FIRST-ORDER PHASE TRANSITION AND MAGNETIC PROPERTIES OF EPITAXIAL FeRh THIN FILMS

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Declaration

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all sources of information which have been used in the thesis.

The thesis has also not been submitted for any degree in any university previously.

________________________________________

Cher Kiat Min, Kelvin

17th December 2012
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Summary

The equiatomic FeRh alloy is known to exhibit first-order anti-ferromagnetic to ferromagnetic phase transition when subjected to elevated temperatures of around 100°C depending on sample conditions such as compositional differences, doping and impurities, film thickness, as well as external applications of heat, magnetic fields and pressure. Convenience of the transition temperature has attracted significant interests in areas such as thermo-magnetic switches for heat-assisted magnetic recording (HAMR) media, and microelectromechanical systems (MEMS). However, much of the work done on FeRh was mainly focused on bulk and non-texture thin films. Yet, for many practical applications, textured films are highly desired for integration purposes. Thus firstly in this thesis, the effects of compositional variations on the first-order transition of (001) textured FeRh thin films were studied. A compositional-dependent first-order transition from ferromagnetic to anti-ferromagnetic phase was observed between 47 and 48 at. % when Rh content was progressively increased. The transition was sharp resembling that of bulk FeRh, rather than the gradual decrease in magnetization of non-texture thin films, which occurred over a wide composition range. With Rh content beyond 47 at. %, the anti-ferromagnetic films displayed a sharp increase in magnetization becoming ferromagnetic once again when subject to heating. The transition was distinct and sharp for films of near equiatomic compositions when compared to the broad transitions of its non-texture counterparts. However, with the increase Rh content, the transition of these textured films broadened monotonically.
With the continued trend of device miniaturizations, it is important to understand the behavioral shifts of these textured films as dimensions, in particular thickness, were reduced. To do this, transitional behaviors of textured Fe\textsubscript{52}Rh\textsubscript{48}, Fe\textsubscript{50}Rh\textsubscript{50}, and Fe\textsubscript{48}Rh\textsubscript{52} films of thickness 5nm to 200nm were investigated. With reduction in thickness from 200 nm to 5 nm, textured FeRh films showed broadening of the first-order phase transition indicating the more graduated formation of the ferromagnetic phase. At 5 nm, the films behaved predominantly ferromagnetic with large magnetization and small phase transition within the temperature range of \(-75^\circ\text{C}\) to \(130^\circ\text{C}\) which was a result of surface nucleation mechanism of FeRh which became prominent with reduced thickness. At the same time, lattice parameter-\(a\) of the FeRh FCC unit cell increased, matching the lattice of the MgO substrate at 5 nm suggesting a critical film thickness whereby the film becomes predominantly ferromagnetic.

Lastly, the effects of transition temperature modification through Ir doping among textured Fe\textsubscript{52}Rh\textsubscript{48-x}Ir\textsubscript{x}, Fe\textsubscript{50}Rh\textsubscript{50-x}Ir\textsubscript{x}, and Fe\textsubscript{48}Rh\textsubscript{52-x}Ir\textsubscript{x} films (where \(x = 0, 1, 2, 4, \text{ and } 8\)) were investigated. With increasing Ir content up to 4 at. %, the transition temperature could be monotonically delayed to higher temperatures. Magnetization of the ferromagnetic phase right after the phase transition decreased with higher Ir content. At the same time, the thermal hysteresis characteristic of first-order phase transition diminished when Ir content was increased suggesting that with the addition of Ir could have disrupted the formation of the ferromagnetic phase. With 8 at. % Ir however, no transitions could be observed suggesting either the transition was destroyed by 8 at. % Ir or the transition was delayed beyond \(260^\circ\text{C}\).
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## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>FeRh</td>
<td>Iron Rhodium</td>
</tr>
<tr>
<td>AFM</td>
<td>Anti-Ferromagnetic</td>
</tr>
<tr>
<td>FM</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>BCC</td>
<td>Body-Centered Cubic</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-Centered Cubic</td>
</tr>
<tr>
<td>HAMR</td>
<td>Heat-Assisted Magnetic Recording</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical Systems</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectrometry</td>
</tr>
<tr>
<td>AGFM</td>
<td>Alternating Gradient Forced Magnetometer</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting Quantum Interference Device</td>
</tr>
<tr>
<td>VSM</td>
<td>Vibrating Sample Magnetometer</td>
</tr>
<tr>
<td>PIPS</td>
<td>Passivated Implanted Planar Silicon</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
</tbody>
</table>
List of Symbols

\( \mu_B \) Bohr Magneton
\( k_U \) Magnetocrystalline Anisotropy
\( H_{\text{saturation}} \) Saturation field
\( M_s \) Saturation Magnetization
\( H_c \) Coercivity
\( M_r \) Remnant Magnetization
\( \Delta T \) Transition Width
\( \Delta T_{\text{Hysteresis}} \) Hysteresis Width
\( \Delta T_{\text{Heating}} \) Transition on-set temperature (heating)
\( \Delta T_{\text{Cooling}} \) Transition on-set temperature (cooling)
\( \Delta\theta_{50} \) Full-widths of half maximum of rocking curve
\( \theta-2\theta \) Theta-2Theta
\( \langle e^2 \rangle^{1/2} \) Root-mean-square strain
Chapter 1: Introduction

1.1 Anti-ferromagnetic/Ferromagnetic Transitions of FeRh

Early measurements by Fallot and Hocart\textsuperscript{1,2} on equiatomic bulk FeRh (Iron-Rhodium) alloy revealed an unusual magnetic transition from anti-ferromagnetic state to ferromagnetic state. The transition, coupled with an increase in volume, is known to exist at low temperatures of about 350K subjected to conditions of environment and sample preparation conditions. Temperature hysteresis accompanied the abrupt magnetization changes suggested the transition was of a first-order nature exhibiting discontinuity in one or more of its properties. X-ray diffractions (XRD) performed showed that FeRh, in ferromagnetic state, had an ordered CsCl structure, and retained its CsCl structure at temperatures below the transition. Despite the similar structures, the transition from anti-ferromagnetic to ferromagnetic yielded a rapid yet uniform volume expansion of approximately 1% of this ordered cubic structure.\textsuperscript{3,4}

Magnetization-temperature measurements of bulk FeRh below the transition temperature showed a slow increase in magnetization linear with increasing temperature. At 350K, magnetization experienced an abrupt increase, and continues to rise sharply till saturation. Further increases in temperature beyond the transition resulted in behaviors similar to normal ferromagnets with gradual decrease in magnetization becoming paramagnetic phase at Curie temperature of 670K\textsuperscript{5} indicative of a second-order transition\textsuperscript{6}. Subsequent work in neutron diffraction\textsuperscript{7,8} and Mössbauer spectroscopy\textsuperscript{9} showed collinear spin structure with moments of approximately 3.2 \(\mu_B\) per Fe atom and 0.9 \(\mu_B\) per Rh atom for the ferromagnetic state indicating that the Rh atoms do contribute
to the total ferromagnetically aligned moments. Collinear spin structure was also observed with the anti-ferromagnetic state with moment of 3.3 $\mu_B$ per Fe atom. No magnetic moment was however observed in the Rh atoms due to the magnetic symmetry of its structure. \(^{10}\)

Electrical measurements of bulk equiatomic FeRh showed abrupt decreases in resistivity at 350K, consistent with the first-order anti-ferromagnetic to ferromagnetic transition. Thermal hysteresis was noted and further increases in temperature beyond transition led to a more gradual increase in resistivity and eventual plateau at the Curie temperature.

### 1.2 Extrinsic and intrinsic factors on phase transition and properties of FeRh

The magnetic properties and phase transition of FeRh were well known to be highly sensitive to a variety of conditions both during the fabrication process as well as external influences. \(^{11}\) This indicated the possible problems in sample reproduction. As such, careful control and understanding to these conditions are critical to the repeatability and reliable cross comparison of samples. However, such sensitivity would also allow FeRh to be finely manipulated to specific needs and properties, as well as the possibility in developing high-resolution sensing devices keenly associated with these conditions. Some of the properties are described in the following.
1.2.1 Composition dependence

It was well established that the temperature induced first-order anti-ferromagnetic to ferromagnetic phase transition of bulk FeRh occurred approximately between the narrow window of 48 and 52 at. % Rh. Deviations from near equiatomic ratios resulted in formation of other phases with composition dependent magnetic behaviors as seen in Figure 1.  

![Phase diagram of the FeRh alloy](image)

*Figure 1.1  Phase diagram of the FeRh alloy.*

The initial addition of Rh to pure Fe led to increasing Fe magnetic moment which reached a maximum at approximately 25 at. % Rh. The structure was of disordered Body-Centered Cubic (BCC) until 20 at. % Rh, commonly designated as α-phase in phase diagrams, and is ferromagnetic in nature. Beyond 20 at. % Rh, structurally ordered CsCl
\( \alpha' \)-phase were observed, and extended to 52 at. \% Rh. \(^{12,13}\) FeRh within this composition continues to behave ferromagnetically until approximately 50 at. \% Rh in which its magnetic moment experienced a sharp decline becoming anti-ferromagnetic. Further increase in Rh, resulted in the formation of a Face-Centered Cubic (FCC) \( \gamma \)-phase that is paramagnetic.

1.2.2 Form factor effects

Initial work on FeRh were mainly focused on bulk form. However, much of subsequent works were carried out on polycrystalline thin films 200 nm or less, deposited on amorphous substrates such as glass. \(^{14}\) In contrast to the sharp and narrow thermal hysteresis of the first-order anti-ferromagnetic to ferromagnetic transitions experienced in bulk equiatomic FeRh, thin films exhibited broad and incomplete transitions accompanied by large thermal hysteresis. This was often attributed to the presence of stress distribution, as well as concentration variations of Rh due to its slow diffusivity which formed mixed \( \alpha'/\gamma \) phases, where the presence of \( \gamma \) phase impeded the anti-ferromagnetic/ferromagnetic transition. \(^{15}\)

Composition dependence magnetization behavior at 25°C of thin films also differed significantly from bulk form. Instead of an abrupt decrease in moment for bulk FeRh near equiatomic ratios, the decrease in moment for thin films occurred gradually between 30 and 59 at. \% Rh. Even at Rh content of 59 at. \%, magnetization was still observable and the film not fully anti-ferromagnetic. \(^{16,17}\) This was due to the
compositional fluctuations and the presence of FCC phase which destabilized the ordered CsCl structure resulting in an incomplete anti-ferromagnetic phase.

1.2.3 Elemental doping and impurities

Earlier works on modified Mn$_2$Sb showed that the addition of a third elemental dopant, $X$, resulted in changes to its first-order anti-ferromagnetic to ferrimagnetic transition temperature.$^{18, 19}$ These results prompted modifiers to be added to FeRh in order to study dopant effects on the first-order anti-ferromagnetic to ferromagnetic transitional behaviors of equiatomic bulk FeRh.$^{20, 21}$ Observable changes to FeRh included decreased transition temperature, increased transition temperature, or the elimination of the phase transition. Addition of as little as 2 at. % of modifiers such as Co, Ni, Cu, Nb, Mo, Ta, or W eliminated the phase transition resulting in FeRh-$X$ becoming ferromagnetic at all temperatures below Curie temperature.$^5$ Modifiers such as Pd, V, Mn, or Au decreased the FeRh-$X$ transition temperature, while Ru, Os, Ir, and Pt increased it. With the increased dopant content, modifications of transition temperature became enhanced with larger Pt content leading to higher transition temperatures, while larger Pd content resulted in further reduced transition temperatures with stabilized ferromagnetic state at temperatures as low as -195°C. However, both Curie temperatures and maximum magnetization decreased with larger doping. This potentially allowed the transition behavior to be modified in accordance to different needs by introduction of dopant and strict compositional control.
Modifications of the phase transition could also be achieved through introduction of various gases during post-deposition annealing. Thin films of FeRh typically exhibit incomplete and broad transitions. Upon annealing in dry $N_2$ environment with traces of several hundred ppm of $O_2$ however, a complete transition was observed with a narrower transition width. Maximum magnetization decreased due to the surface oxidation of the film. The process could be reversed by further annealing in dry $H_2$ environment resulting in a thermal transition similar to the original partial hysteresis transformation.

1.2.4 Thermal and mechanical treatment

FeRh samples prepared by mechanical means such as ball milling, press forging or rolling, often suffered from severe plastic deformation which resulted in the formation of disordered paramagnetic FCC phase. Highly ordered CsCl structure, which exhibit the first-order anti-ferromagnetic to ferromagnetic transition, could be recovered through high temperature post-annealing which undergoes three distinct phases of transformation. The first phase consisted of a rapid disappearance of FCC phase and the formation of the ordered CsCl phase. The sample became predominantly ferromagnetic at all temperatures below Curie point but with intermediate values of magnetization. The second phase of post-annealing showed no visible changes to structure in x-ray diffraction spectrums. However, with prolonged annealing times, magnetization-temperature measurements displayed the manifestation of a broad thermal hysteresis associated with the first-order transition. Large magnetization present at temperatures below the transition indicated an incomplete change, while the magnetization at the ferromagnetic region of the transition
increased with annealing time. The third phase consisted of a slow and long recovery process where the first-order transition regained much of its pre-deformed characteristics. Continuous anneal resulted in sharper and narrower thermal hysteresis. Magnetization at temperatures below transition decreased while magnetization at the ferromagnetic region of the transition increased indicating the transition becoming more complete. 22, 23

1.2.5 Pressure effect

Studies carried out on equiatomic FeRh revealed the existence of a triple point in its pressure-temperature phase diagram. 24, 25 With increased external pressure applied, the first-order anti-ferromagnetic to ferromagnetic transition temperature increased, while the second-order ferromagnetic to paramagnetic (Curie temperature) transition temperature decreased. At high pressures of approximately 6 GPa, ferromagnetic phase in the pressure-temperature phase diagram became non-existent as the two transition temperatures coincide resulting in a direct transition from anti-ferromagnetic to paramagnetic phase at pressures beyond the triple point. 26, 27 The triple point in sensitive to a number of parameters such as FeRh composition and elemental dopants such as Ir and Pd. 28 The inclusion of 6 at. % Ir dramatically reduced the triple point such that the ferromagnetic phase disappeared from the pressure-temperature phase diagram at pressure of 1.5 GPa.
1.2.6 Field induced transition

Isothermal measurements of magnetization with respect to magnetic field demonstrated that increasing an applied external field allowed magnetization of FeRh to be increased under constant temperature conditions suggesting a field-induced transition from anti-ferromagnetic to ferromagnetic state. Such transitions were reversible with the removal of applied field, but possessed field hysteresis between the application and removal of field. The field required to induce complete transition to ferromagnetic state could be reduced with the increase in temperature. Similarly, the application of a fixed field to FeRh was known to reduce the transition temperature of the first-order transition. Increasing the applied fields resulted in a shift of its thermal hysteresis towards lower temperature. Under the field-temperature phase diagram, the first-order phase transition could thus be described by the empirical relationship:

\[
\frac{H}{H_0} = 1 - \left( \frac{T}{T_0} \right)^2
\]  

(1.1)

where \(H_0\) and \(T_0\) are composition dependent quantities describing the transition field at 0K and transition temperature at 0T respectively.

1.3 Application of FeRh

Equiatomic FeRh with CsCl structure is known for its unusual first-order anti-ferromagnetic to ferromagnetic phase transition when subjected to elevated temperatures of approximately 350K. The ease of accessibility of the FeRh transition temperature, typically 50 to 100K above room temperatures, had attracted significant interests in
multiple fields such as heat assisted magnetic recording disk drives (HAMR), and microelectromechanical devices (MEMS).

1.3.1 Heat Assisted Magnetic Recording Media

One of the key challenges faced by the magnetic recording industry is to maintain the continued increase in recording areal densities.\textsuperscript{31} This is typically achieved through scaling of the media by continued reduction in both grain size and distribution, thereby increasing the total grain density while maintaining the signal-to-noise ratio. The difficulty with this approach is that with reduction in grain size, the magnetic anisotropy energy of the grains, given by the product of magnetocrystalline anisotropy of the material ($k_u$) and the volume of the grain, decreased. This subjected the grains to be more susceptible to ambient thermal fluctuations eventually resulting in uncontrolled magnetization reversals when the limit of grain size reduction was reached. In order to maintain the stability of small grains, materials with high magnetocrystalline anisotropy such as FePt were required. Yet conventional recording heads were unable to write on FePt-based media due to limitations of the write field not being able to overcome the media’s large anisotropy. To that, heat assisted magnetic recording (HAMR) was proposed to delay the onset of the superparamagnetic limit in which the coercivity of FePt could be reduced through heating to temperatures close to Curie point. At such high temperatures however, large thermally-induced stress was induced, loss of perpendicular anisotropy and magnetization, as well as severe degradations of the lubrication layer.
would pose significant problems. Thus a bilayer structure comprising of FeRh and FePt was proposed.

Such structure when heated to temperatures above FeRh transition but well below FePt Curie temperature acted like a thermal-magnetic switch, allowing the low magnetocrystalline anisotropy ferromagnetic FeRh to reduce the coercivity of FePt via an exchange spring mechanism. This allowed the writing of data to be done in a lower field than would be required of a single FePt layer. The data were subsequently stored at temperatures below FeRh transition where it behaved anti-ferromagnetically. Thermal stability of the stored data was therefore determined solely by the high anisotropy FePt layer. Overall, the proposed structure could reduce the switching field of FePt media at significantly lower temperatures without compromising thermal stability.

Since then, much work had been focused on prevention of interlayer diffusion between FeRh and FePt arising from the high deposition temperatures of 500°C and above. Interlayer diffusion posed a large problem for the bilayer structure as it not only broadens the anti-ferromagnetic/ferromagnetic transition of FeRh but also deteriorates the epitaxial growth and ordering of FePt, as well as dampened the exchange coupling among the bilayer. The interlayer diffusion could be however reduced through addition of buffer layers between FeRh and FePt, or the acceleration of FePt ordering under lower temperatures through doping of FePt with Ag or C. If successful, HAMR media would require less heating for data writing thus reducing energy consumptions on HAMR hard disk drives. At the same time, severity of thermally induce lubricant degradation would also be reduced while the strict criteria for high temperature disk overcoat and lubricant could be relaxed opening up more options.
1.3.2 Other applications

Other applications of FeRh include being employed in microelectromechanical systems (MEMS), as well as spin-valve sensors. The large volume expansion of about 1% arising from both simultaneous anti-ferromagnetic to ferromagnetic phase transition and large electrical resistivity change allowed FeRh to be employed as electrostatic and magnetically actuated micro-switches, micro-motors and accelerometers. \(^{36,37}\) However, much work are still required as FeRh in thin film form could not be easily deployed in such applications due to the inability to obtain sharp and complete transitions in very thin films.

Thin anti-ferromagnetic films in particular FeRh are attracting much attention as they could be employed as pinning layers in spin-valve structures. The high pinning force coupled with strong corrosion resistance of FeRh were two key reasons for such interest. Work on NiFe/FeRh-Ir had shown considerably high coercivity originating from NiFe/FeRh-Ir interface which could be employed as pinning layer in spin-valve structures. \(^{38}\)

1.4 Research objectives

Equiatomic FeRh and its unique anti-ferromagnetic to ferromagnetic phase transition had garnered much interest due to the convenience of its transition temperature. Much studies performed on FeRh were focused on bulk form, nanoparticles, or polycrystalline thin films that were randomly oriented. Yet for many practical applications, highly textured FeRh thin films are highly desired for the integration into
devices through heteroepitaxial growth of multilayered film structures, which up till now are not yet widely investigated. Thus the objectives of this work are,

1. To determine the effects of composition variation on highly (001) texture FeRh thin films and its first order anti-ferromagnetic to ferromagnetic phase transition. Discussions will focus on both the composition dependence behaviors of FeRh as well as the thermal behaviors with respect to the different compositions.

2. Investigate the structural, magnetic and phase transition behaviors with reduction of film thicknesses at various compositions both of stoichiometric and off-stoichiometric compositions.

3. Study the behavior of textured FeRh thin films doped with various amounts of Ir. This portion would focus on the effects of Ir doping, in particular the differences between different Fe-Rh compositions.

1.5 Outline of dissertation

This dissertation is organized into 6 chapters. The first chapter would give an introduction on the unique properties of the FeRh alloy and its potential applications. Chapter 2 gives an overview of the experimental techniques employed for this study. In Chapter 3, the effects of compositional variation on (001) texture FeRh thin films would be investigated. Chapter 4 addressed the changes to textured FeRh with reduction in tin film thickness. The changes to structure, magnetic properties and phase transition with Ir doping into FeRh of various compositions would be investigated in chapter 5. In chapter 6, a summary of the dissertation was compiled.
Chapter 2: Experimental Techniques

This chapter focuses on the methods of sample fabrication and characterization that were employed during the course of investigation. Fabrication of samples was carried out by means of con-focal magnetron sputtering. Composition of the films were determined by means of Rutherford Backscattering Spectrometry (RBS). Magnetic properties were characterized by Alternating Gradient Forced Magnetometer (AGFM), Superconducting Quantum Interference Device (SQUID), and Vibrating Sample Magnetometer (VSM). Structural determinations were carried out using X-ray Diffraction (XRD). These methods are further detailed in this chapter.

2.1 Sample Fabrication

The FeRh thin films in this work were deposited by magnetron sputtering. This method is widely used in thin film deposition works due to its enhanced sputter yield, excellent film uniformity, and ability to utilize a wide selection of metallic and non-metallic materials. Control over a variety of parameters such a working gas and pressure, deposition power and rates, and in-situ temperature allow for manipulation of the films’ structure and related properties making this method highly versatile.

Magnetron sputtering is accomplished by ejecting atoms from material targets by bombarding these target surfaces with highly energized particles. The ejected atoms would be adsorbed on the substrate surface forming a thin film. More in-depth knowledge about sputter and its related physics could be found in many textbooks. 39
The deposition system utilized in this work is a high vacuum magnetron sputtering system with four confocal cathodes each containing a target material lined in a circular fashion directed at the substrate centered and above the four cathodes. Base pressure of $3 \times 10^{-8}$ Torr or lower was obtained before the introduction of 99.999% purity Argon working gas, in order to minimize contamination. Chamber pressure was held at $3 \times 10^{-3}$ Torr during the deposition process through varying the throttle valve position of the cryogenic pump. Fe-Rh and Fe-Rh-Ir alloys were deposited on MgO single crystal substrates by co-sputtering two or three cathodes respectively. Three of the cathodes were utilized containing in each a Fe target (99.99% purity), Rh target (99.9% purity) and Ir (99.99% purity). Composition of the films were varied by tuning the sputtering power of Rh and Ir targets, while keeping the Fe target sputtering power/rate fixed.

### 2.2 Compositional Determination using Rutherford Backscattering Spectrometry

Rutherford Backscattering Spectrometry (RBS) is a commonly used non-destructive technique for characterization of the elemental composition, thickness, and depth profiles of thin films. Typically in the quantitative analysis of elemental compositions, a beam of mono-energetic $\text{H}^+$ or $\text{He}^+$ ions is directed at the sample. The ion beam generated in a mass accelerator is accelerated, and mass- and charge-selected producing a mono-energetic beam in the MeV range. Of the incident ions, a fraction is scattered backwards from the atoms near the sample surface and detected by a passivated implanted planar silicon (PIPS) detector located at an angle from the incident beam. The backscattered ions, upon collision, undergo transfer of energy to the target atoms. Thus
through evaluation of the energies of the backscattered particles, information such as composition, depth as well as thickness of the different films could be determined.  

2.3 Magnetic Characterization

Magnetic properties of FeRh thin films such as saturation magnetization, magnetic hysteresis loop, and thermal-magnetic hysteresis loops were of particular interest. As such, various techniques were employed to extract such information.

2.3.1 Magnetic Hysteresis Loop Measurement

2.3.1.1 Alternating Gradient Force Magnetometer

The Alternating Gradient Force Magnetometer (AGFM) is a system which is highly sensitive and a faster form of magnetic measurement than conventional vibrating sample magnetometer (VSM). It features a piezoelectric incorporated cantilever rod where the sample is mounted on one end. The sample is subjected to a DC field while simultaneously exposed to a small alternating gradient field which exerts an alternating force on the sample. The deflection of the cantilever caused by the force on the sample is measured by the output voltage generated by the piezoelectric element and is greatly amplified when the system operates near the mechanical resonance frequency of the cantilever. The AGFM used in this study was the MicroMag 2900 magnetometer by Princeton Measurement Corporation.
Chapter 2: Experimental Techniques

Figure 2.1 Magnetic hysteresis loop.

For measurements of the magnetic hysteresis loop, a field, $H_{\text{saturation}}$, that is strong enough to saturate the sample was applied. The field was subsequently decreased in steps till $-H_{\text{saturation}}$, and back to $H_{\text{saturation}}$, while the corresponding magnetization values were measured at each interval. A typical hysteresis loop obtained is shown in Figure 2.1. Here, information such as saturation magnetization ($M_s$), remnant magnetization ($M_r$) and coercivity ($H_c$) could be obtained from the hysteresis loop.
2.3.2 *Thermal-Magnetic Hysteresis Loop*

2.3.2.1 *Superconducting Quantum Interference Device*

The Superconducting Quantum Interference Device (SQUID) is a highly sensitive magnetic measurement device capable of sensing extremely subtle magnetic fields. The SQUID used in this study was manufactured by Quantum Design Inc. with a maximum applied field of up to 7 Tesla, and temperature control capable of cooling and heating samples from 4K to 400K. The current set-up used was a direct current (DC) SQUID consisting of two Josephson junctions connect in series in a superconducting loop. A comprehensive review of the working principles of Josephson junctions and SQUID could be found in several textbooks and journal papers.\(^{42, 43, 44}\)

![Figure 2.2 Thermal-magnetic hysteresis loop](image)
As the anti-ferromagnetic to ferromagnetic transition of FeRh alloys are temperature dependent, the SQUID was employed to measure the magnetization values of the samples at different temperatures states. Before the measurement began, a steady magnetic field capable of saturating the sample was applied. In this study, the samples were subjected to a field of 0.5T during the measurement. The samples were cooled to 200K and temperature was increased to 400K in steps. Magnetization was measured at each interval of the heating process. The same was applied to the cooling process from 400K back to 200K. A typical thermal-magnetic hysteresis obtained is shown in Figure 2.2. Parameters such as hysteresis width ($\Delta T_{\text{Hysteresis}}$), width of the transition ($\Delta T$), and transition on-set temperature ($\Delta T_{\text{Heating}}$ and $\Delta T_{\text{Cooling}}$) could be obtained.

2.3.2.2 Vibrating Sample Magnetometer

The Vibrating Sample Magnetometer (VSM) is a very common instrument for magnetic materials characterization. It operates on Faraday’s Law of Induction where changes in magnetic flux $d\phi/dt$ caused by a vibrating magnetic sample produces a proportionally induced voltaged $V(t)$ in the electrical circuit given by,

$$V(t) = -C \frac{d\phi}{dt}$$

(2.2)

The induced voltage could be measured and information regarding the sample could be obtained.\(^4^5\) The VSM employed in this study is the Vector Magnetometer Model-10 VSM by Microsense, LLC (previously known as ADE Technologies). It is capable of multiple different functions including temperature dependence measurements of magnetic
materials. The advantage of the VSM over SQUID in terms of thermal-magnetic hysteresis loop measurement is its capability to measure temperatures up to 550K, whilst the SQUID is limited to a maximum operating temperature of 400K. The measurement method is similar to that used in SQUID to determine the thermal-magnetic hysteresis loop. A steady field of 0.5T was applied to saturate the sample. The loop was obtained by measuring the magnetization at each step of during the heating and cooling process.

2.4 Crystallographic structure determination

The X-ray diffraction (XRD) is a technique used to determine the crystallographic texture and structure of material. The basic principle of the x-ray diffraction is based on Bragg’s Law given by:

\[ 2d_{hkl} \sin \theta = n \lambda \]  

(2.3)

where \( d_{hkl} \) is the inter-planar lattice spacing of the diffracting\{hkl\} plane, \( \theta \) is the angle between the x-ray source and diffracting plane, \( n \) is a positive integer denoting the order of diffraction, and \( \lambda \) the wavelength of the x-ray. The XRD used in this study included Phillips X’pert PRO MRD, Phillips X’Pert PRO with Anton Parr HTK 1200N heating attachment for measurements under non-ambient temperature conditions, and Bruker D8 DISCOVER Thin Film XRD.
2.4.1 Theta-2Theta (θ-2θ) measurements

In theta-2theta x-ray diffraction scans, both the x-ray source and detector move in relation to the sample with the incident x-rays forming an angle $\theta$ with the surface of the sample, and an angle of $2\theta$ with the detector as seen in Figure 2.3.

![Principles of X-ray diffraction](image)

*Figure 2.3  Principles of X-ray diffraction*

The measurement was carried out within a user-defined range of $2\theta$. The intensity of the diffracted x-ray was measured at each $2\theta$ value within the scan range at predefined intervals. The measured intensity was then plotted against diffracted $2\theta$ angles, the
diffraction peaks indexed and the phases were compared with experimental peak positions from the Joint Committee on Powdered Diffraction Standard (JCPDS). The lattice parameters $a$ and $c$ of FeRh could thus be obtained through the following equation $^46$,

$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2)}{a^2} + \frac{t^2}{c^2}$$

(2.4)

Peaks of particular interest to this study are the $\alpha'$-phase FeRh (001) superlattice and (200) fundamental peaks, and $\gamma$-phase FeRh (200) peak. The relative degree of chemical ordering of the $\alpha'$-phase could be obtained by taking square root of the ratio of the normalized integrated intensity of the $\alpha'$-phase FeRh (001) and (002) peaks.

$$\text{ratio of integrated intensities} = \sqrt{\frac{I_{(001)}}{\Delta\theta_{50} (001)}} \frac{I_{(002)}}{\Delta\theta_{50} (002)}$$

(2.5)

Both $I_{(001)}$ and $I_{(002)}$ are the integrated intensities of $\alpha'$-phase FeRh (001) and (002) diffraction peaks, while $\Delta\theta_{50} (001)$ and $\Delta\theta_{50} (002)$ are the corresponding full-widths at half maxima of the rocking curves of the $\alpha'$-phase peaks.

### 2.4.2 Rocking curve measurements

The quality of a film texture could be investigated through rocking curve scans. This method is employed to determine the spread of deviations present in the lattice plane of a diffraction peak away from the axis normal to the lattice plane. The rocking curve is
measured by first determining the $2\theta_{\text{peak}}$ angle of the peak of interest. The detector is then fixed constantly at $2\theta_{\text{peak}}$ with respect to the incident x-rays, while the incident x-ray was swept a range of $\pm \theta_{\text{scan}}$ about $\theta_{\text{peak}}$ and the intensity of the diffracted x-rays measured. The axis dispersion of the lattice plane was determined through the full-width at half maxima ($\Delta \theta_{50}$) of the rocking curve where a small $\Delta \theta_{50}$ signifies smaller dispersion and better texture.

2.4.3 **Non-ambient temperature XRD scan**

The changes in crystallographic texture of the sample when exposed to elevated temperatures were measured using Phillips X’Pert PRO with Anton Parr HTK 1200N heating attachment. The sample chamber was first evacuated to high vacuum of pressure in the range of $10^{-6}$ Torr, and held in high vacuum throughout the measurement in order to minimize reactions with ambient gases during high temperature measurements. The samples were then heated in pre-defined intervals and similarly cooled down to room temperature. At each temperature interval, theta-2theta scan was performed in order to determine the crystallographic texture of the sample. Peak shifts and lattice parameter changes could be determined from the scan.
2.4.4 **Lattice strain determination**

2.4.4.1 **Reciprocal lattice mapping**

In order to examine the epitaxial relations and lattice strain of FeRh thin films deposited on single crystal MgO substrates, reciprocal lattice of both film and substrates were mapped out in the reciprocal space. The strain status of the FeRh layer (complete relaxation, fully matched, or partially matched) could thus be determined by comparison of the relative positions of the reciprocal points of both film and substrate seen in Figure 2.4. The reciprocal space also shows the distribution of diffracted intensities of each reciprocal point. The quality of the film, mosaicity, and macroscopic strain could be observed in these maps, as different forms of imperfections broaden the diffracted intensity in different directions. The reciprocal space map in this study was obtained using D8 Discover high resolution x-ray diffraction (HRXRD) manufactured by Bruker AXS.
2.4.4.2 Strain broadening effect

To investigate the lattice strain within the FeRh thin films, both the full-widths at half maxima, as well as the Bragg peak positions of (001) and (002) peaks of α'-phase FeRh were required. The root-mean-square strain $\langle e^2 \rangle^{1/2}$ of FeRh thin films could be determined through amount of peak broadening of the respective Bragg peaks by plotting the FWHM of the Bragg peaks, $\Delta K$, as a function of the Bragg peaks. The Bragg peak, $K$, was given in terms of momentum transfer by,
Thus, root-mean-square strain $\langle e^2 \rangle^{1/2}$ of FeRh could be determined through strain broadening effects of the Bragg peaks given by $^{47,48}$,

$$\Delta K = A \langle e^2 \rangle^{1/2} K$$ (2.7)

where $A$ is a constant depending on the strain distribution and is approximately taken to be 1 for a random dislocation distribution.
Chapter 3: Compositional dependence on the phase transition of FeRh thin films

As discussed previously in Chapter 1, magnetic and structural behaviors of FeRh alloy are highly sensitive to the compositional variations. Thus, careful study and understanding of the changes in properties of (001) epitaxially textured FeRh thin films is important in its implementations into various applications.

3.1 Experimental Techniques

To investigate the compositional effects of textured FeRh thin films, 100 nm thick Fe$_{100-x}$Rh$_x$ films of compositions $x = 35$ to $65$ were deposited on (001) textured MgO single crystal substrates which were preheated and maintained at 400$^\circ$C with in-situ heating. Base pressure of the chamber during fabrication process was $2 \times 10^{-8}$ Torr while working pressure was $3 \times 10^{-3}$ Torr with Argon as the working gas. The films were deposited by co-sputtering both Fe and Rh targets simultaneously, and adjusting the composition through varying Rh sputter rate by changing its sputtering power while keeping the Fe sputter rate constant. Compositions of the films were then confirmed using Rutherford Backscattering Spectrometry. Film texture and microstructure were characterized using x-ray diffraction while magnetic properties were determined using alternating force gradient magnetometer and superconducting quantum interference device.
3.2 Results and Discussion

3.2.1 Crystallographic structure of $\text{Fe}_{100-x}\text{Rh}_x$ thin films

X-ray diffraction theta-2theta spectra of $\text{Fe}_{100-x}\text{Rh}_x$ samples of different compositions were shown in Figure 3.1. Compositions of between 35 to 55 at. % Rh showed only (001) superlattice and (002) fundamental peaks belonging to the $\alpha'$-phase FeRh suggesting that chemically ordered CsCl structure were obtained. Increasing Rh content resulted in deteriorations in intensity of (001) and (002) $\alpha'$-phase peaks. Further increases beyond 55 at. % Rh led to the appearance of (200) peak belonging to the Face Centered Cubic (FCC) $\gamma$-phase FeRh. Peak intensity of the $\gamma$-phase (200) peak increased with increasing Rh content indicating the dominant presence of the $\gamma$-phase at higher Rh contents. Compositions of the thin films were confirmed using Rutherford Backscattering Spectrometry (RBS) and shown in Figure 3.2, which agreed well with the calculated values of the sputtered films.

Figure 3.3(a) showed the relative chemical ordering parameter represented by the square root of the ratio of normalized integrated intensity of the (001) superlattice and (002) fundamental peaks. Ordering of the $\alpha'$-phase increased initially with increasing Rh content suggesting improved ordering of the superlattice structure and remained constant when Rh content was 47 at. % and above. This suggested that the increased Rh content did not deteriorate the $\alpha'$-phase. Rather, the decreases in $\alpha'$-phase (001) and (002) peak intensities may be more likely due to a decrease in the amounts of $\alpha'$-phase and an increase in the $\gamma$-phase with the larger Rh contents.
Chapter 3: Compositional dependence on the phase transition of FeRh thin films

Figure 3.1 X-ray diffraction theta-2theta spectra of Fe$_{100-x}$Rh$_x$ thin films of different compositions from $x = 35$ to 65.

Figure 3.2 Rutherford Backscattering Spectrometry (RBS) measurement of compositions of Fe$_{100-x}$Rh$_x$ thin film for calculated compositions of Fe$_{55}$Rh$_{45}$ to Fe$_{45}$Rh$_{55}$.

Figure 3.3(b) depicts the changes of lattice parameter-c with Rh content, calculated from the corresponding (001) and (002) peak positions in the x-ray diffraction
spectra. The lattice parameter $c$ gradually increased with Rh content but experienced a sharp and discontinued decrease at Rh content of about 48 at. % Rh indicating a transformation in structure had occur.

![Graph (a)](image-a.png)

![Graph (b)](image-b.png)

**Figure 3.3**  (a) Relative ordering parameter of $\alpha'$-phase $\text{Fe}_{100-x}\text{Rh}_x$ thin films of various compositions from $x = 35$ to 65, and (b) Lattice parameter $c$ of $\text{Fe}_{100-x}\text{Rh}_x$ thin films of various compositions from $x = 35$ to 65.
3.2.2 Magnetic properties of Fe\textsubscript{100-x}Rh\textsubscript{x} thin films

Magnetization of FeRh thin films of various compositions were shown in Figure 3.4. Compositions between 35 to 47 at.% Rh behaved ferromagnetically with large magnetization values of beyond 1400 emu/cm\textsuperscript{3} as seen from the magnetic hysteresis in Figure 3.4 inset. A sharp decrease in magnetization from 1600 emu/cm\textsuperscript{3} to 200 emu/cm\textsuperscript{3} was observed at Rh content of around 48 at. %. Coupled with the sudden decrease in lattice parameter-c seen in Figure 3.3, the combined results suggested that a first-order phase transition from a ferromagnetic phase when Rh content was below 48 at. % to an anti-ferromagnetic phase when Rh was increased to 48 at. % and beyond had occurred. The transition of highly (001) textured FeRh films was much sharper compared to previous works of non-textured randomly oriented thin films which reported a gradual and continuous decrease in magnetization from 1800emu/cm\textsuperscript{3} to 200 emu/cm\textsuperscript{3} between the compositional range of 30 to 57 at. % Rh. \textsuperscript{49}

![Magnetization of 100nm thick Fe\textsubscript{100-x}Rh\textsubscript{x} thin films of various compositions from x = 35 to 65. Inset shows the magnetic hysteresis of Fe\textsubscript{60}Rh\textsubscript{40} and Fe\textsubscript{45}Rh\textsubscript{55} thin films.](image-url)
More rather, the compositional dependent transition of texture thin films resemble closely to the sharp transitions observed in previous works in bulk FeRh\textsuperscript{50}, although occurring at off-equiatomic compositions of between 47 and 48 at. %.

3.2.3 Temperature dependent crystallographic and structural changes

X-ray diffraction measurements were carried out at different temperature steps of between 25°C to 130°C in order to study the effects of heating and cooling on the structure of (001) texture FeRh thin films. Figure 3.5 showed the temperature dependence of XRD spectra of Fe49Rh51 thin film with 100nm thickness. Both (001) and (002) peaks of the $\alpha'$-phase shifted toward lower angles when heated suggesting the occurrence of lattice expansion, but shifted back to higher values upon cooling back to room temperature. The peak positions during both heating and cooling processes did not coincide with each other in the temperature range of between 50 to 100°C suggesting that thermal hysteresis corresponding to the anti-ferromagnetic/ferromagnetic transition were present in the thermal behaviors of lattice parameter-c of FeRh thin films.

As the temperature induced magnetic transition is a first-order transition accompanied by lattice expansion/contraction, the transition for different compositions could thus be studied through the thermal behaviors of the corresponding lattice parameters.
Figure 3.5  
X-ray diffraction measurements of α’-phase FeRh (001) superlattice and (002) fundamental peaks at different temperature steps during heating from 25°C to 130°C, and subsequently cooling from 130°C back to room temperature of 25°C

The lattice parameter-c, derived from x-ray diffraction theta-2theta spectra of the FeRh α’-phase (001) peak, measured at various temperatures between 25°C and 130°C for Fe_{100-x}Rh_x thin films of compositions between x =35 to 53 are shown in Figure 3.6. For films with Rh content of 47 at.% and lower, lattice parameter-c remained constant and was insensitive to temperature suggesting there was no phase transition within the temperature range of 20 to 130°C. Films with Rh content beyond 47 at. % showed distinct increases in lattice parameter-c when heated and decreases when samples were subsequently cooled to room temperature.
Chapter 3: Compositional dependence on the phase transition of FeRh thin films

Figure 3.6 Out-of-plane c lattice parameter of Fe\textsubscript{100-x}Rh\textsubscript{x} thin films of different compositions (x = 35 to 53) at different temperature steps from 25°C to 130°C. Sample was initially heated from 25 to 130°C and subsequently cooled back to 25°C

For compositions exhibiting such lattice transitions, hysteresis behaviors were also observed. Transition of Fe\textsubscript{51}Rh\textsubscript{49} thin film in Figure 3.7 was relatively sharp occurring over a width of 39°C with a hysteresis width of 5.5°C. The hysteresis width is taken to be the difference between the heating path and cooling path at midway of the transitions which increased monotonically to 14.5°C when Rh content was further increased to 53 at. %. Transition width was the range of temperatures through which the change in lattice parameter-c occurred. Similar to the behaviors of hysteresis width, the transition width experienced broadening with larger Rh content. Such behaviors
suggested the anti-ferromagnetic/ferromagnetic transition was not an abrupt change but more graduated with the presence of both the nucleating ferromagnetic phase and remaining anti-ferromagnetic phase together during the transition. This could be attributed to the presence of crystalline imperfections arising from the localized concentration of Rh atoms and that the broadening of the phase transition was likely due to the increased imperfections when Rh content was increased.

![Diagram showing Width of hysteresis (ΔT_{Hysteresis}), width of transition (ΔT), and transition onset temperature (T_{Heating}) of out-of-plane c lattice parameter for Fe_{100-x}Rh_x thin films of various compositions.](image)

**Figure 3.7** Width of hysteresis (ΔT_{Hysteresis}), width of transition (ΔT), and transition onset temperature (T_{Heating}) of out-of-plane c lattice parameter for Fe_{100-x}Rh_x thin films of various compositions.

The onset temperature in which the lattice expansion began was decreased monotonically from 71°C to 25°C when Rh content was increased from 48 to 53 at. %.
However, when temperature was subsequently reduced to room temperature, the lattice contraction began around 110°C with no significant variations regardless of composition.

### 3.2.4 Temperature dependent magnetic properties

![Figure 3.8](image)

Figure 3.8 Plot of magnetization of Fe$_{100-x}$Rh$_{x}$ thin films of different compositions (x = 40 to 55) at different temperature steps from -70°C to 130°C. Films were heated from -70 to 130°C and subsequently cool back down to -70°C. Applied field of 5 kOe was used during measurement.

Figure 3.8 depicts the magnetization behavior for FeRh thin films of various compositions under temperatures ranging from -70°C to 130°C. Films with Rh content below 47 at. % showed no significant changes in film magnetization and remained ferromagnetic throughout the entire temperature range agreeing well with the changes
observed previously in lattice parameter-c in Figure 3.6. Fe$_{53}$Rh$_{47}$ thin film showed no significant changes in magnetization and remained ferromagnetic temperatures of 50°C and above. However, at temperatures below 50°C, large decreases in magnetization was observed suggesting the anti-ferromagnetic phase started to form at lower temperatures. The transition was broad and considered to be a result of magnetic inhomogeneity arising from being off-stoichiometric and iron-rich, which was previously also noted in bulk FeRh.  

Films with Rh content beyond 47 at. % exhibited low magnetization at room temperature as observed in both Figure 3.4 and 3.8. Magnetization of these compositions increased however when heated to 130°C indicating the occurrence of phase transition from anti-ferromagnetic to ferromagnetic, consistent with the previously observed thermally induced lattice expansion behaviors. Films with near equiatomic compositions deposited on (001) textured MgO single crystal substrates exhibited sharp magnetization increases with narrow thermal hysteresis compared to films deposited on glass or quartz, which exhibited wide transitions.  

However, with increasing Rh content from 49 to 55 at. %, the thermally induced transition was observed to broadened much like those deposited on glass. Similarly, the on-set temperature of the transition towards ferromagnetic phase was reduced with increasing Rh content, mirroring the changes in lattice parameter-c. It was also noted in this set of experiments, the magnetization transitions occurred 15°C higher than the transitions in lattive parameter-c. This was attributed to the differences in the application and detection of temperature between SQUID’s sweeping measurements and XRD’s static measurements.
3.3 Summary

In this chapter, the effects of compositional variations on epitaxially (001) textured Fe$_{100-x}$Rh$_x$ thin films of 100nm thickness were presented. Compositional-dependent change in phase from ferromagnetic to anti-ferromagnetic phase with increasing Rh content were observed to be sharp, bearing similarities to bulk FeRh, but at off-equatomic compositions of between 47 and 48 at. % Rh. Temperature-induced first-order phase transitions for FeRh thin films could be studied through its thermal expansion and contractions behaviors in lattice parameters. Temperature-dependent magnetization measurements performed agreed well with the observed lattice parameter changes and showed that the anti-ferromagnetic to ferromagnetic transition for (001) textured FeRh thin films were narrow compared to the broad transitions of their randomly oriented counterparts. The temperature and the range of which such transition occur and the behavior of such transitions could be controlled through varying the Rh content with larger content resulting in broadened transition.
Chapter 4: Thickness effect on the thermal-magnetic behaviors of FeRh thin films

With the continued miniaturization of devices, reduction in film thickness is unavoidable and the effects it posed on films, in particular the broadening of thermal hysteresis, are becoming crucial and of key concern as maintaining sharp first-order antiferromagnetic/ferromagnetic transitions of FeRh thin films are still of upmost importance for any of its applications to be realized. Thus in this chapter, the relation between thickness of (001) textured FeRh thin films, and its magnetic and structural transitions were studied for equiatomic, Fe-rich, and Rh-rich FeRh thin films.

4.1 Experimental Methods

Iron-Rhodium (FeRh) thin films of various thicknesses ranging from 5nm to 200nm were fabricated on (001) textured single crystal MgO substrates through DC confocal magnetron sputtering, similar to the work done in Chapter 3. Thicknesses of the films were controlled through varying the sputtering time while keeping sputter rates constant. Composition of films were varied by adjusting the sputtering rates of Rh target through adjustments done to its sputter power, while keeping Fe sputter rates constant. The effects of thickness variation would be studied on compositions of Fe$_{52}$Rh$_{48}$, Fe$_{50}$Rh$_{50}$, and Fe$_{48}$Rh$_{52}$. 
4.2 Results and discussions

4.2.1 Phase transition and thermal behaviors of epitaxial Fe-rich FeRh thin films

4.2.1.1 Crystallographic structure of Fe-rich Fe\textsubscript{52}Rh\textsubscript{48} thin films

X-ray diffraction spectra of Fe\textsubscript{52}Rh\textsubscript{48} thin films with different thicknesses (Figure 4.1) showed that both (001) superlattice and (002) fundamental peaks belonging to $\alpha'$ phase FeRh were present suggesting that chemically ordered CsCl structure were obtained. Both peak positions shifted towards lower angles with reduction in film thickness suggesting expansions in the lattice parameter-$c$. No (200) peaks belonging to FCC $\gamma$-phase were observed.

![X-ray diffraction theta-2theta spectra of Fe\textsubscript{52}Rh\textsubscript{48} thin films](image)

**Figure 4.1** X-ray diffraction theta-2theta spectra of Fe\textsubscript{52}Rh\textsubscript{48} thin
The square-root of ratio of integrated intensities of the (001) superlattice peak to (002) fundamental peak normalized by full-width at half maximum values of their respective rocking curves in Figure 4.2 showed the relative degree of ordering among the films. With reduction in film thickness, ordering was observed to decrease monotonically with significant decreases especially at thicknesses of 20 nm and below. The reduction in ordering of the Fe$_{52}$Rh$_{48}$ films could be attributed to the presence of a second phase within the $\alpha'$ phase which act as defects creating imperfections.

\[ \text{Normalized } I_{(001)} / \text{Normalized } I_{(002)} \] ^{1/2} \]

**Figure 4.2** Square-root of the ratio of integrated intensities of the (001) superlattice peak to the (002) fundamental peak normalized by the full-width at half maximum values of their respective rocking curves for Fe-rich Fe$_{52}$Rh$_{48}$ thin films of various thicknesses from 5 nm to 200 nm.

\[ \begin{array}{c|c|c|c|c|c|c|c|c|c} \text{Thickness (nm)} & 0 & 50 & 100 & 150 & 200 \\ \hline \text{Normalized } I_{(001)} / \text{Normalized } I_{(002)} & 1.00 & 1.02 & 1.04 & 1.04 & 1.06 \end{array} \]

### 4.2.1.2 Magnetic properties of Fe-rich Fe$_{52}$Rh$_{48}$ thin films

Figure 4.3 showed the magnetization as well as corresponding lattice parameter-c and -a of Fe$_{52}$Rh$_{48}$ films of various thicknesses. The 200 nm thick film exhibited
magnetization of 50 emu/cm$^3$, and not zero as would be expected from a completely anti-ferromagnetic film. This suggested traces of disordered ferromagnetic phase present within the anti-ferromagnetic CsCl ordered phase although no other Bragg peaks, apart from those arising from the MgO substrate, were observed. This observation supported the possible notion of the presence of two phases in which the poorer ordering of the films was a possible consequence of.

![Graph showing the relationship between magnetization, lattice parameter-c, and lattice parameter-a multiplied by a factor of $\sqrt{2}$ of Fe$_{52}$Rh$_{48}$ thin films of thicknesses 5nm, 10nm, 20nm, 50nm, 100nm and 200nm.](image)

Figure 4.3  **Ambient temperature magnetization values, lattice parameter-c, and lattice parameter-a multiplied by a factor of $\sqrt{2}$ of Fe$_{52}$Rh$_{48}$ thin films of thicknesses 5nm, 10nm, 20nm, 50nm, 100nm and 200nm.**

Reduction in film thickness from 200 nm to 5 nm resulted in an increase in magnetization to 979 emu/cm$^3$. Correspondingly, lattice parameter-c behaved similarly to magnetization increasing with thickness reduction which was characteristic of first-order
AFM-FM transitions observed previously in chapter 3. The increases in magnetization and lattice parameter-c were especially prominent at thicknesses of 5 nm and 10 nm. Lattice parameter-a showed no changes between 20 nm to 200 nm, but increased for thicknesses below 10 nm. The increase in lattice parameter-a was especially distinct at 5 nm occurring together with the sharp rise in magnetization. Lattice parameter-a of its corresponding FCC cell was calculated by factoring √2 to the BCC lattice parameter-a (obtained from X-ray diffraction) given that the BCC unit cell was rotated 45° with respect to both its FCC cell and the MgO unit cell. The lattice parameter-a of the FeRh FCC cell at 5 nm thickness was obtained to be at 0.4212 nm, incidentally matching the lattice constant of MgO substrate of 0.4217 nm. Thus, with the reduction in Fe$_{52}$Rh$_{48}$ thickness, the films tended towards ferromagnetic state as observed with the increases in magnetization, lattice parameter-c and lattice parameter-a.

4.2.1.3 Temperature dependent magnetic properties

The magnetization behaviors of Fe$_{52}$Rh$_{48}$ thin films of various thicknesses across temperature range of -75°C to 130°C were shown in Figure 4.4. Distinct magnetic transitions of increased and decreased magnetization during the respective heating and cooling cycles occurred for thicknesses of between 10 nm to 200 nm. The transition was however less distinct for the thinnest film of 5 nm. The hysteresis was broad with small increments to the already large magnetization from 933 emu/cc to 1039 emu/cc upon heating suggesting the predominance of the ferromagnetic phase.
Chapter 4: Thickness effect on the thermal-magnetic behaviors of FeRh thin films

Figure 4.4 Magnetic-Thermal hysteresis of Fe$_{52}$Rh$_{48}$ thin films of thickness 200 nm, 100 nm, 50 nm, 20 nm, 10 nm and 5 nm. Films were heated from -75°C to 130°C and cooled back down to -75°C

The transition for the thicker 200 nm film was sharp with hysteresis width of 8°C. With the thinning of the film, the hysteresis width broadened monotonically to 42°C at 10 nm. The transitions also occurred at lower temperatures with reduced thickness while the slope of the hysteresis became gentler implying a more graduated nucleation of the ferromagnetic phase. At -75°C, the magnetization shifted towards higher values with thinner films suggesting that the fraction of ferromagnetic phase present, before any occurrence of thermally induced phase transition, was higher. Such observations could be attributed to the way FeRh film surface behaved as a catalyst for such transitions. The surface acted as a major defect due to the sudden truncation of bulk periodicity.
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encouraging first the nucleation of the ferromagnetic phase along the film surface propagating to within the bulk when heated. Thus as films become thinner, the proportion of surface area to volume increases, resulting in the increase of both proportion of ferromagnetic phase and magnetization of the film.

4.2.1.4 Temperature dependent crystallographic and structural changes

The thermal hysteresis of lattice parameter-\(c\) of Fe\(_{52}\)Rh\(_{48}\) thin films behaved in agreement with the thermal-magnetic properties shown in Figure 4.4 exhibiting hysteresis which broadened with reduction in film thickness shown in Figure 4.5(a). The root-mean-square strain \(<e^2>^{1/2}\) of Fe\(_{52}\)Rh\(_{48}\) thin films at different temperatures were shown in Figure 4.5(b). With the increase in temperature, lattice strain in the films of thickness 200 nm, 100 nm, and 50 nm generally increased attributing to the differences in thermal expansion between film and substrate. A discontinued decrease was however observed amidst the increasing strain. Conversely, the films displayed reversed behaviors when cooling down exhibiting hysteresis behaviors much like those observed in both magnetization and lattice parameter-\(c\). The temperature at which the discontinued strain decrease occur reduced with film thickness, and happened simultaneously with the sudden increase in both lattice parameter-\(c\) and magnetization as seen in Figure 4.5(a) and 4.4 respectively. This suggested during the phase transition with increasing temperature from an anti-ferromagnetic phase to a ferromagnetic phase, the films experienced a sharp relaxation in strain likely associated with the thermal expansion of the lattice parameter-\(c\). In general, the magnitude of strain was observed to be larger for
thinner films, while the discontinued strain decreased experience with was also more distinct for thinner films as the increase in lattice parameter-c from anti-ferromagnetic to ferromagnetic phase relaxes the lattice strain.

\[
\text{Lattice parameter-c (Å)} \quad \text{Temperature (deg C)}
\]

\[
\text{Lattice strain } \langle e^2 \rangle^{1/2} \quad \text{Temperature (deg C)}
\]

Figure 4.5  (a) Thermal behavior of lattice parameter-c of Fe\textsubscript{52}Rh\textsubscript{48} thin films of thickness 200nm, 100nm, 50nm and 20nm, and (b) thermal behavior of the root-mean-square strain of Fe\textsubscript{52}Rh\textsubscript{48} thin films of 200nm, 100nm and 50nm thickness.
4.2.1.5 Summary

The on-set temperature ($T_{\text{Heating}}$) and thermal hysteresis ($\Delta T_{\text{Hysteresis}}$) width of both magnetization and lattice parameter-c thermal behaviors were shown in Figure 4.6(a) and (b), while the mean strain $<e^2>^{1/2}$ of the films at ambient temperature were shown in Figure 4.6(c).

![Graphs showing various data](image)

**Figure 4.6** (a) On-set transition temperature, $T_{\text{Heating}}$, and (b) Transition hysteresis width, $\Delta T_{\text{Hysteresis}}$ of Fe$_{52}$Rh$_{48}$ films of various thickness for the thermal-magnetic hysteresis, and thermal lattice parameter-c hysteresis. (c) Ambient temperature mean strain $<e^2>^{1/2}$ of Fe$_{52}$Rh$_{48}$ thin film of various thickness.
Decreases in the on-set temperature and broadening of thermal hysteresis were observed with thinner films, indicating a shift towards more heterogeneous nucleation of the ferromagnetic phase. Interestingly, these changes were synonymous with the monotonic increase in lattice mean strain with reduced film thickness. These behaviors accelerated with reduced film thickness and the film became predominantly ferromagnetic at 5 nm thicknesses, exhibiting little heat-induced phase transition as the lattice parameter-a of the film approached and matched that of the substrate. Such behaviors could be attributed to the increased formation of imperfections arising from the presence of ferromagnetic phase within the anti-ferromagnetic phase as the films become thinner, as well as the nucleation mechanism which first occur along the film surface and became more significant as thickness of the films decreases.

4.2.2 Phase transition and thermal behaviors of equiatomic Fe$_{50}$Rh$_{50}$ and Rh-rich Fe$_{48}$Rh$_{52}$ thin films

Similar to the investigation of Fe-rich Fe$_{52}$Rh$_{48}$ thin films, the magnetic properties and crystallographic texture of both equiatomic Fe$_{50}$Rh$_{50}$ and Rh-rich Fe$_{48}$Rh$_{52}$ thin films deposited on MgO (100) single crystal substrates were investigated for thickness varying from 5 nm to 200 nm and reported here.
4.2.2.1 Crystallographic structure of equiatomic and Rh-rich FeRh thin films

The x-ray diffraction spectra of both equiatomic Fe$_{50}$Rh$_{50}$ and Rh-rich Fe$_{48}$Rh$_{52}$ thin films of thicknesses 5 nm to 200 nm were shown in Figure 4.7.

![Figure 4.7 X-ray diffraction theta-2theta spectra of (a) Fe$_{50}$Rh$_{50}$ and (b) Fe$_{48}$Rh$_{52}$ thin films of thicknesses 5 nm, 10 nm, 20 nm, 50 nm, 100 nm, and 200 nm.](image)
Similar to the diffraction spectrum of Fe-rich thin films, only (001) superlattice and (002) fundamental peaks belonging to $\alpha'$-phase FeRh were present suggesting the presence of chemically ordered CsCl structure. No observable peaks belonging to $\gamma$-phase FeRh were present. Both $\alpha'$-phase FeRh (001) and (002) peaks shifted to lower angles with the reduction in film thickness indicating increases in the lattice parameter-c.

4.2.2.2 Magnetic properties of equiatomic and Rh-rich FeRh thin films

Figure 4.8 showed the magnetization of both equiatomic and Rh-rich FeRh films of different thicknesses from 5 nm to 200 nm, together with the corresponding lattice parameter-c and lattice parameter-a. Reduction in thickness from 200 nm to 5 nm resulted in an increase in magnetization for both equiatomic and Rh-rich films indicating a shift towards ferromagnetic phase. The increases were especially significant when thicknesses of the films fall below 20 nm, which increased from 100 emu/cm$^3$ to 920 emu/cm$^3$ for the equiatomic films, and from 110 emu/cm$^3$ to 840 emu/cm$^3$ for the Rh-rich films. Magnetization of films thicker than 20 nm however showed no significant changes for both compositions suggesting the magnetization at room temperature was less sensitive to the thicknesses variations between 20 to 200 nm resulting in no observable ferromagnetic transitions, and the significance of the surface nucleation mechanism of the ferromagnetic phase could become more prominent with thickness below 20 nm.
Chapter 4: Thickness effect on the thermal-magnetic behaviors of FeRh thin films

Figure 4.8  Ambient temperature magnetization values, lattice parameter-c, and lattice parameter-a multiplied by a factor of $\sqrt{2}$ of (a) Fe$_{50}$Rh$_{50}$ and (b) Fe$_{48}$Rh$_{52}$ thin films of thicknesses 5nm, 10nm, 20nm, 50nm, 100nm and 200nm.

Lattice parameter-a for both equiatomic and Rh-rich films displayed similar behaviors as magnetization, remaining relatively insensitive to the reduction in thickness.
Chapter 4: Thickness effect on the thermal-magnetic behaviors of FeRh thin films

from 200 nm down to 20 nm. Further reduction in thickness from 20 nm to 5 nm however saw sharp increases in lattice parameter-a with the FCC cell of the $\alpha'$-phase approaching the lattice parameter of MgO substrate.

Lattice parameter-c displayed monotonic increases for both compositions when thickness was reduced from 200 nm to 20 nm similar to Fe-rich films. The increase however was more significant for films with higher Rh content with the Rh-rich films exhibiting largest lattice parameter-c of 3.03 Å at 20 nm thickness. Further reduction in thickness to 5 nm continued to show increases in lattice parameter-c for the equiatomic films. Lattice parameter-c of the Rh-rich films on the other hand decreased when below 20 nm thickness after reaching the largest of 3.03 Å. Both equiatomic and Rh-rich films displayed increases in magnetization with the reduction in thickness below 20 nm. Coupled with corresponding increases in both lattice parameter-c and -a, the behavior is characteristic of the first-order anti-ferromagnetic to ferromagnetic phase transitions.

4.2.2.3 Temperature dependent crystallographic texture and magnetic properties of equiatomic $Fe_{50}Rh_{50}$ and Rh-rich $Fe_{48}Rh_{52}$ thin films

The thermal responses of the magnetization behaviors of equiatomic $Fe_{50}Rh_{50}$ and Rh-rich $Fe_{48}Rh_{52}$ of various thicknesses from 5 nm to 200 nm were shown in Figure 4.9. Temperature was varied between -75 °C to 130 °C. Films of thickness between 10 nm to 200 nm for both equiatomic and Rh-rich films displayed distinct increases and decreases in magnetization for both compositions when heated and cooled respectively, generating thermal-hysteresis behaviors observed generally in FeRh and associated with the first-
order anti-ferromagnetic/ferromagnetic transition. Similar to the Fe-rich films, the thickest 200 nm films for both compositions displayed the sharpest transition. The phase transition broadened as film thickness was reduced with both hysteresis width and transition width increasing monotonically. The broadening was accompanied with the slope of the hysteresis becoming gentler suggesting a shift towards more heterogeneous nucleation of the ferromagnetic phase. The films also experienced an increase in magnetization at -75°C with reduction in film thickness. These increases were observed when the film thickness was reduced below 20 nm while the films were comparably insensitive to the thickness variations from 200 to 20 nm possessing a small presence of magnetization in the films. These changes happened before any thermally induced transition to ferromagnetic phase could occurred and were similar to what was observed for the Fe-rich films attributing to the surface nucleation mechanism of ferromagnetic phase which became more significant as film thickness was reduced.

However, comparing the films of all three compositions namely Fe$_{52}$Rh$_{48}$, Fe$_{50}$Rh$_{50}$, and Fe$_{48}$Rh$_{52}$, the broadening of the hysteresis were more significant for films with higher Rh content with hysteresis width increasing faster as seen in Figure 4.10(b). The onset of the transition also fell to lower temperatures with higher Rh content for all thickness indicating an earlier onset of the anti-ferromagnetic to ferromagnetic phase transition. Together, both observations suggested that the increased presence of Rh, encouraged the phase transition towards ferromagnetic phase. This was also noticed among non-textured films previously where localized concentration of Rh atoms during film fabrication resulted in increased imperfections leading towards a more
heterogeneous nucleation of the ferromagnetic phase and hence broadening of the phase transition.  

Figure 4.9 Magnetic-Thermal hysteresis of (a) equiatomic Fe$_{50}$Rh$_{50}$ and (b) Rh-rich Fe$_{48}$Rh$_{52}$ thin films of thickness 200nm, 100nm, 50nm, 20nm, 10nm and 5nm. Films were heated from -75°C to 130°C and cooled back down to -75°C and the magnetization were recorded at each temperature interval.
Chapter 4: Thickness effect on the thermal-magnetic behaviors of FeRh thin films

Figure 4.10  (a) Root-mean-square strain strain $<e^2>^{1/2}$ of FeRh thin films of thicknesses 5 nm, 10 nm, 20 nm, 50 nm, 100 nm, and 200 nm at ambient temperature, (b) Hysteresis width, $\Delta T_{Hysteresis}$ and (c) On-set transition temperature, $T_{heating}$. FeRh films of various thickness for the thermal-magnetic hysteresis.
Figure 4.11 show the thermal responses of the lattice parameter-c of both equiatomic Fe$_{50}$Rh$_{50}$ and Rh-rich Fe$_{48}$Rh$_{52}$ thin films of thicknesses between 20 nm to 200 nm. Similar to the thermal-magnetic behaviors, the lattice parameter-c of equiatomic and Rh-rich films displayed increasing and decreasing changes when subjected to heating and cooling respectively while exhibiting hysteresis behaviors. The temperature in which these transitions occurred agreed well with the anti-ferromagnetic/ferromagnetic transitions shown in Figure 4.9. The hysteresis however was incomplete for the 20 nm Fe$_{50}$Rh$_{50}$ film and the Fe$_{48}$Rh$_{52}$ films as the onset of the transition was below room temperature, beyond the operational temperature range of the equipment (Anton Parr heating stage). Despite the incomplete hysteresis, it could be observed that the slope of hysteresis broadened and became gentler with reduction in film thickness in agreement with the corresponding thermal-magnetic hysteresis.

Figure 4.10 depicts the root-mean-square strain, hysteresis width and transition onset temperature of the anti-ferromagnetic to ferromagnetic transition. Mean strain of both equiatomic and Rh-rich films increased with reduction of film thickness much like the behaviors observed in Fe-rich Fe$_{52}$Rh$_{48}$ films which also occurred simultaneously with both the broadening of the phase transition and earlier onset of the first-order phase transition.
Figure 4.11  Thermal behavior of lattice parameter-\(c\) of (a) equiatomic Fe\(_{50}\)Rh\(_{50}\) and (b) Rh-rich Fe\(_{48}\)Rh\(_{52}\) thin films of thickness 200nm, 100nm, 50nm and 20nm
4.2.2.4 Summary

The reduction of film thickness of both equiatomic Fe$_{50}$Rh$_{50}$ and Rh-rich Fe$_{48}$Rh$_{52}$ from 200 nm to 5 nm resulted in the onset of the phase transition from anti-ferromagnetic to ferromagnetic to occur at lower temperatures while the thermal hysteresis broadened. Magnetization of the films increased significantly when thickness was reduced below 20 nm suggesting the films becoming more ferromagnetic as thickness was reduced attributing to the increased significance of the surface nucleation of the ferromagnetic phase. The increasing Rh content within FeRh films led to larger shifts toward the broadening of the transition with thickness reduction due to the presence of larger imperfections causing more heterogenous nucleation of the ferromagnetic phase.

4.3 Summary

In this chapter, the effects of thickness reduction from 200 nm to 5 nm on Fe-rich Fe$_{52}$Rh$_{48}$, equiatomic Fe$_{50}$Rh$_{50}$, and Rh-rich Fe$_{48}$Rh$_{52}$ thin films were studied. With the reduction in film thickness from 200 nm to 5 nm, magnetization of epitaxial FeRh films increased for all three compositions. The increases were most significant when thickness was reduced below 20 nm as shown in Figure 4.12 suggesting the dominance of ferromagnetic phase within thinner films attributing to the increased significance of the surface nucleation of the ferromagnetic as films became thinner. Similarly, lattice parameter-c increased with reduction of film thickness from 200 nm to 5 nm for both Fe-rich and equiatomic films agreeing to the typical lattice expansions observed with anti-ferromagnetic to ferromagnetic transitions. Rh-rich films exhibited similar increases
when thickness was reduced down to 20 nm reaching the largest lattice parameter-\( c \) of 3.03 Å, but decreasing with subsequent reduction in film thickness. The increase in lattice parameter-\( c \) with thickness reduction was more significant in films with higher Rh content. Lattice parameter-\( a \) of all three also increased with reduced thickness. With reduction in thickness down to 5 nm, both Fe-rich and equiatomic FeRh films approached the lattice parameter-\( a \) of the MgO substrate forming a near match. Rh-rich Fe\(_{48}\)Rh\(_{52}\) however showed significant increase in lattice parameter-\( a \) becoming larger than the lattice parameter of the substrate. Overall, with reduction in film thickness causing the films to become more ferromagnetic, both lattice parameter-\( c \) and –\( a \) generally increased resulting in volume expansion in agreement with the previous works on both bulk and thin film FeRh.

The corresponding heat induced first-order transitions for all there compositions were observed to broaden with not only reduction of film thickness but also with the increase in Rh content. The broadening of the transition and shift towards ferromagnetic phase with thickness reduction could be attributed to the increased significance of the film surface in the nucleation of the ferromagnetic phase, which were applicable to films of all three compositions. The broadening was enhanced with films of higher Rh content suggesting the addition of Rh caused more heterogeneous nucleation of the ferromagnetic phase resulting from the increased presence of imperfections with due to local concentration of Rh atoms.
Figure 4.12  Magnetization, lattice parameter-c, and lattice parameter-a multiplied by factor of $\sqrt{2}$, and volume of unit cell of Fe$_{52}$Rh$_{48}$, Fe$_{50}$Rh$_{50}$, and Fe$_{48}$Rh$_{52}$ thin films epitaxially deposited on (001) texture MgO single crystal substrates.
Chapter 5: Effects of Ir doping on the phase transition of FeRh-Ir epitaxial thin films

Earlier works on bulk and non-textured FeRh films doped with modifiers such as Ir, Pt, Mn and Cu to partially replace Rh in FeRh had either modified or eliminated the phase transition behaviors of the FeRh films. In this work, the effects of modifying the transition temperature of textured FeRh films through Ir doping would be investigated. Ir would be doped into textured FeRh thin films of 3 compositions namely Fe$_{52}$Rh$_{48}$, Fe$_{50}$Rh$_{50}$ and Fe$_{48}$Rh$_{52}$ with thickness of the films being kept at 100 nm. The phase transition, magnetic properties and crystallographic texture would be studied.

5.1 Experimental Methods

Iron-Rhodium (FeRh) thin films of compositions Fe$_{52}$Rh$_{48}$, Fe$_{50}$Rh$_{50}$ and Fe$_{48}$Rh$_{52}$ were doped with Ir, deposited on (001) texture MgO single crystal substrates. Ir was used to replace Rh in FeRh films and its content was varied from no doping to 8 at. % Ir. The films were deposited by means of confocal DC magnetron sputtering with Fe sputter rate being fixed while Rh and Ir sputter rates were varied to achieve the various compositions. The films were deposited under in-situ heating conditions of 400°C while the thickness of the films was maintained at 100 nm.
Chapter 5: Effects of Ir doping on the phase transition of FeRh-Ir epitaxial thin films

5.2 Results and discussions

5.2.1 Effects of Ir doping in Fe-rich Fe$_{52}$Rh$_{48}$ thin films

5.2.1.1 Crystallographic texture

Figure 5.1 showed the x-ray diffraction spectra of 100 nm thick Fe$_{52}$Rh$_{48-x}$Ir$_x$ thin films of different Ir doping content.

![X-ray diffraction spectra](image)

*Figure 5.1  X-ray diffraction theta-2theta spectra of Fe$_{52}$Rh$_{48-x}$Ir$_x$ thin film of different Ir content, where $x = 0, 1, 2, 4$, and 8 at. %.*
Both (001) superlattice and (002) fundamental peaks of the $\alpha'$-phase were present indicating the presence of the chemically ordered CsCl structure. No peaks belonging to the FCC paramagnetic $\gamma$-phase were present. Increasing the Ir content led to shifts in both (001) and (002) peak positions toward lower angles indicating an increase in the lattice parameter $c$. Figure 5.2 showed calculated lattice parameter $c$ and lattice parameter $a$ using Bragg’s law. Both lattice parameter $c$ and lattice parameter $a$ increased monotonically with larger Ir substitution which could be attributed to the larger Ir dopants. The root-mean-square strain of the FeRhIr films (Figure 5.3) initially remained insensitive with the substitution of 1 at. % Ir but subsequently increased monotonically as Ir content was increased among the films which coincided with the increases in lattice parameter.

![Figure 5.2](image)

**Figure 5.2** Lattice parameter $c$ and lattice parameter $a$ of Fe$_{52}$Rh$_{48-x}$Ir$_x$ thin film of different Ir content, where $x = 0, 1, 2, 4, 6, 8$ at. %.
Chapter 5: Effects of Ir doping on the phase transition of FeRh-Ir epitaxial thin films

5.2.1.2 Thermal-magnetic properties

The thermal-magnetic properties of Fe-rich FeRh films doped with Ir were shown in Figure 5.4. Fe$_{52}$Rh$_{48}$ film without Ir doping showed a sharp transition occurring at 59.5°C with magnetization increasing from 22 emu/cm$^3$ to 1000 emu/cm$^3$ indicating the film underwent phase transition from anti-ferromagnetic to ferromagnetic phase with the increase in temperature. A similar sharp decrease in magnetization was observed with the reduction of temperature forming a hysteresis behavior as with all previous FeRh thin films.

With the substitution of Ir, the transition began to occur at higher temperatures with its onset temperatures increasing monotonically as shown in Figure 5.5. This
suggested that the transition temperature could be delayed to higher temperatures with the addition of Ir. The maximum magnetization of the film however began to decrease from 1000 emu/cm\(^3\) to 287 emu/cm\(^3\) when Ir content was increased from 0 to 4 at. %. Upon addition of 8 at. % of Ir, the magnetization of the film remained low between 20 emu/cm\(^3\) to 30 emu/cm\(^3\) with no distinct increases/decreases in magnetization throughout the temperature range. The film however still remained dominantly \(\alpha'\)-phase at 8 at.% Ir as no other diffraction peaks apart from \(\alpha'\)-phase (001) and (002) peaks were observed in Figure 5.1.

The transition width of the Fe\(_{52}\)Rh\(_{48-x}\)Ir\(_x\) films remained unchanged with increasing Ir substitution from 0 to 4 at. %. However, the hysteresis width began to decrease diminishing the hysteresis of the first-order anti-ferromagnetic to ferromagnetic transition. Coupled with the reduced magnetization of the films, the increasing substitution of Ir for Rh resulted in a loss in the first-order anti-ferromagnetic to ferromagnetic phase transition. This suggested that the substitution of Ir for Rh while maintaining the \(\alpha'\)-phase, could possibly reduce the ferromagnetic exchange interactions between Fe and Rh atoms and thus the polarizability of Rh atoms. \(^5^9\) The presence of Ir could also disrupt the weakening of the Fe-Fe exchange interactions when subjected to increasing temperatures which together with the ferromagnetic exchange between Fe and Rh atoms are the two driving mechanisms behind the first-order phase transition seen in FeRh.

It is interesting to note that with a mere 4 at. % of Ir the phase transition of FeRh could be drastically reduced, while 8 at. % Ir could render phase transition could no longer be observed. These observations of epitaxially texture Fe\(_{52}\)Rh\(_{48-x}\)Ir\(_x\) thin films tend
to behave similarly with previous work on bulk FeRh, although the effects of Ir doping of epitaxial thin films were more pronounced as the phase transitions could still be observed with up to 12.1 at. % of Ir doping in bulk FeRh, whereas none could be observed with 8 at. % for epitaxial films.  

![Graph showing magnetic thermal hysteresis](image)

**Figure 5.4** Magnetic-Thermal hysteresis of Fe$^{x}_{52}$Rh$^{48-x}_{48}$Ir$_x$ thin films of different Ir content. Ir content was varied from 0 to 8 at. %. Films were heated from -25°C up to 260°C and cooled back down to 25°C and the magnetization were recorded at each temperature interval.
Chapter 5: Effects of Ir doping on the phase transition of FeRh-Ir epitaxial thin films

Figure 5.5  Maximum magnetization, transition width, hysteresis width and on-set temperature of first order anti-ferromagnetic/ferromagnetic phase of Fe$_{52}$Rh$_{48-x}$Ir$_x$ thin films of different Ir content. Ir content was varied from 0 to 8 at. %
5.2.1.3 Summary

With the initial doping and subsequent increase of Ir, the antiferromagnetic/ferromagnetic phase transition temperature of Fe\textsubscript{52}Rh\textsubscript{48-x}Ir\textsubscript{x} thin films increased monotonically with up to 4 at. % Ir suggesting that the transition temperature could be modified through Ir doping. Magnetization of the ferromagnetic phase however decreased with the increasing Ir content suggesting the replacement of Ir for Rh had disrupted the phase transition from antiferromagnetic to the ferromagnetic phase. With Ir content of 8 at. %, no phase transition was observable within the temperature range of between 25°C to 260°C.

5.2.2 Effects of Ir doping in Fe\textsubscript{50}Rh\textsubscript{50-x}Ir\textsubscript{x} and Fe\textsubscript{48}Rh\textsubscript{52-x}Ir\textsubscript{x} thin films

5.2.2.1 Crystallographic texture

The x-ray diffraction theta-2theta spectra of Fe\textsubscript{50}Rh\textsubscript{50-x}Ir\textsubscript{x} and Fe\textsubscript{48}Rh\textsubscript{52-x}Ir\textsubscript{x} thin films were shown in Figure 5.6. Similar to Fe\textsubscript{52}Rh\textsubscript{48-x}Ir\textsubscript{x} films, only (001) superlattice and (002) fundamental peaks belonging to the \(\alpha^\prime\)-phase FeRh were present while no peaks belonging to \(\gamma\)-phase were observed suggesting the presence of \(\alpha^\prime\)-phase.
Figure 5.6  X-ray diffraction theta-2theta spectra of (a) Fe_{50}Rh_{50-x}Ir_{x} and (b) Fe_{48}Rh_{52-x}Ir_{x} thin films of different Ir content, where x = 0, 1, 2, 4, and 8 at. %.
Chapter 5: Effects of Ir doping on the phase transition of FeRh-Ir epitaxial thin films

Figure 5.7  Lattice parameter-c and lattice parameter-a of (a) Fe$_{50}$Rh$_{50-x}$Ir$_x$ and (b) Fe$_{48}$Rh$_{52-x}$Ir$_x$ thin films of different Ir content, where $x = 0, 1, 2, 4, and 8$ at. %.
Chapter 5: Effects of Ir doping on the phase transition of FeRh-Ir epitaxial thin films

Lattice parameter-c and lattice parameter-a obtained from (001) and (101) diffraction peaks respectively were shown in Figure 5.7. With the doping Ir, lattice parameters-c and lattice parameter-a of Fe$_{50}$Rh$_{50-x}$Ir$_x$ and Fe$_{48}$Rh$_{52-x}$Ir$_x$ thin films both showed increases suggesting that the films experience lattice expansions with increasing Ir doping as was observed previously in Fe$_{52}$Rh$_{48-x}$Ir$_x$ films and attributing to the larger Ir atoms substituting for Rh. The root-mean-square strain of both Fe$_{50}$Rh$_{50-x}$Ir$_x$ and Fe$_{48}$Rh$_{52-x}$Ir$_x$ films initially remained insensitive with up to 2 at. % Ir doped, similar to Fe$_{52}$Rh$_{48-x}$Ir$_x$ films. Subsequent increase of Ir up to 8 at. % however led to increases in strain as seen in Figure 5.8.

![Figure 5.8](image-url)

*Figure 5.8* Root-mean-square strain of Fe$_{50}$Rh$_{50-x}$Ir$_x$ and Fe$_{52}$Rh$_{48-x}$Ir$_x$ thin film of different Ir content, where $x = 0, 1, 2, 4, \text{and } 8$ at. %.
5.2.2.2 Thermal-magnetic properties

Figure 5.9 showed the thermal-magnetic response of Fe$_{50}$Rh$_{50-x}$Ir$_x$ and Fe$_{48}$Rh$_{52-x}$Ir$_x$ thin films. Films with up to 4 at. % Ir showed distinct increases and decreases in magnetization upon heating and cooling of the films respectively forming thermal hysteresis. Similar to the Fe-rich films, the anti-ferromagnetic/ferromagnetic transition temperature increased monotonically with Ir content (Figure 5.10). Magnetization of the ferromagnetic phase decreased with the addition of Ir up to 4 at. %. Films with higher Rh content initially exhibited larger magnetization. With the addition of up to 4 at. % Ir however, the magnetization of the ferromagnetic phase decreased to 250 emu/cm$^3$ regardless of composition. At the same time, the thermal hysteresis behavior diminished with increasing Ir content, as seen from the decrease in hysteresis width. With doping of 8 at. % Ir, no phase transition could be observed, similar to the Fe-rich Fe$_{52}$Rh$_{48-x}$Ir$_x$ films suggesting increasing Ir content beyond 8 at. % could either have fully disrupted first-order phase transition from occurring or that the transition itself took place at temperatures beyond 260°C. This could be attributed to the disruption of the Fe-Rh ferromagnetic exchange interactions which reduced the polarizability of the Rh atoms through the introduction of Ir dopants similar to the Fe$_{52}$Rh$_{48-x}$Ir$_x$ films.

Comparing between different compositions of Fe$_{52}$Rh$_{48-x}$Ir$_x$, Fe$_{50}$Rh$_{50-x}$Ir$_x$, and Fe$_{48}$Rh$_{52-x}$Ir$_x$ thin films, the temperature at which the transitions occurred shifted towards lower temperatures with higher Rh/Ir content, similar to what was observed previously in chapter 4. The transition width for film of similar Fe content did not vary with the increasing doping of Ir. However, the transition width increased for films with higher Rh/Ir indicating the broadening of the phase transition as should be expected.
Chapter 5: Effects of Ir doping on the phase transition of FeRh-Ir epitaxial thin films

Figure 5.9  Magnetic-Thermal hysteresis of Fe_{50}Rh_{50-x}Ir_{x} thin films of different Ir content. Ir content was varied from 0 to 8 at. %. Films were heated from -25ºC up to 260ºC and cooled back down to 25ºC and the magnetization were recorded at each temperature interval.
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Figure 5.10  Magnetization of ferromagnetic phase, transition width, and transition onset temperature of Fe\textsubscript{52}Rh\textsubscript{48-x}Ir\textsubscript{x}, Fe\textsubscript{50}Rh\textsubscript{50-x}Ir\textsubscript{x}, and Fe\textsubscript{48}Rh\textsubscript{52-x}Ir\textsubscript{x} thin films of different Ir content. Ir content was varied from 0 to 8 at. %

5.2.2.3 Summary

The Fe\textsubscript{50}Rh\textsubscript{50-x}Ir\textsubscript{x} and Fe\textsubscript{48}Rh\textsubscript{52-x}Ir\textsubscript{x} films displayed similar behaviors to the Fe-rich Fe\textsubscript{52}Rh\textsubscript{48-x}Ir\textsubscript{x} counterparts. The lattice parameters showed increases with the incremental doping of Ir up to 8 at. % attributing to the larger size of the Ir dopants. First-order anti-ferromagnetic to ferromagnetic transition began to diminish with addition of Ir up to 8 at. % for both compositions suggesting the disruption of the Fe-Fe and Fe-Rh
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exchange interactions by the addition of Ir. The transition width however remained unaffected by the addition of Ir but increased only when the total amount of Rh and Ir increased which was in agreement to what was observed earlier in chapter 4.

5.3 Summary

In this chapter, the effects of Ir doping on Fe$_{52}$Rh$_{48-x}$Ir$_x$, Fe$_{50}$Rh$_{50-x}$Ir$_x$, and Fe$_{48}$Rh$_{52-x}$Ir$_x$ thin films were studied. The films experienced increases in both lattice parameter-c and lattice parameter-a with the addition of Ir from 0 to 8 at. % for all three compositions indicating an expansion in the lattice of the films as seen in Figure 5.11 attributing to the substitution of the large Ir atoms.

![Figure 5.11 Volume of unit cell of Fe$_{52}$Rh$_{48-x}$Ir$_x$, Fe$_{50}$Rh$_{50-x}$Ir$_x$, and Fe$_{48}$Rh$_{52-x}$Ir$_x$ thin films of different Ir content. Ir content was varied from 0 to 8 at. %](image-url)
The expansion in lattice however did not indicate a shift towards the ferromagnetic state as seen in previous chapters. Rather, with the addition of Ir to FeRh thin films, the first order anti-ferromagnetic/ferromagnetic transition temperature were shifted to higher temperatures for all compositions as seen from the transition on-set temperature in Figure 5.10. As Ir content was increased from 0 to 4 at. %, the magnetization of Fe\textsubscript{52}Rh\textsubscript{48-x}Ir\textsubscript{x}, Fe\textsubscript{50}Rh\textsubscript{50-x}Ir\textsubscript{x}, and Fe\textsubscript{48}Rh\textsubscript{52-x}Ir\textsubscript{x} films tended to decrease synonymously and monotonically converging at 250 emu/cm\textsuperscript{3}. Thermal hysteresis behaviors typically associated with the first-order transition also began to diminish with the addition of Ir. At 8 at. % Ir content, no transitions were observable suggesting that either the transition occurred at temperatures higher than 260°C or the Ir dopant could have destroyed the phase transition behavior altogether. This could be attributed to the disruption substituting Ir for Rh had on the polarization of Rh atoms through the ferromagnetic exchange interactions between Fe and Rh atoms within FeRh, as well as the preservation of the Fe-Fe anti-ferromagnetic exchange interactions when subjected to increasing temperatures both of which suppresses the first-order phase transition from occurring. Transition width of the first order transition remained constant with up to 4 at. % Ir. Comparing Fe\textsubscript{52}Rh\textsubscript{48-x}Ir\textsubscript{x}, Fe\textsubscript{50}Rh\textsubscript{50-x}Ir\textsubscript{x}, and Fe\textsubscript{48}Rh\textsubscript{52-x}Ir\textsubscript{x} thin films however showed the broadening of the transition when films contain more Rh/Ir (or lesser Fe) agreeing well with the observations in Chapter 3.

Thus the transition temperature of FeRh could be tuned with the addition of Ir up to 4 at. %. However, excessive Ir doping would result in the loss of the phase transition rendering the loss of its unique properties. In comparison to bulk FeRh, the textured films
were more sensitive to the addition of Ir as bulk FeRh still exhibited the first-order transition with up to 12 at. % Ir substitution.
Chapter 6: Summary

The objective of this thesis was to study the various responses of (001) textured FeRh thin films to the changes in composition, thickness, and modification of transition temperature through Ir doping. A first-order phase transition from ferromagnetic to antiferromagnetic state was observed between 47 and 48 at. % Rh when Rh content was increased from 35 to 65 at. %. The transition involved a sharp decrease in magnetization from 1600 emu/cm$^3$ to 200 emu/cm$^3$ accompanied by a distinct and sudden lattice contraction typical of such transitions. Such transition differed significantly from the non-texture thin film in which its transitions were gradual occurring over a large composition range from 30 to 57 at. % Rh. More rather, the behaviors of textured films resembled the sharp transitions seen in bulk FeRh although occurring at off-equatomi compositions of Fe$_{53}$Rh$_{47}$. No thermal responses were obtained from the predominantly ferromagnetic films when Rh content below 47 at. %. With Rh content increased beyond 47 at. %, the anti-ferromagnetic films displayed sharp increases in magnetization with the heating of these films becoming ferromagnetic once again. The transition could be reversed with the cooling of the films back to room temperature although hysteresis behavior could be observed. The hysteresis behavior was sharp with compositions near equiatomic. However, as Rh content was increased, the hysteresis broadens suggesting more heterogeneous nucleation of the ferromagnetic phase which could be attributed to the localized concentration of Rh atoms resulting in increased defects within the films which became more prominent with higher Rh presence.
The effects of thickness reduction were studied for FeRh films of near equiatomic compositions $Fe_{52}Rh_{48}$, $Fe_{50}Rh_{50}$ and $Fe_{48}Rh$. With the reduction in film thickness from 200 nm to 5 nm, FeRh films showed broadening of the first-order phase transition with both increases in hysteresis and transition width, as well as the more graduated formation of the ferromagnetic phase. At 5 nm, the films behaved predominantly ferromagnetic with large magnetization and small phase transition within the temperature range of -75°C to 130°C attributing to the increased significance of the surface nucleation of the ferromagnetic phase when thickness was reduced. At the same time, lattice parameter-a of the FeRh FCC unit cell increased, matching the lattice of the MgO substrate suggesting a critical film thickness whereby the film becomes predominantly ferromagnetic. The transition temperature also shifted to lower temperatures with the reduction in film thickness. Such behaviors were more pronounced with the increase in Rh content again attributing to the increased defects caused by Rh localization.

FeRh films doped with Ir of compositions $Fe_{52}Rh_{48-x}Ir_x$, $Fe_{50}Rh_{50-x}Ir_x$, and $Fe_{48}Rh_{52-x}Ir_x$ showed that with increasing Ir content up to 4 at. %, the transition temperature could be monotonically delayed to higher temperatures. Magnetization of the ferromagnetic phase decreased with higher Ir content. At the same time, the thermal hysteresis behavior characteristic of the first-order transition diminished with increasing Ir substitution suggesting that with the addition of Ir could have disrupted the formation of the ferromagnetic phase. This was due to the disruption by Ir of the two main driving mechanism of the phase transition namely the polarization of Rh by the Fe-Rh ferromagnetic exchange interactions and the weakening of the Fe-Fe anti-ferromagnetic exchange interactions when subjected to increased temperatures. The transition width
however was unaffected by the Ir doping up to 4 at. % and remained constant. Films with higher Rh/Ir content (or lower Fe content) however saw a broadening of the transition width consistent to what was observed in earlier chapters. With 8 at. % Ir however, no transitions could be observed suggesting either the transition was destroyed or the transition was delayed beyond 260°C. In comparison to bulk FeRh, the textured FeRh thin films were more sensitive to Ir doping as bulk FeRh, when doped with up to 12 at. % Ir, still showed distinct anti-ferromagnetic to ferromagnetic transitions.
References

References

References


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