, \quad (6.12)$$

where all the terms are defined above, except A_{hkl} , which is the area of an (hkl) face, and V , which is the volume of the polyhedron. By inputting the equations from Table 6.1, we can get an equation that can be differentiated to find the critical dimensions for nucleation of a certain shape. To simplify these calculations, the free energy of nucleation is normalized by γ_{110} , where $\Delta F'_n = \Delta F_n/\gamma_{110}$ and the ratio of surface energies that can be varied will be $r = \gamma_{100}/\gamma_{110}$. As confirmed by Raja et al., the coefficient in front of the volume term, $\Delta f_v/\gamma_{110}$, can be set to 1 for simplicity; Δf_v for all the shapes will be the same since they have the same crystal structure, and we can assume that γ_{110} is a constant with only γ_{100} varying to produce the

different values of r [83]. In contrast to the previous work with cubes and octahedra, the equations shown in Table 6.1 are continuous between the two end shapes, whereas the FCC shapes could only reach the cuboctahedra continuously; in order to reach the octahedra, the same facet grows but with none of the original cubic edges remaining. No truncation parameter or equation changes, however, are needed here to evaluate the nuclei and growth shapes for BCC-type polyhedra.

Table 6.1: Volume and area calculations for the various crystallographic facets starting either at the cube or the rhombic dodecahedron

	Trunc. Cube	Trunc. Rh. Dod.
A_{100}	x^2	$\frac{4}{3}b^2$
A_{110}	$\sqrt{2} \left(xy + \frac{y^2}{2} \right)$	$\frac{2\sqrt{2}}{3} (2ab + a^2)$
V_T	$x^3 + 6x^2y + 6y^2x + 2y^3$	$\frac{8}{3\sqrt{3}} (b^3 + 6b^2a + 6a^2b + 2a^3)$

We first need to determine the critical nuclei for this system. By differentiating the free energy equations with respect to x , y , a , or b for both the cubic and rhombic dodecahedron and setting these new equations equal to zero, we can get the critical points (x_o , y_o , a_o , and b_o) of the curves as a function of r (see Equations 6.13 and 6.14).

$$\frac{\partial \Delta F'_n}{\partial x} = -3x^2 - 12xy - 6y^2 + 12rx + 12\sqrt{2}y = 0 \quad (6.13)$$

$$\frac{\partial \Delta F'_n}{\partial y} = -6x^2 - 12xy - 6y^2 + 12\sqrt{2}(x + y) = 0 \quad (6.14)$$

By solving the system of equations for x and y , the first derivative analysis yields four solutions in terms of r (referred to below as “Cases”). Only the non-negative solutions of x and y are applicable, since our polyhedra have to have positive edge lengths. Only the cubic equations need to be considered, since the rhombic dodecahedron equations are the same equations with substitutions for x and y , and will therefore yield the same results. The first-derivative solutions are summarized below:

1. $x_o = 0, y_o = 0$ - Trivial Case
2. $x_o = 0, y_o = 2\sqrt{2}$ (Rhombic Dodecahedron) - non-negative for all r ranges
3. $x_o = 4(\sqrt{2} - r), y_o = -2(\sqrt{2} - 2r)$ - non-negative for $\frac{1}{\sqrt{2}} \leq r \leq \sqrt{2}$
4. $x_o = 4(\sqrt{2} - r), y_o = -4(\sqrt{2} - r)$ - non-negative for $r = \sqrt{2}$ (Trivial)

To understand the nature of these critical points, we can look to the second derivative using combinations of x_o and y_o or a_o and b_o . The second derivative analysis relies upon the use of the Hessian matrix (Equation 6.15) and the following conditions [22, 80]:

1. If $\det(H) > 0$ and $f_{xx}(x_o, y_o) < 0$, then (x_o, y_o) is a local maximum
2. If $\det(H) > 0$ and $f_{xx}(x_o, y_o) > 0$, then (x_o, y_o) is a local minimum
3. If $\det(H) < 0$, then (x_o, y_o) is a saddle point
4. If $\det(H) = 0$, then the second derivative test is inconclusive

Therefore, a relative maximum in the surface plot occurs when the determinant of the Hessian matrix is positive but $f_{xx}(x_o, y_o)$ or $f_{aa}(a_o, b_o)$ is negative. This traditionally would give us the critical points we need to look at and their valid regions of application.

$$H = \begin{bmatrix} \frac{\partial^2 f}{\partial x^2} & \frac{\partial^2 f}{\partial x \partial y} \\ \frac{\partial^2 f}{\partial y \partial x} & \frac{\partial^2 f}{\partial y^2} \end{bmatrix} \text{ or } \begin{bmatrix} \frac{\partial^2 f}{\partial a^2} & \frac{\partial^2 f}{\partial a \partial b} \\ \frac{\partial^2 f}{\partial b \partial a} & \frac{\partial^2 f}{\partial b^2} \end{bmatrix} \quad (6.15)$$

The second derivative analysis shows that there is no solution that satisfies our requirements for Case 1. Case 2, however, is applicable when $0 \leq r \leq \sqrt{2}$. This solution does not make conceptual sense, though, since it says that the rhombic dodecahedron is the preferred shape even when the (110) surface energy is infinitely larger than the (100) surface energy. This solution only makes sense above the equality point for the cube and rhombic dodecahedron equations, where the rhombic dodecahedron should be favored. This is found to be at $r = 0.89$, by setting the volumes of the two pure shapes equal to each other, and finding at what surface energy ratio the total energies of the pure shapes are equal too. Case 3 is only applicable when $r = \sqrt{2}$, which reduces to Case 2, and Case 4 has no solution, as expected. The analysis for the rhombic dodecahedron equations yields the same results, since the equations are substitutionally the same.

These solutions, however, are not correct, since the cube is never calculated to be a critical nuclei. Therefore, it can be assumed that the analysis for this system is not trivial, and is not analogous to the process described by [83]. If the maxima of the x-y plot are found through first and second derivatives and the appropriate use of the Hessian matrix, then there is only one maximum that is found at $x = 0$ and $y = 2\sqrt{2}$, even when the surface energy ratio, r , is 0 (meaning that the γ_{110} energy is infinitely larger than the γ_{100} surface energy); yet, the cubic critical nucleus should be found at least at this extreme. So, further inspection of the curves is needed to understand the appropriate maxima and minima.

By inspecting the equations further, it is not just a maximum in the energy space of x-y that should be considered, but saddle points are also important. A lack of consideration of the saddle points would cause

us to miss the actual critical nuclei which is the minimum of all the nucleation energy barriers. There will always be a maximum in the nucleation curve for any shape, yielding a critical nuclei. This maximum can obviously be found by setting the first derivative equal to zero for that shape. However, if we change the shape (meaning the x/a edge-length ratio), we will get a change in the critical nucleus size and energy barrier. By extending this to all possibilities in the x-y plane, we essentially get a series of maxima that line up with each other in polar arrays, which will keep the truncation ratio the same. So if we pick a certain angle in the x-y plane, we have chosen a certain shape and can find the critical nuclei size for the truncation. In combining all these possibilities, however, we want to choose the overall minimum energy barrier to be overcome to nucleate a shape at that desired surface energy ratio, r . As we change that surface energy ratio, the minimum will change, but since we are looking for the minimum in the calculated energy maxima, this point needs to be a saddle point. This is made especially evident when the energies of the rhombic dodecahedron and cube are equal, at $r = 0.89$. It was declared in [83], when the energies are equal, that is when the critical nucleus switches from cube to octahedron, or in our case from cube to rhombic dodecahedron. In contrast, this paper posits that this switch does not happen at a single point but rather over a range of points. For BCC polyhedra, this would be continuous from the cube to the rhombic dodecahedron. For the FCC polyhedra, with an intermediate cuboctahedron, there will be two different transitory regions: one region in between the cube and cuboctahedron, and then another transition region between the cuboctahedron and the octahedron. Figure 6.7 shows the BCC case where $r = 0.89$, and therefore the free-energy of the cube and rhombic dodecahedron are equal. But, as is shown, the energy can still decrease, and it is a minimum at an edge length ratio of $x/a = 3.30963$.

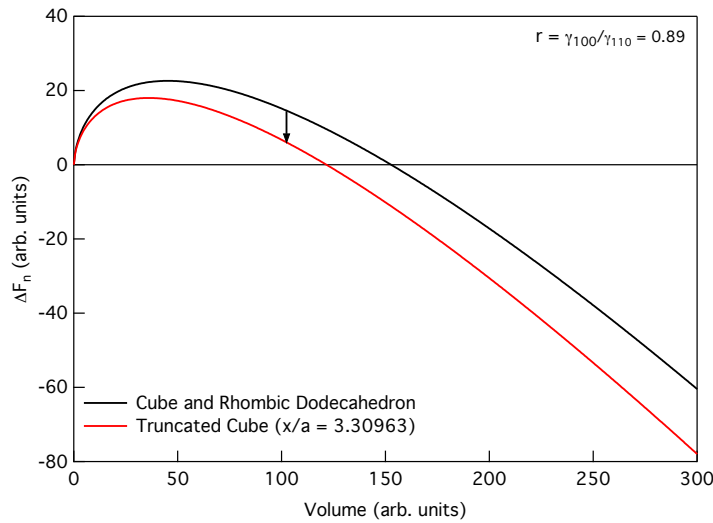


Figure 6.7: Helmholtz Free-Energy of the Nucleation of a Cube, Truncated Cube, and Rhombic Dodecahedron when the surface energy ratio, r , is 0.89.

In choosing the saddle point condition for the Hessian matrix ($\det(H) < 0$), a different set of critical points can be found for the transitions between these regions. For Case 1, the answer is still trivial, although the applicable range is when $0 \leq r < \sqrt{2}$. For Case 2, the Rhombic Dodecahedron is preferred when $r > \sqrt{2}$. For Case 3, solutions can be found when $1/\sqrt{2} \leq r < \sqrt{2}$, which correspond to variable truncations between the cube and rhombic dodecahedron; at the upper limit, the shape is the rhombic dodecahedron, and at the lower limit the shape is a cube. For Case 4, there are no solutions. The cube is again never mentioned in the solutions above, however, this can be correctly understood by looking at the curves and realizing that the cubic energy minimum is not necessarily at a point when the first derivative is zero, since it is an end-point and therefore cannot truly be evaluated with that requirement; a similar problem exists for the rhombic dodecahedron. If $r \leq 1/\sqrt{2}$, then the critical nuclei are cubes; if $r \geq \sqrt{2}$, then the critical nuclei are rhombic dodecahedra. However, if $1/\sqrt{2} \leq r \leq \sqrt{2}$, then it is a truncated shape.

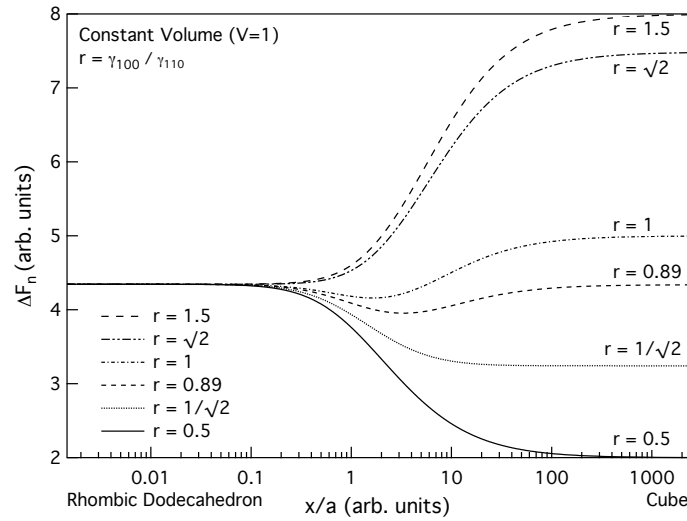


Figure 6.8: A plot of the Free Energy of Nucleation versus truncation parameter for BCC materials (at constant volume).

This is the same condition as seen for the growth shapes. The growth shapes are determined by a minimization of surface energy, which can be calculated by a Wulff construction, where the volume is held constant and only the surface energies are taken into account. While it initially seems necessary to keep the growth shape volume above the critical nuclei size, this is not necessary since the volume only subtracts a constant from all the equations if it is held constant for all polyhedra. By keeping the volume constant, we can see the effect of truncation on the Helmholtz free energy, as depicted in Figure 6.8. The volume is set at 1, and the edge lengths x and a are varied in the appropriate ratios to maintain that volume. These curves are almost identical to those that can be shown for surface to volume ratios as a function of truncation.

Setting the volume free energy to 1, we can see three regimes of growth shapes with changing r values. At low and high r values, there is a smooth transition in energy between the cube and the rhombic dodecahedron truncations, with the minima lying at the pure shapes in accordance with the r values reported above. At middle values of r , however, the minimum lies at some truncated shape. The two transitions when a truncated critical nucleus becomes and ends being stable are $r = 1/\sqrt{2}$ and $r = \sqrt{2}$, again in accordance with above. Figure 6.9 shows pictorially the transition regions for critical nuclei and growth shapes, and the polyhedra that are stable in each region.

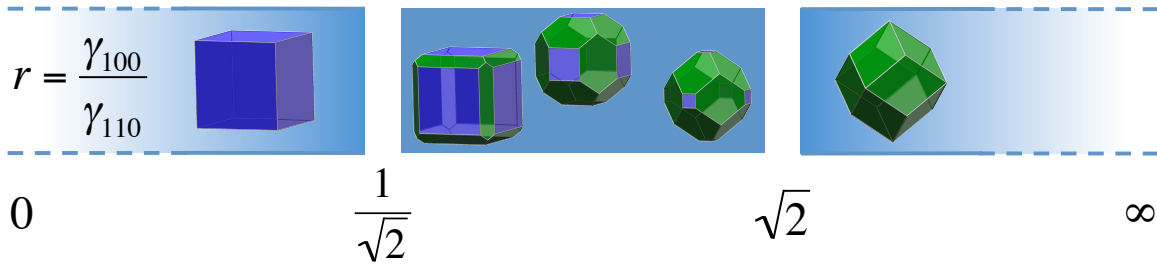


Figure 6.9: The critical points of the surface energy ratio, r , for both the critical nuclei and the growth shapes of BCC materials.

These conclusions agree with the analyses and observations by Wang et al., Saito et al., and Hayashi et al. [27,71,91]. In addition, the particles observed by Jones et al. had similar truncations [39], resembling particles near the rhombic dodecahedron side of the surface energy ratios (or ratio of growth speed for different planes, as described by Wang et al.). While the nanoparticle techniques used by the former papers produced monodispersed powders where sizes can be varied, the techniques used by Jones et al. produced polydispersed powders with a wide particle size distribution. Those particles produced at high temperatures yielded primarily rhombic dodecahedra or truncated rhombic dodecahedra, while those particles produced at room temperature yielded cubes or truncated cubes. This was attributed by Wang et al. to growth kinetics at lower temperatures, which overwhelms the atoms' ability to form the equilibrium shape due to limited atomic motion. At higher temperatures, the atoms have more ability to find their preferred lattice positions and truncation amounts since they are not as constrained to stay in their initial position as determined by the deposition technique. Plasma torch synthesis, therefore, has an interesting possibility to produce many varied shapes and sizes, which depends on where in the argon plasma they nucleate (determining the temperature of nucleation) and the distance remaining for them to grow before reaching temperatures which limit diffusion (determined by the temperature gradient and the nucleation location). Those seen by Jones et al., however, all resemble polyhedra on the side of the rhombic dodecahedra (pure and slightly truncated) or are spherical (as also seen by Wang et al. for the smallest particles).

6.4.2 $\{111\}$ Truncations

The cube and octahedron truncations can be analyzed in the same way, and yield slightly different results from those reported previously. For critical nuclei, it was previously shown that the transition between the Cube and Octahedron occurs at the surface energy ratio of $\gamma_{100}/\gamma_{111} \approx 0.95$. We can see from Figure 6.10 that the free energy maxima for these two polyhedra are equal, and if we plot them against volume, the entire energy curve will be equal. As can be noted, however, the cuboctahedron has a maximum that is lower in energy than both of the assumed critical nuclei; the cuboctahedron, therefore, has a smaller energy barrier that needs to be overcome to nucleate. The cuboctahedron is not actually the lowest energy here, though. The actual preferred shape lies a little further toward the octahedron side. This again prompts a new analysis by utilizing saddle points.

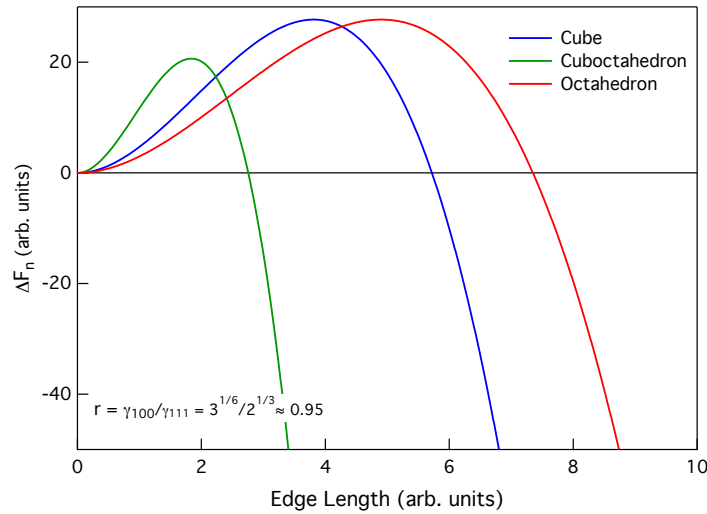


Figure 6.10: Helmholtz Free-Energy of Nucleation of a Cube, Cuboctahedron, and Octahedron when the surface energy ratio, r , is $\gamma_{100}/\gamma_{111} = 3^{1/6}/2^{1/3} \approx 0.95$.

The first derivative analysis for the Cube and Octahedron truncations are the same as reported previously. In these analyses, a pure cube is defined by only x and a pure octahedron is defined by only x_1 . y and y_1 are the truncation parameters for the cube and octahedron, respectively, and are parallel to x and x_1 , extending to the original polyhedra vertices [83]. For the cube the first derivative solutions are:

1. $x = 0, y = 0$ - Trivial Case
2. $x = 4(\sqrt{3} - 3r), y = -2(\sqrt{3} - 3r)$ - non-negative for $r = 1/\sqrt{3}$ (Trivial)
3. $x = 4(\sqrt{3} - 2r), y = -2(\sqrt{3} - 3r)$ - non negative for $1/\sqrt{3} \leq r \leq \sqrt{3}/2$
4. $x = 4r, y = 0$ (Cube) - non-negative for all r ($r \geq 0$)

For the octahedron, they are:

1. $x_1 = 0, y_1 = 0$ - Trivial Case
2. $x_1 = 2\sqrt{6}, y_1 = 0$ (Octahedron) - non-negative for all r
3. $x_1 = -2(\sqrt{6} - 2\sqrt{2}r), y_1 = 2(\sqrt{6} - \sqrt{2}r)$ - non-negative for $\sqrt{3}/2 \leq r \leq \sqrt{3}$
4. $x_1 = -4(\sqrt{6} - \sqrt{2}r), y_1 = 2(\sqrt{6} - \sqrt{2}r)$ - non-negative for $r = \sqrt{3}$ (Trivial)

The second derivative analysis yields different critical nuclei than those reported by Raja et al. due to the criterion of saddle points, rather than maxima. For the cube, we will ignore Case 1, since this does not correspond to any polyhedra. Case 2 also corresponds to no polyhedra. Case 3 is applicable when $1/\sqrt{3} < r \leq \sqrt{3}/2$, and Case 4 is applicable when $0 < r < 1/\sqrt{3}$. So, for the range of Case 4 we will get the cube, and for Case 3, we will have a truncated shape, ending with the cuboctahedron at $\sqrt{3}/2$. The transition between the cube and truncated cubes begins at $1/\sqrt{3}$, which is why neither shape is solely applicable at that r value.

For the Octahedron equations, we will again ignore Case 1. Case 2 corresponds to an Octahedron and is applicable when $r > \sqrt{3}$. Case 3 is applicable when $\sqrt{3}/2 \leq r < \sqrt{3}$, corresponding to truncated octahedra, and ending with the cuboctahedron at $\sqrt{3}/2$. Case 4 is not applicable to polyhedra. So, again we see that the transition between truncated and pure shapes ($r = \sqrt{3}$) could correspond to either shape, since that is the transition point. And, all polyhedra meet at $r = \sqrt{3}/2$, where the cuboctahedron connects the two sets of equations and truncations. This intermediate shape is only stable at one point, but is necessary since the truncation parameters need to change when we get to this Archimedean solid. This is not necessary in the $\{110\}$ case above since there is no intermediate Archimedean solid.

These answers make more conceptual sense than those reported previously, where there was an overlapped region of Cube and Octahedron critical nuclei. Here, however, it is well defined that when r is less than $1/\sqrt{3}$ we will have a pure cube nucleate. When r is between $1/\sqrt{3}$ and $\sqrt{3}$, we will observe continuous truncation shapes between the cube and octahedron, with an intermediate cuboctahedron at $r = \sqrt{3}/2$. Above $r = \sqrt{3}$, the octahedron will be the critical nuclei (see Figure 6.11). It is comforting to note that the cutoffs for this system are determined by $\sqrt{3}$, since these are dealing with truncations with a normal along the cubic body diagonal, and the previous system was determined by $\sqrt{2}$, since that system was concerned with truncation normals along the face diagonals. In both cases, the growth shapes are the same as the critical nuclei, and when the free energy is plotted against volume, rather than truncation parameter, this can be observed. As was noted above, the critical nuclei for $r = 3^{1/6}/2^{1/3}$ is a truncated octahedra, which is

slightly less truncated than the cuboctahedron. This is in agreement with the second derivative analysis, since $3^{1/6}/2^{1/3}$ is larger than $\sqrt{3}/2$, which puts it in the truncated octahedron regime.

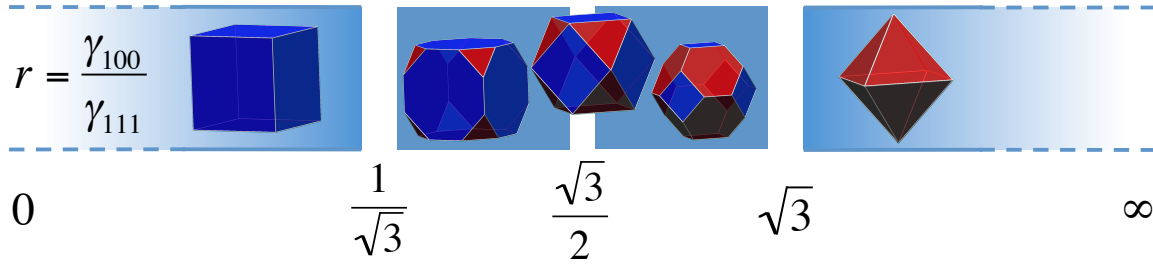


Figure 6.11: The critical points of the surface energy ratio, r , for both the critical nuclei and the growth shapes of FCC materials.

6.5 Summary

It has been shown that critical nuclei and equilibrium growth particles have the same polyhedra, and therefore proceed through self-similar growth, as was previously postulated but not proven. This verification relies upon a graphical analysis comparing the volume of shapes, rather than edge lengths, as is normally done when assuming spherical particles. The critical nucleus analytical analysis utilizes saddle points to find the critical edge length parameters, which combine the search for an energy barrier (local maximum) for a certain particle shape, with the finding of the minimum energy barrier by comparing the nucleation barrier for all possible polyhedra for that crystal structure. This analysis relies primarily upon the surface energy ratio, and not any volumetric considerations.

The critical polyhedra proceed continuously from one pure shape to another pure shape (fully truncated) with changing surface energy ratio, with no intermediate shape taking any precedence through the transition. For BCC polyhedra, this proceeds from a Cube (for $r \leq \sqrt{2}/2$) through all (110)-truncations ($\sqrt{2}/2 \leq r \leq \sqrt{2}$) until the Rhombic Dodecahedron ($r \geq \sqrt{2}$). In the case of FCC polyhedra, the cuboctahedron only holds a transitional place due to the necessity of changing calculation parameters, when the original edge lengths no longer exist. It is, however, just a stopping point for analytical purposes, and nothing more (even though it is an Archimedean solid). The FCC solids proceed from Cube (for $r \leq \sqrt{3}/3$) through all (111)-truncations ($\sqrt{3}/3 \leq r \leq \sqrt{3}$) until the Octahedron ($r \geq \sqrt{3}$).

Chapter 7

CoCrPt Thin Films for AGFM-type Sensors

7.1 Introduction

While analysis of the oxidation properties and nucleation and growth of FeCo alloys is essential to their function in the applications described above, there is also a need to verify the homogeneity of the nanoparticles, whether in the body or in an EMI polymer. Seeing the similar requirements for such a sensor with modern space explorations (especially to Mars), the design of such a sensor has proceeded with the collaboration of the Instituto Nacional de Técnica Aeroespacial (INTA) in Spain. There is current need in space exploration and biomedical applications (in addition to magnetogeological and industrial areas) for a sensor that is portable and rugged. Current interests of INTA lie in analyzing magnetic minerals on Mars, to monitor and further understand its geomagnetic crustal remnant state [49,50]. And, current biomedical interests at the McGowan Institute for Regenerative Medicine have focused on determining the uniformity of the distribution of magnetic nanoparticles placed in tissue scaffolds and those used for magnetic tagging in cancerous tumors. In space exploration, in particular, extra weight and space is very expensive, and the equipment has to be able to withstand drastically varying temperatures and gravitational forces. Traditional magnetometry equipment, however, is bulky and expensive, and therefore not usable. In biomedical applications, the magnetometry equipment (i.e., MRI) needs cryogenic temperatures to image the body and determine the location of nanoparticles. Previous designs for portable magnetometers were consulted with an eye towards updating the material choice for the sensing material, based on modern thin film techniques.

7.2 Thin Film Choice and Fabrication

The current design as proposed by INTA is shown in Figure 7.1. The sensor consists of a silicon membrane ($\sim 15\mu\text{m}$ thick), which is thinned from a silicon substrate. The substrate is constrained from movement, leaving the membrane free to vibrate, and is surrounded by four coils of wires [50]. These coils have an alternating current sent through them, such that if a magnetic material is attached to the center of the membrane (see Figure 7.6a), it will begin to oscillate along the direction of the gradient of the alternating magnetic field. The gradient is produced by having opposite currents through the two vertically adjacent coils. The frequency of oscillation is optimized to be in agreement with the resonance frequency of the system, to maximize the signal to noise ratio. As a magnetic sample passes by the sensor, an additional force will be exerted on the magnetic oscillator and will bring it out of resonance. The shift in the resonance frequency is proportional to the magnetic moment of the sample, based upon its distance from the magnetometer. The oscillation (and change in oscillation) of the magnetic oscillator is monitored by a bundle of optical fibers.

A high moment material is necessary to produce a large enough response, and currently a $1\mu\text{m}$ -thick SmCo disk (Saturation Magnetization, $M_s \approx 800\text{ emu/cc}$; Remnant Magnetization, $M_r \approx 640\text{ emu/cc}$) has been used [49,50,63]. Due to the high cost and reactivity of rare earth elements, FePt was chosen due to the high magnetocrystalline anisotropy of its $L1_0$ structure. It is essential, when choosing a material, that the material have a preferred magnetization direction out of the plane of the film. This will allow the film to oscillate in vibrational mode 1, which is desired; the oscillation will only take place in one direction, which is not only simpler to calculate and model, but will reduce the losses in the system due to a minimization in the torque on the magnetic material. Due to the difficulty in fabricating FePt thin films with the appropriate texture and magnetic properties, CoPt was chosen.

CoPt provides a high magnetization with a close-packed hexagonal structure, and can easily provide the desired (00.1) texture through appropriate underlayers. It is essential for the film to have a preferred out-of-plane easy axis, however this was not initially possible due to the large demagnetization field, due to the high magnetization. It was assumed that by alloying the CoPt with Cr, the magnetization would decrease, enabling the high uniaxial out-of-plane magnetocrystalline anisotropy, along with other contributing magnetic energies, to overcome the demagnetization energy due to the thin film geometry. Besides the large magnetization and high perpendicular anisotropy still provided by the alloy, CoCrPt films also provide corrosion resistance [46,48,58].

CoCrPt thin films of various thicknesses (nominal composition $\text{Co}_{66}\text{Cr}_{15}\text{Pt}_{19}$) were sputtered using an RF sputtering system onto a naturally oxidized Si substrate at 5 to 8nm/min. The thickest film was 500 nm, to be comparable to the SmCo disk. To achieve the desired (00.1) texture, an underlayer stack of Ta (3

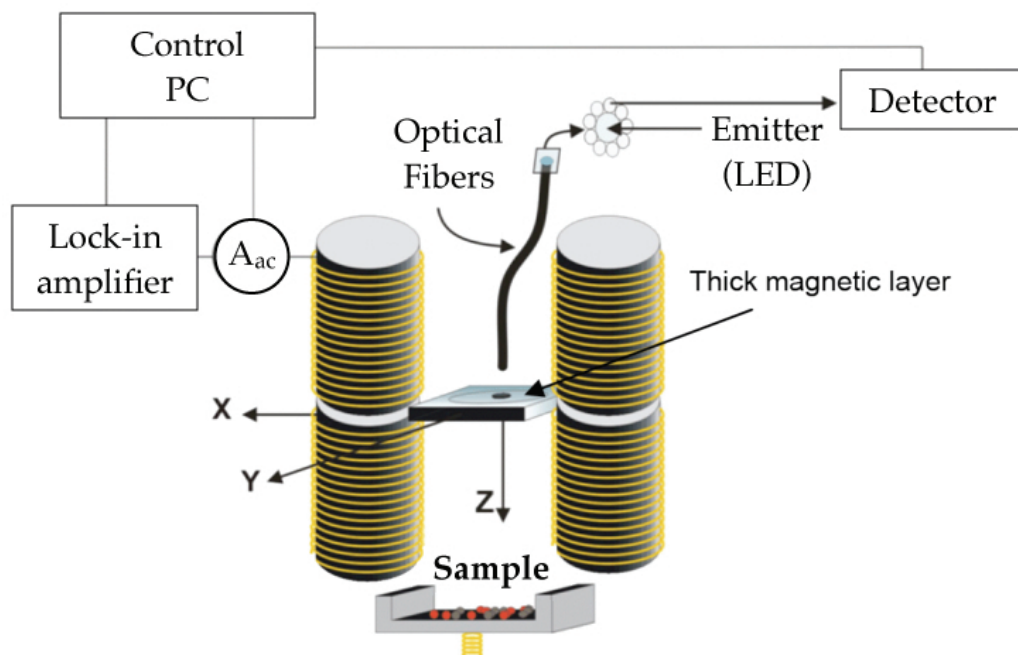


Figure 7.1: AGFM Sensor testing set-up (Image courtesy of INTA).

nm)/Ni₉₀W₁₀ (10 nm)/Ru (20 nm) was first sputtered onto the sample (see Figure 7.2). Ta was used as an amorphous adhesion layer, with the NiW and Ru layers naturally growing as FCC (111) and HCP (00.1), respectively, inducing a strong (00.1) texture in the CoCrPt layer.

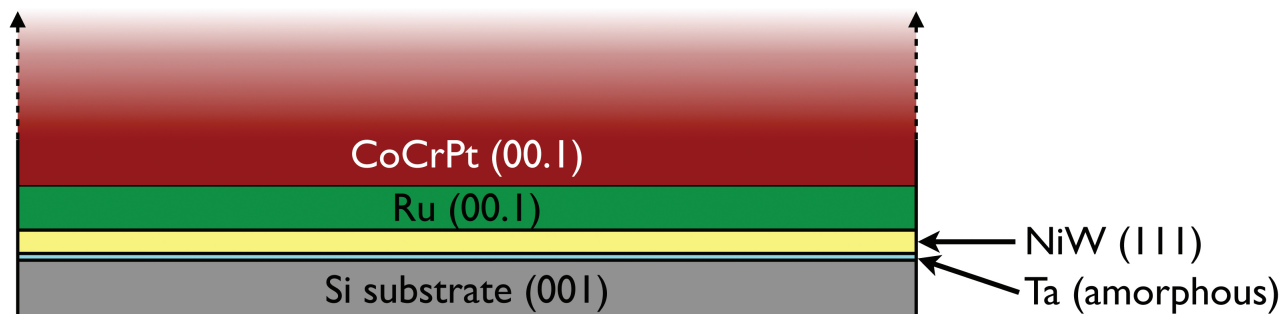


Figure 7.2: CoCrPt multilayer stack.

7.3 X-Ray Diffraction

XRD was used to determine the texture and crystallography of the CoCrPt layer. An out-of-plane 2θ XRD scan (Figure 7.3a) shows good (00.1) orientation, with prominent (002) and (004) peaks. The Si peak intensity was minimized by setting a scan offset of 0.1° . A small Ru peak can also be seen, verifying the

orientation of that layer.

While the out-of-plane scan provides us with important information about the texture of the film, we still have to verify the hexagonal nature of the CoCrPt layer. In-plane XRD scans were performed by tilting the sample until the X-ray beam diffracts off of the planes perpendicular to the surface ($\psi = 88^\circ$; Figure 7.3b). Since the $\{200\}$ planes of the in- and out-of-plane scans do not agree, then we can verify that our crystal structure is not cubic but hexagonal.

By combining the two scans, we can calculate lattice parameters of $a = 2.575 \text{ \AA}$ and $c = 4.186 \text{ \AA}$, which are both larger than the literature values for pure Co [32]. This is due to the dissolution of Pt into the structure, which will expand the lattice; Cr and Co will essentially sit on the same sites and are fairly close in size to each other. By comparing the CoCrPt layer with the Ru underlayer ($a_{Ru} = 2.7058 \text{ \AA}$), we can see that at least the first few layers of the CoCrPt film should be in tension, due to epitaxial stresses at the interface [84]. The layers in tension could not be verified through XRD, using both in-plane and out-of-plane scans, similar to Shimatsu et al. [74]. In fact, the (002) and (004) peaks seem to shift to higher angles with increasing thickness, indicating a compression of the c-axis with increasing thickness, rather than the inverse (which would be predicted using a normal, positive poisson's ratio and an in-plane tensile stress). The c-axis compression using the (002) peak, however, is only $\sim 0.015 \text{ \AA}$. The in-plane scans don't reveal any shifting of peaks. Therefore the c/a ratio decreases from 1.63 at 10 nm to 1.626 at 500 nm, which is the opposite of that found later by Shimatsu et al. for $\text{Co}_{80}\text{Pt}_{20}$ films [75]. As seen through TEM, the grains are not all affected by the underlying Ru, and the observed trend may be due to the averaging nature of XRD scans. The possible interfacial tension will be discussed more below in Section 7.4.2. Due to the mismatch with the underlayer, however, there may be more magnetic energy terms to consider than just the magnetocrystalline and shape anisotropies to determine the easy axis of the film, especially at lower thicknesses.

While our film has the desired orientation and crystal structure, the quality of that texture will directly impact the observed magnetic properties and the desired out-of-plane texture. The quality of the texture will be determined by varying the Ω angle, rather than 2θ , which is known as a rocking curve. The rocking curve keeps the 2θ angle constant, at the appropriate Bragg condition for the desired peak, while changing the angle of the sample. The change in intensity with Ω is analogous to the amount of grains in the film that are misaligned at that angle from the plane normal. By sitting at different 2θ conditions, we can determine the quality of the texture of the different layers in the stack.

Rocking curves were first performed on the (002) peak of the CoCrPt layer in the different films (Figure 7.4 shows the 20 nm and 500 nm films). All films showed a good alignment of crystallites, with a full width at half maximum (FWHM or $\Delta\theta_{50}$) of $\sim 3^\circ$ or less in most cases (the 10 nm film was $\sim 4.6^\circ$); this

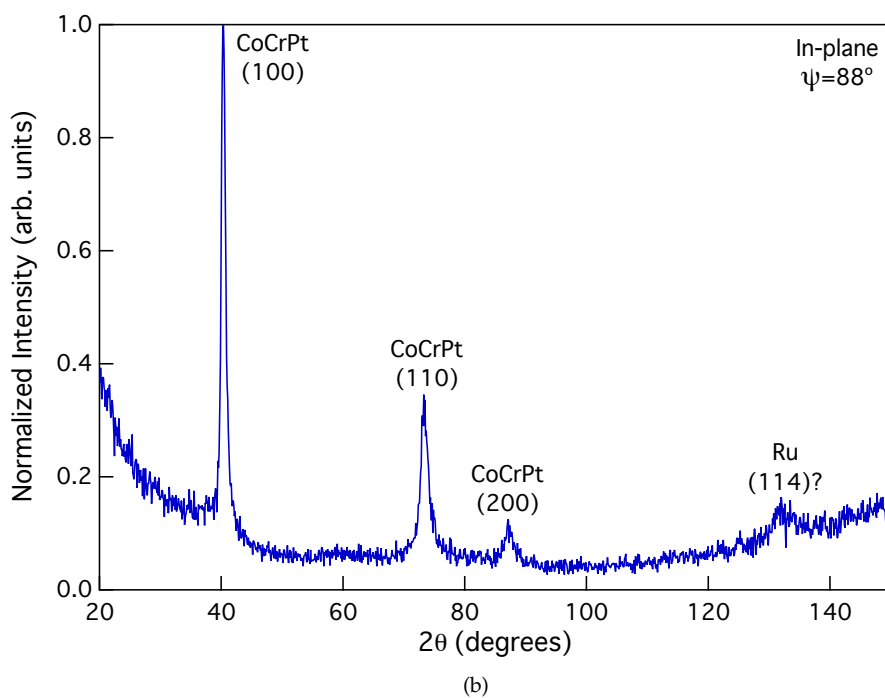
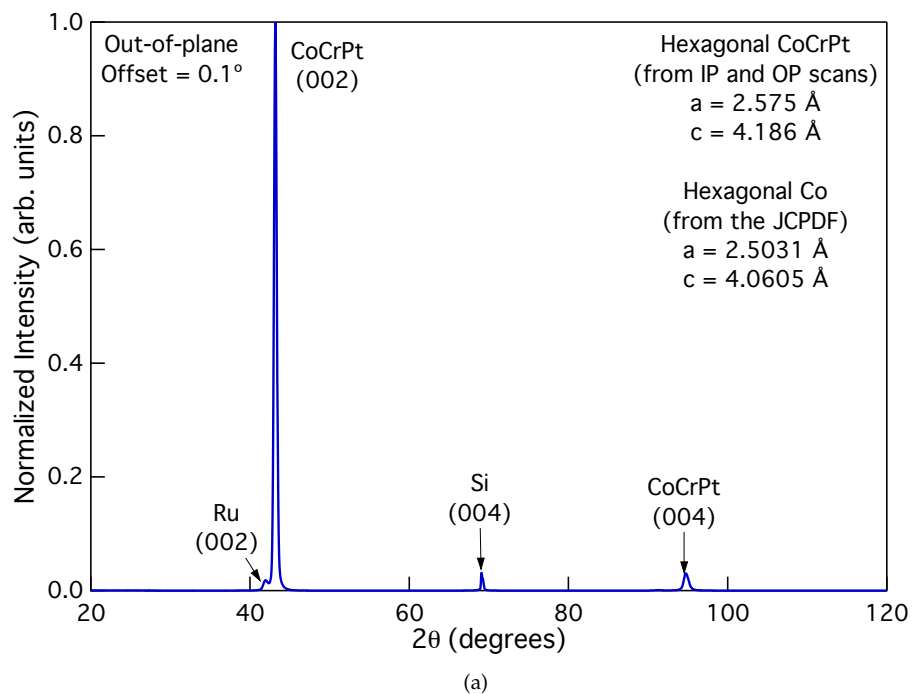


Figure 7.3: θ - 2θ XRD scans of a 500 nm CoCrPt thin film with the $\text{Cu K}\alpha$ radiation (a) out-of-plane ($\psi = 0^\circ$) and (b) in-plane ($\psi = 88^\circ$).

is better alignment than normally desired by the data storage industry. Interestingly, though, the thickest film had a $\Delta\theta_{50}$ of 2.490° , while the thinner 20 nm film was 3° . Since the thinner film is in general closer to the substrate and underlayer, it was assumed that it had less “opportunity” to become misaligned from the desired texture, yet here the thicker film became more aligned as the film grew. To understand the mechanism behind this increase in orientation, a rocking curve was performed on the Ru underlayer of all of the films to see if it was the underlayer that provided the better texture. The Ru underlayer, however, was worse than all of the CoCrPt layers measured, with a $\Delta\theta_{50}$ of 3.3° . It was only as the thickness of the film decreased to 10 nm that the alignment of the CoCrPt layer became the same as the Ru layer (at 10 nm, $\Delta\theta_{50, \text{CoCrPt}} \approx \Delta\theta_{50, \text{Ru}} \approx 4.6$). While the alignment should normally decrease with increasing thickness, here the preferred growth orientation is the (00.1) plane, which minimizes the surface energy of the system, therefore the texture improves with thickness [58].

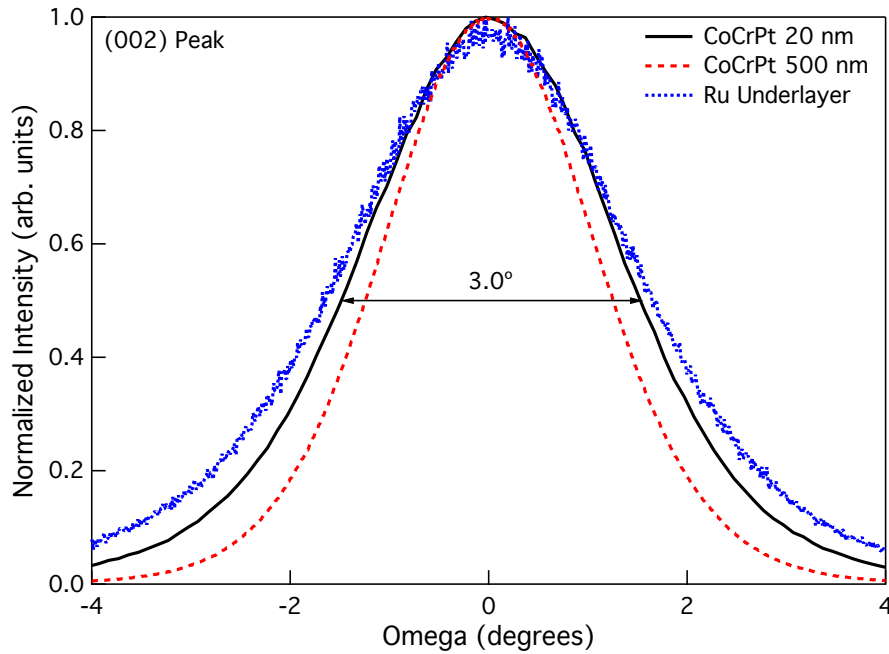


Figure 7.4: Omega Scans (“Rocking Curves”) on the (002) peak of the 20 nm and 500 nm thick CoCrPt films, and the Ru underlayer for the 500 nm–thick film.

7.4 Magnetic Properties

7.4.1 Introduction

While the film texture looks good, the magnetic properties are what are important, and these properties rely upon many factors besides just crystalline texture. Figure 7.5 shows three magnetization versus field

hysteresis loops that preempted the rest of the study. Figure 7.5a was initially sputtered to see if the alloy, through the addition of Cr, was capable of providing a film with a preferred out-of-plane anisotropy, which would agree with the film's texture. As can be seen in the figure, the out-of-plane loop is quite square and easy to saturate at low fields, while the in-plane loop is difficult to saturate and not square, but does have a small jump in magnetization at low fields. Given these results, the addition of Cr was enough to reduce the magnetization and overall demagnetization field, allowing the films to possess the desired out-of-plane anisotropy. While this seemed promising, films that thin (20 nm) are not usable in the AGFM sensor; there would not be enough moment to get the membrane oscillating. So a sensor was sputtered to a 500 nm thickness. Interestingly, even though the film got thicker, the out-of-plane direction became more difficult to saturate. This does not make sense with the simplistic assumption that the only energy terms are magnetocrystalline and shape anisotropy energy, in addition to Zeeman energy. After all, the texture improved with the thicker films and the sample thickness to sample length ratio decreased, all of which point towards the $[00.1]$ direction becoming even softer (better crystal alignment and less shape anisotropy); yet, its slope changed indicating it became harder to saturate, since we now need a stronger applied field to get the same response. We therefore need to look into possible film stresses present due to the epitaxial interface between the Ru and Co-alloy layers. This will be discussed below. For the moment, the discussion will be focused on the hysteresis loops themselves.

All the in-plane hysteresis loops in Figure 7.5 have a jump near zero-field. This is attributed to the variation in the crystallite orientation, as described in the rocking curves of Section 7.2. None of the films are perfectly aligned and therefore will have moments that lie off axis from the rest. These off-axis crystals will be easier to saturate since they are not perfectly aligned perpendicular to the in-plane direction, and the moments will not have to jump as far to align themselves with the applied field (and their final alignment will not be completely hard with respect to the crystal structure). This means that the better aligned films should have a smaller jump, which is what we see; the 20 nm film has a jump around twice as large as the continuous 500 nm film, with the alignment of the 500 nm being better than the 20 nm film. The thicker films all have an interesting out-of-plane loop shape as they approach saturation; the loop opens up near the top. This is mostly due to the domain structure of the films, and these hysteresis loops bear a strong resemblance to those seen by Hehn et al. for Co thin films, with in-plane magnetization [28]. Since the films in the current study are out-of-plane, the domain structure and evolution may be slightly different due to the preference for both in-plane (due to shape) and out-of-plane (Magnetocrystalline and Magnetoelastic) anisotropy. It is possible that the domain wall here will be a combination of both Néel and Bloch walls, creating a helical domain wall that minimizes the energy to switch directions [77], although other shapes are more probable/preferable [33, 53]; this will be discussed in Section 7.4.2. The shape is also an effect

of the continuity of the thin film, and the exchange coupling between adjacent moments/domains. The in-plane loops show a large anisotropy field, ~ 1.2 T, for the 500 nm films. Using this anisotropy field, we can calculate some basic anisotropy values for the films at room temperature, ignoring the curvature of the in-plane hard axis (and thus any second order anisotropy values). This will be discussed in Section 7.4.3.

Since these films are to be used in a very sensitive magnetometer system, we want to ensure that the response from the entire thin film is even. Since there is a build up of magnetic flux lines at the edge of the sample ("edge effects"), this can produce varying responses depending upon the location of the sample (especially comparing a corner with an edge center or the areal center of the film). Therefore, it was proposed by Lucas et. al to change the continuous nature of the thin film to a checkerboard pattern [49]. The etched checkerboard (Figure 7.6b–c) has small squares, each with their own edge effects. While there are many edges now, the overall response is more spatially even since the squares are small. The 500 nm sample was etched to create $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ squares on the film in a checkerboard pattern. It was assumed that these squares would also allow for an improved out-of-plane anisotropy, since the film aspect ratio has been significantly decreased (from an edge:thickness ratio of 6,000 to 40; the 20 nm film had a ratio of 150,000). Figure 7.5c shows the hysteresis loop of the new film. The loop resembles that of the continuous 500 nm film, although the easy axis loop has opened up even further, and the slopes of both etched loops have increased. The decrease in shearing is due to the decrease in the demagnetization field due to the film geometry. While the shearing is less, it does not yet resemble the 20 nm film. This further points towards the effects of other anisotropy energy terms contributing to the out-of-plane magnetic properties in the thin film. While we have decreased the effects from shape even further, we still do not have a completely easy axis, and need other energy terms to help battle against the remaining shape anisotropy. There is still a small in-plane jump at lower fields, which is again due to the crystal orientation distribution, although it is larger than in the continuous film; this is most likely due to the etching away of half of the film, reducing the amount of grains over which the magnetization is averaged, and causing the off-orientation grains to have more of an effect [38].

In hopes of increasing the remnant magnetization of the films, in accordance with Hirayama et al., a 500 nm film was annealed for 1 hour at $450\text{ }^{\circ}\text{C}$ [29]. This should have squared up the hysteresis loop, providing better out-of-plane anisotropy by helping the film to order, and increasing the K_u value. The annealing treatment, however, only minimally altered the hysteresis loops, slightly increasing the slope of the in-plane loop.

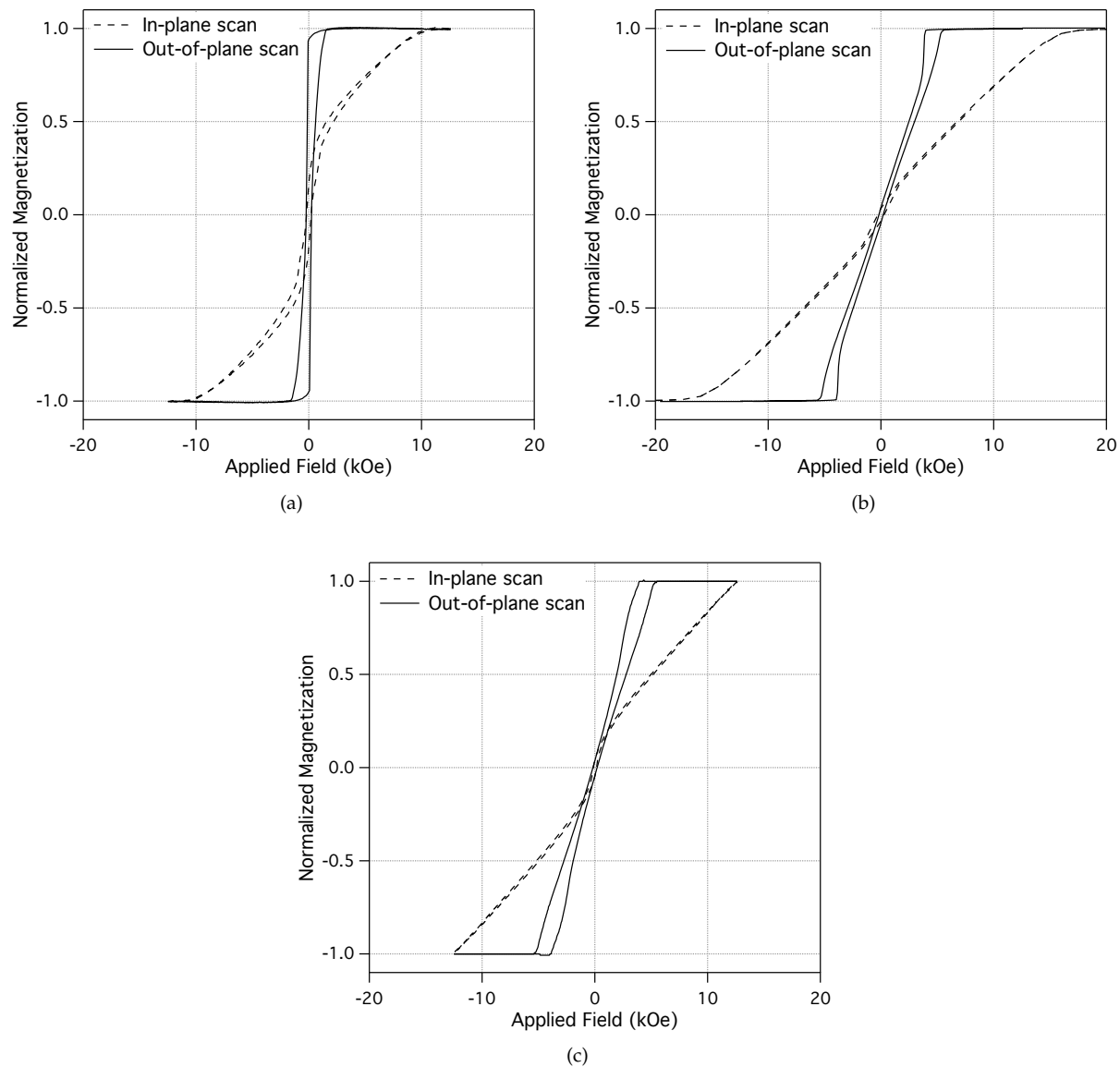


Figure 7.5: Magnetic hysteresis loops with an applied magnetic field oriented parallel and perpendicular to the plane of 15%-Cr CoPt films measured for (a) a continuous 20 nm sputtered film, (b) a continuous 500 nm sputtered film, and (c) a checkerboard patterned 500 nm sputtered film.

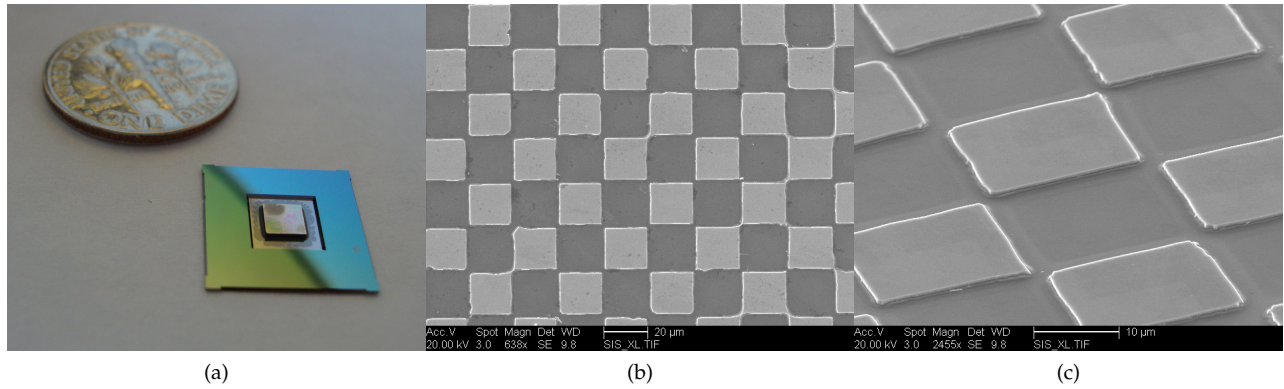


Figure 7.6: (a) Image of a diced, patterned film glued to a Si membrane, and (b–c) SEM images of a checkerboard patterned CoCrPt thin film.

7.4.2 Thickness-dependent Properties

Since there was such a change in properties when comparing the 20 nm and 500 nm films, thickness must have some effect on the overall properties of the film. Films of 10, 20, 30, 40, 50, 100, 300 and 500 nm were sputtered to observe the change with increasing thickness. Out-of-plane hysteresis loops from the AGFM are shown below in Figure 7.7; in-plane loops are shown in Figures 7.13 and 7.14. All out-of-plane loops indicate an easy axis when compared with the in-plane loops. The out-of-plane loops are “square” shaped, although they become more sheared with a decreasing remnant magnetization as thickness increases.

As can be seen from Figure 7.7, there are two things to note in the out-of-plane loops of both the thinnest films and thickest films. The thinnest films (Figure 7.7a) all have the same loop shape, and are quite square. The remnant magnetization, however, drops consistently with thickness. The slope also decreases with thickness, as the loops become more sheared. In the thickest films (Figure 7.7c), there are also two things to note. Here, the hysteresis loops also share basically the same traits, however, the loop shape is different from the thinnest films. The loops are very thin at low fields, but open up at higher fields, as described above. This is attributed to a new domain structure in the films. The slope of these films continues to decrease with increasing thickness, similar to the thinnest films, however the remnance is constant, and does not change with field. Figure 7.7b shows the transition thickness between thinner and thicker films (between 40 and 50 nm), indicating that something is happening around 50 nm.

To highlight these properties even further and inspect the transition thickness, the changes in remnant magnetization along with the out-of-plane anisotropy field have been plotted (Figure 7.8). The out-of-plane anisotropy field has been determined as the extension of the low-field slope to saturation, and is a measure of how much field is necessary to overcome the anisotropy opposing the out-of-plane direction;

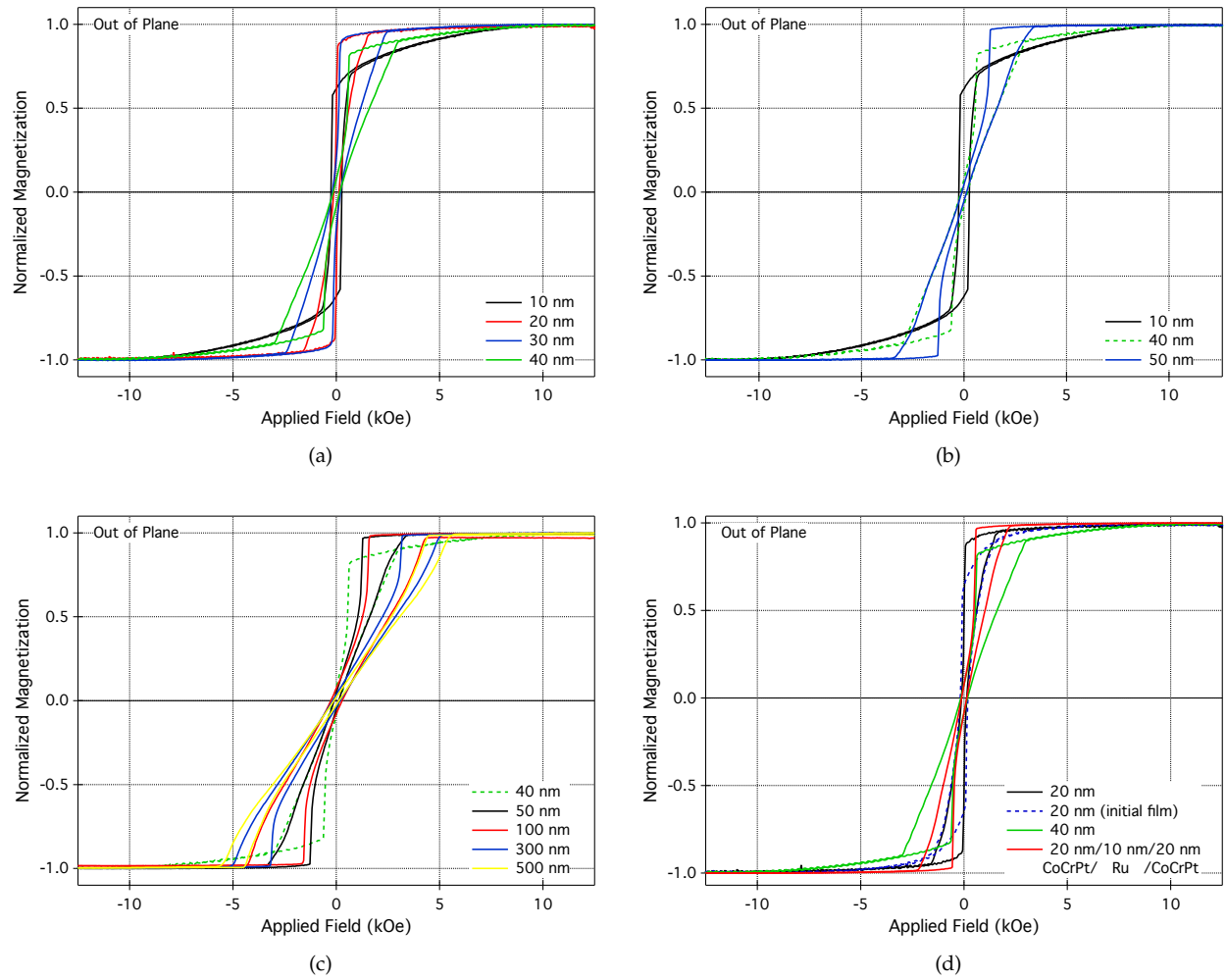


Figure 7.7: Out-of-plane Magnetization versus applied field loops for (a) films of lower thickness, (b) films around the transition region for this system, (c) films of larger thickness, and (d) a comparison between different 20 nm films (including a stacked film).

this calculation, while not technically correct [37], will give us numbers for comparison between the films, which cooperate with our measurement system's limitations and are simpler than a full analysis (although the full analysis has been done for certain films that went to saturation in the in-plane geometry). There are two different trends in the figure: there is a steep drop in the remnant magnetization, approaching 50 nm; oppositely, the anisotropy field increases continuously, plateauing above 500 nm. These two parameters will be discussed individually below.

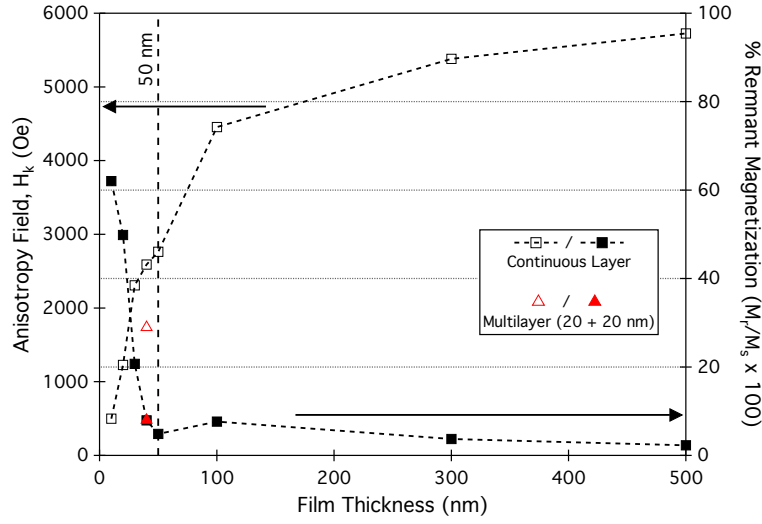


Figure 7.8: A plot of out-of-plane Anisotropy field, H_k , and % Remnant Magnetization (M_r/M_s) as a function of film thickness, for continuous films of $\text{Co}_{66}\text{Cr}_{15}\text{Pt}_{19}$ with Ru/NiW/Ta on a Si (001) substrate; the multilayer film is 20 nm of CoCrPt with an intermediate layer of 10 nm of Ru followed by another 20 nm of CoCrPt.

Remnant Magnetization - M_r/M_s

The remnant magnetization is of great importance, since that is the value of magnetization remaining when the applied field is removed. The larger the value of M_r , the greater the initial response of our film to a field gradient. Therefore, we want a large remnance in our films, and it is important to understand how and why that value changes with thickness. The remnant magnetization shows a precipitous drop approaching 50 nm. After 50 nm, the remnant magnetization stays fairly constant. This reduction is due to the films breaking up into domains while approaching 50 nm. It is essential to understand the domain structure here, and why there is some critical thickness below which our film becomes single domain; traditionally, there would be a transition, but that transition would be between two different domain structures.

Domains are sections of a magnetic material with a homogeneous spin direction (similar to the microstructural concept of grains). In between each domain, there is a wall through which the magnetization

rotates to the direction of the next domain. After being magnetized, when approaching zero applied field, a material often breaks into sections of homogeneous magnetization to minimize the overall magnetostatic energy inside the material. Below a certain critical thickness, however, domains are no longer energetically favorable, and the film will approach a single domain state. In such a state the remnant magnetization will remain high, since the film cannot break into sections of opposite (or varied) magnetization. The remnant magnetization, therefore, is a measure of the extent to which the magnetization in the film volume has broken into domains. The observed drop around 50 nm could be attributed to films that are past a critical thickness for breaking into magnetic domains, reducing the moment to near zero with no applied field.

Since most textbooks consider out-of-plane anisotropy to be a special case, few observations and calculations have been made for domains in films of out-of-plane anisotropy [17]. In traditional thin films, where shape dominates, there are two domain wall geometries: Bloch walls and Néel walls. Bloch walls (Figure 7.9a) have domains with magnetization in the plane of the film, and they transition from one direction to the other by rotating through the plane normal. As the film thickness decreases, the tendency of the domain wall to have an out-of-plane component gets minimized, yielding a Néel wall (Figure 7.9b), with domain magnetization in-plane, and the domain wall rotation also in plane (rotation about the normal, rather than through).

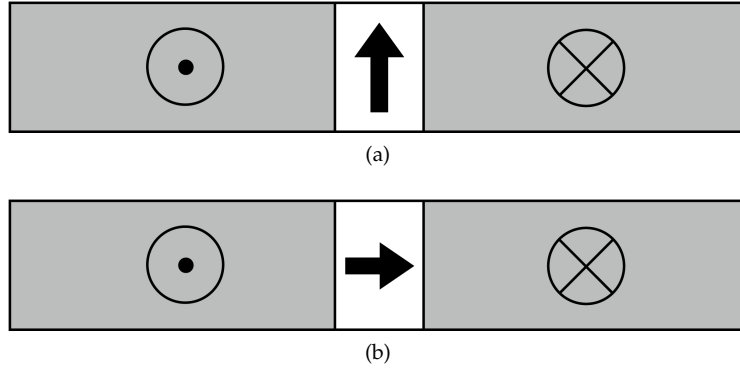


Figure 7.9: Traditional magnetization geometry for thin films with in-plane anisotropy, showing (a) Bloch and (b) Néel walls.

Since our films, however, have an out-of-plane preference, neither of these geometries will work. As proposed by Huber and Smith [33], there's the possibility of a canted magnetization domain structure (Figure 7.10a), however it seems more probable (especially given brief MFM work), to consider the domain walls to be of a modified-Bloch wall geometry (as proposed by Málek and Kamberský) [53]. There are two possible geometries of the modified-Bloch wall. The first (Figure 7.10b) has the magnetization rotating in the plane of the wall. The second (Figure 7.10c). has the magnetization rotating through the normal to the domain

wall. Due to the shape of the domain wall (using similar arguments to Néel for the traditional films), the domain wall magnetization should remain in the plane of the domain wall. There is also the possibility of a mixture of Figures 7.10b and 7.10c, however the structure should again favor a magnetization rotation in the plane of the wall.

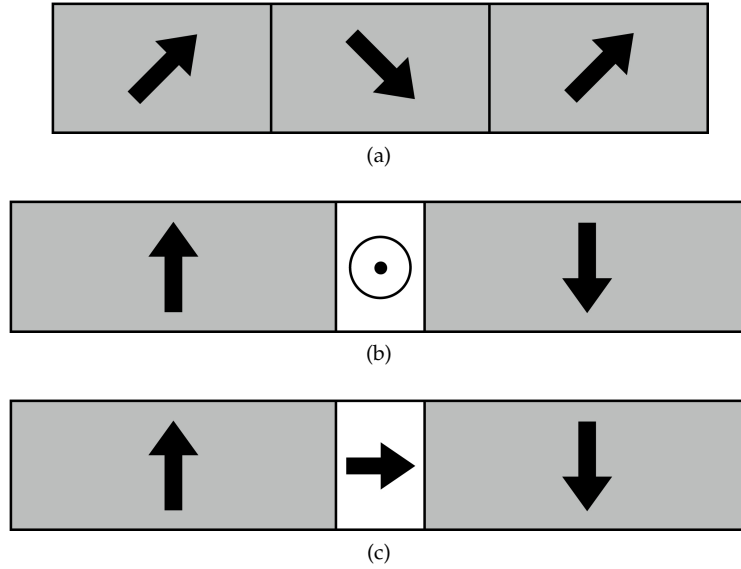


Figure 7.10: Three possible domain wall geometries for thin films with preferred out-of-plane anisotropy: (a) a canted domain structure, and (b-c) two modified Bloch walls.

Having a new film geometry necessitates calculations that are different from what is normally shown. These calculations have been done for MnBi thin films with out-of-plane geometry [53], and can be adapted for our CoCrPt thin films. Figure 7.11 shows adjusted calculations using materials parameters for CoCrPt: Exchange Stiffness, A_{ex} , is 1.85×10^{-6} erg/cm (calculated from [94]), $K_u = 4.83 \times 10^6$ erg/cm³ (from below, removing shape effects), $M_s = 425$ emu/cm³ (from below). We can also calculate the domain wall energy, γ , to be 11.96 erg/cm² from:

$$\gamma = 4\sqrt{A \cdot K_u} \quad (7.1)$$

As film thickness decreases, the domain size initially decreases as well, until a critical thickness (here, just below 200 nm) where the domain size begins to increase again. By 50 nm, the domain size is 0.5 μ m, and it skyrockets shortly thereafter. By 20 nm, the film is essentially single domain. This agrees with the trend seen above in Figure 7.8, showing a critical domain size below 50 nm.

Magnetic Force Microscopy was used to image the domain structure of the CoCrPt thin films in their as-received state, to compare with the theory. The domain structure of both the 20 nm and 500 nm thin films looks the same, exhibiting a maze-type domain morphology (see Figure 7.12). The dark and light regions

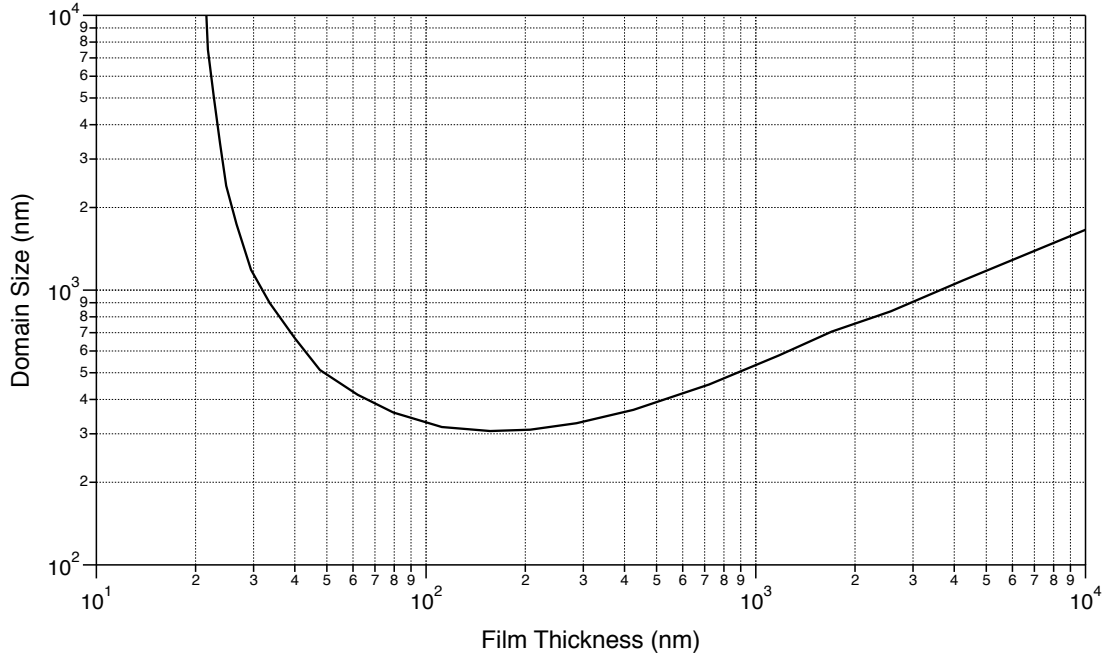


Figure 7.11: Domain Size vs. Film thickness graph (adapted and calculated from [53]).

correspond to sections of opposite magnetization (parallel or antiparallel to the film normal). The domains of the 500 nm thin film are about $0.2 \mu\text{m}$ thick, while the 20 nm film has domains around $0.25 \mu\text{m}$. Using this data, it seems like the theoretical domain size curve should be shifted down and to the left, although it should be noted that magnetizing the samples, and allowing them to return to their remnant state should allow for larger domains.

Anisotropy Field - H_k

The anisotropy field, H_k , shows a different trend compared to the normalized remnant magnetization (M_r/M_s) as a function of film thickness. The anisotropy field increases with increasing thickness, and flattens out near 500 nm. This is opposite to the remnant magnetization, which drops rapidly, and has nearly no change above 50 nm. The change in out-of-plane anisotropy field can be found analogous to both the breaking up of the film into domains and the weighting of different energy terms as a function of thickness.

It is normal to only consider magnetocrystalline anisotropy and shape anisotropy, when thinking of magnetic energy. In these CoCrPt thin films, the magnetocrystalline anisotropy will dominate over the shape. However, as thickness increases, the contribution from shape will decrease (albeit, only slightly, since N_c for the out-of-plane demagnetization factor changes from $4\pi \approx 12.566$ to 12.565), yet there is a large change in the slopes of the M-H loops, indicating that some energy is working against the out-of-plane anisotropy

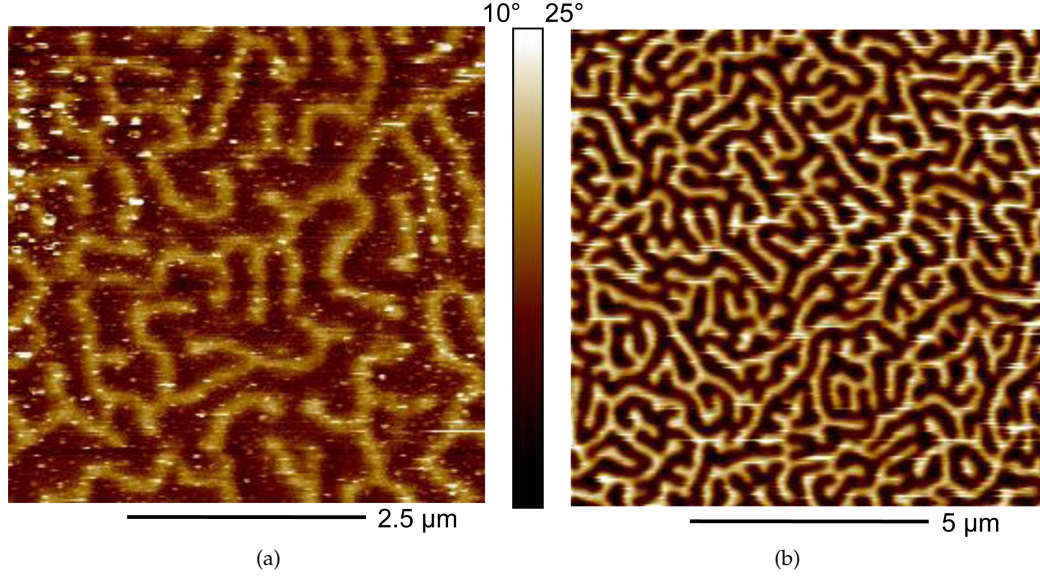


Figure 7.12: Phase-contrast MFM scans of (a) 20 nm and (b) 500 nm CoCrPt Thin Films in their as received magnetic state.

energy. If we assume that the magnetocrystalline anisotropy energy density does not change appreciably with thickness, since the texture actually improves slightly, the thickness variation must be explained by considering other energy terms. We are looking for an energy term that favors out-of-plane anisotropy, but decreases with increasing thickness. There are three major energy terms that could follow this trend.

The first is Surface Anisotropy, which can increase the effective K_u value due to the introduction of different surfaces (here, the Ru and Ta layers). The effective uniaxial magnetocrystalline anisotropy is described by Equation 7.2, where $K_{s,i}$ is the surface anisotropy due to layer i , and t is the thickness of the bulk layer. The effect of surface anisotropy is minimal as shown by Shimatsu et al., and cannot explain the effect seen above [75]; in addition, calculations of surface anisotropy, following Shimatsu et al. [75] and Johnson et al. [37], show K_s to be negative in sign (favoring in-plane magnetization), which is opposite of what is needed. Surface anisotropy, therefore, can not be responsible for the added out-of-plane anisotropy energy.

$$K_{u,\text{eff}} = K_{u,\text{bulk}} + (K_{s,1} + K_{s,2}) / t \quad (7.2)$$

The second possible contribution is from a theoretical enhancement of K_u due to the decrease in the c/a ratio of various materials, including Co [8–10, 30, 75, 93]. This follows the wrong trend, however, since the c/a ratio was shown here to decrease with increasing thickness, which would decrease the out-of-plane anisotropy, and not enhance it. This also does not agree with our films, then.

Magnetoelastic effects are the last contribution discussed. These effects are possible since there is cou-

pling between the elastic and magnetic properties in many materials, including CoCrPt. The shearing of these hysteresis loops agrees with the magnetoelastic coupling constants of CoCrPt, where the magnetostriction is in general negative for these alloy compositions [31,34,87,88]. The Ru underlayer has a lattice constant which is larger than the CoCrPt layer ($a_{\text{CoCrPt}} = 2.575 \text{ \AA}$ vs. $a_{\text{Ru}} = 2.7058 \text{ \AA}$), which will cause the CoCrPt layer to be in tension at the interface [84]; in fact, HRTEM has shown that the interfacial stresses extend to both sides of the interface, leaving the CoCrPt in tension and the Ru in compression (although the overall effect will be less than if the stresses only affected one layer). Since the CoCrPt layer is negatively magnetostrictive at this composition, the tensile stress will cause a preference for perpendicular anisotropy in the moments; this preference is added to the magnetocrystalline anisotropy, rather than the shape anisotropy, which prefers an in-plane magnetization. This causes an increase in the susceptibility in the thinnest films, but will diminish as thickness increases, since the interfacial stresses will only penetrate around 10 nm of film. The total energy equation becomes:

$$E_{\text{mag}} = E_{\text{SA}} - E_{\text{MC}} - E_{\text{ME}}, \quad (7.3)$$

where SA is Shape Anisotropy, MC is Magnetocrystalline Anisotropy, and ME is Magnetoelastic Anisotropy. By inputting the appropriate terms into Equation 7.3, we get Equation 7.4, with a simplified insertion for the hexagonal magnetoelastic energy; K_u is the uniaxial anisotropy coefficient, $\lambda_{s,i}$ is the isotropic saturation magnetostriction coefficient, t_{pd} is the penetration depth of the interfacial strain, and t is the film thickness. The magnetoelastic and magnetocrystalline energies are working together to promote the out-of-plane anisotropy, while the shape energy is favoring in-plane anisotropy.

$$E_{\text{mag}} = (2\pi M_s^2 - K_u) \cos^2 \theta - \frac{3}{2} \lambda_{s,i} \sigma \frac{t_{pd}}{t} \cos^2 (90 - \theta) \quad (7.4)$$

The current results share some similarities with the analysis by Im et al. [34]. They also see a transition region between 40 and 50 nm, in different parameters than were measured here. Their films were grown on Ti, which has a lattice parameter about 0.2 nm larger than Ru, providing even more tension. While we see similar trends in their data and see a correlation between magnetostriction and perpendicular magnetic anisotropy, there are many competing factors in their analysis that make it difficult to believe. In particular, they claim that the magnetostriction constant changes with the thickness of the film layer. While I agree that the observed magnetostrictive response may change with thickness ("effective" magnetostriction), the actual base magnetostrictive property will not change; any nanoscale type effects should be minimal since we are staying in the nanoscale regime. It is argued here that there are competing effects producing per-

pendicular anisotropy in these types of films, and the observed effect of magnetostriction is due to epitaxial stresses in the film, induced by the film underlayer. As the film gets thicker, the effect of those stresses is minimized, since the percentage of film under tension decreases as film thickness goes up. Therefore, the observed magnetostriction may seem to decrease or even change signs, but this is rather due to competing variables in the films.

It is possible to estimate the amount of magnetoelastic energy contributing to our large slope in the thinnest films. This is done by comparing the anisotropy field, in-plane or out-of-plane, in a state where there are multiple energy variables and when there is a minimum of energy variables. This has been done using the out-of-plane variant of Equation 7.5 as calculated at 10 nm and 500 nm. The Magnetocrystalline Anisotropy energy will remain the same, but at 10 nm both Shape and Magnetoelastic energies will affect it's strength, while at 500 nm, the Magnetoelastic effect is much diminished, leaving only the effect of shape on the anisotropy field. From these calculations, the Magnetoelastic energy provides 1.11×10^6 erg/cm³ of energy to produce the hysteresis loop shown for 10 nm.

$$H_{k, \text{OP}} = \frac{2(E_{\text{SA}} - E_{\text{ME}})}{M_s} \quad H_{k, \text{IP}} = \frac{2(K_u + E_{\text{ME}})}{M_s} \quad (7.5)$$

Since the major focus of this sensor is to be very sensitive and comparable to SmCo films, we need a high remnant magnetization. As can be seen by the above discussion of Figures 7.7a–c, the remnant magnetization constantly decreases as thickness increases. What we want is to retain the high magnetization at zero field as seen in the initial 20 nm thin film. Since the previous discussion hoped to illuminate the role of stresses and domains on the out-of-plane anisotropy, an attempt was made to continue the presence of those stresses through thicker films keeping its single domain nature by making a multilayer of CoCrPt. This was intended to “reset” the growing conditions by inserting a 10 nm layer of Ru in between two 20 nm layers of CoCrPt during the sputtering process. This would give us 40 nm of film, hopefully retaining the domain structure of the 20 nm film, and reapply the tension due to Ru. As can be seen in Figure 7.7d, the multilayer film does not resemble either the 20 nm films or the 40 nm film completely. Its remnant magnetization has decreased from the 20 nm film, but its slope has increased from the 40 nm film. Looking at Figure 7.8 helps clarify the situation. The remnant magnetization of the multilayer is exactly the same as the 40 nm film, indicating the Ru interlayer did not decouple the Co layers enough, allowing them to “communicate”, establishing the same domain structure of the 40 nm film, but in the multilayer. The anisotropy field is not the same as the 40 nm film, but has decreased to between that of the 40 and 20 nm films. The Ru interlayer did propagate the interfacial stresses a little further than just the underlayer, however, it didn't improve the properties completely. One issue with mutlilayers may be a reduction in film stresses due to

multiple interfaces, i.e. the first Ru layer will hold the CoCrPt in tension, but the second Ru layer will be held slightly in compression by the first CoCrPt layer, and will reduce the tension applied to the second CoCrPt layer.

Even though the M_r is small for these films, it is still possible to use these films in the linear regime of their hysteresis loop. While the initial response may not be as high as SmCo thin films, the CoCrPt film will invariably stay in first mode if we are operating at the desired resonance frequency. The CoCrPt alloys studied do not have a large coercivity, and can therefore switch easily as the applied field is switched. SmCo, on the other hand, has a very high remnant state, but also a huge coercivity (40+ kOe); when the field is applied opposite of the magnetization of the SmCo thin film, the film may want to flip over to align itself with the applied field. This will cause a torque to the permanent magnet, causing an oscillation outside of the 1st vibrational mode, and decreasing the effectiveness of the sensor. With the correct optimization, CoCrPt, or other such thin films, may still be a viable possibility.

The hard-axis in-plane loops have been included here for completeness. They show primarily moment rotation, but have a small jump in magnetization near zero field, in accordance with the quality of texture, as discussed above. These loops also show a clockwise shearing with thickness, in accordance with the results discussed above. The shearing is not as drastic as the out-of-plane loops, since the area between the loops will get smaller with increasing thickness, indicating that there is a lower energy barrier between the out-of-plane and in-plane loops, due to the reduction in magnetoelastic energy as thickness increases. It is not possible at this time to perform the same analysis as above, however, since the magnetometry equipment used for these experiments was not able to saturate the thicker samples. To demonstrate this more drastically, Figure 7.14 shows the full set of in-plane loops, normalized and as magnetization. It is obvious when looking at Figure 7.14b that some of the films have yet to reach saturation, even though the normalized figure looks opposite. The variation in saturation magnetization shown is due to inaccuracies in the the calculation of the volume of sample in these thin films.

7.4.3 Temperature-dependent Properties

To verify the sensor's capabilities in varying thermal environments, and its stability and usability at RT and below, the CoCrPt thin films were analyzed with the VSM at elevated temperatures, up to 1000 °C. Figure 7.15 shows the normalized magnetization of the 500 nm thin film as a function of temperature, when the field is applied parallel and perpendicular to the surface.

The out-of-plane magnetization looks like a regular MvT curve, which would flatten out below room temperature. This is because the film was saturated perpendicular to the surface with the applied 12.5

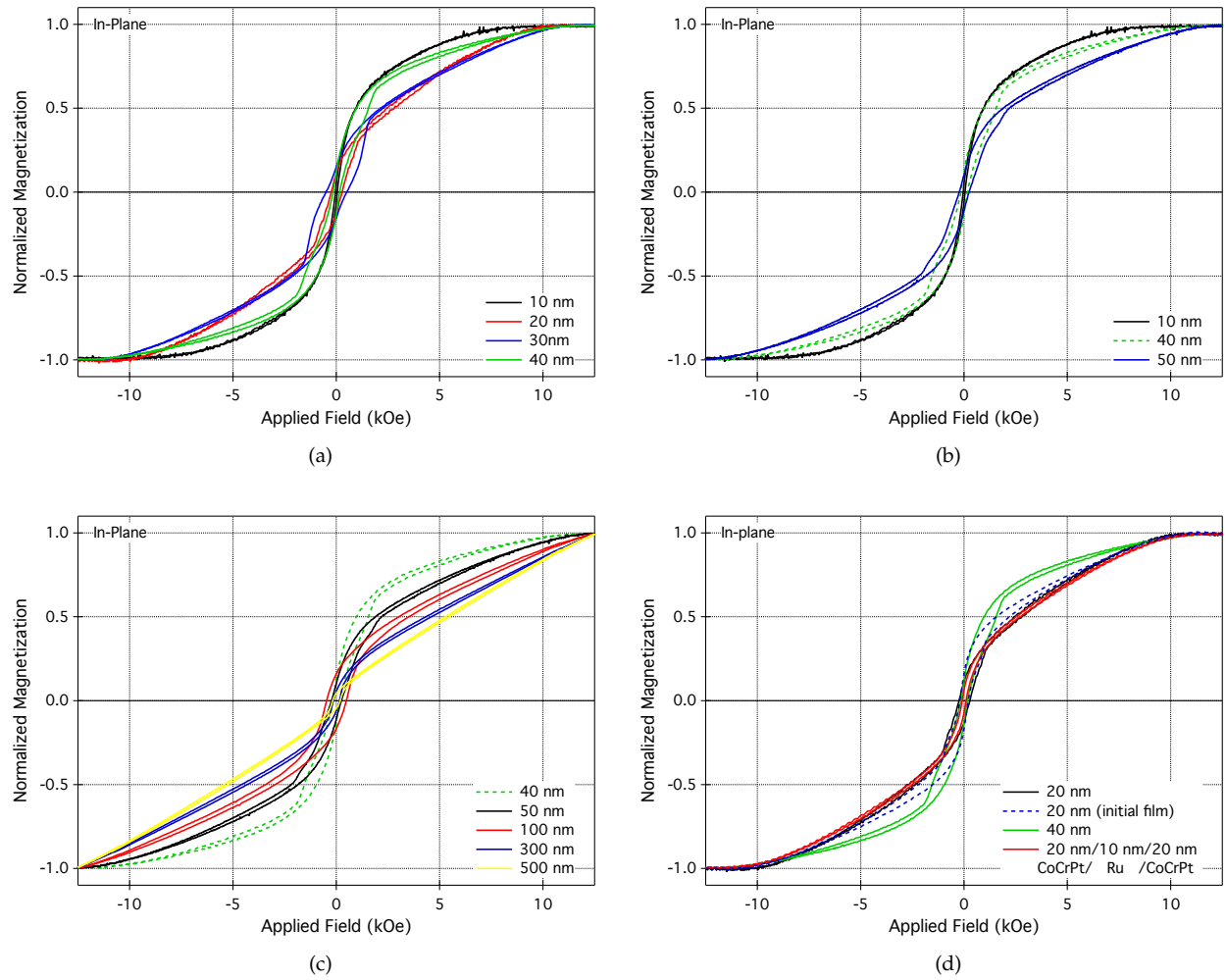


Figure 7.13: In-plane Magnetization versus applied field loops for (a) films of lower thickness, (b) films around the transition region for this system, (c) films of larger thickness, and (d) a comparison between different 20 nm films (including a stacked film).

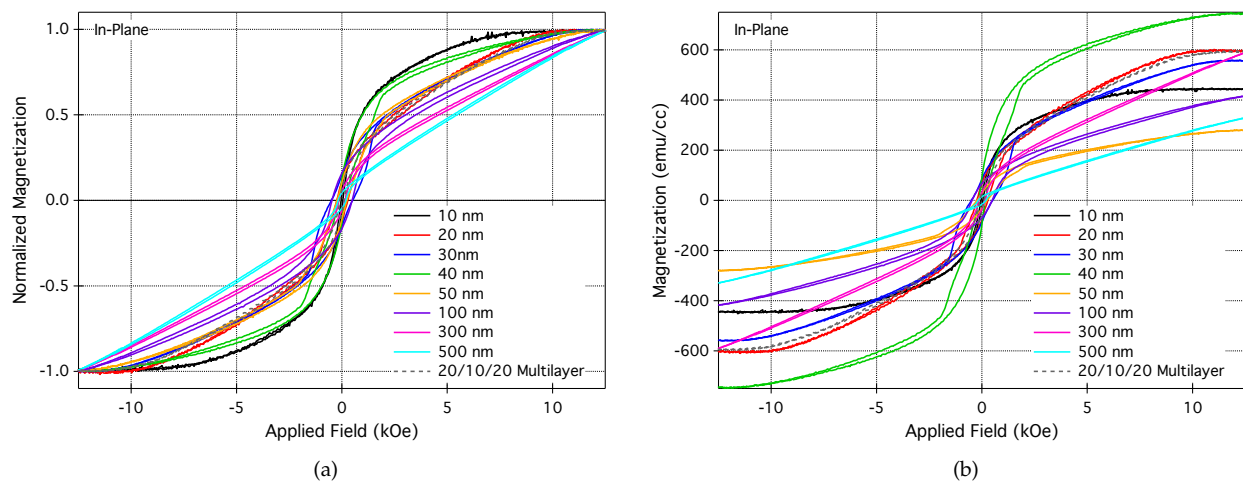


Figure 7.14: Full thickness sets of In-Plane Magnetization versus applied field loops using (a) normalized magnetization and (b) volume magnetization (emu/cc).

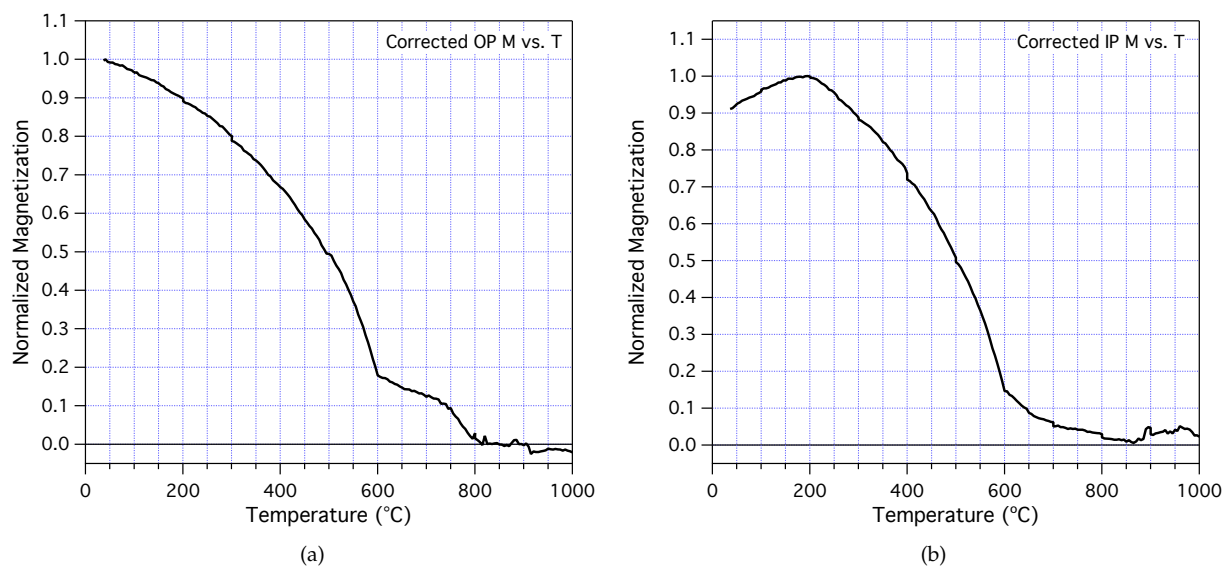


Figure 7.15: Normalized Magnetization versus Temperature curves for a 500 nm thin film of CoCrPt with a 12.5 kOe field applied (a) perpendicular to the surface (out-of-plane, OP) and (b) parallel to the surface (in-plane, IP). The correction was to make the curve continuous with out jumps due to equipment.

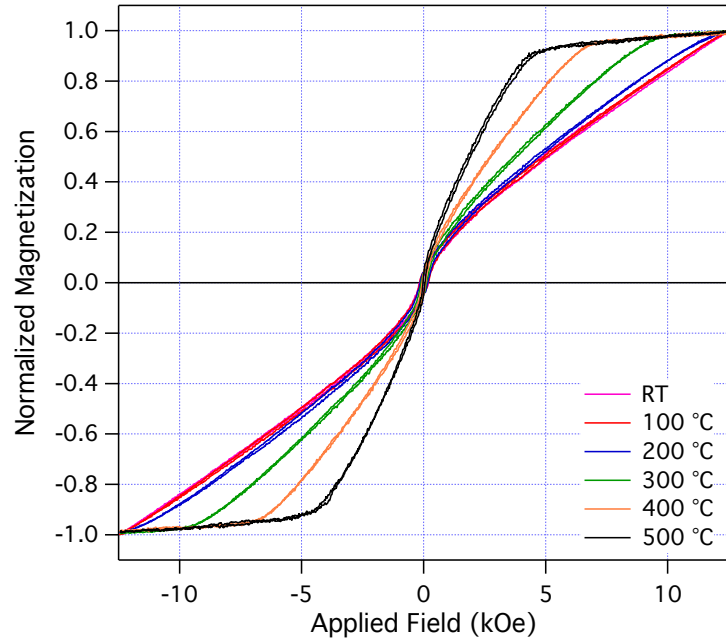
kOe field. The in-plane curve, however, has an initial increase in magnetization with temperature, since the increase in thermal energy makes it easier to saturate the otherwise hard basal plane. This saturation is further confirmed in 7.16a, where the hysteresis loop just reaches saturation in-plane when the ambient temperature is 200 °C. The curie temperature is around 600 °C for both sample orientations. For the results below, only the data below 500 °C was used, since above 600 °C the sample seems to change irreversibly, with the magnetization being reduced by more than a factor of 3 at room temperature. While the nature of the change has not been confirmed through experimental results yet, it is most likely a combination of substrate and underlayer interdiffusion with the magnetic layer, oxidation, and a change in microstructure.

As the film was heated for the temperature dependent magnetization data, magnetization versus field hysteresis loops were also measured at a held temperature. The in-plane loops are shown in 7.16a. The anisotropy field, H_k , continuously decreases with field due to the decreasing magnetic preference for the (00.1) direction. Not only are stresses partly relieved with temperature, but the thermal energy begins to overcome the magnetocrystalline anisotropy as well. Even though the hysteresis loops have curvature, for simplicity we can assume that only K_1 values are applicable. Using Equation 7.6, where K_1 is the first order uniaxial magnetocrystalline anisotropy constant, H_k is the anisotropy field, and M_s is the saturation magnetization, we can calculate K_1 as a function of temperature (see Figure 7.16b); a full anisotropy analysis, done by integrating the area between the in- and out-of-plane hysteresis loops, yields anisotropy energies on the same order as the approximation. The reduced anisotropy constants are compared to the normalized magnetization cubed, $m(T)^3$ as a function of temperature and show a good fit to the calculated constants. Using both the experimentally measured data and a Brillouin fit of the magnetization versus temperature data, the anisotropy calculations show good agreement with Akulov's theory for uniaxial materials, Equation 7.7, where n is the power of the angular terms of the energy equation for that anisotropy constant, $\langle n \rangle$ is the order of the anisotropy constant, and $M_{s,0}$ and $K_0^{\langle n \rangle}$ are the Saturation Magnetization and n^{th} order anisotropy constant at zero kelvin, respectively [2, 17]; for the first order anisotropy constant in uniaxial materials, K_u , the right-hand exponent is 3, since $n = 2$. The actual anisotropy constants calculated from Figure 7.16a, are summarized in Table 7.1.

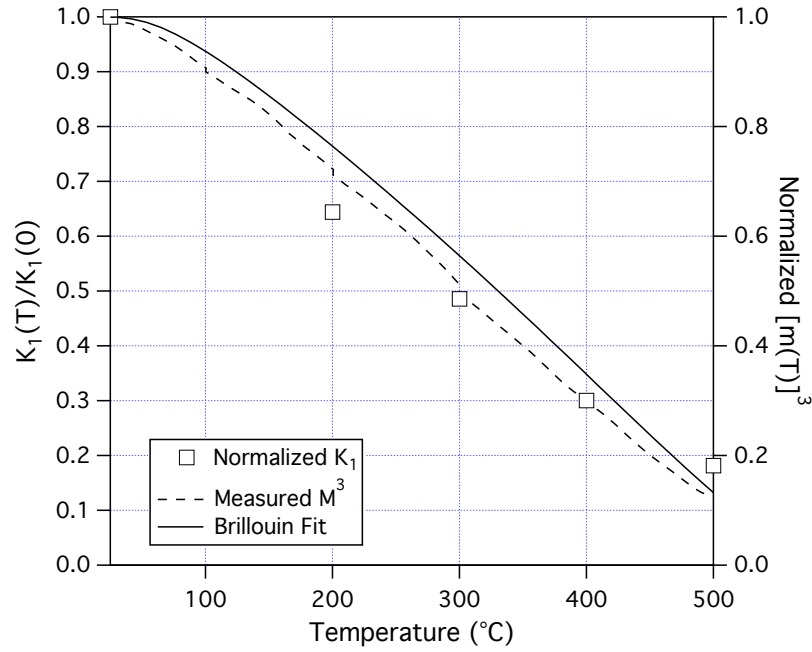
$$K_1 = \frac{1}{2} H_k \cdot M_s \quad (7.6)$$

$$\frac{K^{\langle n \rangle}}{K_0^{\langle n \rangle}} \propto \left(\frac{M_s}{M_{s,0}} \right)^{\frac{n(n+1)}{2}} \quad (7.7)$$

It is possible to estimate second order anisotropy constants from these equations, although the analysis gets more tricky. By plotting the hysteresis loop data with equation 7.8, we can change the values of $K_{u,1}$



(a)



(b)

Figure 7.16: (a) In-plane hysteresis loops for continuous 500 nm CoCrPt films measured at temperatures between 25 and 500 °C and (b) normalized K_1 values determined from (a) for continuous 500 nm CoCrPt films plotted as a function of temperature.

T (°C)	$K_{u,1}$ (ergs/cm ³)
25	3.72×10^6
200	2.40×10^6
300	1.81×10^6
400	1.12×10^6
500	6.76×10^5

Table 7.1: First Order Uniaxial anisotropy constants for a 500 nm CoCrPt thin film.

and $K_{u,2}$ to make the theory agree best with the data, yielding approximate values for $K_{u,1}$ of $(2 \pm 0.3) \times 10^6$ ergs/cm³, and $K_{u,2}$ of $(3.9 \pm 1.4) \times 10^5$ ergs/cm³.

$$H = \frac{2K_1}{M_s} \left(\frac{M}{M_s} \right) + \frac{4K_2}{M_s} \left(\frac{M}{M_s} \right)^3 \quad (7.8)$$

There are many approximations that were made in these calculations that need to be mentioned, and may allow for more refined calculations in the future (see Section 8.1.3). First, the curvature of the in-plane loops and jump at low fields was ignored; further calculations utilizing the area between the out-of-plane and in-plane loops would provide more accurate constants. Second, only magnetocrystalline anisotropy energy was included in these calculations; shape anisotropy and magnetoelastic energies have been ignored, although ignoring the out-of-plane loops in Eq. 7.6 has implicitly taken this into account. Finally, the plot in Figure 7.16b needs points closer to zero kelvin to accurately compare magnetization to anisotropy constants, although the current fit seems quite good.

7.5 Direct CoCrPt Sputtering on a Si Membrane

All of the previous CoCrPt research and analysis was done on thin films, because thin films are easier to handle, and most of the equipment used is set-up for thin films, but not membranes. In particular, many of the techniques used above would require the sample to be cut smaller, thus destroying the sample in the process. Handling the membrane without the thicker Si sides might also become difficult. Nevertheless, the final sensor design would work better with the film sputtered directly on the Si membrane, rather than requiring the Si substrate to be glued to the membrane. The substrate adds a lot of weight to the system, making it more difficult to vibrate, and the glue also interferes with the vibration mechanics of the membrane.

In order to sputter on the membrane, however, it is essential to mask the rest of the surface, since we don't want the active material to be everywhere, but only on the membrane. Also, using a smaller active area will allow the magnetic field gradients to be more uniform [50]; this will allow the sample to stay in

one vibrational mode, without exciting others. An initial mask was made by cutting the center membrane out of one of the membranes, leaving only the thick, unetched Si remaining. The faux mask was placed over an uncut membrane during sputtering, and is shown in the top center of Figure 7.17. The “mask” became misaligned when inserting the sample into the sputtering chamber, which is why the sputtered square of material is tilted. After demonstrating the feasibility of sputtering with a mask, Aluminum masks were machined with two different sized holes, shown in Figure 7.17 around the sputtered sample. These masks can be placed on top of the Si membrane during sputtering to shield the rest of the substrate/membrane from material.

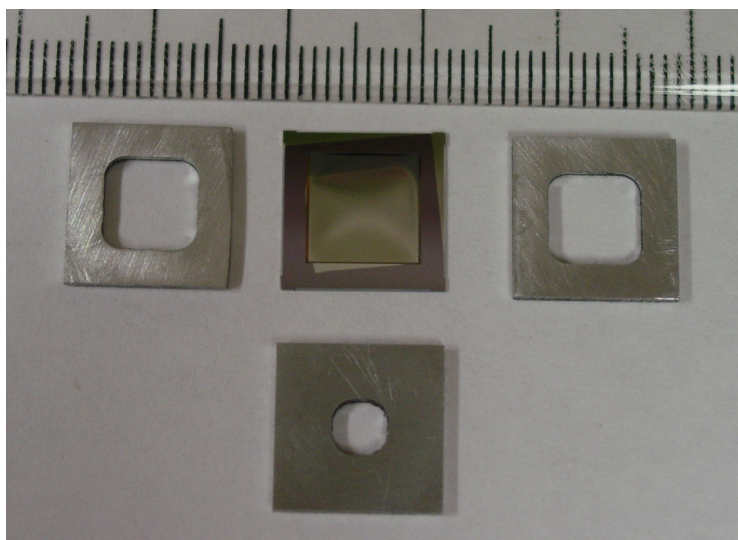


Figure 7.17: Three sputtering masks (the top two are the same dimensions) surrounding a Si membrane sputtered with 500nm of CoCrPt (top-center); each division of the scale bar is 1 mm.

X-ray diffraction was performed on the sample sputtered with the faux mask. The sample was 500 nm thick, and showed good (00.2) CoCrPt texture, with a small Ru peak. A rocking curve could not be performed, however, since the optics used for the out-of-plane XRD scans are focusing optics, and any results would not be comparable with the rest of the rocking curves discussed above, which used parallel optics. The FWHM of the rocking curve would change due to the varied optics.

7.6 Summary

The fabrication of a CoCrPt thin film for use in small, portable AGFM sensors has been demonstrated showing a preferred out-of-plane anisotropy that is a balance between magnetoelastic and shape anisotropy energies. The effect of each of these energies determines the shearing of the hysteresis loop, and the overall remnant magnetization of the sample is a function of the domain structure, which consists of modified

Bloch walls, and has a critical single domain thickness below 50 nm. The remnant magnetization and loop shearing help determine the films usefulness. While it is as yet not possible to extend the 20nm film properties to thicker films, the above results give a better understand of the variables involved in optimizing the properties. A value for the amount of magnetoelastic energy present in the thinnest materials has been calculated. The change in the magnetocrystalline anisotropy constants with respect to temperature has been measured at elevated temperatures, showing good agreement with theory. Multilayers with an intervening Ru layer have been sputtered, showing the same domain structure as the multilayer's thicker counterpart, but an improved anisotropy field. Finally, it has been shown the CoCrPt can be sputtered directly onto Si membranes, yielding the desired (00.2) texture; Aluminum sputtering masks have also been machined.

Chapter 8

Summary

FeCo nanoparticles have been shown to oxidize slowly, up until 400 °C, after which oxidation proceeds more quickly and completely, and the entire structure becomes an oxide. As oxidation progresses, the core becomes voided due to the mobility of Fe and Co cations, with the core eventually collapsing, and particles sintering at higher temperatures. It is assumed, and shown through some techniques, that Fe has a higher mobility than Co, although this mobility is affected by composition, and the activity of the components (and the final oxide structure). The oxide structure has been shown to be primarily Magnetite, although this becomes Maghemite as oxidation progresses.

Nucleation and growth code has been written for both (110)- and (111)-faceted nanoparticles. The code shows that the critical nuclei are the same as the growth shapes for different faceting amounts, although the amount of faceting is surface energy dependent. It was written as both an adaptation of previously published code, but also an update and correcting of that code.

Finally CoCrPt films were fabricated for use in a portable AGFM sensor. Their magnetic properties have been studied as a function of thickness, and temperature, with initial theories proposed about the role of magnetostriction in the out-of-plane anisotropy, and initial calculations of first order uniaxial anisotropy constants as a function of temperature. While these films show potential for use in the portable AGFMs to replace SmCo, more work will be done to increase the remnant magnetization and to understand the system better.

8.1 Future Work

8.1.1 FeCo Oxidation

While many techniques have been used in hopes of complimenting each other, certain aspects of nanoparticle oxidation are still unknown. It would be beneficial to use TEM to fill in the gap between 350 °C and 900 °C, and for various times at lower temperatures (like 350 °C from 0 to 5 hours) to understand the progression of oxidation. It would also be interesting to monitor the void at higher temperatures to note when the void collapses and sintering begins. While some HRTEM has been performed, it would also be helpful to do more specific compositional analyses on the nanoparticles, and to do more tilt series on nanoparticles oxidized at various temperatures to get a more three-dimensional understanding of their shape and connectivity with each other. A further EELS analysis at low and high magnifications will help determine the location of the Cobalt in the system, since it should be located somewhere in the oxidized nanoparticle system; the low magnification will help provide an understanding of the spatial distribution of the Cobalt throughout the clump. Due to nanoparticle clumping from magnetostatic interactions, it would be beneficial to attempt to separate the nanoparticles using a surfactant attached to their surface, which will more easily allow the observation of one nanoparticle at a time, rather than a clump or multiple nanoparticles on top of each other; this will make image analysis easier. Thermogravimetric Analysis (TGA) provided helpful insights into the oxidation rate, however more temperatures would further clarify the picture. The TGA analysis could also be coupled with high temperature XRD data, looking at crystallographic changes over time; this would also help determine any shifting of peaks over time due to epitaxial stresses during the growth of the oxide, and a quantitative analysis for phase composition can be compared to VSM and TGA data.

While these studies have been done with polydispersed nanoparticles, it may be useful to replicate some experiments using monodispersed nanoparticle, to more closely monitor the oxide thickness in the TEM, and with less size variation in the VSM.

It is also desirable to model diffusion through the nanoparticles, to come up with a more concrete understanding of rate limiting factors in the growth of the oxide. While the direct logarithmic rate law seemed to fit the data well, these laws were not developed for nanoparticles which are dominated by a very thin oxide layer. While the model could begin as a spherical particle, it has to be at least noted that there are different facets involved that will oxidize differently. This problem will need many levels of development, since it currently seems that we have a double moving boundary problem, with unlimited oxygen at the oxide-gas interface, and a limited supply of Fe and/or Co to get oxidized, which will eventually have a large compositional gradient in the oxide layer. It currently seems like there are two moving boundaries,

since the oxide is growing out (assuming Fe is the primary mobile oxidizing species), but yet the core is shrinking as well.

More thin film work would also help clarify the growth of the oxide in the nanoparticles. The oxidation rate of different FeCo surfaces can be monitored using TGA and TEM, along with the epitaxial evolution of the oxide layer. The TGA could be used by oxidizing a sample of known orientation and comparing the kinetics with a sample of a different orientation; the initial kinetics (if measurable) will help understand oxidation on a specific FeCo face, while the long term kinetics will help determine diffusion rates through various orientations of oxide. Further XPS analyses along with analytical TEM would also be helpful to understand the elemental composition of the oxide and FeCo layers. XRD and HiT-XRD may also be useful, although initial studies have shown some of the oxide peaks to be hidden by the MgO substrate peaks. Magnetometry analysis of the thin films using a Vector Vibrating Sample Magnetometer (VVSM) and/or a torque magnetometer can help us determine any magnetic coupling between the oxide and metal layers of the thin film (and therefore the nanoparticle), noting the effect of the different anisotropy constants of the oxide and FeCo layers and the effect of their epitaxial relationships. Thin films with capping layers can be used as a control for comparison with those with a native or grown oxide to see if there is any difference in the anisotropy constants without the oxide layer.

8.1.2 Nanoparticle Nucleation and Growth

While the above analyses are completed, it may be of interest to start combining different facets, and proceeding beyond just two planes of interest. This may get very complicated, and may be undoable from a graphical perspective, although the math may still yield answers that are beneficial and can clarify different growth and faceting regions. The model could also be extended for use in analyzing voided particles, adding interior surfaces, in addition to the generic exterior surfaces studied here.

8.1.3 CoCrPt Sensor

In order to increase the remnant magnetization, and improve the overall magnetic properties of these CoCrPt thin films, there are many directions to explore. While it has been shown above that an annealing treatment at 450 °C for 1 hour under argon did not improve the properties of the film, it is possible that another annealing treatment will help to order the system; therefore a more in-depth inspection of the phase diagrams for this system and literature survey on the ordering of CoCrPt systems may be helpful. In-plane magnetization loops going to higher fields will enable the conversion of anisotropy field measurements to energy measurements, by calculating the area between the in-plane and out-of-plane M-H loops;

currently, the in-plane loops were not all complete, and therefore couldn't be used. High resolution TEM on the Ru-CoCrPt interface will also help clarify the change in lattice spacing with thickness in these thin films, and will not have the averaging effects possible with XRD. A further analysis of the MFM properties of these films will be useful, looking at the domain structure in various states (demagnetized, remnant, and with an applied field).

A more accurate analysis of the in-plane and out-of-plane hysteresis loops would refine the anisotropy constant calculations, specifically looking at calculating the area between IP and OP hysteresis loops at various temperatures, and including shape and elastic terms in the calculations. In order to expand the anisotropy constant calculations as a function of temperature, magnetization versus temperature curves and hysteresis loops could also be taken down to 4 K, since many space environments are below room temperature.

Further experimentation on CoCrPt multilayers should likely encompass a comparison between the Ru interlayer tested above and a complete restarting of the underlayer stack as an interlayer (Ta, NiW, followed by Ru). Other interlayers may also be more effective at decoupling the layers, such as an oxide interlayer, although research into correct lattice matches will be necessary, along with experimentation to see how the texture will be affected by different interlayers (especially those that are not hexagonal). An XRD analysis will also be helpful to see if these multilayers are remaining well textured.

Direct sputtering on Si membranes has only briefly been studied. It would be interesting to determine the surface roughness of the membrane before and after sputtering using AFM to see how much of that roughness affects the CoCrPt layer. There are also two sides that could be sputtered, and their roughness may affect the resulting texture and magnetic properties of the film. A more in-depth analysis will be helpful in understanding the texture of the resulting films; this will preferably use parallel optics, although the sample's fragility will have to be considered in setting up the test. The same considerations will need to be made for magnetometry analyses, since the sample cannot be tested easily after being cut up into pieces small enough for AGFM or VSM tests; those tests would also become destructive, and would make the overall research initiative very costly since the membrane could not be used afterward for testing by INTA. Kerr magnetometry may prove useful, since it will be non-destructive and the sample can lie flat on a surface, although that technique performs better with in-plane anisotropy. Further development of the sputtering masks may also be necessary depending upon the results of many of these experiments and the quality of the sputtered membranes.

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