Pathways for tailoring the magnetostructural response of FeRh-based compounds

A Dissertation

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ABSTRACT

Materials systems that undergo magnetostructural phase transitions (simultaneous magnetic and structural phase changes) have the capability of providing exceptional functional effects (example: colossal magnetoresistance effect (CMR), giant magnetocaloric (GMCE) and giant volume magnetostriction effects) in response to small physical inputs such as magnetic field, temperature and pressure. It is envisioned that magnetostructural materials may have significant potential for environmental and economic impact as they can be incorporated into a wide array of devices ranging from sensors for energy applications to actuators for tissue engineering constructs. From the standpoint of fundamental scientific research, these materials are interesting as they serve as model systems for understanding basic spin-lattice interactions.

In this work, the near-equatomic phase of FeRh serves as a test bed for understanding the magnetostructural phenomena in intermetallic alloys due to its relatively simple crystal structure (cubic with B2 (CsCl)-type ordering) and its reported ability to undergo a first-order magnetic phase change from antiferromagnetic (AF) to ferromagnetic (FM) ordering, with an accompanying 1 % volume expansion in the unit cell near room temperature ($T_r \sim 350$ K). Overall, three interrelated but largely unexplored aspects concerning the FeRh system have been examined here: (1) influence of nanostructuring on the magnetostructural response; (2) influence of simultaneous application of pressure and magnetic field on the magnetostructural response; (3) correlations between chemical modification of the lattice and the magnetostructural response. Bulk FeRh-based samples in this study were synthesized using the arc-melting technique and nanostructuring of the system was achieved via rapid solidification processing (melt-spinning) of the arc-melted precursor. Structure-property correlations between the parent equiatomic FeRh compound and its nanostructured/chemically-modified counterparts were examined using a
variety of structural and magnetic probes including x-ray diffraction (synchrotron and laboratory based), transmission electron microscopy (TEM) and magnetometry. Overall, the results achieved in this work provide predictive capability and pathways for tailoring the magnetostructural behavior and the associated functional response of FeRh systems for potential technological applications such as magnetic refrigeration and heat-assisted magnetic recording media. Further, insight is gained into the mechanism of magnetostructural phenomena at the fundamental atomic level. In particular, the experimental evidence obtained in this work suggests that the magnetostructural response of FeRh-based compounds depends upon both the electronic state of the system and the magnetovolume effect.

Despite the success achieved in this Dissertation, many open questions regarding the first-order magnetostructural transition in FeRh systems still persist. The concluding chapter of this Dissertation provides recommendations for future experiments that may be conducted to develop a more advanced understanding of the fundamental thermodynamic and kinetic factors influencing the magnetostructural phase transformation process in FeRh and related intermetallic compounds. Further, it is anticipated that computational studies aimed at modeling the magnetostructural behavior of FeRh-based ternary alloys using ab initio calculations and density functional theory will be useful for providing a theoretical framework to the results obtained in this study.
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1.0 INTRODUCTION

1.1 Motivation

Magnetostructural phase transitions comprise simultaneous magnetic and structural phase changes of an abrupt and hysteretic nature.[1] Such transitions are thermodynamically first-order and thus show a discontinuity in the first derivatives of the Gibbs free energy with respect to a change in a thermodynamic variable, such as temperature and pressure. This behavior emphasizes a strong coupling between the electronic spins, atomic orbitals and crystal lattice of the system. In the vicinity of magnetostructural transition, select materials systems exhibit exceptional functional effects such as the giant magnetocaloric effect (Example: Gd₅(Si₁₋ₓGeₓ)₄ [2]), the colossal magnetoresistance effect (Example: La₀.₆₇Sr₀.₃₃MnO₃ [3]) and the giant magnetostrictive effect (example: Ni₂MnGa [4]). It is therefore envisioned that magnetostructural materials may have significant potential for environmental and economic impact as they can be incorporated into a wide array of magnetic devices including networked environmental sensors and magnetic refrigerators for energy harvesting [2]; heat assisted magnetic recording (HAMR) technology for data storage [5] and magnetic actuators for tissue engineering constructs [6]. From the standpoint of basic scientific research, these materials are interesting as they may serve as testbeds for understanding basic spin-lattice interactions.

An intriguing characteristic of magnetostructural phase transitions is that it can be driven via a multitude of physical inputs such as temperature, pressure and magnetic field. This feature implies that the thermodynamics of these transitions may be manipulated to tailor the functional response of the system. In literature many theoretical and phenomenological models have been proposed to explain the physical and chemical factors influencing the Gibb’s free energy ($G_v$) of a system during the magnetostructural phase transition [7-12]. According to one such model
proposed by Bean and Rodbell in 1962 [8], the total Gibbs free energy per unit volume ($G_{V, tot}$) in a magnetic system may be expressed as:

$$G_v = -\sigma H M_s - \frac{N k T_c \sigma^2}{2} + \frac{1}{2K} \left( \frac{v-v_0}{v_0} \right)^2 + P \frac{v-v_0}{v_0} - T N I \left[ \ln 2 - \frac{1}{2} \ln(1 - \sigma^2) - \sigma \tanh^{-1} \sigma \right]$$

(1)

The terms in Equation (1) can be explained as follows:

- The first term, $\sigma H M_s$, represents the free energy in the system due to application of magnetic field. Here, $M_s$ is the saturation magnetization of the system; $H$ is the applied magnetic field and $\sigma$ is the relative ratio of the magnetization and the saturation magnetization of the system. Typically $\sigma$ varies from 0 to 1.

- The second term, $N k T_c \sigma^2/2$, corresponds to the quantum-mechanical exchange energy of the system. Here, $N$ is the number of atoms in the systems which contribute to the magnetic moment; $k$ is Boltzmann’s constant ($1.38 \times 10^{-23}$ J/K) and $T_c$ is the Curie temperature.

- The third term, $\frac{1}{2K} \left( \frac{v-v_0}{v_0} \right)^2$ and fourth term, $P \frac{v-v_0}{v_0}$, account for strain/pressure effects in the system. Here, $v$ and $v_0$ are the molecular volumes of the magnetostructural system before and after the phase transition respectively; $P$ is the pressure applied and $K$ is the compressibility constant.

- The fifth term, $\left[ \ln 2 - \frac{1}{2} \ln(1 - \sigma^2) - \sigma \tanh^{-1} \sigma \right]$, accounts for the entropy of the temperature dependence of magnetization. Here, $\sigma$ is the relative ratio of the magnetization and the saturation magnetization of the system. Typically it varies from 0 to 1

In nanostructured systems, owing to an enhanced surface-to-volume ratio, dominance of the surface atoms over the bulk atoms is anticipated to change the relative strengths of the energies involved in the magnetostructural phase transition (as shown in Eq. [1]). It is thus hypothesized
that in addition to variations brought on by physical parameters, nanostructuring and dimensionality variation may also provide additional routes for alteration of magnetostructural transitions. In keeping with this line of thought, the overall goal of this Dissertation is to understand, predict and control magnetostructural transitions as a function of extrinsic parameter variation, including microstructural scale. Correlations between chemical modification of the lattice and the magnetostructural response are also of particular interest in this study. In principle, a multidimensional phase space map of the magnetostructural response as driven by the independent variables of size, chemical modification, temperature, magnetic field and pressure is sought (Figure 1). Fundamental knowledge obtained in this Dissertation provides predictive capability and pathways to tailor magnetostructural transitions for optimal effects that may be exploited for new technological applications that depend on the functional response of the system.

**Extrinsic parameters:**
- Pressure
- Magnetic Field
- Temperature
- Structural scale

**Intrinsic parameters:**
- Chemical Modification of lattice

**Figure 1.** Schematic representation of a multidimensional phase space map of the functional response of a magnetostructural materials system as driven by the independent variables of size, chemical modification, temperature, magnetic field and pressure. Graph adapted from [13].
1.2 Overview of research

In this Dissertation, FeRh has been chosen as a test bed for understanding the magnetostructural phenomena in intermetallic alloys due to its relatively simple crystal structure (cubic with B2 (CsCl)-type chemical ordering) and its reported ability to undergo a first-order magnetic phase change from antiferromagnetic (AF) to ferromagnetic (FM) ordering, with an accompanying 1% volume expansion in the unit cell near room temperature ($T_t \sim 350$ K).[9] Overall, three interrelated but largely unexplored aspects concerning the FeRh system have been examined in this work. These are as follows: (1) Influence of nanostructuring on the FeRh magnetostructural transition; (2) Correlations between chemical modification of the FeRh lattice and the magnetostructural response of the system and (3) Influence of simultaneous application of pressure and magnetic field on the magnetostructural response of FeRh. In this work, comparison of the structure-property relations of the parent equiatomic FeRh compound and its nanostructured/chemically-modified counterparts provides insight into the mechanism of magnetostructural phase transition at the fundamental atomic level. For potential applications utilizing magnetostructural materials, it is crucial to understand correlations between the magnetostructural behavior and the functional effects observed in the system. To this end, the magnetocaloric effect – a phenomenon describing the reversible temperature change of a magnetic material upon application or removal of a magnetic field – is of specific interest in this Dissertation. A segment of the research conducted in this Dissertation is dedicated to understanding the effect of hydrostatic pressure and chemical substitution on the magnetocaloric behavior of the FeRh system. Overall, the results obtained in this Dissertation provide potential routes for tuning the magnetostructural behavior and the associated functional response of FeRh systems for promising technological applications. The experimental evidence obtained in this
work also provides insight into the fundamental thermodynamic and kinetic factors influencing the magnetostructural behavior of FeRh and related intermetallic compounds.

1.3 Organization of Dissertation

This Dissertation consists of six chapters: (1) An Introduction (here); (2) Critical Literature Review; (3) Experimental Techniques; (4) Results and Discussion; (5) Summary and (6) Recommendations. Chapter 2 - “Critical Literature Review” - of this Dissertation work provides the reader with fundamental background regarding thermodynamic aspects of first-order magnetostructural transitions and the giant magnetocaloric effect. Additionally, salient features regarding the magnetostructural phase transition response of FeRh-based compounds are reviewed. In Chapter 3 – “Experimental Methods and Techniques” – the rationale for specific experiments is provided followed by a discussion regarding the experimental techniques and apparatus used to characterize the magnetic and structural properties of the FeRh alloy. Chapter 4 – “Results and Discussion” – is sub-divided into four Sections. In the first three Sections, experimental data pertaining to studies aimed at understanding the influence of elemental substitution in the FeRh lattice, extrinsic parameter variation (pressure/strain & magnetic field) and dimensionality variation (bulk to nanoscaled) on the magnetostructural response of FeRh-based alloys has been presented and interpreted. The last segment of Chapter 4 is focused on examining the magnetocaloric behavior of FeRh-based compounds as a function of elemental substitution and hydrostatic pressure. The significance of the results achieved in this Dissertation are concisely summarized in Chapter 5, “Summary and Conclusions”. Finally, recommendations for future experiments are discussed in Section 6, “Outlook and Future Work”.
2.0 CRITICAL LITERATURE REVIEW

In this Ph.D. Dissertation, studies focused on understanding the magnetostructural phase transition of FeRh as a function of dimensionality variation (bulk to nanoscaled), elemental substitution and extrinsic parameter variation (pressure/strain & magnetic field) provides guidance for tailoring phase transitions in this compound, with possible extensions to other intermetallic-based magnetostructural compounds. This critical literature review provides a comprehensive summary of the background information and literature relevant to this thesis. Overall, this chapter has been divided broadly into three segments. In Section 2.1, fundamental aspects concerning the thermodynamics of phase transformations are described. In particular, the Ehrenfest classification of phase transitions is presented followed by a brief discussion regarding salient features of the first-order magnetostructural transition. In Section 2.2, the following aspects regarding FeRh-based compounds will be discussed: (a) the FeRh binary phase diagram; (b) structure-property correlations in the different phases of the FeRh system; (c) functional effects observed in the near-equatomic FeRh phase. The effect of tunable parameters on the magnetostructural character of the FeRh system will be described in Section 2.3. Particular attention will be given to the following variables: magnetic field, pressure/strain, elemental substitution and reduction of microstructural scale. Finally in Section 2.4, proposed mechanisms for the magnetostructural phenomena in the FeRh system, as articulated in the literature, will be discussed.

2.1 Overview of magnetostructural phase transformations

This Section provides basic information essential for developing a comprehensive understanding of phase transformations in solid state material systems. A fundamental overview of the thermodynamics underlying phase transformations is presented first, followed by a brief
discussion regarding phase stability and equilibrium conditions in the context of maxima and minima of the Gibb’s free energy function. These concepts are further developed by defining and comparing the features of first- and second order phase transformations in the framework of the Ehrenfest classification system. Finally, general characteristics of first-order magnetostructural phase transformations are outlined.

2.1.1 Thermodynamics of phase transformations: Definitions and concepts

In classical thermodynamics, a thermodynamic system – a phase – is characterized by a set of thermodynamic parameters associated with the system. These parameters include macroscopic properties, such as pressure ($P$), temperature ($T$), enthalpy ($H$) and Gibbs free energy ($G$). A phase transition is defined as the transformation of a thermodynamic system from one state of matter to another [14]. For phase transformations which occur at a constant temperature and pressure, the stability of the system can be expressed by the Gibbs free energy ($G$) - an extensive property which is proportional to the amount of material in the system. Mathematically, the Gibb’s free energy of a system is expressed as a function of temperature and pressure:

$$G(T,P) = U + PV - TS$$  \hspace{1cm} (2)

Where: $T$ is the temperature of the system (K)
$P$ is the pressure of the system (N/m$^2$)
$U$ is the internal energy of the system (J)
$V$ is the volume of the system (m$^3$)
$S$ is the entropy of the system (J/K)

It is important to note that the entropy term in Eq. (2) represents the total entropy arising from lattice vibrations, electronic contributions and magnetic contributions. Distinguishing between
the relative magnitudes of these contributions in the Gibbs free energy has been particularly important in examining the origin of the FeRh magnetostructural phase transformation (See Section 2.2.4 for more details).

An important consequence of the laws of classical thermodynamics is that at constant temperature and pressure, a closed system (i.e. one of fixed mass and composition) will be in stable equilibrium if it has the lowest possible value of the Gibbs free energy ($G$), or in mathematical terms:

$$dG = 0 \quad (3)$$

To illustrate the definition of equilibrium graphically, a schematic representation of the variation of Gibbs free energy with the system configuration is shown in Figure 2. Configuration A here is the most stable equilibrium state. At this point, small changes in the arrangement of atoms to a first approximation produces no change in $G$ (i.e. Equation (3) is satisfied). Configuration B lies at a local minima in the free energy but it does not have the lowest possible value of $G$. It is therefore the metastable equilibrium state. Thermodynamically, any transformation that results in a decrease in Gibbs free energy is possible. Therefore, a required criterion for phase transformation is:

$$\Delta G = G_2 - G_1 < 0 \quad (4)$$

Where, $G_1$ and $G_2$ are the free energies of the initial and final states, respectively.
Figure 2. Schematic variation of Gibbs free energy with the arrangement of atoms. Configuration “A” has the lowest free energy and is therefore the arrangement when the system is at stable equilibrium. Configuration “B” is a metastable equilibrium. Figure adapted from [14].

Sometimes metastable states can be very short lived; at other times they can exist almost indefinitely. For a transformation to proceed the transforming phase must overcome an initial energy barrier, *i.e.* activation energy ($E_a$), which is the energy separating two equilibrium states (Figure 2). Random thermal motion of the atoms comprising a system may provide sufficient energy for the atoms to reach a thermally-activated state. In general, higher temperatures results in greater atomic mobility and consequently the activation energy barrier of a phase transformation decreases with increase in temperature. The influence of temperature on activation energy can be well understood by examining the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$  \hspace{1cm} (5)

Where: $A$ is the pre-exponential factor (unitless)
$E_a$ is the activation energy (J/mol)

$R$ is the ideal gas constant (8.314 J/K mol)

$T$ is the temperature of the system (K)

$k$ is the rate constant (unitless)

### 2.1.2 Classification of phase transformations

Phase transformations may be categorized based on the behavior of the Gibbs free energy ($G$) as a function of other intensive thermodynamic variables, namely temperature ($T$) and pressure ($P$). In particular, in the Ehrenfest classification scheme, phase transitions are described by the lowest derivative of the free energy that is discontinuous at the transition [14]. Thus, first-order phase transitions exhibit a discontinuity in the first derivatives of the Gibbs free energy, volume ($V$) and entropy ($S$), with respect to temperature ($T$) and pressure ($P$). Mathematically, this can be represented as:

\[
\frac{\partial (G_1 - G_2)}{\partial T} = S_1 - S_2 \neq 0
\]  

(6)

And

\[
\frac{\partial (G_1 - G_2)}{\partial P} = V_1 - V_2 \neq 0
\]  

(7)

Where: $G_1$ and $G_2$ are the Gibbs free energies of phases 1 and 2 respectively (J)

$S_1$ and $S_2$ are the entropies of phases 1 and 2 respectively (J/K)

$V_1$ and $V_2$ are the volumes of phases 1 and 2 respectively (m$^3$)

$T$ is the temperature (K)

$P$ is the pressure (N/m$^2$)

The abrupt discontinuity of the first derivatives of the Gibb’s free energy (volume and entropy) during a first-order phase transition is graphically shown in Figure 3.
Figure 3. Graphical representation of a first-order phase transition at $T_t$: (a) Abrupt change in the Gibbs free energy at $T_t$; (b) Discontinuity in the volume at $T_t$; (c) Discontinuity in the entropy at $T_t$. Figure adapted from [14].

Second-order phase transitions exhibit a discontinuity in the second derivatives of the Gibbs free energy with respect to temperature ($T$) and pressure ($P$). Mathematically, this relationship can be represented as:

$$\left(\frac{\partial^2 (G_1 - G_2)}{\partial T^2}\right)_P = \left(\frac{\partial (S_1 - S_2)}{\partial T}\right)_P = C_{p,1} - C_{p,2} \neq 0$$  \hspace{1cm} (8)

And

$$\left(\frac{\partial^2 (G_1 - G_2)}{\partial P^2}\right)_T = \left(\frac{\partial (V_1 - V_2)}{\partial P}\right)_T = K \neq 0$$  \hspace{1cm} (9)

Where: $G_1$ and $G_2$ are the Gibbs free energies of phases 1 and 2 respectively (J)

$S_1$ and $S_2$ are the entropies of phases 1 and 2 respectively (J/K)

$V_1$ and $V_2$ are the volumes of phases 1 and 2 respectively (L)

$C_{p,1}$ and $C_{p,2}$ are the specific heat capacities at constant pressure of phases 1 and 2 respectively (J/Kg K)

$K$ is the compressibility constant (atm$^{-1}$)

No enthalpy of transition ($\Delta H$) is associated with second-order phase transitions. The abrupt change of the second derivative of the Gibb’s free energy (specific heat capacity) during a second-order phase transition is graphically shown in Figure 4.
In this Ph.D. Dissertation, first-order phase transformations comprising of simultaneous magnetic and structural phase changes – magnetostructural phase transitions - are of particular interest. In magnetic materials systems, in addition to the intensive variables (temperature and pressure), the state of a system is described by its magnetization ($M$). Change in Gibbs free energy in a magnetic system during phase transformation is expressed as [15]:

$$dG = -S \, dT + V \, dP - M \, dH$$  \hspace{1cm} (10)

Where: $G$ is the Gibbs free energy (J)

$T$ is the temperature of the system (K)

$P$ is the pressure of the system (N/m$^2$)

$U$ is the internal energy of the system (J)

$V$ is the volume of the system (m$^3$)

$S$ is the entropy of the system (J/K)

$M$ is the magnetization of the system (Am$^{-1}$)

$H$ is the external magnetic field applied to the system (T)
In accordance with Ehrenfest’s classification, in addition to a discontinuity in volume and entropy, first-order magnetic transitions exhibit a discontinuity in magnetization ($M$) at the phase transition temperature. This is distinctly different from the undisputed second-order magnetic transition observed in Fe where magnetization decreases gradually with increasing temperature before disappearing at the Curie temperature. Figure 5 provides examples of the second-order magnetic phase change found in Fe [15] and the very abrupt first-order magnetic phase change found in a single crystal of the Heusler alloy Ni$_2$MnGa [4].

![Figure 5](image)

**Figure 5.** Data illustrating the change in magnetization found in a typical thermodynamically second-order demagnetization process (a) and a thermodynamically first-order demagnetization process (b). Figures adapted from [4] and [15].

### 2.1.3 General characteristics of magnetostructural phase transformations

Typically, magnetostructural materials systems are characterized by three common features: (a) hysteresis in a measured physical property (example: magnetization, volume) as the control variable (example: temperature, magnetic field) is varied across the phase transition point; (b) evolution of latent heat and (c) presence of amplified functional effects in the vicinity
of the magnetostructural response. In the following paragraphs, each characteristic feature of magnetostructural materials system is described individually.

(a) Hysteresis in magnetostructural systems: Overall concepts and implications

In a magnetostructural system, an increase in the thermodynamic driving force ($\Delta G$) occurs when a system is cooled (or heated) past its equilibrium transformation temperature; this phenomenon is known as undercooling (or superheating) a system. A general schematic diagram illustrating the principle of undercooling a liquid below its melting temperature, represented by $T_m$, is shown in Figure 6. Here, solidification below $T_m$ is accompanied by a decrease in the free energy, represented by $\Delta G$. It is critical to recognize that $\Delta G$ provides the necessary driving force for a spontaneous transformation to occur.

![Figure 6. Graphical representation of difference in free energy between liquid and solid ($\Delta G$) close to the melting point ($T_m$). Figure adapted from [14].](image)

Characteristically, supercooling or superheating effects in a magnetostructural system results in hysteresis in a measured physical property (example: magnetization, volume) as the control variable (which may be temperature $T$, or pressure $P$, or magnetic field $H$) is varied
across the phase transition point [1]. Hysteresis in magnetostructural systems provides information regarding the kinetics of the phase transformation process. In first-order magnetostructural materials, phase transformations typically proceed via the nucleation and growth of a product phase from a parent phase. Characteristically, nucleation can proceed homogeneously or heterogeneously. Homogeneous nucleation occurs when nuclei form randomly throughout the system; in comparison, during heterogeneous nucleation, nuclei form at the interfaces or at defects in a system. Growth of the product phase can occur simultaneously during phase nucleation (i.e. continuous nucleation) or after the nucleation process is complete (i.e. site saturated nucleation). As relevant to this Dissertation, it is important to note that hysteresis and the degree of undercooling during a phase transformation (i.e., $\Delta T$ in Figure 6) is directly proportional to the activation energy barrier that the system must overcome to drive nucleation ($\Delta G$ in Figure 6). Overall, hysteresis indicates the presence of metastable states across a first-order phase transition [1]. A familiar example of temperature-induced first-order phase transition is the boiling of water. At the boiling point, water does not instantly turn into vapor, but instead forms a turbulent mixture of liquid water and vapor bubbles. Examples of magnetic-field induced first-order phase transitions are less obvious in nature. Coexistence of magnetic phases across first-order magnetostructural phase transitions has been confirmed theoretically and experimentally in a number of magnetostructural materials systems such as Ru-doped CeFe$_2$ compounds [16] and La-based manganites [17].

By definition, hysteresis is an extrinsic property of a system that may be influenced by a number of physical factors such as the quenched disorder in the system, microstructure of the sample and the sweep rate of the control variable [1]. As an example, Figure 7 demonstrates the
temperature-sweep rate dependence of the thermal hysteresis associated with the first-order martensitic transformation of a Heusler compound of composition, Ni$_{45}$Co$_{5}$Mn$_{38}$Sb$_{12}$ [18].

![Temperature-sweep rate dependence of thermal hysteresis](image)

Figure 7: Variable heating rate temperature-dependent magnetic measurements of the Ni$_{45}$Co$_{5}$Mn$_{38}$Sb$_{12}$ system. Data shown here indicates that thermal hysteresis width of the sample depends on the temperature-sweep rate of the measurement. Figure taken from [18].

**b) Evolution of latent heat during a magnetostructural phase transformation**

The rigorous test of first-order phase transitions involves the detection of discontinuous change in a thermodynamic observable, namely the latent heat of the system ($Q$). From the second law of thermodynamics, it is known that a change in the entropy ($S$) of a system is the infinitesimal transfer of heat ($Q$) to a closed system driving a reversible process, divided by the equilibrium temperature ($T$) of the system:

$$S_1 - S_2 = \frac{Q}{T} \quad (11)$$

Where: $S_1$ and $S_2$ are the entropies of phase 1 and 2 respectively (J/K)

$Q$ is the latent heat of reaction (J)

Combining Equations (10) and (5):
\[
\left( \frac{\partial (G_1 - G_2)}{\partial T} \right)_P = S_1 - S_2 = \frac{Q}{T} \quad (12)
\]

Where: \( S_1 \) and \( S_2 \) are the entropies of phases 1 and 2 respectively (J/K)

\( G_1 \) and \( G_2 \) are the Gibbs free energies of phases 1 and 2 respectively (J)

\( Q \) is the latent heat of reaction (J)

\( T \) is the temperature (K)

\( P \) is the pressure (N/m²)

The presence of latent heat (\( Q \)) across a first-order magnetostructural phase transition has been determined experimentally using calorimetry for many magnetostructural materials systems [2, 19-26]. The ability to monitor the evolution of latent heat during a magnetostructural phase transition is particularly useful for investigating the functional response of magnetostructural materials, namely the giant magnetocaloric effect [2, 19-26].

(c) Functional effects observed in magnetostructural materials systems

In the vicinity of the magnetostructural phase transformation, magnetostructural materials systems exhibit amplified functional effects in response to physical inputs such as temperature and magnetic field [1]. Three classes of magnetostructural materials, based on their functional effect are described below: (1) Magnetocaloric materials (Example: Gd₅Ge₄ [20]) and (2) Magnetic shape memory alloys (Example: Ni-Ti alloys [27]) and (3) Colossal magnetoresistance materials (CMR). As applicable to this Dissertation, the functional effects observed in the FeRh system are described in details in Section 2.2.3.

The magnetocaloric effect (MCE): The magnetocaloric effect (MCE) is a thermodynamic phenomenon in which a change in the temperature of a magnetic material is caused by exposing the material to a changing magnetic field. Magnetic refrigeration based on the MCE has been used to achieve cryogenic temperatures in a laboratory setting (\( T < 10 \)K) since
the 1950s. The discovery of room-temperature giant magnetocaloric compounds, such as Gd$_3$Si$_{4-x}$Ge$_x$ [2] and MnFeP (As, Ge) [28] has driven development of magnetic refrigeration closer to ambient conditions. Currently, magnetic refrigeration is considered to be an environmentally friendly and energy-efficient technology with the potential to outperform conventional gas-compression refrigeration for everyday applications. In this Dissertation the magnetocaloric effect of the FeRh system is of specific interest. Thermodynamic aspects regarding this functional effect are outlined in the supplementary section (Appendix B).

**The shape memory alloy effect (SMA):** Shape memory alloys (SMA) are metallic systems that have the ability to remember a predetermined shape [1]. They return back to that shape after being bent, stretched or otherwise mechanically deformed [1]. This shape memory effect is caused by a ‘thermoelastic martensitic transition’—a reversible transition between two different crystal microstructures in the concerned metallic system. Typically shape memory alloys have application in automotive, aerospace and biomedical industries. In the 1990s it was discovered that magnetostructural materials such as Heusler compounds of composition Ni$_{0.5}$Mn$_{0.5-x}$M$_x$ (M=In, Sn) can undergo large reversible deformations in an applied magnetic field [27]. These materials are now known as magnetic shape memory alloys (MSMA).

**The colossal magnetoresistance effect (CMR):** Magnetoresistance is the property of a material to change the value of its electrical resistance when an external magnetic field is applied to it. Numerically, it is calculated as: \[ \delta_H = \frac{R(0) - R(H)}{R(H)} \], where \( R(H) \) is the resistance of the sample in a magnetic field \( H \) and \( R(0) \) corresponds to \( H=0 \) T [17]. In select magnetostructural materials systems, mostly manganese-based perovskite oxides, a giant change in magnetoresistance is observed with change in magnetic field near the first-order phase transition temperature. Typically, called the colossal magnetoresistance effect (CMR), this functional effect is generally
explained in the framework of the double exchange theory. The fundamental mechanism underlying CMR is beyond the scope of this study and will not be discussed in this work. As relevant to this dissertation, it is important to note that “colossal magnetoresistance-like”, enhanced magnetoresistance has also been observed in many intermetallic magnetostructural compounds such as Ni_{0.5}Mn_{0.5-x}In_x [27], MnAs [29] and GdSiGe [30]). Potential applications of these materials include magnetic field sensors which may be used to read data in hard disk drives, biosensors and microelectromechanical systems (MEMS).

2.1 Overview of the FeRh system

In this Dissertation, FeRh has been selected as a prototypical system for understanding the fundamental science behind the magnetostructural phenomena in intermetallic alloys. This Section describes the general characteristics of this compound. In Section 2.2.1, the equilibrium and metastable phases observed in the Fe_{1-x}Rh_x system are identified and compared. Salient aspects regarding the magnetostructural phenomena observed in the near-equiaatomic \( \alpha'' \)-FeRh phase are presented in Section 2.2.2.

2.2.1 Equilibrium and metastable phases observed in the Fe_{1-x}Rh_x system

The equilibrium phases of the Fe_{1-x}Rh_x system, as shown in the equilibrium phase diagram in Fig. 8 and Table 1, are as follows [31]: (1) \( L \), the liquid phase persists above approximately above 1550 °C; (b) \( \gamma \), the paramagnetic (PM) face-centered cubic (fcc) phase which represents a complete range of solid solubility between approximately 1300 and 1394 °C; (c) \( \delta \), the high-temperature paramagnetic body-centered cubic (bcc) phase, with a solubility of up to 3 atomic % of Rh; (d) \( \alpha \), the low-temperature ferromagnetic bcc phase; (e) \( \alpha' \), an chemically-ordered phase with B2 (CsCl)-type crystal structure and (f) \( \alpha'' \), a phase with a chemically-ordered CsCl
structure which forms from the $\alpha'$ phase upon cooling by a first-order ferromagnetic to antiferromagnetic transition.

In this Ph.D. Dissertation, the near equiatomic $\alpha''$ phase ($0.48 \leq x \leq 0.52$) of Fe$_{1-x}$Rh$_x$ alloys (marked in grey in Figure 8) is of singular interest. From this point onwards, in this Dissertation the $\alpha''$ phase will be referred to as the AF phase and the $\alpha'$ phase will be referred to as the FM or the PM phase depending on its magnetic state. Details regarding the magnetic and structural properties of this phase and the functional effects observed in this system are provided in subsequent Sections.

Figure 8. Equilibrium phase diagram of FeRh alloys. Here: PM is paramagnetic, FM is ferromagnetic and AF is antiferromagnetic. In this Ph.D. Dissertation, the near equiatomic $\alpha''$ phase ($0.48 \leq x \leq 0.52$) of Fe$_{1-x}$Rh$_x$ alloys (marked in grey) is of singular interest. Figure adapted from [31].
Table 1. Summary of magnetic and structural properties of the equilibrium phases of the Fe_{1-x}Rh\textsubscript{x} system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Approx. composition (atomic % Rh)</th>
<th>Structure</th>
<th>Magnetic ordering</th>
<th>Supplementary facts</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma) phase</td>
<td>0-100</td>
<td>Face centered cubic (space group: (Fm\overline{3}m))</td>
<td>Paramagnetic</td>
<td>Stable only at high temperatures (1394-1538 °C)</td>
</tr>
<tr>
<td>(\delta) phase</td>
<td>0-3</td>
<td>Body centered cubic (space group: (Im\overline{3}m))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha) phase</td>
<td>0-19</td>
<td>Body centered cubic (space group: (Im\overline{3}m))</td>
<td>Ferromagnetic at room temperature</td>
<td>Stable only at low temperatures (below ~ 900 °C)</td>
</tr>
<tr>
<td>(\alpha') phase</td>
<td>11-55</td>
<td>Cubic with B2 (CsCl)-type ordering (space group: (Pm\overline{3}m))</td>
<td>Ferromagnetic at room temperature</td>
<td></td>
</tr>
<tr>
<td>(\alpha'') phase</td>
<td>48-55</td>
<td>Cubic with B2 (CsCl)-type ordering (space group: (Pm\overline{3}m))</td>
<td>Antiferromagnetic at room temperature</td>
<td>Stable only at low temperatures; Undergoes a first order magnetic transition to FM phase upon heating</td>
</tr>
</tbody>
</table>

As relevant to this Dissertation, few studies in the literature have reported formation of a non-equilibrium L1\(_0\) (CuAu 1)-ordered phase in equiatomic FeRh alloys subjected to mechanical deformation by mild cold rolling or high-speed compression [32, 33]. The L1\(_0\) crystal structure of FeRh, shown in Figure 9(a), is a chemically-ordered crystallographic derivative of the face-centered tetragonal (\(f\overline{4}c\)) crystal structure, where four of the tetragonal unit cell faces are occupied by one type of atom and the corner and the other faces are occupied with the second type of atom. This metastable phase is recognized as a stress-induced martensite of the
equilibrium B2-ordered \( \alpha' \) phase [33]. The relationship between the B2 and L1\(_0\) crystal phases of FeRh (also known as a Bain correspondence) is shown schematically in Fig. 9(b).

![Figure 9](image)

**Figure 9.** (a) Crystal structure of the metastable L1\(_0\)-ordered phase of FeRh. (b) Schematic illustration of the relationship between the B2 and L1\(_0\)-ordered crystal phases of FeRh (also known as Bain correspondence).

2.2.2 Magnetostructural phase transition in near-equiatomic FeRh compounds

In this Dissertation, the near-equiatomic phase of Fe\(_{1-x}\)Rh\(_x\) (0.48 \( \leq x \leq 0.52\)) has been selected as a test bed for understanding the magnetostructural phenomena in intermetallic alloys. Discovered in 1938 by M. Fallot [34], this phase of FeRh is reported to possess a chemically-ordered cubic CsCl-type structure that exhibits a hysteretic antiferromagnetic (AF) \( \rightarrow \) ferromagnetic (FM) transition around \( T \sim 350 \text{ K} \) (Figure 10 (a)) accompanied by a uniform unit cell volume increase of 1 \% upon heating (Figure 10 (b)) that preserves the cubic structure [9]. When the temperature of bulk FeRh is raised above the Curie temperature (\( T_c \sim 670 \text{ K} \)), the system undergoes a second-order transition from a ferromagnetic to paramagnetic (PM) state [9]. As shown in Figure 11, FeRh has been shown to have a magnetic moment of 3.04 \( \mu_B \) for Fe and 0.62 \( \mu_B \) for Rh in the FM state; whereas, at room temperature, in the AF state, the CsCl-structure has zero net magnetic moment with the Fe spins ordered antiferromagnetically with spin moments of 3.3 \( \mu_B \) per Fe and 0 \( \mu_B \) per Rh [35].
Figure 10. The magnetostructural response in nominally-equiatomic FeRh alloys: (a) Temperature-dependant magnetization behavior of FeRh showing a first-order AF→FM magnetic phase transition at $T_f=350$ K and a second order FM→PM magnetic phase transition at $T_c=670$ K; (b) Temperature dependence of the lattice parameter of FeRh indicates 1% volume expansion at $T_f=350$ K. Image adapted from and [9] and [11].

Figure 11. Magnetic ordering in equiatomic FeRh alloys: (a) At room temperature, FeRh is antiferromagnetic. In this configuration, the CsCl-structure of FeRh has zero net magnetic moment with the Fe spins ordered antiferromagnetically with spin moments of 3.3 $\mu_B$ per Fe and 0 $\mu_B$ per Rh; (b) At temperatures above 350 K, FeRh is ferromagnetic. In this configuration, the Fe and Rh atoms possess a magnetic moment of 3.04 $\mu_B$ and 0.62 $\mu_B$, respectively.
In the vicinity of the magnetostructural phase transition temperature exceptional functional effects have been reported in the FeRh system in response to physical inputs such as pressure and magnetic field. In particular, giant volume magnetostriction (volume magnetostriction, $\omega = 8.2 \times 10^{-3}$), giant magnetoresistance (resistivity change $\Delta R/R = 50\%$ at $H_{app} = 15$ T) and giant magnetocaloric (adiabatic temperature change, $\Delta T_{ad} = 12.9$ K at $H_{app} = 2$ T) effects have been reported in this compound [26, 36-38]. In this Dissertation, the giant magnetocaloric effect is of special interest. Details regarding thermodynamic aspects of the phenomena are outlined in the supplementary Section (Appendix B). As applicable to this literature review, it is sufficient to note that the magnetocaloric effect is a thermodynamic phenomenon in which a change in temperature of a magnetic material is caused by exposing the material to a changing magnetic field. Typically, magnetocaloric materials are evaluated by two critical parameters [39]: (1) The magnetic entropy change observed in the system ($\Delta S_{mag}$) and (2) The adiabatic temperature change observed in the system upon application and subsequent removal of a magnetic field ($\Delta T_{ad}$). In Figure 12, the $\Delta S_{mag}$ values of select room temperature magnetocaloric materials have been plotted as a function of their corresponding $\Delta T_{ad}$ values. From this plot it is evident that at the current time FeRh holds the record for the largest adiabatic temperature change per Tesla for any room temperature magnetocaloric material.
Figure 12. Plot of adiabatic temperature change ($\Delta T_{ad}$) and magnetic entropy change ($\Delta S_{mag}$) of select technologically important room temperature magnetocaloric materials systems. Plot adapted from [40].

2.3 Tailoring the FeRh magnetostructural transition

An intriguing feature of the FeRh system is that its first-order magnetostructural phase transition can be tuned in a variety of ways. The following Sections describe the changes observed in the magnetostructural response of bulk FeRh alloys with the variation in the following parameters: (a) External magnetic field ($H$); (b) Pressure/strain ($P$); (c) Reduction in the microstructural scale and (d) Addition of transition metal impurities.

2.3.1 Influence of applied magnetic field on the FeRh magnetostructural transition temperature

The magnetostructural response in the FeRh system is extremely sensitive to applied magnetic field. Typically, in bulk FeRh alloys, the magnetostructural transition temperature ($T_t$) decreases with increase in the applied magnetic field at a rate of $\sim 8$ K/T [41] (See Figure 13(a)}
for example). Additionally, magnetization isotherms measured in the vicinity of the magnetostructural transition temperature indicate the presence of a field-driven antiferromagnetic to ferromagnetic transition [11]. Figure 13(b) shows magnetization isotherms of an equiatomic FeRh compound in the temperature range 300-380 K and in magnetic fields as high as 14 T, as measured by Ibarra et al. [11]. It is observed that the critical magnetic field at which the field-driven AF → FM transition occurs ($H_k$) decreases linearly with increase in temperature at a rate of $-1.7 \times 10^3$ Oe/K [11].

Figure 13. (a) Temperature-dependant magnetic behavior of FeRh samples indicates that the magnetostructural temperature ($T_t$) of the system decreases with applied magnetic field at a rate of $-8$ K/T (b) Magnetization isotherms of FeRh alloys indicates that the critical magnetic field at which the AF → FM field-driven transition occurs ($H_k$) decreases linearly with increase in temperature at a rate of $-1.7 \times 10^3$ Oe/K. Figures adapted from [42] and [11].

2.3.2 Influence of pressure/strain on the FeRh magnetostructural transition temperature

The effect of pressure on the magnetostructural transition temperature ($T_t$) of near-equiaxial ordered Fe$_{1-x}$Rh$_x$ (0.48 ≤ x ≤ 0.52) alloys has been extensively investigated [10, 11, 41-48]. From Figure 14(a) it is evident that the $T_t$ of FeRh increases with increasing compressive strain, $dT_t/dP = 4.33 \times 10^{-3}$ K/atm [10, 11, 48]. Figure 14(b) shows the temperature-dependant
resistivity behavior of an alloy of composition Fe₄₉Rh₅₁, as measured by Annaroaza et al. It is observed that the application of tensile strain decreases the transition temperature of FeRh \(dT/t/dP = -2 \times 10^{-3} \text{ K/atm} [47]\).

![Graph showing the effect of hydrostatic pressure on resistivity](image)

**Figure 14. Pressure dependence of the magnetostructural transition temperature of FeRh:** (a) Magnetic phase diagram of nominally equiatomic FeRh alloys shows that hydrostatic compressive pressure increases the magnetostructural phase transition temperature \(T_t\). (b) Temperature-dependence of resistivity of an alloy of composition Fe₄₉Rh₅₁ shows that \(T_t\) decreases with application of uniaxial pressure. Figures adapted from [11] and [49].

Epitaxially clamping a thin film to a substrate surface simulates the effect of pressure by creating strain in the regions nearest to the interfaces. Two common approaches to modify the strain character of a thin film are to grow the films on substrates with varying degrees of lattice mismatch or to grow films of various thicknesses on a substrate. A comparison of films grown on Al₂O₃ and MgO substrates shows that strain from the Al₂O₃ substrate is equal in magnitude but opposite in direction to strain from the MgO substrate. Contrary to results reported for bulk pressure studies on FeRh [11], compressive strain caused by deposition of thin films of varied thicknesses to an MgO substrate, results in reduction of the onset of \(T_t\) (Figure 15(a)) [42].
Conversely, FeRh films grown epitaxially on Al₂O₃ substrates demonstrate an increase in the onset of the transition temperature (Figure 15(b)) [42].

![Figure 15: Temperature-dependant magnetization behavior of 110-nm-thick FeRh films grown on: (a) MgO (001) substrate and (b) Al₂O₃ (0001) substrate. The red line corresponds to the magnetostructural temperature (\(T_t\)) of equiatomic FeRh compounds. Compressive strain caused by clamping FeRh thin films to an MgO substrate, results in reduction of the onset of \(T_t\). Conversely, FeRh films grown epitaxially on Al₂O₃ substrates demonstrate an increase in the onset of \(T_t\). Figure adapted from [42].](image)

In FeRh thin films, surface strain is believed to foster stabilization of a retained ferromagnetic phase below the magnetostructural transition temperature [43-45]. Recently, Loving et al. reported that when FeRh is grown at thicknesses less than 10 nm, the topography of the surface exhibits a discontinuous island-like morphology, shown in Figure 16 (a) [50]. In Figure 16(b), the temperature-dependant magnetization behavior of an ultrathin FeRh film of thickness 10 nm is shown along with that of a 50-nm thick film. Both systems exhibit an abrupt AF→FM transition upon heating which is reduced by 30 K in the nano-island system relative to the 50 nm film \((T_{t,10\,nm} = 250\,K,\,T_{t,50\,nm} = 380\,K)\). The cooling branch of the 10 nm film is substantially broader than that of the 50 nm film, leading to an overall decrease in the transition symmetry and increase in the thermal hysteresis width of the sample \((\Delta T_{t,10\,nm} = 15\,K,\,\Delta T_{t,50\,nm} =\)
100 K). While a very tiny retained magnetism is observed in the 50 nm thick film, a large retained magnetization of \(~815\) emu/cc persists in the 10 nm thick film. The unusual magnetostructural features of the FeRh nanoislands are attributed to the crystallographic arrangement of the nano-islands which consists of a gradient of lattice parameters corresponding to an antiferromagnetic core surrounded by a ferromagnetic shell (Figure 17). Overall, these results demonstrate the influence of substrate-induced strain on the magnetostructural response of FeRh thin films.

Figure 16. Magnetic and structural properties of ultrathin FeRh films: (a) Topography of the surface of a FeRh thin film of thickness 10 nm shows a discontinuous island-like morphology; (b) Temperature-dependant magnetization behavior of an ultrathin FeRh film of thickness 10 nm and a 50-nm thick FeRh film.

Figure 17. Schematic illustration of the core–shell crystallographic arrangement of a single FeRh nanoisland in the AF state. The light regions correspond to lattice parameters with AF ordering (core) which relax to the dark regions of the retained FM components (shell). Figure adapted from [50].
2.3.3 Influence of chemical modification on the FeRh magnetostructural transition temperature

An intriguing characteristic of FeRh alloys is that in addition to variation in extrinsic physical parameters such as temperature, pressure/strain and magnetic field, the magnetostructural transition temperature \( T_t \) of FeRh alloys can also be tuned over a wide temperature range \( (100 \text{ K} \leq T_t \leq 600 \text{ K}) \) by tweaking the chemical composition of the compound slightly [9-12, 41, 46, 48, 51-66]. Figure 18 shows that the \( T_t \) of Rh-rich FeRh compounds is lower than that of the \( T_t \) of equiatomic FeRh compounds \( (T_t, \text{bulk FeRh} \sim 360 \text{ K}) \) [67]. Further, it is possible to increase the bulk FeRh \( T_t \) with small additions of Os, Ru, Ir, and Pt [9, 10, 12, 41, 48, 51, 53, 54, 57-60]. Conversely, small additions of Al, V, Cr, Mn, Co, Ni, Pd and Au is known to decrease the \( T_t \) of bulk FeRh [9, 41, 46, 48, 51, 55, 57-61, 63-65, 68, 69].

![Figure 18](image)

**Figure 18.** Magnetic phase diagram for the near-equiatomic \( \alpha' \) phase of Fe\(_{1-x}\)Rh\(_x\) \((0.48 < x< 0.52)\). Here, the square and circle markers show the magnetostructural transition temperature during the heating and cooling process, respectively. The blank square and circle plots refer to data collected for FeRh thin films by J. Cao [63]. Overall, it is observed that the magnetostructural temperature of Rh-rich FeRh compounds is lower than that of equiatomic FeRh compounds \( (T_t, \text{bulk FeRh} \sim 360 \text{ K}) \). Figure adapted from [64].
In FeRh$_{1-x}$Pt$_x$ and FeRh$_{1-x}$Pd$_x$ alloys, at high doping levels ($x>0.2$), a highly ordered body-centered tetragonal (bct) structure with L10-type ordering is obtained [55, 57, 70-73]. It is evident from the magnetic phase diagram of FeRh$_{1-x}$Pt$_x$ and FeRh$_{1-x}$Pd$_x$ compounds, shown in Figure 19, that the bct alloys are predominantly antiferromagnetic [73]. In a narrow composition range - $0.72 < x < 0.81$ and $0.53 < x < 0.61$ for FeRh$_{1-x}$Pt$_x$ alloys and FeRh$_{1-x}$Pd$_x$ alloys respectively – an antiferromagnetic to ferromagnetic phase transition is observed upon heating [73].

![Figure 19: Magnetic phase diagram of Fe(Rh$_{1-x}$Pd$_x$) and Fe(Rh$_{1-x}$Pt$_x$) systems.](image)

Figure 19: Magnetic phase diagram of Fe(Rh$_{1-x}$Pd$_x$) and Fe(Rh$_{1-x}$Pt$_x$) systems. In FeRh$_{1-x}$Pt$_x$ and FeRh$_{1-x}$Pd$_x$ alloys, at high doping levels ($x>0.2$), a ferromagnetic body-centered tetragonal (bct) structure with L10-type ordering is obtained. In a narrow composition range - $0.72<x<0.81$ and $0.53<x<0.61$ for FeRh$_{1-x}$Pt$_x$ alloys and FeRh$_{1-x}$Pd$_x$ alloys respectively - a suppressed antiferromagnetic to ferromagnetic phase transition is observed upon heating. Figure adapted from [73].

2.3.4 Influence of nanostructuring on the FeRh magnetostructural transition temperature

As previously shown in Section 1, the Gibbs free energy of a first-order phase transformation is governed by a balance of energy terms. In nanostructured FeRh, it is
anticipated that free energy contributions associated with the increased surface to volume ratio may lead to variations in the overall driving force of the magnetostructural transition. In keeping with this hypothesis, one of the major goals of this Dissertation is to understand the influence of microstructural scale reduction on the magnetostructural transition of FeRh. Details regarding experimental studies aimed at fulfilling this objective are provided in Section 4.1. This Section describes the general features associated with nanostructured FeRh.

Prior to the studies conducted in this Dissertation, nanoscaled FeRh has been fabricated using three techniques: (a) rapid solidification processing (melt spinning) [74]; (b) mechanical alloying (ball milling) [75, 76] and (c) chemical synthesis (solution phase method) [77, 78]. Depending upon the synthesis approach, diverse magnetic properties have been observed in nanostructured FeRh [74-80]. While melt spinning produces nanograined FeRh ribbons which exhibit paramagnetism [74], ball milling results in formation of nanocrystalline FeRh alloys consisting of a ferrimagnetic core surrounded by an external shell which exhibits spin-glass like characteristics [75, 76]. FeRh nanoparticles of controllable composition and size (4-20 nm) synthesized using chemical synthesis methods show broad asymmetric magnetostructural transitions [77, 78]. A representative $M(T)$ measurement carried out on chemically-synthesized FeRh nanoparticles is shown in Figure 19. Here, the transformation asymmetry is clearly noted by an abrupt AF-FM transformation at 150 °C and a broad FM-AF transformation which persists to low temperatures (T ~ 100 to -100 °C).
2.4 Proposed mechanisms for the magnetostructural phenomena in the FeRh system

Although many attempts have been made to clarify the underlying mechanism of the AF-to-FM phase transition in FeRh alloys, the origin of the magnetostructural phase transition remains under debate for both bulk and thin-film forms of this system [7, 8, 10-12, 41, 53, 71, 81-87]. This Section serves to provide a general overview of the theories which have been proposed to understand the fundamental factors which drive the magnetostructural transformation.

The first proposed explanation of the FeRh magnetostructural transformation was made in the framework of an exchange inversion theory [7]. This theory is essentially derived from the concept that the interatomic distance determines the exchange energy between the atoms. Exchange energy is a quantum mechanical term which increases or decreases the expectation...
value of the energy between two or more identical particles when their wave functions overlap
[21]. For a pair of atoms, the exchange interaction, $E_{ex}$ is calculated as:

$$E_{ex} = -2J_{ex}S_iS_j = -2JS_iS_j \cos \phi$$  \hspace{1cm} (13)

where: $J_{ex}$ is the exchange integral;

$i$ and $j$ are the indices of the two atoms;

$S$ is the electron spins of atoms $i$ and $j$;

$\Phi$ is the angle between the spins;

The basic assumption of Kittel’s exchange inversion theory is that the exchange interaction
integral ($J_{ex}$) between the Fe-Fe atoms in the FeRh lattice depends linearly on the lattice
parameter and changes sign at a certain critical value of that parameter. This theory has since
been disproved based on inconsistencies between the total entropy of the transformation and the
change in the lattice entropy of the transformation [11, 41, 81].

Theoretical studies suggest that an electronic difference in the density of states (i.e. the
concentration of energy levels within the valence band) between the antiferromagnetic and
ferromagnetic state is the primary driving force for the transformation [57, 83, 88, 89]. In 1992
Moruzzi and Marcus performed first-principle band structure calculations using spin-polarized
density functional theory in the framework of the local density approximation (LDA) and the
augmented spherical wave (ASW) formalism [83, 84]. They calculated the total energy of FeRh
as a function of volume for three different magnetic configurations of FeRh: (a) ferromagnetic
configuration in which the Fe atoms polarize the neighboring Rh layers (Figure 21(a)); (b)
layered antiferromagnetic configuration where ferromagnetic Fe planes are separated by a
nonmagnetic Rh plane and the Fe planes are antiferromagnetically coupled with its nearest-
neighboring Fe planes (This configuration called antiferromagnetic I is shown in Figure 21(b))
and (c) in-plane antiferromagnetic configuration in each Fe plane, the Rh atoms staying unpolarized (This configuration also called antiferromagnetic II is shown in Figure 21(c)). The calculations of Moruzzi and Marcus reveal the coexistence of AF-II and FM solutions over a wide range of volume. The ground state of the FeRh system was found to be AF-II. A metastable ferromagnetic state with local moments of 3.1 \( \mu_B \) per Fe atom and 1 \( \mu_B \) per Rh atom was found just above the AF-II state. The overall energy differences in the computed ground states of the AF and FM phase in the FeRh system was determined to be very small, and it was shown that the ground state configuration of FeRh could be altered easily by variation of external parameters, such as field and pressure. The work of Moruzzi and Marcus is largely accepted by the FeRh community and most recently Gunner et al. extended this study by investigating the temperature dependence of the free energy states of the FM and AF phases using Monte Carlo simulations [90]. Accordingly to Grunner et al., the FeRh transformation is also strongly influenced by the instability of the magnetic states of the Rh atom, which is known to have a magnetic moment of 0 or 1 \( \mu_B \), depending on the magnetic order of the system [90].

Figure 21: Theoretically possible magnetic configurations in the FeRh system: (a) Ferromagnetic configuration in which the Fe atoms polarize the neighboring Rh layers; (b) Layered antiferromagnetic I configuration where the intra-plane coupling is ferromagnetic while inter-plane coupling is antiferromagnetic; (c) Antiferromagnetic II configuration where both intra-plane and inter-plane coupling are antiferromagnetic
Understanding the origin of the magnetostructural transformation has also been approached from a thermodynamic framework [42, 71, 85, 87, 91, 92]. In particular, it is to be noted that the theoretical work of Ricodeau and Melville suggests that the total driving force of the FeRh transformation ($\Delta G$) is driven by magnetic, electronic and lattice contributions ($\Delta G_{\text{mag}}$, $\Delta G_{\text{el}}$ and $\Delta G_{\text{lat}}$ respectively) [81]. In Figure 22 a plot from Ricodeau and Melville’s paper is reproduced. Here, the free energy contributions to the FeRh magnetostructural transition are plotted as a function of temperature. It is observed that $\Delta G_{\text{lat}}$ increases with increasing temperature (i.e. the lattice vibrations prevent the AF → FM phase transformation). Conversely, $\Delta G_{\text{el}}$ decreases with increasing temperature. Since, $\Delta G_{\text{lat}}$ and $\Delta G_{\text{el}}$ are equal and opposite in magnitude, the two contributions cancel each other out. From this work it is evident that the magnetic entropy change ($\Delta G_{\text{mag}}$) is the primary driving force of the FeRh magnetostructural phase transformation. Finally it is important to note from Figure 22 that the total driving force for the phase transition is higher at higher temperatures. Calorimetry studies have been useful in experimentally validating the results shown by Ricodeau and Meville. Recently, Cooke et al. proposed that thermally-driven magnetic fluctuations play the largest role in driving the FeRh magnetostructural phase transformation, while electronic effects provide a small contribution and lattice vibrations actually stabilize the AF phase relative to the FM phase [87]. This conclusion is consistent with time resolved x-ray diffraction and magneto-optical Kerr microscopy (MOKE) experiments, which suggest that in FeRh compounds lattice expansion occurs after the magnetic transformation [93-95]. Alternatively, time-resolved X-ray magnetic circular dichroism (XMCD) measurements suggest that the magnetic and structural transformation occur simultaneously [95].
Figure 22. Schematic diagram of the competing contributions to the total driving force of the AF $\rightarrow$ FM FeRh magnetostructural phase transformation. Here, $\Delta G_{\text{mag}}$ is the magnetic contribution, $\Delta G_{\text{el}}$ is the electronic contribution and $\Delta G_{\text{lat}}$ is the lattice contribution to the total driving force $\Delta G$. Image taken from [81].

2.5 Summary

In this chapter, salient aspects regarding the thermodynamics of magnetostructural phase transformations have been presented. This information provides a context for understanding the magnetostructural phase transition phenomena in FeRh-based compounds. The magnetic and structural properties of the equilibrium B2-ordered FeRh phase and the metastable L1$_0$-ordered FeRh phase has been described, followed by a detailed discussion regarding the influence of extrinsic (pressure, magnetic field, microstructural scale) and intrinsic (chemical modification) parameters on the FeRh magnetostructural transition. Finally, a brief overview of the current understanding of the origin of the FeRh phase transformation has been provided.
3.0 EXPERIMENTAL METHODS AND TECHNIQUES

The overarching objective of this Dissertation is to understand, predict and control the magnetostructural response of FeRh as a function of extrinsic parameter variation, elemental substitution and microstructural scale. A synopsis of the experimental techniques used in this Dissertation is described in the following Sections. Section 3.1 describes the preparation of the FeRh bulk and nanostructured samples. Fundamental aspects concerning the structural and magnetic probes used in this study are discussed in Section 3.2. Finally, Section 3.3 provides a brief summary of the synthesis and characterization techniques discussed in this chapter.

3.1 Materials synthesis and processing

This Section describes the preparation of the bulk and nanostructured FeRh samples under investigation in this Dissertation; a complete list of the samples examined is provided in Table 2. Bulk FeRh-based samples were synthesized via the arc-melting technique. Nanostructuring of the FeRh system was achieved by rapid solidification of an arc-melted alloy of composition Cu_{95}(FeRh)_{5} using the melt-spinning technique. In Section 3.1.1, the rationale behind choosing the above mentioned synthesis techniques is presented. A general overview of the instrumentation and operating principles of arc melting and melt-spinning is provided in Section 3.1.2. Specific details regarding the sample preparation conditions for the various experiments conducted in this thesis are provided later in Chapter 4 (See Sections 4.1.2, 4.2.3, 4.3.2 and 4.4.2).
Table 2. List of samples studied in this Dissertation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Method of synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeRh</td>
<td>Bulk ingot</td>
<td>Arc-melting</td>
</tr>
<tr>
<td>Fe_{50}(Rh_{49}Cu_{1})</td>
<td>Bulk ingot</td>
<td>Arc-melting</td>
</tr>
<tr>
<td>Fe_{50}(Rh_{48}Cu_{2})</td>
<td>Bulk ingot</td>
<td>Arc-melting</td>
</tr>
<tr>
<td>Fe_{50}(Rh_{47}Pd_{3})</td>
<td>Bulk ingot</td>
<td>Arc-melting</td>
</tr>
<tr>
<td>(Fe_{47.5}Ni_{1.5})Rh_{51}</td>
<td>Bulk ingot</td>
<td>Arc-melting</td>
</tr>
<tr>
<td>Cu_{95}(FeRh)_{5}</td>
<td>Rapidly-solidified ribbons</td>
<td>Arc-melting followed by melt-spinning</td>
</tr>
<tr>
<td>Cu_{98}Fe_{2}</td>
<td>Rapidly-solidified ribbons</td>
<td>Arc-melting followed by melt-spinning</td>
</tr>
<tr>
<td>Cu_{98}Rh_{2}</td>
<td>Rapidly-solidified ribbons</td>
<td>Arc-melting followed by melt-spinning</td>
</tr>
</tbody>
</table>

3.1.1 Rationale for using arc-melting and melt-spinning for sample synthesis

Depending upon the motivation of the experimental study, FeRh-based samples in this Dissertation were synthesized using two different techniques. For experiments aimed at examining the influence of elemental substitution and extrinsic parameter variation on the magnetostructural response, bulk alloys of chemical composition Fe(Rh_{1-x}M_{x}) or (Fe_{1-x}M_{x})Rh (M=Cu, Ni, Pd and Au; 0<x<0.04) were fabricated using the arc-melting technique. For studies focused on investigating effects of nanostructuring on the magnetostructural response, the melt-spinning technique was used to synthesize FeRh nanoparticles in a metallic Cu matrix. Melt spinning is a non-equilibrium synthesis technique where a balance between thermodynamics and kinetics is exploited to trap metastable phases and nanostructures in a 3-dimensional matrix [96]. In this method, a molten charge is solidified at high quench rates in the range of 10^6 degree/sec and the equilibrium transformation of a liquid to solid is thus suppressed [97]. Typically, melt-spinning of alloys results in formation of supersaturated solid solutions. A number of non-equilibrium phases have been obtained during aging of super-saturated solid solutions [98]. For example, thermal annealing of rapidly solidified ribbons of composition TiNi results in
formation of Ti2Ni nanoprecipitates in a TiNi matrix [99]. In determining which system is amenable for production of nanocomposites by melt-spinning, features of the phase diagram play an important role [96, 98]. An overview of fundamental aspects regarding phase diagrams of binary alloys, as relevant to this study, is presented in Appendix A.

As applicable to this Dissertation, Cu was chosen as a matrix for the realization of the nanostructured FeRh system because the equilibrium phase diagram of the element end-member pairs (Rh, Cu) and (Fe, Cu) are characterized by large miscibility gaps spanning wide composition ranges (Figure 23) [100, 101]. Based on the limited solid solubility of the elements Fe and Rh in Cu, it was hypothesized that rapid solidification processing and subsequent annealing of an arc-melted precursor alloy of composition, (FeRh)5Cu95 would result in the formation of a phase-separated nanocomposite system consisting of non-interacting FeRh nanoprecipitates embedded in a Cu matrix. Results outlined in Section 4.1 confirm this hypothesis.

![Figure 23: Equilibrium phase diagrams of the immiscible elemental pairs: (a) (Fe, Cu) and (b) (Rh, Cu). Figures adapted from [100] and [101].](image)
3.1.2 Operating principle of arc-melting and melt-spinning

In this Dissertation, bulk FeRh-based samples were synthesized via the arc-melting technique. Subsequently, nanostructuring of the FeRh system was achieved by rapidly-solidifying arc-melted FeRh-based precursors using the melt-spinning technique. In this Section, a brief overview of the instrumentation and operating principles of arc melting and melt-spinning is provided.

(a) Synthesis of bulk FeRh-based samples via arc-melting

Synthesis of the bulk FeRh-based alloys under consideration in this Dissertation (See Table 2) were achieved using a Edmund Buhler MAM-1 mini-arc melting system operated in an argon atmosphere (Figure 24(a)). The arc melting chamber is shown in Figure 24(b). During the arc melting process, a DC current is applied between a tungsten tip and a water-cooled copper hearth to create sustained plasma that reaches a temperature of 3500 °C. Sample material placed on the copper hearth is melted by the plasma and consequently a nominally homogenous alloy is created when the sample is cooled to room temperature. To prevent contamination by oxidation, a titanium getter that absorbs oxygen is placed in the crucible along with the sample.
(b) Synthesis of the FeRh nanocomposite system via melt-spinning

For studies focused on investigating the effect of reduction of microstructural scale on the magnetostructural response of FeRh, the melt-spinning technique was used to synthesize FeRh nanoparticles in a metallic Cu matrix. In this Section, the operating principle of melt-spinning is described. The melt-spinning apparatus used in this work, shown in Figure 25(a), was manufactured by Edmund Buhler GmbH (Tübingen, Germany). During sample processing using this technique, the bulk ingot is first placed in a quartz crucible containing a small orifice at the bottom (Figure 25(b)). The crucible is then positioned inside the melt-spinning chamber followed by evacuation and backfilling of the chamber with Ar several times. RF induction heating is then used to melt the bulk alloy. Once the desired temperature is reached (as determined by the color of the melt), the melt is ejected through the orifice onto a rapidly-spinning water-cooled copper wheel to solidify the liquid. The resulting product, ribbon, is then thrown off the rapidly rotating wheel. The microstructure as well as the properties of melt-spun materials systems depends strongly on three operating factors: (a) the dimensions of the orifice
of the crucible; (b) the distance between the Cu wheel and the orifice and (c) the speed of rotation of the Cu wheel [96]. In this Dissertation work, quartz crucibles with an orifice diameter of 0.8 mm were used during melt-spinning and the effective rotating speed of the Cu wheel was set at 31 m/sec. The distance between the orifice and the Cu wheel was set at 3 mm.

Figure 25: (a) The Edmund Buhler melt-spinning system. (b) During melt-spinning, the crucible containing the sample is placed in an induction coil. Once the desired temperature is reached, the liquid melt is ejected through the orifice at the bottom of the crucible onto a rotating Cu wheel which solidifies the liquid into a ribbon at cooling rates up to 106 K/s. Image adapted from [102].

3.2 Characterization techniques: Chemical, Structural and Magnetic

In this Section the characterization techniques used for investigating the structural and magnetic properties of the bulk and nanostructured FeRh samples are described. In Section 3.2.1, fundamental aspects regarding compositional analysis of the FeRh-based samples using energy dispersive x-ray spectroscopy (EDS) are described. In Section 3.2.2.1, experimental methods for obtaining information regarding the crystallographic and microstructural properties of FeRh-based compounds are discussed. Salient features and the operating principles of transmission electron microscopy (TEM) and X-ray diffraction (laboratory and synchrotron-based) are discussed in Section 3.2.2.2. An overview of the analysis methods pertaining to the magnetic
properties of FeRh-based systems is given in Section 3.2.3.1. Finally, the operating principles of SQUID and VSM magnetometry are presented in Section 3.2.3.

3.2.1 Chemical characterization using Energy Dispersive X-ray Spectroscopy (EDS)

In this Dissertation, a field-emission scanning electron microscope (FE-SEM), Hitachi S4800, equipped with energy dispersive x-ray analysis (EDS) capability was used for compositional analysis of the FeRh-based samples (Figure 26).

A schematic representation of the operating principle of EDS is shown in Figure 27. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of X-rays is focused onto the sample under study. In its native state, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was originally located. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an x-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive
spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, the elemental composition of the specimen may be quantified. The limit of detection of EDS is approximately ± 0.5 weight percent [104]. It is important to note that accuracy of EDS is low when the specimen being analyzed consists of elements with overlapping characteristic energies [104].

Figure 27. Schematic of operating principle of Energy-dispersive X-ray spectroscopy (EDS). Figure adapted from [104].

3.2.2 Structural Characterization Techniques

In this research, information pertaining to the crystallographic properties (crystal structure, lattice parameter, chemical ordering) and the microstructure (grain size, matrix/precipitate orientation, lattice misfit strain, interparticle distance) of the bulk and nanostructured FeRh systems was obtained using transmission electron microscopy (TEM) equipped with selected area electron diffraction (SAED) functionality and X-ray diffraction (XRD, laboratory and synchrotron-based). An outline of the essential terminology and analysis necessary for interpreting the data obtained from TEM and XRD experiments is provided in
Section 3.2.2.1. In the subsequent Sections, information regarding the operating principles of the techniques used in this study (TEM and XRD) is provided.

3.2.2.1 Overview of terminology and analysis methods for structural characterization

This Section is subdivided into two major segments. In the first segment, analytical methods for determining the crystallographic properties of the bulk and nanostructured FeRh-based compounds are described. In the second segment, concepts associated with microstructural analysis of the nanoscaled FeRh system are presented.

(a) Analysis of crystallographic properties of bulk and nanostructured FeRh systems

The crystal structure of a materials system describes the arrangement of atoms within a given type of crystal in terms of its simplest repeating unit - the unit cell. Typically, the unit cell is represented in terms of its lattice parameters which are the lengths of the cell edges \((a, b\) and \(c)\) and the angles between them \((\alpha, \beta\) and \(\gamma)\). Miller indexing is a common notation used to describe lattice planes in a crystalline system. In this notation, the inverse intercepts of the lattice plane may be described by an integer value \((hkl)\). As applicable to this study, it is important to note that FeRh in its equilibrium form is cubic \((a=b=c=2.9987\ \text{Å at room temperature}; \ a=\beta=\gamma=90^\circ)\). Lattice planes with different Miller indices in cubic crystals are schematically shown in Figure 28.
In this study, lattice parameters of the FeRh bulk and nanostructured systems were determined using two comparable techniques: (a) X-Ray Diffraction and (b) Selected area electron diffraction (SAED, in conjunction with TEM). In electron diffraction experiments, constructive interference patterns emerge when waves are scattered by the electrons constituting the plane of atoms in the unit cell (Figure 29). Thus, depending on the orientation of the lattice planes in the unit cell, a specific pattern will be produced. The spacing between the planes of atoms, $d$, can be determined when the conditions for constructive interference, as described by Bragg’s law, are satisfied:
\[ 2d \sin \theta = n\lambda \quad (13) \]

Where:
- \(d\) = Interatomic spacing (nm)
- \(\lambda\) = Wavelength of incoming radiation (nm)
- \(\theta\) = Angle of incident x-ray radiation (degrees)
- \(n\) = Order of reflection (usually taken as one)

![Schematic representation of the operating principle of X-ray diffraction. Figure adapted from [105].](image)

The \(d\)-spacing values obtained from Equation (13) can then be used to compute the lattice constants of the unit cell. For a cubic system such as FeRh in its equilibrium form, the characteristic lattice parameter, \(a\), can be obtained from:

\[ \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (14) \]

Where:
- \(a\) = Lattice constant (nm);
- \(D\) = Interatomic spacing (nm);
- \((hkl)\) = Miller indices (unitless)

The bulk FeRh-based compounds in this study are chemically-ordered in a B2 (CsCl)-type crystallographic configuration where Rh sits in the body centered position in the unit cell (i.e. at the center) and Fe occupies the corners of the unit cell (See Figure 30(b)).
crystallographic arrangement is fundamentally different from the chemically-disordered body-centered cubic structure, shown in Figure 30(a) where the atoms are indistinguishable from one another. During x-ray diffraction, each plane in a chemically-disordered body-centered cubic structure has an average atomic scattering factor (measure of the scattering amplitude of a wave by an isolated atom, $F_{av}$) that is the same for \{001\} and \{002\} planes. The x-ray beams diffracted from the \{001\} planes will be perfectly in phase with each other and perfectly out of phase with beams diffracted from the \{002\}-planes, so that the diffracted beams interfere destructively. However, in the B2-ordered FeRh structure, the \{001\} and \{002\} planes have different scattering factor ($F_{Fe}$ and $F_{Rh}$ for Fe and Rh respectively) so the diffracted beams interfere constructively. This results in additional peaks in the XRD pattern called superstructure peaks.

**Figure 30.** (a) Crystal structure of a chemically-disordered body-centered cubic (bcc) unit cell; (b) Crystal structure of a chemically-ordered B2 (CsCl)-type cubic unit cell. It is important to note that in the B2-ordered FeRh structure, the \{001\}-planes and \{002\}-planes have different scattering factor $F_{Fe}$ and $F_{Rh}$. This results in additional peaks in the XRD pattern called superstructure peaks.

The FeRh system is considered to have perfect chemical ordering if all the Fe and Rh atoms are perfectly situated in their respective lattice sites as shown in Figure 30 (b). The degree of chemical ordering in this system can be determined by the calculation of an order parameter,
$S$, which takes values between 0 and 1, where $S=1$ represents perfect chemical ordering and $S=0$ represents complete chemical disordering. The order parameter may be calculated based on the integrated intensity ratio of the superlattice reflections (Bragg peaks corresponding to the chemically-ordered B2 structure) and the fundamental peak reflections (Bragg peaks corresponding to the chemically-disordered $bcc$ structured):

$$S = \sqrt{\frac{I_{\text{exp}}^{\text{calc}}}{I_{\text{calc}}^{\text{calc}}}}$$  \hspace{1cm} (15)

Where: $I_{\text{exp}}^{\text{exp}}(001)$ and $I_{\text{exp}}^{\text{exp}}(002)$ are the experimental intensities of the (001) and (002) Bragg reflections; $I_{\text{calc}}^{\text{calc}}(001)$ and $I_{\text{calc}}^{\text{calc}}(002)$ are the experimental intensities of the (001) and (002) Bragg reflections.

In this Dissertation, the value of $I_{\text{calc}}^{\text{calc}}(001) / I_{\text{calc}}^{\text{calc}}(002)$ was considered as 1.07 in accordance to previous literature calculations of the order parameters of the FeRh system [107]. Equation [15] may therefore be re-written as:

$$S = \sqrt{\frac{I_{\text{exp}}^{\text{exp}}(001)}{I_{\text{exp}}^{\text{exp}}(002)}}$$  \hspace{1cm} (16)

It is well known that the degree of chemical ordering plays an important role in influencing the magnetostructural response of FeRh-based compounds. To this end, it is important to note that the bulk compounds studied in this research were found to have a high degree of chemical ordering ($S>0.8$).

(b) **Analysis of microstructural properties of the nanostructured FeRh system**

For studies focused on investigating effects of nanostructuring on the magnetostructural response of FeRh, a phase-separated nanocomposite system consisting of FeRh nanoparticles in
a Cu matrix was synthesized via thermal annealing of a rapidly-solidified (FeRh)_{5}Cu_{95} ribbon (See Section 3.1 for details). This Section describes the analysis methods used to obtain information regarding the microstructure of the (FeRh)_{5}Cu_{95} sample. In particular, the Williamson-Hall method for simultaneous determination of crystallite size and strain in the FeRh nanoprecipitates is discussed. Further, the concept of matrix-induced strain is explained.

(i) Williamson-Hall Analysis

Broadening of X-ray diffraction peaks in nanostructured materials systems is an experimental signature of finite crystallite size and possible lattice strain. In this Dissertation, the Williamson-Hall method was used to investigate the microstructural size and strain effects in the FeRh nanoprecipitates. In this method, the peak widths of the Bragg reflections (β*) obtained via XRD experiments were plotted as a function of inverse d-spacing (d*):

$$\beta^* = \frac{1}{D_{hkl}} + 2\varepsilon d^* \quad (17)$$

Here, β* = (FWHM) cos(θ)/λ, where FWHM is the full-width at half-maximum intensity of the Bragg peaks in radians and λ is the wavelength of the incident radiation and

$$d^* = \frac{2 \sin(\theta)}{\lambda}.$$ 

Typically, the $D_{hkl}$ intercept provides an estimation of the crystallite size (i.e. distance between two coherently diffracting planes in a crystal) of the FeRh precipitates and the slope yields the strain parameter (ε). In a nanostructured system, there may be many sources of strain. For example: strain due to distribution of lattice constants arising due to crystal imperfections such as lattice dislocation. In this Dissertation, strain induced due to lattice-mismatch between the matrix and the nanoparticles is important. This concept is explained in the following paragraph.

(ii) Matrix-induced strain in a nanocomposite system

In a nanocomposite system comprising of a two-phase microstructure, the nanoprecipitate phase is often dispersed in the matrix phase. In such a scenario, matrix-induced strain plays an
important role in determining the microstructure of the sample. Matrix-induced strain in a nanoparticle system may be visualized via a schematic representation of the precipitate/matrix atomic interface. A coherent interface in a nanocomposite system is achieved when the lattices of the precipitate and the matrix phase match perfectly at the interface plane so that the two lattices are continuous across the interface, See Figure 31. This scenario can only be achieved if the interfacial plane has the same atomic configuration in both phases. For example, such an interface is formed between hexagonal close-packed ($hcp$) Si-rich surface and the fcc Cu-rich $\alpha$-matrix in Cu-Si alloys [14]. The lattice parameters of these two phases are such that the $(111)_{fcc}$ phase is identical to the $(0001)_{hcp}$ phase. Therefore when the two crystals are joined along these planes, the resultant interface is completely coherent. A graphical representation of this concept is shown in Figure 31(b).

![Schematic representation of a strain-free coherent interface between two phases, $\alpha$ and $\beta$.](image)

**Figure 31.** Schematic representation of a strain-free coherent interface between two phases, $\alpha$ and $\beta$. In scenario (a), the two phases $\alpha$ and $\beta$ have the same crystal structure and consequently they have perfect plane-on-plane crystallographic orientation. In scenario (b), the two phases $\alpha$ and $\beta$ have different crystal structures and they form a coherent interface only along the crystallographic planes which have the same lattice parameters. Figure adapted from [14].
When the distance between the atoms in the interface is not identical, it is still possible to maintain coherency by straining one or both of the two lattices as illustrated in Figure 31. The resultant lattice distortions are known as coherency strains. The degree of lattice mismatch between the nonoparticle and the matrix lattice parameters may be calculated as follows:

\[
\varepsilon_{\text{lat mis}} = \frac{a_{\text{nanoparticle}} - a_{\text{matrix}}}{a_{\text{nanoparticle}}}
\]

(18)

Where: \(\varepsilon_{\text{lat mis}}\) is the strain due to lattice mismatch

- \(a_{\text{nanoparticle}}\) is the lattice parameter of the nanoparticle system
- \(a_{\text{matrix}}\) is the lattice parameter of the matrix

Lattice fitting arguments are often used to predict the crystallographic orientational relationship between a coherent nanoparticle system and its matrix. In many circumstances, the matrix orientation which provides the smallest lattice mismatch is often the observed matrix-nanoparticle orientation.

Figure 32. Schematic representation of a coherent interface between two phases (α and β) with slightly different lattice parameters. Figure adapted from [14].
3.2.2.2 Operating principles of structural probes: Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD)

In this Section, a general overview of the instrumentation and operating principles of the probes used for structural characterization of the bulk and nanostructured FeRh samples is provided.

(a) Transmission Electron Microscopy (TEM) equipped with Selected Area Electron Diffraction (SAED) functionality

In this Dissertation work, transmission electron microscopy (TEM) imaging of the FeRh nanostructured samples was done in collaboration with colleagues at Professor. Jeffery E. Shield’s laboratory at the University of Nebraska at Lincoln. Specifically, a JEOL 2010 TEM operating at 200 kV was used for this study (Figure 33(a)). TEM sample preparation was accomplished by mechanically polishing the melt-spun (FeRh)$_5$Cu$_{95}$ ribbons to a thickness of ~10 μm, followed by ion milling to perforation using a Gatan Precision Ion Polishing System (PIPS) operated at 5 kV (Figure 33(b)).

Figure 33. (a) JEOL 2010 Transmission Electron Microscope (TEM) with Selected Area Electron Diffraction (SAED) capability; (b) Gatan Precision Ion Polishing System (PIPS) used for TEM sample preparation. Image taken from [108].
The operating principle of TEM may be briefly outlined as follows: Typically, a transmission electron microscope is composed of several components, including an electron emission source for generation of the electron stream, vacuum system in which the electrons travel, a series of electromagnetic lenses, as well as electrostatic plates (See Figure 34 for the layout of the optical components in a basic TEM). In this technique, a focused high energy beam of electrons is transmitted through an ultra-thin specimen. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device such as a fluorescent screen, and is detected by a sensor such as a CCD camera.

Figure 34. Layout of optical components in a basic transmission electron microscope (TEM). Image adapted from [109].
Typically, TEM is performed in conjunction with selected area (electron) diffraction (SAED) [109]. It is to be noted that the wavelength of the high-energy electrons during TEM imaging is typically a few thousandths of a nanometer and the spacing between atoms in a solid is about a hundred times larger. The atoms therefore act as a diffraction grating to the electrons. SAED patterns are a projection of the reciprocal lattice, with lattice reflections shown as sharp diffraction spots. SAED is referred to as "selected" because the end-user can easily choose from which part of the specimen to obtain the diffraction pattern [110]. Located below the sample holder on the TEM column is a selected area aperture, which can be inserted into the beam path. This is a thin strip of metal that will block the beam. It contains several different sized holes, and can be moved by the user. The effect is to block the entire electron beam except for the small fraction passing through one of the holes; by moving the aperture hole to the Section of the sample that the user wishes to examine, this particular area is selected by the aperture, and only this Section will contribute to the SAED on the screen. As a diffraction technique, SAED can be used to identify crystal structures and examine crystal defects. It is similar to X-ray diffraction (described in Section 3.2.2.2), but unique in that areas as small as several hundred nanometers in size can be examined, whereas X-ray diffraction typically investigates areas several centimeters in size.

(b) Operating principle of X-ray Diffraction (Laboratory and Synchrotron-based)

In this study, the crystallographic structure of bulk FeRh-based samples was determined using a PANanalytical X’Pert PRO MPD X-ray diffractometer available at Northeastern University’s George J. Kostas Nanoscale Technology and Manufacturing Research Center (Figure 35(a)). The basic geometry of an X-ray diffractometer involves a source of monochromatic radiation and an X-ray detector situated on the circumference of a graduated
circle centered on the powder specimen (Figure 35(b)). The detector and specimen holder are mechanically coupled with a goniometer so that a rotation of the detector through $2\theta$ degrees occurs in conjunction with the rotation of the specimen through $\theta$ degrees, a fixed 2:1 ratio. As the sample holder and detector rotate, the intensity of the reflected x-rays is recorded. Constructive interference of the outgoing x-rays produces a Bragg peak in the XRD pattern which corresponds to a lattice plane in the sample’s unit cell.

Figure 35. (a) Image of a standard laboratory PANanalytical X’Pert PRO MPD X-ray Diffractometer (XRD). Image taken from [111]; (b) Schematic of operation of a X-ray diffractometer - A monochromatic x-ray beam irradiates a sample at an angle and a detector records the reflected intensity at an angle $0$. Figure adapted from [105].

In this Dissertation, the Bragg peaks of the FeRh nanoparticles fabricated in the Cu$_{95}$(FeRh)$_5$ nanocomposite were too small in intensity to be detected using standard laboratory X-ray diffraction which employs Cu-$K\alpha$ radiation (See Section 4.1 for details). Information regarding the microstructure of the FeRh nanocomposite sample was therefore obtained via XRD
experiments conducted in the transmission mode at the National Synchrotron Light Source (NSLS) Beamline X16C at Brookhaven National Laboratory (Figure 36). Synchrotron- and laboratory-based diffractometers differ in the process of the generation of the x-rays and in the intensity of the resultant x-ray beam [112]. In a laboratory diffractometer x-rays are generated in an x-ray tube when a filament is heated to produce electrons. The electrons are liberated from the heated filament and accelerated by a high voltage towards the metal target. The X-rays are produced when the electrons dislodge the inner shell electrons of the target material. The diffractometer employed in this current study employs a Cu target. Thus the characteristic x-ray spectra of this diffractometer consist of Cu-K$_\alpha$ and K$_\beta$ components. A monochromatic x-ray beam is desired for structural analysis; therefore the beam is filtered through a material, typically Ni, to produce only Cu-K$_\alpha$ radiation which has a wavelength of 0.154 nm. In contrast, at a synchrotron facility, electrons are produced by cathode that is heated to about 1,100 °C. The electrons thus produced are accelerated to 99.999% of the speed of light in a linear accelerator. From the linear accelerator, the electrons are injected into the booster synchrotron. Here, the electrons are sent around an oval racetrack of electromagnets, providing further acceleration. Within one-half second, the electrons reach 99 % of the speed of light. Upon reaching that speed, the electrons are injected into a circular storage ring consisting of more than 1,000 electromagnets. Once in the storage ring, the electrons produce x-ray beams that are available for use in experimentation. A schematic of this phenomenon is shown in Figure 37. In synchrotron x-ray facilities specialized accessories such as undulators, wigglers and bending magnets are used to tune the emitted x-rays to a desired wave length [112]. This allows synchrotron-based XRD experiments to use more intense radiation during characterization. In this thesis, the energy of the incident radiation at Beamline X16C at the National Synchrotron
Light Source (NSLS) at Brookhaven National Laboratory (BNL), was set to 17 keV (photon wavelength $\lambda=0.7$ Å). To minimize error due to the texture of the melt-spun ribbons, the sample was mounted in the axial direction and rotated at a speed of 50 m/sec during data collection. Error due to instrumental broadening was estimated as negligible.

Figure 36. (a) Experimental floor at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL); (b) Powder X-ray diffraction set-up at Beamline X16C.

Figure 37. Schematic representation of a synchrotron radiation accelerarator. Here: $e^-$ refers to electrons and $h\nu$ refers to the photon source. Figure adapted from reference [112].
3.2.3 Magnetic Characterization: Methods and Techniques

Characterization of magnetic properties of the synthesized bulk and nanostructured FeRh systems was carried out using a superconducting quantum interference device (SQUID) magnetometer and a vibrating sample magnetometer (VSM). Temperature- and field-dependant magnetization measurements in fields up to 5 T and in the temperature range $2 \text{ K} \leq T \leq 800 \text{ K}$ were used to identify the magnetic phases and magnetic transitions in the bulk and nanostructured systems. Additionally, the effects of annealing temperature, external magnetic field and hydrostatic pressure on magnetic transition temperatures, particularly the magnetostructural temperatures ($T_t$), were examined. An overview of the basic terminology and analysis methods necessary for interpreting the magnetic data obtained in this study is provided in Section 3.2.3.1. The basic operating principle of the magnetometers used in this study is described in Section 3.2.3.2.

3.2.3.1 Overview of magnetic terminology and analysis methods

Atoms contain many electrons; in a simplistic sense each spins about its own axis and moves in its own orbit. The magnetic moment associated with each atom is a vector quantity which is a sum total of its spin and orbital angular momentum. Materials may be classified according to the response of a magnetic moment ($\vec{M}$) and an externally applied field ($H_{app}$); this term is generally referred to as magnetic susceptibility ($\chi$). Salient features regarding four common types of magnetic materials are outlined below:

Diamagnetic materials: In a metal, the orbital motion of electrons creates tiny atomic current loops, which produce magnetic fields. When an external magnetic field is applied to a material, these current loops tend to align in a way that opposes the applied field. This may be viewed as an atomic version of Lenz's law: “induced magnetic fields tend to oppose the change which
“creates them”. Materials in which this effect is the only response to a magnetic field are called diamagnetic materials. Typically diamagnetic materials are composed of atoms which have no net magnetic moments (i.e., all the orbital shells are filled and there are no unpaired electrons). Figure 38(a) shows that when diamagnetic materials are exposed to an external magnetic field, a negative magnetization is produced and thus the susceptibility is negative (See Figure 38(a)). Typically, the susceptibility of diamagnetic materials is temperature independent (See Figure 38(b)).

![Figure 38. Magnetic moment of diamagnetic materials as a function of: (a) Magnetic field and (b) Temperature. Figure taken from [113].](image)

(a) **Paramagnetic materials:** In this class of materials, some of the atoms or ions in the material have a net magnetic moment due to unpaired electrons in partially filled orbitals. However, the individual magnetic moments do not interact magnetically, and like diamagnetism, the magnetization is zero when the field is removed. In the presence of a field, there is a partial alignment of the atomic magnetic moments in the direction of the field, resulting in a net positive magnetization and positive susceptibility (Figure 39(a)). The efficiency of the field in aligning
the moments is opposed by the randomizing effects of temperature. This results in a temperature dependent susceptibility, known as the Curie Law (Figure 39(b)):

\[
\chi = \frac{c}{T}
\]  

(19)

Where: \( C \) is the Curie constant (cm\(^3\) K/g);

\( T \) is the temperature of the system;

\( \theta \) is the paramagnetic Curie temperature (K)

**Figure 39. Magnetic moment of paramagnetic materials as a function of (a) Magnetic field and (b) Temperature. Figure taken from [113].**

It is important that in the framework of classical physics, the Curie law is based theoretically on the Langevin theory of paramagnetism. This theory assumes that the individual carriers of magnetic moments in a paramagnetic material do not interact with one another but are acted on only by the applied field or by thermal agitation. Many paramagnetic materials, however do not obey this law; they instead obey a more general equation called the Curie-Weiss law:
\[ \chi = \frac{C}{T - \theta} \quad \text{(20)} \]

Where: 
- \( C \) is the Curie constant (cm\(^3\) K/g);
- \( T \) is the temperature of the system;
- \( \theta \) is a measure of the exchange interaction between the atoms in the system.

Exchange interaction is a quantum mechanical term which increases or decreases the expectation value of the energy between two or more identical particles when their wave functions overlap [21]. For a pair of atoms, the exchange interaction, \( E_{ex} \) is calculated as:

\[ E_{ex} = -2J_{ex}S_iS_j, \]

where \( J_{ex} \) is the exchange integral; \( i \) and \( j \) are the indices of the two atoms and \( S \) is the electron spins of atoms \( i \) and \( j \). Experimentally, both positive and negative values of \( \theta \) are observed. A positive value of \( \theta \) implies parallel (i.e. ferromagnetic) exchange interaction between the atoms. Conversely, a negative value of \( \theta \) implies antiparallel (i.e. antiferromagnetic) exchange interaction between the atoms.

In metallic systems, the conduction electrons exhibit a weak temperature-independent paramagnetism known as Pauli paramagnetism. In such systems, the Curie-Weiss law is modified as follows:

\[ \chi = \frac{C}{T - \theta} + \chi_{pp} \quad \text{(21)} \]

Where: 
- \( C \) is the Curie constant (cm\(^3\) K/g);
- \( T \) is the temperature of the system;
- \( \theta \) is a measure of the exchange interaction between the atoms in the system;
- \( \chi_{pp} \) is the Pauli paramagnetic susceptibility (cm\(^3\) K/g)
**Ferromagnetic Materials:** Ferromagnetic materials exhibit parallel alignment of atomic moments resulting in large net magnetization even in the absence of a magnetic field (Figure 40(a)). In such a system the exchange coupling constant, $J_{ex}$, is always greater than 0. Typically, the temperature-dependant magnetization behavior of FeRh-based compounds is characterized by a magnetic hysteresis loop (shown in Figure 40(b)). The hysteresis loop is explained as follows: At point “a”, the material system is initially demagnetized. As the external magnetic field ($\vec{H}$) is increased, the induced magnetization ($\vec{M}$) also increases. The induced magnetization eventually saturates at point “b”. This point is called the saturation magnetization $M_s$. The curve between points “a” and “b” is called the initial magnetization curve. When the $\vec{H}$ is reduced, $\vec{M}$ also decreases, but it does not follow the original curve. Instead, the material retains a certain permanent magnetization termed the remanent magnetization $M_r$ (point “c”). The remanent magnetization is the permanent magnetization that remains after the external field is removed. If $H$ is further reduced, $M$ decreases till $H=0$ (point “d”). The external field for which the $M_r$ goes to zero is termed the coercitivity, $H_c$. As the external field continues to reverse, permanent magnetization of the opposite sign is created in the agnet. A similar curve is traced for the negative direction with $M_s$ (point “e”), $M_r$ (point “f”) and $H_c$ (point “g”). The hysteresis curve then retraces points b-e if the field cycles. Even though electronic exchange forces in ferromagnets are very large, thermal energy eventually overcomes the exchange and produces a randomizing effect. This occurs at a particular temperature called the Curie temperature ($T_c$) (See Figure 5(a)) in Section 2.1.2 for an example of Curie temperature behavior in Fe).
Antiferromagnetic Materials: Antiferromagnetism is a weak form of magnetism which is similar to paramagnetism in the sense that antiferromagnetic materials exhibit a small positive susceptibility. As shown in Figure 41(a), the temperature-dependent susceptibility of this type of magnetism is characterized by the presence of a kink in the $\chi$ vs. $T$ plot. This kink is generally referred to as the Néel temperature ($T_N$). Below the Néel temperature, antiferromagnetic materials exhibit antiparallel spins which completely cancel each other out (See Figure 41(b) for spin configuration in the antiferromagnetic state). When an external magnetic field is applied to an antiferromagnetic material, the negative interaction of the antiparallel spin prevents the spin from aligning to the direction of the magnetic field and thus the susceptibility of the material decreases with decreasing temperature, contrary to the usual paramagnetic behavior. Above the Néel point, the spin arrangement becomes random as expected in a paramagnetic material (See...
Figure 41(c) for spin configuration in the paramagnetic state). Consequently, the susceptibility decreases with increasing temperature.

![Figure 41](image)

**Figure 41.** Temperature-dependant magnetization behavior of antiferromagnetic materials systems. Figure taken from [113].

As applicable to this study, it is to be noted that the bulk FeRh systems investigated in this study are antiferromagnetic at room temperature. At $T \sim 350$ K, FeRh is known to undergo a first-order hysteretic magnetostructural transition. In this Dissertation, values of the magnetostructural transition temperature ($T_t$) and thermal hysteresis ($\Delta T_t$) were obtained from $M$ vs. $T$ measurements in the temperature range of $100$ K $\leq T \leq 400$ K at various applied fields ($H$) up to 5 T. The FeRh magnetostructural phase transition temperature ($T_t$) was determined as the maximum of the derivative of $M$ with respect to $T$ plotted against $T$ (i.e. $dM/dT$ vs. $T$), while the width of the thermal hysteresis, $\Delta T_t$, was calculated as the difference between the temperatures at which a maximum was noted in the $dM/dT$ heating and cooling curves. A schematic of the graphical method used for determination of $T_t$ and $\Delta T_t$ is shown in Figure 42.
Figure 42. Schematic representation of the temperature-dependant magnetization curves of FeRh-based compounds (a) and its corresponding derivative curves (b). The maximum of the derivative curve represents the magnetostructural temperature ($T_t$). The difference in temperature between the maximum of the heating and the cooling magnetization curves represents the thermal hysteresis of the samples ($\Delta T$). Figure adapted from [42].

In dilute nanocomposite magnetic systems such as the phase-separated Cu$_{95}$(FeRh)$_5$ ribbons synthesized in this work, sometimes a spin-glass-like magnetic phase is observed at low temperatures. A spin glass is a disordered magnet with frustrated interactions, augmented by stochastic positions of the spins, where conflicting interactions, namely both ferromagnetic and also antiferromagnetic bonds, are randomly distributed with comparable frequency (Figure 43). The term "glass" comes from an analogy between the magnetic disorder in a spin glass and the positional disorder of a conventional, chemical glass, e.g., a window glass.
Figure 43. Schematic representation of the random spin structure of a spin glass (a) and the ordered one of a ferromagnet (b). Figure adapted from [114].

Experimentally, the easiest way to identify a spin glass phase is by studying its temperature-dependant magnetization behavior. Figure 44 shows the magnetization vs. temperature (M-T) curves of a typical spin glass material. Above the spin glass transition temperature, $T_b$, the spin glass exhibits typical magnetic behavior (such as paramagnetism). If a magnetic field is applied as the sample is cooled to the transition temperature, magnetization of the sample increases as described by the Curie law. Upon reaching $T_b$, the sample becomes frustrated and further cooling results in little change in magnetization. This is referred to as the field-cooled (FC) magnetization. When the external magnetic field is removed, the magnetization of the spin glass falls rapidly to a lower value known as the remanent magnetization. Magnetization then decays slowly as it approaches zero. This decay is non-exponential and no simple function can fit the curve of magnetization versus time adequately. It is critical to note that this slow decay is particular to spin glasses. Experimentally, the blocking temperature of spin glasses is identified as the temperature at which the field-cooled and zero-field cooled magnetization curves meet.
Figure 44. Field-cooled (FC) and zero-field cooled (ZFC) temperature-dependant magnetization curves of a material exhibiting the spin-glass phase. The blocking temperature \((T_b)\) of the sample is defined as the cusp of the ZFC curve. Figure adapted from [114].

3.2.3.2 Operating principles of magnetic probes: Vibrating Sample Magnetometry (VSM) and Superconducting Quantum Interference Device (SQUID) Magnetometry

In this Section, a general overview of the instrumentation and operating principles of the probes used for magnetic characterization of the bulk and nanostructured FeRh samples is provided.

(a) Operating principle of a Vibrating Sample Magnetometer (VSM)

In this Dissertation, a Quantum Design (QD) Versalab vibrating sample magnetometer (VSM) was used to investigate the magnetic properties of bulk FeRh-based samples in magnetic fields upto 3 Tesla and in the temperature range 50 - 1000 K (Figure 45(a)). In this technique, the sample is mounted in a polypropylene holder (an injection molded plastic part) that snaps into a brass trough (Figure 45(b)). A schematic representation of the operating principle of a
Vibrating Sample Magnetometer (VSM) is shown in Figure 46. The VSM detects the magnetization of a sample by mechanically vibrating the sample inside an inductive pickup. The oscillating magnetic flux from the sample induces a voltage in the pickup coils by Faraday's law of induction. The magnitude of this voltage is proportional to the magnetic moment of the sample. Typically, the sample in the VSM is vibrated using a motor or a piezoelectric actuator. It is important to note that the VSM is not as sensitive as the SQUID magnetometer which has a limit of detectability of $1 \times 10^{-8}$ emu. The VSM used in this Dissertation is capable of detecting high moments up to the range of 40 emu [115].

Figure 45. (a) A Quantum Design (QD) Versalab vibrating sample magnetometer (VSM) (b) Sample holder for the Versalab consists of a polypropylene holder that snaps into a brass trough. Figure adapted from [114].
(b) Operating principle of a Superconducting Quantum Interference Device magnetometer (SQUID)

The Quantum Design MPMS-XL5 SQUID magnetometer is a very sensitive instrument that is capable of measuring magnetic moments as small as $10^{-8}$ emu in the temperature regime, $1.8 \, \text{K} \leq T \leq 400 \, \text{K}$, in magnetic fields up to 5 T (Figure 57) [117]. When required, the operating temperature range of the SQUID magnetometer can be extended to 800 K by inserting an oven manufactured by Quantum Design into the sample chamber. The SQUID magnetometer is made of three primary components: a superconducting magnet, superconducting detection coils, and a SQUID connected to the detection coils. These components are described in further detail in the following paragraphs:

(a) **Superconducting magnet:** A superconducting magnet is a solenoid made of superconducting wire. Figure 47 shows a cross-sectional view of a typical superconducting magnet used in a SQUID magnetometer. This solenoid must be kept at liquid helium temperature
in a liquid-helium dewar. A uniform magnetic field is produced along the of producing magnetic fields up to 5 Tesla with an accuracy of $10^{-5}$ T in the longitudinal direction.

![Cross-Sectional view of a superconducting magnet. Figure adapted from [118].](image)

**Figure 47. Cross-Sectional view of a superconducting magnet. Figure adapted from [118].**

**b) Detection coil:** The detection coil in the SQUID chamber is a single piece of superconducting wire configured as a second-order gradiometer. The pick-up coil system is placed in the uniform magnetic field region of the solenoidal superconducting magnet.

**c) SQUID:** The SQUID device itself is usually superconducting thin film (usually made of pure niobium or a lead alloy with 10% gold or indium) that functions as an extremely sensitive current-to-voltage-converter. When the sample (typically mounted in a straw) moves through the second-order gradiometer, the magnetic moment of the sample induces an electric current in the pickup coil system (Figure 48(b)). A change in the magnetic flux of these coils changes the current in the detection circuit. The change in the current in the detection coils produces a SQUID output voltage proportional to the magnetic moment of sample (Figure 48(a)).
Figure 48. Schematic of a typical SQUID measurement: (a) shows the ideal SQUID response for a dipole and (b) shows the movement of a sample (mounted in a straw) within the SQUID pickup coils. Figure adapted from [118].

For experiments involving pressure-based magnetic measurements, hydrostatic pressure (up to 10 kbar) was applied ex-situ on the FeRh-based bulk samples using a CuBe pressure cell (Mcell 10) manufactured by EasyLab. In Figure 49(a), the components of the pressure cell are shown. The sample is placed in the PTFE cell together with an appropriate pressure transmitting fluid and a Sn manometer. Pressure is applied on the sample using a hydraulic press ram (Figure 49(b)). In principle, the Mcell 10 is pressurized by the application of a known force on a tungsten carbide piston pushing onto the ceramic pistons (Figure 50). In turn, the PTFE cap, where the sample is sitting surrounded by the transmitting medium, has its volume reduced and hence the pressure increases. Once the pressure has been applied to the sample, the pressure cell is loaded onto the MPMS using a standard DC transport rod (Figure 49(c)). It is anticipated that measurements of samples with magnetic moments as low as $10^{-5}$ is possible using this set-up.
Figure 49. (a) Schematic of the assembly of the EasyLab pressure cell (MCell 10); (b) Hydraulic press ram used for exerting pressure on the sample inserted in MCell 10; (c) Loading the pressure cell into the SQUID magnetometer using the standard DC transport rod. Figures adapted from [119].

Figure 50. Schematic representation of the manner in which a sample is pressurized in the Cu-Be pressure cell (MCell 10). Figures adapted from [119].
One of the difficulties faced when measuring the magnetization of a sample inside the Mcell 10 is that the signal detected by the SQUID is in fact the superposition of the magnetic trace of the cell and the sample:

\[ V_{\text{Sample}} = V_{\text{Measured}} - V_{\text{Background}} = V_{\text{Measured}} - V_{\text{Mcell10}} \]  \hspace{1cm} (22)

In this Dissertation, this feature was corrected by first studying the pressure-dependence of the pressure transmitting medium as a function of temperature. The Automated Background Subtraction (ABS) option of the MPMS MultiVu software was used to record the background raw data signals associated with the pressure cell. When the measurements with the sample inside the pressure cell were performed, the option ‘Subtract Background’ was selected.

Due to the differential thermal contraction between the metallic components and the transmitting medium, one can expect some pressure variations within the Mcell 10, particularly at low temperatures. Based on the pressure dependence of the superconducting transition temperature of the Sn manometer placed in the pressure transmitting fluid (Figure 48), the precise pressure exerted on the sample in the PTFE cell was determined using the following equation [119]:

\[ P = a [T_{\text{sb,0}} - T_{\text{sb,P}}]^2 + b[T_{\text{sb,0}} - T_{\text{sb,P}}] \]  \hspace{1cm} (23)

Where: 
- \( P \) is the hydrostatic pressure within the pressure cell (kbar)
- \( T_{\text{sb,0}} \) is the superconducting temperature of the Sn manometer at ambient pressure (K)
- \( T_{\text{sb,P}} \) is the superconducting temperature of the Sn manometer at applied pressure (K)
- \( a \) and \( b \) are arbitrary constants of value 5.041 kbar/K^2 & 17.813 kbar/K respectively
3.3 Summary

This section describes the synthesis and characterization experimental techniques that were used to accomplish the objectives associated with this Dissertation. In this study, bulk FeRh-based samples were synthesized via the arc-melting technique. Subsequently, nanostructuring of the FeRh system was achieved by rapidly-solidifying arc-melted FeRh-based precursors using the melt-spinning technique. Chemical characterization of the FeRh-based samples synthesized in this study was achieved via Energy Dispersive Spectroscopy (EDS). Structural characterization of the bulk and nanostructured samples were accomplished via transmission electron microscopy (TEM) and X-ray diffraction (XRD, laboratory and synchrotron-based). While XRD experiments were performed at Northeastern University and at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), TEM studies were done in collaboration with the Department of Mechanical Engineering at the University of Nebraska at Lincoln. Magnetic characterization of the FeRh-based samples was
done using superconducting quantum interference device (SQUID) magnetometry and vibrating sample magnetometry (VSM). For experiments involving pressure-based magnetic measurements, hydrostatic pressure was applied on the FeRh-based samples using a CuBe pressure cell (Mcell 10) manufactured by EasyLab. This accessory has been specifically engineered to enable end-users to perform SQUID measurements under high-pressure (up to 10 kbar) in the temperature range, 2-350 K.
4.0 Results and Discussion

The overarching goal of this Ph.D. Dissertation is to understand, predict and control the magnetostructural response of the FeRh system as a function of extrinsic and intrinsic parameter variation. Overall, in this study, three pathways were explored to tailor the magnetostructural response of FeRh-based compounds: (a) reduction of structural scale (Nanostructuring); (b) chemical modification of the FeRh lattice via elemental substitution and (c) simultaneous variation of two or more extrinsic parameters, namely temperature, magnetic field and pressure. Results obtained from these experiments are presented in Sections 4.1, 4.2 and 4.3 respectively. From the viewpoint of applied science, the relationship between the magnetostructural response and the magnetocaloric effect of FeRh-based compounds is interesting for development of potential magnetic micro cooling devices such as thermal pumps for microfluidics [153]. In Section 4.4, results pertaining to experimental studies aimed at understanding the influence of hydrostatic pressure and chemical substitution on the magnetocaloric behavior of the FeRh system are presented.

4.1 Tailoring the magnetostructural response of FeRh via nanostructuring

Results obtained from experiments focused on investigating the effect of nanostructuring on the magnetostructural transition response of near-equatomic Fe$_{1-x}$Rh$_x$ alloys are presented in this Section. For organizational clarity, this Section has been divided into five parts: Section 4.1.1 provides an introduction and justification for this study; Section 4.1.2 provides specific details pertaining to the sample synthesis and characterization techniques; Section 4.1.3 provides an overview of the structural and magnetic results obtained; Section 4.1.4 provides a discussion and interpretation of the results and finally Section 4.1.5 highlights the overall significance of this work.
4.1.1 Background and justification: Influence of nanostructuring on the FeRh magnetostructural response

Based on thermodynamic studies aimed at explaining the mechanism of the magnetostructural phase transitions (See Section 1.1 for more details), it is recognized that in addition to modification of extrinsic variables—temperature ($T$), pressure ($P$), and magnetic field ($H$)—reduction of the characteristic dimensions of the system via nanostructuring may also provide an alternative route for engineering magnetostructural phase transitions in functional materials systems [8]. In this work, FeRh serves as a test bed to explore the effects of nanostructuring on the magnetostructural response. It is important to note that although extensive research has been carried out on bulk and thin film forms of FeRh [9-12, 32, 35, 41, 43, 44, 50-53, 62-65, 69, 74, 79-82, 86, 87, 107, 120-122], limited work has been performed on nanoscaled FeRh systems [77-80, 123, 124].

Previous reports indicate that chemically synthesized FeRh nanoparticles of controlled composition and size (4–20 nm) undergo a hysteretic magnetic transition at around $T_{t}$ ($H_{app}$ =1T)≈320K; this transformation is very broad, a feature that may be attributed either to reduced particle size or to surface oxidation effects [77]. Attainment of the ordered CsCl phase in the chemically synthesized FeRh nanoparticles is inconclusive. In sharp contrast to these results, FeRh nanoparticles (~10-150 nm) synthesized in metallic/insulating and amorphous matrices via sputtering and cluster deposition were found to be completely ferromagnetic up to temperatures as low as 2 K [79, 80]. To date, the relationship between the structural and magnetic properties of FeRh systems with nanoscaled dimensions remains unclear. To fill this gap in the FeRh literature, in this Dissertation, FeRh nanoprecipitates were synthesized by melt-spinning and annealing a nanocomposite system of chemical composition, (FeRh)$_5$Cu$_{95}$ [123, 124]. Characterization of this heterogeneous Cu-based system using structural and magnetic probes
emphasizes the sensitivity of the magnetostructural properties of FeRh to changes in microstructural scale.

4.1.2 Experimental Details: Influence of nanostructuring on the FeRh magnetostructural response

The influence of nanostructuring on the magnetostructural transition response of near-equiatomic Fe$_{1-x}$Rh$_x$ alloys was investigated by synthesis of nanoscaled FeRh precipitates in a rapidly solidified Cu(Fe) matrix. As outlined in Section 3.1, this phase separated system was fabricated by melt-spinning a pre-alloyed (arc-melted) charge of nominal atomic composition (FeRh)$_5$Cu$_{95}$. The resultant ribbons were ~3 mm wide and ~100 μm thick, with lengths > 2 cm (see Figure 51). It is critical to note that a copper matrix was selected for this study because the equilibrium phase diagrams of the elemental pairs (Fe,Cu) and (Rh,Cu) indicate that Fe and Rh are both immiscible in Cu (See Fig 23 in Section 3.1.1). It was thus hypothesized that the (FeRh)$_5$Cu$_{95}$ ribbons would yield non-interacting nanoscaled FeRh precipitates in a Cu matrix upon moderate annealing. For comparison purposes and to facilitate identification of the magnetic phases in the (FeRh)$_5$Cu$_{95}$ nanocomposite, control samples consisting of melt-quenched ribbons of Cu containing dilute amounts of Fe or Rh were also synthesized, annealed, and measured under the same conditions. The nominal compositions of the control samples were Cu$_{98}$Fe$_2$ and Cu$_{98}$Rh$_2$. 
Figure 51: Photograph of as-quenched melt-spun ribbons of atomic composition (FeRh)$_5$Cu$_{95}$. Overall, the physical dimensions of (FeRh)$_5$Cu$_{95}$ ribbons were as follows: ~3 mm wide, ~100 μm thick, lengths > 2 cm.

Precipitation of FeRh nanoparticles in the melt spun (FeRh)$_5$Cu$_{95}$ nanocomposite was induced by annealing at temperatures below 800 °C in a multiple position tube furnace 1200C manufactured by MTI corporation (see Figure 52(a)). Isochronal annealing for 30 minutes was done in a tube furnace in the temperature range 100 °C to 800 °C at intervals of 100 °C. During annealing, to avoid oxidation, the samples in amounts in the range of 20-40 mg were sealed in nominal vacuum of 1 x 10$^{-6}$ Torr in a sample holder consisting of a hollow, fused silica tube and two solid silica rods that fit precisely within the tube, sandwiching the sample (shown in Figure 52(b)) [125]. The evolution of the magnetic and structural properties of the nanocomposite Cu$_{95}$(FeRh)$_5$ system was studied using the following probes: (a) Scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDS) capability; (b) Transmission electron microscopy (TEM) equipped with selected area diffraction (SAED) functionality; (b) Laboratory and synchrotron X-ray diffraction and (d) SQUID magnetometry. Details regarding
the experimental methods used to analyze the nanostructured FeRh system are provided in Section 3.2.

Figure 52: (a) The multiple-position tube furnace 1200°C manufactured by MTI corporation. Image adapted from [126]; (b) Schematic of sample holder design. The dotted line represents the points where constrictions were made in the hollow tube.

4.1.3 Experimental Results: Influence of nanostructuring on the FeRh magnetostructural response

This Section is divided into two sub-parts. In the first Section, Section 4.1.3.1, results pertaining to the structural properties of the Cu$_{95}$(FeRh)$_5$ system is discussed. Following this, in Section 4.1.3.2, experimental data obtained via magnetic characterization of the Cu$_{95}$(FeRh)$_5$ ribbons are presented.

4.1.3.1 Structural characterization of Cu/FeRh nanocomposite system

As discussed in Section 3.1, the chemical homogeneity and composition of rapidly-solidified (FeRh)$_5$Cu$_{95}$, Cu$_{98}$Fe$_2$, and Cu$_{98}$Rh$_2$ ribbons were confirmed using SEM-EDS. In all the as-spun samples, no crystalline phases other than face-centered cubic (fcc) Cu with a slightly expanded lattice parameter, $a=3.620\pm0.001$ Å (relative to the standard Cu lattice parameter of $a=3.615$ Å (Ref. [105]) was observed using laboratory Cu Kα-XRD (Figure 53). However, the TEM studies performed on the sample indicate that the microstructure of (FeRh)$_5$Cu$_{95}$ ribbons
annealed to 500 °C consists of micron-scale polycrystalline grains containing nanoscale (~10 nm) precipitates, shown in Fig. 54(a). TEM selected-area electron diffraction (SAED) patterns taken along the [1\bar{1}0] zone axis show the presence of Bragg reflections arising from both the matrix and the precipitates, shown in Fig. 54(b). The TEM SAED pattern of the matrix indexes to an fcc structure consistent with the XRD data. Intriguingly, instead of the expected B2 (CsCl)-type structure found in bulk FeRh, diffraction information obtained from the nanoprecipitates is consistent with the L1\textsubscript{0} (CuAu 1)-type crystal structure with lattice parameters \(a=4.32\) Å and \(c=4.20\) Å. The lattice parameters of the L1\textsubscript{0}-ordered precipitates are estimated to have accuracy of 2%-3% [127], resulting in an estimated error on the order of 0.13 Å. The presence of L1\textsubscript{0}-ordered structure in the precipitates was determined through the appearance of superlattice reflections in the SAED pattern [128]. In Figure 54(b), the L1\textsubscript{0}-reflections corresponding to the precipitate phase are clearly marked. As expected, the intensity of the superlattice reflection from the \{110\} set of planes of the L1\textsubscript{0}-ordered FeRh phase is weak. A definite cube-on-cube orientational relationship is observed between the Cu matrix and the precipitate phase: \(<110> Cu // <110> FeRh\) for directions and \{001\} Cu // \{001\} FeRh for planes.

The population of L1\textsubscript{0}-ordered FeRh nanoparticles within the sample annealed to 500 °C is too small and dilute to be detected XRD. However, the synchrotron XRD data of the (FeRh)\textsubscript{5}Cu\textsubscript{95} ribbons annealed to 800 °C, shown in Fig. 55, clearly indicate the presence of B2-ordered FeRh precipitates (\(a=2.983\pm0.002\) Å) in a Cu matrix (\(a=3.62\pm0.001\) Å). The lattice constant of the B2-ordered FeRh nanoprecipitates is only slightly smaller than that of bulk FeRh at room temperature (\(a_{\text{bulk \ FeRh}}=2.987\) Å, Ref. [31]). Williamson-Hall analysis of the XRD data, shown in Figure 56, reveals that the crystallite size of the B2-ordered FeRh precipitates is ~90 ± 13 nm. The lattice strain in the FeRh precipitates was determined as ~0.1%. The increased size
of the FeRh precipitates in ribbons annealed to 800 °C was also confirmed via TEM imaging (See Figure 57).

Figure 53. X-ray diffraction intensity of as-spun (FeRh)$_5$Cu$_{95}$ ribbons as a function of diffraction angle. Measurements were taken using a standard laboratory Cu Kα radiation. The observed Bragg peaks correspond to that of the face-centered cubic (fcc) Cu matrix with a slightly expanded lattice parameter, $a=3.620\pm 0.001$ Å, Å (relative to the standard Cu lattice parameter of $a=3.615$ Å Ref. [105]).

Figure 54. (a) Plan-view TEM images of (FeRh)$_5$Cu$_{95}$ ribbons annealed to 500 °C show the presence of FeRh nanoprecipitates with $\sim$10–15nm diameters in micron-scaled grains of Cu. (b) TEM diffraction pattern of annealed (FeRh)$_5$Cu$_{95}$ ribbons indicate that the FeRh precipitates have an orientational relationship with the Cu matrix. Arrows indicate the crystallographic orientation corresponding to the precipitate reflections.
Figure 55. X-ray diffraction intensity of as-spun and annealed (FeRh)$_5$Cu$_{95}$ ribbons as a function of diffraction angle. The population of L1$_0$-ordered FeRh nanoparticles within the sample annealed to 773K is too small and dilute to be detected XRD. The Bragg peaks seen in the ribbon annealed at 1073K corresponds to B2-ordered FeRh precipitates (a=2.983±0.001 Å) in a strained Cu matrix (a=3.620±0.001 Å).
Figure 56. Williamson–Hall plot of XRD data obtained from the B2-ordered FeRh precipitates and the Cu matrix in the Cu$_{95}$(FeRh)$_5$ sample annealed to 1073 K. The data points are identified by their Bragg peak crystallographic indices. The broken line represents a least-squares linear fit to the data for the FeRh precipitates. From the inverse of the intercept of the linear fit, the crystallite size of the FeRh precipitates is estimated as $90 \pm 13$ nm. The lattice strain in the FeRh precipitates was determined from the slope as $\sim0.1\%$.

Figure 57. Plan-view TEM image of the cross-Section of a (FeRh)$_5$Cu$_{95}$ ribbon annealed to 800 °C yields evidence of annealing-induced coarsening of the FeRh precipitates embedded in the Cu matrix.
4.1.3.2 Magnetic characterization of Cu/FeRh nanocomposite system

Temperature- and field- dependent magnetization of rapidly solidified ribbons of composition (FeRh)$_5$Cu$_{95}$, Cu$_{98}$Fe$_2$ and Cu$_{98}$Rh$_2$ was studied using SQUID magnetometry in fields up to 50 kOe and temperatures in the range 2 K < T < 800 K. In the following Sections, results obtained for the control samples - Cu$_{98}$Fe$_2$ and Cu$_{98}$Rh$_2$ – is briefly discussed first, followed by a detailed discussion regarding the magnetic properties of the (FeRh)$_5$Cu$_{95}$ nanocomposite.

(a) Magnetic properties of control samples (Cu$_{98}$Fe$_2$ and Cu$_{98}$Rh$_2$ ribbons)

The magnetic behavior of the rapidly-solidified Cu$_{98}$Fe$_2$ and Cu$_{98}$Rh$_2$ ribbons synthesized in this study is consistent with previous reports in literature [129-131]. The as-quenched Cu$_{98}$Fe$_2$ ribbons exhibited a multiphase state encompassing spin glass, paramagnetic and ferromagnetic phases (Figure 58), while the as-quenched Cu$_{98}$Rh$_2$ ribbons are diamagnetic with a mass susceptibility of -7.3 e$^{-7}$ emu/g at room temperature (Figure 59). The blocking temperature ($T_b$) of the spin-glass phase in the as-quenched CuFe ribbons, defined as the peak of the dc susceptibility curves $\chi(T)$, was $T_b=6.5$ K. As expected from earlier studies on this alloy [129, 131], annealing the ribbons to 500 °C reduces $T_b$ to 3 K. No unexpected magnetic phases or phase transitions were observed in the Cu$_{98}$Fe$_2$ and Cu$_{98}$Rh$_2$ ribbons upon annealing.
Figure 58. Zero-field-cooled temperature-dependent magnetization curves of Cu$_{98}$Fe$_2$ ribbons showing evidence of a spin-glass, paramagnetic and ferromagnetic phases.

Figure 59. Field-dependent magnetization behavior of Cu$_{98}$Rh$_2$ sample at room temperature indicates that the ribbons are diamagnetic with a mass susceptibility of 7.3 x 10$^{-7}$ emu/g.
(a) Magnetic properties of rapidly-solidified (FeRh)$_5$Cu$_{95}$ ribbons

The magnetic behavior of the (FeRh)$_5$Cu$_{95}$ ribbons may be categorized into three temperature regimes: (1) low temperature ($2 \text{ K} \leq T \leq 15 \text{ K}$); (2) intermediate temperature ($15 \text{ K} \leq T \leq 200 \text{ K}$); and (3) high temperature ($T > 200 \text{ K}$).

(i) Magnetic behavior of the (FeRh)$_5$Cu$_{95}$ ribbons at low temperatures ($2 \text{ K} \leq T \leq 15 \text{ K}$)

In the low-temperature regime ($2 \text{ K} \leq T \leq 15 \text{ K}$), the (FeRh)$_5$Cu$_{95}$ ribbons show spin-glass-like behavior. Fig. 60 displays the low-temperature zero-field-cooled (ZFC) susceptibility curves of the ribbons in as-quenched and annealed states. The blocking temperature ($T_b$) of the spin-glass phase in the as-quenched (FeRh)$_5$Cu$_{95}$ ribbons was determined as $T_b = 10 \text{ K}$. Annealing the ribbons to $500 \text{ °C}$ reduces $T_b$ to $6.5 \text{ K}$. No blocking behavior was observed in samples annealed to $800 \text{ °C}$.

![Figure 60. Low-temperature zero-field-cooled susceptibility of (FeRh)$_5$Cu$_{95}$ ribbons showing evidence of a spin-glass phase. The blocking temperature ($T_b$) of the spin-glass phase is defined at the peak of the susceptibility curves $\chi(T)$. Annealing decreases $T_b$.](image-url)
(ii) Magnetic behavior of (FeRh)$_5$Cu$_{95}$ ribbons in the temperature range, 20 K ≤ T ≤ 200 K

In Fig. 61, the zero-field cooled temperature-dependent magnetization curves of as-quenched and annealed (FeRh)$_5$Cu$_{95}$ ribbons in the intermediate temperature range (15 K ≤ T ≤ 200 K) are shown. In the as-quenched state, the ribbons demonstrate paramagnetic behavior (Figure 61(a)). Following Bitter *et al.*, the overall paramagnetic susceptibility ($\chi_{\text{tot}}$) can be described by the sum of Curie-Weiss-type susceptibility (first term) and temperature-independent Pauli paramagnetic susceptibility (second term) [132]:

$$\chi_{\text{tot}} = \frac{C}{T-\theta} + \chi_{\text{pp}}$$  \hspace{1cm} (24)

Where: $C$ is the Curie constant (cm$^3$ K/g);

$\theta$ is the paramagnetic Curie temperature (K);

$\chi_{\text{pp}}$ is the temperature-independent Pauli paramagnetic susceptibility (cm$^3$/g).

A fit to the data obtained from the as-spun material using Eq. (24) provided the following parameters: $C=1.98 \times 10^{-3}$ cm$^3$ K/g of (FeRh)$_5$Cu$_{95}$; $\theta=0.69$ K; $\chi_{\text{pp}}=1.93 \times 10^{-5}$ cm$^3$/g of (FeRh)$_5$Cu$_{95}$. In the annealed ribbons (473 K ≤ $T_a$ ≤ 873 K) a magnetic transition at $T_t=100$ K is observed (Figure 61(b) and 62(c)). The paramagnetic background of the annealed (FeRh)$_5$Cu$_{95}$ ribbon was obtained by fitting the $M(T)$ data in the temperature range 10 K ≤ $T$ ≤ 90 K to Eq. (24). From Fig. 62(a), it is clear that the temperature dependence of the magnetic moment of the annealed (FeRh)$_5$Cu$_{95}$ ribbons after subtraction of the paramagnetic contribution is remarkably similar to the magnetostructural phase transition trend observed in equiatomic FeRh at $T_t=350$ K (AFM → FM transition, See Figure 10(a) in Section 2.2.2). The net magnetization of the (FeRh)$_5$Cu$_{95}$ ribbons at the transition increases upon annealing to higher temperatures and additional broadening is seen in the sample upon annealing to 800 °C. It is critical to note that at low annealing temperatures ($T_a \leq 500$ °C), the field-cooled temperature-dependent magnetization
curve of the (FeRh)$_5$Cu$_{95}$ ribbons exhibit thermal hysteresis – a characteristic feature of first-order magnetostructural transitions (Figure 63).

Figure 61. Magnetization versus temperature curves (H$_{app}$=100 Oe) of (FeRh)$_5$Cu$_{95}$ ribbons in the following conditions: (a) as-quenched state; (b) annealed to 500 °C and (c) annealed to 800 °C. The paramagnetic backgrounds (marked in red) were calculated by fitting the data in the temperature range 10K < T < 90K to \( \chi_{tot} = \frac{C}{T-\theta} + \chi_{pp} \). Here, C is the Curie constant, \( \theta_p \) is the Curie temperature, and \( \chi_{pp} \) is the Pauli paramagnetic susceptibility.
Figure 62. (a) Zero-field-cooled magnetization (with paramagnetism subtracted) versus temperature ($H_{app}=100$ Oe) of $(\text{FeRh})_5\text{Cu}_{95}$ ribbons for various annealing temperatures; (b) the high-temperature magnetization behavior ($H_{app}=1000$ Oe) of a ribbon annealed to 1073 K, indicating a Curie temperature of $T_c = 810$ K.

Figure 63. Thermal hysteresis in the field-cooled magnetization curve of $(\text{FeRh})_5\text{Cu}_{95}$ ribbons annealed to 500 °C identifies a first-order-like transition that is typical of bulk FeRh.
(iii) Magnetic behavior of (FeRh)$_5$Cu$_{95}$ ribbons above 200 K

At higher temperatures ($T > 200$ K), field-dependent magnetization measurements indicate a coexistence of paramagnetic and ferromagnetic phases. Figure 64(a) shows the development of the field-dependent magnetization behavior of the (FeRh)$_5$Cu$_{95}$ ribbons as a function of annealing temperature. Annealing at higher temperatures increases the saturation magnetization ($M_s$) of the ferromagnetic phases while decreasing the susceptibility ($\chi$) of the paramagnetic phase, as shown in Fig. 64(b). From Figure 62(a), it appears that annealing increases the apparent Curie temperature ($T_c$) ferromagnetic phase of the (FeRh)$_5$Cu$_{95}$ ribbons. The high temperature magnetization behavior ($H_{app}=1000$ Oe) of (FeRh)$_5$Cu$_{95}$ ribbons annealed to 1073 K ($400 \text{ K} < T < 780 \text{ K}$) is shown in Fig. 62(b). It is to be noted that the $T_c$ of this sample is the same as that of bulk Fe$_{0.54}$Rh$_{0.46}$ alloys where $T_c=810 \text{ K}$ [41].
4.1.3 Discussion: Influence of nanostructuring on the FeRh magnetostructural response

In this study, nanoprecipitates of FeRh were synthesized via heat treatment of a rapidly-solidified phase-separated system of overall composition \((\text{FeRh})_5\text{Cu}_{95}\). Characterization of this
heterogeneous Cu-based system using structural and magnetic probes indicates that the magnetostructural behavior of the FeRh nanoparticles is dependent upon the annealing conditions of the system, and in this manner, potential pathways are provided to modify the phase transition. The results obtained in this study have been schematically summarized in Figure 65 below.

Figure 65. Schematic representation of the variation of Gibbs free energy with the arrangement of atoms in the FeRh system. Upon annealing induced coarsening from $\sim$10 nm to $\sim$94 nm, the crystal structure of the FeRh precipitates evolves from the metastable L1$_0$-structure to the anticipated equilibrium B2 structure. The L1$_0$ $\rightarrow$ B2 phase transformation in the FeRh precipitates is accompanied by a gradual broadening of the first-order magnetic transition observed at $\sim$100 K.
At low annealing temperatures \((T_a=500 \, \text{C})\), the FeRh nanoprecipitates (~10–15 nm) exhibit a metastable L1\textsubscript{0}-ordered structure, with a hysteretic magnetothermal transition at \(T_t\sim100\) K. It is interesting to note that the L1\textsubscript{0} structure has been frequently observed in various intermetallic binary compounds that comprise transition metals and noble metals \([133]\). In most systems, the L1\textsubscript{0} structure forms an equilibrium phase in the bulk alloys (example: FePt \([134]\), FePd \([135]\)). In other cases, L1\textsubscript{0}-ordered structures have been observed only in nanoclusters (example: FeAu) \([136]\). In the FeRh system, the L1\textsubscript{0}-ordered structure is a metastable phase which is recognized as a stress-induced martensite form of the equilibrium B2-ordered phase \([33, 137]\). In Table 3, the lattice parameter values of the L1\textsubscript{0}-ordered FeRh nanoprecipitates obtained in this study are reported along with those of related intermetallic compounds, namely, L1\textsubscript{0}-ordered FePt and FePd. It is important to note that although the lattice parameters of the L1\textsubscript{0} FeRh nanoprecipitates are greater than those of FePd and FePt, the lattice distortions (as quantified by the \(c/a\) ratio of L1\textsubscript{0} structure) are comparable.

**Table 3. Crystallographic properties of the L1\textsubscript{0} crystal structure of FeRh, FePt and FePd.**

<table>
<thead>
<tr>
<th>System</th>
<th>Lattice parameters (Å)</th>
<th>Lattice distortion ((c/a) ratio)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeRh</td>
<td>(a=4.32), (c=4.20)</td>
<td>0.97</td>
<td>Current study</td>
</tr>
<tr>
<td>FePt</td>
<td>(a=3.85), (c=3.71)</td>
<td>0.96</td>
<td>Ref. [134]</td>
</tr>
<tr>
<td>FePd</td>
<td>(a=3.83), (c=3.66)</td>
<td>0.96</td>
<td>Ref. [135]</td>
</tr>
</tbody>
</table>

At high annealing temperature \((T_a = 800 \, \text{C})\), the FeRh precipitates adopt the equilibrium B2-ordered crystal structure. The crystallite size of these B2-ordered precipitates, 90±13 nm, is considerably larger than the 10–15 nm particle size of the L1\textsubscript{0}-ordered precipitates observed in ribbons annealed to 500 °C. It is therefore proposed that the L1\textsubscript{0} \(\rightarrow\) B2 phase transformation in
the FeRh precipitates is due to annealing-induced coarsening of the FeRh precipitates. Similar conclusions were reached in the previous reports on rapidly solidified Cu(Fe) and Cu(FeCo) nanocomposite systems, where the Fe and FeCo particles initially precipitate out of the supersaturated Cu matrix as a coherent fcc phase [138, 139]. Upon annealing, the Fe/FeCo particles ultimately transform to their equilibrium body-centered cubic (bcc) crystal structure [138, 139].

Temperature- and field-dependent magnetization studies of rapidly-solidified (FeRh)$_5$Cu$_95$ ribbons indicate the existence of a complex multiphase state that includes spin-glass, ferromagnetic and paramagnetic phases. The paramagnetic and spin-glass phases in the (FeRh)$_5$Cu$_95$ ribbons are ascribed to the formation of a dilute metastable solid solution of Cu(Fe) upon rapid solidification [129, 131]. The temperature-independent component of the paramagnetic signal ($\chi_{pp}$) is largely attributed to the Cu matrix. As noted from Table 4 and Figure 66, the decrease in the Curie-Weiss constant ($C$) and increase in the Pauli paramagnetic susceptibility ($\chi_{pp}$) with increasing annealing temperature are indicative of the changing microstructure of (FeRh)$_5$Cu$_95$ ribbons upon annealing.
Figure 66. Dependence of the Curie-Weiss constant \((C)\) and the Pauli paramagnetic susceptibility \((\chi_{pp})\) of the Cu\(_{95}\)(FeRh)\(_5\) ribbons on annealing temperature.

Table 4. Curie constant \((C)\), paramagnetic Curie temperature \((\theta)\) and Pauli paramagnetic susceptibility \((\chi_{pp})\) of the as-spun and annealed \((\text{FeRh})_5\text{Cu}_{95}\) ribbons as obtained from fit of data to Equation 19 \(\chi_{\text{tot}} = \frac{C}{T-\theta} + \chi_{pp}\).

<table>
<thead>
<tr>
<th>Annealing temperature (^\circ\text{C})</th>
<th>Curie constant, (C) ((\text{cm}^3/\text{g of Cu}_{95}\text{(FeRh)}_5))</th>
<th>Paramagnetic Curie temperature, (\theta) ((\text{K}))</th>
<th>Pauli paramagnetic susceptibility, (\chi_{pp}) ((\text{cm}^3/\text{g of Cu}_{95}\text{(FeRh)}_5))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-spun</td>
<td>(1.98 \times 10^{-3})</td>
<td>0.69</td>
<td>(1.93 \times 10^{-3})</td>
</tr>
<tr>
<td>200</td>
<td>(1.98 \times 10^{-3})</td>
<td>0.51</td>
<td>(3.09 \times 10^{-5})</td>
</tr>
<tr>
<td>400</td>
<td>(1.66 \times 10^{-3})</td>
<td>2.65</td>
<td>(9.29 \times 10^{-5})</td>
</tr>
<tr>
<td>600</td>
<td>(4.26 \times 10^{-4})</td>
<td>4.4</td>
<td>(2.47 \times 10^{-4})</td>
</tr>
<tr>
<td>800</td>
<td>(1.04 \times 10^{-4})</td>
<td>3.61</td>
<td>(6.52 \times 10^{-4})</td>
</tr>
</tbody>
</table>

\(a\) The data reported in this table was calculated by fitting the \(M(T)\) data in the temperature range \(10 \text{ K} \leq T \leq 90 \text{ K}\) to Equation (18).

Annealing fosters precipitation of FeRh-based nanoparticles as evident by the increase in saturation magnetization of the ferromagnetic phase and the decrease in susceptibility of the
paramagnetic phase in the (FeRh)$_5$Cu$_{95}$ ribbons with increased annealing time and temperature (Figure 64). As such, two observations obtained via magnetic characterization of the (FeRh)$_5$Cu$_{95}$ ribbons strongly support the conclusion that the nanoprecipitates are indeed comprised of FeRh: (1) the remarkable similarity between the hysteretic magnetic transition at T~100 K observed in annealed (FeRh)$_5$Cu$_{95}$ ribbons and the magnetostructural phase transition response of bulk FeRh alloys at T~350 K (See Fig. 60(a) and Fig. 10(a)) and (2) the conspicuous absence of a low temperature magnetic phase transition in the annealed control samples - rapidly solidified Cu$_{98}$Rh$_2$ and Cu$_{98}$Fe$_2$ ribbons (See Figures 58 and 59).

In magnetic materials, the crystallographic structure plays a critical role in determining the magnetic properties of the system. While it is well-known that near-equivalent B2-type FeRh alloys have a magnetostructural transition temperature of $T_t \sim 350$ K, the existence of the magnetostructural phase transition in the pure L1$_0$ FeRh phase has not been confirmed in the literature. The L1$_0$-ordered FeRh nanoparticles (10–15 nm) synthesized in this study demonstrate a significant reduction in $T_t$ when compared to that of bulk FeRh ($T_t = T_{t}^{Bulk\text{FeRh}} - T_{t}^{\text{nanostructuredFeRh}} = 250$ K). This observed reduction in $T_t$ may be attributed to a combination of a few potential factors: (a) finite size effects; (b) interfacial strain derived from the coherent orientational relationship between the FeRh precipitates and the fcc Cu matrix; and (c) chemical modification due to the postulated inclusion of Cu in the FeRh nanoprecipitates. It is speculated that the fcc crystal structure of the Cu matrix serves as a template for the stabilization of the L1$_0$ structure in the FeRh nanoprecipitates. Upon annealing-induced coarsening to ~90 nm, the FeRh precipitates exhibit the B2-ordered structure with a broad magnetic transition ranging from 100–350K (Fig. 61). The results presented here may be compared with the previous studies of Fe$_x$Rh$_{1-x}$ ($x=35–55$) nanoparticles (~2–20 nm) that were
synthesized using the solution phase chemical method [78]. In these studies, depending upon the composition, the nanoparticles exhibit a broad magnetic transition ranging from 275 K to 423 K, a feature that those authors attribute to inhomogeneous chemical composition and possibly surface oxidation effects. Lastly, it is important to note that as the rapidly solidified \((\text{FeRh})_5\text{Cu}_{95}\) nanocomposite ribbons are complex and multiphase, with a rather dilute presence of nanoprecipitates (less than 5 at. %), the role of interparticle interaction on the magnetic behavior of the system is unclear.

4.1.5 Significance of work: Nanophase stability of the \(\text{L1}_0\) crystal structure in the FeRh system

The experimental evidence presented here indicates that in addition to the extrinsic variables (temperature, pressure, and magnetic field), nanostructuring may also provide a potential route for controlling magnetostructural phase transitions in functional materials systems such as FeRh. In this work, nanoprecipitates of FeRh (~10 nm) were synthesized via thermal annealing of a rapidly-solidified alloy of nominal atomic composition \((\text{FeRh})_5\text{Cu}_{95}\). These FeRh nanoparticles exhibit a \(\text{L1}_0\) (CuAu 1)-type structure, instead of the anticipated B2 (CsCl)-type structure found in bulk FeRh. A thermally hysteretic magnetic transition, remarkably similar to the magnetostructural transition of bulk CsCl-type FeRh reported at \(T_T\sim350\) K, is observed in the nanostructured material at \(T\sim100\) K. Upon annealing-induced coarsening to a size of ~94 nm, these nanoparticles undergo a structural phase transformation from a metastable tetragonal \(\text{L1}_0\) (AuCu-1-type) structure to a more stable B2 (CsCl-type) structure. A gradual broadening of the magnetothermal transition commencing at ~100 K accompanies this crystal structure transition. Overall, these results emphasize the sensitivity of the magnetic and structural properties of FeRh to changes in nanostructural scale. It is further critical to note that prior to this study, formation
of the L1_0-ordered structure in FeRh systems of nanoscaled dimension has never been reported before.

4.2. Tailoring the magnetostructural response of FeRh via chemical modification of the lattice

Results obtained from experiments aimed at understanding the influence of elemental substitution on the magnetostructural response of near-equiaxial Fe_{1-x}Rh_x alloys are presented in this Section. For organizational clarity, this study has been divided into five sub-Sections. First, Section 4.1.1 provides an introduction and justification for this study. In Section 4.1.2, magnetostructural trends observed in transition-metal substituted FeRh compounds are presented. Based on these data trends, an empirical model is established for predicting the magnetic transition temperatures and crystal structures of doped FeRh alloys. In Section 4.1.3, confirmation of this phenomenological model is provided through investigation of the influence of Cu and Au additions on the magnetostructural response of FeRh alloys. Section 4.1.4 provides a discussion and interpretation of the results and finally Section 4.1.5 highlights the overall significance of this work.

4.2.1 Background and justification: Influence of elemental substitution on the FeRh magnetostructural response

A general characteristic of FeRh alloys is that its magnetostructural transition temperature (T_t) can be tuned over a wide temperature range (100 K ≤ T_t ≤ 600 K) by elemental substitution [9-12, 41, 46, 48, 51-66]. Previous reports in literature indicate that it is possible to increase the bulk FeRh T_t with small additions of Os, Ru, Ir, and Pt [9, 10, 12, 41, 48, 51, 53, 54, 57-60]. Conversely, small additions of Al, V, Cr, Mn, Co, Ni, Pd and Au is known to decrease the T_t of bulk FeRh [9, 41, 46, 48, 51, 55, 57-61, 63-65, 68, 69]. Despite this large body of work on elemental substitutions into FeRh that spans almost 50 years, very little has been reported
concerning correlations between structure, magnetism and chemical modification in the different FeRh-based ternary alloys. To fill this gap, correlations between the characteristic magnetic transition temperatures and the averaged weighted valence band electron concentration ($(s+d)$ electrons/atom) of chemically-modified alloys of composition Fe(Rh$_{1-x}$M$_x$) or (Fe$_{1-x}$M$_x$)Rh (M = transition elements; x < 6 atomic %), as reported in the literature, are presented here. Based on the deduced relationships between the dependence of the magnetostructural transition temperature and valence electron concentration of FeRh-ternary compounds, an empirical model is proposed to predict the influence of elemental substitution on the magnetostructural behavior of bulk FeRh-based compounds with the B2 (CsCl)-type crystal structure. Confirmation of this phenomenological model is provided through investigation of the influence of Cu and Au additions, previously unreported, on the magnetostructural response of FeRh alloys.

4.2.2 Analysis of magnetostructural data trends in FeRh-based ternary compounds

Overall, this Section is divided into two major segments. In the first segment, Section 4.2.2.1, a consolidated list of the magnetostructural transition temperature and the Curie temperature of all the FeRh compounds considered in this study is provided along with corresponding references. In the subsequent Section, Section 4.2.2.2, qualitative and quantitative trends in the characteristic magnetic transition temperatures of these compounds, are presented

4.2.2.1 Considerations during data analysis

The experimental values of $T_t$ and $T_c$ of the B2- and L1$_0$-ordered FeRh-based ternary alloys considered in this study are presented in Table 5 and 6 respectively, along with corresponding references. The average weighted valence band electron concentration of the Fe(Rh$_{1-x}$M$_x$) and (Fe$_{1-x}$M$_x$)Rh alloys (M = 3d, 4d or 5d transition metals) listed in Table 5 and 6 were calculated using Equation (20):
\[
e_{v}/\text{atom} = f_{Fe}e_{v}^{Fe} + f_{Rh}e_{v}^{Rh} + f_{M}e_{v}^{M}
\]

(20)

Here, \(f_{Fe}, f_{Rh}\) and \(f_{M}\) represent the atomic fraction of the elements in the alloy for Fe, Rh and M, and \(e_{v}^{Fe}, e_{v}^{Rh}\) and \(e_{v}^{M}\) are the corresponding number of valence electrons of Fe, Rh and M, respectively. Valence electrons are electrons in the outermost principal quantum level of an atom. For transition metals, the valence electrons are usually considered as the number of \(d\) and \(s\) electrons for an atom.

In all the FeRh-based systems listed in Table 5 and 6, thermal hysteresis – a characteristic of the phase nucleation behavior found in Ehrenfest-type first-order phase transitions - is accounted for by utilizing the average transition temperature:

\[
T'_{t} = \frac{(T^{cc}_{t}+T^{hc}_{t})}{2}
\]

(25)

Here, \(T^{cc}_{t}\) and \(T^{hc}_{t}\) represent the transition temperature \(T_{t}\) obtained upon cooling through the FM \(\rightarrow\) AF transition and upon heating through the AF \(\rightarrow\) FM transition, respectively. As the magnetostructural temperature \(T_{t}\) in FeRh-based alloys is reported to vary linearly with applied magnetic field \(H_{app}\) at the rate \(\left(\frac{\partial T_{t}}{\partial H}\right)_{Bulk\ FeRh} = -8\ K/T\) [41], the \(T_{t}\) values of the ternary alloys reported in references [23, 55-57, 61-63, 70-73, 140] have been normalized to zero applied field using the formula:

\[
T'_{t,H=0\,OE} = T'_{t,Happ} - \left(\frac{\partial T_{t}}{\partial H}\right)_{Bulk\ FeRh} \cdot H_{app}
\]

(26)

Here, \(T'_{t,H=0\,OE}\) and \(T'_{t,Happ}\) are the average transition temperatures of the sample at zero applied field and at an applied field of \(H_{app}\) respectively.
Table 5. Magnetic transition temperatures of B2-ordered FeRh-based binary and ternary compounds (as reported in literature)

<table>
<thead>
<tr>
<th>Composition of alloy</th>
<th>Substituting Element</th>
<th>Atomic radii (pm)(^a)</th>
<th>Valence electron per atom</th>
<th>Magneto-structural Temperature (K) (^b,c)</th>
<th>Curie Temperature T(_c) (K)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(<em>{0.51})Rh(</em>{0.49})</td>
<td>-</td>
<td>-</td>
<td>8.49</td>
<td>325</td>
<td>692</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.50})</td>
<td>-</td>
<td>-</td>
<td>8.50</td>
<td>374</td>
<td>-</td>
<td>[56]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.50})</td>
<td>-</td>
<td>-</td>
<td>8.50</td>
<td>390</td>
<td>-</td>
<td>[54]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.50})</td>
<td>-</td>
<td>-</td>
<td>8.50</td>
<td>384</td>
<td>-</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.50})</td>
<td>-</td>
<td>-</td>
<td>8.50</td>
<td>367</td>
<td>-</td>
<td>[55]</td>
</tr>
<tr>
<td>Fe(<em>{0.49})Rh(</em>{0.51})</td>
<td>-</td>
<td>-</td>
<td>8.51</td>
<td>330</td>
<td>680</td>
<td>[59]</td>
</tr>
<tr>
<td>Fe(<em>{0.49})Rh(</em>{0.51})</td>
<td>-</td>
<td>-</td>
<td>8.51</td>
<td>320</td>
<td>680</td>
<td>[46]</td>
</tr>
<tr>
<td>Fe(<em>{0.49})Rh(</em>{0.51})</td>
<td>-</td>
<td>-</td>
<td>8.51</td>
<td>310</td>
<td>-</td>
<td>[53]</td>
</tr>
<tr>
<td>Fe(<em>{0.49})Rh(</em>{0.51})</td>
<td>-</td>
<td>-</td>
<td>8.51</td>
<td>328</td>
<td>-</td>
<td>[12]</td>
</tr>
<tr>
<td>Fe(<em>{0.49})Rh(</em>{0.51})</td>
<td>-</td>
<td>-</td>
<td>8.51</td>
<td>316</td>
<td>667</td>
<td>[10]</td>
</tr>
<tr>
<td>Fe(<em>{0.49})Rh(</em>{0.51})</td>
<td>-</td>
<td>-</td>
<td>8.51</td>
<td>299</td>
<td>640</td>
<td>[52]</td>
</tr>
<tr>
<td>Fe(<em>{0.49})Rh(</em>{0.51})</td>
<td>-</td>
<td>-</td>
<td>8.51</td>
<td>325</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.52})</td>
<td>-</td>
<td>-</td>
<td>8.52</td>
<td>338</td>
<td>668</td>
<td>[51]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.52})</td>
<td>-</td>
<td>-</td>
<td>8.52</td>
<td>340</td>
<td>640</td>
<td>[41]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.52})</td>
<td>-</td>
<td>-</td>
<td>8.52</td>
<td>303</td>
<td>641</td>
<td>[52]</td>
</tr>
<tr>
<td>Fe(<em>{0.47})Rh(</em>{0.53})</td>
<td>-</td>
<td>-</td>
<td>8.53</td>
<td>315</td>
<td>661</td>
<td>[10]</td>
</tr>
<tr>
<td>Fe(<em>{0.47})Rh(</em>{0.53})</td>
<td>-</td>
<td>-</td>
<td>8.53</td>
<td>296</td>
<td>643</td>
<td>[52]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.49})Al(_{0.01})</td>
<td>Al</td>
<td>118</td>
<td>8.44</td>
<td>194</td>
<td>-</td>
<td>[56]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.48\text{75}})Al(_{0.0125})</td>
<td></td>
<td></td>
<td>8.43</td>
<td>174</td>
<td>-</td>
<td>[56]</td>
</tr>
<tr>
<td>Fe(<em>{0.455})Rh(</em>{0.52})Cr(_{0.025})</td>
<td>Cr</td>
<td>171</td>
<td>8.47</td>
<td>340</td>
<td>-</td>
<td>[51]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.48})Mn(_{0.04})</td>
<td>Mn</td>
<td>161</td>
<td>8.44</td>
<td>229</td>
<td>-</td>
<td>[51]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.49})Co(_{0.01})</td>
<td>Co</td>
<td>152</td>
<td>8.50</td>
<td>278</td>
<td>675</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.48})Co(_{0.02})</td>
<td></td>
<td></td>
<td>8.50</td>
<td>176</td>
<td>685</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.49})Ni(_{0.01})</td>
<td>Ni</td>
<td>149</td>
<td>8.51</td>
<td>333</td>
<td>670</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.49\text{75}})Ni(_{0.025})</td>
<td></td>
<td></td>
<td>8.525</td>
<td>280</td>
<td>670</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.51})Ni(_{0.01})</td>
<td></td>
<td></td>
<td>8.53</td>
<td>250</td>
<td>675</td>
<td>[59]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.51})Ni(_{0.01})</td>
<td></td>
<td></td>
<td>8.53</td>
<td>275</td>
<td>668</td>
<td>[41]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.46})Ni(_{0.04})</td>
<td></td>
<td></td>
<td>8.54</td>
<td>188</td>
<td>670</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.50})Ni(_{0.025})</td>
<td></td>
<td></td>
<td>8.54</td>
<td>200</td>
<td>-</td>
<td>[69]</td>
</tr>
<tr>
<td>Fe(<em>{0.47})Rh(</em>{0.51})Ni(_{0.02})</td>
<td></td>
<td></td>
<td>8.55</td>
<td>130</td>
<td>665</td>
<td>[58]</td>
</tr>
<tr>
<td>Fe(<em>{0.47})Rh(</em>{0.51})Ni(_{0.02})</td>
<td></td>
<td></td>
<td>8.55</td>
<td>155</td>
<td>-</td>
<td>[41]</td>
</tr>
<tr>
<td>Fe(<em>{0.46\text{5}})Rh(</em>{0.51})Ni(_{0.025})</td>
<td></td>
<td></td>
<td>8.56</td>
<td>164</td>
<td>665</td>
<td>[41]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.48})Ru(_{0.04})</td>
<td>Ru</td>
<td>178</td>
<td>8.48</td>
<td>368</td>
<td>-</td>
<td>[51]</td>
</tr>
<tr>
<td>Formula</td>
<td>Substituting Element</td>
<td>Atomic Radius</td>
<td>Transition Temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>----------------------</td>
<td>---------------</td>
<td>------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.49}Rh_{0.50}Pd_{0.01}</td>
<td>Pd</td>
<td>169</td>
<td>8.52 225 -</td>
<td>[64]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.49}Rh_{0.495}Pd_{0.015}</td>
<td></td>
<td>8.525 274 -</td>
<td>[61]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.49}Rh_{0.49}Pd_{0.02}</td>
<td></td>
<td>8.53 233 665</td>
<td>[64]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.51}Pd_{0.01}</td>
<td></td>
<td>8.53 272 661</td>
<td>[10]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.49}Rh_{0.48}Pd_{0.03}</td>
<td></td>
<td>8.53 274 -</td>
<td>[61]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.50}Pd_{0.02}</td>
<td></td>
<td>8.54 222 664</td>
<td>[41]</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fe_{0.49}Rh_{0.48}Pd_{0.03}</td>
<td></td>
<td>8.54 175 671</td>
<td>[58]</td>
<td></td>
<td></td>
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<tr>
<td>Fe_{0.49}Rh_{0.47}Pd_{0.04}</td>
<td></td>
<td>8.55 166 -</td>
<td>[58]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.49}Pd_{0.03}</td>
<td></td>
<td>8.55 169 650</td>
<td>[41]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.49}Pd_{0.03}</td>
<td></td>
<td>8.55 240 691</td>
<td>[51]</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Fe_{0.49}Rh_{0.47}Pd_{0.04}</td>
<td></td>
<td>8.55 211 -</td>
<td>[63]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.49}Rh_{0.47}Pd_{0.04}</td>
<td></td>
<td>8.55 210 -</td>
<td>[53]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.49}Rh_{0.47}Pd_{0.04}</td>
<td></td>
<td>8.55 154 -</td>
<td>[61]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Pd_{0.04}</td>
<td></td>
<td>8.56 170 670</td>
<td>[51]</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fe_{0.48}Rh_{0.47}Pd_{0.05}</td>
<td></td>
<td>8.57 140 661</td>
<td>[51]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Os_{0.04}</td>
<td>Os</td>
<td>185</td>
<td>8.48 436 -</td>
<td>[51]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Os_{0.04}</td>
<td></td>
<td></td>
<td>[51]</td>
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<td></td>
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<tr>
<td>Fe_{0.48}Rh_{0.48}Ir_{0.03}</td>
<td>Ir</td>
<td>180</td>
<td>8.52 463 -</td>
<td>[51]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Ir_{0.03}</td>
<td></td>
<td></td>
<td>[51]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Ir_{0.04}</td>
<td></td>
<td>8.52 499 643</td>
<td>[41]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Ir_{0.04}</td>
<td></td>
<td>8.52 545 630</td>
<td>[41]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Ir_{0.06}</td>
<td></td>
<td>8.52 585 613</td>
<td>[41]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Ir_{0.04}</td>
<td></td>
<td>8.52 528 -</td>
<td>[12]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Ir_{0.05}</td>
<td></td>
<td>8.52 519 -</td>
<td>[51]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.50}Rh_{0.475}Ir_{0.025}</td>
<td></td>
<td>8.52 521 628</td>
<td>[57]</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Ir_{0.01}</td>
<td></td>
<td>8.52 555 -</td>
<td>[51]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.50}Rh_{0.45}Ir_{0.10}</td>
<td></td>
<td>8.52 577 626</td>
<td>[57]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.50}Rh_{0.45}Pt_{0.01}</td>
<td>Pt</td>
<td>177</td>
<td>8.51 470 630</td>
<td>[57]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.50}Rh_{0.45}Pt_{0.05}</td>
<td></td>
<td>8.55 485 -</td>
<td>[57]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.49}Pt_{0.03}</td>
<td></td>
<td>8.55 413 636</td>
<td>[41]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Pt_{0.04}</td>
<td></td>
<td>8.56 411 -</td>
<td>[51]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{0.48}Rh_{0.48}Au_{0.04}</td>
<td>Au</td>
<td>174</td>
<td>8.6 140 -</td>
<td>[51]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ a \] Values of the atomic radii of the substituting element were taken from Reference [141]

\[ b \] Thermal hysteresis in the magnetostructural response of the alloys was accounted for by considering an average value of the transition temperature obtained by cooling through the FM to AF transition and heating through the AF to FM transition.

\[ c \] In FeRh-based alloys, \( T_t \) varies with applied magnetic field \( (H_{app}) \) at the rate \( \frac{\partial T_t}{\partial H_{app}} \). The \( T_t \) values of the ternary alloys reported here have been normalized to zero applied field.
Table 6. Magnetostructural transition temperatures of L1\textsubscript{0}-ordered FeRh-based ternary compounds (as reported in literature)

<table>
<thead>
<tr>
<th>Composition of alloy</th>
<th>Substituting Element</th>
<th>Valence electron per atom</th>
<th>Magnetostructural Temperature (K) \textsuperscript{a,b}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsubscript{0.50}Rh\textsubscript{0.23}Pd\textsubscript{0.27}</td>
<td>Pd</td>
<td>8.80</td>
<td>100</td>
<td>[71]</td>
</tr>
<tr>
<td>Fe\textsubscript{0.50}Rh\textsubscript{0.21}Pd\textsubscript{0.29}</td>
<td></td>
<td>8.79</td>
<td>200</td>
<td>[71]</td>
</tr>
<tr>
<td>Fe\textsubscript{0.50}Rh\textsubscript{0.20}Pd\textsubscript{0.30}</td>
<td></td>
<td>8.77</td>
<td>370</td>
<td>[71]</td>
</tr>
<tr>
<td>Fe\textsubscript{0.50}Rh\textsubscript{0.14}Pt\textsubscript{0.36}</td>
<td>Pt</td>
<td>8.86</td>
<td>345</td>
<td>[72]</td>
</tr>
<tr>
<td>Fe\textsubscript{0.50}Rh\textsubscript{0.10}Pt\textsubscript{0.40}</td>
<td></td>
<td>8.90</td>
<td>145</td>
<td>[72]</td>
</tr>
<tr>
<td>Fe\textsubscript{0.50}Rh\textsubscript{0.15}Pt\textsubscript{0.35}</td>
<td></td>
<td>8.85</td>
<td>388</td>
<td>[70]</td>
</tr>
<tr>
<td>Fe\textsubscript{0.48}Rh\textsubscript{0.135}Pt\textsubscript{0.365}</td>
<td></td>
<td>8.865</td>
<td>344</td>
<td>[70]</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Thermal hysteresis in the magnetostructural response of the alloys was accounted for by considering an average value of the transition temperature obtained by cooling through the FM\textsuperscript{→}AF transition and heating through the AF\textsuperscript{→}FM transition.

\textsuperscript{b} In FeRh-based alloys, \(T_t\) varies with applied magnetic field (H\textsubscript{app}) at the rate \(\frac{\Delta T_t}{\Delta H} \approx -8 \text{ K/T.}^2\) The \(T_t\) values of the ternary alloys reported here have been normalized to zero applied field.

4.2.2.2 Trends in the magnetic transition temperatures of B2- and L1\textsubscript{0}-ordered FeRh-ternary compounds

The influence of elemental substitution on the magnetostructural transition temperatures of chemically-modified FeRh alloys may be visualized qualitatively using the Periodic Table of the Elements (shown in Fig. 67). The shaded boxes in Fig. 67 represent those elements whose effect on the magnetostructural response of B2-type FeRh compounds have previously been studied in the literature and are investigated here [9-12, 41, 46, 48, 51-64, 69, 71-73]. It is observed that 3\textit{d} transition metal substituents decrease the FeRh transition temperature while 5\textit{d} transition metal additions increase it. No unique trend is noted in the \(T_t\) of FeRh alloys where the Rh atom is substituted by 4\textit{d} transition metal elements.
The starting point for quantitative analysis of the magnetostructural behavior of FeRh-based alloys is a review of the body of knowledge concerning dependence of the properties of metals and alloys on their average valence electron concentration. The parameter “valence electrons per atom” is a powerful tool for predicting the physical and electronic behavior of metals and alloys. In the early twentieth century, Hume-Rothery and his co-workers demonstrated the importance of the valence electron concentration in controlling the range of stability of solid solutions and intermetallic compound formation in metals and alloys [142]. Since then, this parameter has been shown to vary in a systematic manner with a number of other properties such as the axial ratio of unit cell parameters of hexagonal phases, the electronic specific heat coefficient, the superconducting transition temperature, the activation energy for diffusion etc. [106]. Indeed, the well-known Slater-Pauling curve (Figure 68), whose regularities and trends are routinely used to accurately predict the magnetic moment of typical itinerant
electronic magnetic systems such as Co-Ni and Ni-rich Fe-Ni alloys, is based on correlations between the average saturation magnetization ($M_s$) of 3$d$ transition metal alloys and the total number of 3$d$ and 4$s$ valence electrons per atom [113]. More information regarding the Slater-Pauling curve is provided in Appendix C in the Supplementary Information Section. Since its introduction in the 1938, the Slater-Pauling curve has been modified to determine trends in the Curie temperature ($T_c$) of intermetallic alloys (See Figure 60) [143] and, most recently, has been applied to the analysis of the martensitic transformation temperature ($T_m$) of Heusler alloys [5, 144]. Here the dependence of the thermodynamically first-order magnetostructural transition temperature ($T_t$) and the second-order Curie temperatures ($T_c$) of FeRh-based ternary alloys on their corresponding values of averaged weighted valence band electron concentration ($(s+d)$ electrons per atom) is demonstrated.

Figure 68. Dependence of the average saturation magnetization ($M_s$) of 3$d$ transition metal alloys on their corresponding valence electron concentration (Slater-Pauling plot). Image taken from [113]. For more information regarding the Slater-Pauling curve refer to Appendix C in the Supplementary Information Section.
Figure 69. Dependence of the Curie Temperature ($T_C$) of 3$d$ transition metal alloys on their corresponding valence electron concentration (modified Slater-Pauling plot). Image taken from Reference [143]

A plot of the magnetostructural transition temperatures ($T_t$) of the alloys listed in Table 5 and 6 as a function of the averaged weighted valence band electrons in the system reveals a pronounced Slater-Pauling-type trend, Fig. 70. A maximum in the transition temperature occurs around a critical valence band electron concentration ($e_v^*$) of 8.50 electrons/atom for substitution of both 3$d$ or 4$d$ elements ($x < 6.5$ at%) into B2-type FeRh. Substitution of 5$d$ transition metal atoms into the B2 FeRh lattice echoes this trend but exhibits an overall increase in $T_t$ and a shift in $e_v^*$ to higher values, with a peak at $e_v^*$ of 8.52 electrons/atom. For $e_v > 8.65$ electrons/atom, FeRh-based alloys cease to adopt the B2-ordered crystallographic structure in favor of the chemically-disordered A1-type structure or the ordered L1$_0$-type structure. In L1$_0$-ordered Pd- and Pt-substituted FeRh alloys, the magnetostructural transition is observed in a narrow valence
electron concentration range: 8.77-8.80 electrons/atom for Fe(Rh\textsubscript{1-x}Pd\textsubscript{x}) and 8.84-8.90 electrons/atom for Fe(Rh\textsubscript{1-x}Pt\textsubscript{x}) alloys.

Figure 70. Plot of zero-field normalized magnetostructural temperature (\(T'_t\)) vs. the average weighted valence band electrons ((s+d) electrons/atom) of FeRh-based ternary alloys. The \(T'_t\) values of the ternary alloys plotted here were taken from the literature. The bold black data markers in the plot refer to the \(T'_t\) values of the Fe(Rh\textsubscript{1-x}Cux) and Fe(Rh\textsubscript{1-x}Aux) alloys synthesized in this study.

Note: No magnetostructural transition is observed in A1-ordered FeRh-ternary compounds

In Figure 71, the Curie temperatures (\(T_c\)) of the alloys listed in Table 5 are plotted as a function of the average weighted valence band electrons in the system. Correlations between the thermodynamically second-order magnetic phase transition at the Curie temperature (\(T_c\)) and the valence electron concentration (e\textsubscript{v}/atom) of FeRh-based ternary alloys are rather weak. While the magnetostructural transition temperature \(T_t\) in FeRh-ternary alloys varies from 100 K to 600 K.
depending on the valence band electron concentration, $T_c$ decreases gradually from 690 K to 610 K as the number of valence electron concentration increases from 8.51 to 8.60 electrons/atom.

Figure 71. Plot of Curie temperature ($T_c$) vs. the average weighted valence band electrons ($(s+d)$ electrons/atom) of FeRh-based ternary alloys. The $T_c$ values of the ternary alloys plotted here were taken from the literature.

4.2.3 Experimental validation of trends in the magnetostructural temperature ($T_t$) of FeRh-based ternary alloys

The generalized behavior of the $T_t$ vs. $e_v/atom$ plot of the FeRh-based ternary alloys, Fig. 60, invites validation through investigation of other chemically-modified FeRh alloys. To this end, experimental studies were conducted to determine the influence of Cu and Au addition on the magnetostructural transition temperature of FeRh alloys. To date, very little work has been performed on Au-modified FeRh systems [51, 65], while the influence of substitution of Cu for Rh in near-equiatomic FeRh alloys has never been previously studied. Bulk FeRh-ternary alloys of composition $\text{Fe}(\text{Rh}_{1-x}\text{M}_x)$ ($\text{M} = \text{Cu, Au; } x < 0.08$) with mass in the range 15 – 50 mg, were synthesized from constituent elements (99.9% purity) arc-melted in Ar and subsequently sealed under vacuum in vitreous silica tubes ($1 \times 10^{-6}$ Torr) for annealing at 1000 °C for 48 hours. The chemical composition and homogeneity of the alloys were confirmed using energy-dispersive X-
ray spectroscopy in a scanning electron microscope (SEM-EDS, Hitachi S4800). Standard Laboratory Cu Kα X-ray diffraction (PANanalytical X’Pert PRO MPD) was employed to verify the B2-type crystal structure in the FeRh-based compounds. Magnetic characterization was carried out using a Vibrating Sample Magnetometer (VSM, Quantum Design model VersaLab) in magnetic fields up to $H = 3$ Tesla and temperatures in the range $50 \text{ K} \leq T \leq 400 \text{ K}$ at a temperature sweep rate of 10 K/min. The magnetostructural transition temperatures ($T_t$) of the chemically-modified FeRh alloys were determined from the inflection point of the $M$ vs. $T$ transition as the maximum of the derivative of $M$ with respect to $T$ (i.e. $dM/dT$).

The temperature-dependent magnetization ($M$-$T$) behavior of the Fe(Rh$_{1-x}$M$_x$) ($M = $ Cu, Au; $x < 0.08$) alloys measured at an applied field of $H_{app} = 1$ T is shown in Fig. 72. All samples exhibit an AFM-FM phase transition upon heating and a thermal hysteresis of the order of 15-35 K. It is observed that $T_t$ decreases rapidly as the substitution level ($x$) of Cu and Au in the FeRh lattice increases. Further, an increased substitution of Rh with the alloying element Au results in broadening of the magnetic transition and increase in the net magnetization of the samples below $T_t$. The thermal hysteresis values and the magnetic field dependence of $T_t$ in the Fe(Rh$_{1-x}$M$_x$) ($M = $ Cu, Au; $x < 0.08$) compounds were normalized using the Equations 20 and 21. Table 7 summarizes features of the AFM-FM and FM-AFM transitions as well as the lattice constants of all samples synthesized in this study. Referring back to Fig. 70, the normalized magnetostructural transition temperatures of the samples synthesized here, Fe(Rh$_{1-x}$M$_x$) ($M = $ Cu, Au; $x < 0.08$), all fall on the generalized Slater-Pauling-type curve deduced earlier, thus validating the empirical trend.
Figure 72. The temperature-dependent magnetization ($M-T$) behavior of Fe(Rh$_{1-x}$M$_x$) (M=Cu, Au; x < 0.08) alloys at an applied field of $H_{app}=1$ T.

Table 7. Structural and magnetic properties of Fe(Rh$_{1-x}$M$_x$) alloys (M=Cu, Au)

<table>
<thead>
<tr>
<th>Composition of alloy</th>
<th>Lattice constant, $a$ (Å)</th>
<th>$T_{c,H=1T}^{hc}$ (K)$^a$</th>
<th>$T_{c,H=1T}^{cc}$ (K)$^a$</th>
<th>$\frac{dT_t}{dT_H}$ (K/T)</th>
<th>$T'_t$ (K) $^b,c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{0.50}$Rh$</em>{0.49}$Cu$_{0.01}$</td>
<td>2.979 ± 0.004</td>
<td>337</td>
<td>320</td>
<td>8.7</td>
<td>337</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{0.50}$Rh$</em>{0.48}$Cu$_{0.02}$</td>
<td>2.979 ± 0.008</td>
<td>190</td>
<td>224</td>
<td>9.7</td>
<td>217</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{0.50}$Rh$</em>{0.48}$Au$_{0.02}$</td>
<td>2.989 ± 0.005</td>
<td>385</td>
<td>371</td>
<td>9.6</td>
<td>388</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{0.50}$Rh$</em>{0.46}$Au$_{0.04}$</td>
<td>2.997 ± 0.006</td>
<td>202</td>
<td>240</td>
<td>9.4</td>
<td>230</td>
</tr>
</tbody>
</table>

$^a$ $T_{c,H=1T}^{hc}$ and $T_{c,H=1T}^{cc}$ represents the transition temperature obtained upon heating and cooling through the AFM$\rightarrow$FM and the FM$\rightarrow$AFM transition respectively, at an applied magnetic field ($H_{app}$) of 1T

$^b$ Thermal hysteresis in the magnetostructural response of the alloys was accounted for by considering an average value of the transition temperature obtained by cooling through the FM$\rightarrow$AF transition and heating through the AF$\rightarrow$FM transition.

$^c$ The $T_t$ values of the ternary alloys have been normalized to zero applied field using the formula, $T'_t = T_{t,H_{app}} - \left(\frac{dT_t}{dH}\right) \cdot H_{app}$
4.2.4. Discussion: Insight into the driving forces underlying the magnetostructural transition in FeRh and related systems

In this work, a phenomenological model has been established to predict the influence of elemental substitution on the first-order magnetostructural transition temperatures in bulk FeRh-based compounds with the B2 (CsCl)-type crystal structure. From the viewpoint of fundamental scientific achievement, this empirical model provides fresh insight into the driving forces underlying the magnetostructural transition in FeRh and related systems. The unmistakable resemblance between the generalized magnetostructural transition temperature ($T_t$) vs. valence electrons per atom ($e_v$/atom) curve obtained in this work for FeRh-based ternary alloys (Figure 62) and the Slater-Pauling curve (Figure 60) allows a direct conceptual correspondence to be drawn. In particular, the magnetostructural transition temperature in FeRh, and therefore the transition itself, may be understood in the context of the rigid-band model of transition metal magnetism (for a detailed description of the Slater-Pauling curve in terms of the rigid band structure model, see Appendix C). Self-consistent band structure calculations of FeRh reveal that the magnetostructural transition phenomena in these alloys is accompanied by a large change in the density of electronic states (DOS) at the Fermi level [85]. The results obtained in our study (Fig. 70) are consistent with the addition of electrons to antiferromagnetic bonding states of a spin-split conduction band that reaches a stability maximum around 8.50 electrons per atom. Insight is gained from the computational body of work by Moruzzi et al. that evaluated the total energy and the local moments of FeX and Fe$_2$XY compounds in the CsCl structure of both antiferromagnetic (AFM) and ferromagnetic (FM) configurations, where X and Y are 4d elements ranging from Tc to Ag [83, 84, 145]. Moruzzi et al. found data trends similar to what is reported here, with valence electron concentration range $8.5 < e_v$/atom $< 9.0$ providing very
small differences in energy between the Type-II AFM configuration and the FM configuration in FeRh.

In addition to electronic considerations, magnetovolume effects likely contribute to the stability of the antiferromagnetic FeRh phase as 3d-, 4d- or 5d-elements substituted into the lattice alter the lattice volume [57]. Results obtained in this current study clearly indicate that the lattice constant of the Au-modified FeRh-ternary alloys is noticeably larger than that of Cu-modified FeRh-ternary compounds (See Table 7). As the atomic radii of 5d-elements is greater than that of 3d-elements, it is reasonable to postulate that the overall increase in the magnetostructural transition temperature observed in 5d-substituted FeRh compounds (Figure 70) may be attributed, at least in part, to a magnetovolume effect. Broadly speaking, the data trends reported in this work suggest that the lattice and electronic free energies are both equally important in driving the magnetostructural transition in FeRh-based alloys.

The dissimilar sensitivity of the first-order magnetostructural temperature ($T_t$) and the second-order Curie temperature ($T_c$) of FeRh-ternary alloys to changes in valence electron concentrations ($e/\text{atom}$) emphasizes the differences between the thermodynamic characters of the two magnetic phase transitions. Insight regarding the weak correlation between the $T_c$ and the valence electron concentration may be obtained by examining the lattice parameters of the FeRh alloys considered in this study. From Table 8, it is observed that depending upon the type and concentration of the substituting element, the lattice constant of FeRh-based alloys can vary from 2.97 Å to 3.00 Å. Theoretical studies indicate that in this narrow range of lattice spacing, the local moments of the Fe and Rh atoms in the FeRh lattice is nearly constant [91]. Considering that the Curie temperature of intermetallic alloys is directly proportional to the atomic magnetic moments in the system (See Equation 22 below), it is reasonable that the $T_c$ of FeRh-ternary
alloys is weakly dependent on valence electron concentration changes due to chemical modification.

\[ T_c = \frac{2J_{ex}S(s+1)}{3k_B} \]  

(27)

Here, \( Z \) is the nearest neighbor coordination number;

\( J_{ex} \) is the exchange integral;

\( S \) is the total spin angular momentum;

\( k_B \) is the Boltzman constant.

### Table 8. Lattice constants of FeRh-based binary and ternary alloys
(as reported in literature)

<table>
<thead>
<tr>
<th>Composition of alloy</th>
<th>Substituting Element</th>
<th>Lattice parameter (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(<em>{0.51})Rh(</em>{0.49})</td>
<td></td>
<td>2.979</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.49})Rh(</em>{0.51})</td>
<td></td>
<td>2.987</td>
<td>[52]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.52})</td>
<td></td>
<td>2.990</td>
<td>[41]</td>
</tr>
<tr>
<td>Fe(<em>{0.48})Rh(</em>{0.52})</td>
<td></td>
<td>2.986</td>
<td>[52]</td>
</tr>
<tr>
<td>Fe(<em>{0.47})Rh(</em>{0.53})</td>
<td></td>
<td>2.987</td>
<td>[52]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.49})Co(_{0.01})</td>
<td>Co</td>
<td>2.989</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.48})Co(_{0.02})</td>
<td></td>
<td>2.984</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.49})Ni(_{0.01})</td>
<td>Ni</td>
<td>2.989</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.475})Ni(_{0.025})</td>
<td></td>
<td>2.984</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.46})Ni(_{0.04})</td>
<td></td>
<td>2.978</td>
<td>[54]</td>
</tr>
<tr>
<td>Fe(<em>{0.49})Rh(</em>{0.47})Pd(_{0.04})</td>
<td>Pd</td>
<td>2.997</td>
<td>[63]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.475})Ir(_{0.025})</td>
<td>Ir</td>
<td>2.985</td>
<td>[54]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.45})Ir(_{0.10})</td>
<td></td>
<td>2.986</td>
<td>[54]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.49})Pt(_{0.01})</td>
<td>Pt</td>
<td>2.991</td>
<td>[54]</td>
</tr>
<tr>
<td>Fe(<em>{0.50})Rh(</em>{0.45})Pt(_{0.05})</td>
<td></td>
<td>3.000</td>
<td>[54]</td>
</tr>
</tbody>
</table>

**Note:** The lattice parameters values of the FeRh-alloys were determined at room temperature conditions.

At the current time, the empirical model that has been developed in this work is based on phenomenological grounds. A simple choice of the parameter, “valence electron concentration” (\( e_{/atom} \)) may therefore only be considered as a guideline for examining
systematic changes in B2-type FeRh based alloys. Chemical disorder and local lattice distortions, together with variations in the local interatomic exchange are expected to occur simultaneously with alterations of the valence electron concentration in the FeRh ternary system. Indeed, if the magnetostructural transition of chemically-modified FeRh were driven solely by electronic effects, then the magnetostructural behavior of all isoelectronic compounds would be largely identical. However, an evaluation of isoelectronic alloys obtained by substituting Rh for Co or Ir shows that although electron concentration $e_{\text{v/atom}}$ remains unchanged, the structural and magnetic transition temperatures of Fe($\text{Rh}_{1-x}\text{Co}_x$) and Fe($\text{Rh}_{1-x}\text{Ir}_x$) alloys vary considerably. This observation demonstrates the importance of local lattice distortions and chemical order for determination of the characteristic magnetic transition temperatures of FeRh-based ternary systems.

4.2.5 Significance of work: Influence of elemental substitution on the FeRh magnetostructural response

Empirical models based on universal curves can often serve as simple, cost-effective screening tools to guide the search for new functional materials systems for future technological applications. Similar to the results reported here, trends between the magnetostructural transition temperature and valence electron concentration have also been reported in Heusler compounds, particularly in of Ni-Mn-M Heusler systems such as Ni$_{2-x}$Mn$_{1-x}$Ga and Ni$_2$Mn$_{1+x}$In$_{1-x}$ [5, 144]. The deduced valence electron dependence of $T_t$ in Heusler compounds has been extensively used to predict the magnetic and structural behavior of new ferromagnetic shape memory alloys [5]. As applicable to our system, it may be suggested that the generalized behavior of the $T_t'$ vs. $e_{\text{v/atom}}$ plot of the FeRh-based ternary alloys represents an empirical model that allows prediction of the magnetostructural behavior and the associated functional response of chemically-modified FeRh compounds. The success of this phenomenological model in
confirming existing data trends in chemically-substituted FeRh and predicting new composition-transition temperature correlations not only emphasizes the strong interplay between the electronic spin configuration, the electronic band structure and crystal lattice of this system but also allows for tailoring of the magnetostructural FeRh phase transition for technological applications. Further, the data trends presented in this work indicate that the stability of the ground state antiferromagnetic phase of the FeRh-based systems depends both on the electronic structure of the system and on the magnetovolume effect.

4.3 Tailoring the magnetostructural response of FeRh-based compounds via extrinsic parameter variation

Results obtained from experiments aimed at understanding the influence of extrinsic parameter variation (namely, temperature, pressure and magnetic field) on the magnetostructural transition response of Fe_{1-x}Rh_{x} alloys are presented in this Section. For organizational clarity, this study has been divided into five sub-Sections: Section 4.3.1 provides an introduction and justification for this study; Section 4.3.2 provides specific details pertaining to the sample synthesis and characterization techniques; Section 4.3.3 provides an overview of the structural and magnetic results obtained; Section 4.3.4 provides a discussion and interpretation of the results and finally Section 4.3.5 highlights the significance of this work.

Overall, the experimental evidence presented in this Section demonstrates that external pressure and magnetic field influence the magnetostructural temperature of FeRh-based compounds in opposite ways (ie. \( T_t \) increases with increased applied pressure and decreases with increased applied magnetic field). Further, it is observed that when the FeRh transition is shifted to low temperatures \( (T < 200 \text{ K}) \), either by elemental substitution or by application of a magnetic field, the magnetostructural response of the system shows many peculiar features. In particular, significant broadening of the magnetostructural transition width is observed accompanied by an
anomalous increase in the ferromagnetic signal in antiferromagnetic temperature regime below the magnetostructural transition temperature ($T < T_t$). Complete stabilization of the high temperature ferromagnetic phase and abrupt disappearance of the magnetostructural response in FeRh-based compounds is noted at an estimated threshold temperature of $T \sim 75$ K. Considering that the magnetostructural phase transformation process in FeRh-based systems is a thermally activated process, these results are tentatively attributed to the sluggish kinetics of the phase transformation process at low temperatures.

4.3.1 Background and justification for study: The influence of extrinsic parameter variation on the magnetostructural response of FeRh-based systems

The physical and chemical factors relevant to magnetostructural transitions may be understood by examining a very general expression of the total Gibbs free energy per unit volume $G_{V,\text{tot}}$ in a magnetic system [following Bean and Rodbell, Ref [8]):

$$G_{V,\text{tot}} = (T,S) + G_{\text{magnetostatic}} + G_{\text{magnetocrystalline}} + G_{\text{lattice}} + G_{\text{pressure}} + G_{\text{surface}} + \ldots \ldots \ldots (28)$$

Explicit expressions for the self-explanatory energy terms of Eq. [28] are not included here as they have been presented before in Chapter 1 (See Eq.[1]). As such, Eq. [28], allows a broad categorization of the parameters affecting magnetostructural phase transitions. In particular, it is important to recognize from Eq. 24 that the magnetostructural response in the FeRh system can be driven via a multitude of physical inputs, including pressure and magnetic field. Typically, hydrostatic pressure and magnetic field are reported to have an opposing influence on the magnetostructural temperature ($T_t$) of FeRh-based compounds [10, 11, 41, 48]. In bulk equiatomic FeRh, $T_t$ increases with increased hydrostatic pressure ($dT_t/dP = 4.33 \times 10^{-3}$ K/atm) [23, 35, 140] . Conversely, a decrease in $T_t$ is noted with increased magnetic field ($dT_t/dH = -8\text{K}/\text{T}$ [41]. To date, little work has been done in understanding the simultaneous influence of
pressure and magnetic field on the magnetostructural response of FeRh-based compounds [10, 146].

To fill this gap in the literature, in this study \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) serves as a test bed for understanding the relative and simultaneous effects of temperature (2-400 K), magnetic field (up to 5 T) and pressure (up to 10 kbar) on the magnetostructural response of FeRh-based systems. Based on experimental data obtained in this work, correlations between chemical composition and hence the “valence electron concentration” of FeRh-ternary compounds and the sensitivity of the magnetostructural temperature to pressure and magnetic field \((dT_\text{t}/dP\) and \(dT_\text{t}/dH\)) are established. (See Section 4.2 for more information regarding the parameter, “valence electron concentration”). Further, insight is obtained into the underlying factors influencing the thermal hysteresis behavior of this material system.

4.3.2 Experimental Details: The influence of extrinsic parameter variation on the magnetostructural response of FeRh-based systems

A bulk Ni-doped FeRh-based sample of composition \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) was synthesized by arc melting the constituent elements (99.9% purity) in an Ar atmosphere. The arc-melted ingot was sealed under vacuum (1 x 10^{-6} Torr) in vitreous silica tubes and annealed at 1000 °C for 48 hours. As described previously in Section 3.2, the chemical composition and homogeneity of the sample were confirmed by energy-dispersive X-ray spectroscopy in a scanning electron microscope (SEM-EDS, Hitachi S4800) and attainment of the B2-ordered crystal structure was verified using powder X-ray diffraction (PANanalytical X’Pert PRO). Magnetization measurements at ambient and at hydrostatic pressures (up to 6 KBar) were performed using SQUID magnetometry in fields up to 5 T. A clamp-type CuBe hydrostatic pressure cell (Mcell 10 manufactured by EasyLab) was used for the high pressure experiments. From the perspective of experimental design, it is critical to note that in this study, \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) was specifically
chosen as the model system because its magnetostructural transition temperature was found to be well within the operating temperature range of the pressure cell ($T_t \sim 150$ K; Operating temperature range of MCell 10 =2-350 K). Overall, the thermomagnetic behavior of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system was studied in three different conditions: (a) zero-field cooled (ZFC); (b) field-cooled (FC) and (c) field-heated (FH). In the ZFC mode, the sample was initially cooled to 50 K under zero applied magnetic field and the data were taken upon increasing the temperature in an applied field. In the FC mode, the data were collected while cooling in a magnetic field and subsequently in FH mode data were collected during heating. To minimize errors due to differential thermal contraction between the metallic components of the pressure cell and the pressure transmitting medium, the temperature sweep-rate during magnetic measurements was set at 1 K/min.

4.3.3 Experimental results: Understanding the influence of extrinsic parameter variation on the magnetostructural response of FeRh-based systems

Experimental data obtained from studies aimed at understanding the simultaneous influence of pressure and magnetic field on the magnetostructural response of FeRh-based compounds are presented in this Section. Information pertaining to the crystallographic structure of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system is presented first. These structural results are followed by a detailed description of the temperature-dependant magnetic behavior of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ compound in the presence of magnetic field (upto 5 T) and pressure (upto 6 kbar).

4.3.3.1 Structural characterization of (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$

The X-ray diffraction pattern of the annealed (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ sample is shown in Figure 73. The Bragg peaks observed in the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ sample (marked in red) were found to be consistent with those of the chemically-ordered cubic B2 (CsCl)-type crystal structure observed in the parent equiatomic FeRh compound (marked in black). Using the least squares
procedure for Bragg peak fitting [147], it was determined that the room-temperature lattice parameter of the (Fe\textsubscript{47.5}Ni\textsubscript{1.5})Rh\textsubscript{51} sample is lower than that of the parent equiatomic FeRh compound ($a_{FeRh-Ni}$=2.983 Å; $a_{FeRhi}$=2.987 Å). The degree of chemical ordering in the system, as determined by the order parameter $S$, was estimated as 0.8. The width of the Bragg peaks observed in Figure 80 is predominantly due to instrumental broadening (see Section 3.2.2.1 for more information regarding “instrumental broadening”). The background noise at low intensities is attributed mostly to error due to sample placement in the X-ray diffraction beam. As such, no crystalline phases other than the B2-ordered FeRh phase were found in the (Fe\textsubscript{47.5}Ni\textsubscript{1.5})Rh\textsubscript{51} sample.

Figure 73: X-ray diffraction pattern of the (Fe\textsubscript{47.5}Ni\textsubscript{1.5})Rh\textsubscript{51} compound. No crystalline phases other than the B2 (CsCl)-ordered crystal structure was observed in the annealed sample.

4.3.3.2 Magnetic characterization of the (Fe\textsubscript{47.5}Ni\textsubscript{1.5})Rh\textsubscript{51} system

The magnetic behavior of the (Fe\textsubscript{47.5}Ni\textsubscript{1.5})Rh\textsubscript{51} system in the temperature range 50 K < $T$ < 300 K was investigated using SQUID magnetometry in fields up to 50 kOe and pressures up to

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6 kbar. In the following Sections, results obtained for the sample at ambient pressure ($P_{\text{app}}=0$ kbar) are presented first. The magnetic behavior of (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ under simultaneous application of magnetic field and pressure is discussed thereafter.

(a) **Temperature-dependant magnetization behavior of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system at ambient pressure**

Figure 74 shows the zero-field cooled (ZFC), field-cooled (FC) and field-heated (FH) temperature-dependant magnetization curves of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system at an applied magnetic field of $H_{\text{app}}=1$ T and in the absence of applied pressure ($P=0$ kbar). Consistent with previous studies in the literature, the magnetostructural temperature of (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ is found to be much lower than that of the equiatomic parent FeRh compound ($T_{t,\text{FeRh}} \approx 360$ K [41]; $T_{t,\text{(FeNi)Rh}} \approx 150$ K at $H_{\text{app}}=1$ T). Below the transition temperature, a difference in magnetization is observed between the ZFC and the FC/FH magnetization curves ($\Delta M_{\text{ZFC-FC}}$) of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system. This result is indeed surprising because typically the ZFC and the FC $M(T)$ plots of bulk FeRh-based compounds are expected to be indistinguishable from each other [9]. At the current time, $\Delta M_{\text{ZFC-FC}}$ is identified as the magnetization of a portion of the high-temperature ferromagnetic phase that is retained in the antiferromagnetic temperature regime ($T < T_{t}$) due to the presence of an external applied magnetic field.
Figure 74: Zero-field cooled (ZFC), field-cooled (FC) and field-heated (FH) temperature-dependant magnetic behavior of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system at an applied magnetic field of $H_{app}=1$ T and in the absence of applied pressure ($P=0$ kbar)

In Figure 75(a), the field-cooled temperature-dependent magnetization curves of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system at different applied magnetic fields (up to 5 T) are shown. It is observed that the remnant magnetization of the high temperature ferromagnetic phase below the FM $\rightarrow$ AFM transition ($\Delta M_{ZFC-FC}$) increases with increased applied magnetic field. At $H_{app} = 3$ T, complete stabilization of the ferromagnetic state is noted and the magnetostructural phase transition in the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system is completely suppressed. The magnetic field-induced stabilization of the high temperature ferromagnetic phase is accompanied by a decrease in the magnetostructural transition temperature and a gradual broadening of the thermal hysteresis width ($\Delta T_t$). From Figure 75(b) it is observed that the sensitivity of the transition temperature to
applied magnetic field \((dT/dH_{app})\) is different in the heating and cooling branches of the \(M(T)\) plots (Note: \((dT/dH_{app})_{AFM} = 28.16 \text{ K/T}; (dT/dH_{app})_{FM} = 20.38 \text{ K/T}).

Figure 75: (a) Field-cooled temperature-dependant magnetization measurements of the \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) system at different applied magnetic fields (up to 5 T) but in the absence of applied pressure \((P=0 \text{ kbar})\); (b) Plot of transition temperature \((T_t)\) as a function of applied magnetic field.

(b) Temperature-dependent magnetization behavior of the \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) system upon application of pressure

In Figure 76, the field-cooled temperature-dependent magnetization behavior of the \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) system is shown under the condition of simultaneous application of magnetic field (up to 5 T) and hydrostatic pressure \((P=1.25, 2.7 \text{ and } 5.4 \text{ kbar})\). Overall, the data shown in these plots suggest that applied pressure increases the magnetostructural transition temperature \((dT/dP)_{FeRhNi} = 15.6 \text{ K/kbar}) and decreases the thermal hysteresis width \((\Delta T_t)\) of the sample. At a given pressure, magnetic-field-induced lowering of the transition temperature is accompanied by coincident broadening of the thermal hysteresis width and pronounced increase in the metastable ferromagnetic signal below \(T_t\). Further, it is interesting to note that the magnetic field required to suppress the magnetostructural transformation in the \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) compound
$(H_{sup})$ increases with increased pressure ($H_{sup} = 3$ T and 5 T for $P = 1.5$ and 2.7 kbar, respectively; $H_{sup} > 5$ T for $P = 5.4$ kbar).

Figure 76: Field-cooled temperature-dependant magnetization measurements under simultaneous application of magnetic field (up to 5 T) and hydrostatic pressure (up to 6 kbar).

Based on data collected from temperature-dependent magnetization measurements under simultaneous application of magnetic field (up to 5 T) and pressure (up to 6 kbar), the magnetic field–pressure–temperature $(H–P–T)$ phase diagram for the first-order
magnetostructural transition in the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system is constructed (see Figure 77). It is important to note that in Figure 77, the thermal hysteresis in the magnetostructural response of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ sample was quantified by utilizing the average transitions temperature obtained upon cooling through the FM$\rightarrow$AF transition ($T^{cc}_t$) and heating through the AF$\rightarrow$FM transition ($T^{hc}_t$) (i.e. $T_t = (T^{hc}_t + T^{cc}_t)/2$). The experimental values of $T^{cc}_t$ and $T^{hc}_t$ obtained at different applied pressure and magnetic fields is presented in Table 9. Corresponding values of the thermal hysteresis width are provided in Table 10. The surface in the H-P-T phase diagram shown in Figure 77 presents the average surface of the magnetostructural transition response in the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system. The space underneath the surface represents the low temperature antiferromagnetic (AF) state while the space above it represents the ferromagnetic (FM) state. It is observed that the magnetostructural temperature $T_t$ decreases with increased magnetic field and increases with increased hydrostatic pressure. The surface develops an abrupt jump to 0 K when the transition temperature is shifted below ~75 K by application of magnetic field.

Figure 77: Phase diagram derived from magnetic measurements in temperature, magnetic field and pressure space for (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$. 

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Table 9. Experimental values of the transition temperatures at different pressures and magnetic fields.*

<table>
<thead>
<tr>
<th>P (kbar)</th>
<th>( T_{hc}^T ) (K)</th>
<th>( T_{cc}^T ) (K)</th>
<th>( T_{hc}^T ) (K)</th>
<th>( T_{cc}^T ) (K)</th>
<th>( T_{hc}^T ) (K)</th>
<th>( T_{cc}^T ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>158</td>
<td>108</td>
<td>145</td>
<td>87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>169</td>
<td>132</td>
<td>144</td>
<td>82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>204</td>
<td>178</td>
<td>195</td>
<td>168</td>
<td>168</td>
<td>150</td>
</tr>
<tr>
<td>5.4</td>
<td>251</td>
<td>230</td>
<td>234</td>
<td>215</td>
<td>217</td>
<td>200</td>
</tr>
</tbody>
</table>

* The transition temperatures, \( T_{hc}^T \) and \( T_{cc}^T \), were obtained upon heating through the AF \( \rightarrow \) FM transition and cooling through the FM \( \rightarrow \) AF transition respectively.

Table 10. Experimental values of the thermal hysteresis width obtained at different pressures and magnetic fields.

<table>
<thead>
<tr>
<th>P (kbar)</th>
<th>( \Delta T_1 ) at ( H_{app} = 1) T</th>
<th>( \Delta T_1 ) at ( H_{app} = 2) T</th>
<th>( \Delta T_1 ) at ( H_{app} = 3) T</th>
<th>( \Delta T_1 ) at ( H_{app} = 4) T</th>
<th>( \Delta T_1 ) at ( H_{app} = 5) T</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>27</td>
<td>62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>24</td>
<td>27</td>
<td>42</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>17</td>
<td>19</td>
<td>21</td>
<td>22</td>
<td>28</td>
</tr>
</tbody>
</table>

Decreasing thermal hysteresis width
4.3.4 Discussion: Insight into the relative energies influencing the magnetostructural transition in FeRh compounds

An analysis of the influence of simultaneous application of temperature, pressure and magnetic field on the magnetostructural properties of FeRh-based compounds is presented here. For organization clarity this Section is divided broadly into two segments. The effect of extrinsic parameter variation on the inherent magnetostructural properties of the \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) system is discussed first in Section 4.3.4.1. Particular attention is given to the magnetostructural temperature \((T_t)\) and the pressure and magnetic field dependence of transition temperature \((dT_t/dP)_{H=0}\) and \((dT_t/dH)_{P=0}\). The influence of pressure and magnetic field on the thermal hysteresis width \((\Delta T_t)\) of the \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) system is discussed next in Section 4.3.4.2. Overall, the experimental evidence presented in this Section demonstrates that external pressure and magnetic field influence the magnetostructural properties of FeRh-based compounds in completely opposite ways. Further, it is observed that when the FeRh transition is shifted to low temperatures \((T < 200\text{ K})\) the magnetostructural response of the system shows many unusual features. In particular, significant broadening of the magnetostructural transition width is observed accompanied by an anomalous increase in the ferromagnetic signal below the magnetostructural transition temperature \((T < T_t)\).

4.3.4.1 Influence of extrinsic parameter variation on the intrinsic magnetostructural properties of the \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) system

The results obtained in this study indicate that at zero applied magnetic field and zero applied pressure, \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) exhibits a hysteretic first-order magnetostructural response at \(T_t \sim 150\text{ K}\). At ambient pressure, magnetic-field-induced lowering of the transition temperature in this sample \(((dT_t/dH)_{P=0\text{ kbar}} = -25\text{ K/T})\) is accompanied by broadening of the thermal hysteresis width and metastable retention of a fraction of the high temperature ferromagnetic
phase below the magnetostructural temperature \((T_{c} < T_{f})\) (Figure 82). At \(H_{app} = 3\ T\), complete stabilization of the ferromagnetic phase is noted and the magnetostructural transition in the \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) system is totally suppressed. Hydrostatic pressure applied to \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) produces an overall increase in \(T_{f}\) with increased pressure \(((dT_{f}/dP)_{H=0} = 15.6\ \text{K/kbar})\) and it is observed that at higher pressures, larger magnetic fields are required to suppress the magnetostructural phase transformation process (Figure 76).

Insight into the origin of the anomalous magnetostructural behavior of \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) may be obtained from the experimental work of Feng et al. where magnetic-field-influenced arrest of the magnetostructural phase transformation process was reported in a Pd-doped FeRh compound of composition \((\text{Fe}_{0.45}\text{Rh}_{0.45})\text{Pd}_{0.1}\) [148]. For reference, Figure 78 shows the reported temperature-dependant magnetic behavior of \((\text{Fe}_{0.45}\text{Rh}_{0.45})\text{Pd}_{0.1}\) at ambient pressure. Close comparison of the field-dependence of the thermomagnetic behavior of \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) (this work) and \((\text{Fe}_{0.45}\text{Rh}_{0.45})\text{Pd}_{0.1}\) (Feng et al. [148]) indicates many fundamental similarities (See Figures 75, 76 and 78). Most importantly, it is intriguing to note that in both these compounds suppression of the magnetostructural transition occurs at an average critical temperature of approximately \(T \sim 75\ \text{K}\). Based on this observation, it is hypothesized that when the FeRh transition is shifted to lower temperatures (in the present system achieved by Ni doping and by applying magnetic field) the atomic motion within the sample is hindered due to low thermal energy. Consequently, nucleation and growth of the antiferromagnetic phase in the sample becomes sluggish. The unusual magnetostructural behavior of Ni- and Pd-doped FeRh systems at low temperatures is therefore tentatively ascribed to the critically slow dynamics of the phase transformation process at low temperatures \((T < 100\ \text{K})\). This hypothesis is consistent with the observation that no FeRh-ternary compound is known to exhibit magnetostructural behavior.
below \textasciitilde 75 \textdegree K (See Table VI in Section 4.2.4 for a complete list, to date, of the $T_t$ values of FeRh-ternary compounds). Similar kinetic arrest of the magnetostructural transition response has also been observed in other thermally-driven magnetostructural systems such as in Cr-substituted Mn$_2$Sb alloys, Pr-substituted La$_{0.67}$Ca$_{0.33}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ [149-151].

Figure 78. Magnetization as a function of temperature under different applied magnetic fields in a Pd-doped FeRh compound of composition (Fe$_{0.45}$Rh$_{0.45}$)Pd$_{0.1}$. Magnetic-field induced lowering of the transition temperature in this sample ($(dT_t/dH)_{P=0 \text{ kbar}} = -23$ K/T) is accompanied by a broadening of the thermal hysteresis width and metastable retention of the ferromagnetic phase below the magnetostructural temperature. Figure taken from [148].

The pressure and field dependence of the magnetostructural temperature in (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ is approximately three times greater than that of the parent FeRh compound (see Table 11 for details). This result is consistent with the work of Wayne and Kamenev \textit{et al.} where an increase in the $dT_t/dP$ of Ir-, Pd- and Ni-doped FeRh compounds was observed with decrease in temperature (See Table 11) [10, 46]. By comparing high pressure data with the magnetic field dependence of $T_t$, as obtained by Kouvel \textit{et al.} [41], Wayne found that the ratio of
$dT_t/dP$ and $dT_t/dH$ in FeRh-based ternary compounds is almost constant (~1.73 kbar/T) [42]. In this Dissertation, the ratio of $dT_t/dP$ and $dT_t/dH$ in the $(\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}$ system was found to be 1.68. The $(dT_t/dP)_{H=0\text{T}}$ and $(dT_t/dH)_{P=0\text{ kbar}}$ values of the FeRh-ternary compounds listed in Table 11 are plotted as a function of their corresponding average transition temperature in Figure 79. It is apparent that at higher temperatures ($T > 250$ K), $(dT_t/dP)_{H=0\text{T}}$ and $(dT_t/dH)_{P=0\text{ kbar}}$ of equiatomic FeRh and its ternary counterparts varies linearly with temperature. However, near 200 K, a distinct deviation from linearity is noted. It is postulated that the anomalous increase in $(dT_t/dP)_{H=0\text{T}}$ and $(dT_t/dH)_{P=0\text{ kbar}}$ is a signature of the sluggish kinetics of the phase transformation process at low temperatures. To confirm this hypothesis, future work aimed at investigating the kinetic behavior of the magnetostructural phase transformation process in the $(\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}$ system is anticipated. Comparison of the kinetic parameters (example: activation energy $(E_a)$, isothermal time-dependence of the phase transformation etc.) of equiatomic FeRh and its ternary counterparts is anticipated to provide insight into the kinetic factors influencing the magnetostructural phase transition phenomena in FeRh-based compounds.
Table 11: Pressure- and field dependence of the magnetostructural temperature of FeRh-based compounds (as reported in literature and as obtained in this Dissertation)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition Temperature, (T_t) (K)</th>
<th>Pressure Dependence of (T_t) (K/kbar) (\frac{dT_t}{dP}) (_{H=0\ T})</th>
<th>Field Dependence of (T_t) (K/T) (\frac{dT_t}{dH}) (_{P=0\ kbar})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeRh</td>
<td>340</td>
<td>3.78</td>
<td>8.07</td>
<td>[41]</td>
</tr>
<tr>
<td>FeRh</td>
<td>372</td>
<td>4.19</td>
<td>8.6</td>
<td>[10]</td>
</tr>
<tr>
<td>FeRh</td>
<td>388</td>
<td>4.42</td>
<td>9.35</td>
<td>This work</td>
</tr>
<tr>
<td>FeRh</td>
<td>336</td>
<td>4.91</td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>Fe(<em>{48})Rh(</em>{52})</td>
<td>315.5</td>
<td></td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>Fe(<em>{49})Rh(</em>{51})</td>
<td>318</td>
<td></td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>Fe(<em>{49})Rh(</em>{51})</td>
<td>321</td>
<td></td>
<td></td>
<td>[61]</td>
</tr>
<tr>
<td>(Fe(<em>{47.5})Ni(</em>{1.5}))Rh(_{51})</td>
<td>153.5</td>
<td>15.38</td>
<td>25.22</td>
<td>This work</td>
</tr>
<tr>
<td>(Fe(<em>{48})Ni)Rh(</em>{51})</td>
<td>155</td>
<td>13</td>
<td>9.94</td>
<td>[46]</td>
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<tr>
<td>(Fe(<em>{47.8})Ni(</em>{1.2}))Rh(_{51})</td>
<td>162</td>
<td>11.4</td>
<td>9.4</td>
<td>[46]</td>
</tr>
<tr>
<td>(Fe(<em>{48.4})Ni(</em>{1.6}))Rh(_{51})</td>
<td>190</td>
<td>9</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>(Fe(<em>{48.75})Ni(</em>{1.25}))Rh(_{50})</td>
<td>300</td>
<td></td>
<td></td>
<td>[69]</td>
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<tr>
<td>Fe(<em>{50})(Rh(</em>{48})Cu(_2))</td>
<td>217</td>
<td></td>
<td>9.7</td>
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</tr>
<tr>
<td>Fe(<em>{50})(Rh(</em>{49})Cu(_1))</td>
<td>337</td>
<td></td>
<td>8.7</td>
<td>This work</td>
</tr>
<tr>
<td>(FeRh)(<em>{30})Pd(</em>{10})</td>
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<td>23.2</td>
<td>[148]</td>
</tr>
<tr>
<td>Fe(<em>{49})(Rh(</em>{48})Pd(_3))</td>
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<td>5.73</td>
<td>17.07</td>
<td>[41]</td>
</tr>
<tr>
<td>Fe(<em>{49})(Rh(</em>{47.4})Pd(_{3.6}))</td>
<td>180</td>
<td></td>
<td>14.44</td>
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<tr>
<td>Fe(<em>{49})(Rh(</em>{48})Pd(_3))</td>
<td>212</td>
<td></td>
<td>12.47</td>
<td>[61]</td>
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<tr>
<td>Fe(<em>{49})(Rh(</em>{47.5})Pd(_{3.5}))</td>
<td>217</td>
<td></td>
<td>12.77</td>
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<tr>
<td>Fe(<em>{49})(Rh(</em>{49})Pd(_3))</td>
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<td>11.65</td>
<td>[10]</td>
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<td>Fe(<em>{49})(Rh(</em>{50.7})Pd(_{1.6}))</td>
<td>269</td>
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<td>Fe(<em>{49})(Rh(</em>{49.5})Pd(_{1.5}))</td>
<td>274</td>
<td></td>
<td>9.62</td>
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<td>Fe(<em>{49})(Rh(</em>{50.5})Pd(_{0.5}))</td>
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<td>10.6</td>
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<td>Fe(<em>{50})(Rh(</em>{47})Pd(_{3}))</td>
<td>325</td>
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<td>[143]</td>
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<tr>
<td>Fe(<em>{50})(Rh(</em>{49})Au(_1))</td>
<td>230</td>
<td>9.4</td>
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<td>This work</td>
</tr>
<tr>
<td>Fe(<em>{48})(Rh(</em>{48})Pt(_4))</td>
<td>420</td>
<td>7.34</td>
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<td>[41]</td>
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<tr>
<td>Fe(<em>{48})(Rh(</em>{49})Ir(_3))</td>
<td>499</td>
<td>2.7</td>
<td>5.2</td>
<td>[41]</td>
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<tr>
<td>Fe(<em>{50})(Rh(</em>{47.5})Ir(_{2.5}))</td>
<td>529</td>
<td>2.2</td>
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<td>[115]</td>
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<tr>
<td>Fe(<em>{48})(Rh(</em>{48})Ir(_4))</td>
<td>545</td>
<td></td>
<td>4.9</td>
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<tr>
<td>Fe(<em>{48.5})(Rh(</em>{45.9})Ir(_{5.8}))</td>
<td>570</td>
<td></td>
<td>2.6</td>
<td>[10]</td>
</tr>
<tr>
<td>Fe(<em>{48})(Rh(</em>{47})Ir(_5))</td>
<td>585</td>
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<td>[41]</td>
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</table>
Figure 79: Magnetic field and pressure dependence of the magnetostructural transition temperature of FeRh-based compounds. Data plotted here is reported in Table IX. It is evident that at high temperatures \((T>150 \text{ K})\), \((dT_t/dP)_{H=0.7}\) and \((dT_t/dH)_{P=0 \text{ kbar}}\) of FeRh and its ternary counterparts varies linearly with temperature. Below 150 K, distinct deviation from linearity is noted.

4.3.4.2 Influence of extrinsic parameter variation on the thermal hysteresis width of the \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) system

Thermal hysteresis in magnetostructural materials is an experimental manifestation of a first-order phase transition occurring in the system. It is an extrinsic property of a magnetostructural system that has important implications for potential technological applications of these materials. In Section 2.1 of this Dissertation, the physical basis of thermal hysteresis in
magnetostructural materials has been explained from a thermodynamic point of view. As relevant to the current Section of this Dissertation, thermal hysteresis gives information regarding the kinetics of the phase transformation process. As such, it provides insight into the barriers to nucleation and growth mechanisms in magnetostructural material systems. To date, very few experimental studies in literature have investigated the relative role of an external parameter in the broadening of a first-order magnetostructural phase transition.

In this current study, the effect of pressure, temperature and magnetic field on the thermal hysteresis width ($\Delta T$) of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system has been investigated. In particular, it is observed that $\Delta T$ increases with increased magnetic field and decreases with increased hydrostatic pressure (See Tables 9 and 10). To clarify the role that temperature plays in influencing the thermal hysteresis width of FeRh-based systems, results from three sets of measurements are shown in Figure 80. The y-axis of the graph of Figure 80 represents the temperature derivative of the magnetic moment and the x-axis represents the temperature. The average transition temperatures of the data shown in Figure 80 (a), (b) and (c) correspond to 191 K, 171 K and 150 K respectively. It is observed although the values of the applied pressure and magnetic field are distinctly different; the thermal widths ($\Delta T$) of the transition character of the samples are almost identical for all the curves in a given set. These trends suggest that while pressure and magnetic field shift the magnetostructural transition temperature of the FeRh system, they contribute very little to the activation energy barriers that the system must overcome to achieve nucleation of the antiferromagnetic or ferromagnetic phase. Thus, it appears that nucleation and growth in the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system is driven primarily by temperature.

In Figure 81, the thermal hysteresis width of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ sample obtained under different pressure and magnetic field conditions is plotted as a function of transition temperature.
It is observed that in the temperature range 100-200 K, $\Delta T_t$ decreases linearly with increase in temperature. The linear broadening of the thermal hysteresis at low temperatures is tentatively recognized as an experimental sign of the sluggish kinetics of the nucleation and growth process in the system due to low thermal activation energy. At temperatures above 200 K, $\Delta T_t$ becomes almost constant at around ~20 degrees. At the current time, the underlying mechanism for this change in the slope of the temperature-dependence of the thermal hysteresis width is not clearly understood. Based on the theoretical study of Imry and Wortis which shows that local defects and microscopic quenched order can influence the thermodynamic behavior of phase transitions, it is conjectured that the transition width of the sample at high temperatures is dominated by the chemical disorder in the sample. To validate this hypothesis, experimental and theoretical studies aimed at investigating the temperature-dependence of the kinetic behavior of the magnetostructural phase transformation process in the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ system are desired.
Figure 80: Plots of derivative of the temperature-dependant magnetization curve of the (Fe_{47.5}Ni_{1.5})Rh_{51} system at different applied fields and pressures as a function of temperature. It is intriguing to observe that though the applied pressure and magnetic field values are distinctly different, the thermal width of the samples are almost identical for all the curves in a given set.
Figure 81. Plot of hysteresis width of the (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$ sample under different pressure and magnetic field conditions and transition temperature.

4.3.5 Ongoing research: Development of a theoretical model to predict the effect of extrinsic parameter variation on the FeRh magnetostructural transition

At the current time, efforts are underway in this study for development of a semi-empirical model that will facilitate quantitative prediction of the relative energies influencing the magnetostructural phase transition response in FeRh-based compounds. A schematic representation of this model is provided in Figure 82 which is described in the next paragraph.

Based on previous thermodynamic studies in the FeRh literature, the fundamental assumption of this model is that at 0 K the internal energy ($U$) of the antiferromagnetic phase of FeRh is lower than its corresponding ferromagnetic phase by an amount $\Delta U_0$ (i.e. $\Delta U_0 = U_{FM} - U_{AFM}$). A magnetostructural transition is expected to occur when the driving force for the magnetostructural phase transition response ($\Delta G_{\text{phase transition}}$) is equal to $\Delta U_0$. In the absence of applied magnetic field and pressure, $\Delta G_{\text{phase transition}}$ depends principally on the ambient thermal
energy of the system (marked in yellow in Figure 82(a)). It is postulated that $\Delta E_{thermal}$ is proportional to the energy expression, $E = kT_t$ (Here, $k$ is the Boltzmann constant and $T_t$ is the magnetostructural transition temperature). Application of a magnetic field lowers the thermal energy required to drive the magnetostructural transition, producing a decrease in $T_t$ (See Figure 82(b)). Conversely, it is anticipated that application of hydrostatic pressure increases the overall internal energy of the system (Figure 82(c)). Consequently, greater thermal energy is required to drive the magnetostructural transition and an increase in $T_t$ is observed (Figure 79(c). Based on these arguments, it is postulated that a thermodynamic condition required to overcome the energy difference between the antiferromagnetic and ferromagnetic state of the FeRh compound $(\Delta U_0)$ maybe expressed as:

$$\Delta G_{phase\ transition} = \Delta U_0 = \Delta E_{thermal} + \Delta E_{magnetic\ field} + \Delta E_{pressure} \quad (29)$$

In Eq. [25]:

$\Delta E_{pressure}$ = Change in energy of the system due to application of pressure

$\Delta E_{thermal}$ = Change in energy of the system due to application of temperature

$\Delta E_{magnetic\ field}$ = Change in energy of the system due to application of magnetic field.

When pressure and magnetic field are both applied to the sample, magnetic and pressure contributions to the overall energy of the system are expected to oppose each other (See Figure 79(d). At the current time, the biggest challenge for refining this rather rudimentary model lies in identifying the precise physical expressions for the energy terms described in Eq. [25]. Future work to this end is desired.
Figure 82. Schematic representation of an empirical model developed to understand the effect of extrinsic parameter variation (temperature, magnetic field and pressure) on the relative energies influencing the magnetostructural response.

4.3.6 Conclusions and significance of work

In this study, \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\) serves as a model system for understanding the relative and simultaneous effects of temperature (2-400 K), magnetic field (up to 5 T) and pressure (up to 10 kbar) on the magnetostructural response of FeRh-based systems. The experimental data and trends presented in this work indicate that external pressure and magnetic field influence the magnetostructural properties of FeRh-based compounds in opposing ways (Example: The
magnetostructural temperature ($T_t$) increases with increase in pressure and decreases with increases in magnetic field; Conversely, the thermal transition width ($\Delta T_t$) decreases with increase in pressure and increase in magnetic field). It is further, proposed that when the FeRh transition is shifted to low temperatures ($T < 200$ K), either by elemental substitution or by application of a magnetic field, the motion of the atoms involved in the transition becomes sluggish or arrested in metastable regimes due to low thermal activation energy. Consequently, at low transition temperatures, significant broadening of the magnetostructural transition width is observed accompanied by an anomalous increase in the sensitivity of the magnetostructural temperature to pressure and magnetic field. At a critical temperature of 50 K, complete kinetic arrest of the phase transformation process is observed. Overall, these results emphasize that the magnetostructural phenomena in FeRh-based compounds is a thermally-activated process. It is important to note that the conclusions presented in this work are based primarily on results obtained from magnetic characterization of the ($\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}$ sample. Future research aimed at advanced structural characterization of FeRh-based ternary compounds using temperature-, magnetic field- and pressure-dependant x-ray diffraction is recommended for obtaining information regarding the influence of extrinsic parameter variation on the structural component of the FeRh magnetostructural transition.

4.4. Towards tailoring the magnetocaloric response of FeRh-based ternary compounds

The primary objective of this Dissertation is to explore pathways for tailoring the magnetostructural response of FeRh-based compounds. This objective is motivated by a desire to understand the fundamental physics underlying the functional response associated with this system. In this Dissertation, specific attention has been given to the magnetocaloric effect observed in FeRh-based compounds. In this Section, results obtained from experiments aimed at understanding the influence of elemental substitution and hydrostatic pressure on the
magnetocaloric properties (working temperature range ($\delta T_{FWHM}$), magnetic entropy ($\Delta S_{mag}$) and magnetic refrigeration capacity ($RC$)) of FeRh-based compounds are described. For organizational clarity, this Section has been divided into five broad segments: Section 4.4.1 provides an introduction and justification for this study; Section 4.4.2 provides specific details pertaining to the sample synthesis and characterization techniques; Section 4.4.3 provides an overview of the results obtained; Section 4.4.4 provides a discussion and interpretation of the results and finally Section 4.4.5 highlights the overall significance of this work.

4.4.1 Background and Justification: Tailoring the magnetocaloric response of FeRh-based ternary compounds

In the past 20 years, there has been a surge in research on the magnetocaloric response of magnetic materials, mainly due to the possibility of applying this effect for several possible technological applications, including magnetic refrigeration in the room-temperature regime [39], energy harvesting through thermomagnetic transitions [152] and development of microfluidic pumps [153]. But interest in studying the MCE does not lie only with practical applications; understanding of this phenomenon also provides advanced comprehension of the fundamental characteristics of phase transitions [39]. To this end, it is important to note that the common underlying cause of a large MCE in many technologically-important materials systems (Example: La(FeSi)$_{13}$ and Gd$_5$(SiGe)$_4$ and their variants) is attributed to a first-order magnetostructural phase transition [39]. FeRh is no exception to this generalization. Direct calorimetry-based measurements of the MCE of a nominally equiatomic FeRh alloy indicate a large adiabatic temperature change of $\Delta T_{ad} \sim 13$ K and a magnetic entropy change of $\Delta S_{mag} \sim 16$ J/kg K in an external magnetic field change ($H_{app}$) of 1.95 T (See Figure 82) [26]. It is intriguing to note that to date, very little has been reported concerning the effect of extrinsic and intrinsic parameter variation on the magnetocaloric behavior of FeRh-based systems [61, 69]. To fill this
knowledge gap, here the influence of elemental substitution and hydrostatic pressure on the magnetocaloric properties of FeRh-based alloys is reported.

![Figure 82. Plot of adiabatic temperature change ($\Delta T_{ad}$) and magnetic entropy change ($\Delta S_{mag}$) of select technologically important room temperature magnetocaloric materials systems. Plot adapted from Ref [40].]

### 4.4.2 Experimental Details: Tailoring the magnetocaloric response of FeRh-based ternary compounds

Bulk FeRh-based alloys of composition $[\text{Fe}(\text{Rh}_{1-x}\text{A}_x)]$ or $[(\text{Fe}_{1-x}\text{B}_x)\text{Rh}]$ (A=Cu, Pd; B=Ni; 0<$x$<0.06) were synthesized by arc melting the constituent elements (99.9% purity) in an Ar atmosphere. The arc-melted ingots were subsequently sealed under vacuum ($1 \times 10^{-6}$ Torr) in vitreous silica tubes for annealing at 1000 °C for 48 hours. The chemical composition and homogeneity of the FeRh-based compounds were confirmed by energy-dispersive X-ray spectroscopy in a scanning electron microscope (SEM-EDS, Hitachi S4800) and attainment of the B2-ordered crystal structure was verified using powder X-ray diffraction (PANalytical X’Pert PRO). Depending upon the motivation of the study, magnetic characterization of the
FeRh-based compounds was carried out in the temperature range 2 K < T < 400 K, using two different kinds of magnetometers. In studies aimed at understanding the influence of elemental substitution of the magnetocaloric behavior of FeRh-based compounds, a Vibrating Sample Magnetometer (VSM, Quantum Design model VersaLab) was used. The effect of hydrostatic pressure (upto 10 kbar) on the magnetocaloric behavior of FeRh-based compounds was investigated using an EasyLab diamond anvil pressure cell (MCell 10) in conjunction with a SQUID magnetometer. An overview of the figures of merit of a magnetocaloric material and the experimental methods used to determine them are provided in Appendix B. Specific details, as relevant to the FeRh-based samples examined in this Dissertation are provided below.

In this study, the magnetostructural transition temperatures (Tt) of the chemically-modified FeRh alloys were determined from the inflection point of the M vs. T transition as the maximum of the derivative of M with respect to T (i.e. [\frac{\partial M}{\partial T}]_{max}). Characteristically, the thermal behavior of magnetocaloric compounds is strongly correlated with the magnetic entropy change (\Delta S_{mag}) of the system [39]. The magnetic entropy change (\Delta S_{mag}) achieved in the FeRh-ternary compounds was therefore determined from the Maxwell relation using isothermal M(H) curves measured at temperature intervals of 2.5 K in the vicinity of the magnetostructural transition temperature:

$$\Delta S_{mag} \left( \frac{T_1 - T_2}{2} \right) = \frac{1}{T_1 - T_2} \left[ \int_{0}^{H_{max}} M(T_2, H) dH - \int_{0}^{H_{max}} M(T_1, H) dH \right] \quad (30)$$

The area encompassed by the two magnetization curves at temperatures T_1 and T_2 was divided by the temperature difference, \Delta T = T_2 - T_1, to determine the entropy change \Delta S_{mag} at temperature, \( T = \frac{(T_2 + T_1)}{2} \). To ensure reproducibility of the results, prior to measurement of each M(H) curve the magnetic history of the sample was reset by cooling the sample down to the
antiferromagnetic temperature range \((T=250 \text{ K for FeRh, Fe}_{50}(\text{Rh}_{49}\text{Cu}_1)\text{ and } \text{Fe}_{50}(\text{Rh}_{47}\text{Pd}_3); T=150 \text{ K for Fe}_{50}(\text{Rh}_{48}\text{Cu}_2); T=25 \text{ K for } (\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51})\).

It is important to note that during the discovery of the large MCE in FeRh-based compounds, Nikitin et al. noted that the MCE vanished after the first field cycle and a reproducible MCE could not be achieved [26]. This observation was believed for a long time and in the early magnetocaloric literature many studies have pointed out this finding while comparing the merits of newly discovered materials showing large MCE near room temperature [2, 154, 155]. However, in 2008, Manekar et al. showed that the vanishing MCE in FeRh is actually a misinterpretation of the generic thermomagnetic history effects arising across any first-order magnetostructural transition [62]. By taking into account the metastability and phase coexistence across the FeRh transition, Manekar et al. proposed an experimental protocol to achieve a reproducible entropy change in the case of FeRh system [62]. In this Dissertation, the protocol articulated by Manekar et al. was followed and accordingly the the magnetic entropy changes \(\Delta S_{\text{mag}}\) of all the FeRh samples were calculated using the second magnetization cycle rather than the initial magnetization curve.

The magnetic refrigeration capacity (RC) of the FeRh-based systems at a given applied magnetic field \((H_{\text{app}})\) was estimated from the entropy curves \((\Delta S_{\text{mag}} \text{ vs. } T)\) plot as:

\[
RC(H_{\text{app}}) = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S_{\text{mag}}(T, H_{\text{app}}) dT
\]

Here, the temperatures, \(T_{\text{hot}}\) and \(T_{\text{cold}}\), correspond to the extreme temperature ends of the full width at half maximum \((\delta T_{\text{FWHM}})\) of the peak of the \(\Delta S_{\text{mag}} \text{ vs. } T\) curve. The refrigeration cycle in the FeRh system is characteristically accompanied by hysteresis losses that heat the material. The net refrigeration capacity \((RC_{\text{net}})\) was therefore calculated as:

\[
RC_{\text{net}} = RC(H_{\text{app}}) - \text{Hysteresis Loss}
\]
The hysteresis loss was computed from the data using the following equation:

\[
Hysteresis \ Loss = \frac{1}{\delta T_{FWHM}} \int_{T_{cold}}^{T_{hot}} \left( \int_0^{H_{max}} M_{desc}(T, H) \, dH - \int_0^{H_{max}} M_{asc}(T, H) \, dH \right) \, dT \tag{33}
\]

Where, \( M_{desc} \) and \( M_{asc} \) represent the ascending and descending field-dependant magnetization curves of the material system, respectively.

4.4.3 Experimental Results: Tailoring the magnetocaloric response of FeRh-based ternary compounds

For organizational clarity, this Section is divided into two sub-parts. Results obtained while investigating the effect of elemental substitution of the magnetocaloric properties (namely, magnetic entropy change (\( \Delta S_{mag} \)), net refrigeration capacity (\( RC \)) and working temperature range (\( \delta T_{FWHM} \)) of bulk FeRh-based compounds are described in Section 4.4.3.1. In studies aimed at understanding the influence of hydrostatic pressure on the magnetocaloric behavior of FeRh compounds, a Ni-doped FeRh compound of composition Fe_{47.3}Ni_{1.3}Rh_{51} was used as a model system. Results obtained via magnetic characterization of this sample are discussed in Section 4.4.3.2.

4.4.3.1 Influence of elemental substitution on the magnetocaloric behavior of FeRh-based compounds

Figure 83 shows the temperature-dependent magnetization curves of the FeRh-based alloys synthesized in this study in an applied magnetic field of \( H_{app} = 1 \) T. The magnetostructural properties of the FeRh-compounds, as deduced from these curve, are summarized in Table 12. Consistent with previous reports in the literature, the equiatomic parent FeRh alloy possesses a saturation magnetization value of \( \sim 140 \) emu/g and exhibits a first-order AFM \( \rightarrow \) FM phase transition upon heating to \( \sim 390 \) K. Depending upon the type and concentration of the dopant,
elemental substitution decreases the saturation magnetization ($M_s$) and the magnetostructural transition temperature ($T_t$) of the FeRh-ternary compounds, relative to those of the equiatomic parent FeRh alloy, while consistently increasing the thermal hysteresis width ($\Delta T_t$) of the magnetostructural transition.

Figure 83. Temperature-dependant magnetization curves of the 3d- and 4d-transition metal substituted FeRh-ternary compounds at an applied magnetic field of $H_{app} = 1$ T. Depending upon the type and concentration of the dopant, elemental substitution decreases the saturation magnetization ($M_s$) and the magnetostructural temperature ($T_t$) of the FeRh-ternary compounds, relative to that of the equiatomic parent FeRh alloy, while consistently increasing the thermal hysteresis width ($\Delta T_t$) of the magnetostructural transition.

<table>
<thead>
<tr>
<th>Composition of alloy</th>
<th>$M_s$ (emu/g)</th>
<th>$T_{t}^{AFM\rightarrow FM}$ (K)</th>
<th>$T_{t}^{FM\rightarrow AFM}$ (K)</th>
<th>$\Delta T_t$ (K)</th>
<th>$dT_t/dH_{app}$ (K/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{50}$Rh$</em>{50}$</td>
<td>137</td>
<td>387</td>
<td>373</td>
<td>15</td>
<td>8.7</td>
</tr>
<tr>
<td>Fe$<em>{0.50}$(Rh$</em>{0.49}$Cu$_{0.01}$)</td>
<td>109</td>
<td>346</td>
<td>322</td>
<td>24</td>
<td>9.7</td>
</tr>
<tr>
<td>Fe$<em>{0.50}$(Rh$</em>{0.48}$Cu$_{0.02}$)</td>
<td>96</td>
<td>233</td>
<td>188</td>
<td>45</td>
<td>9.6</td>
</tr>
<tr>
<td>Fe$<em>{0.50}$(Rh$</em>{0.47}$Pd$_{0.03}$)</td>
<td>107</td>
<td>292</td>
<td>324</td>
<td>32</td>
<td>10.3</td>
</tr>
<tr>
<td>(Fe$<em>{0.475}$Ni$</em>{0.125}$)Rh$_{0.49}$</td>
<td>125</td>
<td>123</td>
<td>171</td>
<td>48</td>
<td>18.1</td>
</tr>
</tbody>
</table>

$^a$ $T_{t}^{AFM\rightarrow FM}$ and $T_{t}^{AFM\rightarrow FM}$ represent the transition temperatures obtained upon heating through the AF$\rightarrow$FM transition and cooling through the FM$\rightarrow$AFM transition at an applied magnetic field ($H_{app}$) of 1T.

$^b$ The temperature mid-point between $T_{t}^{AFM\rightarrow FM}$ and $T_{t}^{AFM\rightarrow FM}$ was considered during determination of the magnetic field dependence of the magnetostructural transition temperature ($dT_t/dH_{app}$).
Magnetic entropy curves ($\Delta S_{\text{mag}}$ vs. $T$ plots) of the chemically-modified FeRh alloys, were constructed from magnetization isotherms measured in the vicinity of the magnetostructural transition. As an example, magnetization isotherms of the Fe$_{50}$(Rh$_{49}$Cu$_1$) sample in the temperature range 325-345 K are shown in Figure 84. Initially, at temperatures below 325 K, the Fe$_{50}$(Rh$_{49}$Cu$_1$) alloy is predominantly antiferromagnetic and very little change in magnetization ($M$) is observed at an applied field of 2T. At 327.5 K a field-driven meta magnetic transition is noted at a critical applied field of $H_c=1.95$ T. Increase in the temperature, in the range 327.5 to 335 K, moves the field-driven transition to lower critical fields. At 337.5 K, a peculiar step-like two-phase behavior is noted and finally at temperatures greater than 340 K, the sample is ferromagnetic with a saturation magnetization of 107 emu/g. Based on previous reports on the magnetocaloric properties of systems which exhibit first-order magnetostructural transitions (Example: Gd$_5$Si$_{4-x}$Ge$_x$, MnAs$_{1-x}$Sb$_x$ and La$_{1-x}$Fe$_{11.83}$Si$_{1.17}$), the curious “step-like” behavior observed in the Fe$_{50}$(Rh$_{49}$Cu$_1$) sample is attributed to coexistence of the ferromagnetic and the antiferromagnetic phases near the magnetostructural transition temperature [28, 156, 157]. This “step-like” feature at a certain critical temperature was observed in the magnetization isotherms of all the FeRh-based alloys synthesized in this study.
In systems which exhibit abrupt first-order magnetic transitions, when magnetic entropy curves are constructed from isothermal magnetic measurements, an unrealistic spike is observed at the temperature corresponding to that of the magnetic isotherm which exhibits the peculiar “step-like” behavior (See Figure 85 for example) [28, 156, 157]. This spike is identified as an artifact of the measurement technique and it is never observed when magnetic entropy curves are calculated from calorimetric measurements [34]. In this study, the $\Delta S_{\text{mag}}$ vs. $T$ plots of the FeRh-ternary compounds were corrected by employing a method developed by Liu et al. [156]. A detailed description of this method is provided in Appendix C.
Figure 85: Magnetic entropy curve of the Fe$_{50}$(Rh$_{49}$Cu$_1$) sample. The red curve shows a spike which is recognized as an artifact of the magnetic measurement technique. The spike was corrected using an experimental protocol developed by Liu et al. [156].

The magnetic entropy curves of all the FeRh-based systems considered in this study are shown in Figure 86. It is evident from Figure 86 that the $\Delta S_{mag}^{peak}$ of the FeRh-based ternary alloys is consistently lower than that of the parent FeRh compound ($\Delta S_{mag,FeRh}^{peak}\sim 17$ J/kgK; $\Delta S_{mag,FeRh-X}^{peak} = 7$-14 J/kgK at $H_{app}=2$T). However, despite high hysteresis losses during the refrigeration cycle, the net refrigeration capacity of the doped FeRh systems is significantly higher than that of equiatomic FeRh system ($RC_{FeRh} \sim 150$ J/kg; $RC_{FeRh-ternary} = 170$-210 J/kg at $H_{app}=2$T). The peak magnetic entropy change ($\Delta S_{mag}^{peak}$), working temperature range ($\delta T_{FWHM}$) and net refrigeration capacity ($RC_{net}$) of these compounds are summarized in Table 13.
Figure 86. Magnetic entropy curves ($\Delta S_{mag}$ vs. $T$) of 3$d$- and 4$d$-transition metal substituted FeRh-ternary compounds at an applied magnetic field of $H_{app}=2T$.

Table 13. Magnetocaloric properties of the FeRh-based ternary compounds

<table>
<thead>
<tr>
<th>Composition of alloy</th>
<th>Valence electrons per atom</th>
<th>$\Delta S_{mag}^{peak}$ (J/kg K)</th>
<th>Working Temperature range (K)</th>
<th>Refrigeration capacity (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_{hot}$ $T_{cold}$ $\delta T_{FWHM}$</td>
<td>RC</td>
<td>Hysteresis Loss</td>
</tr>
<tr>
<td>Fe$<em>{50}$Rh$</em>{50}$</td>
<td>8.50</td>
<td>16.37</td>
<td>400 385 15</td>
<td>201 53   148</td>
</tr>
<tr>
<td>Fe$<em>{0.50}$(Rh$</em>{0.49}$Cu$_{0.01}$)</td>
<td>8.52</td>
<td>14.40</td>
<td>345 324 21</td>
<td>267 76   191</td>
</tr>
<tr>
<td>Fe$<em>{0.50}$(Rh$</em>{0.48}$Cu$_{0.02}$)</td>
<td>8.54</td>
<td>9.91</td>
<td>235 201 34</td>
<td>300 92   208</td>
</tr>
<tr>
<td>Fe$<em>{0.50}$(Rh$</em>{0.47}$Pd$_{0.03}$)</td>
<td>8.53</td>
<td>10.68</td>
<td>315 291 24</td>
<td>219 50   169</td>
</tr>
<tr>
<td>(Fe$<em>{0.475}$Ni$</em>{0.125}$)Rh$_{0.49}$</td>
<td>8.54</td>
<td>7.37</td>
<td>175 115 60</td>
<td>289 107 182</td>
</tr>
</tbody>
</table>

* The magnetocaloric properties reported in this table were measured at an applied magnetic field of $H_{app}=2T$
4.4.3.2 Influence of pressure on the magnetocaloric behavior of the \((\text{Fe}_{0.475}\text{Ni}_{0.125})\text{Rh}_{0.49}\) system

In this study, the \(\text{Fe}_{47.5}\text{Ni}_{1.5}\) sample serves as a test bed for understanding the influence of hydrostatic pressure on the magnetocaloric behavior of FeRh-based compounds. Details regarding the structural and magnetic properties of this particular compound have already been provided in Section 4.3. Here, special attention will be given to changes in the magnetic entropy \((\Delta S_{\text{mag}})\) and the refrigeration capacity \((RC)\) of the \(\text{Fe}_{47.5}\text{Ni}_{1.5}\) compound as a function of applied pressure.

Figure 87 shows the temperature-dependant magnetization behavior of the \(\text{Fe}_{47.5}\text{Ni}_{1.5}\) sample under application of pressure (up to 6 kbar). At an applied field of \(H_{\text{app}}=1\) T, the dependence of the magnetostructural transition temperature on applied pressure \((i.e. dT_t/dP)\) in the Ni-doped FeRh sample was determined as 15.78 K/kar. Additionally, it is interesting to note that the thermal hysteresis width \((\Delta T_t)\) of the sample decreases with increase in applied pressure.

![Figure 87: Temperature-dependant magnetization behavior of the \(\text{Fe}_{47.5}\text{Ni}_{1.5}\) sample under application of pressure (Note: \(H_{\text{app}}=1\) T).](image)
The magnetic entropy curves of the Fe_{47.5}Ni_{1.5}Rh_{51} system at a magnetic field of $H_{app}=2T$ are shown as a function of applied hydrostatic pressure in Figure 88. It is observed from Figure 88 that pressure increases the $\Delta S_{mag}^{peak}$ of Fe_{47.5}Ni_{1.5}Rh_{51} while decreasing the net refrigeration capacity of the sample. A summary of the magnetocaloric properties of Fe_{47.5}Ni_{1.5}Rh_{51} compound is provided in Table 14.

![Figure 88: Magnetic entropy curves of the Fe_{47.5}Ni_{1.5}Rh_{51} system (at a magnetic field of $H_{app}=2T$) as a function of applied hydrostatic pressure (upto 5.5 kbars).](image)

<table>
<thead>
<tr>
<th>Pressure (KBar)</th>
<th>Magnetostructural Temperature (K)</th>
<th>$\Delta S_{mag}^{peak}$ (J/kg K)</th>
<th>Refrigeration capacity (J/kg)</th>
<th>Working Temperature range (K)</th>
<th>$T_{hot}$</th>
<th>$T_{cold}$</th>
<th>$\delta T_{FWHM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>145</td>
<td>16.37</td>
<td>182</td>
<td>175</td>
<td>115</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>192</td>
<td>14.40</td>
<td>167.16</td>
<td>206</td>
<td>182</td>
<td>24</td>
<td>24</td>
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<tr>
<td>5.4</td>
<td>241</td>
<td>9.91</td>
<td>91.8</td>
<td>247</td>
<td>235</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

* The magnetocaloric properties reported in this table were measured at an applied magnetic field of $H_{app}=2T$
4.4.4 Discussion: General trends in the magnetocaloric properties of FeRh-based compounds

In this work, the magnetocaloric behavior of FeRh-based systems of composition Fe(Rh$_{1-x}$A$_x$) or (Fe$_{1-x}$B$_x$)Rh (A=Cu, Pd; B=Ni; 0<x<0.06) is found to vary systematically over a wide temperature range, 100 K ≤ $T$ ≤ 400 K. Despite a lower peak magnetic entropy change value ($\Delta S_{mag}^{peak}$), the refrigeration capacity ($RC$) of the FeRh-based ternary alloys were found to be appreciably higher than that of the parent FeRh compound. In accordance to previous findings in this Dissertation (See Section 4.2), the decrease in $\Delta S_{mag}^{peak}$ in the FeRh system is attributed to changes in the electronic band structure due to elemental substitution. Insight into the possible reason for increase in the refrigeration capacity in doped FeRh compounds may be obtained from the theoretical study of Imry and Wortis which shows that microscopic random quenched chemical impurities and local defects can influence the thermodynamic behavior of phase transitions [158]. Considering that the thermal hysteresis width and the field-dependence of the ternary FeRh compounds is consistently higher than that of the equiatomic FeRh compound (See Table 12), it is reasonable to state that chemical disorder results in broadening of the magnetostructural transition in the FeRh system. Similar chemical-disorder induced broadening of the magnetic phase transition has also been observed in a few other magnetocaloric materials systems such as in Gd$_5$Ge$_2$Si$_{x-2}$Fe$_x$ [156] and CoMnGe$_{1-x}$Sn$_x$ [159] alloys. Additionally, it is worthwhile to note that results reported in Section 4.3 of this Dissertation indicate that thermal hysteresis and therefore the nucleation and growth process in FeRh-based compounds is driven primarily by temperature. As applicable to this current Section, it is observed that the magnetostructural temperatures of the FeRh-based ternary compounds examined in this study are consistently lower than that of the parent FeRh compound (See Table 13).
Results presented in Section 4.2 demonstrates that the parameter, “valence band electron concentration,” plays a critical role in determining the magnetostructural temperature of FeRh-based compounds. Extending this work, the peak magnetic entropy change ($\Delta S_{mag}^{\text{peak}}$) of the FeRh-based compounds synthesized in this study has been plotted as a function of their corresponding valence band concentration in Figure 89(a). For comparison, $\Delta S_{mag}^{\text{peak}}$ of FeRh-based compounds previously studied in the literature have also been included in this figure. The linear dependence of the $\Delta S_{mag}^{\text{peak}}$ values on the valence electron concentration of the chemically-modified FeRh compounds is reminiscent of the linear relationship between the magnetostructural transition temperature ($T_t$) and the valence electron concentrations of these same compounds (shown in Figure 89(b)). To this end, it is interesting to note that a plot of $\Delta S_{mag}^{\text{peak}}$ as a function of the magnetostructural phase transition temperature (shown in Figure 90), indicates that for 3d- and 4d-transition metal doped FeRh compounds, $\Delta S_{mag}^{\text{peak}}$ increases linearly with $T_t$ in the temperature range, 150-400 K:

$$\Delta S_{mag}^{\text{peak}} = \Delta S_{0\ mag}^{\text{peak}} + AT$$  \hspace{1cm} (35)

Where $\Delta S_{0\ mag}^{\text{peak}} = 2 \text{ J/kg}$ and $A = 0.035 \text{ J/kgK}$. This result compares exceptionally well with the value of $\Delta S_{0\ mag}^{\text{peak}} = 1.94 \text{ J/kg}$ and $A = 0.036 \text{ J/kgK}$ obtained from Kouvel’s measurements on FeRh-ternary samples. Overall, these data trends confirm that the magnetic entropy of the FeRh system is strongly influenced by the electronic structure of the system. It is further speculated that the generalized plots shown in figures 89 and 90 may provide pathways for predicting magnetic entropy changes in FeRh-based alloys.
Figure 89: Dependence of the magnetostructural properties of FeRh-based compounds on their corresponding valence band electron concentration: (a) Magnetic entropy change ($\Delta S_{mag}^{peak}$) and (b) Magnetostructural Temperature ($T_s$).
Figure 90: Plot of $\Delta S_{mag}^{peak}$ as a function of the magnetostructural phase transition temperature, $T_t$. It is observed that in the temperature range 150-400 K, $\Delta S_{mag}^{peak}$ increases linearly with increase in $T_t$.

In Figure 91, the magnetic refrigeration capacity (RC) of the FeRh-based compounds synthesized in this study has been plotted as a function of their corresponding valence band concentration. In confirmation with results reported in Section 4.4.3.1, Figure 91 indicates that the RC of FeRh-based ternary compounds is significantly higher than that of nominally equiatomic binary FeRh compounds. However, this plot does not allow prediction of the RC of FeRh-based ternary compounds. It follows from Equation (30) that quantitative assessment of the magnetic refrigeration capacity of magnetocaloric compounds requires the capability of predicting the width of the magnetostructural transition width ($\Delta T_t$) of the system. To this end, it is important to realize that although it is known that the $\Delta T_t$ of FeRh-based compounds is strongly influenced by the quenched chemical disorder in the system, to date, no theoretical or empirical study has been conducted to systematically investigate the effect of substitutional
doping on the thermal hysteresis width of FeRh-based alloys. It is anticipated that future work to this end would be useful in predicting the net refrigeration capacity of FeRh-based alloys.

Figure 91: Dependence of the magnetic refrigeration capacity of FeRh-based compounds on their corresponding valence band electron concentration.

4.4.5 Significance of work

In this Dissertation, it is demonstrated that the magnetocaloric response of FeRh-based compounds may be tailored for potential magnetic refrigeration applications by chemical modification of the FeRh lattice or by application of hydrostatic pressure. Figure 92 shows the relationship between the absolute value of the maximum magnetic entropy change and the corresponding transition temperature for nine technologically important families of magnetocaloric compounds. The brown shaded area here represents the magnetocaloric properties of the FeRh family, as shown by Franco et al. in reference [34]. Overall, Figure 92 suggests that prior to this Dissertation, FeRh-based compounds were known to exhibit the magnetocaloric effect in a narrow temperature range spanning from 300 to 250 K only. Results obtained in this work suggest that the temperature range in which the magnetocaloric effect is observed in FeRh-doped compounds is actually much wider, 100 K ≤ T ≤ 400 K (as represented
by the brown dotted lines). Further, the experimental trends presented in this work suggests that while elemental substitution consistently decreases the magnetic entropy change ($\Delta S_{mag}$) of the FeRh-based ternary alloys relative to that of the parent FeRh compound ($\Delta S_{mag, FeRh}=\sim 17$ J/kgK; $\Delta S_{mag, FeRh-ternary} = 7-14$ J/kgK at $H_{app} = 2$T), the net refrigeration capacity ($RC$) of the ternary systems are significantly higher ($RC_{FeRh}=\sim 120$ J/kg; $RC_{FeRh-ternary}=150-200$J/kg at $H_{app} = 2$T).

While the decrease in $\Delta S_{mag, peak}$ is attributed to changes in the electronic band structure of the FeRh system due to elemental substitution, the enhanced RC in chemically-modified FeRh is ascribed partially to local chemical-disorder-induced broadening of the magnetostructural phase transition. It is important to realize that broadening of the magnetostructural transition width in the FeRh-ternary compounds is also recognized as an experimental sign of the low thermal activation energy available to the system for nucleation and growth of the secondary phase (See Section 4.3 for more information).

Based on previous studies which have shown that the RC of magnetocaloric materials can be enhanced using multiphase materials [160], it is anticipated that the working temperature range ($\delta T_{FWHM}$) and the magnitude of the refrigeration capacity in the FeRh system may be optimized in a laminated composite of compositionally-tuned (Fe(Rh$_{1-x}$M$_x$) or (Fe$_{1-x}$M$_x$)Rh components where $0.48 \leq x \leq 0.52$ and M=3$d$ or 4$d$ transition element). While the thermal hysteresis effect found in the FeRh system may lower the magnitude of the MCE, possible optimal cooling cycles have been suggested in the literature [38]. Further, the results obtained in this study indicate that thermal hysteresis in FeRh-based compounds may be reduced by application of hydrostatic pressure. Finally, correlations between the valence band electron concentration and the magnetic entropy change of 3$d$- and 4$d$- substituted FeRh compounds have
been presented. These generalized trends allowing prediction of the magnetic entropy changes in this system.

Figure 92: Maximum magnetic entropy change versus peak temperature for different families of magnetocaloric compounds. The brown shaded area here represents the magnetocaloric properties of the FeRh family, as shown by Fraco et al. in Reference [34]. Previously, FeRh-based compounds were known to demonstrate the magnetocaloric effect in a narrow temperature range spanning from 300 to 250 K only. In this study, we demonstrate that by elemental substitution the magnetocaloric behavior of FeRh-based systems can be tuned in the temperature range, $100 \, \text{K} \leq T \leq 400 \, \text{K}$ (as represented by the brown dotted lines). Typically, the $\Delta S_{\text{mag}}$ of FeRh-ternary compounds is smaller than that of the parent FeRh alloy.
5.0 CONCLUSIONS & SUMMARY

The overarching goal of this Ph.D. Dissertation is to understand, predict and control the magnetostructural response of the FeRh system as a function of extrinsic and intrinsic parameter variation. Overall, in this study, three pathways were explored to tailor the magnetostructural response of FeRh-based compounds: (a) Reduction of structural scale (Nanostructuring); (b) Simultaneous variation two or more extrinsic parameters, namely temperature, magnetic field and pressure; (c) Chemical modification of the FeRh lattice via elemental substitution. In this work, comparison of the structure-property relations of the parent equiatomic FeRh compound and its nanostructured/chemically-modified counterparts provides insight into fundamental physics underlying the magnetostructural phase transition phenomenon. From the perspective of applied science, it is interesting to investigate correlations between the magnetostructural behavior and functional effects observed in the FeRh system. A small segment of the research conducted in this Dissertation involves understanding the magnetocaloric response of FeRh compounds as a function of hydrostatic pressure and elemental substitution. This Section serves to briefly summarize the results achieved in this Dissertation.

The experimental evidence presented in Section 4.1 indicates that in addition to the extrinsic variables (temperature, pressure, and magnetic field), nanostructuring may also provide a potential route for controlling magnetostructural phase transitions in functional materials systems such as FeRh. In this work, nanoprecipitates of FeRh (~10 nm) were synthesized via thermal annealing of a rapidly-solidified alloy of nominal atomic composition (FeRh)$_5$Cu$_{95}$. These FeRh nanoparticles exhibit a L$_{10}$ (CuAu 1)-type structure, instead of the anticipated B$_2$ (CsCl)-type structure found in bulk FeRh. A thermally hysteretic magnetic transition, remarkably similar to the magnetostructural transition of bulk CsCl-type FeRh reported at $T_c$ ~350 K, is
observed in the nanostructured material at $T \sim 100$ K. Upon annealing-induced coarsening to a size of $\sim 94$ nm, these nanoparticles undergo a structural phase transformation from a metastable tetragonal $L1_0$ (AuCu-1-type) structure to a more stable B2 (CsCl-type) structure. A gradual broadening of the magnetothermal transition commencing at $\sim 100$K accompanies this crystal structure transition. Overall, these results emphasize the sensitivity of the magnetic and structural properties of FeRh to changes in nanostructural scale. It is further important to note that prior to this study, formation of the $L1_0$-ordered structure in FeRh systems of nanoscaled dimension has never been reported before.

In Section 4.2, correlations between the characteristic magnetic transition temperatures and the averaged weighted valence band electron concentration ($(s+d)$ electrons/atom) of chemically-modified alloys of composition Fe($\text{Rh}_{1-x}\text{M}_x$) or ($\text{Fe}_{1-x}\text{M}_x$)Rh ($\text{M} =$ transition element), as reported in the literature, are presented. Based on the deduced relationships between the dependence of the magnetostructural transition temperature and valence electron concentration of FeRh-ternary compounds, an empirical model is proposed to predict the influence of elemental substitution on the magnetostructural behavior of nominally-equiaxial bulk FeRh-based compounds with the B2 (CsCl)-type crystal structure. Confirmation of this phenomenological model is provided through investigation of the influence of Cu and Au additions, previously unreported, on the magnetostructural response of FeRh alloys. The success of this generalized model in confirming existing data trends in chemically-substituted FeRh and predicting new composition-transition temperature correlations not only emphasizes the strong interplay between the electronic spin configuration, the electronic band structure and crystal lattice of this system but also allows for tailoring of the magnetostructural FeRh phase transition for technological applications. Further, the data and associated trends presented in this work
indicate that the stability of the ground state antiferromagnetic phase of the FeRh-based systems depends both on the electronic structure of the system and on the magnetovolume effect.

In Section 4.3, a Ni-doped FeRh-ternary compound of composition, \((\text{Fe}_{47.5}\text{Ni}_{1.5})\text{Rh}_{51}\), serves as a model system for understanding the relative and simultaneous effects of temperature, magnetic field and pressure on the magnetostructural response of FeRh-based systems. The experimental data and trends presented in this work indicate that external pressure and magnetic field influence the magnetostructural properties of FeRh-based compounds in contradictory ways (Example: the magnetostructural temperature \(T_t\) increases with increase in pressure and decreases with increases in magnetic field; conversely, the thermal transition width \(\Delta T_t\) decreases with increase in pressure and increase in magnetic field). It is further, proposed that when the FeRh magnetostructural transition is shifted to low temperatures \((T < 200 \text{ K})\), either by elemental substitution or by application of a magnetic field, the motion of the atoms involved in the transition becomes sluggish or arrested in metastable regimes due to low thermal activation energy. Consequently, at low transition temperatures, significant broadening of the magnetostructural transition width is observed, accompanied by an anomalous increase in the sensitivity of the magnetostructural temperature to pressure and magnetic field. At a critical temperature of 50 K, complete kinetic arrest of the phase transformation process is observed. Overall, these results emphasize that the magnetostructural phenomena in FeRh-based compounds is a thermally-activated process.

Results obtained in Section 4.4 demonstrate that the magnetocaloric response of FeRh-based compounds may be tailored for potential magnetic refrigeration applications by chemical modification of the FeRh lattice or by application of hydrostatic pressure. In this study, it was found that the magnetocaloric working temperature range \(\delta T_{FWHM}\) of FeRh-based can be
systematically tuned in the temperature range, \(100 \, \text{K} \leq T \leq 400 \, \text{K}\), by elemental substitution. It is intriguing to note that while chemical substitution consistently decreases the magnetic entropy change \(\Delta S_{\text{mag}}\) of the FeRh-based ternary alloys from that of the parent FeRh compound \(\Delta S_{\text{mag,FeRh}} \approx 17 \, \text{J/kgK}\; \Delta S_{\text{mag,FeRh-ternary}} = 7-14 \, \text{J/kgK} \, \text{at} \, H_{\text{app}} = 2 \, \text{T}\), the net refrigeration capacity \(RC\) of the doped systems are significantly higher \(RC_{\text{FeRh}} \approx 150 \, \text{J/kg}; \; RC_{\text{FeRh-ternary}} = 170-210 \, \text{J/kg at} \, H_{\text{app}} = 2 \, \text{T}\). These results are attributed to stoichiometry-induced changes in the FeRh electronic band structure and beneficial broadening of the magnetostructural transition due to local chemical disorder. It is intuitively understood that the thermal hysteresis effect found in the FeRh system may reduce the magnitude of the magnetocaloric effect (MCE) in this compound. To this end, it is important to note that application of hydrostatic pressure reduces thermal hysteresis in the FeRh compound. Finally, correlations between the valence band electron concentration and the magnetic entropy change of 3d- and 4d- substituted FeRh compounds are presented in this study. These generalized trends allow prediction of the magnetic entropy changes in this system.
6.0 Outlook and Recommendations for Future Work

In this Dissertation, the magnetostructural response of the FeRh system has been studied as a function of dimensionality variation (bulk to nanoscaled), elemental substitution and extrinsic parameter variation (hydrostatic pressure/strain & magnetic field). The results achieved in this work provide predictive capability and pathways for tailoring the magnetostructural behavior and the associated functional response of FeRh systems for potential technological applications. Further, insight is gained into the fundamental thermodynamic and kinetic factors influencing the magnetostructural phase transformation process in FeRh and related intermetallic compounds. Despite the success achieved in this Dissertation, many open questions regarding the first-order magnetostructural transition in FeRh systems still persist, namely:

1. What role does matrix-induced interfacial strain play in stabilizing the metastable L1_0-ordered structure in the FeRh nanoprecipitates found in the Cu_95(FeRh)_5 nanocomposite?

2. Is there a correlation between the magnetic and the structural properties of B2- and L1_0-ordered FeRh compounds?

3. Can the magnetostructural trends provided in this Dissertation (Section 4.2, 4.3 and 4.4) be explained by theoretical studies?

4. Can the magnetocaloric effect in FeRh-based compounds be tailored by synthesizing a heterostructured system consisting of compositionally-tuned FeRh layers?

In addition to the ongoing experiments briefly described in the results and discussion Section (Sections 4.1.3); this current chapter provides guidelines for future research that may be useful in answering these questions. It is anticipated that results obtained from experiments recommended in this Section will provide an enhanced understanding of the physics underlying the magnetostructural phase transformation in FeRh compounds.
Recommendation 1: Investigate the role that matrix-induced strain plays in stabilizing the metastable L1₀-ordered structure in the FeRh nanoprecipitates found in the Cu₉₅(FeRh)₅ nanocomposite.

Results focused on understanding the influence of nanostructuring on the magnetostructural response of FeRh-based alloys indicate that FeRh nanoparticles (~10 nm) coherently embedded in a Cu matrix adopt a L1₀-type (CuAu 1) structure, in contrast to the anticipated B2 (CsCl)-type structure found in bulk FeRh (See Section 4.1 for details). It is hypothesized that interfacial strain between the matrix and the precipitate plays a critical role in stabilizing the L1₀-ordered FeRh phase in the nanostructured FeRh system. It is proposed that future work employing advanced structural and chemical characterization of the (FeRh)₅Cu₉₅ ribbons will be useful in understanding the effect of matrix-induced strain on the magnetostructural response of the FeRh nanoprecipitates. The application of probes such as temperature-dependant high-resolution transmission electron microscopy (HR-TEM) and electron energy-loss spectroscopy (EELS) are recommended for this purpose.

Recommendation 2: Examine structure-magnetic property correlations between the B2- and the L1₀-ordered FeRh phase

The results described in Section 4.1 of this Dissertation represents the first report on the observation of the L1₀-ordered crystal structure in FeRh nanoparticles [122, 123]. In the FeRh system, prior to this study, the L1₀-crystal structure has been observed only in bulk Fe(Rh₁₋ₓPdx) and Fe(Rh₁₋ₓPtₓ) compounds (x>0.2) [55, 70, 71, 73]. It is anticipated that computational and experimental studies aimed at systematically investigating the possibility of the presence of the L1₀-ordered structure in other doped FeRh compounds will be useful for developing a deeper understanding of the structure-property correlations between the B2- and the L1₀-ordered FeRh phase. As a starting point for these experiments, it is important to note that the magnetostructural trends identified in Section 4.2 of this Dissertation indicate that FeRh-ternary alloys cease to
adopt the B2-ordered crystallographic structure in favor of the face-centered cubic (fcc) or the ordered L10-type structure when their average valence electron concentration exceeds a critical value of 8.65 electrons/atom. To this end, it is expected that L10-ordering may be present in FeRh-based compounds of composition, Fe(Rh1−xMx) or (Fe1−yMy)Rh (x ≥ 0.06, y ≥ 0.04, M= Cu, Ag or Au).

**Recommendation 3: Conduct computational studies aimed at explaining the empirical magnetostructural trends identified in this Dissertation**

In Section 4.2 of this Dissertation, correlations between the characteristic magnetic transition temperatures and the averaged weighted valence band electron concentration ((s+d) electrons/atom) of chemically-modified alloys FeRh compounds were presented. Based on deduced relationships between the dependence of the magnetostructural transition temperature and the valence electron concentration of FeRh-ternary compounds, an empirical model was proposed to predict the influence of elemental substitution on the magnetostructural behavior of nominally-equiatomic bulk FeRh-based compounds with the B2 (CsCl)-type crystal structure. At the current time, a major drawback of this generalized model is that it is based on phenomenological grounds only. A simple choice of the parameter, “valence electron concentration” (e/atom) may therefore only be considered as a guideline for examining systematic magnetostructural changes in FeRh based alloys. Chemical disorder and local lattice distortions, together with variations in the local interatomic exchanges are expected to occur simultaneously with alterations of the valence electron concentration in the FeRh ternary system. Indeed, if the magnetostructural transition of chemically-modified FeRh were driven solely by electronic effects, then the magnetostructural behavior of all isoelectronic compounds would be largely identical. However, an evaluation of isoelectronic alloys obtained by substituting Co or Ir for Rh shows that although electron concentration e/atom remains unchanged, the structural and
magnetic transition temperatures of Fe(Rh$_{1-x}$Co$_x$) and Fe(Rh$_{1-x}$Ir$_x$) alloys vary considerably (See Table 5 and 8 in Section 4.2). This observation demonstrates the need for computational studies that will provide insight into the effect of local lattice distortions and chemical order on the magnetostructural response of FeRh-based ternary systems. Further, it is anticipated that future work aimed at modeling the magnetostructural behavior of FeRh-based ternary allows using \textit{ab initio} calculations and density functional theory will be useful for providing a theoretical framework to the phenomenological model presented in this study.

**Recommendation 4: Investigate the magnetocaloric properties of a heterostructured system consisting of doped FeRh layers**

In Section 4.4 of this Dissertation, it was shown that the magnetic refrigeration capacity ($RC$) of the FeRh-based ternary alloys is appreciably higher than that of the parent FeRh compound. At the current time, it is speculated that the enhanced RC in chemically-modified FeRh is predominantly due to local chemical-disorder-induced broadening of the magnetostructural phase transition. Based on previous studies in literature that have shown that the RC of magnetocaloric materials can be enhanced using multiphase materials [161], it is anticipated that the working temperature range ($\delta T_{FWHM}$) and the magnitude of the refrigeration capacity in the FeRh system may be optimized through synthesis and characterization of a laminated composite consisting of compositionally-tuned (Fe(Rh$_{1-x}$M$_x$) or (Fe$_{1-x}$M$_x$)Rh layers where $0.48 \leq x \leq 0.52$ and M=3$d$ or 4$d$ transition element). Experimental investigation to this end is proposed. It is anticipated that these experiments will be useful in tailoring the magnetocaloric properties of FeRh-based compounds for micro-applications such as energy harvesting through thermomagnetic transitions [162] and the development of microfluidic pumps [163].
### 7.0 NOMENCLATURE

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<td>$\Delta T_t$</td>
<td>Thermal hysteresis width, K</td>
</tr>
<tr>
<td>$\Delta T_{ad}$</td>
<td>Adiabatic temperature change, K</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$\delta T_{FWHM}$</td>
<td>Working temperature range of a magnetocaloric material, K</td>
</tr>
<tr>
<td>U</td>
<td>Internal energy of a system, J</td>
</tr>
<tr>
<td>V</td>
<td>Volume, L</td>
</tr>
<tr>
<td>VSM</td>
<td>Vibrating sample magnetometer</td>
</tr>
<tr>
<td>XMCD</td>
<td>X-ray magnetic circular dichroism</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>Z</td>
<td>Nearest neighbor coordination number</td>
</tr>
<tr>
<td>ZFC</td>
<td>Zero field cooled</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Internal strain parameter</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Excess free energy at the interface of a nanoparticle, J/m$^2$</td>
</tr>
<tr>
<td>$\gamma_{ch}$</td>
<td>Chemical contribution to the interfacial energy, J/m$^2$</td>
</tr>
<tr>
<td>$\gamma_{st}$</td>
<td>Structural contribution to the interfacial energy, J/m$^2$</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>Angle of incident radiation, degree</td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>Bohr Magneton, 9.27x10$^{-24}$ J/T</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Magnetic mass susceptibility, cm$^3$/g</td>
</tr>
<tr>
<td>$\chi_{pp}$</td>
<td>Temperature-independent Pauli paramagnetic susceptibility, cm$^3$/g</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>Relative magnetization, unitless</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of radiation, Å</td>
</tr>
</tbody>
</table>
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9.0 APPENDICES
Appendix A: Fundamental aspects of binary phase diagrams

One of the fundamental objectives of this Dissertation is to understand the influence of nanostructuring on the magnetostructural response of FeRh-based compounds. In this work nanocomposites of FeRh were synthesized via the rapid-solidification (melt-spinning) technique. In determining which system is amenable for production of nanocomposites using this synthesis method, features of the phase diagram play an important role. An overview of fundamental aspects regarding phase diagrams of binary alloys, as relevant to this study, is presented in the following paragraphs.

By definition, phase diagrams represent the thermodynamic phase equilibria of multicomponent systems and reveal useful insights into fundamental material aspects regarding the processing and reactions of materials. Phase diagrams and the systems they describe are often classified and named for the number (in Latin) of components in the system. For example: An univariant phase diagram consists of one component only (see Figure 1 for example) According to the phase rule, three phases can exist in stable equilibrium only at a single point on a unary diagram:

\[ F = c - p + 2 = 1 - 3 + 2 = 0 \]  \hspace{1cm} (36)

Here, \( F \) is the number of independent variables (called degrees of freedom), \( c \) is the number of components and \( p \) is the number of stable phases in the system. This limitation is illustrated as point O in the hypothetical pressure-temperature (\( P-T \)) diagram shown in Fig. 93. In this diagram, the three states (or phases)--solid, liquid, and gas--- are represented by the three correspondingly labeled fields. Stable equilibrium between any two phases occurs along their mutual boundary, and equilibrium among all three phases occurs at the so-called triple point, O, where the three boundaries intersect. The three curves that issue from the triple point are called
triple curves: line 1, representing the reaction between the solid and the gas phases is the sublimation curve; line 2 is the melting curve; and line 3 is the vaporization curve. The vaporization curve ends at point 4, called a critical point, where the physical distinction between the liquid and gas phases disappears.

Figure 93: Schematic illustration of a pressure-temperature phase diagram of a univariant system. Stable equilibrium between any two phases occurs along their mutual boundary, and equilibrium among all three phases occurs at the so-called triple point, “O”. Lines 1, 2 and 3 represent the sublimation, melting and vaporization curves respectively. The vaporization curve ends at point 4, called a critical point, where the physical distinction between the liquid and gas phases disappears. Figure adapted from [14].

If the system under consideration is comprised of two components, a composition axis must be added to the $P$-$T$ plot, requiring construction of a three-dimensional graph. Most metallurgical problems, however, are concerned only with a fixed pressure of 1 atm and the graph reduces to a two-dimensional plot of temperature and composition ($T$-$X$ diagram). Many binary systems are comprised of components having the same crystal structure, and the components of some of these systems are completely miscible (completely soluble in each other) in the solid form, thus forming a continuous solid solution. When this occurs in a binary system, the phase diagram usually has the general appearance of that shown in Fig. 94. The diagram
consists of two single-phase fields ($L$ and $\alpha$) separated by a two-phase field ($L+\alpha$). The boundary between the liquid field ($L$) and the two-phase field ($L+\alpha$) in Fig. 93 is called the liquidus; that between the two-phase field ($L+\alpha$) and the solid field is the solidus. In general, a liquidus is the locus of points in a phase diagram representing the temperatures at which alloys of the various compositions of the system begin to freeze on cooling or finish melting on heating; a solidus is the locus of points representing the temperatures at which the various alloys finish freezing on cooling or begin melting on heating. The phases in equilibrium across the two-phase field in Fig. 93 (the liquid and solid solutions) are called conjugate phases.

![Phase diagram schematic](image)

**Figure 94.** Schematic illustration of a phase diagram consisting of two single-phase fields ($L$ and $\alpha$) separated by a two-phase field ($L+\alpha$). The boundary between the liquid field ($L$) and the two-phase field ($L+\alpha$) in Fig. 93 is called the liquidus; that between the two-phase field ($L+\alpha$) and the solid field is the solidus Figure adapted from Reference [14].

If the solidus and liquidus meet tangentially at some point, a maximum or minimum is produced in the two-phase field, splitting it into two portions as shown in Fig. 95. It also is possible to have a gap in miscibility in a single-phase field; this is shown in Fig. 96. Point $T_c$,
above which phases $\alpha_1$ and $\alpha_2$ become indistinguishable, is a critical point similar to point 4 in Fig. 96. Lines $a-T_c$ and $b-T_c$, called solvus lines, indicate the limits of solubility of component B in A and A in B, respectively. The configurations of these and all other phase diagrams depend on the thermodynamics of the system.

![Figure 95](image1.png)

**Figure 95.** Schematic binary phase diagrams with solid-state miscibility where the liquidus between the liquid field ($L$) and the two-phase field ($L+\alpha$) shows a maximum (a) and a minimum (b). Figure adapted from [10].

![Figure 96](image2.png)

**Figure 96.** Schematic binary phase diagram with a minimum in the liquidus and a miscibility gap in the solid state. Here, the point $T_c$ marks the critical temperature above which phases $\alpha_1$ and $\alpha_2$ become indistinguishable. Figure adapted from [10].
As applicable to this work, it is important to note that while Fe and Rh are completely miscible (see phase diagram of the Fe-Rh system in Figure 8), these compounds have very limited solid-solubility in Cu (see phase diagram of the Cu-Fe and the Cu-Rh system in Figure 23). It was thus hypothesized rapid solidification processing and subsequent annealing of an arc-melted precursor alloy of composition, \((\text{FeRh})_5\text{Cu}_{95}\) may result in formation of a phase-separated nanocomposite system consisting of non-interacting FeRh nanoprecipitates embedded in a Cu matrix. Results outlined in Section 4.1 confirm this hypothesis.
Appendix B: Experimental protocol for measuring the magnetocaloric effect (MCE) in magnetostructural materials systems.

In magnetostructural systems interesting functional effects are observed in the vicinity of the magnetostructural phase transition. Three classes of magnetostructural materials have emerged during the last two decades with much promise for technological applications [1]. These are: (1) colossal magnetoresistance materials; (2) magnetocaloric materials and (3) magnetic shape memory alloys. In this Dissertation, the giant magnetocaloric effect (GMCE) is of specific interest. By definition, the magnetocaloric effect is a magneto-thermodynamic phenomenon in which a change in temperature of a magnetic material is caused by exposing the material to a changing magnetic field. In this Section, a brief overview of the figures of merit of a magnetocaloric material is provided first, followed by a description of the experimental protocols used for measuring the magnetocaloric behavior of first-order magnetostructural systems.

(a) Figures of merit of a magnetocaloric material

To characterize a magnetocaloric material, there are several relevant parameters that need to be experimentally determined. The most intuitive one is the adiabatic temperature change, $\Delta T_{ad}$, which is the temperature change of the material when adiabatically magnetized/demagnetized. Less obvious, but easier to determine experimentally is the magnetic entropy change ($\Delta S_{mag}$) of the system. As temperature changes in a magnetocaloric material are due to changes in the order of magnetic moments, it is intuitively understood that materials with large $\Delta S_{mag}$ values are likely to be good candidates for magnetic refrigerants. From equations (32) and (33) it is evident that both magnitudes are related to the dependence of magnetization on temperature $\left( \frac{\partial M}{\partial T} \right)$ and the specific heat capacity of the sample at constant pressure ($C_p$):
\[
\Delta T_{ad} = \int_0^{H_{\text{max}}} \frac{T}{C_p} \left( \frac{\partial M}{\partial T} \right)_H dH \tag{37}
\]

and

\[
\Delta S_{\text{mag}} = \int_0^{H_{\text{max}}} \left( \frac{\partial M}{\partial T} \right)_H dH \tag{38}
\]

where \( H_{\text{max}} \) is the maximum applied field. Usually \( C_p \) is approximated in the literature as field independent and, therefore, Equation 38 may be replaced by:

\[
\Delta T_{ad} \approx \frac{T \Delta S_{\text{mag}}}{C_p} \tag{39}
\]

It is important to note that for first-order phase transitions, \( C_p \) exhibits a divergence at the transition temperature. This divergence is either strongly smeared out or the \( C_p \) peak is shifted to different temperatures by application of magnetic field. As a consequence, Equation (14) is not valid for determining the \( \Delta T_{ad} \) of magnetostructural systems. Another relevant parameter for evaluating the performance of a magnetocaloric system is its refrigerant capacity (\( RC \)). This parameter is a measure of the amount of heat that can be transferred between the cold and hot reservoirs in one ideal refrigerant cycle [155]. Typically, \( RC \) at a particular applied magnetic field (\( H_{\text{app}} \)) is estimated from the magnetic entropy curves (\( \Delta S_{\text{mag}} \) vs. \( T \) plot) of the material system using the following equation (See Figure 97 for example):

\[
RC(H_{\text{app}}) = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S_{\text{mag}}(T, H_{\text{app}}) dT \tag{40}
\]

Here, the temperatures of the reservoirs, \( T_{\text{hot}} \) and \( T_{\text{cold}} \), correspond to the extreme temperature ends of the full width at half maximum (\( \delta T_{\text{FWHM}} \)) of the peak \( \Delta S_{\text{mag}} \). Before comparing the RC of different materials, it is essential to subtract the energy losses that cause the material to heat up, such as hysteresis losses [164].
(b) Experimental methods for evaluating the magnetocaloric effect

Conceptually, the most straightforward procedure for characterizing a magnetocaloric material is to adiabatically isolate a sample, place a temperature sensor on it, and record the temperature change of the sample when the magnetic field is swept. In this way, $\Delta T_{ad}(H)$ curves would be recorded as a function of the material’s temperature [23-25]. However, indirect measurements of the magnetocaloric effect of magnetic materials systems are much simpler to perform, as they involve readily available experimental devices, such as magnetometers and calorimeters. Perhaps the most common indirect characterization technique is to measure the isothermal field-dependent magnetization curves and then use Maxwell’s equation to calculate $\Delta S_{mag}$ (See Figure 98(a) for example using a single-crystal of Gd). Magnetization measurements are especially suitable for characterizing the MCE of samples with small mass. Another alternative method is to measure the temperature dependence of the specific heat for different values of the applied field (See Figure 98(b) for an example using a single-crystal of Gd).
the definition of the mathematical definition of entropy, isofield curves of $S$ as a function of $T$ can be obtained:

$$ S (T, H) = \int \frac{C_p(H)}{T} dT $$  \hspace{1cm} (41)

The magnetic entropy change can be calculated as the isothermal difference between two isofield curves, and the adiabatic temperature change can be calculated as the isentropic difference using the following Equation 14. A comparison of the results provided by the different measurement procedures can be found in Reference [22].

![Figure 98](image)

Figure 98. (a) Field-dependant magnetization isotherms in single-crystal Gd in the temperature range 221-324 K. (b) The heat capacity of a Gd single crystal measured in 0 and 5T applied fields. The magnetic field vector was applied parallel to the [0001] direction in the Gd single crystal. Figure adapted from [22].

Although Equation 33, which is the integral version of one of the Maxwell relations, is extremely helpful in calculating the magnetic entropy change of MCMs using simple magnetic measurements, its limitations should be considered before applying it [39]. Otherwise, spurious results may occur, with calculated $\Delta s_{mag}^{peak}$ values one order of magnitude larger than the actual values [20, 21, 166]. To understand the main reason for occurrence of this specious result, it is
important to realize the intrinsic difference between first-and second-order phase transitions (FOPT and SOPT, respectively). In SOPT’s, there is a continuous change from the low-temperature phase to the high-temperature phase, without there being a temperature range in which both phases coexist. FOPTs, however, involve a latent heat (absorbed or released without a change in temperature) and a coexistence of phases, which plays an important role in the calculation of the magnetic entropy change using Equation 33. Typically in FOPT materials such as Gd₅(SiGe)₄, La₁₋ₓPrₓFe₁₁₋ₓSi₁.₅ or MnAs, there is a field-induced magnetic transition whose critical field depends upon the temperature [34]. At a certain critical temperature, a curious step-like behavior is observed in many first-order magnetostructural materials (an example for the compounds, La₁₋ₓPrₓFe₁₁₋ₓSi₁.₅, is shown in Figure 99). When $\Delta S_{mag}$ is calculated from isothermal magnetic measurements, a spike is typically obtained at precisely the same temperature where the “step-like behavior” is noted. This spike is recognized as an artifact of the magnetic measurement technique and it is important to realize that it is never observed when $\Delta S_{mag}$ is determined from calorimetry measurements (See Figure 100 for example). Many experimental protocols have been suggested in literature to correct for this false spike [34]. Here a method developed by Liu et al. is described [157].
Figure 99. Magnetization isotherms of La$_{1-x}$Pr$_x$Fe$_{11.5}$Si$_{1.5}$ (x=0.3 and 0.4 respectively) measured in the field increase process. A spurious spike is observed at $T=184$ K and 181 K for $x=0.3$ and 0.4, respectively. The hatched region here marks the area that contributes to entropy change. Numbers in the figure indicate the temperature in units of kelvin. Figure taken from [156].

Figure 100: Temperature-dependant entropy changes in the magnetostructural system, La$_{0.7}$Pr$_{0.3}$Fe$_{11.5}$Si$_{1.5}$ calculated from magnetometry and calorimetry methods. The spike observed in the $\Delta S_{mag}$ value in the magnetic data is an artifact of the measurement technique. Figure adapted from [157].
As a starting point to explain Liu et al's analytical technique, a schematic diagram of the isothermal field-dependant magnetization curves in a materials system showing idealized stepwise magnetic behavior is shown in Figure 101. Here, the area surrounded by the two $M$-$H$ curves at $T_1$ and $T_2$ are denoted as $\Sigma_1$ and $\Sigma_2$, respectively. The Maxwell relation here can be expressed as:

$$\Delta S_{mag} \left( \frac{T_1 - T_2}{2} \right) = \frac{\Sigma_1 + \Sigma_2}{T_1 - T_2}$$

(42)

Considering the fact that the field-induced metamagnetic transition takes place only partially at $T_1$, it is reasonable to state that only $\Sigma_1$ contributes to $\Delta S$ of the sample. Thus Equation (37) can be modified as:

$$\Delta S_{mag} \left( \frac{T_1 - T_2}{2} \right) = \frac{\Sigma_1}{T_1 - T_2}$$

(43)

Figure 101. Schematic diagram showing the calculation of entropy change when stepwise magnetic behaviors occur. Figure adapted from [157].

It is obvious from Liu et al's study on the magnetic compound, La$_{1-x}$Pr$_x$Fe$_{11.5}$Si$_{1.5}$, that spurious spikes in the magnetic entropy curves of first-order magnetostructural compounds is due to the
inadequate inclusion of $\Sigma_2$ in the calculation. This method has also been used to determine magnetic entropy changes of other first-order magnetocaloric compounds, including MnAs and Mn$_{1-x}$Fe$_x$As (see Figure 102 for example). It is important to note that in this Dissertation this experimental protocol has been employed to calculate the magnetic entropy curves of FeRh-based compounds (see Section 4.4).

![Figure 102. Entropy changes of MnAs under a pressure of 0.18 GPa, as determined by Reference [152].Inset plot shows the magnetization isotherms measured under the pressure of 0.18 GPa. Solid symbols represent the results calculated by the Maxwell relation. The spike observed in the magnetic entropy curve occurs at the temperature where a step-like behavior is noted in the magnetization isotherms. The magnetic entropy curve was corrected using the experimental protocol of Liu et al. [157]. Open symbols shown here are the contributions from the metamagnetic transition only.](image-url)
Appendix C: Description of the Slater-Pauling curve in terms of the rigid band structure model

In solid-state physics, the band theory describes the electronic structure of solids. It has been used to explain many physical properties of solids, such as electrical resistivity and optical absorption, and it essentially forms the foundation of the understanding of all solid-state devices (transistors, solar cells, etc.). When the band theory is applied specifically to magnetic systems, it is sometimes called the collective-electron theory. This application of band theory was first made in 1933 – 1936 by E. C. Stoner and N. F. Mott in the United Kingdom and by J. C. Slater in the United States. As a starting point, for understanding band theory it is essential to review the electronic structure of free atoms, ie. atoms located at large distances from one another, as in a monoatomic gas. In free atoms, the electrons occupy sharply defined energy levels in accordance with the Pauli exclusion principle which states that each energy level in an atom can contain a maximum of two electrons, and they must have opposite spin. Table 15 lists the various energy levels and the number of electrons each can hold in terms of x-ray notation (K, L,...) and quantum-mechanical notation (1s, 2s,...). The 2p shell is actually composed of two sub-shells of the same energy, each capable of holding two electrons. The 3 shell has a as a similar kind of substructure with 5 sub-shells and a total capacity of 10 electrons.

Table 15. Summary of atomic energy levels

<table>
<thead>
<tr>
<th>Shell</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subshell</td>
<td>1s</td>
<td>2s</td>
<td>2p</td>
<td>3s 3p 3d 4s</td>
</tr>
<tr>
<td>Electron capacity</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2 6 10 2</td>
</tr>
</tbody>
</table>
The filling up of energy levels proceeds regularly across the periodic table in the elements from hydrogen to argon, which has 18 electrons. At this point all levels up to and including the $3p$ are filled. As we go to heavier elements, however, irregularities are found in the way that the $3d$ and $4s$ levels are filled, because these two have nearly the same energy and they shift their relative positions almost from atom to atom. The transition elements, in which an incomplete $3d$ shell is present, are of interest in this Dissertation.

When atoms are brought close together to form a solid, the positions of the energy levels are profoundly modified. Suppose that two atoms of Fe approach each other from a large distance. When they are well separated, their $1s$ levels, each containing two electrons, have exactly the same energy. When they approach so closely that their electron clouds begin to overlap, the Pauli principle now applies to the two atoms as a unit and prevents them from having a single $1s$ level containing four electrons; instead, the $1s$ level must split into two levels with two electrons in each. Similarly, when $N$ atoms come together to form a solid, each level of the free atom must split into $N$ levels, because the Pauli principle now applies to the whole group of $N$ atoms. There are a great many energy levels in a band, even for a small bit of crystal. For example, 55.85 g of iron (the gram atomic weight) contain $6.02 \times 10^{23}$ atoms (Avogadro's number). Thus 1 mg of iron contains about $10^{19}$ atoms, and the Pauli principle therefore requires that each separate energy level in the free atom split into about $10^{19}$ levels in a 1 mg crystal. This means that the levels in a band are so closely spaced as to constitute almost a continuum of allowed energy. It is therefore easiest to visualize bands as a function of its density of states (DOS). The product of the density $N(E)$ and any given energy range gives the number of energy levels in that range; thus $N(E)dE$ is the number of levels lying between the energies $E$ and $E+dE$. 
An important and difficult problem of the band theory is to calculate the “shape” of energy bands, i.e., the form of the \( N(E) \) vs. \( E \) curve for the band. The result of one such calculation, for the 3\( d \) band of nickel, is shown in Fig. 103.

![Density of states diagram](image)

**Figure 103.** Density of states diagram (i.e. \( N(E) \) vs. \( E \) plot) in the 3\( d \) band of nickel. Figure taken from [113].

Since the 3\( d \) and 4\( s \) bands overlap in energy, it is convenient to draw the responding density curves side by side, as in Fig. 104. Here the density of 3\( d \) levels increases outward to the left, and that of 4\( s \) levels outward to the right. The density of 3\( d \) levels is far greater than that of 4\( s \) levels, because there are five 3\( d \) levels per atom, with a capacity of 10 electrons, whereas there is only one 4\( s \) level, with a capacity of two electrons, as noted in Table 15. The area under each \( N(E) \) vs. \( E \) curve is equal to the total number of levels in the band. This figure forms the basis for understanding the electronic structure of metallic systems. *The rigid-band model which is of interest in this section makes a first-approximation assumption that the shape of the bands of transition-metals does not change from one element to another.*
Figure 104. Schematic representation of the density of energy levels of the 3d and 4s electrons in 3d transition elements. Figure taken from [113].

It is important to note that the $N(E)$ curves show the density of available levels. The extent to which these levels are occupied by electrons depends on the number of (3d and 4s) electrons in the atom. The 3d band can hold a total of 10 electrons per atom, but in the transition elements it is never completely full. The extent to which it is filled in several metals is shown by dashed lines in Fig. 105. The topmost filled level for any metal is called the Fermi level. Nickel has a total of 10 ($3d + 4s$) electrons, in the solid or the free atom, and therefore its Fermi level is drawn just near the top of the 3d zone. Cu has one more electron and its 3d zone is therefore full. In Zn both the 3d and 4s zones are full.
Filled energy levels cannot contribute to the atomic moment and this situation is shown in Figure 104(a), where a band of levels, imagined to consist of two half bands, contains an equal number of spin-up and spin-down electrons. If one of the electrons reverses its spin, there is a spin imbalance, as shown in Figure 104(b). In the Stoner model of ferromagnetism, this spin imbalance is attributed to exchange interactions. The ferromagnetism of Fe, Co, and Ni is due to spin unbalance in the $3d$ band. The $4s$ electrons are assumed to make no contribution. The density of levels in the $4s$ band is low, which means that the levels themselves are widely spaced. Since the $3d$ band can hold five electrons with spin up and five with spin down, the maximum unbalance, i.e., the saturation magnetization, is achieved when one half-band is full of five electrons. Suppose $n$ is the number of $3d$ and $4s$ electrons per atom, $n_d$ is the number of $d$ electrons per atom and $n- n_d$ is the number of $s$ electrons. At saturation, five $3d$ electrons have spin up and $(n_d-5)$ have spin down. The magnetic moment per atom is therefore:

$$\mu_H = 5 - (n_d-5) \mu_B = (10 - n_d) \mu_B \quad (44)$$
This equation also shows that the maximum spin unbalance is equal to the number of unfilled electron states in the $3d$ band. By alloying one can achieve non-integral values and, in this way, Equation [44] is applicable for a wide range of solid solutions. This result is shown in Fig. 106 and it is generally called the Slater –Pauling curve.

![Figure 106. The Slater-Pauling model showing moment per atom (in Bohr magnetons) for transition metal based compounds as a function of valence electron concentration or alloy composition. Figure taken from [113].](image)

It is important to note that for alloys, say for a composition $A_{1-x}B_x$, the number of $d$ electrons in the system alloy $A_{1-x}B_x$ is given by:

$$n_d^{\text{alloy}} = (1 - x)n_d^A + xn_d^B \quad (45)$$

If the atomic number of species B differs from that of A by $\Delta Z$, then $n_d^B \approx n_d^A + \Delta Z$. Thus,

$$n_d^{\text{alloy}} \approx (1 - x)n_d^A + x(n_d^A + \Delta Z) = n_d^A + x\Delta Z \quad (46)$$

When this result is used in place of $n_d$ in Equation (4), the alloy moment is given by:

$$\mu_m^{\text{alloy}} = (10 - n_d^A - x\Delta Z)\mu_B \quad (47)$$

Noting that $10 - n_d^A = \mu_{\text{host}}$.
Basically Equation (48) implies that the magnetic moment per average atom in a strong ferromagnetic alloy, \( A_{1-x}B_x \) differs from that of the host by an amount proportional to the atomic number difference of B relative to A. For alloys such as Fe\(_{1-x}\)Cr\(_x\) located on the left-hand side of the Slater Pauling curve, the spin-up and spin-down bands are both partially empty and \( \mu_m \) decreases with decreasing \( n_d \). These alloys are thus referred to as weak ferromagnets. It is important to note that the rigid-band model is not applicable for weak ferromagnetic alloys because it is not simple to identify the band into which the impurity electrons go. The shortcomings of the rigid-band model can be accounted for by more robust models such as the virtual bound-state model or the split-band model. Alloys to the right of the Slater-Pauling model with valence electron concentrations greater than 8.3 are essentially strong ferromagnets.

As applicable to this dissertation, it is critical to note that FeRh and its ternary variants are strong ferromagnets with valence band concentrations ranging from 8.4-8.6. Since this alloy is comprised of a 3d element and a 4d element, the Slater-Pauling model cannot be directly applied to it. However, the unmistakable resemblance between the generalized magnetostructural transition temperature \( (T_t) \) vs. valence electrons per atom \( (e_v/atom) \) curve obtained in this work for FeRh-based ternary alloys (Figure 62) and the Slater-Pauling curve (shown above) allows a direct conceptual correspondence to be drawn.

\[
\mu_m^{\text{alloy}} = \mu_{\text{host}} - x\Delta Z\mu_B
\]