EPITAXIAL THIN FILM DEPOSITION OF MAGNETOSTRICTIVE MATERIALS
AND ITS EFFECT ON MAGNETIC ANISOTROPY

by

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APPROVAL

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Magnetostriction means that the dimensions of a material depend on its magnetization. The primary goal of this dissertation was to understand the effect of magnetostriction on the magnetic anisotropy of single crystal magnetostrictive thin films, where the epitaxial pinning of the material to a substrate could inhibit its conversion to new dimensions.

In order to address this goal, several Fe-based binary alloys were deposited onto various substrates by molecular beam epitaxy. The samples were characterized by an array of techniques including electron diffraction, Rutherford backscattering, vibrating sample magnetometry, ferromagnetic resonance, and x-ray absorption spectroscopies.

The attempted growths of crystalline magnetostrictive thin films resulted in successful depositions of Fe$_{1-x}$Ga$_x$ and Fe$_{1-x}$Zn$_x$. Depositions onto MgO(001) substrates result in an in-plane cubic magnetic anisotropy, as expected from the cubic symmetry of the Fe-based thin films, and a strong out-of-plane uniaxial anisotropy that forces the magnetization to lie in the plane of the films. Depositions onto ZnSe/GaAs(001) substrates feature an additional in-plane uniaxial anisotropy. The magnitudes and signs of the in-plane anisotropies depend on the Ga content. Furthermore, the cubic anisotropy constant of Fe$_{1-x}$Ga$_x$ samples deposited onto MgO substrates switches sign at a lower Ga concentration than is seen in bulk Fe$_{1-x}$Ga$_x$.

The effect on the magnetic anisotropy of depositing a magnetostrictive material as an epitaxial thin film is influenced by the material’s magnetostrictive properties and the substrate upon which it is deposited. In particular, pinning a magnetoelastic material to a substrate will modify its cubic anisotropy, and depositions on substrates compliant to an anisotropic strain relaxation may result in a strong in-plane uniaxial anisotropy.
CHAPTER ONE

INTRODUCTION TO DISSERTATION

The primary purpose of this work was to determine the effect of magnetostriction on the magnetic anisotropy of single crystal magnetostrictive thin films. The main idea inspiring this work was that bulk magneto-elastic materials deform under the application of a magnetic field, so how might the magnetic properties of a magneto-elastic material, in particular its magnetic anisotropy, be affected if the material is inhibited from deforming in a magnetic field by pinning it to a substrate as a single crystal? In order to answer this question, we studied the properties of several Fe-based binary alloys that were deposited onto various substrates by molecular beam epitaxy.

The overall scope of this project was three-fold. Because I was the individual responsible for making the samples to be studied, I first had to determine if and how certain magnetostrictive materials could be synthesized as crystalline thin films. Once a growth recipe was established, we studied the properties of the sample through a number of techniques. Again, the primary goal was to characterize the magnetic anisotropy of the materials that were made and look for connections to magnetostriction. The characterization of the magnetic anisotropy was primarily accomplished by vibrating sample magnetometry and angle dependent ferromagnetic resonance (FMR). (For an in depth review of the FMR studies, see [1]).

The final part of this project was to lay the groundwork for future investigations into how the epitaxial pinning of a magnetostrictive material may affect its spin
dynamics. This was accomplished primarily by developing reliable thin film growth recipes, and also by noting certain pitfalls that I encountered which future investigators hopefully can avoid.

The possibility of controlling the spin damping parameter (known as $\alpha$ from the Landau-Lifshitz-Gilbert equation [2]) originates when a highly magnetostrictive material is pinned to a substrate as a single crystal thin film so that it cannot alter its in-plane lattice constants in response to an applied field. It is believed that the subsequent magnetoelastic stress energy generated in the sample will be converted into controllable spin damping. As an example, the magnetostrictive constants of Fe$_{1-x}$Ga$_x$ single crystals are highly anisotropic and dependent on the alloy concentration. Preliminary ferromagnetic resonance linewidth and microwave stripline measurements on these samples indicate that the damping parameter is anisotropic, dependent on the magnetoelastic properties of the material, and sensitive to the applied field [1, 3].

Furthermore, the magnetoelastic stress energy generated in magnetostrictive materials is sensitive to strain. This opens up the possibility for some important technological applications. The switching of a magnetic bit has reached speeds whereby the standard methods of applying an anti-aligned magnetic field are losing their usefulness. As demands for faster switching speeds continue, new paths for the magnetization reversal of magnetic bits are required. Some recent developments in this field include heat assisted magnetic reversal (HAMR) [4], spin torque transfer [5, 6], transverse ultra short magnetic pulses [5, 7], and induced reversal with simultaneous heating [8, 9]. We believe that a new approach could be realized using magnetostrictive
materials by coupling such materials to ultrafast piezoelectric straining materials, resulting in the possibility of ultrafast control of the local magnetic moment.

**Introduction to Magnetostriction**

Magnetostriction refers to the change in dimensions of a sample as a result of magnetic interactions, and is typically divided into two categories: spontaneous magnetostriction and forced magnetostriction.

Spontaneous magnetostriction is a non volume conserving effect related to internal magnetic interactions within a sample. For example, when iron is cooled through its Curie temperature ($T_c$), an isotropic expansion occurs leading to a type of volume magnetostriction [10, 11]. The isotropic volume magnetostriction arising from the spontaneous magnetization of nickel causes such a sample to contract [10, 11]. This effect allows for the creation of materials whose size is invariant with temperature for a certain temperature range, known as perminvars [11].

Forced magnetostriction reflects the magnetic interaction between a spontaneously magnetized sample (i.e., a sample below its $T_c$) and an applied magnetic field. This type of magnetostriction has isotropic and anisotropic components. The isotropic component is another type of volume magnetostriction, and occurs when the applied magnetic field reaches strengths above technical saturation. Above technical saturation, the spontaneous magnetization of the sample increases with field at a rate similar to its paramagnetic state above its Curie temperature, causing a forced spontaneous magnetostriction.
Among many of his discoveries, James Prescott Joule discovered the anisotropic component of the forced magnetostriction in a bar of polycrystalline iron in 1842 [12]. He found that the length of the bar along an applied field direction depended on the strength of the applied field, sometimes referred to as longitudinal magnetostriction. Joule also measured a deformation perpendicular to the applied field direction which had half the magnitude and opposite sign of the longitudinal magnetostriction. The orthogonal deformation is sometimes referred to as transverse magnetostriction. Longitudinal and transverse magnetostriction are two aspects of the same effect which today we refer to as Joule magnetostriction. Joule magnetostriction conserves the volume of a sample and reaches saturation when the applied field technically saturates the magnetization. Unless explicitly stated otherwise, the use of ‘magnetostriction’ throughout this dissertation will always refer to Joule magnetostriction.

In parts per million (ppm), the Joule magnetostriction of polycrystalline iron, nickel and cobalt at room temperature are -7, -34, and -62 respectively [13]. The minus signs indicate a contraction with applied field. The largest room temperature Joule magnetostriction, reported for TbFe$_2$ and Tb$_{0.3}$Dy$_{0.7}$Fe$_{1.92}$, is around 2600 ppm [13-15].

Just as the application of a magnetic field can change the size of an iron rod, changing the rod’s size by straining it will produce a change in its magnetic properties (magneto-elastic coupling is discussed in more detail in Chapter 2). This inverse of Joule magnetostriction is known as the Villari effect [16]. I would like to point out that an external strain does not magnetize a demagnetized ferromagnetic sample in the absence of an applied field. A strain only changes the magnitude of the magnetization in a sample.
if applied in the presence of a magnetic field or if the sample possesses a remanent magnetization [17].

The combined phenomena of magnetostriction and the Faraday effect open up the possibility for devices based on the conversion of electrical signals into mechanical ones and vice versa. For example, magnetic actuators, ultrasonic cleaning devices, and sonar incorporate magnetostriction into their design [18-21]. Furthermore, there is current interest in the Villari effect relating to energy harvesting applications [22]. Magnetostriction becomes an unwanted phenomenon in certain applications. For instance, the low frequency hum from transformers is a direct result of magnetostriction [17, 23].

More information on magnetostriction is presented in Chapter 2.

Overview of Dissertation

Definitions and descriptions of relevant terms and techniques are presented in chapter two. Chapter three describes some basic properties of single crystal Fe$_{1-x}$Ga$_x$ thin films. It includes a discussion of why Fe$_{1-x}$Ga$_x$ was chosen, and details of its deposition on ZnSe/GaAs substrates. Also provided is the GaAs substrate cleaning process. Chapter four presents further information on the magnetic properties of Fe$_{1-x}$Ga$_x$ thin films. The magnetic properties of Fe$_{1-x}$Ga$_x$ thin films deposited on ZnSe/GaAs(001) and MgO(001) substrates are compared and contrasted. The MgO substrate cleaning process is also given. Chapter five characterizes the magnetic anisotropy of the Fe$_{1-x}$Ga$_x$ thin films deposited on both substrates in more detail, and compares the thin film behavior to
that of bulk Fe$_{1-x}$Ga$_x$. X-ray absorption studies on the electronic and magnetic structure of Fe$_{1-x}$Ga$_x$ thin films deposited on GaAs(001) substrates is given in chapter six. This chapter also provides a method to at least qualitatively measure the anisotropic spin-orbit coupling in the samples. Chapter seven reports some properties of ordered Fe$_{1-x}$Zn$_x$ thin films. In chapter eight I summarize the major results of this work.
References


CHAPTER TWO

TERMS AND TECHNIQUES

Molecular Beam Epitaxy (MBE)

All of the samples reported on in this thesis were made by Molecular Beam Epitaxy (MBE) at the Montana State University Magnetic Nanostructure Growth and Characterization Facility. Epitaxy essentially refers to single crystal growth, where the crystallographic orientation of the film is related to that of the substrate. However, certainly not all films deposited by MBE are epitaxial. In general, it is much easier to grow a non single crystal film than it is to produce a single crystal one. The term molecular beam describes a type of flow, where the mean free path of the evaporated material is equal to or larger than the source to sample distance, i.e. a non-interacting flow. In order to justify the use of this term, the mean free path in our MBE chamber for a typical deposition pressure of \(4 \times 10^{-9}\) Torr is about 22 km!

MBE is an evaporative deposition technique. The growth process involves controlling the flux of the source materials by manipulation of the source temperature and the use of shutters. The flux is directed at a single crystal substrate, maintained at the appropriate temperature so as to achieve epitaxial growth. Too much flux (very high deposition rates) can trap defects within the film. Too little flux allows contamination from the background gases present in the system. However, this issue can be minimized by achieving an ultra high vacuum environment. Deposition rates for the Fe based samples used in this study were 2 – 2.5 Å/min. The substrate temperature is an important
parameter concerning epitaxial depositions for the following reasons. Substrate temperatures that are too high tend to cause the source material to ball up on the substrate surface. Substrate temperatures that are too low freeze in defects. Additionally, only a substrate which has been properly prepared, usually by a chemical and thermal treatment, will result in a clean, single crystal surface upon which the film can be epitaxially deposited with reproducible quality. It is generally accepted that MBE sets the standard regarding the quality of single crystal thin films.

During my use of our MBE system, I have gained some information concerning the cleaning of certain source materials and the operation of an Al source which does not seem to be common knowledge, and as I feel it is important I would like to mention it here.

First I will discuss the operation of the Al source. Crucibles containing Al are delicate to work with. The Al is contained within a Pyrolytic Boron Nitride (PBN) crucible. (The crucible rests within another ceramic bowl which houses a thermocouple. Tantalum wire is wound around the outside of the ceramic bowl, and can be resistively heated.) Aluminum has a melting point very near 660 °C (this is exceeded by the typical deposition temperature of 1100 °C). The change in volume associated with the change in density from the solid to liquid phase transition is 13.7%! A problem arises should the Al become liquid and have no place to go. For instance, if the Al at the bottom of the crucible melts first and continues to have a solid Al cap on top, the Al could relieve its pressure by cracking the bottom of the crucible and spilling its contents all over the internals of the effusion cell. Unfortunately, this has occurred more than once in our lab.
However, I feel like we have finally gained an understanding of the problem and how to minimize its impact. First, it is critical to increase the temperature very gradually when passing through the melting point. This allows the Al to melt more uniformly, and at the very least allows the Al along the walls of the crucible to melt, providing an escape for any liquid Al formed below and freeing any potential solid Al plug to float in a liquid Al bath. Second, it is important to limit the Al in the crucible to a minimal amount. This limits the area that a potential Al plug could cling to. We have never had an issue with running out of source material, so I would recommend filling the Al crucible to no more than ¼ full.

Now I will discuss the cleaning of the source materials. Our source materials are almost exclusively purchased from Alfa Aesar®. The bulk purity of the materials ranges from 99.95% for Fe, to 99.99999% for Ga. The bulk purity is not a problem. However, the materials are shipped in plastic bottles, and the plastic can result in trace amounts of hydrocarbon residue on the surface of the materials. Due to the extremely low vapor pressure of carbon, the residue does not necessarily contaminate the film. Instead, the residue disrupts the reproducibility of flux vs. source temperature, primarily for molten sources. As the source material melts, the lower density carbon floats to the top of the source, thereby reducing the effective area of evaporation, thereby reducing the flux. To make matters worse, the C surface area coverage varies every time the source is cooled and reheated. This disrupts the correlation between the source temperature and the resulting flux. Fortunately this problem is easily resolved. Based on work done at the Advanced Photon Source [1], we are now cleaning most of our source materials using
potassium hydroxide (KOH), a strong alkaline base. Since adopting this practice, I have not noticed any carbon soot on the surface of our source materials, and the flux vs. source temperature has been very consistent.

A representation of the Fe$_{1-x}$Ga$_x$ multistructures discussed in this work are shown in Figure 2.1. The Fe$_{1-x}$Ga$_x$ samples were deposited onto ZnSe/GaAs(001) buffer layers and directly onto the MgO(001) substrates. The thickness of the MgO substrates is about 0.5 mm, while the GaAs substrates are about 0.25 mm thick. We chose to deposit the Fe$_{1-x}$Ga$_x$ samples onto the ZnSe buffer layer instead of directly onto the GaAs substrate for several reasons. First of all, Fe samples deposited onto ZnSe have shown better quality than those deposited directly onto GaAs primarily due to the lack of diffusion at the interface; Ga and As readily diffuse into the Fe [2]. Also, the GaAs surface is rather rough after the thermal cleaning of the substrate and the ZnSe buffer layer smoothes the surface on which the Fe$_{1-x}$Ga$_x$ samples will be deposited. The final reason is related to our x-ray absorption measurements. These techniques are element specific and we wanted to make sure that any Ga signal we measured was from our Fe$_{1-x}$Ga$_x$ sample and not from the underlying substrate. By burying the GaAs substrate under 75 nm of ZnSe we eliminate any Ga signal from the GaAs substrate. Furthermore, the ZnSe/GaAs structure is preferred to using a single crystal ZnSe substrate for several reasons. Because the thermal treatment of GaAs leaves the surface rough, that can probably be expected for a thermal cleaning of a ZnSe single crystal. But more importantly, ZnSe single crystal substrates are really expensive. A 1cm$^2$ x 0.5mm ZnSe substrate costs about $500. This is about the cost of a large GaAs wafer which will produce many
samples. Also, optical grade bulk 99.999% pure ZnSe costs about $42 for 5 grams of material, which will produce a lifetime of ZnSe buffer layers.

The ZnSe buffer layer and Fe$_{1-x}$Ga$_x$ samples grow single crystal on the substrates due to their very close lattice match. GaAs and ZnSe are both zinc-blende structures with lattice constants $a_{\text{GaAs}} = 5.654$ Å and $a_{\text{ZnSe}} = 5.668$ Å. The close lattice match of only -0.25% allows single crystal growth with GaAs(001) = ZnSe(001) and GaAs<100>/<ZnSe<100>. The lattice constant of body centered cubic Fe ($a_{\text{Fe}} = 2.866$ Å) means that Fe can grow single crystal on the ZnSe buffer layer under 1.1% bi-axial compression (assuming the Fe remains fully strained) with ZnSe(001) = Fe(001) and ZnSe<100>/<Fe<100>. The situation is different for Fe deposited onto MgO(001) substrates. The lattice constant of our MgO substrates is $a_{\text{MgO}} = 4.216$ Å. The epitaxial mismatch of Fe on MgO is minimized when Fe undergoes a 45° rotation. Therefore, Fe grows single crystal on MgO under a 4.0% bi-axial tensile strain (assuming Fe remains fully strained) with MgO(001) = Fe(001) and MgO<100>/<Fe<110>. Furthermore, the lattice constants of the Fe$_{1-x}$Ga$_x$ samples increase linearly from that of pure Fe, meaning that the Fe$_{1-x}$Ga$_x$ samples become more compressively strained on the ZnSe and experience less tensile strain on the MgO substrates with increasing Ga content.

**Magnetic Anisotropy**

Magnetic Anisotropy means that a material’s magnetic properties are directionally dependent. The term almost always refers to a sample’s magnetization, and means that a sample’s magnetization prefers to point in a particular direction. Magnetic anisotropy
results in magnetic easy and hard axes. The three primary factors that determine a sample’s magnetic anisotropy are shape anisotropy, magneto-crystalline anisotropy, and magneto-elastic anisotropy. Other sources of magnetic anisotropy include edge effects and induced anisotropy.

Shape anisotropy is a consequence of an object having directionally dependent dimensions. It affects nearly every object; only a sphere has no shape anisotropy. Shape anisotropy results from the interaction between a sample’s magnetization and its own dipolar field [3]. For example, it is easier to magnetize a needle along its long axis than its short axis because the dipolar field has much less material of opposing magnetization to pass through when magnetized along its long axis. However, when the needle is magnetized along its short axis the dipolar field has much more material of opposing magnetization to fight through, making it more difficult to magnetize in that direction. A sphere has no shape anisotropy, so it is equally difficult/easy to magnetize in all directions.

In general, it can be very complicated to calculate the interaction between a sample’s magnetization and its own dipolar field because the magnetization can vary throughout the sample. However, the situation is much simplified for ellipses of revolution because they have uniform magnetizations, therefore uniform demagnetization fields, $H_d$ (see [4, 5]). The internal demagnetization fields for prolate and oblate spheroids are parameterized by the demagnetization factor, $N$, such that $H_d = -NM$; where $N$ is a constant between 0 and 1, and $M$ is the magnetization. Shape anisotropy is simply
the difference in the magneto-static energy density between two magnetization directions, such that:

$$E_{ms} = \frac{1}{2} \mu_o (N_2 - N_1) M^2.$$  

Magneto-crystalline anisotropy results from the symmetry of a crystal structure through partial orbital quenching, with the spins, thus the magnetization, coupled to the preferred atomic orbitals via the spin-orbit interaction. In other words, magneto-crystalline anisotropy arises from an interaction between the crystalline electric field and spin-orbit coupling, and manifests itself by making certain crystallographic directions easier to magnetize than others. In a spherically symmetric structure all atomic orbitals are degenerate. As the symmetry is lowered from spherical, certain orbitals have preference over others based on energetics of the system. The magnetization of the transition metals is largely due to the spin of the electron. Because the electron spin, thus the magnetization, is tied to the orbital through the spin-orbit interaction, the symmetry of the system will result in the magnetization preferring certain crystal directions over others. Because the spin-orbit interaction of the valence electrons responsible for magnetism in the transition metals is very weak (of order $\approx 10 \mu$eV), theoretical modeling of the magneto-crystalline anisotropy is very difficult. This also means that very small energy differences (for example, from a modified orbital moment at an interface) can lead to entirely different magnetic properties of a sample. (I would also like to point out that most textbooks refer to the spin-orbit coupling as being very weak, like the approximately 10 $\mu$eV stated above. What they are referring to is either the spin-orbit coupling of light elements or more usually the spin-orbit coupling of the valence
electrons. I would like to distinguish this from the case of spin-orbit coupling in the core level electrons which can be quite large. For instance, the L$_{2,3}$-edges of Fe are spin-orbit split by about 13 eV!)

The contribution of the magneto-crystalline anisotropy to the energy density of a cubic crystal is:

$$E_{mc} = K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2(\alpha_1^2 \alpha_2^2 \alpha_3^2);$$

where the $K_i$'s are the cubic magneto-crystalline anisotropy constants, and the $\alpha_i$'s are the direction cosines of the magnetization with respect to the cubic crystalline axes. The most commonly reported parameter for describing magneto-crystalline anisotropy in cubic systems is the first order cubic anisotropy constant, $K_1$. When $K_1$ is positive, the <100> directions are easy to magnetize, and <111> hard. When $K_1$ is negative, <111> directions become the easy axes, and <100> hard. $K_2$ primarily modifies the anisotropy surface in the <111> directions.

Magneto-elastic anisotropy reflects the connection between the magnetic and elastic properties of a material. It results in strain dependent magnetic properties, as well as magnetostriction, which refers to the change in size of a material as it is magnetized. These properties come about by minimizing the free energy density of a material with respect to its strain to determine its equilibrium strain state. The strain dependent energy terms for a material are the elastic and magneto-elastic energy densities. The elastic energy density of a cubic crystal is:

$$E_{el} = \frac{1}{2} c_{11}(\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2) + c_{12}(\epsilon_1 \epsilon_2 + \epsilon_2 \epsilon_3 + \epsilon_3 \epsilon_1) + 2c_{44}(\epsilon_4^2 + \epsilon_5^2 + \epsilon_6^2);$$
where the $c_{ij}^{\text{el}}$ are the elastic stiffness constants, and the $\epsilon_i^{\text{el}}$ are the strains. An additional energy term of a cubic crystal due to magneto-elastic coupling is:

$$E_{me} = B_1 \left( (\alpha_1^2 - \frac{1}{3}) e_1 + (\alpha_2^2 - \frac{1}{3}) e_2 + (\alpha_3^2 - \frac{1}{3}) e_3 \right) + 2B_2 \alpha_1 \alpha_2 \epsilon_4 + \alpha_2 \alpha_3 \epsilon_5 + \alpha_3 \alpha_1 \epsilon_6;$$

where the $B_i^{\text{me}}$ are the magneto-elastic coupling coefficients, the $\alpha_i^{\text{me}}$ are again the direction cosines of the magnetization with respect to the cubic crystalline axes, and the $\epsilon_i^{\text{me}}$ are the strains. After performing the appropriate steps, it can be shown that the strain, $\frac{\partial l}{l}$, in direction $\beta$ for magnetization in direction $\alpha$ is given by [3, 6, 7]:

$$\frac{\partial l}{l} = -\frac{B_1}{c_{11}-c_{12}} \left( \alpha_1^2 \beta_1^2 + \alpha_2^2 \beta_2^2 + \alpha_3^2 \beta_3^2 - \frac{1}{3} \right) - \frac{B_2}{c_{44}} (\alpha_1 \alpha_2 \beta_1 \beta_2 + \alpha_2 \alpha_3 \beta_2 \beta_3 + \alpha_3 \alpha_1 \beta_3 \beta_1).$$

The previous equation also helps to define the magnetostrictive constants, $\lambda$. Magnetostriction is the change in length, or strain, produced by a magnetization in that direction, so:

$$\lambda_{100} = -\frac{2}{3} \left( \frac{B_1}{c_{11}-c_{12}} \right) \text{ and } \lambda_{111} = -\frac{1}{5} \left( \frac{B_2}{c_{44}} \right).$$

Furthermore, substituting the equilibrium strains determined earlier into the magneto-elastic energy density, and re-writing the magneto-elastic coupling coefficients in terms of the magnetostrictive constants reveals a contribution from magnetostriction to the magneto-crystalline anisotropy, $K_1$. If we write $K_1$ as $K + \Delta K$, it can be shown that [3, 6]:

$$\Delta K = \frac{9}{4} ((c_{11} - c_{12}) \lambda_{100}^2 - 2c_{44} \lambda_{111}^2).$$
Edge effects occur at boundaries of samples, where the change of symmetry influences the orientation of spins. Understanding edge effects is growing in importance as devices become smaller and their surface to volume ratio increases.

Induced anisotropy, in general, refers to any extrinsic factors which affect a sample’s magnetic anisotropy. Induced anisotropy may result from in-situ influences, such as growing a sample in a magnetic field or depositing a thin film with the source targeting the substrate at a grazing angle, or from post-growth processing of a sample, such as annealing. Incorporating induced anisotropy has become particularly relevant to manufacturers of hard disk drives consisting of magneto-resistive sandwiches.

At room temperature, iron has a saturation magnetization of about 1,700 emu/cm$^3$, $K_I \approx 4.8 \times 10^4$ J/m$^3$, and $B_I \approx -2.9 \times 10^6$ N/m$^2$. For a single crystal thin film (for a film $N_{out of plane} \approx 1$, $N_{in plane} \approx 0$) of Fe on MgO(001), using these bulk values and assuming a uniform bi-axial tensile strain of 4% (the lattice mismatch for Fe/MgO), the corresponding magnetic anisotropy energy terms are (at room temperature):

$$E_{ms} \approx 1.8 \times 10^6 \text{ J/m}^3, \ E_{mc} \approx 1 \times 10^4 \text{ J/m}^3, \text{ and } E_{me} \approx 2.3 \times 10^5 \text{ J/m}^3.$$

The results show that the magnetic anisotropy is dominated by shape anisotropy, which prefers an in-plane magnetization. The next most significant term is magneto-elastic coupling, which also prefers an in-plane magnetization. The magneto-crystalline anisotropy is the weakest of the three, and prefers any $<100>$ direction, including out of plane.

When trying to understand the influence of the magnetic anisotropy terms, it is often helpful to visualize the anisotropy contributions as energy surfaces. Shown in
Figure 2.2 is the energy surface corresponding to cubic anisotropy and a positive value for the first order cubic anisotropy constant, $K_1$. The distance from the origin to the object’s surface represents the energy density for the magnetization in that direction; i.e., a measure of the ease or difficulty in magnetizing the object in that direction. As can be seen in Fig. 2.2, a positive value of $K_1$ makes the \(<100>\) directions easy, the \(<111>\) direction hard, and \(<110>\) intermediate. A negative value of $K_1$, whose corresponding energy surface is depicted in Fig. 2.3, results in the \(<111>\) directions being easiest to magnetize, \(<100>\) hardest, and \(<110>\) again intermediate. The second order cubic anisotropy constant, $K_2$, modifies the cubic anisotropy surface along the cube diagonals. A positive value for $K_2$, as shown in Fig. 2.4, makes the \(<111>\) directions more difficult to magnetize, while a negative value for $K_2$ makes the \(<111>\) directions easier to magnetize, as shown in Fig. 2.5.

Along with cubic anisotropies, there are also uniaxial anisotropies. Some materials have a uniaxial magnetocrystalline anisotropy, such as Co. Other forms of uniaxial anisotropies can originate from shape or magneto-elastic contributions. Again, it can be helpful to visualize these energy surfaces, represented in Fig. 2.6 for a positive value of $K_u$, and in Fig. 2.7 for a negative value of $K_u$. Please note that these shapes were drawn using $E = K_u \cdot \sin^2(\theta)$, for $\theta$ ranging from 0 to pi. Regardless of the definitions concerning the sign of $K_u$, it is important to note that a uniaxial anisotropy will result in an easy axis and a hard plane (Fig. 2.6), or a hard axis and an easy plane (Fig. 2.7).
Reflection High Energy Electron Diffraction (RHEED)

The crystalline structures of the substrate, any buffer layer, and the Fe based alloys were monitored *in situ* by Reflection High Energy Electron Diffraction (RHEED). In RHEED, energetic electrons (I have used 10 keV and 15 keV electron guns) impinge on the sample at a very grazing angle (~1-3°), rendering this technique surface sensitive. The resulting RHEED patterns provide qualitative information regarding the quality of the crystal surfaces (‘smooth’ vs. ‘rough’), the ordering of the deposited material (single crystal vs. polycrystalline), and insight into the possible formation of potential crystal types. Though rarely done, quantitative information can also be derived from RHEED patterns.

Perhaps the most straightforward way to understand the RHEED patterns is to use the Ewald construction. In this scheme, the condition for diffraction is satisfied when the Ewald sphere intersects a reciprocal lattice point. This is simplified for scattering in 2-D, and for a surface the condition for diffraction is satisfied when the Ewald sphere intersects a reciprocal lattice *rod*. The surface forms reciprocal lattice rods, rather than points, due to the lack of periodicity in the third dimension.

Lattice constants can be derived from the RHEED patterns. From the RHEED geometry, I think the most general starting point for extracting lattice constants is the following expression:

$$\frac{D_{\text{recip}}}{R_{\text{Ewald}}} = \frac{D_{\text{screen}}}{D_{\text{chamber}}}$$
Here, \( D_{\text{recip}} \) is the reciprocal lattice spacing, \( R_{\text{Ewald}} \) is the radius of the Ewald sphere, \( D_{\text{screen}} \) is the distance between the diffraction spacings on the phosphorescent screen, and \( D_{\text{chamber}} \) is the distance in the growth chamber between the screen and the sample.

The distances between the sample to screen and diffraction spacings are measured. The reciprocal lattice spacing is constructed from knowledge of the real space structure. The radius of the Ewald sphere is inversely proportional to the wavelength of the electrons, with the wavelength being calculated from the energy of the electrons.

**Vibrating Sample Magnetometry (VSM)**

Hysteresis loops of the samples were acquired at 305K using the Vibrating Sample Magnetometer (VSM) option for a Quantum Design Physical Properties Measurement System (QDPPMS). The room temperature magnetic moments and coercivities of the samples, along with qualitative information regarding uniaxial and cubic anisotropy constants, were determined from these hysteresis loops.

The basic principle of operation is to oscillate the sample near a pickup coil. From Faraday’s Law, a changing magnetic flux through the pickup coil induces an emf in the coil which can then be related to the magnetic moment of the sample. In practice, the VSM has two counter wound coils (in the x-y plane), between which the sample oscillates (along the z axis), and all of which reside in a homogeneous, controllable magnetic field (applied along the z axis). The magnetic moment depends on the applied field, and in this way hysteresis loops can be created with respect to the applied field direction.
Samples were prepared for the VSM by gluing them to a quartz sample paddle using Duco® Cement. The quartz paddle is then attached to a rod which is driven by a linear motor. In order to obtain hysteresis loops along various crystallographic directions of a single sample, the sample had to be dismounted from the quartz holder, re-mounted at the appropriate angle, and re-inserted into the machine.

There are two important things to keep in mind concerning results obtained from VSM. First, the measured moment is due to any material that creates an inhomogeneous magnetic field between the pickup coils. We are only interested in the response of the ferromagnetic thin film to an applied field. However, the measured moment is a result of the combination of moments due to the ferromagnetic thin film, the substrate, the glue, and any capping or buffer layers. Fortunately, all of the extraneous material only contributes to a linear paramagnetic/diamagnetic effect. By collecting a hysteresis loop out to a large enough field (1T in this case), the linear contribution can be eliminated, resulting in a hysteresis loop intrinsic to the ferromagnetism of the thin film. Second, the actual magnetic moment of the sample must be corrected for the sample’s size. The magnetic moment measured by the VSM assumes a point-like particle. Therefore, the actual moments were determined by correcting for the length of the sample using Table 3-1 of the QDPPMS VSM option user’s manual. No correction was made for the width of the sample.
Rutherford Backscattering Spectrometry (RBS)

Rutherford Backscattering Spectrometry (RBS) was used to determine the compositions and thicknesses of the thin film samples made by MBE. In RBS, a beam of highly energetic (~MeV) light ions is directed at a target. Ions which get backscattered at a particular angle, thru a particular solid angle are detected and sorted according to their energy. The collected spectrum is essentially a number of detected backscattered ions as a function of energy of the detected ion. A target model is then constructed in an analysis simulation program and compared to the data to extract the target composition and thickness.

In RBS, scattering between incident ions and target nuclei is treated as an elastic, billiard ball type collision. An important descriptor for this type of collision is the kinematic factor, $K$, which is the ratio of the final, scattered ion energy, $E_f$, to the initial, incident ion energy, $E_i$, and depends only on the scattering angle and the masses of the incident ion and target nuclei. Mass resolution is enhanced by minimizing $K$, which occurs at a backscattering angle of 180°. However, due to practical considerations the detector is placed at as large a backscattering angle as possible without interfering with the incident beam of particles.

A portion of the backscattered ions is detected by a silicon surface barrier detector. In this type of detector, an energetic particle striking the detector creates electron-hole pairs along its penetration path, and the electron-hole pairs are converted into a voltage pulse. The strength, or height, of the voltage pulse is proportional to the number of electron-hole pairs created which is directly related to the energy of the
detected particle. The voltage pulses are binned according to their height, so the resulting RBS spectrum displays the number of voltage pulses versus voltage pulse strength, and is equivalent to the yield of backscattered ions versus the energy of the backscattered ion. The intensity of the peaks is determined by the scattering cross section, which for a fixed experimental arrangement depends only on the square of the charge of the target atoms’ nuclei. For more information on RBS and atomic collisions in general, see [8].

The analysis of the RBS spectra is accomplished using the backscattering simulation program SIMNRA [9]. SIMNRA allows the user to adjust the target parameters until a close match between the measured spectrum and the simulated spectrum is achieved. In the end, the analysis program provides a reliable count of the areal density of target atoms in units of atoms/cm$^2$. The computed areal number density is equal to the volume number density multiplied by the sample’s thickness, so the thickness of the sample can be determined if the density of the sample is known. In general, the density of the thin film samples is unknown. When I extract a thickness from the RBS analysis on my Fe alloy samples, I assume a bulk density for pure Fe films. As elements are alloyed into the Fe, the density is calculated by assuming that the volume stays the same but the mass changes according to the appropriate concentrations of elements.

The RBS data for my samples was collected in the Ion Beams Laboratory of Montana State University using incident $^4$He$^+$ ions of about 1.3 MeV generated from a 2 MV van de Graaff accelerator. The detector was positioned at a backscattering angle of 165°.
X-ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is a powerful synchrotron based technique that uses tunable, monochromatic photons to probe the electronic structure of a specific element of interest in a sample. The resulting spectrum is indicative of the chemical and structural environment of that element [10].

In XAS, the absorption of incident x-rays is measured as a function of x-ray energy. There is an enhanced, resonant absorption of x-rays when the x-ray energy closely matches a binding energy of the electrons in an atom, leading to what is known as an absorption edge. Elemental specificity results from the fact that binding energies are unique to each element. During a resonant absorption event in XAS, a core level electron is promoted to an unoccupied state just above the Fermi level. Therefore, the probability of this transition is governed not only by the dipole selection rules, but also by the density of states near the Fermi level. XAS creates a core hole, leaving the absorbing atom in an excited state. The atom relaxes by filling the core hole with an electron of lower binding energy, resulting in the emission of a fluorescence photon or an Auger electron. The overall process of XAS (the absorption of an x-ray, followed by the production of fluorescence photons and Auger electrons) provides experimentalists with several measurement options.

The direct method of determining the absorption of an x-ray is in transmission, where the intensities of the incident and transmitted x-rays are measured and related to one another by the Beer-Lambert law [11]. However, it is impractical to use this method on most of the samples that I have made because most of the samples were deposited on
substrates that are about 500 μm thick. (A series of Fe_{1-x}Ga_x samples was deposited onto 100 nm Si₃N₄ membranes.) Another method of measuring the absorption of x-rays, although not used by our group, is an indirect technique that takes advantage of the radiative decay of the core hole, and is termed Fluorescence Yield (FY) [12]. I have a few details to add in the succeeding paragraphs that are relevant to this technique, but for now would just like to mention that FY and transmission provide equivalent information [12, 13].

Perhaps the most commonly used detection scheme in XAS is another indirect method, known as Total Electron Yield (TEY), which also provides information equivalent to transmission [14, 15]. In TEY, all of the electrons emitted from a sample are measured. The sample is typically connected to a picoammeter and the current necessary to keep the sample neutral is measured. In order to correct for errors due to any variations in the flux of the incident x-rays, the sample current is normalized by the incident flux. The incident flux is measured using a gold mesh located just before the experimental chamber.

The TEY detection method might seem counterintuitive given that the resonant absorption of x-rays only promotes the core level electrons to near the Fermi level, not ejected from the sample. (I would like to point out that this description of XAS only applies to x-rays absorbed near the absorption edge, termed X-ray Absorption Near Edge Spectroscopy (XANES) or Near Edge X-ray Absorption Fine Structure (NEXAFS). The spectrum above the absorption edge, typically within several hundred eV of the edge, also contains useful information and is known as Extended X-ray Absorption Fine
Structure (EXAFS). In EXAFS, a bound core level electron receives enough energy from an incident x-ray to be ejected from the sample, which also contributes to the TEY signal. Our group focuses exclusively on XANES.) It is the de-excitation processes which provide many electrons, called secondary electrons, with enough energy to be freed from the sample. As previously mentioned, core hole decays produce fluorescence photons or Auger electrons. (These are competitive processes. Their relative yield depends on the excitation energy of the incident x-rays, and for core levels below a few keV, the probability of producing Auger electrons exceeds that of photons [16-18].) Both the incident x-rays and the fluorescence photons can produce Auger electrons. Very few of the Auger electrons escape without being inelastically scattered. Therefore, the signal in TEY is dominated by a cascade of secondary electrons generated by the inelastic scattering of Auger electrons [16, 19-21]. For a more in depth review of TEY, I found Physical Review B 37, 2450 to be a particularly thorough and insightful discussion [21].

All of the XAS spectra presented in this thesis were collected using TEY at the Advanced Light Source on either beamline 4.0.2 or 6.3.1.

**X-ray Magnetic Circular Dichroism (XMCD)**

In addition to VSM, magnetic information was acquired using X-ray Magnetic Circular Dichroism (XMCD). XMCD is an element specific technique with strong magnetic contrast that has been successfully employed to measure induced magnetic moments [22], identify element specific magnetic ordering [23], acquire element specific
magnetic hysteresis loops [24], and determine individually the orbital [25] and spin [26] contributions to the overall moment of a specific element [27].

In this technique, two XAS spectra are alternatively acquired using circularly polarized light collinear with the magnetization direction, with the magnetization direction of the sample reversed at each photon energy. An equivalent measurement can be performed using a fixed magnetization and reversing the photon helicity at each photon energy [28], but in practice it is usually advantageous to fix the photon helicity and switch the magnetization direction. The use of circularly polarized light preferentially promotes transitions of either up spin or down spin electrons to the corresponding empty states near the Fermi level. Because a magnetized material has more unfilled states near the Fermi level for one electron spin orientation than the other, the absorption is enhanced for the corresponding magnetization direction. The XMCD intensity is related to the difference between the two spectra, and directly proportional to the atomic magnetic moment [29].

In order for proper comparisons with theory to be made, the measured XMCD value must be corrected for incomplete polarization of the photons, incomplete alignment of the magnetization and photon propagation direction, incomplete magnetization, and the presence of any secondary non-ferromagnetic phase that contains the same element of interest.

All of the XMCD spectra presented in this thesis were collected at the Advanced Light Source on beamlines 4.0.2 or 6.3.1.
Figure 2.1: Representation of the Fe$_{1-x}$Ga$_x$ films discussed in this work. The Fe$_{1-x}$Ga$_x$ samples were deposited onto a ZnSe/GaAs(001) buffer layer, and directly onto the MgO(001) substrates.

Figure 2.2: Cubic anisotropy energy surface for a positive $K_1$. 

Figure 2.3: Cubic anisotropy energy surface for a negative $K_1$.

Figure 2.4: Cubic anisotropy energy surface for a positive $K_2$. 
Figure 2.5: Cubic anisotropy energy surface for a negative $K_2$.

Figure 2.6: Uniaxial anisotropy energy surface for a positive $K_u$. ($E = K_u \sin^2(\theta)$)
Figure 2.7: Uniaxial anisotropy energy surface for a negative $K_u$. ($E = K_u \cdot \sin^2(\theta)$)
References


CHAPTER THREE

PROPERTIES OF SINGLE CRYSTAL Fe$_{1-x}$Ga$_x$ THIN FILMS

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The purpose of this manuscript is to familiarize the reader with our motivation for pursuing studies of epitaxially pinned magnetostrictive materials, and to describe some introductory properties of the Fe$_{1-x}$Ga$_x$/ZnSe/GaAs(001) single crystal thin films. Because the properties of the films depend on how they are made and the surface onto which they are deposited, we also wished to describe the substrate preparation and thin film deposition processes in some detail. Anticipating more work to come on these materials, this also allows us to reference these processes without having to incorporate the descriptions into every upcoming paper.

**Abstract**

Molecular beam epitaxy (MBE) was used to deposit single crystal thin film Fe$_{1-x}$Ga$_x$ samples on ZnSe buffer layers grown on (001) and (110) single crystal GaAs substrates. The crystal quality of the GaAs surface and each deposited layer was monitored *in situ* by reflection high energy electron diffraction (RHEED). The magnetic properties of the samples were characterized by vibrating sample magnetometry (VSM) and ferromagnetic resonance (FMR). The FMR linewidth increases dramatically with Ga concentration, while the cubic anisotropy term $K_1$ switches sign.

**Introduction**

Since the initial demonstration by Prinz and Krebs [1], high quality single crystal Fe films have been grown on the semiconductors GaAs [1-7], ZnSe [8-12], Si [13], Ge [14], and the insulator MgO [15] by various deposition techniques. Of these, the
depositions of single crystal Fe on ZnSe by molecular beam epitaxy (MBE) have been shown to be of superior quality, primarily due to the lack of diffusion at the interface [12] and the sharpness of the ferromagnetic linewidth [8].

Alloys of Fe$_{1-x}$Ga$_x$ have generated recent interest because of their unique magnetostrictive and high tensile loading properties [16-26], and as possible spin polarized current injectors into GaAs-based light emitting diodes [27-29]. Of particular interest is the anisotropic behavior of the magneto-elastic constants as a function of Ga concentration, where $\lambda_{100}$ is observed to increase 10 fold while $\lambda_{111}$ remains small and changes sign [18]. Furthermore, at the appropriate alloy concentrations, these materials have the ability to induce large magnetostriction with a small applied magnetic field [22]. Pinning a highly magnetostrictive material to a substrate and applying a magnetic field will impart an anisotropic strain controllable by the magnetic field in the Fe$_{1-x}$Ga$_x$ film that may modify other magnetic properties of the film including magnetic anisotropy and magnetization dynamics. The role of magnetic anisotropies in single crystal films determines much of their desirable magnetic properties (for instance, see [30]). Therefore, the ability to control the magnetic anisotropy of a magnetic element would allow one to tailor its magnetic properties for a particular need.

**Experimental**

Single crystal thin films of Fe$_{1-x}$Ga$_x$ were deposited on ZnSe buffer layers grown on single crystal GaAs(001) and GaAs(110) substrates in an MBE system with a base pressure of $\sim$5x10$^{-11}$ Torr. The deposition procedure used here was similar to the
deposition procedures for single crystal Fe films grown on similar substrates as described by Prinz et al. [8]. The polished GaAs surface was prepared by first sonicating in acetone for 5 minutes, then rinsing in methanol, followed by rinsing in de-ionized water and drying with nitrogen. Carbon contaminants were further removed with a 45 minute ozone treatment. The last step in the cleaning process was to heat the substrates to 620 °C for 45 minutes in ultra high vacuum conditions to remove any surface oxides and other contaminants. It is important to note that the final bake out temperature, duration, and rate at which the substrate is heated all affect the quality of the GaAs surface. Our substrates were warmed to 200 °C uniformly over the course of ten minutes, then rapidly heated to 620 °C in the next three minutes.

After the thermal cleaning, an 800 Å epitaxial ZnSe buffer layer was deposited on the GaAs from a single source ZnSe crucible at a rate of 13 Å/min while the substrate was held at 175 °C. A UTI instruments quadrupole mass spectrometer (QMS) monitored the flux of the source materials. After the ZnSe deposition, the sample was allowed to cool to 150 °C and the growth of the iron-gallium film ensued from independent Fe and Ga Knudsen cell sources. The Fe$_{1-x}$Ga$_x$ thin films reported here are 210 - 250 Å thick, and in the composition range of $x = 0 - 0.36$, with deposition rates of 2.3 – 2.8 Å/min, as determined by Rutherford backscattering (RBS) of the films post growth. The multilayer was concluded by capping the Fe$_{1-x}$Ga$_x$ alloy films with 40 Å Al to protect the samples from the formation of any oxides. The capping layer was deposited at a substrate temperature of 100 °C and a deposition rate of 3.5 Å/min.
Results and Discussion

The crystal quality of the GaAs surface and each deposited layer was monitored in situ by reflection high energy electron diffraction (RHEED) using 10 keV electrons. Representative RHEED patterns of a GaAs(001) substrate and the subsequent depositions (except for the capping layer) are shown in Figure 3.1. (Deposition on the GaAs(110) surface results in similar quality RHEED patterns.) It is evident from the non-continuous lines that the clean GaAs surface is rough (Figure 3.1a), and that the epitaxially deposited ZnSe buffer layer significantly improves the surface quality (Figure 3.1b). This is to be expected, as the very close lattice match between GaAs ($a_o = 5.654$ Å) and ZnSe ($a_o = 5.668$ Å) facilitates the formation of the highly crystalline and flat ZnSe layer [8]. The high quality ZnSe layer allows for the deposition of a uniform, single crystal Fe$_{1-x}$Ga$_x$ thin film, and also physically separates signals from the Ga in the alloy film from any Ga signal in the buried GaAs substrate. The RHEED pattern for an Fe$_{0.89}$Ga$_{0.11}$ thin film is shown in Figure 3.1(c) and indicates a (2x1) surface reconstruction of a bcc single crystal grown in registry with the ZnSe surface. The bcc structure is stabilized because the lattice constant of bcc Fe$_{0.82}$Ga$_{0.18}$ ($a_o \sim 2.9$ Å) is close to half that of ZnSe [8, 31].

Magnetic characterization of the Fe$_{1-x}$Ga$_x$ thin films was carried out in part by taking hysteresis loops of the films using the vibrating sample magnetometer (VSM) option on a Quantum Design Physical Property Measurement System (PPMS). The magnetic field was applied in the plane of the samples along the primary high symmetry directions. Figure 3.2 highlights two fundamental magnetic properties of Fe$_{1-x}$Ga$_x$ thin films, namely the change in sign of the cubic magnetic anisotropy constant $K_1$, as
indicated by the migration of the easy axis from [100] for a 5% Ga film to [110] for a 
28% Ga film, and a growing uniaxial anisotropy as indicated by the increasing 
inequivalence between the [110] and [1-10] directions. These VSM results demonstrate 
that the magnetic anisotropy of FeGa thin films can be very different from the purely 
cubic nature of Fe.

The magnetic properties of the Fe$_{1-x}$Ga$_{x}$ thin films were further determined from 
Q-band (35 GHz) ferromagnetic resonance (FMR) measurements acquired at room 
temperature using a Bruker EleXsys 560 system. An FMR spectrum of a pure iron 
reference sample deposited in our MBE chamber using a GaAs(001) substrate is shown 
in Figure 3.3. The line shape is symmetric with a peak-to-peak linewidth of 43 Oe, and is 
fit very accurately by a Lorentzian derivative. The linewidth is found to depend strongly 
on the relative sample orientation with the applied field direction, and the values reported 
here are the minimum linewidths. The inset of Figure 3.3 shows the dependence of the 
minimum linewidth of the Fe$_{1-x}$Ga$_{x}$ samples on the concentration of Ga. It is evident that 
the damping in these samples, as indicated by the FMR linewidths [32-34], can be varied 
by nearly an order of magnitude by the substitutional incorporation of Ga. A strong 
angular dependence of the FMR linewidth suggests that the pinning of the magnetoelastic 
Fe$_{1-x}$Ga$_{x}$ thin films by the substrate and the subsequent generation of a magnetocrystalline 
strain energy can strongly modify dynamics in a non-isotropic manner within these films.
Summary

Thin film Fe$_{1-x}$Ga$_x$ single crystals of $x = 0 - 0.36$ were epitaxially deposited on ZnSe buffer layers grown on (001) and (110) single crystal GaAs substrates by MBE. RHEED indicates single crystal bcc growth in registry with the ZnSe surface. A measure of the quality of the samples is taken from the narrow FMR linewidth of only 43 Oe for the pure iron sample. The FMR linewidth increases with Ga concentration, to a value for a 36% Ga sample that is almost 10 times that of pure iron. VSM measurements indicate a change in sign of the cubic anisotropy constant $K_1$ as evidenced by the change in the easy axis from $<100>$ for a 5% Ga sample to $<110>$ for 28% Ga.

Acknowledgements

This research was supported by the Army Research Office under grant W911NF-08-1-0325 and the Office of Naval Research under grant N00014-03-1-0692. The authors wish to thank C. Key and W. Priyantha for assistance in the Ion Beam Laboratory at Montana State University, supported by DOI and DOE subcontract to PNNL, No. 3917 (413060-A) and NSF grant DMR0516603. We also wish to thank G. Malovichko of Montana State University for access to the Magnetic Resonance Laboratory and for useful discussions.
Figure 3.1: RHEED patterns of (a) the clean GaAs(001) surface, (b) the ZnSe(001) buffer layer, and (c) the bcc Fe$_{0.89}$Ga$_{0.11}$(001) film. The incident electron beam is along the in-plane direction shown.

Figure 3.2: Normalized hysteresis loops for a) (001) Fe$_{0.95}$Ga$_{0.05}$ and b) (001) Fe$_{0.72}$Ga$_{0.28}$ thin films. Note the change in easy axis from [100] for $x = 0.05$ (a) to [110] for $x = 0.28$ (b) and the growing inequivalence between the [110] and [1-10] axes.
Figure 3.3: The FMR spectrum from our pure Fe(001) reference sample taken at 35 GHz. The inset tracks the linewidth as a function of the Ga concentration.
References


CHAPTER FOUR

FERRIMAGNETIC ORDERING OF SINGLE CRYSTAL Fe$_{1-x}$Ga$_x$ THIN FILMS

Contribution of Authors and Co-Authors

Manuscript in Chapter 4

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Contributions: Made the samples to be studied, collected and analyzed the RBS data, captured the RHEED patterns, collected and analyzed the VSM data, collected the x-ray absorption and magnetic hysteresis data, and wrote the manuscript.

Co-Author: Elke Arenholz

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Contributions: Prepared the synchrotron beamlines for acquisition of x-ray absorption data, and helped train students on the use of the facility. Also provided useful discussions.

Co-Author: Yves U. Idzerda

Institution: Department of Physics, Montana State University, Bozeman, Montana 59717

Contributions: Obtained funding for the project, analyzed the x-ray absorption data, and edited the manuscript.

Additional Contributions: I would like to thank C. Key of the Ion Beams Laboratory for help in acquiring the RBS data. I would also like to thank R. Bollinger for help in acquiring the VSM data presented in Figure 2b.
The purpose of this manuscript is to provide more details on the magnetic properties of Fe$_{1-x}$Ga$_x$ single crystal thin films. In addition to samples deposited on ZnSe/GaAs(001) substrates, samples were also deposited onto MgO(001) substrates. Inspiration for depositions onto MgO substrates came while perusing a poster session at an MMM (Magnetism and Magnetic Materials) conference devoted to Fe/MgO/Fe magnetic tunnel junctions. It occurred to me that depositions of Fe$_{1-x}$Ga$_x$ onto MgO(001) might be a fruitful way to proceed. If nothing else, the mass separation of the elements would allow for a more accurate determination of the concentrations of the samples from RBS.

The magnetic properties of samples deposited onto ZnSe/GaAs(001) and MgO(001) substrates are compared and contrasted. Also, the cleaning treatment for the MgO substrates is described, and is very different than the GaAs procedure.

**Abstract**

Molecular beam epitaxy (MBE) was used to deposit body centered cubic single crystal Fe$_{1-x}$Ga$_x$ thin films on MgO(001) and ZnSe/GaAs(001) substrates well beyond the bulk stability concentration of about 28%. The crystal quality of the substrate surface and each deposited layer was monitored *in situ* by reflection high energy electron diffraction (RHEED). The magnetization of the samples as a function of Ga is found to decrease more rapidly than a simple dilution effect, and element specific X-ray magnetic circular dichroism (XMCD) ascribes this trend to a decrease in the Fe moment and an induced moment in the Ga that is anti-aligned to the Fe moment.
**Introduction**

Alloys of Fe$_{1-x}$Ga$_x$ have generated recent interest because of their unique magnetostrictive and high tensile loading properties [1-4] and as possible spin polarized current injectors into GaAs-based light emitting diodes [5]. Of particular interest is the anisotropic behavior of the elastic constants as a function of Ga concentration, where $\lambda_{100}$ is observed to increase 10 fold while $\lambda_{111}$ remains small and changes sign [3]. Furthermore, at the appropriate alloy concentrations, these materials have the ability to induce large magnetostriction with a small applied magnetic field [4]. Pinning a highly magnetostrictive material to a substrate and applying a magnetic field will impart an anisotropic stress, controllable by the magnetic field, in the Fe$_{1-x}$Ga$_x$ film that may modify other magnetic properties of the film including magnetic anisotropy and magnetization dynamics, particularly the rate of precessional energy loss (damping).

**Experimental**

Single crystal thin films (~17nm) of Fe$_{1-x}$Ga$_x$ (0<x<0.60) were deposited on MgO(001) and ZnSe(80nm)/GaAs(001) substrates by molecular beam epitaxy (MBE). Details of the Fe$_{1-x}$Ga$_x$ growth on the epitaxial ZnSe buffer layer have been previously reported [6]. The polished MgO surface was prepared by first sonicating in acetone for 5 minutes, then rinsing in methanol, followed by drying with flowing nitrogen. The typical third step in the triple clean process, the rinsing in de-ionized water, was skipped due to the hygroscopic nature of the substrate. The last step in the cleaning process was to heat
the substrates to 800°C for 2 minutes in ultra high vacuum conditions to remove any other surface contaminants, as this treatment promotes layer-by-layer growth [7].

The 17nm epitaxial Fe_{1-x}Ga_x thin films were deposited at a rate of 1.9Å/min from independent Fe and Ga Knudsen cell sources at a substrate temperature of 150°C. The samples were capped with 40Å of Al to protect the Fe_{1-x}Ga_x films from the formation of any oxides. The Al layer was deposited at a substrate temperature of 100°C and a deposition rate of 3.5Å/min. Film thicknesses and compositions were determined by Rutherford backscattering (RBS) and X-ray absorption spectroscopy (XAS). RBS spectra was collected at multiple angles to eliminate the effects of channeling.

**Results and Discussion**

The crystal quality of the MgO surface and each deposited layer was monitored *in situ* by reflection high energy electron diffraction (RHEED) using 10keV electrons. Representative RHEED patterns of the MgO(001) substrates and the Fe_{1-x}Ga_x(001) depositions are shown in Figure 4.1. The sharp and continuous streaks seen for the FeGa(001) layer indicate a bcc growth of high crystal quality. RHEED of the MgO(001) substrate shows a clean, single crystal surface, however the insulating nature of MgO makes obtaining a sharp RHEED pattern difficult, and the MgO RHEED images shown in Figure 4.1 have been digitally modified. The RHEED patterns and subsequent vibrating sample magnetometry (VSM) measurements confirm the epitaxial relationship of \(<110>\text{FeGa}(001) // <100>\text{MgO}(001) [8,9]\, and reveal a thin film crystal stability limit of about 45% Ga, higher than the bulk but less than growths on ZnSe/GaAs(001) [6].
Above that Ga concentration the RHEED patterns become increasingly complex, while the hysteresis loops display multi-phase behavior.

The substrate temperature of 150°C was chosen to optimize the crystal quality of the samples. Interestingly, RHEED images of pure Fe deposited on MgO(001) for a range of substrate temperatures look similar to those displayed in Figure 4.1, indicating quality single crystal surfaces; however, the internal structure of the films, probed by measuring the magnetic hysteresis of the samples, depends strongly on the deposition temperatures. As can be seen in Figure 4.2 (a), magnetic hysteresis loops taken along the hard axis (<110>) of the Fe films show much improved magnetic properties for the films deposited at a substrate temperature below 200°C. Figure 4.2 (b) shows hysteresis loops taken along the easy axis (<100>) of the Fe films deposited at 90°C and 150°C, and establishes 150°C as the preferred deposition temperature due to the much reduced coercivity. A similar improvement in coercivity is measured for the hard axis.

Magnetometry measurements can also be used to monitor the magnetic anisotropy of these films as a function of Ga concentration. Figure 4.3 shows in-plane magnetic hysteresis loops taken on 17nm (a) Fe$_{0.85}$Ga$_{0.15}$(001) and (b) Fe$_{0.735}$Ga$_{0.265}$(001) samples and highlights two fundamental magnetic properties of Fe$_{1-x}$Ga$_x$ thin films deposited on MgO(001): the purely cubic nature of the magnetic anisotropy, in contrast to an additional Ga dependent in-plane uniaxial anisotropy term for Fe$_{1-x}$Ga$_x$ thin films deposited on ZnSe(80nm)/GaAs(001) substrates [6], and the change in sign of the cubic magnetic anisotropy constant $K_1$, indicated by the exchange of the easy and hard axes as the Ga concentration is increased.
Although there is a difference in the behavior of the magnetic anisotropy and the limits of stability for Fe$_{1-x}$Ga$_x$ films deposited on MgO(001) and ZnSe/GaAs(001) substrates, the behavior of the magnetization and electronic structure are found to be independent of the underlying substrate. Vibrating sample magnetometry and Rutherford Backscattering (RBS) were used to determine the magnetizations of our films. The magnetizations for films grown on MgO(001) and ZnSe/GaAs(001) display an identical linear reduction with increasing Ga concentration up to about 23% Ga, then decreasing more rapidly at higher concentrations. The initial decline in the magnetization is slightly reduced from the effect of adding a non-magnetic element (Ga) to a magnetic host (Fe) of constant moment.

To further investigate the origin of the magnetization reduction, we performed X-ray magnetic circular dichroism (XMCD) at the Fe and Ga L$_{2,3}$-edges for growths on both substrates, acquired by sample total current yield with the films magnetically saturated at beamline 4.0.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory. XMCD is an element-specific technique using circular polarized photons and measuring the differential X-ray absorption spectra (XAS) between having the photon helicity and sample magnetization aligned and anti-aligned. The peak intensity of the XMCD signal is proportional to the elemental magnetic moment [10-12].

Figure 4.4 shows the aligned and anti-aligned Fe L$_{2,3}$ XAS of an Fe$_{0.80}$Ga$_{0.20}$ sample and the resultant dichroism spectra, taken at fixed photon helicity and reversing the magnetization of the sample at each photon energy. The inset tracks the Fe L$_3$ peak XMCD intensity as a function of Ga concentration, showing that the Fe XMCD decreases
gradually out to about 23% Ga, where the Fe moment is still about 95% that of pure Fe, and where the Fe XMCD intensity decreases more precipitously.

The trend of the Fe XMCD as a function of Ga resembles that of the magnetization, and does enhance the magnetization reduction. Additional information concerning the magnetization reduction can be found in the Ga moment behavior. Therefore, we performed XMCD measurements at the Ga L\textsubscript{2,3} edges for each film. By comparing to theoretical electronic structure calculations for FeGa alloys \cite{13,14} and other experimental Ga spectra for Mn-doped GaAs \cite{15}, we conclude that the presence and sign of the signal, as shown in Figure 4.5 (a) for Fe\textsubscript{0.83}Ga\textsubscript{0.17}, establishes an induced local moment in the Ga that is aligned anti-parallel to the Fe moment, in agreement with the theoretical calculations \cite{13-15}.

One remaining concern is that the Ga may have segregated into a secondary magnetic phase independent of the majority of the Fe. To eliminate this possibility, element specific magnetic hysteresis (MHY) loops of the Fe and Ga were separately acquired for the films. Element specific MHY loops are X-ray absorption intensities collected using fixed helicity circularly polarized light, at the photon energy corresponding to the peak L\textsubscript{3} XMCD intensity, while sweeping the magnetic field \cite{16, 17}. Figure 4.5 (b) shows normalized MHY loops for Fe and Ga in an Fe\textsubscript{0.78}Ga\textsubscript{0.22} film, along with the total moment VSM hysteresis data collected on the same sample. In all instances the field was applied along the <110> easy axis of the sample, and the results demonstrate that the Fe and Ga moments are inherently linked.
Summary

Molecular beam epitaxy (MBE) was used to deposit single crystal Fe\textsubscript{1-x}Ga\textsubscript{x} thin films on MgO(001) substrates up to 45% Ga concentration. These depositions show a purely cubic magnetic anisotropy, in contrast to an additional Ga dependent in-plane uniaxial anisotropy for Fe\textsubscript{1-x}Ga\textsubscript{x} thin films deposited on ZnSe(80nm)/GaAs(001) substrates, though a similar change in sign of the cubic magnetic anisotropy constant, $K_1$, is seen for both sets of samples. The decrease in the magnetization with the incorporation of Ga also shows a similar trend for the depositions on both substrates, and has been attributed to a decrease in the Fe moment along with an induced moment in the Ga that is anti-aligned to the Fe moment.

Acknowledgements

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Figure 4.1: RHEED patterns recorded at an electron energy of 10keV with the electron beam incident along the <100> and <110> crystallographic directions, respectively, of the bare MgO(001) substrate ((a) and (b)) and the 17nm Fe\textsubscript{0.82}Ga\textsubscript{0.18} film ((c) and (d)). The MgO RHEED images have been digitally modified to enhance the contrast.

Figure 4.2: (a) Normalized magnetic hysteresis loops for 17nm thin film Fe samples deposited on MgO(001) substrates for various substrate temperatures with the magnetic field applied along <110>. (b) Normalized hysteresis loops measured along Fe <100> for substrate deposition temperatures of 90°C and 150°C.
Figure 4.3: Normalized hysteresis loops taken along the indicated applied field directions for (a) Fe$_{0.85}$Ga$_{0.15}$ and (b) Fe$_{0.735}$Ga$_{0.265}$ thin films. Note the change in easy axis from $<100>$ for $x = 0.15$ (a) to $<110>$ for $x = 0.265$ (b) as well as the cubic symmetry.
Figure 4.4: The normalized Fe L$_{23}$ edge XAS and XMCD for Fe$_{0.80}$Ga$_{0.20}$ film at room temperature. Inset: The measured variation of the Fe L$_3$ XMCD peak intensity as a function of Ga concentration. The dashed line is a guide to the eye.
Figure 4.5: (a) Ga L\textsubscript{2,3} XMCD for 17 nm Fe\textsubscript{0.83}Ga\textsubscript{0.17} film. (b) Element specific magnetic hysteresis loops for Fe and Ga. Included is the total moment hysteresis loop as measured by VSM. The high degree of similarity between these loops shows that the Fe and Ga are strongly coupled and no secondary magnetic phase is present.
References


Contribution of Authors and Co-Authors

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Contributions: Obtained funding for the project and edited the manuscript.

Additional Contributions: I would like to thank C. Key of the Ion Beams Laboratory for help in acquiring the RBS data.
The purpose of this manuscript is to present information more focused on the magnetic anisotropy of Fe$_{1-x}$Ga$_x$ thin films deposited onto ZnSe/GaAs(001) and MgO(001) substrates, and to compare this behavior with that observed in bulk Fe$_{1-x}$Ga$_x$ samples. The magnetocrystalline anisotropy constant $K_1$ switches sign at a lower Ga concentration in single crystal thin films than it does in bulk, and an origin for this reduction is presented in terms of the epitaxial pinning. The uniaxial anisotropy present for depositions onto GaAs substrates is quantified for a range of Ga concentrations.

There also exist differences between predicted thin film and bulk magnetostrictive constants due to the difference in free parameters. Another purpose of this manuscript is to highlight this difference because the material properties required for robust magnetostriction in thin films differ from the requirements for bulk magnetostriction.

Abstract

The magnetic properties of single crystal Fe$_{1-x}$Ga$_x$ thin films deposited on ZnSe/GaAs(001) and MgO(001) substrates by molecular beam epitaxy (MBE) were investigated by vibrating sample magnetometry (VSM) and angle dependent ferromagnetic resonance (FMR). Depositions on the ZnSe buffer layer feature a strong uniaxial anisotropy that scales with the thin film magnetostriction of the samples, while depositions on MgO(001) substrates result in a purely cubic anisotropy whose cubic anisotropy constant, $K_1$, switches sign at a lower Ga concentration than is seen in bulk Fe$_{1-x}$Ga$_x$ samples.
Introduction

Pinning a highly magnetostrictive material to a substrate and applying a magnetic field will impart an anisotropic stress, controllable by the magnetic field, that may modify the magnetic properties of the film including the magnetic anisotropy and magnetization dynamics. Candidates for these pinned films are often found in materials that have had success in bulk applications. Alloys of bulk Fe$_{1-x}$Ga$_x$ have generated recent interest because of their unique magnetostrictive and high tensile loading properties [1,2]. Of particular interest is the large and anisotropic behavior of the magnetostriction as a function of Ga concentration, where $(3/2)\lambda_{100}$ features a double peak with values exceeding 400 ppm [1,2]. The first peak near $x = 0.19$ is due to a maximum in the magnetoelastic coupling constant, $B_1$, while the second peak around $x = 0.27$ is related to the softening of the elastic shear constant, $(c_{11} - c_{12})/2$, as a result of the crystal undergoing a bcc to bct transition [2-4]. Furthermore, it is possible to induce large magnetostriction in these materials with a small applied magnetic field [5]. In thin film form, the epitaxial pinning of this highly magnetostrictive material may generate large variations in the magnetic anisotropy with Ga concentration that can be compared to the bulk behavior.

Experimental

Single crystal Fe$_{1-x}$Ga$_x$ thin films (~17 nm) of various Ga concentrations were prepared on GaAs(001), with an 80 nm ZnSe buffer layer, and MgO(001) substrates by molecular beam epitaxy (MBE) as previously described [6, 7]. All samples were capped
with 4 nm Al to prevent the formation of any oxides. The thicknesses and concentrations of the films were determined by Rutherford backscattering (RBS). The magnetic properties of the samples were investigated using vibrating sample magnetometry (VSM) and angle dependent ferromagnetic resonance (FMR).

Results and Discussion

As shown by the magnetic hysteresis loops in Figure 5.1, Fe$_{1-x}$Ga$_x$ thin films grown on MgO(001) and ZnSe/GaAs(001) substrates have very different responses to an applied magnetic field. The Fe$_{0.85}$Ga$_{0.15}$ samples deposited on MgO have a purely cubic anisotropy (Figure 5.1 (a)), whereas samples deposited on the directionally bonded ZnSe buffer layer feature a strong uniaxial anisotropy (Figure 5.1 (b)).

The cubic and uniaxial anisotropies in our Fe$_{1-x}$Ga$_x$ samples deposited on ZnSe/GaAs(001) have been quantified by angle dependent ferromagnetic resonance (FMR) using the following form for the free energy density of a ferromagnetic thin film:

$$E = -M \cdot H + K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + 2\pi(M \cdot \hat{n})^2 + K_u^{eff} \sin^2(\alpha - \alpha_u) - K_n (M \cdot \hat{n}/M)^2. \quad (5.1)$$

The five terms are the Zeeman energy; the cubic magnetocrystalline anisotropy, with $\alpha_1$, $\alpha_2$, and $\alpha_3$ being the typical direction cosines; the demagnetization energy for a film; the in-plane uniaxial magnetic anisotropy, where $K_u^{eff}$ includes any effective contributions from the substrate, capping layer, magnetoelastic coupling, etc., and $\alpha$ being the angle of the magnetization in the film plane and $\alpha_u$ the angle of the easy axis of the in-plane uniaxial anisotropy (in this case along [110]); and lastly the large perpendicular anisotropy that forces the magnetization in the film plane. The magnetic anisotropies
were computed using the above expression for the free energy and the equations for the FMR condition [8], and the experimental data acquired at 34.6 GHz (Q-band) and fit for a pure iron film are shown in Figure 5.2 (a) using $K_{u}^{eff} = 8 \times 10^3 \text{erg/cm}^3$ and $K_1 = 5.2 \times 10^5 \text{erg/cm}^3$. The strength of the uniaxial anisotropy as a function of Ga concentration is shown in Figure 5.2 (b) and exhibits a single peak near $x = 0.20$.

The presence of a uniaxial magnetic anisotropy for Fe thin films deposited on zinc-blende surfaces has been well established [9-11], and has been attributed to magnetostriction and an anisotropic strain relaxation that has its origins in the directional bonding from the zinc-blende surface [11, 12]. The anisotropic strain relaxation creates an elastic shear strain, and through magnetoelastic coupling introduces an energy term that has a uniaxial angle dependence [12], which is accounted for in our $K_{u}^{eff}$ term. Epitaxial depositions on substrates lacking an anisotropic strain relaxation (e.g., MgO(001)) will lack a magnetoelastically coupled uniaxial magnetic anisotropy. However, for substrates compliant to an elastic shear strain, the effect of an enhanced magnetostriction is to enhance the anisotropy of the strain relaxation. Therefore, one would expect the strength of the uniaxial term to scale with the magnetostriction.

The trend of the FMR extracted uniaxial anisotropy as a function of Ga concentration, including the single peak near Fe$_{0.80}$Ga$_{0.20}$, is reminiscent of the magnetostriction of bulk Fe$_{1-x}$Ga$_x$ alloys, but an expected second peak in the uniaxial anisotropy is not observed in thin films. The absence of a second peak can be explained as follows. A first principles calculation of magnetostriction is determined by minimizing the free energy of a material with respect to the elastic constants. In bulk
form, all of the elastic constants are free parameters and the minimization results in the usual expression for the magnetostriction: \( \frac{3}{2} \lambda_{100}^{bulk} = -B_1/(c_{11} - c_{12}) \) \[13, 14\]. However, there is only one free parameter for any thin film epitaxially pinned to a substrate, and the resulting magnetostriction is: \( \frac{3}{2} \lambda_{100}^{film} = -B_1/c_{11} \) \[15\]. Bulk magnetoelastic and elastic constants are listed in Table 5.1 for several Ga concentrations (data taken from Ref. \[16\]), along with the corresponding thin film magnetostriction, assuming the bulk values remain valid. It is interesting to note that the strength of the uniaxial anisotropy seen in the Fe\(_{1-x}\)Ga\(_x\) thin films deposited on ZnSe/GaAs(001) substrates scales with the predicted thin film magnetostriction, most importantly that they both feature a single peak near a Ga concentration of 19%.

Comparing Figures 5.1 (a) and (c) reveals that the easy axis of magnetization has switched from \(<100>\) for Fe\(_{0.85}\)Ga\(_{0.15}\) to \(<110>\) for Fe\(_{0.825}\)Ga\(_{0.175}\) samples deposited on MgO substrates. This signals that the cubic anisotropy constant, \(K_1\), has become negative by 17.5% Ga, in contrast to bulk Fe\(_{1-x}\)Ga\(_x\) alloys where \(K_1\) switches sign near 20% Ga \[17\]. Also, the shape of the hysteresis loops for the Fe\(_{0.825}\)Ga\(_{0.175}\) sample and the low magnetic remanence of only 86% along the easy axis suggest that \(K_1\), though negative at this Ga concentration, likely has a very small value.

It is well established that for cubic crystals the effect of magnetostriction is to modify the cubic anisotropy, where \(K_1\) can be written as \((K + \Delta K)\) with \(\Delta K = ((c_{11} - c_{12})(3/2\lambda_{100})^2 - 2c_{44}(3/2\lambda_{111})^2)\) being the contribution from magnetostriction \[13, 14\]. For FeGa alloys this modification is to enhance \(K_1\), but the much reduced thin film values of \(\frac{3}{2} \lambda_{100}^{film}\) shown in Table 5.1 result in a negligible enhancement. However, the
magnetostriction for bulk Fe$_{0.83}$Ga$_{0.17}$ alloys results in an enhancement of about $4 \times 10^4$ erg/cm$^3$ [16], and can explain why $K_1$ remains positive for bulk Fe$_{0.825}$Ga$_{0.175}$ alloys, whereas in thin films $K_1$ has become negative by 17.5% Ga.

**Summary**

Depositions of Fe$_{1-x}$Ga$_x$ single crystal thin films grown on MgO(001) and ZnSe/GaAs(001) substrates have very different magnetic properties. The samples deposited on MgO have a purely cubic anisotropy, and it is found that the cubic anisotropy constant, $K_1$, switches sign at a lower Ga concentration than is seen in bulk Fe$_{1-x}$Ga$_x$. The enhancement of the bulk cubic anisotropy is attributed to the much larger bulk magnetostriction. Depositions on the ZnSe buffer layer feature a strong uniaxial anisotropy that scales with the thin film magnetostriction of the samples, and is attributed to an interplay between the magnetostriction and an anisotropic strain relaxation.

This work demonstrates that the effect of depositing magnetostrictive materials as thin films can be heavily influenced by the substrate. Depositions on substrates that allow anisotropic strain relaxation, such as GaAs and InAs [18], may feature a strong uniaxial anisotropy, while depositions on non-directionally bonded substrates can have a strongly modified cubic anisotropy. It is also important to highlight that the difference between the bulk and thin film magnetostriction values due to the bonding of the material to a substrate predicts that some highly magnetostrictive materials in the bulk, such as Fe$_{0.81}$Ga$_{0.19}$, may have significantly reduced values as thin film single crystals.
Conversely, there possibly exist materials whose bulk magnetostriction is insignificant but have dramatically enhanced magnetostriction in the form of single crystal thin films.

Acknowledgements

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Table 5.1: The magnetoelastic energy constants, elastic constants, and bulk and thin film magnetostriction values of Fe$_{1-x}$Ga$_x$ alloys for several Ga concentrations ($\lambda$ in ppm). Note the much reduced magnetostriction in thin film form, as well as the single peak. (data taken from [16])
Figures 5.1: Depositions of single crystal Fe$_{1-x}$Ga$_x$ thin films on ZnSe/GaAs(001) substrates (b) have a strong uniaxial anisotropy, while depositions on MgO(001) substrates ((a) and (c)) are purely cubic. The switching of the easy and hard axes between Fe$_{0.85}$Ga$_{0.15}$ (a) and Fe$_{0.825}$Ga$_{0.175}$ (c) indicates a change in sign of the cubic anisotropy constant, $K_1$. 
Figure 5.2: The reduced experimental Q-band FMR data for a 17nm pure iron film deposited on the ZnSe buffer layer (triangles) (a), and the effective uniaxial anisotropy of Fe$_{1-x}$Ga$_x$ samples deposited on ZnSe/GaAs(001) as a function of Ga concentration, which features a single peak near 20% Ga (b) ($K_u^{eff} = 0$ for depositions on MgO).
References


CHAPTER SIX

ELECTRONIC AND MAGNETIC STRUCTURE OF Fe$_{1-x}$Ga$_x$ THIN FILMS

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Contributions: Helped conceive the study and edited the manuscript.
The purpose of this manuscript is to further investigate the properties of Fe\(_{1-x}\)Ga\(_x\) thin films using x-ray absorption spectroscopy techniques. The use of XAS and XMCD allow us to determine the impact on the band structure of Fe as it is alloyed with Ga. We find that there is charge transfer from the Ga atoms to the Fe, and that an enhanced reduction of the Fe moment coincides with the filling of the majority band.

A related technique, x-ray magnetic linear dichroism (XMLD), is used to measure anisotropic charge distributions of a magnetic nature. We wished to apply this technique because it is a measure of the anisotropic spin-orbit interaction, which is a measure of the magnetocrystalline anisotropy. Furthermore, G. van der Laan and E. Arenholz are essentially the theoretical and experimental pioneers of this technique, and we wished to use their expertise to provide insight into our samples. Although some theoretical details concerning the absolute magnitude of the magnetocrystalline anisotropy derived from such measurements are yet to be ironed out, a qualitative analysis is performed. The use of XMLD also reveals some surprising structural information about our samples. We find that our samples are multiphase crystals, and that the fraction of the D0\(_3\) phase increases with increasing Ga content.

Abstract

The electronic as well as magnetic properties of Fe\(_{1-x}\)Ga\(_x\) films were studied by soft x-ray measurements. Using x-ray magnetic circular dichroism (XMCD) the Fe majority spin band was found to be completely filled for \(x \approx 0.3\). With further enhanced Ga content, the Fe moment as well as the angular dependence of the x-ray magnetic
linear dichroism decrease strongly, which we attribute to the formation of D0₃ precipitates. Moreover, the magnetocrystalline anisotropy drops significantly.

**Introduction**

In a magnetic material, the spin-orbit interaction, a purely relativistic effect between the electron spin and its orbital moment, couples the magnetic moments to the lattice. It is at the electronic origin of magnetocrystalline anisotropy, i.e., the energy associated with the (re)orientation of the magnetization relative to the lattice, as well as magnetostriction referring to the deformation of a magnetic material when subjected to an external magnetic field. In magnetostrictive thin films, the adaptation to new dimensions is inhibited by bonding to the substrate and the application of a magnetic field in the film plane does not result in an expansion or contraction along the field direction. Instead a magnetoelastic stress is created that leads to a change in magnetocrystalline anisotropy.

Here we study the magnetic as well as electronic properties of Fe₁₋ₓGaₓ films deposited on GaAs(001). In bulk form, Fe₁₋ₓGaₓ exhibits extraordinary magnetostrictive properties as function of composition implying a strong dependence of the underlying spin-orbit coupling on x [1-3]. Fe₁₋ₓGaₓ thin films [4-6] are therefore an ideal candidate to study the composition dependence of the magnetic anisotropy and to correlate this with its electronic structure.
Using soft x-ray absorption spectroscopy, we find that the magnetic as well as electronic properties of Fe\(_{1-x}\)Ga\(_x\) films change significantly for Fe content near \(x=0.3\). The holes in the Fe majority-spin band disappear with increasing Ga content and the Fe majority-spin band is completely filled for \(x \approx 0.3\). With further enhanced Ga content, the Fe moment as well as the x-ray magnetic linear dichroism (XMLD) angular dependence decrease strongly, which we attribute to the formation of D0\(_3\) precipitates.

For this study, 20 nm single crystalline Fe\(_{1-x}\)Ga\(_x\) thin films, \(0 \leq x \leq 0.6\), were deposited by molecular beam epitaxy as described in Ref. 5. X-ray absorption (XA) spectra were measured at ALS beamline 4.0.2 at ambient temperature with either 90% circularly or 100% linearly polarized x rays in total electron yield mode by monitoring the sample drain current. External fields of 0.5 T were provided by an eightpole electromagnet [7]. X-ray magnetic circular dichroism (XMCD) was derived from XA spectra measured with the magnetic field collinearly aligned to the incident x-ray beam, which in turn impinged at an angle of 30° to the sample surface. XMLD spectra are obtained as the difference between XA spectra in external fields parallel and perpendicular to the x-ray polarization in normal incidence geometry.

**Results and Discussion**

Figure 6.1(a) shows the average of XA spectra obtained from Fe\(_{1-x}\)Ga\(_x\) films with \(0 \leq x \leq 0.6\). In the concentration dependence of the Fe \(L_{3,2}\) XMCD shown in Fig. 6.1(b), we can distinguish two regions exhibiting distinct magnetic characteristics. For \(x \leq 0.28\), the
Fe $L_3$ XMCD signal—and with that to a good approximation the average Fe magnetic moment—is nearly constant and starts at 55% of the Fe $L_3$ XA intensity in agreement with previous results for Fe films [8]. For $x \geq 0.3$, the Fe $L_3$ XMCD decreases almost linearly with Fe concentration. It is generally accepted that hybridization of the Fe and Ga states reduces the Fe magnetic moment [9-12]. Detailed calculations aimed at determining the concentration dependence of the Fe moment in different lattice structures and sites have been performed. However, there are significant variations in the results suggesting that an estimate of the average Fe moment as a function of Fe concentration using theory is not unambiguous at present.

The inset in Fig. 6.1(b) shows the spectral features at the high-photon-energy side of the Fe $L_3$ edge for $x \leq 0.3$. For the pure Fe film, a small positive XMCD feature is observed at $\sim 711$ eV, which can be ascribed to transitions from the $2p$ core level to the unoccupied majority-spin band [13,14]. The main negative Fe XMCD $L_3$ feature is due to transitions to the unoccupied minority-spin band. The intensity of the XMCD feature at $\sim 711$ eV reduces with increasing Ga content, i.e., the majority-spin band is gradually filled. For $x \approx 0.3$, the Fe $L_3$ XMCD becomes fully negative indicating that the majority-spin band is completely filled. We also see a shift in both the XA and XMCD $L_3$ peak energy to lower photon energy (inset Fig. 6.1(a)) consistent with band filling argument.

The occupation of majority-spin states is closely correlated with the magnetostriction. Berger [15] showed that the magnetoelastic energy—and hence the magnetostriction—is determined by the electronic states located near the Fermi level, $E_F$, and that it is directly proportional to the spin-orbit splitting. Consequently, the
magnetostriction changes sign, i.e., zero magnetostriction is observed if $E_f$ is located between the spin-orbit split bands. Filling of the majority-spin band also affects the magnetocrystalline anisotropy energy (MAE) [16,17]. Using second-order perturbation theory, i.e., considering the spin-orbit coupling to be small compared to energy differences caused by the crystalline electric field (CEF) and exchange interaction, one can distinguish two contributions to the MAE; those due to spin-conserved terms and those arising from spin-flip processes. An incompletely filled majority-spin band allows low-energy spin-flip excitations near $E_f$. When the majority-spin band is full, however, such excitations require an energy in the order of the exchange interaction. Hence, unoccupied majority-spin states enable spin-flip excitations, thereby changing the MAE. While the spin-flip contributions are usually not the dominant contribution in the total MAE, they will lead to a change in MAE [12,16,17].

Previous studies on transition metal and lanthanide oxide thin films [18–21] have shown that the angular dependence of the XMLD provides a sensitive measure of the CEF symmetry and strength as well as magnetic and electronic characteristics of the absorber. We determined the Fe $L_{3,2}$ XMLD spectra, $I_{\text{xmld}}(\phi)$, for varying angle $\phi$ between the linear x-ray polarization, $E$, and the [100] lattice direction of Fe$_{0.8}$Ga$_{0.2}$. The XMLD spectrum is defined here as the difference between XA spectra with $H$ parallel and perpendicular to $E$, i.e., at angles $\phi$ and $\phi+90^\circ$ to the [100] direction:

$$I_{\text{xmld}}(\phi) = I_{\text{xa}}(H_{\phi},E_{\phi}) - I_{\text{xa}}(H_{\phi+90},E_{\phi}).$$  \hspace{1cm} (6.1)

The averaged Fe XA signal is shown in Fig. 6.2(a) and the XMLD angular dependence for $0^\circ \leq \phi \leq 45^\circ$ in Fig. 6.2(b). A pronounced variation in the Fe XMLD signal
with \( \varphi \) is observed. In lattices with cubic symmetry, the angular dependent XMLD can be very well described by a linear combination of two fundamental spectra accounting for the XA photon energy dependence in selected orientations [19-21]. Their relative contributions are determined by the symmetry of the experimental geometry. In the (001) plane, the XMLD angular dependence is described by:

\[
I_{\text{xmld}}(\varphi) = \frac{1}{2}[(I_0 + I_{45}) + (I_0 - I_{45})\cos4\varphi],
\]

where \( I_0 \) and \( I_{45} \) refer to the XMLD spectra obtained with the x-ray polarization \( E \) at 0° and 45° to the [100] direction, i.e., along the [100] and [110] directions, respectively. Equation (6.2) allows us to separate the angular-dependent XMLD into an angle-independent or isotropic contribution to the XMLD signal, \((1/2)(I_0+I_{45})\), and an angular part or anisotropic contribution, \((1/2)(I_0-I_{45})\), which gives the difference in the XMLD along two principal directions. Figure 6.2(c) shows the experimental results for \((1/2)(I_0+I_{45})\) and \((1/2)(I_0-I_{45})\). Applying Eq. (6.2) and using the results from Fig. 6.2(c), leads to the calculated spectra shown in direct comparison with the experimental data in Fig. 6.2(b). The agreement is excellent indicating that the approach of separating the anisotropy due to CEF from the detailed electronic structure of the excited atom originally developed for transition-metal oxides is also valid for itinerant electron systems such as Fe and Fe\(_{1-x}\)Ga\(_x\).

We determined the concentration dependence of the Fe XMLD spectra \( I_0 \) and \( I_{45} \) for \( 0 \leq x \leq 0.6 \). The experimental results for \((1/2)(I_0+I_{45})\) and \((1/2)(I_0-I_{45})\) are shown in Fig. 6.3(a). Both contributions decrease significantly with increasing Ga content. The XMLD signal was shown to be proportional to the square of the magnetic moment [18].
To account for the observed change in Fe moment with Ga content (see Fig. 6.1(b)), we normalized the XMLD signals to the square of the Fe $L_3$ XMCD signal that to good approximation is a measure for the Fe magnetic moment. The results are shown in Fig. 6.3(b) for the isotropic XMLD contribution and we find a constant $(1/2)(I_0+I_{45})$ signal for the entire concentration range. We conclude that the magnitude of the isotropic XMLD signal $(1/2)(I_0+I_{45})$ is solely determined by the magnitude of the Fe magnetic moment. Small changes in the spectral shape are attributed to changes in the detailed electronic structure also seen in the Fe XMCD as discussed above. Using the same normalization for the angle-dependent signal $(1/2)(I_0-I_{45})$ leads to a still strongly decreasing XMLD signal with decreasing Fe concentration. As shown in Fig. 6.3(c) normalizing $(1/2)(I_0-I_{45})$ to the Fe concentration, i.e., scaling it by $(1-x)^{-1}$ as well as the square of the average Fe moment, leads to a constant anisotropic XMLD signal for $x\leq 0.28$ as well as for $x\geq 0.3$. This indicates that additional factors beyond the concentration dependence of the Fe moment play a role in determining the XMLD angular dependence. One possible explanation is that for $x\geq 0.3$ a volume fraction of the Fe$_{1-x}$Ga$_x$ film consists of a phase where the Fe XMLD signal does not exhibit an angular dependence, i.e., is highly isotropic. The volume fraction of Fe atoms in this phase increases with decreasing Fe content to account for the decrease in $(1/2)(I_0-I_{45})$ with $x$.

In case of a completely disordered or isotropic system, no angular dependence is expected, i.e., $I_0-I_{45}=0$. Our reflection high-energy electron diffraction (RHEED) measurements during film deposition indicate that the structural quality of the Fe$_{1-x}$Ga$_x$
does not dependent significantly on the Fe concentration, i.e., structural disorder cannot account for the reduction in $(1/2)(I_0-I_{45})$ with increasing Ga content.

In epitaxial EuO thin films, the Eu $M_{5,4}$ XMLD shows only a very small angular dependence, which could be explained by the nearly perfect spherical shape of the half filled Eu $4f$ shell [21]. For Fe$_{1-x}$Ga$_x$, Lei et al. [10] calculated the anisotropy of the Fe $3d$ orbitals for D0$_3$, B2-like, and L1$_2$ lattice structures [11]. They showed that the D0$_3$ structure has an almost isotropic $3d$ charge density and that there is hardly any difference between the two Fe sites in this lattice structure. By contrast, a pronounced anisotropy was found for the other two phases. This suggests that Fe in local D0$_3$ environments could be responsible for the reduction in the Fe XMLD angular dependence with decreasing Fe concentration. Moreover, van’t Erve et al. [4] concluded from RHEED measurements during deposition of Fe$_{1-x}$Ga$_x$ films on AlGaAs/GaAs quantum-well structures that the D0$_3$ phase is present for $x\geq 0.25$. These results lead us to conclude that with increasing Ga content the D0$_3$ phase develops and the fraction of Fe in these D0$_3$ precipitates increases with decreasing Fe concentration. This accounts for the change in the angular dependent XMLD with Fe concentration 1–$x$.

Having discussed concentration dependence of the magnitude of the XMLD signal we now consider the variation in the Fe XMLD spectral shape with Ga concentration. The XMLD spectral shape is influenced by the CEF symmetry and strength as well as the magnetic and electronic characteristics of the absorber. In case of Fe$_{1-x}$Ga$_x$ alloys, the CEF created by the nearest neighbors of the Fe absorber is not expected to be very sensitive to change in the elemental species between Fe and Ga for
identical structural parameters. As a consequence the spectral shape of the Fe XMLD signal is expected to be the same for bcc Fe and a disordered $\text{Fe}_{1-x}\text{Ga}_x$ alloy with the same bcc structure, i.e., $\text{Fe}_{1-x}\text{Ga}_x$ in A2 phase. The experiments show that the spectral shape of $(1/2)(I_0-I_{45})$ is the same for all Ga concentrations $x$, i.e., identical to pure bcc-Fe ($x=0$). Therefore, we attribute the $(1/2)(I_0-I_{45})$ signal to Fe atoms in the A2 phase.

To determine the impact of the concentration dependence of the Fe electronic structure in $\text{Fe}_{1-x}\text{Ga}_x$ films on their magnetic anisotropy, we applied the XMLD sum rules to the experimental results for $(1/2)(I_0+I_{45})$ and $(1/2)(I_0-I_{45})$ [22]. The integrated intensities, $A_{L3}$ and $A_{L2}$ of the Fe $L_3$ and $L_2$ XMLD signal, respectively, were determined using the experimental results for $(1/2)(I_0+I_{45})$ and $(1/2)(I_0-I_{45})$ shown in Fig. 6.3(a). The integrated signal $A=A_{L3}-2A_{L2}$ is related via the sum rule to the anisotropic spin-orbit interaction, which in turn is a measure of the MAE. Previous experiments suggest that it is not straightforward to directly relate the integrated signals to the absolute value of the MAE [23]. However, here we measure a material where the composition gradually changes and therefore the trend in the MAE should be qualitatively correct. Moreover, by evaluating the ratio $R=A_{10-145}/A_{10+145}$ we eliminate the impact of factors such as degree of magnetization and polarization, $3d$ localization, number of holes, etc. The dimensionless quantity $R$ is a measure for the magnetic anisotropy between the [100] and [110] directions. The results shown in Fig. 6.3(d) indicate that the MAE is approximately constant for $x\leq0.28$ and abruptly drops by a factor of two with further decreasing Fe concentration. The MAE and magnetostriction are sensitive properties of the crystal structure, band filling, and $E_f$ position. Our results indicate that for $x>0.28$, i.e., for
concentrations with the majority-spin band filled, the MAE is much reduced. As mentioned above, spin-flips inhibited by the filled majority-spin band are a possible origin of the reduced MAE, however, they do not necessarily form the main cause.

Summary

We summarize that the magnetic as well as electronic properties of Fe$_{1-x}$Ga$_x$ films change significantly for Fe content near $x=0.3$. The holes in the Fe majority-spin band disappear with increasing Ga content and the Fe majority-spin band is completely filled for $x \approx 0.3$. With further enhanced Ga content, the Fe moment as well as the XMLD angular dependence decrease strongly, which we attribute to the formation of D0$_3$ precipitates. In bulk Fe$_{1-x}$Ga$_x$, the formation of D0$_3$ precipitates has been observed near $x=0.19$ and is associated with a maximum in magnetostriction. A second maximum of the magnetostriction is observed near $x=0.28$ attributed to a softening of the shear modulus, coinciding with our observation of Fe majority-spin band filling. Further experimental and theoretical studies are certainly warranted to explain the differences in structure, magnetic, and electronic between bulk and thin film Fe$_{1-x}$Ga$_x$ samples.

Acknowledgements

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Figure 6.1: Fe $L_{3,2}$ XA and XMCD spectra for Fe$_{1-x}$Ga$_x$. (a) Average XA spectrum. Inset: change in photon energy of the Fe $L_3$ edge derived from the XA (solid symbols) and XMCD spectra (open symbols). (b) XMCD spectra for varying Ga concentrations, 0 ≤ x ≤ 0.6. Lighter colored lines correspond to data obtained from samples with higher Ga concentration. Top inset: Fe XMCD spectra near 711 eV for x ≤ 0.28. Bottom inset: concentration dependence of the Fe $L_3$ XMCD signal.
Figure 6.2: Fe $L_{3,2}$ XA and XMLD spectra for Fe$_{0.8}$Ga$_{0.2}$. (a) XA spectrum. (b) XMLD spectra for varying angle $\phi$ between the x-ray polarization and the [100] direction. The (black) symbols indicate the experimental data while the (red) lines represent the results of the model discussed in the text. (c) Derived XMLD spectra $(1/2)(I_0+I_{45})$ and $(1/2)(I_0-I_{45})$, where $I_0$ and $I_{45}$ refer to the XMLD spectra obtained for $\phi=0^\circ$ and $\phi=45^\circ$, respectively.
Figure 6.3: Concentration dependence of the Fe $L_{3,2}$ XMLD signal in $\text{Fe}_{1-x}\text{Ga}_x$. The results for $x=0$ are shown in black while lighter colored lines correspond to data obtained from samples with higher Ga concentration. (a) $\frac{1}{2}(I_0 + I_{45})$ (top) and $\frac{1}{2}(I_0 - I_{45})$ (bottom) for $x \leq 0.28$. (b) $\frac{1}{2}(I_0 + I_{45})$ normalized to the Fe $L_3$ XMCD signal for $x \leq 0.3$ (top) and for $x \geq 0.3$ (bottom). (c) $\frac{1}{2}(I_0 - I_{45})$ normalized to the square of the Fe $L_3$ XMCD signal and the Fe concentration, $1-x$, for $x \leq 0.28$ (top) and for $x \geq 0.3$ (bottom). (d) Concentration dependence of the ratio $R = \frac{A_{10-145}}{A_{10+145}}$, see text.
References


CHAPTER SEVEN

MAGNETIC AND STRUCTURAL PROPERTIES OF SINGLE CRYSTAL Fe_{1-x}Zn_x THIN FILMS

Contribution of Authors and Co-Authors

Manuscript in Chapter 7

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Additional Contributions: I would like to thank C. Key and N. Childs of the Ion Beams Laboratory for help in acquiring the RBS data.
The purpose of this manuscript is to report the properties of Fe$_{1-x}$Zn$_x$ thin films made by MBE. This work was inspired by recent theoretical predictions that single crystal Fe$_{1-x}$Zn$_x$ alloys should have a slightly enhanced magnetostriction compared to their Fe$_{1-x}$Ga$_x$ counterparts. However, single crystal Fe$_{1-x}$Zn$_x$ alloys have not been made in the bulk, primarily due to the large vapor pressure difference between Fe and Zn. We reasoned that MBE might be suitable for realizing single crystal Fe$_{1-x}$Zn$_x$ thin films, and our efforts are described.

**Abstract**

Single crystal Fe$_{1-x}$Zn$_x$ thin films ($x = 0 – 0.85$) have been prepared on MgO(001) substrates by molecular beam epitaxy. Reflection high energy electron diffraction monitored the crystal quality of the films *in situ*, and reveals a phase transition of the crystal structure from the $\alpha$-Fe phase to primarily the $\Gamma$ phase near a Zn concentration of 40%. Vibrating sample magnetometry shows a lack of any uniaxial anisotropy and a change in sign of the first order cubic magnetic anisotropy constant, $K_1$, at a Zn concentration near 40%. The Fe$_{1-x}$Zn$_x$ samples maintain the high easy axis remanence and low coercivity of pure iron out to about 40% Zn, where the samples show a dramatic increase in the coercivity, at least in part due to an increased roughness of the films, as the formation of the $\Gamma$ phase becomes preferred.
Introduction

It has been important to understand the microstructures formed during the galvannealing process in order to optimize the corrosion resistance of Zn coated steel, particularly for use in the automotive and roofing industries [1-3]. Apart from that motivation, Fe_{1-x}Zn_x alloys have generated recent interest for their magnetostrictive properties, as they are predicted to exhibit a magnetostriction comparable to the highly magnetostrictive Fe_{1-x}Ga_x alloys [4]. But the synthesis of bulk Fe_{1-x}Zn_x samples proves difficult due to the high vapor pressure of Zn and the large difference in melting points of the constituent elements. However, the process of depositing thin films of Fe_{1-x}Zn_x alloys is well suited for molecular beam epitaxy (MBE) because thin film deposition is kinematically limited and often performed far from thermodynamic equilibrium. When a highly magnetostrictive material is atomically pinned to a substrate as an epitaxial thin film, the application of a magnetic field will generate a stress in the film which modifies the magnetic anisotropy of the material and allows for control of its magnetization dynamics.

Experimental

Single crystal thin films of Fe_{1-x}Zn_x have been prepared on MgO(001) substrates using an MBE system with a base pressure of 2x10^{-10} Torr. The procedure to effectively prepare the substrates for deposition has been previously described [5]. The samples were deposited at a substrate temperature of 60 °C, are 20 – 22 nm thick with compositions ranging from x = 0 – 0.85, and deposition rates of 2.2 – 2.5 Å/min. The
chamber pressure during growth was typically 3-5x10^{-9} Torr. The growth was concluded by capping the Fe_{1-x}Zn_{x} layer with 30 Å of Al, also at a substrate temperature of 60 °C, to protect the samples from the formation of oxides or any other contaminants.

A UTI instruments quadrupole mass spectrometer was used to monitor the flux of the source materials, while the film thicknesses and compositions were determined by Rutherford backscattering and X-ray absorption spectroscopy (XAS).

Results and Discussion

The crystal quality of the MgO and Fe_{1-x}Zn_{x} surfaces was monitored in-situ by reflection high energy electron diffraction (RHEED) using a 10 kV electron gun source. The RHEED images shown in Figure 7.1 reveal a gradual crystal structure transition from the body centered cubic (bcc) α-Fe phase at low Zn concentrations (x<0.35) to primarily the Γ phase at Zn concentrations between 40-70%. Single crystal growths could not be stabilized above about 85% Zn.

RHEED of the pure Fe depositions, as seen in Figs. 7.1 (a, b), show a single crystal film, but the somewhat diffuse and non-continuous nature of the streaks indicate a slightly rough crystal surface. (The crystal quality of pure Fe can be improved by raising the substrate temperature to 150 °C (see reference [5] for more details), however the incorporation of Zn in Fe at that temperature is low due to the high vapor pressure of the Zn.) The incorporation of Zn into the Fe lattice appears to immediately improve the crystal quality, possibly by enhancing the mobility of the Fe, as shown by the continuous and sharp streaks seen in Figs. 7.1 (c, d). It is important to note the appearance of some
spots in Figs. 7.1 (c, d), particularly the spots located 1/3 of the way between the 1st and 2nd order streaks in Fig. 7.1 (d). Figs. 7.1 (e, f) are representative of the RHEED patterns seen for Fe_{1-x}Zn_x thin films with Zn concentrations between about 40-65%, and look very different to the RHEED patterns seen at lower concentrations, indicating that a structural phase transition has taken place.

The Fe_{1-x}Zn_x phase diagram [6, 7] is relatively straightforward to understand, with a striking feature being that mixed phases are present for much of its extent. At the temperatures at which the samples were deposited, a homogeneous α-Fe phase (a_{Fe}=2.866 Å for Fe) exists for only very low Zn concentrations. Then there is a large region of Zn incorporation where the α phase co-exists with the Γ (γ-brass) phase (a_0=8.932 Å, ≈3 a_{Fe}) bcc type structure, until a homogeneous Γ phase is reached at a Zn concentration near 70%. Above this concentration, the Γ phase gradually converts into the Γ_1 phase (a_1=17.963 Å, ≈6 a_{Fe}) fcc structure until a homogeneous Γ_1 phase occurs near 77% Zn. Additional Zn incorporation prefers the hexagonal and monoclinic crystal structures.

The importance of understanding the Fe_{1-x}Zn_x phases that can occur lies in the epitaxial relationships between these phases and the MgO substrate. The substrates used in this study have a lattice constant of 4.216 Å, so half of the diagonal leads to a lattice mismatch of +4.0% for a pure iron film. Surprisingly, the lattice mismatches for the Γ and Γ_1 phases are only +0.1% and -0.4%, respectively. Now the RHEED patterns can be more readily understood in the context of the formation of these various cubic phases. For pure iron and very low Zn concentrations, a homogeneous α-Fe bcc phase is formed (Figs. 7.1 (a, b)). At slightly higher Zn concentrations, the α phase is preferred, but some
Γ phase is formed, indicated by the additional spots present in Figs. 7.1 (c, d). Above Zn concentrations of about 40%, the RHEED patterns show a tripling of diffraction planes (Figs. 7.1 (e, f)), indicating that a crystal structure with 1/3 the periodicity of the α-Fe phase has formed, i.e. the Γ phase becomes preferred. Evidently the competition between the α and Γ phases in this Zn concentration range results in a rough film, as spots are seen in the RHEED pictures instead of lines. As seen in Figs. 7.1 (g, h), the RHEED pictures again show sharp and continuous lines, also with the tripling of the diffraction planes, at a Zn concentration of 71%, evidence that a nearly homogeneous Γ phase crystal structure has formed. Rings seen in the RHEED images for quite high Zn concentrations suggest that single crystal films cannot be stabilized for samples containing more than about 80-85% Zn.

Magnetic characterization of the Fe$_{1-x}$Zn$_x$ thin films was carried out in part using the vibrating sample magnetometer (VSM) option of a Quantum Design Physical Properties Measurement System, with hysteresis loops of the films acquired at room temperature with the magnetic field applied in the sample plane along the primary high symmetry directions. The field was applied up to 10 kOe (1 T), well above the saturation fields of 3-5 kOe, in order to accurately subtract the diamagnetic signal of the substrate, with the resulting hysteresis loops representing the intrinsic ferromagnetic signature of the Fe$_{1-x}$Zn$_x$ films. Magnetometry measurements for a 30% Zn sample are shown in Figure 7.2. The <100> easy axes and <110> hard axes of this sample indicate a positive first order cubic anisotropy constant, $K_1$. Subsequent magnetometry measurements show that $K_1$ remains positive out to about 40% Zn, the same concentration at which the
RHEED patterns begin to show a preference for the formation of the \( \Gamma \) phase, and above which \( K_I \) switches sign with the <100> becoming the hard axes and <110> the easy axes. As can be seen in Fig. 7.2, the samples have a high magnetic remanence along the easy axis (>97%) and a low coercivity (<15 Oe), even at a Zn concentration of 30%. The hard axis hysteresis loops display a remanence very near 71%, precisely the theoretical value associated with a magnetization oriented 45° from the magnetometer analysis direction. The lack of a uniaxial anisotropy is representative for all of the samples, and is confirmed by subsequent angle dependent ferromagnetic resonance measurements. Slight variations in the magnetometry data for equivalent sets of crystallographic directions are likely a result of the uncertainty in the alignment of the crystal axis with the applied field.

The inset to Fig. 7.2 shows the easy axis coercivity of the \( \text{Fe}_{1-x}\text{Zn}_x \) samples as a function of Zn concentration. The coercivity of a pure iron sample deposited on MgO at a substrate temperature of 60 °C is about 8 Oe. The coercivity of the \( \text{Fe}_{1-x}\text{Zn}_x \) films remains low (<15 Oe) out to about 40% Zn, and interestingly is reduced from the value of pure iron for the first 20% or so of Zn incorporation. This initial reduction in coercivity can be attributed to less crystalline roughness [8, 9], as indicated by the RHEED patterns (Fig. 7.1). The large rise seen in the coercivity around 40% Zn occurs with the onset of the phase transition of the samples to primarily the \( \Gamma \) phase, though it is unclear whether the increased coercivity is intrinsic to the samples at these Zn concentrations or is associated with the increased roughness of the films. However, the dip in coercivity for a 71% Zn sample, whose RHEED patterns (Figs. 7.1 (g, h)) indicate a smooth crystal
growth, suggests that much of the increased coercivity in the 40-60+\% Zn range is related to an increased crystalline roughness.

**Summary**

Single crystal $\text{Fe}_{1-x}\text{Zn}_x$ thin films, with $x = 0 - 0.85$, were prepared on MgO(001) substrates at a temperature of 60 °C by molecular beam epitaxy. The low substrate temperature is critical for the incorporation of the Zn. The crystal quality of the films was monitored *in-situ* using reflection high energy electron diffraction with 10 keV electrons, and reveals an evolution of the crystal structure from the $\alpha$-Fe bcc phase at low Zn concentrations to primarily the $\Gamma$ (\&-brass) phase at Zn concentrations above 40\%. Subsequent vibrating sample magnetometry measurements show no uniaxial anisotropy and a change in sign of the first order cubic magnetic anisotropy constant, $K_1$, at a Zn concentration near 40\%. The $\text{Fe}_{1-x}\text{Zn}_x$ samples retain a high easy axis magnetic remanence and low coercivity out to about 40\% Zn. As the formation of the $\Gamma$ phase becomes preferred above 40\% Zn, the samples show a dramatic increase in the easy axis coercive field, at least in part due to an increased roughness of the films.

**Acknowledgements**

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Figure 7.1: Representative 10 keV RHEED patterns for Fe$_{1-x}$Zn$_x$ thin films deposited on MgO(001) substrates taken along the in plane directions shown for (a, b) pure Fe, (c, d) low Zn concentrations, (e, f) a mid range Zn concentration illustrating the $\alpha$ to $\Gamma$ phase transition, and (g, h) a $\Gamma$ phase Fe$_{0.29}$Zn$_{0.71}$ film.

Figure 7.2: Magnetic hysteresis loops taken along various in plane crystalline axes for a 22 nm thick Fe$_{0.70}$Zn$_{0.30}$ film. (Inset) The easy axis coercivity of the Fe$_{1-x}$Zn$_x$ films as a function of Zn concentration, displaying a drastic increase near 40% Zn as the crystal structure begins to favor the $\Gamma$ phase, simultaneously increasing the roughness of the films. The dashed line is a guide to the eye.
References

SUMMARY OF DISSERTATION

Magnetostriction is expected to affect the magnetic anisotropy of single crystal thin films, where the adaptation to new film dimensions is inhibited by the epitaxial coupling to a substrate. To investigate the effects of magnetostriction on the magnetic anisotropy of single crystal magnetostrictive thin films, single crystal bcc Fe$_{1-x}$Ga$_x$ thin films (~20nm) were deposited onto MgO(001) and ZnSe buffer layers grown on (001) and (110) GaAs substrates by MBE. Crystalline Fe$_{1-x}$Zn$_x$ thin films (~20nm) were also prepared on MgO(001) substrates by MBE. The magnetostrictive strain of Fe$_{1-x}$Ga$_x$ alloys is very large and can exceed 400ppm, and the magnetostrictive properties of Fe$_{1-x}$Zn$_x$ alloys are predicted to also be very large.

In order to make samples with reproducible quality, the substrates must be properly prepared so that a clean single crystal surface results. The cleaning procedure consists of a chemical and thermal treatment. The GaAs substrates were prepared by first sonicating in acetone for 5 minutes, then rinsing in methanol, followed by rinsing in de-ionized water and drying with flowing nitrogen. The last step in the cleaning process was to heat the substrates to 620°C for 45 minutes in high vacuum conditions. The MgO substrates were prepared by sonicating in acetone for 5 minutes, rinsing in methanol, followed by drying with flowing nitrogen. The typical third step in the cleaning process, rinsing in de-ionized water, was skipped due to the hygroscopic nature of MgO.
final cleaning step was to heat the substrates to 800°C for 2 minutes in high vacuum conditions.

Once the substrates were suitably prepared, the growth of the Fe$_{1-x}$Ga$_x$ or Fe$_{1-x}$Zn$_x$ films could commence. On the GaAs substrates, an 800Å epitaxial ZnSe buffer layer was first deposited from a single source ZnSe crucible at a rate of 13Å/min while the substrate was held at 175°C. After the ZnSe deposition, the substrate temperature was reduced to 150°C and the growth of the iron-gallium film ensued from independent Fe and Ga Knudsen cell sources. Depositions of Fe$_{1-x}$Ga$_x$ on the MgO substrates were also performed at a substrate temperature of 150°C. These substrate temperatures were chosen to optimize the crystal quality of the films, determined by RHEED, VSM, and angle dependent FMR. The Fe$_{1-x}$Zn$_x$ samples were deposited at a substrate temperature of 60°C in order to incorporate Zn into the Fe host. The incorporation of Zn in Fe at a substrate temperature of 150°C is low due to the high vapor pressure of Zn. The Fe based samples were typically about 20nm thick using a deposition rate of 2 - 2.5Å/min, and the deposition pressure was generally around 4x10$^{-9}$ Torr. The growths were concluded by capping the films with 40Å or so of Al to protect the samples from the formation of oxides.

RHEED images of the Fe$_{1-x}$Zn$_x$ samples indicate some sample inhomogeneity and suggest an evolution of the crystal structure from the α-Fe bcc phase at low Zn concentrations to primarily the Γ (γ-brass) phase at Zn concentrations above 40%. Subsequent VSM measurements show no uniaxial anisotropy and a change in sign of the first order cubic magnetic anisotropy constant, $K_1$, at a Zn concentration near 40%. The
Fe$_{1-x}$Zn$_x$ samples retain a high easy axis magnetic remanence and low coercive field out to about 40% Zn. As the formation of the Γ phase becomes preferred above 40% Zn, the samples show a large increase in the easy axis coercivity, at least in part due to an increased roughness of the films.

The Fe$_{1-x}$Ga$_x$ samples were studied in a bit more detail. The RHEED patterns and subsequent VSM measurements for Fe$_{1-x}$Ga$_x$ samples deposited on ZnSe/GaAs show that the crystal ordering persists to 75+% Ga, while the same measurements for samples deposited on MgO reveal a thin film bcc crystal stability limit of about 45% Ga, both of which exceed the bulk stability limit of about 28% Ga. As more Ga is added to the samples deposited on MgO, the RHEED patterns become increasingly complex, while the hysteresis loops display multiphase behavior.

Although there is a difference in the limits of stability for Fe$_{1-x}$Ga$_x$ films deposited on MgO and ZnSe/GaAs substrates, the behavior of the magnetization and electronic structure are found to be independent of the underlying substrate. The magnetizations for films grown on both substrates display a similar linear reduction with increasing Ga concentration up to about 23% Ga, decreasing more rapidly at higher concentrations. The initial decline in the magnetization is slightly reduced from the effect of adding a non-magnetic element (Ga) to a magnetic host (Fe) of constant moment. XMCD results show that the enhanced reduction of the magnetization originates from two sources. First, the Fe moment is not constant. As Ga is added to the Fe, the Fe moment gradually decreases out to about 23% Ga. Increasing the Ga content further causes the Fe moment to drop off more rapidly. Second, the Ga is not non-magnetic. When incorporated into
the Fe, the Ga atoms develop a small induced magnetic moment aligned anti-parallel to the Fe moment.

Additional x-ray absorption studies show that the holes in the Fe majority-spin band decrease with increasing Ga content, completely filling the Fe majority-spin band by $x \approx 0.3$. The filling of the Fe majority-spin band coincides with a strongly decreasing Fe moment. The XMLD angular dependence also decreases strongly for $x \geq 0.3$ and is attributed to the formation of D0$_3$ precipitates. Furthermore, the XMLD results provide qualitative information on the magnetic anisotropy, and show that it is much reduced for $x \geq 0.3$. Another achievement of this work was the demonstration that the separation of XMLD terms into angle-dependent and angle-independent terms, an approach originally developed for transition metal oxides [1], is also valid for itinerant electron systems.

In contrast to the behavior of the magnetization and electronic structure, depositions of Fe$_{1-x}$Ga$_x$ single crystal thin films on MgO(001) and ZnSe/GaAs(001) substrates have quite different magnetic anisotropies.

Samples deposited on MgO have a purely cubic anisotropy, and it is found that the cubic anisotropy constant, $K_1$, switches sign by 17.5% Ga, whereas $K_1$ remains positive in bulk Fe$_{1-x}$Ga$_x$ alloys out to about 20% Ga. Recalling that $K_1$ can be written as $K + \Delta K$, where $\Delta K = \frac{9}{4} \left((c_{11} - c_{12})\lambda_{100}^2 - 2c_{44}\lambda_{111}^2\right)$, the enhancement of the bulk cubic anisotropy is attributed to the very large bulk magnetostriction which is absent in epitaxially pinned thin films. However, the $\Delta K$ contribution is only about 25% of the bulk value of $K_1$ near 17.5% Ga. This is insufficient to fully explain the change in sign of
by 17.5% Ga for Fe$_{1-x}$Ga$_x$ thin films, and suggests intrinsic differences in material properties between strained Fe$_{1-x}$Ga$_x$ thin films and their bulk counterparts.

Fe$_{1-x}$Ga$_x$ samples deposited on ZnSe/GaAs substrates have a similar cubic anisotropy to samples deposited on MgO substrates, but also feature an additional Ga dependent in-plane uniaxial anisotropy. This has been attributed to an interplay between magnetostriction and an anisotropic strain relaxation. The anisotropic strain relaxation originates from the substrate, and generates a uniaxial anisotropy by coupling through the $B_2$ magneto-elastic term. Let’s take a look at the origins of the uniaxial anisotropy in more detail. Thomas et al. have found an anisotropic strain relaxation for a 13nm Fe film deposited directly onto a GaAs(001) substrate [2]. They found that the [110] direction is more relaxed than the [1-10] direction. The effect of this anisotropic strain relaxation is a shear strain, which they found to be 0.2% for this sample. This shear strain modifies the magnetic anisotropy by generating a uniaxial anisotropy in the material through magneto-elastic coupling, and the magnitude of the uniaxial anisotropy depends on the magnitude of the strain and $B_2$. For example, from angle dependent ferromagnetic resonance measurements, we find a value for the uniaxial anisotropy of an Fe$_{0.82}$Ga$_{0.18}$ sample deposited on ZnSe/GaAs(001) to be 6x10$^3$ J/m$^3$ [3]. Using a bulk value for $B_2$ of 4x10$^6$ N/m$^2$ [4] (and assuming it applies in these highly strained thin films) and the same shear strain that Thomas et al. found of 0.2% (assuming this applies to our 20nm FeGa sample deposited on ZnSe/GaAs(001)), we would predict a uniaxial anisotropy of 8x10$^3$ J/m$^3$. This very close agreement with the measured value leads us to believe that the anisotropic strain relaxation coupled with magnet-elastic anisotropy is the mechanism
responsible for generating a uniaxial anisotropy in the Fe$_{1-x}$Ga$_x$/ZnSe/GaAs(001) samples.

The explanation for the origins of the in-plane uniaxial anisotropy predicts that the anisotropy should scale with magnetostriction, and because the bulk value of $B_2$ switches sign, the direction of the uniaxial easy axis should also change. Both of these effects are seen in the Fe$_{1-x}$Ga$_x$/ZnSe/GaAs(001) thin films but are somewhat modified from what the bulk properties imply. The strength of the in-plane uniaxial anisotropy does scale with magnetostriction until a single peak near 20% Ga is reached. An expected second peak of the uniaxial anisotropy, corresponding to the second peak in magnetostriction near 28% Ga, is missing, likely due to the substrate stabilization of the bcc structure. The in-plane uniaxial anisotropy changes direction, from [110] to [1-10], above a Ga concentration of about 33%. In bulk Fe$_{1-x}$Ga$_x$ materials, $B_2$ switches sign near 20% Ga, so the delayed switching of the uniaxial easy axis once again suggests that the intrinsic properties of Fe$_{1-x}$Ga$_x$ thin films may be altered from bulk values.

These results demonstrate that the effect of depositing magnetostrictive materials as thin films can be heavily influenced by the substrate. Depositions on substrates that allow anisotropic strain relaxation may develop a strong in-plane uniaxial anisotropy, while depositions on non-directionally bonded substrates can have a strongly modified cubic anisotropy. Furthermore, the epitaxial mismatch between the film and the substrate can be used to adjust the out-of-plane uniaxial anisotropy.
References


APPENDIX A

FIELD DEPENDENT MAGNETIC ANISOTROPY OF Fe$_{0.8}$Ga$_{0.2}$ THIN FILMS
Contribution of Authors and Co-Authors

Manuscript in Appendix A

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Contributions: Proposed the experiment, discussed the results, and edited the manuscript.
The purpose of this manuscript is to investigate the influence of magnetostriction on the magnetic anisotropy of Fe$_{0.8}$Ga$_{0.2}$ thin films epitaxially deposited onto ZnSe/GaAs(001) substrates. More specifically, the focus of this work is to determine if there is a magnetic field dependence to the magnetic anisotropy. The idea behind this work is that a magnetoelastic material epitaxially pinned to a substrate is inhibited from deforming, so the application of a magnetic field will generate a field dependent magnetostrictive stress in the sample which is believed to create a field dependent magnetic anisotropy.

Abstract

Using longitudinal MOKE in combination with a variable strength rotating magnetic field, called the rotational MOKE (ROTMOKE) method, we show that the magnetic anisotropy for an Fe$_{0.8}$Ga$_{0.2}$ single crystal film with a thickness of 17 nm, grown on GaAs(001) with a thick ZnSe buffer layer, depends linearly on the strength of the applied magnetic field. The torque moment curves generated using ROTMOKE are well fit with a model that accounts for the uniaxial, cubic or fourfold anisotropy, as well as additional terms with a linear dependence on the applied magnetic field. The uniaxial and cubic anisotropy fields, taken from both the hard and easy axis scans, are seen to remain field independent. The field dependent terms are evidence of a large effect of the magnetostriction and its contribution to the effective magnetic anisotropy in Fe$_{1-x}$Ga$_x$ thin films.
Introduction

Alloys of Fe$_{1-x}$Ga$_x$ have garnered much interest recently because of their magnetostrictive and high tensile loading properties, [1-11] as well as possible spin polarized current injectors into GaAs based light emitting diodes [12-14]. These materials can induce large magnetostriction with a small applied magnetic field; therefore pinning the in-plane lattice constant of ultrathin films of these materials by epitaxial growth to a substrate and applying a field should induce an anisotropic magnetoelastic stress and a subsequent strain that will create an additional field dependent anisotropy within the film. In this paper, we show evidence of how this effect is the most straightforward way to explain the atypical torque curves produced by Fe$_{0.8}$Ga$_{0.2}$ grown on GaAs(001) with a thick ZnSe buffer layer. In fact, only by taking into account terms that linearly depend on the applied magnetic field can the torque curves be well modeled.

In the past, the rotational magneto-optic Kerr effect (ROTMOKE) has been used to measure the anisotropy fields for magnetic thin films [15,16]. For magnetic thin films with uniaxial anisotropy such as pure Fe, the anisotropy field changes very little when measured at different magnetic field strengths, i.e., there is no applied field dependence to the anisotropy. However, for magnetostrictive films pinned to a substrate, the magnetoelastic strain caused by applying a magnetic field is thought to greatly affect the total anisotropy, resulting in an additional magnetic anisotropy that depends on the magnitude and direction of an applied field.
**Experimental**

Single crystal Fe$_{0.8}$Ga$_{0.2}$ thin films (~17 nm) were prepared on GaAs(001) substrates, with a 75 nm ZnSe buffer layer, by molecular beam epitaxy (MBE) as previously described [17,18]. The sample was capped with 4 nm Al to prevent the formation of any oxides. The thickness and concentration of the film were determined by Rutherford backscattering spectrometry (RBS).

The magnetic anisotropy studies of the Fe$_{0.8}$Ga$_{0.2}$ films were done using the ROTMOKE method, first used to determine the anisotropy fields for uniaxial films [15] and uniaxial and cubic anisotropies [16]. The ROTMOKE experimental setup used in this study uses a basic longitudinal MOKE setup combined with a rotating magnetic field in a setup very similar to that used by Mattheis and Quednau [15] and outlined by Qiu and Bader [19]. A ~1 mW intensity stabilized laser beam passes through a filter and a polarizer before reflecting off of a sample in the presence of a magnetic field generated by a small electromagnet. As the constant strength magnetic field is rotated with respect to the fixed scattering geometry, the reflected light intensity is observed to change. This intensity change is proportional to the component of the magnetic moment of the sample along the axis, which is at the intersection of the sample plane and the reflection plane. (The perpendicular anisotropy of these thin films restricts the moment so that it lies within the sample plane.) The light then passes through another polarizer, called the analyzer, at nearly crossed polarization (~2° offset), allowing for the sensitive detection of any small rotation in the polarization of the reflected light, the Kerr signal, by a diode detector [19]. The Kerr signal, which for small light polarization rotations is directly
proportional to the change in the intensity of the detected light \[19\], is measured as the applied magnetic field is rotated in the plane of the sample for various field strengths.

Traditional M versus \(H\) hysteresis curves taken with this setup along both the easy and hard axis directions are shown in Figure A.1 for this thin film. Because the Kerr intensity is a measure of the projection of the magnetic moment into the reflection plane, it can be used to determine the direction of the magnetic moment of the sample relative to the plane (as long as the magnetization of the sample is saturated, which it will be at high enough fields). A comparison of the direction of the magnetic moment to that of the applied field can be used to determine the magnetic anisotropy field at that field strength. This is done by creating a set of torque density curves as outlined by Mattheis and Quednau \[15\]. These data are then modeled to determine the anisotropy fields.

For a simple uniaxial anisotropic film, the torque density curves, \(l(\theta)\), have a simple \(\sin(2\theta)\) behavior, with the amplitude corresponding to half of the anisotropy field \(H_k\).

\[
l(\theta) = \frac{1}{2}H_k \sin(2\theta)
\]

If other anisotropies are present in the film, they can also affect the shape of the torque curves \[16\]. For instance, if a cubic anisotropy is also present, the torque curves include a \(\sin(4\theta)\) behavior in addition to the uniaxial term (the uniaxial and cubic terms have a common easy axis for this film) \[17,18\]:

\[
l(\theta) = \frac{1}{2}H_{K1} \sin(2\theta) - \frac{1}{4}H_{K2} \sin(4\theta);
\]

where \(H_{K1}\) is the uniaxial anisotropy field and \(H_{K2}\) is the cubic, or fourfold, anisotropy field, while \(\theta\) corresponds to the direction of the magnetic moment \[16\].
In this study, measurements were taken at increasing magnetic fields. Figure A.2 shows 14 torque curves taken along the easy axis ranging from 300 to 900 Oe. Each torque curve is taken using a constant strength magnetic field. Because the amplitude of these curves is proportional to the anisotropy, the change in the peak heights as the field increases is an indicator that magnetostriction may be affecting the anisotropy. Similar measurements were taken along the hard axis.

**Results and Discussion**

The changing peak intensities of the torque curves taken at different magnetic fields exhibit behavior inconsistent with this simple model, and the effect of the magnetostriction on the anisotropy must be included. Given that, for relatively low fields, the magnitude of the magnetostriction is proportional to the applied magnetic field $H$, it is reasonable to anticipate that the anisotropy should depend linearly on $H$ as well. For this Fe$_{0.8}$Ga$_{0.2}$ film, the magnetostriction itself is anisotropic with a large magnetostriction constant along the $<100>$ direction, $\lambda_{100}$, and a smaller one along the $<110>$ direction, $\lambda_{110}$ [1-3]. The net effect of this anisotropy is that the magnetic field dependent anisotropy has a relative easy axis in a direction different than that of the purely crystalline anisotropy (a 45° rotation). Unfortunately, the effect of the magnetostriction is difficult to represent in this model because the tetragonal distortion generated by the uniaxial strain depends on both the strength of the field and the direction of the magnetization of the sample in a non-symmetric way. Furthermore, the conversion of magnetoelastic strain energy to magnetic anisotropy is not well understood, and higher
order Fourier terms are required to model the data well at all fields. To take this into account, and to be as general as possible, additional terms were added to our torque density curves:

\[ l(\theta, H) = A_1 \sin2\theta + A_2 \sin4\theta + H(A_3 + A_4 \sin2\theta + A_5 \sin4\theta + A_6 \sin6\theta + A_7 \sin8\theta); \]

where \( A_1 \) and \( A_2 \) are related to the typical uniaxial and cubic anisotropy fields while the other terms account for the effect of the magnetostriction. The above model was applied simultaneously to eight different torque curves, taken at eight different fields ranging from 350 to 700 Oe, with the sample oriented along the easy as well as the hard axis. This approach results in a description of the field dependency of the torque curves while maintaining a common model for the field independent portion of the eight different torque curves.

The problem of optimizing the model parameters was formulated as an ordinary least squares problem resulting in the linear system:

\[
\sum_{(\text{fields})} \sum_{(\text{angles})} l_{ij} \cdot f_i(\theta_j, H_i) = \sum_{(\text{functions})} A_m \sum_{(\text{fields})} \sum_{(\text{angles})} f_m(\theta_j, H_i) \cdot f_k(\theta_j, H_j); \]

where \( k = (1\ldots \# \text{ of functions}) \), \( l_{ij} \) is the torque measured when applying the \( i^{\text{th}} \) field at the \( j^{\text{th}} \) angle, and \( f_i(\theta, H) \) is the component of \( l(\theta, H) \) multiplying the \( i^{\text{th}} \) parameter. The parameters were found by solving this system using standard matrix methods. It should be noted that this technique is a way of determining parameters simultaneously for all of the fits.

Figure A.3 shows data taken at 600 Oe fit to three different models. The quality of fit for the models was measured by comparing the sum squared error per degree of freedom, or mean square error (MSE), which normalizes for the number of parameters.
The first two models are a simple uniaxial model followed by a combined uniaxial and cubic model. Clearly the poor quality of fit of the uniaxial model and the much better fit of the uniaxial + cubic model suggest that there is a significant cubic anisotropy present in the film (as anticipated [17,18]). Table A.1 reports the parameters and MSE's for the different models fit to all eight curves simultaneously. The first two terms of the full model give $H_{K1} = 2A_1 = 91.4$ Oe, and $H_{K2} = -4A_2 = -120$ Oe, which are similar to values found for iron alloys with both uniaxial and cubic anisotropies [16].

**Summary**

ROTMOKE torque curves from Fe$_{1-x}$Ga$_x$ thin films were shown to exhibit a dependence on the applied magnetic field of the sample. This is seen by a large increase in the quality of fit for a model that incorporates linear field terms fit simultaneously to several different torque curves taken at different fields. This demonstrates that the magnetostriction of the sample has a strong effect on the total anisotropy energy of pinned thin films. In addition, the extracted coefficients used in the field dependent fit function are all significant and should not be ignored, alluding to the complex nature of the conversion of magnetoelastic strain energy to magnetic anisotropy. The use of ROTMOKE may give added insight into the eventual extraction of the magnetostriction coefficients.
Acknowledgements

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Tables

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Table A.1: The parameters for the fits to the different models are shown along with the mean square error (MSE) for those fits. These models were fit simultaneously to eight different torque curves so that the curves for all eight fields have the same parameters.
Figure A.1: Hysteresis curves of the sample along the easy and hard axis directions. ROTMOKE scans were done along both of these directions.
Figure A.2: Torque curves taken at fields ranging from 300 to 900 Oe. The size and shape of the curves change in a significant way as the field is increased. The increase in the peak heights with larger fields demonstrates the effect of the magnetostriction.
Figure A.3: Torque curve taken at 600 Oe fit to a uniaxial model, to a uniaxial + cubic model, and with the new model taking into account the magnetic field dependence.
References


APPENDIX B

ON Fe_{1-x}In_x THIN FILMS
Here I will describe my efforts to make Fe$_{1-x}$In$_x$ thin films. We wanted to continue working with Fe because it was already in our MBE system, it is a material we were familiar with, and as a host material Fe has the tendency to exhibit interesting magnetic properties as it is alloyed. We chose to attempt to alloy the Fe with In for two reasons. First, because Fe$_{1-x}$Ga$_x$ alloys are strongly magnetoelastically coupled and because In lies directly beneath Ga in the periodic table, we reasoned that Fe$_{1-x}$In$_x$ alloys might also exhibit enhanced magnetostrictive properties. Another motivation for this work was that we wanted to try to make something entirely new. Candidates for thin film materials are typically selected from those that have demonstrated interesting properties in bulk. However, Fe and In are essentially immiscible in the bulk as In is only 0.28% soluble in bulk Fe [1, 2]. Previously, it has been shown that metastable and forced structures can be stabilized through interfacial interactions by depositions on closely lattice matched substrates [3-10]. Therefore, we were hoping to stabilize Fe$_{1-x}$In$_x$ as thin films by depositing it on MgO(001) substrates.

The Fe$_{1-x}$In$_x$ thin films described here were deposited using MBE through the simultaneous deposition of Fe and In from independent sources. The In source was cleaned using KOH before being added to the MBE system. Typical source temperatures for the deposition of In were 660°C to 850°C, and the system pressure during deposition was around 3x10$^{-9}$ Torr. The substrate temperature was maintained at its lowest controllable temperature, 70°C. I wanted to deposit the Fe$_{1-x}$In$_x$ thin films at the lowest possible substrate temperature because thermal energy seems a likely culprit to disrupt the stabilization of a new structure. Because our MBE system has no cooling lines for
the sample holder, and because the thermal radiation from the 1410°C Fe source is so intense, 70°C is the lowest controllable substrate temperature. The samples were capped with about 35Å of Al to protect them from the formation of any oxide. The samples were characterized using RHEED, field emission microscopy (FEM), energy dispersive x-ray analysis (EDX), XAS, XMCD, and VSM. No determination on the absolute amounts of Fe and In incorporated into the samples has yet been made, but relative amounts are known by measuring the flux of the source materials using a quadrupole mass analyzer (QMA). Different Fe$_{1-x}$In$_x$ alloys were made by keeping the Fe flux constant and varying the In flux by adjusting its source temperature.

Images of the Fe$_{1-x}$In$_x$ RHEED patterns were taken for all of the film growths using 15keV electrons, and representative RHEED patterns of the Fe$_{1-x}$In$_x$ surfaces are shown in Figure B.1. Figs. B.1 a,b) show that a pure Fe film deposited on MgO(001) at a substrate temperature of 70°C results in a rough surface, and the angled, comet-like appearance of the spots are typical of a faceted surface. From previous work [11] we know that the crystal quality and the magnetic properties of the as-deposited Fe film can be improved by elevating the substrate temperature to 150°C. However, the substrate temperature was held at its lowest controllable temperature, 70°C in this case, in hope that the decreased mobility of the impinging atoms due to the lowered substrate temperature would aid in forcing the Fe$_{1-x}$In$_x$ alloys into the bcc structure. As some In is incorporated into the film growth process for low In fluxes (Figs. B.1 c,d)), we see that the streaks initially sharpen, accompanied by a slightly increasing diffuse background. The initial sharpening of the streaks was also seen for Fe$_{1-x}$Zn$_x$ depositions [12], and
indicates that the crystal surface has gotten smoother, perhaps by increasing the mobility of the Fe atoms. Figs. B.1 e,f) represent the medium range of In flux, and the arcing rings signify that the samples have become polycrystalline. Also, the diffuse background has continued to grow, and an increase in the In flux results in a uniform and featureless bright green diffuse background on the RHEED screen. The increasing diffuse background is concerning, and when compared to the FeIn phase diagram suggests that not all of the In is incorporating into the Fe host.

Along with the \textit{in-situ} RHEED observations, a visual inspection of the films is also revealing. Once enough In flux is reached, near the onset of the polycrystalline transition, the samples start to develop a somewhat cloudy, fingerprinted appearance easily visible to the naked eye. This development was further investigated using a field emission microscope (FEM), and FEM images of some of the Fe$_{1-x}$In$_x$ samples are shown in Figure B.2. These images were acquired post growth, after the deposition of the Al capping layer. Fig. B.2 a) shows an FEM image of a pure Fe film, and the small scale spatial variability vanishes at larger scales and looks uniform and shiny to the naked eye. Even at a very low In flux, the films start to show small surface agglomerations, as shown in Fig. B.2 b). These miniscule adsorbates are too small to be seen by the eye so the samples again appear uniform and shiny, although the small scale inhomogeneity is very evident in the FEM images. In general, additional In flux leads to an increased adsorbate size, increased surface area coverage, and a shape altered from spherical to plate-like. Eventually the size of the adsorbates becomes sufficient to be seen by the naked eye.
FEM images for a high In flux sample are shown in Figs. B.2 c,d), and the large (≥30μm) agglomerations are easily seen by the eye.

The FEM images present clear evidence that the samples are inhomogeneous. The identity of the adsorbates was determined using the energy dispersive x-ray analysis (EDX) capabilities of the FEM machine. The EDX results, obtained using a 15keV electron source, are shown in Figure B.3. Fig. B.3 a) shows the x-ray intensity vs. x-ray energy collected at a spot on the sample between the large surface agglomerations, and the primary feature in the spectra comes from the MgO substrate. Fig. B.3 b) shows the EDX results collected when centered on a large adsorbate. The spectra is dominated by an In signal and leaves little doubt that the surface adsorbates are In. Also, the relative intensity of the In signal to the other signals present and not present in Fig B.3 b), especially the lack of any Mg or O signal, suggests that the adsorbates at a high In flux are relatively thick (≥10nm).

It is very evident from the previous measurements that much of the In is not incorporating into the Fe\(_{1-x}\)In\(_x\) films. But is any In incorporating into the films? In order to address this question, we conducted x-ray absorption studies on the Fe\(_{1-x}\)In\(_x\) samples. X-ray absorption spectroscopy (XAS) at the Fe L\(_{2,3}\)-edge was used to look for any telling changes in the Fe electronic structure. The data, shown in Figure B.4, was collected at normal incidence at the Advanced Light Source on beamline 6.3.1 using total electron yield, and is normalized to the peak absorption intensity. The most telling difference between the spectra is the abrupt change in slope near 707.5 eV that occurs only for the pure Fe film, and disappears as soon as any In is added to the samples. The change in the
Fe XAS as some In flux gets included into the growth process is evidence that at least some In is incorporating into the films. It is also reasonable to expect a shift in energy for the absorption peak. The energy shift occurs as the bonding electrons involved slightly transfer charge between the alloying elements which in turn affects the screening process. For example, we have seen peak absorption energy shifts at the Fe L$_3$-edge in the Fe$_{1-x}$Ga$_x$ and Fe$_{1-x}$Zn$_x$ systems of about 1eV. We have not seen any compelling peak absorption energy shifts in the Fe$_{1-x}$In$_x$ system, suggesting that any In incorporation is small.

We also used x-ray magnetic circular dichroism (XMCD) to study our samples. The XMCD spectra shown in Figure B.5 were measured in saturation at beamline 6.3.1 of the Advanced Light Source using a fixed photon helicity and reversing the magnetization at each photon energy. The full Fe L$_{2,3}$-edge spectra shown in Fig. B.5 a) are nearly identical, again suggesting only a small incorporation of In regardless of In flux. This conclusion stems from the fact that the peak Fe XMCD intensity is proportional to the magnetic moment of the Fe atoms [13-16]. If more and more In was incorporating into the films, the increased hybridization would tend to decrease the exchange interaction [17, 18], thus reducing the Fe moment and leading to a decreased XMCD signal. For example, in the well-incorporated Fe$_{1-x}$Ga$_x$ and Fe$_{1-x}$Zn$_x$ systems the peak Fe L$_3$ XMCD intensity remains mostly constant down to about 80% Fe, where the XMCD intensity is seen to drop rapidly.

The main difference between the spectra shown in Fig. B.5 a) is the absorption intensity near 706.5eV, and this part of the spectra is shown in more detail in Fig. B.5 b).
The small absorption bump seen only for the pure Fe film has been related to transitions to the majority band empty states [19-21]. The lack of this absorption feature once any In is added to the growth again indicates that at least some In is incorporated into the Fe$_{1-x}$In$_x$ films.

Additional magnetic properties of the Fe$_{1-x}$In$_x$ samples were measured using vibrating sample magnetometry (VSM). Some representative VSM hysteresis loops for varying In fluxes are shown in Figure B.6 with a linear diamagnetic background removed in order to reveal the intrinsic ferromagnetic properties of the samples. As can be seen in Fig. B.6 a), a small In flux during the growth results in a film with a well developed magnetocrystalline anisotropy and a positive first order cubic anisotropy constant, $K_1$. The small amount of In actually incorporated into the film results in magnetic properties very similar to that of pure Fe, as expected for such a small incorporation. Fig. B.6 b) shows the effect on the magnetic properties of adding more In flux to the growth process. The identical open S shape to the hysteresis loops measured at many different angles is indicative of polycrystalline samples, consistent with the RHEED observations (see Figs. B.1 e,f)). Because the amount of In actually incorporated into the films remains small independent of the In flux, the onset of polycrystalline growths is likely related to the growth dynamics as the In gets forced to the surface. The hysteresis loops shown in Fig. B.6 c) for high In flux depositions are typical of amorphous materials, and demonstrates that the additional In flux disrupts the growth process enough to prevent the Fe from forming any coherent structure.
In summary, Fe$_{1-x}$In$_x$ samples were deposited onto MgO(001) substrates by MBE. RHEED patterns of the FeIn layer made in-situ during the growth indicate single crystal bcc samples for a low In flux and polycrystalline samples for a medium In flux. Also seen in the RHEED observations was a growing diffuse background with increasing In flux until only a bright, uniform diffuse background was observed at a high In flux. FEM images and EDX analysis show a distinct separation of the Fe and In, with the In primarily organizing itself into large surface adsorbates. Changes in the spectra of XAS and XMCD x-ray absorption measurements as some In flux is added to the growth process reveal that at least some In is incorporating into the Fe host, though likely very little. Magnetic properties derived from VSM measurements show similarities to pure Fe in various ordered and disordered forms. As a whole, the array of measurements performed on the Fe$_{1-x}$In$_x$ samples suggests that the technique presented here has failed to produce Fe$_{1-x}$In$_x$ thin films with much, if any, enhancement of the In concentration compared to bulk samples.
Figure B.1: RHEED patterns of Fe$_{1-x}$In$_x$ thin films taken using 15 keV electrons incident along the $<100>$ and $<110>$ directions as shown for a,b) pure Fe, c,d) some In, and e,f) medium In flux samples. As even higher In concentration films are attempted, the RHEED patterns only show a bright, uniform diffuse background.
Figure B.2: FEM images of a) a pure Fe film, b) a sample with a small In deposition flux, and c) and d) a sample with a high In deposition flux. The scale in the lower left of the images is 1 μm for a) and b), 100 μm for c), and 2 μm for d).
Figure B.3: EDX spectra a) taken between the surface agglomerations, and b) taken on one of the large surface adsorbates.

Figure B.4: Fe L$_{2,3}$-edge XAS for the Fe$_{1-x}$In$_x$ thin films.
Figure B.5: Fe XMCD a) taken at the Fe L\textsubscript{2,3}-edge, and b) zoomed in to highlight the differences in intensity centered near 706.5 eV as a function of In.
Figure B.6: Representative VSM hysteresis loops for a) small In flux, b) medium In flux samples (whose corresponding RHEED patterns are shown in Figures 1 e,f), and c) high In flux samples.
References


