Towards Rare-Earth-Free Permanent Magnets: Exchange Bias In Binary Mn-based Alloys

A Thesis Presented

by

Joshua Leland Marion

to

The Department of Chemical Engineering

In partial fulfillment of the requirements for the degree of

Master of Science

In the field of

Chemical Engineering

Northeastern University

Boston, Massachusetts

March 13, 2013
ABSTRACT

Quantum-mechanical exchange interactions between phases in ferromagnetic/antiferromagnetic (FM/AF) magnetic nanocomposite systems can result in useful effects such as exchange bias ($H_{ex}$) and remanence enhancement. These effects are more pronounced in nanostructured systems than in their coarse-grained counterparts due to improved interphase contact and can be developed to create good permanent magnetic behavior, but are currently poorly understood in bulk three-dimensional systems. To achieve this goal, factors such as the magnetic and structural phase identity, chemistry, size, shape, and character are investigated. To this end, synthesis, characterization and analysis of the magnetic and structural properties of nanocomposites are carried out on MnX (X = Cu, Al) alloys comprised of nanostructured FM and AF phases. It is recommended for future work that Fe be added to augment the FM response of the nanostructured MnX alloys.

$Cu_{30}Mn_{70}$ and $Al_{45}Mn_{55}$ ribbons are fabricated using the nonequilibrium technique of rapid solidification via melt-spinning to access and retain metastable nanostructured states, then subject to post-synthesis processing techniques – thermal annealing and cryogenic milling – to investigate the effects of structural modifications on the magnetic response. X-ray diffraction (XRD) analyses of the crystal structure show the as-quenched ribbons consist of two majority crystallographic phases with slightly different lattice dimensions. Superconducting quantum interference device (SQUID) magnetometry reveals prominent hysteresis shifts of $\sim$10-13 kOe at $T = 10$ K, attributed to the $H_{ex}$ effect. These data suggest that nanoscopic disproportionation of local Mn content causes a structural and corresponding magnetic phase separation into FM Mn-
poor and AF Mn-rich regions; exchange interactions between these regions produce the large low-temperature $H_{c\alpha}$ values observed.

Interestingly, magnetic and calorimetric analyses of $\text{Al}_{45}\text{Mn}_{55}$ melt-spun ribbons also revealed the onset of the massive transformation of the parent hexagonal $\varepsilon$-$\text{AlMn}$ phase to the tetragonal $L1_0$-type $\tau$-$\text{AlMn}$ phase, which reportedly exhibits robust permanent magnetic character due to high magnetocrystalline anisotropy, after the ribbons are annealed for 30 minutes at $\sim275$ °C, signifying a nearly 100 °C reduction in the transformation temperature over previous reports. A reduction of this magnitude in the transformation temperature may have a substantial impact on the fabrication and engineering of advanced RE-free permanent magnetic materials.
ACKNOWLEDGEMENTS

I would first like to gratefully acknowledge the input, support, and patience of my thesis advisor, Prof. Laura H. Lewis. Her academic and personal insights and advice will surely be invaluable to my life and career for years to come. I am thankful to my other thesis committee members, Prof. Teiichi Ando and Prof. Vincent Harris, for taking time out of their busy schedules to provide useful insights when needed. I want to thank Dr. Félix Jiménez-Villacorta for his sense of humor and friendship, his professional expertise, and his close assistance with my research. I am also grateful to each of my current and former lab members – Radhika Barua, Nina Bordeaux, Dr. John Boyle, Tom Dusseault, Piers Echols-Jones, Pegah Hosseinpour, Dr. Barbara Kaeswurm, Melissa Loving, Nathan Mahlmeister, Ian McDonald, Dillon McDowell, Ana María Montes Arango, Dr. John Oldham, Tara Sepehrifar, Bradley West, and Mehdi Zamanpour – for their helpful conversations and friendship throughout my time in 476 Snell Engineering. I would also like to thank Rob Eagan for all of the time and technical help as we continually received new equipment, Dr. Don Heiman for his help with SQUID magnetometry, and Bill Fowle for his assistance with electron microscopy. I am grateful to Dr. Matthew Willard and Dr. Maria Daniil at the Naval Research Laboratory for their assistance with the melt-spinning process. I want to extend special acknowledgements to the Northeastern Department of Chemical Engineering for the opportunity to advance my education and personal development, and to the Office of Naval Research for the funding to be able to do so (grant #N00014-10-1-0553).

Even though words fail to express the true depth of my appreciation, I would also like to acknowledge my entire family and other loved ones for the unending love,
encouragement, and unwavering support they have given to me throughout my academic career, without which I would most definitely not be where I am today. To my future mother- and father-in-law Patricia and Matt: I’ll never be able to thank the two of you enough for all of your sacrifices, for taking me in, but most of all for so wholeheartedly accepting me as a member of your family. To my mother Colleen, my brother Luke, and my father Jay: everything I am today and everything I will become tomorrow was shaped by you three and all the things you’ve taught me, and for that I’m eternally grateful. Finally, I want to thank my wonderful fiancée Emily for her incredible love and devotion. Our future together keeps me going, inspires and motivates me, and puts the smile on my face every day – all of this is for you.
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1.0 INTRODUCTION

Advanced permanent magnets are materials used to convert mechanical-to-electrical energy (and vice-versa) in many critical alternative energy, consumer electronics, and military applications due to their large maximum energy product \((BH)_{\text{max}}\) values, which describe their magnetic energy storage [1-3]. Rare-earth elements (REs) such as Sm, Nd, and Dy are currently the principle components of strong permanent magnets because of the high magnetocrystalline anisotropy they contribute, which conveys to the material a high resistance to demagnetization, or magnetic coercivity \((H_c)\). Recent socioeconomic pressures associated with global RE supplies, however, have made it necessary to explore routes to the development of more economically-viable RE-free alternative permanent magnetic materials [4].

One possible route to the development of RE-free permanent magnets is through the investigation and engineering of exchange-biased magnetic nanocomposite systems. The exchange bias \((H_{\text{ex}})\) effect, the uniaxial shift of the major magnetic hysteresis loop along the applied field \((H)\) axis, is conferred by quantum-mechanical exchange interactions between nanostructured ferromagnetic (FM, exhibiting parallel electron spin magnetic moments) and antiferromagnetic (AF, exhibiting antiparallel electron spin magnetic moments) phases [5, 6]. These FM/AF exchange interactions result in a unidirectional exchange anisotropy that causes the \(H_{\text{ex}}\) shift, which effectively augments the material’s intrinsic coercivity \((H_{\text{ci}})\) and magnetic remanence \((M_r)\) to yield enhanced values of the maximum energy product \((BH)_{\text{max}}\), the figure of merit in permanent magnets. The \(H_{\text{ex}}\) effect becomes increasingly significant as the material’s grain or
crystallite size descends to the nanoscale due to improved interphase contact [1, 7, 8], and can be developed to create good permanent magnetic behavior.

However, the exchange bias and remanence enhancement phenomena are poorly understood, especially in bulk three-dimensional FM/AF magnetic nanocomposite systems. The goal of this thesis research is to clarify the conditions controlling $H_{ex}$ and $M_r$ enhancement in nanostructured magnetic materials comprised of Mn-based metallic compounds. To achieve this goal, factors such as the magnetic and structural phase identity, chemistry, size, shape, orientation, and parameters that control the magnetization stability must be investigated; elucidation of these phenomena is anticipated to enable tailoring of the functional magnetic response of the material. To this end, synthesis, characterization and analysis of the magnetic and structural properties of nanocomposites has been out on Mn-based metallic magnetic systems comprised of nanostructured FM and AF phases (i.e. Mn-rich Cu-Mn and near-equatomic Al-Mn [9-14]). At the later stages of this research, Fe will be added to augment the FM response of the nanostructured Mn-based alloys. In this manner it is anticipated that both the magnetization and the coercivity of the Mn-based alloys may be manipulated, thus contributing to the development of novel permanent magnet materials with zero rare-earth content.

This thesis work represents initial steps towards fulfillment of the overarching research goal to elucidate the underpinnings of the $H_{ex}$ phenomenon in bulk FM/AF nanocomposite systems, using Fe as a model FM component and MnX ($X = Cu, Al, etc.$) alloys as model AF components. Two MnX ($X = Cu, Al, etc.$) metallic magnetic systems of composition Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$ have been synthesized using the non-equilibrium
technique of rapid solidification via melt spinning to access and retain metastable nanostructured states. Isochronal heat treatment at low-to-moderate annealing temperatures ($T_{\text{anneal}}$) is used to induce small progressive changes in the structure, and the effect of each material’s structural evolution on its magnetic response has been investigated and analyzed. X-ray diffraction (XRD) measurements were carried out to identify the crystallographic phase or phases present and to determine the chemistry and size of each phase. The MnX alloys’ microstructural character and volume-averaged chemical composition have been examined by scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX), respectively. The magnetic behavior of each alloy was characterized as a function of temperature ($T$) and applied field ($H$) using superconducting quantum interference device (SQUID) magnetometry. The thermal character of any observed phase transformations that altered the material’s structure (and thereby its magnetic response) which may have occurred as a result of heat treatment has been investigated using differential scanning calorimetry (DSC).

Magnetic measurements obtained from as-quenched Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$ melt-spun ribbons revealed that hysteresis loops collected at $T = 10$ K exhibit unprecedented large $H_{\text{ex}}$ shifts of 10-13 kOe, high $H_{\text{ci}}$ values of 11-19 kOe, and low saturation magnetization ($M_s$) values of 0.2-2 emu/g. In both alloys, XRD measurements showed the coexistence of two distinct crystallographic phases with identical chemically-disordered crystal structures but with slightly different unit cell dimensions. Heat treatment of the melt-spun alloys for 30 minutes at $150 \degree C \leq T_{\text{anneal}} \leq 300 \degree C$ caused homogenization of the unit cell lattice parameters and resulted in slight increases in the saturation magnetization ($M_s$) and small decreases in $H_{\text{ex}}$ and $H_{\text{ci}}$. Additionally, heat
treatment of rapidly-solidified Al_{45}Mn_{55} at $T_{\text{anneal}} \geq 275$ °C was found to cause the growth of a phase with strong ferromagnetic (FM) character at room temperature.

Interpretations of these data suggest that nanoscopic fluctuations in the alloys’ local Mn content cause a structural and corresponding magnetic phase separation into FM and antiferromagnetic (AF) regions. Quantum-mechanical exchange interactions between these regions produce the large $H_{\text{ex}}$ values observed in the as-spun state at low temperature. The increases in $M_s$ and simultaneous small decreases in $H_{\text{ex}}$ and $H_{\text{ci}}$ point to a decrease in AF character upon annealing the melt-spun alloys. The FM phase that began to nucleate upon annealing treatment of the melt-spun Al_{45}Mn_{55} ribbons at $T_{\text{anneal}} \geq 275$ °C has been identified as the face-centered-tetragonal $L1_0$-ordered $\tau$-AlMn phase, which is reported to exhibit robust permanent magnetic character [1-3, 10-12, 15-27]. Nucleation of the $\tau$-AlMn phase at 275 °C is nearly 100 °C lower than previously reported values for the nucleation of the $\tau$-phase, which ranged from between 350 °C and 800 °C [11, 12, 17-21, 23, 27-30]. The reduced nucleation temperature is ascribed to an enhanced density of heterogeneous nucleation sites conveyed by rapid solidification processing, in contrast to other reports which mostly focused on oil- and water-quenched alloys, or mechanically-milled powders.

Once the magnetic and structural character of the MnX alloys has been thoroughly investigated and analyzed, future work should focus on augmenting the FM response by implanting the Mn-based nanostructured alloys in a FM Fe-rich matrix, which is anticipated to enhance $M_s$ and the maximum energy product ($BH_{\text{max}}$). It is recommended that cryogenic mechanical milling (cryomilling) be used to promote intimate FM/AF interphase contact and implant the nanostructured MnX alloys in the Fe
matrix. Correlations between the magnetism and structural character in these new, more complex FM/AF nanocomposites should be developed to enable engineering of the permanent magnetic character.

Section 2.0 of this thesis work provides the reader with a fundamental background of basic concepts and important terminology in magnetism and crystallography. Section 3.0 gives an overview of nanomagnetism from a total energy standpoint, then reviews the literature on bulk three-dimensional nanocomposite magnetic materials, including exchange-spring magnets and exchange-biased magnets. Section 4.0 contains a discussion of the experimental techniques and apparatus used to characterize the magnetic, structural, and thermal attributes of the alloys. Section 5.0 provides the rationale for specific experiments and outlines the investigations will be carried out to investigate the magnetic, structural, and thermal character of the MnX alloys studied in this thesis work. Section 6.0 presents the reader with results of the characterization experiments outlined in Section 5.0 and gives brief analyses of the data, and Section 7.0 contains discussions and interpretations of the data. Finally, Section 8.0 draws conclusions based on the results and recommends work for future researchers.
2.0 BACKGROUND INFORMATION

This thesis research aims to elucidate the conditions controlling exchange bias and magnetic remanence enhancement in nanostructured bulk magnetic systems comprised of ferromagnetic (FM) and antiferromagnetic (AF) phases. Since a material’s magnetic response is intimately related to its structure, development of a fundamental knowledge of crystallography, magnetism, and the important terminology and concepts associated with both subjects is critical. The sections of this Chapter will develop a basic foundation in the relevant principles of crystallography and magnetism, including nomenclature and definitions of important terms and concepts. Key concepts and terminology in crystallography will be outlined Section 2.1, while Section 2.2 will focus on defining some of the fundamental principles of magnetism and magnetic properties.

2.1 Important concepts and terminology in crystallography

A crystalline material is defined as one which exhibits long-range order, wherein the atoms or molecules are arranged in a regular three-dimensional periodic pattern [31]. The smallest repeated unit in the three-dimensional ordered array is the crystallographic unit cell, which is then classified based on its size, shape, and atomic arrangement. The general shape of unit cells is discussed in Section 2.1.1. Section 2.1.2 focuses on identifying specific surfaces and directions within each unit cell, while Section 2.1.3 details the determination of the size of the unit cell. These characteristics of the crystallographic unit cell can significantly affect many of the important intrinsic magnetic properties of the material, which are defined in Section 2.2.2.
2.1.1 Crystallographic unit cells and the seven different crystal systems

Crystallographic unit cells are the smallest repeated structural units of crystalline materials that, when stacked in three dimensions, form a periodic lattice with long-range order (Figure 1a) [32]. The shape and size of a particular unit cell is described by first selecting a convenient \(xyz\) coordinate system, as illustrated in Figure 1b, where the axes coincide with basis vectors \(a, b,\) and \(c\) along which the unit cell is translated to generate the periodic lattice [33]. The lengths of the basis vectors \(a, b,\) and \(c,\) often called the lattice parameters \((a, b, c)\), define the size of the unit cell, while the angles between them \((\alpha, \beta, \gamma)\) define the unit cell shape [31]. In this thesis work \(a, b,\) and \(c\) coincide with the unit cell edges and the lattice parameters \(a, b,\) and \(c\) are used to denote crystal axes.

![Figure 1](image)

**Figure 1:** a) Representative crystal lattice. b) Generalized crystallographic unit cell.

The unit cell shape is broadly classified under one of the seven different crystal systems: cubic, tetragonal, hexagonal, rhombohedral, orthorhombic, monoclinic, and triclinic [32]. Table 1 shows definitions for the symmetry of each crystal system.
Table 1: Relationships between crystallographic axis lengths and angles between crystallographic axes for each crystal system.

<table>
<thead>
<tr>
<th>Lattice system</th>
<th>Lattice parameter relationships ((a, b, c))</th>
<th>Angular relationships ((\alpha, \beta, \gamma))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>(a = b = c)</td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>(a = b \neq c)</td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>(a = b \neq c)</td>
<td>(\alpha = \beta = 90^\circ \neq \gamma = 60^\circ)</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>(a = b = c)</td>
<td>(\alpha = \beta = \gamma \neq 90^\circ)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>(a \neq b \neq c)</td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(a \neq b \neq c)</td>
<td>(\alpha = \gamma = 90^\circ \neq \beta)</td>
</tr>
<tr>
<td>Triclinic</td>
<td>(a \neq b \neq c)</td>
<td>(\alpha \neq \beta \neq \gamma \neq 90^\circ)</td>
</tr>
</tbody>
</table>

2.1.2 Miller index notation for representation of crystal planes and directions

The \((hkl)\) Miller index notation system is used to identify directions or lattice planes in crystalline materials based on their intersections with the major crystallographic axes [34-36]. The direction vector \([hkl]\) is drawn from the origin of the chosen \(abc\) crystal axis system to the point \((a \cdot h, b \cdot k, c \cdot l)\); the family of equivalent directions is denoted as \(<hkl>\). The crystallographic plane denoted as \((hkl)\) is the surface orthogonal to the vector \([hkl]\), which intercepts the \(a, b,\) and \(c\)-axes at \((a/h, 0, 0), (0, b/k, 0),\) and \((0, 0, c/l)\), respectively (Figure 2); the family of equivalent planes is represented by \{hkl\}. 
Figure 2: $(hkl)$ Miller indices identifying crystallographic planes in a cubic unit cell. Each plane intersects the x, y, and z axes at $(a\cdot h, 0, 0)$, $(0, b\cdot k, 0)$, and $(0, 0, c\cdot l)$ respectively.

2.1.3 Evaluation of lattice plane spacings

The unit cell dimensions $a$, $b$, and $c$ are calculated based on the interplanar spacing ($d$), which depends on the symmetry of the unit cell [32]. The formulae in Table 2 (Eq. (1)-(7)) give the relationships between interplanar spacing and crystal system for the generalized unit cell shown in Figure 1b [34].

2.2 Magnetism definitions and terminology

The magnetic character of a material provides important information about the microscopic ordering of its magnetic moments. Magnetic fields are produced by electric charges in motion [37]. Magnetic materials may be broadly classified as exhibiting diamagnetic order, paramagnetic order, ferromagnetic order, or antiferromagnetic order. The magnetic response is often probed as a function of applied magnetic field ($H$) and temperature ($T$) and is quantified by a variety of metrics which may be either intrinsic and depend only on the crystal structure or atomic arrangement of a specimen or may be extrinsic and also be affected by its microstructure. Important intrinsic magnetic properties include the saturation magnetization ($M_s$) and magnetocrystalline anisotropy,
while extrinsic magnetic properties include the magnetic susceptibility ($\chi$), the coercivity ($H_c$), and shape and exchange anisotropies.

Table 2: Dependence of the interplanar spacing $d$ on unit cell symmetry.

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>$1/d^2 = \cdots$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$\frac{h^2 + k^2 + l^2}{a^2}$ (1)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$\frac{h^2 + k^2 + l^2}{a^2} + \frac{l^2}{c^2}$ (2)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$\frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$ (3)</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$\frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)\cos^2\alpha - \cos\alpha}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$ (4)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$ (5)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$\frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$ (6)</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$\frac{1}{V^2} \left(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{31}hl\right)$ (7)</td>
</tr>
</tbody>
</table>

where: $V$ = unit cell volume, $S_{11} = b^2c^2\sin^2\alpha$, $S_{22} = a^2c^2\sin^2\beta$, $S_{33} = a^2b^2\sin^2\gamma$, $S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma)$, $S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha)$, and $S_{31} = ab^2c(\cos\alpha\cos\gamma - \cos\beta)$.

2.2.1 Origin of the magnetic moment and fundamental magnetic quantities

The magnetic moment is, in the most basic sense, a quantum mechanical phenomenon resulting from the motion of electrons [37, 38]. The magnetic moment is a
vector since it has both magnitude and direction, but the magnitude is aspecific of the amount of material being studied. The magnetization ($M$) is an extrinsic property, equal to the vector sum of the magnetic moments normalized to the specimen quantity (i.e. mass, volume, moles, etc.), which defines the extent of magnetization in a sample of finite size [37, 39].

The response of $M$ to changes in temperature ($T$) or an externally-applied magnetic field ($H$) is studied in several different materials in this thesis work. The magnetic susceptibility ($\chi = M/H$) describes the ease with which $M$ responds to $H$ for a given material. The combination of magnetic flux from the magnetization $M$ of a material and from an applied magnetic field $H$ gives the total magnetic response of the material to an applied field, or the magnetic induction ($B$) (Eq. (8)).

$$B = H + 4\pi M \rho$$

(8)

where:

$B$ = Magnetic induction (G)

$H$ = Applied magnetic field (Oe)

$M$ = Magnetization (emu/g)

$\rho$ = Sample density (g/cm$^3$)

2.2.2 Intrinsic magnetic properties vs. extrinsic magnetic properties

The magnetic properties of a material may be either intrinsic or extrinsic in nature. Extrinsic magnetic properties are those determined by the specimen quantity, microstructure, or geometry, and include the magnetic susceptibility ($\chi$) and the intrinsic coercivity ($H_c$), which defines the resistance of the material to demagnetization [37].
Other extrinsic quantities of interest include the remanent magnetization ($M_r$), or the magnetization upon removal of an applied field, and the exchange bias field ($H_{ex}$), defined as the shift of a magnetic hysteresis loop along the $H$-axis as a result of a unidirectional anisotropy conferred by quantum mechanical exchange interactions between ferromagnetic and antiferromagnetic materials [5]. Intrinsic magnetic properties are independent of the microstructure and geometry of the specimen, but rather are determined only by the crystal structure and atomic arrangement of the material [38]. Intrinsic magnetic properties include the saturation magnetization ($M_s$), the magnetocrystalline anisotropy field ($H_k$), and the ferromagnetic or antiferromagnetic ordering temperature, i.e. the Curie temperature ($T_C$) or the Néel temperature ($T_N$), respectively. Refer to the discussions of magnetization curves in Section 2.2.4, magnetic hysteresis loops in Section 2.2.5, and magnetic anisotropy in Section 2.2.6 for clarifications of the definitions of the intrinsic and extrinsic magnetic properties of interest.

### 2.2.3 Classifications of magnetic ordering

The magnitude of the magnetic susceptibility ($\chi$) may be roughly indicative of whether the material exhibits diamagnetic order, paramagnetic order, ferromagnetic (FM) order, or antiferromagnetic (AF) order. Diamagnetic materials exhibit no permanent net magnetic moment per atom due to lack of unpaired electron spins and repel applied magnetic fields ($H_f$), giving negative values of $\chi$ on the order of $-10^{-6}$-$10^{-5}$ [37]. All materials exhibit some diamagnetic behavior, but the diamagnetic effect is negligible in materials containing unpaired electron spins which can lead to paramagnetism or other types of magnetic ordering. Paramagnetic materials, which possess small positive values
of $\chi$ on the order of $0$-$10^{-3}$, have a net magnetic moment in the presence of an applied field $H$ but return to a demagnetized state when $H$ is removed.

Other materials may exhibit spontaneous FM or AF ordering below a certain material-specific temperature as a result of interactions between electrons on neighboring atoms; above the ordering temperature such materials are paramagnetic. Ferromagnetic materials ($\chi \gg 0$) respond strongly to small changes in $H$ and have large magnetization values below the Curie temperature ($T_C$), as exchange interactions between nearby electrons cause neighboring magnetic moments to align parallel to one another in $H$ [37]. These materials are divided into small regions, known as magnetic domains, that contain several magnetic moments pointed in the same direction which tend to coherently rotate into alignment with $H$ (illustrated in Figure 3) [38]. Several factors, such as the size and shape of the domain and the presence of impurities, defect structures, and grain boundaries may render alignment of a domain’s overall magnetization with an applied field $H$ more difficult [37]. As a result, many FM substances may display magnetic hysteresis and retain a net magnetization after $H$ is removed. Exchange interactions between adjacent atomic moments in antiferromagnetic (AF) materials ($\chi \sim 0$) cause neighboring magnetic moments to align antiparallel and effectively cancel one another out, rendering near-zero magnetization values below the Néel temperature ($T_N$) [37].

![Figure 3: Orientation of $M$ within magnetic domains (a) before and (b) after application of $H$.](image)
2.2.4 Magnetization vs. temperature \((M \text{ vs. } T)\) curves

The magnetic response of a material is often probed as a function of temperature \((T)\) under a constant applied magnetic field \((H)\) to gain insight into the microscopic ordering of its magnetic moments. Figure 4 shows typical magnetic susceptibility \((\chi)\) vs. \(T\) curves for substances exhibiting paramagnetic, ferromagnetic (FM), and antiferromagnetic (AF) order as discussed in Section 2.2.3.

![Diagram showing paramagnetism, ferromagnetism, and antiferromagnetism](image)

**Figure 4**: Typical \(\chi\) vs. \(T\) curves for paramagnetic, ferromagnetic, and antiferromagnetic materials.

The susceptibility \(\chi\) of a FM substance increases sharply as it is cooled through the Curie temperature \((T_C)\), when ferromagnetic ordering becomes energetically favorable and neighboring magnetic moments are able to align spontaneously [37]. The susceptibility of an AF material declines as it is cooled through the Néel temperature \((T_N)\), when antiferromagnetic order becomes energetically favorable and adjacent magnetic moments begin to align antiparallel to one another, conveying reduced magnetization values. For paramagnetic substances or FM or AF materials above the magnetic ordering temperature, \(\chi\) decreases as \(T\) rises because thermal energy causes increasingly violent fluctuations of the magnetic moments which prevent the magnetization from aligning with \(H\). Valuable information about the magnetic properties
of a material may be gathered from the shape of the paramagnetic regions of $\chi$ vs. $T$ curves collected from FM and AF materials.

### 2.2.5 Magnetic hysteresis ($M$ vs. $H$) loops

The magnetization of a material ($M$) may also be measured as a function of applied field ($H$) at constant temperature ($T$) by sweeping the applied field between the positive and negative directions, from $+H$ to $-H$ then back to $+H$, to form a hysteresis loop. A typical hysteresis loop for a ferromagnetic (FM) material is shown in Figure 5.

![Figure 5: Typical hysteresis loop for a ferromagnetic material. Includes normal $B(H)$ loop in black and intrinsic $M(H)$ loop in blue.](image)

All of the magnetic moments in a FM material are aligned parallel with one another in sufficiently large applied fields, bringing the magnetization of the material to the saturation magnetization ($M_s$) value. Reducing the field $H$ lowers $M$ to the magnetic remanence ($M_r$) value at $H = 0$, then to $M = 0$ at the intrinsic coercive field ($H_{ci}$) of the material. The applied field $H$ is swept back up after negative magnetic saturation to form
a full major hysteresis loop; if $H$ is insufficient to induce saturation in either the positive or negative directions the loop is known as a minor hysteresis loop.

2.2.6 Magnetic anisotropy

Magnetic anisotropy is the preference of a material’s magnetization to lie in one or more directions over others [37]. This directional dependence, which often enhances the coercivity of the material, may come from a variety of sources, including the crystal structure, the microstructure, and the intimate mixture of materials with different types of magnetic ordering [1, 37]. Magnetocrystalline anisotropy, an intrinsic effect of the crystal structure and atomic arrangement of the material, causes a specimen to be more easily magnetized along certain crystallographic axes than along others [40]. Figure 6 illustrates the relative ease of magnetization along various crystallographic axes in a typical chemically-disordered face-centered-cubic ($fcc$) unit cell – the lowest energy orientation of the magnetization is along the $<111>$ “easy” axis while the highest energy orientation is along the $<100>$ “hard” axis.

Shape anisotropy is an extrinsic effect of the microstructure and sample geometry. Demagnetization effects from aspherical microstructures or specimen geometries render one or more magnetization directions energetically unfavorable [37, 39]. For a detailed discussion of demagnetization effects, see Section 3.1.1.3 or refer to reference [41].
Figure 6: Various possible axes of magnetization in an fcc unit cell. In this example <111> is the easy axis while <100> is the hard axis.

Exchange anisotropy is an extrinsic phenomenon resulting from quantum mechanical exchange interactions across interfaces between two different magnetic phases [42]. Such interactions may occur between low-coercivity and high-coercivity “soft” and “hard” ferromagnetic (FM) phases or between FM and antiferromagnetic (AF) phases [1, 8, 39]. In the latter case the interfacial moments of the FM become pinned to those of the AF, essentially applying a unidirectional torque which prevents the magnetization of the FM from rotating into alignment with \( H \) [5]. This unidirectional exchange anisotropy causes a characteristic shift of the hysteresis loop along the \( H \)-axis known as the exchange bias (\( H_{\text{ex}} \)) shift (Figure 7) [1, 7]. Exchange-biased materials may exhibit enhanced values of coercivity (\( H_c \)), magnetic remanence (\( M_r \)), and maximum energy product (\( BH \))\textsubscript{\text{max}}, the figure of merit in permanent magnetic materials. For a more detailed review of exchange anisotropy, refer to Section 3.1.1.4.
Figure 7: Effect of exchange anisotropy on hysteresis loop of a FM/AF film bilayer system. For $T_N < T < T_C$, the hysteresis loop is that of the FM component (left). For $T < T_N$, the hysteresis loop is shifted by $H_{ex}$ (right).
3.0 CRITICAL LITERATURE REVIEW

Exchange-biased magnetic nanocomposites are materials composed of ferromagnetic (FM) and antiferromagnetic (AF) components which, when combined at the nanoscale, are anticipated to exploit the beneficial properties of each phase to convey enhanced coercivity ($H_c$), magnetic remanence ($M_r$), and maximum energy product ($BH_{\text{max}}$) values over those of the individual FM or AF components [1, 6, 43]. The goal of this thesis work is to investigate the origins and underpinnings of this exchange bias ($H_{\text{ex}}$) and remanence enhancement phenomenon in bulk FM/AF magnetic nanocomposite systems. To this end, nanostructured metallic MnX (X = Cu, Al, etc.) binary alloys with antiferromagnetic character will be implanted in a ferromagnetic Fe-rich matrix and used as model materials for study. The objectives of this work, outlined in Section 5.2, are then threefold: 1) synthesis, characterization, and understanding of the relationships between the magnetic and structural behaviors of the AF MnX component, 2) control of the structure of the binary MnX alloys on the nano- and microscopic scales, and 3) implantation of the AF MnX alloys into an FM Fe-rich matrix and investigation of the FM/AF exchange coupling.

This study is carried out with a mind towards fundamental research, but the enhanced $BH_{\text{max}}$ values anticipated in these nanocomposite systems render them attractive for potential alternative permanent magnetic material applications. Advanced permanent magnets play a critical role in modern energy technologies due to their ability to convert electrical to mechanical energy and vice-versa [1-3, 8, 44, 45]. Current high-performance permanent magnetic materials contain rare-earth metals such as neodymium (Nd), samarium (Sm), gadolinium (Gd), and dysprosium (Dy), which donate an
extremely high magnetocrystalline anisotropy when alloyed with ferromagnetic transition metals like Fe or Co [1]. The rapidly-escalating demand for rare-earth metals, Dy in particular, due primarily to the flourishing alternative energy and electric vehicle industries recently outstripped the global supply, leading to a nearly order-of-magnitude increase in the price of these strategic elements between 2010-2012 [1, 2]. The issue was compounded by the fact that China, which accounted for ~95% of the international production of rare-earth elements at the time, decided to curtail their rare-earth exportation and mining operations in order to control domestic reserves and pollution problems. The soaring costs have since stabilized somewhat, but the “rare-earth crisis” has made clear the need to develop alternative rare-earth-free permanent magnetic materials [1-4, 46].

The significant magnetocrystalline anisotropy conveyed by the rare-earth metals’ highly-localized 4f electrons has proved difficult, if not impossible, to replace [2]. Options do, however, exist to create permanent magnetic materials which exploit both magnetocrystalline anisotropy and other additional types of magnetic anisotropy (Section 2.2.6) to obtain moderately high coercivity ($H_c$) and maximum energy product ($BH_{\text{max}}$) values. Next-generation high anisotropy permanent magnets currently under investigation include materials with crystallographic phases with high intrinsic magnetocrystalline anisotropy, such as tetragonal $L1_0$-structured Al-Mn or Fe-Ni alloys [16, 17, 21, 47, 48] or multiphasic nanocomposites with exchange spring or exchange bias behavior [1, 7, 10, 49-53]. Whereas a vast majority of work in exchange-biased systems has been carried out on thin films – see the review articles in [5, 6, 43] – this
thesis study will be concentrated on aspects of exchange-biased nanocomposites in the bulk form.

This literature review is divided into two basic sections. Section 3.1 gives a brief synopsis of the effects of nanostructuring on a material’s magnetic properties from a total energy minimization standpoint. Quantum mechanical interatomic exchange interactions and their role in determination of the critical length scale for nanomagnetism, the exchange length \( l_{ex} \), are discussed and explained. An overview of contributions to the magnetic anisotropy energy of nanostructured magnetic materials of particular relevance to this thesis research, including bulk \( (i.e. \) particle volume) effects – magnetocrystalline, shape, and stress anisotropy energies – and surface \( (i.e. \) particle interface) effects – surface and exchange anisotropy energies – is also given. Phenomena that have been observed as a result of the unique energy considerations in nanoscaled magnetic materials, including superparamagnetism, single-domain behavior, and exchange spring or exchange bias behavior, will also be discussed. Section 3.2 provides specific examples of magnetic nanocomposite systems materials which have been reported to exhibit exchange bias phenomena in the literature, in particular MnX \( (X = Cu, Al, etc.) \) and Fe/MnX alloys.

3.1 **Magnetic phenomena in nanostructured materials**

As nanostructured magnetic materials \( (i.e. \) one or more dimension less than 100 nm in size) descend to a size comparable to some critical length scales, the proportion of surface atoms increases dramatically \([54, 55]\). The reduced dimensionality and lowered symmetry experienced by atoms at the surface of a particle may dramatically alter the
magnetic properties of the system [56]. The following sections contain a discussion of the relevant thermodynamics and energy considerations – magnetic anisotropy energy and interatomic exchange energy in particular – which lead to determination of a characteristic length scale of nanoscale magnetic materials, the exchange length $l_{ex}$ (Section 3.1.1). Bulk contributions to the magnetic anisotropy energy barrier such as magnetocrystalline, shape, and magnetoelastic anisotropy energy are discussed, along with surface contributions to the magnetic anisotropy such as surface and exchange anisotropy energies. Section 3.1.2 will examine the manner in which minimization of the total energy leads to several phenomena observed in one- and two-phase nanostructured materials, including single-domain behavior, superparamagnetism and magnetic blocking behavior, exchange-averaging of the magnetic anisotropy energy, exchange-spring magnetic nanocomposites, and exchange-biased magnetic nanocomposites.

3.1.1 Total energy considerations of relevance in nanomagnetism

All systems tend towards a more stable equilibrium or, thermodynamically speaking, they seek to minimize some appropriate thermodynamic potential such as the Gibbs free energy [57]. Maxwell relations for magnetic materials define the Gibbs free energy ($G$) as a function of three independently-variable thermodynamic state variables, including the pressure ($P$), applied magnetic field ($H$), and temperature ($T$) [58]. The change in Gibbs free energy of a magnetic material at a constant pressure ($P$) can be written as Eq. (9) [58].
\[ dG = -\overrightarrow{M} \, d\overrightarrow{H} - S \, dT \]  

where: \( G \) = Gibbs free energy of the material (erg)

\( \overrightarrow{M} \) = Magnetization vector (emu/cm\(^3\))

\( \overrightarrow{H} \) = Applied magnetic field vector (Oe)

\( S \) = Entropy (erg/K)

\( T \) = Temperature (K)

Since all systems tend towards their lowest thermodynamic energy state or thermodynamic equilibrium (i.e. \( dG = 0 \)), the magnitude of \( dG \) from Eq. (9) determines the magnetization response of a material [58]. Energy considerations of particular relevance to this thesis research on nanostructured materials are the interatomic exchange energy (\( E_{\text{exchange}} \)) and magnetic anisotropy energy (\( E_{\text{anisotropy}} \)) [58-60]. The quantum mechanical exchange energy is an atomic-scale phenomenon that determines how the electrons of different atoms interact with one another [61]. Magnetic anisotropy energy is a nano- to micro-scale phenomenon that defines the energy per unit volume required to reorient the magnetization from its lowest-energy configuration to its highest-energy configuration [1]. The magnetic anisotropy energy thereby renders one or more preferential orientations for the magnetization; both the bulk of a material (Section 3.1.1.3) and its surface (Section 3.1.1.4) contribute to the magnetic anisotropy energy, but in different ways [55, 60, 62]. The bulk of the material contributes magnetocrystalline anisotropy energy (\( E_{\text{mc}} \)), shape anisotropy energy (\( E_{\text{shape}} \)), and magnetoelastic or stress anisotropy energy (\( E_{\text{me}} \)). The surface of the material contributes surface anisotropy...
energy \( E_{\text{surface}} \) and may contribute exchange anisotropy energy \( E_{\text{ex}} \). The competition between the magnetic anisotropy energy \( E_{\text{anisotropy}} \) and the interatomic exchange energy \( E_{\text{exchange}} \) determines the critical length scale of nanostructured magnetic materials, the exchange length \( l_{\text{ex}} \) [56, 63].

This portion of the literature review contains a discussion of the exchange length \( l_{\text{ex}} \) (Section 3.1.1.1) and quantum mechanical interatomic exchange energy \( E_{\text{exchange}} \) (Section 3.1.1.2). Section 3.1.1.3 presents an overview of the bulk contributions to the magnetic anisotropy energy \( E_{\text{anisotropy}} \), including the magnetocrystalline anisotropy energy \( E_{\text{mc}} \), shape anisotropy energy \( E_{\text{shape}} \), and magnetoelastic anisotropy energy \( E_{\text{mc}} \). Surface contributions to the magnetic anisotropy energy including surface anisotropy energy \( E_{\text{mc}} \) and exchange anisotropy \( E_{\text{ex}} \) are discussed in Section 3.1.1.4.

### 3.1.1.1 The critical length scale of nanomagnetism, the exchange length \( l_{\text{ex}} \)

The critical length scale of nanomagnetism, the exchange length \( l_{\text{ex}} \) given by Eq. (10), is determined by competition between interatomic exchange energy \( E_{\text{exchange}} \), defined in Section 3.1.1.2) and magnetic anisotropy energy \( E_{\text{anisotropy}} \), defined briefly in Section 2.2.6 and discussed in more detail in Sections 3.1.1.3 and 3.1.1.4) [1, 56, 63, 64]. The exchange length \( l_{\text{ex}} \) – typically on the order of 10 nm for many ferromagnetic materials [56, 65, 66] – is given by Eq. (10) [63, 64].
\[ l_{\text{ex}} = \sqrt{A/K_{\text{eff}}} \tag{10} \]

where: \( l_{\text{ex}} = \) Exchange length (cm)

\( A = \) Exchange stiffness parameter (erg/cm)

\( K_{\text{eff}} = \) Effective magnetic anisotropy constant (erg/cm\(^3\))

The effective uniaxial magnetic anisotropy constant \( K_{\text{eff}} \) determines the magnitude of the energy barrier to reorientation of the magnetization from its lowest-energy orientation to its highest-energy orientation [66, 67]. The exchange stiffness \( A \) – typically on the order of \( 10^{-11} \) J/m for ferromagnetic materials [8] – describes the relative ease of rotating the spins out of parallel or antiparallel alignment, or the relative ease of overcoming the interatomic exchange energy barrier (Section 3.1.1.2) [67]. In this manner, the exchange length \( l_{\text{ex}} \) determines the width of magnetic domain walls (\( \delta_w \)) in ferromagnetic materials; so particles with dimensions slightly larger than \( l_{\text{ex}} \) may consist of a single magnetic domain [1, 8, 64]. Figure 8 illustrates schematically the structure of a magnetic domain wall [67, 68].

In particles with dimensions near the exchange length \( l_{\text{ex}} \), exchange forces overcome the ability of the magnetic anisotropy to hold the magnetization along certain low-energy magnetic “easy” axes and interatomic exchange interactions dominate the magnetic response, permitting the material to exist in a single-domain state [64]. In particles with dimensions far larger than the exchange length \( l_{\text{ex}} \), the orientations of magnetic moments within a particle can vary significantly based on the orientations of the magnetic easy axes, determined by the magnetic anisotropy energy [56].
3.1.1.2 Interatomic exchange interaction energy

The interatomic exchange energy $E_{\text{exchange}}$ is an atomic-scale phenomenon that occurs as a result of the overlap of the electron orbitals of different atoms [1, 39]. For clarification, consider two separate atoms whose electron wavefunctions overlap. The atoms will interact with one another by classic Coulombic repulsive and attractive forces. There will also be an additional force that can be explained by the quantum mechanical Pauli Exclusion Principle, which states that two electrons cannot exist in the same quantum state, i.e. occupy the same space and have the same spin [69, 70]. The electron spins will then be forced to be either parallel or antiparallel to one another in order to minimize $E_{\text{exchange}}$, resulting in an interatomic exchange force. Heisenberg found that the energy of the exchange interaction between two atoms $i$ and $j$ is given by Eq. (11) [69].
\[ E_{\text{exchange}} = -2J_{\text{ex}} \vec{S}_i \cdot \vec{S}_j = -2J_{\text{ex}} S_i S_j \cos \phi \quad (11) \]

where: \( E_{\text{exchange}} \) = Interatomic exchange energy (erg)

\( J_{\text{ex}} \) = Exchange integral (erg)

\( \vec{S}_{i,j} \) = Spin angular momentum vector of atom \( i \) or atom \( j \) (unitless)

\( \phi \) = Angle between the atomic spins (degrees)

and:

\[ h \vec{S}_{i,j} / 2\pi = \text{Spin angular momentum of atom } i \text{ or } j \text{ (erg} \cdot \text{sec)} \]

\( h \) = Planck’s constant (6.626 x 10^{-27} erg \cdot sec)

The magnitude of the exchange integral \( J_{\text{ex}} \) determines whether parallel or antiparallel spin alignment minimizes the exchange energy [69]; the magnitude of \( J_{\text{ex}} \) may be extremely large in ferromagnetic (FM) and antiferromagnetic (AF) materials and often depends on the interatomic spacing. Positive values of \( J_{\text{ex}} \) signal parallel alignment \((\phi = 0^\circ)\) or FM exchange between the two spin moments minimizes \( E_{\text{exchange}} \). Negative values of \( J_{\text{ex}} \) indicate antiparallel alignment \((\phi = 180^\circ)\) or AF exchange coupling minimizes \( E_{\text{exchange}} \) [70, 71]. Since \( E_{\text{exchange}} \) is minimized at either extreme \( \phi = 0^\circ \) or \( \phi = 180^\circ \), interatomic exchange interactions essentially maintain the smoothest possible rotation of electron spin magnetic moments out of parallel or antiparallel alignment.

3.1.1.3 Bulk contributions to the magnetic anisotropy energy

The magnetic anisotropy energy \( E_{\text{anisotropy}} \), defined in Section 2.2.6) is the energy required to reorient the magnetization of a material from its lowest-energy orientation to its highest-energy orientation; magnetic anisotropy conveys a certain preferential
orientation for the magnetic moments of the system. There are both bulk and surface contributions to the magnetic anisotropy energy [54] – the extrinsic surface contribution grows more significant as the dimensions of a material descend to the nanoscale, due to an increased proportion of atoms at the surface relative to in the bulk. Within the bulk of a material there are both intrinsic (i.e. material-specific or particle geometry-independent) contributions to the magnetic anisotropy and extrinsic contributions to the anisotropy which are strongly dependent on the microstructure or processing of the material. This portion of the literature review considers only the case of particles with uniaxial magnetic anisotropy (unless otherwise noted), whereby magnetic energy is minimized when the magnetic moments are oriented in either of two directions along a certain axis, rendering the material “easiest” to magnetize along said axis. The magnitude of the uniaxial magnetic anisotropy energy ($E_{\text{anisotropy}}$) is given by Eq. (12) [1].

\[
E_{\text{anisotropy}} = K_{\text{eff}} \sin^2 \theta
\]  

(12)

where: $E_{\text{anisotropy}} = \text{Uniaxial magnetic anisotropy energy density (erg/cm}^3\text{)}$

$K_{\text{eff}} = \text{Effective uniaxial anisotropy constant (erg/cm}^3\text{)}$

$\theta = \text{Angle between the magnetization and the easy axis (degrees)}$

*Magnetocrystalline anisotropy*

Magnetocrystalline anisotropy energy ($E_{\text{mc}}$) is defined as the energy required to overcome the spin-orbit coupling interaction – relatively weak in comparison to the strong interatomic exchange interaction (Section 3.1.1.2) – to reorient the magnetization from its lowest-energy orientation along the crystallographic “easy” axis to its highest-
energy orientation along the crystallographic “hard” axis [1, 56, 70, 72]. The anisotropic spin-orbit coupling interaction depends on the symmetry of the material’s crystal lattice. The effect of magnetocrystalline anisotropy energy on the magnetic response is illustrated in Figure 6. The magnitude of the magnetocrystalline anisotropy energy density $E_{mc}$ is given by Eq. (13) [72].

$$E_{mc} = K_1 \sin^2 \theta + K_2 \sin^4 \theta$$

where:

$E_{mc}$ = Magnetocrystalline anisotropy energy density (erg/cm$^3$)

$K_1$ = First-order magnetic anisotropy constant (erg/cm$^3$)

$K_2$ = Second-order magnetic anisotropy constant (erg/cm$^3$)

$\theta$ = Angle between the magnetization direction and the crystallographic magnetic easy axis (degrees)

Note that the first term in Eq. (13) is generally a sufficient approximation [1, 60].

Shape (magnetostatic) anisotropy energy

The shape of a particle, grain, or crystallite leads to demagnetization effects which occur at all length scales and contribute an additional magnetic anisotropy energy [72, 73]. Magnetic materials form “stray” fields at surfaces normal to a component of the magnetization as a means of minimizing free energy by closing magnetic flux paths [74]. Stray fields are accompanied by internal demagnetizing fields ($H_d$) in opposition to the direction of an external applied field [41]. The magnitude of $H_d$ is given by Eq. (14).
\[ H_d = N_d \rho M \quad (14) \]

where: \( H_d \) = Demagnetizing field (Oe)

\( N_d \) = Demagnetization factor (unitless, \( 0 \leq N_d \leq 4\pi \))

\( \rho \) = Sample density (g/cm\(^3\))

\( M \) = Magnetization (emu/g)

The demagnetization factor \( N_d \) is often determined by the aspect ratio of the material [41]; demagnetization effects increase the energy cost to magnetize a material along its short “hard” axis over that required to magnetize the sample along its long “easy” axis. For an aspherical particle, the shape anisotropy energy \( (E_{\text{shape}}) \) is given by Eq. (15) [72].

\[ E_{\text{shape}} = \frac{1}{2} \Delta N_d \rho M^2 \sin^2 \theta \quad (15) \]

where: \( E_{\text{shape}} \) = Shape anisotropy energy density (erg/cm\(^3\))

\( \Delta N_d \) = Difference in demagnetization factors between the magnetic hard and easy axes (unitless, \( 0 \leq N_d \leq 4\pi \))

\( \rho \) = Sample density (g/cm\(^3\))

\( M \) = Magnetization (emu/g)

\( \theta \) = Angle between the magnetization and the easy axis (degrees)

Magnetic domains (Section 2.2.3) in ferromagnetic and antiferromagnetic materials arise as a means of minimizing the magnetostatic energy associated with \( H_d \).
[72, 73]; if the magnetostatic energy saved by dividing the material into smaller regions of lower uniform magnetization (i.e. domains) is greater than domain wall energy ($\gamma$), given by Eq. (16), the material will divide into magnetic domains (Figure 9) [8, 73].

$$\gamma = 2\pi\sqrt{A \cdot K_{\text{eff}}}$$  \hfill (16)

where: $\gamma$ = Domain wall energy per unit area (erg/cm²)  
$A$ = Exchange stiffness parameter (erg/cm)  
$K_{\text{eff}}$ = Effective uniaxial anisotropy constant (erg/cm³)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{domainFormation.png}
\caption{Minimization of magnetostatic energy plays a key role in the formation of magnetic domains.}
\end{figure}

**Stress (magnetoelastic) anisotropy energy**

Magneetoelastic anisotropy energy ($E_{\text{me}}$) is the energy required to reorient the magnetization from its lowest-energy orientation to its highest-energy orientation upon application of a tensile or compressive stress [39]. The magnetoelastic anisotropy contains an intrinsic contribution – the magnetostriction – which, much like magnetocrystalline anisotropy energy ($E_{\text{mc}}$), is due to spin-orbit coupling [73]. The electron cloud is rotated into alignment with an applied field, and if the electron cloud is
aspherical, the spacing between the atoms may increase slightly due to Coulombic repulsion [72]. Magnetoeleastic anisotropy energy $E_{me}$ also contains an extrinsic contribution from applied stress; compressive or tensile applied stresses will result in different lowest-energy magnetization orientations. For the case of isotropic magnetostriction the magnetoelastic anisotropy energy is given by Eq. (17).

$$E_{me} = \frac{3}{2} \lambda_{si} \sigma \sin^2 \theta$$

(17)

where: $E_{me}$ = Magnetoelastic anisotropy energy density (erg/cm$^3$)

$\lambda_{si}$ = Isotropic magnetostriction (unitless, material-specific)

$\sigma$ = Applied stress (dyne/cm$^2$)

$\theta$ = Angle between the magnetization and the easy axis (degrees)

In materials with positive values of $\lambda_{si}$, application of a compressive stress ($\sigma > 0$) minimizes the magnetoelastic anisotropy energy $E_{me}$ when the magnetization is parallel to the easy axis ($\theta = 0^\circ$), whereas application of tensile stress ($\sigma < 0$) minimizes $E_{me}$ when the magnetization is perpendicular to the easy axis ($\theta = 90^\circ$).

### 3.1.1.4 Surface contributions to the magnetic anisotropy energy

The lower degree of symmetry at the surface of a material (relative to the symmetry in the bulk) also has an impact on the magnetic anisotropy energy barrier [54, 75, 76]. Since the number of magnetic moments at the surface is inversely related to particle size, these surface contributions become increasingly significant as the particle descends to the nanoscale [56]. For example, approximately 60% of the atoms will be on
the surface of a spherical Co nanoparticle with diameter $d \sim 1.6 \text{ nm}$ [54, 77]. Surface contributions to the magnetic anisotropy energy are entirely extrinsic due to the intense dependence of the surface shape and total surface area on how a material is processed.

**Surface anisotropy**

Magnetic moments at the surface of a material experience a different atomic environment than those in the bulk due to broken bonds, structural defects, and strain, and as such, magnetic moments at the surface may be misaligned from their bulk counterparts [54, 75, 78, 79]. These misaligned surface moments are still exchange-coupled to those in the particle bulk (or core) and induce an additional directionally-dependent energy barrier, or surface anisotropy energy ($E_{\text{surface}}$), which influences the orientation of the particle’s magnetization [60]. Surface anisotropy increases the effective uniaxial anisotropy constant ($K_{\text{eff}}$) of a spherical particle by an amount given by Eq. (18), which may increase the uniaxial magnetic anisotropy energy density ($E_{\text{anisotropy}}$) an order of magnitude if the particle is very small [54, 75, 76, 78, 79].

\[
K_{\text{eff}} = K_{\text{bulk}} + \frac{6}{D} K_{\text{surface}}
\]  

(18)

where: $K_{\text{eff}} =$ Total effective uniaxial anisotropy constant (erg/cm$^3$) 

$K_{\text{bulk}} =$ Bulk uniaxial anisotropy constant (erg/cm$^3$) 

$K_{\text{surface}} =$ Surface uniaxial anisotropy constant (erg/cm$^2$) 

$D =$ Spherical particle diameter (cm)

**Exchange coupling across grain boundaries or interfaces**
While isolated particles may exhibit the magnetic anisotropy energy ($E_{\text{anisotropy}}$) contributions discussed in Section 3.1.1.3 and the earlier part of this Section, real systems with intimate interparticle interfaces may exhibit an additional contribution to the anisotropy energy $E_{\text{anisotropy}}$ from quantum mechanical exchange interactions between interface atoms (Section 3.1.1.2) [80]. These exchange interactions between interfacial atoms introduces a unidirectional exchange anisotropy energy barrier, given by Eq. (19), wherein the interfacial magnetization of the particle with lower $K_{\text{eff}}$ is effectively pinned in a single direction to that of the particle with higher $K_{\text{eff}}$ [5, 6, 73].

$$E_{\text{ex}} = -K_{\text{ex}} \cos \theta$$  \hspace{1cm} (19)

where: $E_{\text{ex}}$ = Unidirectional exchange anisotropy energy density (erg/cm$^2$)

$K_{\text{ex}}$ = Unidirectional exchange anisotropy constant (erg/cm$^2$)

$\theta$ = Angle between the magnetization and the easy direction (degrees)

The exchange anisotropy energy $E_{\text{ex}}$ becomes increasingly significant in smaller particles with higher proportions of atoms at the interface. In nanostructured materials with grain size near the exchange length ($l_{\text{ex}}$) (Section 3.1.1.1), the exchange force overcomes the ability of the grain boundaries to determine the orientation of the magnetization at the interface and the system acts as a single particle [1]. The consequences of interparticle exchange interactions will be discussed more thoroughly in the Section 3.1.2.
3.1.2 Phenomena in nanostructured magnetic materials

Magnetic particles with dimensions near the exchange length \((l_{ex})\) (Section 3.1.1.1) may possess strikingly different magnetic properties than their bulk counterparts [73, 80]. Isolated nanoparticles of just a few nanometers may be superparamagnetic at a sufficiently high temperature \((T)\) and possess zero coercivity \((H_c)\). Below the magnetic blocking temperature \((T_B)\) of an assembly of superparamagnetic particles, the magnetic moments may become essentially “stuck” in place for a period of time [81]. Slightly larger particles on the same order of magnitude as the exchange length \((l_{ex})\) or the domain wall width \((\delta_w)\) may consist of a single magnetic domain and possess dramatically-enhanced \(H_c\) values over their bulk counterparts [55, 65].

Interparticle exchange interactions between nearby nanoparticles of identical phase may convey enhanced magnetic remanence \((M_r)\) values via exchange-averaging of the magnetic anisotropy (Section 3.1.2.1). Two or more magnetic phases may also be combined at the nanoscale to form a magnetic nanocomposite system that exploits the beneficial properties of each constituent phase through interparticle exchange interactions [1]. Exchange-spring magnetic nanocomposites, for example, are comprised of a nanostructured magnetically-soft \((i.e.\) low coercivity) ferromagnetic (FM) component and a magnetically-hard \((i.e.\) high coercivity) FM component, and may display improved maximum energy product \((BH)_{max}\) values, the figure of merit in permanent magnetic materials (Section 3.1.2.2) [8]. Exchange-biased magnetic nanocomposites are comprised of exchange-coupled nanostructured FM and antiferromagnetic (AF) components and display a characteristic shift of the major magnetic hysteresis loop along the field axis that effectively augments \(H_c, M_r,\) and \((BH)_{max}\) (Section 3.1.2.3) [42].
3.1.2.1 Nanostructured magnetic materials consisting of a single ferromagnetic phase

Nanoscale particles with dimensions only slightly larger than the exchange length ($l_{ex}$) may be uniformly magnetized and consist of a single magnetic domain (Section 3.1.1.1) [63]. The critical size for observation of single domain behavior ($D_{sd}$, on the order of 10-100 nm for many materials) is given by Eq. (20) [39, 60, 65].

$$D_{sd} = 36\kappa l_{ex}$$  \hspace{1cm} (20)

where: $D_{sd} =$ Critical particle size for observation of single-domain behavior in spherical magnetic nanoparticles (cm)

$l_{ex} =$ Exchange length (cm)

and: $\kappa = 2K_{eff}/4\pi\rho^2M_s^2 =$ Magnetic hardness parameter (unitless)

$K_{eff} =$ Effective uniaxial anisotropy constant (erg/cm$^3$)

$\rho =$ Sample density (g/cm$^3$)

$M_s =$ Saturation magnetization (emu/g)

The magnetic hardness parameter $\kappa$ determines whether the magnetostatic energy of a material is sufficient to overcome the magnetic anisotropy energy barrier to permit the material to, in essence, demagnetize itself [2]. Magnetic moments within a monodomain particle rotate into alignment with an applied field $H$ [67]. If the particle is large enough to contain multiple domains, the magnetization will likely change by either domain wall motion or domain rotation. Since either of these magnetization reversal modes is generally less energy-intensive than rotation of a large number of spins, the
resistance to demagnetization or coercivity ($H_c$) of a material is maximized at the critical single-domain size $D_{sd}$, which is on the order of 10-50 nm in Fe and Co and may be hundreds of nm for more magnetically-hard materials like Nd$_2$Fe$_{14}$B [56, 60]. Leslie-Pelecky’s plot of coercivity vs. particle size in Figure 10 illustrates graphically the maximization of coercivity $H_c$ at the critical single domain particle size $D_{sd}$.

![Figure 10: Typical plot of coercivity ($H_c$) vs. particle size ($D$), showing the superparamagnetic, single domain, and multidomain size regimes [55].](image)

Superparamagnetism and magnetic blocking behavior

As Figure 10 shows, the coercivity of the particle begins to decline as the particle size decreases through the critical single domain size $D_{sd}$ (Eq. (20)), and the coercivity reaches zero when the particle size enters the superparamagnetic regime [55]. Thermal energy overwheels the magnetic anisotropy energy barrier of superparamagnetic particles and thermal fluctuations cause the magnetization to spontaneously reverse above a certain temperature ($T$). The relaxation time between spontaneous magnetization reversals for a particle with uniaxial anisotropy is given in Eq. (21) [56, 81].
\[ \tau = \tau_0 \exp\left(\frac{E_B}{k_B T}\right) \]  \hspace{1cm} (21)

where: \( \tau \) = Relaxation time between magnetization flips (sec)

\[ \tau_0 = \text{Attempt time (\sim 1 \times 10^{-9} \text{ sec})} \]

\[ E_B = \text{Energy barrier to magnetization reversal (erg)} \]

\[ k_B = \text{Boltzmann’s constant (1.38 \times 10^{-16} \text{ erg/K})} \]

\[ T = \text{Temperature (K)} \]

At low fields, \( E_B \approx K_{eff} V \) where \( V \) is the volume of the particle [81]. When \( T \) is below the average blocking temperature of the system \( (T_B) \), thermal energy is insufficient to affect spontaneous magnetization flips and the relaxation time drops rapidly. Field-cooling to \( T < T_B \) causes the magnetization \( (M) \) to become stuck, or “blocked”, in alignment with the cooling field or the magnetic easy axis throughout measurement [56, 80]. Cooling to \( T < T_B \) in zero-field causes \( M \) to decline with decreasing \( T \), since only particles with “free” or unblocked magnetic moments contribute to the magnetization \( (i.e. \) those particles with blocking temperature \( T_B < T) \) [82]. Assuming the magnetization of the superparamagnetic particle flips spontaneously immediately after magnetic measurements stop, the relaxation time \( \tau \) is equal to the measuring time, which is generally around 100 seconds in superconducting quantum interference device (SQUID) magnetometers [81]; Eq. (21) then simplifies to Eq. (22).
\[ K_{\text{eff}} V / k_B T_B \approx 25.3 \]  \hspace{1cm} (22)

where: \( K_{\text{eff}} \) = Effective uniaxial anisotropy constant (erg/cm\(^3\))

\[ V = \text{Average superparamagnetic particle volume (cm}^3) \]

\[ k_B = \text{Boltzmann’s constant (1.38 x 10}^{-16} \text{ erg/K)} \]

\[ T_B = \text{Average blocking temperature of the system (K)} \]

Based on the assumptions made for Eq. (22), the critical size for observation of magnetic blocking behavior in spherical particles – typically on the order of 1-100 nm [65] – is given by Eq. (23).

\[ D_b \leq \left( \frac{152 k_B T_B / \pi K_{\text{eff}}}{1} \right)^{1/3} \]  \hspace{1cm} (23)

where: \( D_b \) = Critical particle size for observation of magnetic blocking behavior in spherical superparamagnetic particles (cm)

\[ k_B = \text{Boltzmann’s constant (1.38 x 10}^{-16} \text{ erg/K)} \]

\[ T_B = \text{Average blocking temperature of the system (K)} \]

\[ K_{\text{eff}} = \text{Effective uniaxial anisotropy constant (erg/cm}^3) \]

**Exchange averaging of the anisotropy in bulk nanostructured materials**

Bulk nanostructured materials consisting of a single ferromagnetic phase with grain or crystallite size (\( D \)) on the order of the exchange length (\( l_{\text{ex}} \)), given by Eq. (10) in Section 3.1.1.1, may exhibit strong interparticle exchange coupling that dominates the magnetization response (Section 3.1.1.4) [1]. Consider a cubic volume of \( l_{\text{ex}}^3 \) that
contains \((l_{ex}/D)^3\) randomly-oriented spherical crystallites; the exchange-averaged anisotropy constant in this volume is given by Eq. (24) [1, 39, 56, 63, 64].

\[
\langle K \rangle = K_{\text{eff}}^4 D^6 / A^3
\]  

(24)

where: \(\langle K \rangle\) = Exchange-averaged uniaxial anisotropy constant (erg/cm³)

\[D = \text{Spherical particle diameter (cm)}\]

\[A = \text{Exchange stiffness parameter (erg/cm)}\]

The sixth-degree dependence of the magnetic anisotropy energy on the particle diameter shown in Eq. (24) signifies a strong relationship between the magnetic anisotropy and thereby the coercivity \((H_c)\) on the crystallite size \(D\) in systems where \(D < l_{ex}\), as illustrated in the typical plot of \(H_c\) vs. \(D\) in Figure 10 [55].

An important consequence of exchange averaging of the magnetic anisotropy energy is magnetic remanence \((M_r)\) enhancement [56]; systems comprised of noninteracting single-domain particles with randomly-oriented magnetic easy axes possess a magnetic remanence ratio \(M_r/M_s = 0.5\), where \(M_s\) is the saturation magnetization. Interparticle exchange interactions lead to \(M_r/M_s > 0.5\).

Kita et al. confirmed exchange-induced remanence enhancement in randomly-oriented single-phase Ni nanocrystals [83]. McCallum, Kadin, Clemente, and Keem reported large magnetic remanence \(M_t > 9-10\) kG, remanence ratio (i.e. \(M_t\) divided by the saturation magnetization, \(M_s\)) of between \(M_t/M_s \sim 0.56-0.62\), and maximum energy product values of \((BH)_{\max} > 20\) MGOe in randomly-oriented rapidly-solidified Nd₂Fe₁₄B-
based alloys [84]. Manaf et al. also observed enhanced values of $M_r > 9$ kG in single-phase rapidly-solidified melt-spun ribbons of composition Nd$_{13.1}$Fe$_{82.4}$B$_{4.5}$ [85].

3.1.2.2 Nanostructured magnetic materials consisting of two phases: exchange-spring magnetic nanocomposites

Magnetic nanocomposites are materials composed of at least two magnetic phases combined at the nanoscale to exploit the advantageous properties of each phase [1]. Interphase exchange interactions enhance the magnetic character of the nanocomposite over that of either individual component to give, ideally, high values of the coercivity ($H_c$), magnetic remanence ($M_r$), or maximum energy product ($BH_{\text{max}}$), the figure of merit in permanent magnetic materials. Exchange-spring magnetic nanocomposite systems are comprised of a magnetically soft ferromagnetic (FM) phase that conveys a large saturation magnetization ($M_s$) and a magnetically-hard FM phase which contributes high anisotropy, high $H_c$, and thereby an enhanced ($BH_{\text{max}}$) [1, 8]. Figure 11 depicts typical demagnetization curves (2nd quadrant) for exchange spring and exchange-biased magnets, which will be discussed in Section 3.1.2.3 [1]. Hysteretic measurements of exchange spring magnetic nanocomposites appear to show a single magnetic phase with a magnetization loop symmetric about the origin.

The unidirectional exchange anisotropy energy barrier (Eq. (19), Section 3.1.1.4) becomes significant only when the dimensions of the constituent phases are on the order of the exchange length $l_{\text{ex}}$ (Section 3.1.1.1) [63, 64, 72]. In larger particles, the magnetic moments in the bulk far outnumber those at the interface, and the surface moments lose the ability to significantly affect the orientation of those in the bulk [1].
Kneller and Hawig determined that the maximum coercivity ($H_c$) value of an exchange-spring magnet is obtained when the soft FM regions possess a crystallite size ($D$) given by Eq. (25) [8, 63, 64].

$$D_{soft} = \frac{\pi \sqrt{A_{soft}/2K_{hard}}}{2}$$ \hspace{1cm} (25)

where: $D_{soft}$ = Diameter of the magnetically-soft ferromagnetic phase (cm) 

$A_{soft}$ = Exchange stiffness of the soft ferromagnetic phase (erg/cm) 

$K_{hard}$ = Uniaxial magnetic anisotropy constant of the magnetically hard ferromagnetic phase (erg/cm$^3$)
The optimal size of the soft-FM regions may be far less than the exchange length $l_{ex}$ of the soft phase because $K_{hard} \gg K_{soft}$ [8, 63]. The magnetization loop behaves like a “spring” when the above criteria are satisfied; the demagnetization curve is 100% reversible until the magnetization of the hard-FM phase begins to rotate into alignment with the applied field ($H$); the material behaves as a single magnetic phase under these conditions [50, 86]. Kneller and Hawig suggested that $(BH)_{max}$ is optimized when the exchange-spring consists of a soft-FM matrix phase that contains ~10 vol. % spherical hard phase precipitates, when the hard-FM precipitates are in a face-centered-cubic-like arrangement [8]. Theoretical predictions by Skomski and Coey have shown that such exchange-spring magnetic nanocomposites would exhibit magnetic remanence ($M_r$) and $(BH)_{max}$ values three to four times higher than in conventional single-phase ferromagnetic materials [87, 88].

Experimental maximum energy product $(BH)_{max}$ enhancements of less than the theoretically-predicted factor of three-to-four have been reported in several hard/soft Nd$_2$Fe$_{14}$B/$\alpha$-Fe exchange-spring nanocomposite systems. Harland et al. [50] reported magnetic remanence ($M_r$) enhancement in melt-spun Nd$_2$Fe$_{14}$B/$\alpha$-Fe alloys containing approximately ~23 at. % excess $\alpha$-Fe with magnetic remanence ratios ($i.e. M_r$ divided by the saturation magnetization, $M_s$) ranging from $M_r/M_s \sim 0.57$ in melt-spun single-phase Nd$_2$Fe$_{14}$B nanostructures to $M_r/M_s \sim 0.60$ in melt-spun Nd$_9$Fe$_{86}$B$_5$ two-phase nanostructures. It was found that addition of Fe past the stoichiometric 2:14:1 ratio of Nd:Fe:B raised the magnetic remanence but lowered the maximum energy product $(BH)_{max}$ by approximately 10%, from 16.6 MGOe to 14.9 MGOe. Müller et al. reported
\[ M_r/M_s \approx 0.75 \] in melt-spun Nd\(_4\)Fe\(_{77}\)B\(_{19} \) ribbons [89]. Coehoorn et al. also observed exchange spring behavior in melt-spun Nd\(_2\)Fe\(_{14}\)B/Fe\(_3\)B ribbons [88, 90-92].

Exchange-spring behavior has also been reported extensively in many magnetic nanocomposites comprised of Sm-Co. O’Sullivan, Rao, and Coey [93] found a small degree of remanence enhancement in Sm\(_2\)Fe\(_{17}\)N\(_3\)/Fe\(_{65}\)Co\(_{35}\) exchange spring magnets [87]. Zaigham and Khalid reported that mechanically-alloyed/sintered SmCo\(_5\) alloys doped with \(~0.2\) at. % Sn contained magnetically-hard precipitates of the ferromagnetic (FM) Sm\(_2\)Co\(_{17}\) and Sm\(_2\)Co\(_7\) phases embedded in a SmCo\(_5\) matrix, leading to \((BH)_{\text{max}}\) values as high as 7.4 MGOe and magnetic remanence ratio of \(M_r/M_s \approx 0.67-0.97\) [53, 94]. Ding et al. [95] observed remanence ratios as high as \(M_r/M_s \approx 0.8\) in mechanically-alloyed isotropic nanocrystalline samples of Sm\(_{12}\)Co\(_{87.5}\) powder, and also observed magnetic remanence enhancement and high \((BH)_{\text{max}} \approx 26\) MGOe in Sm\(_2\)Fe\(_{17}\)N\(_3\)/\(\alpha\)-Fe powders [96]. Shield et al. [97] reported an intergranular-exchange-enhanced magnetic remanence ratio \(M_r/M_s \approx 0.7\) in melt-spun Sm\(_{12}\)Co\(_{88}\) alloys containing a hard SmCo\(_7\) phase and a soft \(\text{fcc}\) Co phase. Chen, Tsai, and Chin [98] observed exchange-spring behavior in Sm\(_2\)Co\(_{17}\)/Co alloys fabricated by mechanical alloying; they reported a significant magnetic remanence \(4\pi M_s \approx 9.4\) kG, and magnetic remanence ratio of 0.82.

Micromagnetic calculations by Kronmüller et al. [99] demonstrated enhanced \(M_r\) at room temperature in a Pr\(_2\)Fe\(_{14}\)B/\(\alpha\)-Fe exchange spring magnet with between 0-30 at. % of the magnetically-soft FM \(\alpha\)-Fe phase. Their model showed that raising the content of the low-coercivity phase led to decreased coercivity \((H_c)\) but increased \(M_r\) values. Lewis and Crew [49] established a parasitic relationship between the magnetic remanence \((M_r)\) and the coercivity \((H_c)\) of 2:14:1 rare-earth intermetallic exchange-spring magnets –
engineering an exchange-spring with increased $M_r$ results in a lower $H_c$ value, and vice-versa. Shield et al. [92] reported that domain wall processes dominate the magnetization reversal process in exchange-spring magnets and suggested that engineering a material with significant domain-wall pinning ability may be helpful in development of optimal exchange-spring magnets.

Unfortunately, a myriad of issues have all but prevented optimal exchange-spring nanocomposite geometries from being realized in bulk materials including (but not limited to) impurities and inhomogeneities in the hard and soft phases, crystallographic incoherency, and small crystallite size requirements for the soft-FM phase. As an example, it has been determined that the ideal crystallite size for an exchange-spring magnet comprised of a Nd$_2$Fe$_{14}$B or other rare-earth-intermetallic hard-FM phase enveloping a soft-FM $\alpha$-Fe phase is on the order of 10 nm [1, 49].

3.1.2.3 Nanostructured magnetic materials consisting of two phases: exchange-biased magnetic nanocomposites

Analogous to exchange-spring magnetic nanocomposites (Section 3.1.2.2) whereby a soft ferromagnetic (FM) phase is exchange-coupled to a hard FM phase, exchange-biased nanocomposites are comprised of a FM phase exchange-coupled to an antiferromagnetic (AF) phase [1, 5, 6, 42, 45, 80]. Here, the FM component contributes high saturation magnetization ($M_s$) while the AF component contributes high magnetic anisotropy. Mutual exchange-coupling between the FM and AF phases introduces an exchange anisotropy energy barrier ($E_{ex}$, given by Eq. (19) in Section 3.1.1.4) that exerts a unidirectional torque on the interfacial magnetization of the FM component and pins it
along a single low-energy “easy direction” determined by the anisotropy of the AF component, rather than in either direction along the “easy axis” determined by the uniaxial magnetic anisotropy energy. In this manner, the major field-cooled (FC) magnetization loop of the FM component collected after cooling through both the Néel temperature \( T_N \) of the AF component and the Curie temperature \( T_c \) of the FM component is shifted along the field \( H \) axis by an exchange bias \( H_{\text{ex}} \) field \([2]\). The \( H_{\text{ex}} \) shift effectively augments the coercivity \( H_c \) and magnetic remanence \( M_r \) to convey large values of the maximum energy product \( (BH)_{\text{max}} \), the figure of merit in permanent magnetic materials (Figure 11, from \([1]\)).

It is important to note that the \( H_{\text{ex}} \) shift manifests only in FM + AF composite materials that meet certain criteria. The Néel temperature \( T_N \) of the AF component must be less than \( T_c \) of the FM component \([5]\); for systems that exhibit magnetic blocking behavior at low temperatures (Section 3.1.2.1), \( H_{\text{ex}} \) vanishes above the blocking temperature \( T_B \), which is usually below \( T_N \) \([6, 43]\). The magnetic anisotropy energy of the AF component must be significantly greater than that of the FM component \((i.e. K_{AF} \gg K_{FM})\). There must also be enormous FM/AF interfacial area to maximize the proportion of exchange-coupled magnetic moments; ideally the crystallite size \( D \) of both the FM and AF components are on the order of the exchange length \( l_{\text{ex}} \), Section 3.1.1.1), similar to the requirements for exchange-spring behavior (Section 3.1.2.2) \([1, 8, 63]\). In this case, FM/AF exchange coupling dominates the magnetic response rather than the bulk anisotropy energy. If \( D_{\text{soft}} \gg l_{\text{ex}} \), the magnetic anisotropy energy in the bulk of the FM component overcomes the FM/AF interatomic exchange interaction energy at the surface (Sections 3.1.1.2 and 3.1.1.4), and the interfacial moments no longer determine
the orientations of those in the bulk. The FM magnetization then becomes easier to reverse and the coercivity of the composite decreases to its bulk decoupled value.

For a comprehensive overview of the mechanism of the exchange anisotropy phenomenon in thin films, the reader is referred to the review articles by Meiklejohn, Berkowitz, and Nogués [5, 6, 42]. This thesis work, however, is focused exclusively on clarification of the exchange-bias and exchange anisotropy phenomenon in bulk FM/AF nanocomposite systems. Several literature examples of bulk materials reported to exhibit the exchange bias phenomenon will be discussed in more depth in Section 3.2.

3.2 Reports of the magnetic and structural properties of exchange-biased nanostructured materials

A comprehensive review of literature examples of materials exhibiting each of the phenomena described in Section 3.1.2 is far beyond the scope of this thesis work. This portion of the literature review is therefore devoted exclusively to an overview of bulk materials reported to exhibit the exchange bias ($H_{\text{ex}}$) effect, whereby the major field-cooled (FC) hysteresis loop displays a characteristic shift along the applied field ($H$) axis (Section 3.1.2.3) [1, 5, 6, 42, 45, 80]. The $H_{\text{ex}}$ shift augments the coercivity ($H_c$) and magnetic remanence ($M_r$) of the FM component, resulting in enhanced maximum energy product ($BH_{\text{max}}$) values and thereby improved permanent magnetic character over either of the individual components.

The exchange anisotropy phenomenon was first observed by Meiklejohn and Bean in their seminal 1956 paper regarding the magnetic character of Co/CoO core-shell nanoparticles [42]. They attributed the $H_{\text{ex}}$ shift to a unidirectional anisotropy conveyed
by quantum mechanical exchange interactions between magnetic moments at the interface between the ferromagnetic (FM) Co core and an antiferromagnetic (AF) CoO shell. Exchange anisotropy has since been extensively studied in thin film materials due to the relative ease of controlling and characterizing the FM/AF interface [1, 5, 6] and the fact that many current technological applications utilize exchange-biased thin films, including so-called “spin-valves” and other magnetoresistive devices [100, 101]. Thin film composites are not, however, suitable for permanent magnet applications due to the implicitly large material requirements [2, 3]. The $H_{\text{ex}}$ effect has not been thoroughly investigated and understood in bulk magnetic nanocomposite systems to date, in part due to difficulty in obtaining suitable uniform phase separation and texturing during processing [1, 7]. Investigations of exchange-biased nanocomposites containing no rare-earth-elements are even more disparate.

This portion of the literature review presents an overview of bulk rare-earth-free exchange-biased magnetic nanocomposites, divided into subsections according to the number of constituent structural phases. Section 3.2.1 first discusses briefly those systems comprised of a single nanoscale structural phase, intended for use as antiferromagnetic components in FM/AF nanocomposite systems, including MnX (X = Cu, Al, etc.) alloys. Section 3.2.2 examines the literature on the magnetic character of two-phase bulk exchange-biased magnetic nanocomposite systems, including Fe/MnX alloys.
3.2.1 Bulk magnetic nanocomposites consisting of a single phase

As mentioned in the introductory chapter (Section 1.0), it is the ultimate goal of this thesis work and the recommended future work to elucidate the underpinnings of the exchange bias ($H_{ex}$) phenomenon in bulk ferromagnetic/antiferromagnetic (FM/AF) magnetic nanocomposite systems for potential rare-earth-free permanent magnet applications. Such materials should be easy-to-manufacture, corrosion-resistant, and consist of easily-obtainable and cost-effective components [1]. It is prudent to understand each single-phase component prior to investigation of the magnetic and structural character of the more complex two-phase nanocomposite materials. Table 3 shows magnetic character data for three of the more commonly-used transition metal elements – Co, Ni, and Fe [102]. It is clear that Co has the highest Curie temperature ($T_c$) while still possessing a saturation magnetization of nearly 200 emu/g at room temperature, but unfortunately Co is a strategic element with a crustal abundance approximately 2000 times lower than that of Fe and therefore much more expensive [2]. For the purposes of this thesis work, Fe will be employed as the model FM matrix phase for study due to its low cost and high Curie temperature [2, 102].

<table>
<thead>
<tr>
<th>Table 3: Magnetic character data for common ferromagnetic transition metal elements Fe, Co, and Ni [102].</th>
</tr>
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<tbody>
<tr>
<td>20 °C</td>
</tr>
<tr>
<td>$M_s$ (emu/g)</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Co</td>
</tr>
<tr>
<td>Ni</td>
</tr>
</tbody>
</table>
Ideal model AF components are corrosion-resistant, possess crystallographic compatibility with the Fe (or Co) matrix, and have easily-controllable microstructures [1]. One such alloy, Ir-Mn, has been reported to exhibit the exchange anisotropy phenomenon in IrMn/Co bilayer systems below the high magnetic blocking temperature \(T_B\) of IrMn alloys (~ 500 K) [103, 104]. However, as Coey recently reported, the extremely low crustal abundance of Ir results in a prohibitive cost of more than $10,000/kg, rendering Ir unsuitable for permanent magnet applications [2]. Other more reasonably-priced Mn-based binary metallic alloys, including Al-Mn and Cu-Mn, possess lower reported \(T_B\) values, and Cu and Al are each immiscible in Fe over certain concentration regimes (Figure 12a and b), rendering it possible to fabricate FM/AF nanocomposites of the form Fe/MnX \((X = Cu, Al, etc.)\) [51, 105, 106].

![Figure 12: Binary equilibrium phase diagrams for the (a) Cu-Fe [106] and (b) Al-Fe [105] systems, to illustrate immiscibility of Cu and Al in Fe.](image)

An additional advantage of these MnX alloys is the reported ability to modify the AF character by simply adjusting the Mn content in the alloy [10, 14, 51, 82]. Néel temperatures \(T_N\) above room temperature have been reported in \(Cu_{10}Mn_{90}\) alloys [14, 107, 108], and giant exchange bias \(H_{ex}\) values of ~ 13 kOe have been observed in rapidly-solidified Al-Mn ribbons at 10 K [51]. The following subsections address the
magnetic and structural properties of each of these alloys by first presenting the binary
equilibrium phase diagram, then discussing the magnetic and structural properties of each
relevant phase.

3.2.1.1 Cu-Mn alloys: Magnetic and structural character

The magnetic and structural behaviors of Cu-Mn alloys have been studied
extensively over essentially the entire composition regime [9, 14, 82, 107-120]. A
majority of these studies are on water- or oil-quenched alloy samples. Rapidly-solidified
Cu-Mn alloys have not, however, been thoroughly investigated, especially with reference
to possible applications as AF components in exchange-biased nanocomposites for
advanced permanent magnet applications (Section 3.1.2.3) [1].

Predel compiled experimental data reported by several investigators to develop
the Cu-Mn binary equilibrium phase diagram in the Landölt-Bornstein database [121],
shown below in Figure 13.
Figure 13: Cu-Mn binary equilibrium phase diagram [121].

Crystal structures of Cu-Mn alloys

Predel [121] and Pearson [122] have compiled structural data for each phase in the Cu-Mn binary equilibrium phase diagram (Figure 13). The δ-Mn phase is stable between ~1100-1250 °C [109] and adopts an A2-type body-centered cubic (bcc) crystal structure with unit cell lattice parameter $a = 3.0806$ Å [121, 122]. The γ-Mn phase is stable between ~1100-1150 °C and adopts an A1-type face-centered-cubic (fcc) crystal structure...
with lattice parameter $a = 3.8624$ Å, and undergoes a tetragonal unit cell distortion along the c-axis of approximately $c/a \sim 0.945$ at low temperatures [123, 124]. The $\beta$-Mn phase is stable between ~700-1100 °C and adopts an $A13$-type complex cubic structure with 20 atoms per unit cell (Figure 14a [125]) that possesses a unit cell lattice parameter $a = 6.3145$ Å [121, 122]. The $\alpha$-Mn phase is stable at room temperature and adopts an $A12$-type complex cubic structure with 58 atoms per unit cell (Figure 14b [126]) that possesses a unit cell lattice parameter $a = 8.9139$ Å [121, 124, 127]. The solubility limit of Cu in either the $\alpha$-Mn or $\beta$-Mn phases is found to be only a few tenths of an atomic percent [128]. The magnetic attributes of each of these phases will be discussed in the latter portion of this Section.

![Figure 14: (a) Crystal structure of the $\beta$-Mn phase (A13-type) [125]. (b) Crystal structure of the $\alpha$-Mn phase (A12-type), with different oxidation states of Mn shown in different shades; Mn$^{1+}$ in light green, Mn$^{4+}$ in dark green [126].](image)

The Cu-Mn crystallographic phase of most interest in this thesis work is the chemically-disordered face-centered-cubic (fcc) $\gamma$-CuMn phase which occurs across the entire composition range in the phase diagram in Figure 13. Turchanin, Agraval, and Abdulov note that, interestingly, Cu-Mn alloys are one of the few transition metal systems that demonstrate such complete mutual solubility [128]. They observed that $\gamma$-
CuMn alloys with lower Mn content tended to have stoichiometric chemically-ordered structures (Figure 13); the $\gamma_1$ phase corresponds to the compound Cu$_5$Mn (10-20 at. % Mn, stable to ~675 K), the $\gamma_2$ phase corresponds to the compound Cu$_3$Mn (23-28 at. % Mn, stable to ~708 K), and the $\gamma_3$ phase corresponds to the high-temperature modification the $\gamma_1$-Cu$_5$Mn compound (5-30 at. % Mn, stable to ~970 K). Alloys with higher Mn content reportedly exhibit some degree of metastable immiscibility [121]. Yin et al. and Turchanin et al. noted that heat treatment of $\gamma$-CuMn alloys with more than approximately 40 at. % Mn in the temperature range $T \sim 400$-$600$ °C resulted in segregation into metastable Mn-rich and Mn-poor fcc phases [128, 129].

Using powder x-ray diffraction and stereographic x-ray diffraction analysis, respectively, Ellsworth and Blake [130] and Basinski and Christian [131] observed that above approximately 72 at. % Mn, fcc $\gamma$-CuMn alloys underwent a diffusionless martensitic transformation over a range of ~ 30 °C at some low temperature that depended on the Mn content. Basinski and Christian found that an fcc alloy containing ~82 at. % Mn transformed to the fct phase on cooling through the approximate temperate range 20 °C to 0 °C.

Bacon et al. [107] and several others [117-120, 130, 132] analyzed x-ray and neutron diffraction measurements to probe the nature of the martensitic $fcc \rightarrow$ face-centered-tetragonal (fct) phase transformation, its precise concentration- and temperature-dependence, and its relationship to the magnetic character of the system (Figure 15a and b). Cowlam et al. carried out a fit of the dependence of the unit cell a-parameter on Mn concentration (Figure 15b) and extrapolated to the axis limits to predict the lattice
parameter of the face-centered-cubic (fcc) $\gamma$-CuMn phase [117]; they found the dependence is given by Eq. (26).

$$a = 3.6145 + 0.4364x_{Mn} - 0.3273x_{Mn}^2$$  \hspace{1cm} (26)$$

where: $a =$ Unit cell a-lattice parameter (Å)

$x_{Mn} =$ Mn content of the fcc $\gamma$-CuMn phase (at. % Mn)

The empirical curve fit in (26) intersects with the tetragonal cell distortion at approximately 83.5 at. % Mn [117]. The martensitic transformation has been observed to be intimately related to the transition to antiferromagnetic (AF) ordering, which will be discussed in the latter portion of this section [107].
The magnetic properties of Cu-Mn are dependent on the crystal structure of the alloy. Franse and Gersdorf [124] compiled previous experimental data of the magnetic character of the Mn allotropes appearing in the Cu-Mn binary equilibrium phase diagram (Figure 13). Little about the magnetic behavior of the body-centered-cubic (bcc) δ-Mn phase has been reported [124]. Franse and Gersdorf also report a simple temperature-independent paramagnetic behavior for the $A_{13}$-type complex cubic $\beta$-Mn phase (Figure 14a) [124]. The $A_{12}$-type complex cubic $\alpha$-Mn phase (Figure 14b) is observed to have an extremely complicated antiferromagnetic (AF) structure where Mn atoms at each of the four nonequivalent lattice sites possess highly different magnetic moments (Table 4). The Néel temperature ($T_N$) of the $\alpha$-Mn phase is given as $T_N = 95$ K.

<table>
<thead>
<tr>
<th>Site</th>
<th>Atoms/unit cell</th>
<th>Magnetic moment/Mn atom ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2</td>
<td>1.9</td>
</tr>
<tr>
<td>II</td>
<td>8</td>
<td>1.7</td>
</tr>
<tr>
<td>III</td>
<td>24</td>
<td>0.6</td>
</tr>
<tr>
<td>IV</td>
<td>24</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Franse and Gersdorf also report the high-temperature face-centered-cubic ($fcc$) $\gamma$-Mn allotropic phase possesses antiferromagnetic (AF) character with $T_N \sim 500$ K (327 °C), concomitant with a tetragonal distortion of the $fcc$ unit cell [124]. Most research on the magnetic and structural properties of the Cu-Mn system has focused on the $fcc$ modification, with varying amounts of Mn dissolved in the $fcc$-Cu lattice or some Cu dissolved in the $fcc$-Mn lattice.
The first major investigation regarding the AF character of Mn-rich $\gamma$-CuMn alloys was carried out by Bacon et al. on argon plasma arc-melted and subsequently water-quenched Cu-Mn specimens containing between 0.780-0.950 at. % Mn [107]. Bacon conducted neutron diffraction analyses and Sucksmith magnetic force measurements as a function of temperature ($T$) only – the magnetic response to changes in the applied magnetic field ($H$) were not reported – and found a magnetic moment per Mn atom of $\sim 2.4 \pm 0.1 \mu_B$, based on an assumed outer-shell electron configuration of $3d^64s^1$. Morris and Williams investigated the magnetic character of Ag-Mn alloys containing 7-38.1 at. % Mn as a function of $T$ and found remarkable parallels with the $\gamma$-CuMn system [133]. They compiled previous experimental data and developed a plot of the paramagnetic Curie temperature $\theta$ as a function of Mn content in the $fcc \gamma$-CuMn phase (Figure 16), noting that the paramagnetic Curie temperature $\theta$ rose to a peak value of $\theta \sim 120$ K at an Mn concentration of $\sim 22$ at. % Mn, and then rapidly decreased back to approximately $\theta \sim 5$ K at about 45 at. % Mn.
Figure 16: Plot of the paramagnetic Curie temperature $\theta$ against Mn content for face-centered-cubic Cu-Mn and Ag-Mn alloys [133].

Derived from the Curie-Weiss law (Eq. (27)) that describes the paramagnetic behavior of an antiferromagnetic (AF) or ferromagnetic (FM) material above its magnetic ordering temperature (Sections 2.2.3 and 2.2.4), the paramagnetic Curie temperature $\theta$ is directly related to the effective magnetic moment ($\mu_{\text{eff}}$) of a material [69]. The maximization of the paramagnetic Curie temperature $\theta$ at a Mn concentration of approximately 22 at. % Mn (Figure 16) is thus analogous to maximization of the magnetic moment at that concentration [133].

$$\chi = \frac{C}{(T - \theta)}$$

where: $\chi$ = Magnetic susceptibility (emu/cm$^3$·Oe)

$T$ = Temperature (K)

$\theta$ = Paramagnetic Curie-Weiss temperature (K)
\[ C = \text{Curie constant} = N_A \rho \mu_{\text{eff}}^2 / 3A k_B \text{ (emu}\cdot\text{K/cm}^3\cdot\text{Oe)} \]

and: \( N_A = \text{Avogadro’s number} (6.022 \times 10^{23} \text{ atoms/mol}) \)

\( \rho = \text{Density (g/cm}^3\) \)

\( \mu_{\text{eff}} = \text{Effective magnetic moment (emu)} \)

\( A = \text{Atomic molar mass (g/mol)} \)

\( k_B = \text{Boltzmann’s constant} (1.38 \times 10^{-16} \text{ erg/K}) \)

In his seminal papers regarding the magnetic character of quenched Cu-Mn alloys with low Mn content (5-25 at. % Mn), Kouvel collected magnetization loops from water-quenched single-phase atomically-disordered \( fcc \) CuMn alloys at \( T = 4.2 \text{ K} \) after cooling in various fields parallel and perpendicular to the measurement axis \([9, 110, 111]\). He found that the field-cooled (FC) major hysteresis loops – \( i.e. \) magnetically saturated in both directions and thus symmetric about the field \( (H) \) axis – collected from Cu\(_{75.9}\)Mn\(_{24.1}\) were shifted along the field axis at 4.2 K, as shown in Figure 17a. Kouvel observed that the magnetization \( (M) \) increased with increasing cooling field \( (H_{\text{cool}}) \) while the loop shift increased from zero at \( H_{\text{cool}} \sim 0 \text{ kOe} \) to about 6 kOe at \( H_{\text{cool}} \sim 5 \text{ kOe} \), but then the shift decreased to 4 kOe after the cooling field was raised to \( H_{\text{cool}} \sim 10 \text{ kOe} \) \([110]\). The loop shift occurred after field-cooling through the peak magnetization temperature \((\sim 100 \text{ K}, \text{ Figure 17b})\), but only if \( H_{\text{cool}} \) was parallel to the measuring axis, as can be seen through comparison of the dashed loop in Figure 17a to that collected after cooling in \( H_{\text{cool}} \sim 5 \text{ kOe} \).
Kouvel noted that this shifted-loop behavior was similar to that observed by Meiklejohn and Bean in their groundbreaking report on the magnetic properties of Co/CoO core-shell nanoparticles [9, 110]. Meiklejohn and Bean had observed the first occurrence of a major hysteresis loop shift after field-cooling to low temperatures [42]. They attributed the shift to a new type of unidirectional anisotropy (now known as exchange anisotropy, see Sections 3.1.1.4 and 3.1.2.3) conferred by quantum mechanical exchange-coupling between the ferromagnetic (FM) Co-core and the inadvertently-oxidized antiferromagnetic (AF) CoO-shell.

To account for the exchange bias ($H_{ex}$) shift $\sim$ 4-6 kOe observed in major FC magnetization loops collected from Cu$_{75.9}$Mn$_{24.1}$ at 4.2 K (Figure 17a) without two distinct FM and AF phases present, Kouvel proposed a phenomenological model that hypothesized a competitive nature of the Mn-Mn interatomic exchange interaction energy
(\(E_{\text{exchange}}\), Section 3.1.1.2) [9]. He suggested that the exchange integral \(J_{\text{ex}}\) (Eq. (11)) was intensely dependent on the interatomic distance between Mn atoms in each Mn-Mn atomic pair; nearest-neighbor Mn atoms interacted antiferromagnetically with one another to minimize \(E_{\text{exchange}}\) \(i.e.\ J_{\text{ex}} < 0\), while next-nearest-neighbor Mn atoms interacted ferromagnetically with one another to minimize \(E_{\text{exchange}}\) \(i.e.\ J_{\text{ex}} > 0\) [9, 111, 114]. Since the alloy’s Mn concentration determines the Mn-Mn interatomic distance, he inferred that the exchange correlation – either ferromagnetic or antiferromagnetic Mn-Mn exchange-coupling – could be controlled through modification of the Mn content.

Gibbs, Harders, and Smith [14] and Banerjee and Majumdar [82] expanded on Kouvel’s phenomenological model and developed experimental magnetic phase diagrams for water-quenched disordered \(fcc\) \(\gamma\)-CuMn alloys (shown in Figure 18a and b, respectively) to accentuate the strong dependence of the magnetic character on Mn content. Gokcen’s [108] extension of the linear dependence of the Néel temperature \(T_N\) on Mn concentration attempted to clarify the transition from cluster glass behavior to antiferromagnetic (AF) ordering (Figure 18c). The miscibility gaps in the high-temperature region of Gokcen’s magnetic phase diagram in Figure 18c show the transformations of the disordered \(fcc\) \(\gamma\)-CuMn phase to the ordered \(\gamma_1\)-Cu₅Mn, \(\gamma_2\)-Cu₃Mn, and \(\gamma_3\)-Cu₅Mn phases (Figure 13) [128]; reports of the magnetic character of these ordered phases could not be located.
Figure 18: Experimental magnetic phase diagrams for $\gamma$-CuMn alloys, developed by (a) Gibbs, Harders, and Smith [14] and (b) Banerjee and Majumdar [82]. (c) Gokcen’s extension of the $T_N$ line [108].

Abbreviations: PM, P = paramagnetic; SG = spin glass; CG = cluster glass; AF = antiferromagnetic; Mix, M = mixed CG + AF order.

Cowlam and Shamah developed another magnetic phase diagram for quenched $\gamma$-CuMn alloys using neutron powder diffraction analysis [118, 132] that is in at least qualitative agreement with all three experimental magnetic phase diagrams in Figure 18 [14, 82, 108].
Gibbs et al., Guy, and Mukhopadhyay et al. found that at low temperatures, Cu-Mn alloys containing below about 15 at. % Mn have a tendency towards a type of short-range magnetic order known as spin-glass-like behavior (Figure 18) [14, 116]. Spin-glass-like behavior is caused by magnetic frustration, wherein the interatomic exchange interaction energy (Section 3.1.1.2) of each magnetic atom pair in an assembly cannot be minimized simultaneously [39, 112, 134, 135]. Frustrated magnetic moments are essentially unbound from the exchange-induced short-range magnetic order in the rest of the assembly, and may align freely with an applied field \( (H) \) as a means of reducing the total interatomic exchange energy of the material [14]. Similar to superparamagnetic particles cooled below their magnetic blocking temperature (Section 3.1.2.1), the frustrated moments become locked or “frozen” in an energetically-favorable orientation below a spin-glass freezing temperature \( (T_f) \) [111, 112]. Many of the intriguing magnetic properties of spin-glass systems are irreversible and point to metastability, including the time-dependent nature of the magnetization [82, 111, 112, 116]. An in-depth review of the complex behaviors of spin glasses and other magnetically-frustrated systems is far beyond the scope of this thesis work; the interested reader is referred to references [134, 136].

As the Mn content in \( \gamma \)-CuMn alloys increases above \( x_{\text{Mn}} > 15 \) at. % Mn, Mn-rich “clusters” start to form and the average Mn-Mn interatomic distance decreases [135]. Direct exchange interactions (Section 3.1.1.1) between Mn-Mn atomic pairs become increasingly prevalent and begin to dominate the magnetic response of the material [14]. As the Mn content continues to rise above 20 at. % Mn the number of ferromagnetic (FM) correlations between next-nearest-neighbor Mn-Mn atomic pairs increases.
However, long-range FM order never occurs due to competing short-range antiferromagnetic (AF) correlations between nearest-neighbor Mn-Mn atomic pairs [9, 110, 112, 135]. The peak in the plot of paramagnetic Curie temperature $\theta$ as a function of Mn content at $\sim 22$ at. % Mn (Figure 16) is likely the “tipping point”, where the AF exchange interactions begin to and govern the magnetization response of the alloy as they begin to outnumber the FM correlations.

Long-range antiferromagnetic order eventually sets when the Mn content ($x_{Mn}$) is raised further to $x_{Mn} > 70$ at. % Mn [82, 115, 119]. The advent of long-range AF order is accompanied by the previously-discussed tetragonal distortion of the fcc unit cell at low temperatures [107, 118, 120]. The Néel temperature ($T_N$) rises as the Mn content increases past this threshold, reaching as high as 484 K at 83 at. % Mn [82]. At much lower temperatures, these Mn-rich alloys display a complex mix of long-range AF order and spin glass-like behavior [14, 118, 132].

The reader will notice that most of these investigations were primarily focused on the magnetic character at the low-Mn portion of the magnetic phase diagram, which, while scientifically-intriguing, is not of particular interest for this thesis work. Few (if any) similar investigations have been carried out on nanostructured or rapidly-solidified Cu-Mn alloys, to say nothing of their use as an antiferromagnetic component in possible exchange-biased nanocomposite permanent magnets.

3.2.1.2 Al-Mn alloys: Magnetic and structural character

Near-equiatomic Al-Mn alloys are reported to display antiferromagnetic (AF) character [10]. The Al-Mn binary equilibrium phase diagram developed by McAlister
and Murray, with addition of the metastable τ-AlMn phase by Yanar et al., is shown in Figure 19 [29, 137-140]. This portion of the literature review is divided such that the crystal structure of each phase in the Al-Mn binary equilibrium phase diagram will be discussed, then the magnetic properties of each relevant phase will be reviewed.

![Al-Mn binary equilibrium phase diagram](image)

**Figure 19**: Al-Mn binary equilibrium phase diagram, courtesy of [29, 140].

**Crystal structure of Al-Mn alloys**

At low Mn concentrations, Al-Mn alloys have a tendency to form several intermetallic compounds like Al$_{12}$Mn, Al$_6$Mn, Al$_4$Mn, Al$_{10}$Mn$_3$, Al$_{11}$Mn$_4$, and Al$_8$Mn$_5$ [137-139, 141]. The Al$_{12}$Mn intermetallic phase occurs as a result of decomposition of supersaturated fcc-Al alloys, possesses a body-centered-cubic (bcc) structure (space group $Im\overline{3}$) with unit cell lattice parameter $a \sim 7.54$ Å. The Al$_6$Mn intermetallic phase
adopts an orthorhombic structure (space group \(Cmcm\)) with unit cell lattice parameters \(a = 7.5518 \text{ Å}, \ b = 6.4978 \text{ Å}, \ c = 8.8703 \text{ Å}\). The \(\text{Al}_4\text{Mn}\) intermetallic phase adopts a hexagonal unit cell structure (space group \(P6_3/mmc\)) with unit cell lattice parameters \(a = 1.998 \text{ Å}\) and \(c = 2.4673 \text{ Å}\). The \(\text{Al}_{10}\text{Mn}_3\) intermetallic phase is metastable and adopts a hexagonal unit cell structure with lattice parameters \(a = 7.543 \text{ Å}\) and \(c = 7.898 \text{ Å}\). The \(\text{Al}_{11}\text{Mn}_4\) intermetallic phase adopts a triclinic unit cell structure (space group \(P\overline{1}\)). The \(\text{Al}_8\text{Mn}_5\) intermetallic compound \((i.e.\) the \(\gamma_2\)-\AlMn phase\) is formed by a peritectic reaction between the \(\text{bcc}\ \gamma\)-\AlMn (space group \(Im\overline{3}m\)) and \(\gamma_1\)-\AlMn phases [140, 141]. \(\text{Al}_8\text{Mn}_5\) is stable over the composition range 32-48 at. % Mn up to around \(\sim1000 \text{ °C}\) and adopts a \(D8_{10}\)-type rhombohedral structure (space group \(R\overline{3}m\)) with unit cell lattice parameters \(a = 7.756 \text{ Å}\) and \(\alpha = 109.03^\circ\). An intermediate phase known as \(\text{B}2\)-\AlMn results from an order-disorder transformation of the \(\gamma\)-\AlMn phase and adopts a chemically-ordered body-centered-cubic (bcc) CsCl-type structure with no unit cell lattice parameter reported [137, 138]. Rapidly-solidified Al-Mn alloys containing between 10 and 25 at. % Mn may retain metastable quasicrystalline phases with long-range order and 5- or 10-fold symmetry [138].

Al-Mn alloys containing higher Mn concentrations display more of a tendency to form solid solutions than intermetallic compounds (Figure 19) – it is these phases that this thesis work will be focused on. The \(\delta\)-\AlMn phase (space group \(Im\overline{3}m\)) is Al dissolved in an allotropic modification of Mn, is stable in the temperature range \(\sim1100-1250 \text{ °C}\) and the composition range \(\sim60-100 \text{ at. % Mn}\) [109], and adopts an \(A2\)-type body-centered cubic (bcc) crystal structure with unit cell lattice parameter \(a = 3.0806 \text{ Å}\), as was noted in Section 3.2.1.1 [121, 122]. The \(\beta\)-\AlMn phase is Al dissolved in another
allotropic modification of Mn, is stable in the approximate temperature range ~250-1350 °C and over the composition range ~60-100 at. % Mn, and adopts an $A_{13}$-type complex cubic structure with 20 atoms per unit cell (Figure 14a [125]) that possesses a unit cell lattice parameter $a = 6.3145 \text{ Å}$, as noted in Section 3.2.1.1 [121, 122]. The $\gamma$-AlMn phase is stable in the temperature range ~950-1175 °C and over the composition range ~35-45 at. % Mn, and adopts an $A_{2}$-type $bcc$ crystal structure with unit cell lattice parameter $a = 3.062 \text{ Å}$ [138, 141].

The $\varepsilon$-AlMn phase of particular relevance to this thesis work is stable in the temperature range ~900-1300 °C and over the composition range 53-65 at. % Mn, and adopts a disordered $A_{3}$-type hexagonal (hcp) structure with unit cell lattice parameters $a = 2.697 \text{ Å}$ and $c = 4.356 \text{ Å}$ [15, 26, 137, 138]. Kono [15] reported the first observation of a transformation of the hcp $\varepsilon$-AlMn phase into a metastable chemically-ordered face-centered-tetragonal (fct) $L_{10}$-type $\tau$-AlMn phase in the approximate composition range 48-58 at. % Mn (Figure 20). This metastable tetragonal $\tau$-AlMn phase possesses unit cell lattice parameters $a = 3.54 \text{ Å}$ and $c = 3.92 \text{ Å}$ [15, 21, 138], and is typically stabilized by addition of a small amount of carbon (< 2 at. %) to the alloy to prevent decomposition into the equilibrium $\gamma_2$-AlMn and $\beta$-AlMn phases [3, 12, 17, 20, 25, 27, 28, 142, 143].
Figure 20: $L_1^0$-type unit cell of the metastable $\tau$-AlMn phase.

Since the initial studies by Kono [15] and Koch et al. [21], the transformation of the $hcp$ $\varepsilon$-AlMn phase to the $L_1^0$-ordered $\tau$-AlMn phase has been extensively studied. The $\varepsilon \rightarrow \tau$ transformation is reported to occur by a compositionally-invariant diffusional nucleation and growth process – *i.e.* a massive transformation – upon controlled cooling at rates between 10 to 30 °C/sec [1, 15, 140, 144, 145] or by heating at temperatures between 350-800 °C [11, 12, 17-21, 23, 27-30, 140]. Liu et al. observed that Al$_{45}$Mn$_{55}$ ribbons melt-spun with a tangential wheel surface velocity of 40 m/s in an Ar protective atmosphere consisted of a single hexagonal $\varepsilon$-AlMn phase which transformed to the $L_1^0$-type $\tau$-phase at 500 °C [27].

Most reports on the mechanism of the $\varepsilon \rightarrow \tau$ transformation suggest a two-step process whereby the $\varepsilon$-phase transforms to the intermediate orthorhombic $\varepsilon'$-phase ($B_{19}$ structure) which then transforms to the $L_1^0$-type $\tau$-phase, albeit with significantly different proposed reaction mechanisms [16, 19, 20, 24, 29, 30, 146, 147]. Several groups postulate that $\varepsilon$-AlMn undergoes an ordering reaction to form the $\varepsilon'$-phase, which then undergoes a diffusionless martensitic transformation to the $\tau$-phase, as shown in
Figure 21 [16, 24, 25, 144, 146]. Other groups have hypothesized a reaction mechanism whereby the ε-phase transforms to the intermediate ε'-AlMn phase and then to τ-AlMn via a short-range diffusional compositionally-invariant nucleation and growth process, i.e. a massive transformation [19, 29, 30, 147]. For more details on the mechanism and kinetics of the ε → τ transformation, see references [19, 25, 29, 30].

Investigations of the kinetics of the ε → τ transformation agree in that the transformation occurs via a short-range diffusional heterogeneous nucleation and growth process from the ε-AlMn grain boundaries (Figure 22a [29]) and imparts a high defect density into the τ-phase, but diverge from there [19, 29, 30, 148]. Yanar et al. observed a “polytwinned” morphology in the τ-AlMn phase and noticed that the advancing interphase interfaces were faceted but displayed no orientation relationship with the parent phase (Figure 22b) [29]. Yanar et al. also characterized the activation energy of the transformation by determination of the velocity of the advancing τ-AlMn phase.
boundaries using electron microscopy analysis, and found the activation energy ($E_a$) of the transformation to be approximately 154 kJ/mol [29].

![Figure 22](image)

Figure 22: (a) Optical microscope image of the growth of the $\tau$-AlMn phase from the grain boundaries of the parent $\varepsilon + \varepsilon'$ phase. (b) Electron image of the faceted interfaces developed during $\tau$-phase growth [29].

Mulyukov and Khaphizov [28] reported growth of $\tau$-AlMn at a minimum temperature of 500 °C and suggest that $\tau$-phase formation is favored in fine-grained $\varepsilon$-phase because heterogeneous nucleation occurs at defects such as grain boundaries and crystal imperfections. Kim and Perepezko [25, 144] carried out containerless rapid solidification of the hcp $\varepsilon$-AlMn phase in order to minimize defect structures. They hypothesized that the transformation originates on the surface of nanoscopic islands (~40 nm) of the orthorhombic $B_{19}$-structured $\varepsilon'$-phase at approximately 400 °C then proceeds from $\varepsilon$-phase AlMn grain boundaries. Dobromyslov et al. suggested that the reactions that form the $B_{19}$-type $\varepsilon'$-phase and the $L1_0$-type $\tau$-AlMn phase from the $\varepsilon$-AlMn parent phase are competitive in nature, but not explicitly linked to one another [30]. They proposed that the orthorhombic $\varepsilon'$-phase is essentially an extraneous product, rather than
an intermediate product required for formation of \( \tau \)-AlMn; the reaction proceeds as \( \epsilon \rightarrow \epsilon + \epsilon' \rightarrow (\epsilon + \epsilon') + \tau_{\text{heterogeneous}} \rightarrow \tau \), where the stacking faults introduced by formation of the \( \epsilon' \)-phase assist in the heterogeneous nucleation of the \( \tau \)-phase at the parent \( \epsilon \)-phase grain boundaries. Jakubovics et al. agree with Dobromyslov’s conclusion that stacking faults along the \{111\} plane of the \( \epsilon \)-phase may be helpful to \( \tau \)-phase nucleation [148], but also note that antiphase boundaries (APBs) developed during the massive transformation to the \( \tau \)-phase may be detrimental to both its nucleation and its eventual permanent magnetic character. They reported that APBs act as domain wall nucleation centers, whereas stacking faults act as domain wall pinning sites.

**Magnetic behavior of near-equatomic Al-Mn alloys**

The magnetic character of Al-Mn alloys is intensely dependent on their crystal structure. The rhombohedral \( \gamma_2 \)-AlMn phase and the complex cubic \( \beta \)-AlMn phase are both reported as paramagnetic at unspecified temperatures [12, 20]. The hexagonal \( \epsilon \)-AlMn phase is reported as antiferromagnetic (AF) with a Néel temperature (\( T_N \)) \( \sim 97 \) K [10-12, 26, 149] – the \( \epsilon \)-phase is of primary interest for this thesis work. However, there have been very few investigations into the AF character of the hexagonal \( \epsilon \)-phase [26], especially with reference to possible use in exchange-biased permanent magnet applications [1, 10]. Wyslocki et al. carried out one of the only studies of the magnetic character of the non-oriented \( \epsilon \)-AlMn phase. They performed a Curie-Weiss analysis (Eq. (27) in Section 3.2.1.1) on measurements of the magnetic susceptibility (\( \chi \)) of the \( \epsilon \)-phase as a function of temperature (\( T \)) and verified that the non-oriented hexagonal-close-packed (hcp) \( A3 \)-type \( \epsilon \)-AlMn phase was AF with \( T_N = 97 \) K (Figure 23a) [26]. They attributed the positive paramagnetic Curie temperature (\( \theta \)) they calculated to a number of
ferromagnetic (FM) exchange correlations between Mn-Mn next-nearest-neighbor atomic pairs, similar to the behavior of Cu-Mn alloys reported by Kouvel (Section 3.2.1.1) [9, 110]. Jiménez-Villacorta et al. observed the first occurrence of an exchange bias ($H_{ex} \sim 10$ kOe at 10 K) shift in rapidly-solidified hcp $\varepsilon$-AlMn alloys (Figure 23b) [10], and ascribed the shift to exchange interactions between intimately-coupled nanosize Mn-rich and Mn-poor regions.

![Figure 23](image)

**Figure 23:** (a) Plot of $\chi$ and $\chi^{-1}$ as a function of $T$ obtained from an $\varepsilon$-MnAlC alloy to illustrate the antiferromagnetic character of the hexagonal phase [26]. (b) Magnetization loops collected from melt-spun $\varepsilon$-Al$_{45}$Mn$_{55}$ alloy displayed an $H_{ex}$ shift $\sim 13$ kOe at 10 K [10].

The vast majority of prior research on the magnetic and structural character of near-equiatomic Al-Mn alloys centers on stabilization of the tetragonal $L1_0$-type $\tau$-AlMn phase (Figure 20) and its potential as an alternative permanent magnetic material [1-3, 11, 12, 15-19, 21-23, 25, 28, 30, 142-144, 150, 151]. The $\tau$-phase is reported to be resistant to corrosion and possesses attractive hard ferromagnetic (FM) character: robust magnetocrystalline anisotropy ($K_1 \sim 10^7$-$10^8$ erg/cm$^3$), high room-temperature coercivity ($H_c \sim 1.5$-$3.0$ kOe) and saturation magnetization ($M_s \sim 88$-$98$ emu/g, a moderate Curie
temperature \( (T_c) \sim 250 \, ^\circ\text{C} \), and favorable maximum energy product values \((BH)_{\text{max}} \sim 2-7 \, \text{MGOe} \) \[2, 3, 10-12, 15-27\].

3.2.2 Bulk magnetic nanocomposites consisting of two or more phases

The ultimate goal of this thesis work is the clarification of the mechanisms of exchange bias \((H_{\text{ex}})\) and magnetic remanence \((M_r)\) enhancement in bulk ferromagnetic/antiferromagnetic (FM/AF) magnetic nanocomposite systems. In reports to date, these systems have been mostly fabricated by mechanical milling. Sort et al. reported significant magnetic remanence \((M_r)\) enhancement \((M_r/M_s \sim 1\) at room temperature after 1 minute of milling, shown in Figure 24\) and an approximately 60% enhancement in the maximum energy product \((BH)_{\text{max}}\) values upon mechanical milling of FM/AF nanocomposites of composition SmCo\(_5\)/NiO and SmCo\(_5\)/CoO \[152, 153\]. They attributed the \(M_r\) enhancement above \(M_r/M_s > 0.8\) to short-range exchange interactions between the small SmCo\(_5\) particles, and further \(M_r/M_s\) enhancement to exchange interactions between SmCo\(_5\) and the antiferromagnetic oxide particles \[153\]. They reported no exchange bias \((H_{\text{ex}})\) shift in the field-cooled (FC) magnetization loops.
Mishra et al. observed small $H_{ex}$ shifts on the order of 100 Oe at 5 K in mechanically-milled FeNi/CoO nanocomposites (Figure 25a) [154]. Anhøj, Jacobsen, and Mørup reported similarly small $H_{ex}$ shifts of approximately 10-30 Oe at room temperature in mechanically-milled Fe$_{100-x}$Mn$_x$/Fe nanostructured powders (Figure 25b) [155].

Each of these papers reported small exchange bias shifts in mechanically-milled composite systems and, while several similar studies exist, reports concerning bulk
FM/AF nanocomposites containing no rare-earth elements are few and far between [1]. Lewis et al. reported a small $H_{ex}$ shift of a few Oe and a resultant maximum energy product $(BH)_{max}$ enhancement in field-cooled magnetization loops collected at 10 K from nanostructured melt-spun $(\text{Fe}_{65}\text{Co}_{35})_{100-x}(\text{Au}_{50}\text{Mn}_{50})_{x}$ ribbons, where $\text{Fe}_{65}\text{Co}_{35}$ was employed as the FM component and $\text{Au}_{50}\text{Mn}_{50}$ was the AF component [7]. The weakness of the unidirectional exchange anisotropy effect in the alloy was attributed to poor FM/AF interfacial contact, small magnetocrystalline anisotropy in the antiferromagnetic $\text{Au}_{50}\text{Mn}_{50}$ component, and random atomic disorder in the $\text{Au}_{50}\text{Mn}_{50}$ alloy [1]. Additionally, as was mentioned in Section 3.2, Co is a strategic element and, as such, supply issues may arise. The cost of Au (greater than $10,000$/kg) is also a consideration that renders the $(\text{Fe}_{65}\text{Co}_{35})_{100-x}(\text{Au}_{50}\text{Mn}_{50})_{x}$ nanocomposite potentially unattractive as an alternative permanent magnetic material [2]. Significant further research is needed to realize the prospect of rare-earth-free permanent magnetism conferred by the exchange bias phenomenon.

3.3 Summary

In summary, this literature review has provided a fundamental background of the thermodynamic properties of interest in bulk magnetic materials at the nanoscale. Intriguing behaviors that occur in nanostructured materials as a result of these unique energy considerations, such as single-domain behavior, magnetic blocking behavior, and exchange-spring and exchange bias behavior are discussed. The magnetic and structural attributes of three reportedly-antiferromagnetic (AF) MnX binary metallic alloys (i.e. Cu-Mn, Ag-Mn, and Al-Mn) which either exhibit or are anticipated to exhibit such phenomena are reviewed. This literature review points out deficiencies in the literature
with regards to investigations of the AF character of these MnX alloys, as far as their potential use as AF components in exchange-biased nanocomposite systems for rare-earth-free permanent magnet applications. This information will be relevant when investigating the nature of exchange bias and remanence enhancement in ferromagnetic/antiferromagnetic nanocomposites.
4.0 EXPERIMENTAL TECHNIQUES

The goal of this thesis work is to clarify the conditions controlling exchange bias and remanence enhancement in nanostructured bulk magnetic systems comprised of ferromagnetic (FM) and antiferromagnetic (AF) phases. A material’s magnetic behavior is intimately related to its structure, so understanding both attributes and the interactions between them is important. Elucidation of the relationships between magnetism and structure in FM/AF nanostructured systems will be facilitated through comprehensive characterization and analysis of the magnetic and structural properties of the bulk Mn-based FM/AF metallic nanocomposites outlined in Section 3.1.2.

Bulk FM/AF Mn-based metallic nanocomposites will be synthesized using nonequilibrium solidification methods to access and retain a nanostructure, and the evolution of the nanostructure due to post-solidification processing will be followed with structural and magnetic probes. In particular, after synthesis by melt-spinning and low-temperature isochronal annealing, x-ray diffraction (XRD) will be used to examine the crystal structure and phase constitution, while scanning electron microscopy (SEM) will be employed to examine grain/phase structure and morphology and to confirm the composition by energy dispersive x-ray spectroscopy (SEM-EDX, or EDX).

The magnetic response of the materials will be characterized by superconducting quantum interference device (SQUID) magnetometry and vibrating sample magnetometry (VSM). Important parameters such as the saturation magnetization \( M_s \), the magnetic susceptibility \( \chi \), the intrinsic coercivity \( H_{ci} \) and the exchange bias field \( H_{ex} \) will be measured as functions of temperature \( T \) and applied magnetic field \( H \) –
refer to Section 2.2 for more detailed definitions of magnetic properties of interest. Multiphase demagnetization curves collected using the SQUID magnetometry and VSM techniques will be decomposed into their components using a phenomenological model to determine the relative contributions of each component to the total magnetization. The thermal character of magnetic and structural transformations will be evaluated with differential scanning calorimetry (DSC).

The following sections of this Chapter will provide an overview of the operation principles of and the motivation for using each experimental technique, and give relevant information concerning the obtained data. Section 4.1 outlines the methods used to synthesize samples of bulk Mn-based metallic nanocomposites. Processing procedures are detailed in Section 4.2. The compositional and structural characterization techniques are described in Section 4.3. Section 4.4 details the magnetic characterization methods. The techniques used to investigate the evolution of the alloys’ magnetic and structural properties as a result of relaxation and diffusive processes are outlined in Section 4.5.

4.1 Synthesis of bulk Mn-based metallic nanocomposites

Nanostructured samples of Mn-based alloys are synthesized by plasma arc melting followed by subsequent rapid solidification via melt spinning. Melt-spun ribbons will be used as precursors in mechanical milling. The synthesized nanocomposites will undergo post-synthesis processing as described in Section 4.2.

4.1.1 Synthesis and homogenization of Mn-based alloys by plasma arc melting

The plasma arc melting technique is used to synthesize a homogeneous mixture of component metals in an alloy. This technique uses an electrode to heat a constricted flow
of inert gas to an extremely high temperature \( T \) so that the gas becomes electrically conductive. The ionized gas, or plasma, transfers an electric arc from the electrode to the sample, which is then melted by the intense heat from the plasma arc. Surface tension and forced convection in the melt provide effective mixing of the molten metals during exposure to the arc [156]. The melt cools in an inert atmosphere and solidifies after the arc is removed by disengaging the electrode.

In the initial stages of this research, alloys with nominal compositions \( \text{Cu}_{30}\text{Mn}_{70} \), \( \text{Al}_{50}\text{Mn}_{50} \), \( \text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10} \) and \( \text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10} \) are synthesized by arc-melting. Initial charges of Cu wire (Alfa Aesar, 99.999% purity, metals basis), Mn granules (Alfa Aesar, 99.98% purity, metals basis), Fe granules (Alfa Aesar, 99.98% purity, metals basis), and Al foil (Alfa Aesar, 99.9% purity, metals basis) are arc-melted in an Ar atmosphere (Medtech, 99.995% purity) using an Edmund Bühler-GmbH MAM1 mini plasma arc melting system. An additional 5 wt.% of the required amount of Mn has been added to offset Mn volatilization during melting in all cases [157]. The arc melting chamber is typically flushed with Ar three times, then backfilled with Ar to a pressure \( (P) \) of -0.2 bar. After a slug of Ti is melted as a getter to scavenge remaining oxygen in the chamber atmosphere, the arc is moved to the sample materials for melting. After the initial melting and solidification, the chamber is opened and the ingots are flipped over and remelted at least twice more for increased homogenization. The homogenized alloys’ surfaces are lightly ground to minimize surface oxides, then the ingots are ultrasonicated in ethanol to remove grinding debris.
4.1.2 Rapid solidification of nanostructured Mn-based alloys via melt spinning

Melt spinning is a rapid solidification technique used to access and retain nanostructured materials and metastable states through rapid quenching. An ideally-homogenized slug of precursor material is placed in a crucible (comprised of a refractory electrically-insulating material such as quartz or boron nitride, BN) and melted by induction coils under an inert atmosphere. A small backpressure of \( \leq 1 \text{ atm} \) then extrudes the melt through a small orifice in the crucible bottom onto a Cu wheel, which is spinning at \( \sim 20-70 \text{ m/s} \) to effectively increase the surface area over which heat transfer occurs. The melt hits the wheel and solidifies into thin metallic ribbons at quench rates as high as \( 1 \times 10^6 \text{ K/s} \) [158]. Melt spinning was carried out at the Naval Research Laboratory (NRL) and at Northeastern University.

The arc-melted ingots described in Section 4.1.1 are used as melt spinning precursors in this study. The ingots are placed in quartz crucibles with circular orifices of different diameter based on the respective melt’s viscosity. The orifice diameters used for processing each ingot, in order of decreasing melt viscosity, are \( \sim 0.61 \text{ mm} \) for \( \text{Al}_{50}\text{Mn}_{50} \), \( \sim 0.57 \text{ mm} \) for \( \text{Cu}_{30}\text{Mn}_{70} \) and \( \text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10} \), and \( \sim 0.48 \text{ mm} \) for \( \text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10} \). At NRL, an optical pyrometer monitors the temperature of the melt, and the melt-spinning process is carried out under 0.3 atm He gas. An additional 1.0 atm backpressure of He is applied to eject the melt from the crucible; the material solidifies as it contacts the Cu wheel spinning at a tangential velocity of \( \sim 64 \text{ m/s} \).

Additional Mn-based metallic nanocomposite specimens will be melt spun with an Edmund Bühler-GmbH Melt-Spinner SC at Northeastern University. Here, the arc-
melted charges are placed in a reusable BN crucible with a rectangular slit of diameter ~0.6 mm. The melt spinning chamber is purged to $P \sim 5 \times 10^{-7}$ mbar, then backfilled with Ar (MedTech Gases, 99.95% purity) to $P \sim 790$ mbar. A backpressure of 1.0 bar is used to eject the melt onto a spinning Cu wheel that has a tangential velocity of ~32 m/s.

### 4.1.3 Pulverization of melt-spun ribbons via mechanical milling for phase mixing

Mechanical milling will be used to foster improved interphase mixing. Mechanical milling is a simple and inexpensive technique of pulverizing materials into fine powders that can contain nonequilibrium phases such as supersaturated solids, metastable phases, and nanostructures [159]. A crucible containing the sample material and grinding media violently spins or shakes and inelastic collisions between the two materials store mechanical energy in the sample as plastic deformation. The energized material is then effectively “quenched” into a configurationally-frozen state to retain desirable nonequilibrium properties [160].

One mechanical milling technique employed in this work is planetary ball milling, a low-energy milling method with a high grinding media velocity but low collision frequency [160]. The planetary milling technique pulverizes the sample material in a rapidly-rotating crucible (100-1000 rpm [161]) that contains grinding media which cascade around and pulverize the specimen by frequent impaction. The Fritsch Pulverisette 6 planetary mill employed in this work is typically operated with a stainless steel crucible and grinding media at a rotational speed in the range 100-650 rpm [161, 162]. Friction between the grinding media and crucible walls generates heat and raises the milling temperature (estimated by as much as 590 °C in Al-Cu-Mn [163]) in
traditional comminution techniques such as room temperature \(T\) planetary ball milling. High milling \(T\) results in increased atomic mobility and interdiffusion which may lead to recovery of crystal defects (recrystallization) and deterioration of desirable metastable states [160]. Milling at lower \(T\) may minimize oxygen contamination and diffusive processes such as recrystallization and phase transformations [164].

An additional mechanical milling technique employed in this work is shaker milling carried out at cryogenic temperatures (or cryomilling). Cryomilling is a low-energy milling method with a low grinding media velocity, collision frequency, and operating \(T\) [160]. A crucible containing the sample material and grinding media is submerged in liquid nitrogen (L-N\(_2\), \(T \sim 77\) K) to lower \(T\). The low milling \(T\) embrittles the specimen, which is then pulverized with a magnetically-oscillated steel impactor rod.

The Mn-based nanocomposites studied in this work, synthesized as described in Section 4.1.2, are used as precursors for cryomilling. The SPEX SamplePrep 6770 Freezer/Mill Cryogenic Grinder uses a 440C stainless steel crucible submerged in L-N\(_2\) containing a magnetized steel impactor rod and the sample material. The crucible is pre-cooled in the L-N\(_2\) for 10 minutes. Cryomilling is then carried out in 5-minute intervals, interspersed by a two-minute recooling period, by applying an oscillating magnetic field to drive the impactor rod rapidly up and down (10 cycles/sec) to pulverize the sample.

4.2 **Heat treatment of bulk Mn-based metallic nanocomposites**

The melt-spun ribbons or cryomilled powders synthesized by methods outlined in Section 4.1 will be sealed in evacuated vitreous silica tubes to prevent oxidation during heat treatment. The evolution of the alloys’ magnetic and structural properties induced
by annealing will be investigated with the structural and magnetic probes described in Sections 4.3 and 4.4.

4.2.1 Prevention of oxidation of specimens during annealing

A small aliquot (< 100 mg) of each material is sealed in a thin evacuated vitreous silica tube, configured as in Figure 26, to provide an inert atmosphere for annealing and magnetic measurements by the techniques described in Section 4.4 [165]. The silica tube is evacuated to $P \sim 1 \times 10^{-6}$ torr and closed with a propane torch to seal under vacuum.

![Figure 26: Straw/quartz tube configuration for annealing. Rods & glass wool prevent sample movement.](image)

4.2.2 Heat treatment of melt-spun ribbons and cryomilled powders

Annealing is a technique used to modify a material’s structure by adding thermal energy to drive diffusion and/or structural relaxation. During isochronal heat treatment the sample is held at an elevated temperature for a set time. The Mn-based metallic nanocomposites in this study, vacuum-sealed using the method in Section 4.2.1, are isochronally annealed by placing the specimens in the middle of the heating zone of a programmable MTI GSL1100X tube furnace and treating at the desired temperature for 30 minutes. The actual temperature in the middle of the hot zone is measured using a calibrated K-type thermocouple and digital thermometer.

4.3 Characterization of structure & composition of melt-spun Mn-based alloys

The crystal structure, composition and microstructure of a magnetic material significantly affect its important technical (extrinsic) magnetic properties such as
magnetic susceptibility ($\chi$), magnetic remanence ($M_r$), coercivity ($H_c$), and exchange bias field ($H_{ex}$) [1, 7, 166, 167], as discussed in Section 4.4. The volume-averaged chemical composition of the Mn-based nanocomposites synthesized and processed with the techniques in Sections 4.1 & 4.2 is verified using scanning electron microscope energy-dispersive x-ray spectroscopy (EDX). The structure is investigated on a variety of length scales – x-ray diffraction (XRD) will be used to determine crystallographic phase identity and dimensions, while scanning electron microscopy (SEM) will be used to examine the morphology and microstructure. The operational principles of these techniques are described below.

### 4.3.1 Compositional determination of samples

The material’s volume-averaged chemical composition is probed using the SEM-based technique of EDX as follows. The material is subjected to electron bombardment that penetrates the specimen surface approximately 1 μm and induces ejection of a small fraction of electrons from the inner-shell orbitals of atoms in the sample [168], creating electronic vacancies and producing an excited state in the electron (Figure 27a) [169]. Outer-shell electrons fill the inner-shell vacancies and emit x-rays with characteristic element-specific energies. The intensity of characteristic x-ray emissions is measured to determine the material’s chemical composition averaged over the interaction volume (described below) [170].
Figure 27: (a) Basic illustration of characteristic x-ray emission in a Bohr atom. (b) Typical specimen-electron interaction volume – more energetic beam electrons penetrate deeper into sample.

Eq. (28) is used to approximate the depth which beam electrons will penetrate into the specimen, while Eq. (29) approximates the interaction volume width [170].

\[ x = 0.1E_0^{1.5}/\rho \]  

\[ y = 0.077E_0^{1.5}/\rho \]  

where: \( x \) = Beam electron penetration depth (μm) \( y \) = Width of interaction volume (μm) \( E_0 \) = Accelerating voltage of electron beam (keV) \( \rho \) = Sample density (g/cm³)

The SEM examinations and EDX measurements of samples in this work are carried out on a Hitachi S4800 field-emission SEM. An electron beam with an accelerating voltage \( E_0 \) ranging from 12-15 keV is used to probe the volume-averaged composition at a working distance of 15 mm. For a metallic material with a density of roughly 7 g/cm³ (Al₄₅Mn₅₅ has a calculated density of 7.2 g/cm³ [127]), Eq. (28) and Eq. (29) can be used to approximate the dimensions of the interaction volume – the lateral
spatial resolution is ~0.5-0.7 μm while the beam penetrates the specimen ~0.6-0.8 μm [170]. If the excitation volume is assumed to be spherical with a diameter of 0.6 μm, the chemical composition detected by EDX is the average over a volume of 0.036 μm³ [170].

4.3.2 Crystallographic structure investigation and analysis

The crystal structures of materials studied in this work are investigated using x-ray diffraction (XRD). The specimen is placed in the XRD sample holder and exposed to a beam of monochromatic x-ray waves incident to the sample surface at an angle $\theta$. As the incident beam interacts with the sample, specimen atoms diffract secondary x-rays (see Figure 28a) [32], and a detector measures the intensity of the diffracted x-ray beam.

![Figure 28: (a) X-ray diffraction by a regularly-spaced array of atoms. (b) Miller indices used for denoting orientation of crystallographic planes in a primitive cubic unit cell.](image)

The diffracted x-ray waves interfere destructively unless the incident beam is at an angle parallel to a crystallographic plane in the specimen (the orientation of a crystal plane is denoted by the Miller indices of the plane, depicted in Figure 28b). This criterion is satisfied at a Bragg angle ($\theta_B$) where x-rays are coherently diffracted and thus interfere constructively with one another, causing an increase in the diffracted beam intensity measured by the detector. The location of peaks on a plot of the intensity of the
diffracted beam vs. $2\theta$ can provide information about the size and shape of the crystallographic unit cell [32], the smallest repeated arrangement of atoms in a crystal phase (for a clarification of the characteristics of a crystal phase and of a unit cell, refer to the discussion of crystallography in Section 2.1). The Bragg angles of each crystallographic phase present will be derived from the parameters of a Gaussian fit (Eq. (30)) to each peak in the plot of relative intensity vs. $2\theta$.

\[
I = m_1 + \sum m_2^{(i)} \exp \left( \frac{(2\theta - m_3^{(i)})^2}{m_4^{(i)}^2} \right) \tag{30}
\]

where: $I$ = Relative intensity of diffracted x-rays ($0 \leq I \leq 1$) (unitless)

$m_1$ = Constant background term (unitless)

$m_2$ = Gaussian peak scaling factor ($0 \leq m_2 \leq 1$) (unitless)

$m_3$ = Bragg angle, the center of the Gaussian peak (degrees $2\theta$)

$m_4$ = Peak width factor (degrees $2\theta$)

The summation in Eq. (30) is carried out over the number of crystallographic phases contributing to each Bragg reflection. The unit cell lattice dimensions (and the error in such) of each crystallographic phase present in the materials in this study are quickly calculated with a least-squares cell parameter fitting program tailored to each space group [171]. The program user first inputs the Bragg diffraction angles of each phase where $\theta_B = m_3^{(i)}$ in Eq. (30), then the program evaluates the average spacing between crystal planes in the phase, the interplanar spacing ($d$), using Bragg’s law (Eq. (31)) [172]:
\[ d = \frac{n\lambda}{2\sin \theta_B} \]  

(31)

where: \( d \) = Interatomic/interplanar spacing (Å)

\[ \lambda = \text{Wavelength of incident Cu-K}_{\alpha1} \text{ radiation (Å)} \]

\[ \theta_B = \text{Bragg diffraction angle (degrees } \theta) \]

\[ n = \text{Reflection order, } i.e. \text{ an integral number of incident x-ray wavelengths (unitless)} \]

The \( d \)-spacing calculated from Eq. (31) is then used to determine the unit cell lattice parameters. The user then guesses \( (hkl) \) Miller indices (Section 2.1.2) which correspond to each Bragg peak. Unit cell lattice parameters are calculated by the methods detailed in Section 2.1.3 (Eq. (1)-(7)). The volume-averaged crystallite size will then be calculated by first evaluating the full-width at half the maximum (FWHM) of the Gaussian fits (Eq. (30)) to the most intense Bragg reflection, as shown in Eq. (32).

\[ FWHM = 2m_4 \sqrt{\ln \left( \frac{2m_2}{m_2 - m_1} \right)} \]  

(32)

where: \( FWHM = \text{Full-width at half the maximum (degrees } 2\theta) \)

\[ m_1 = \text{Constant background term (unitless)} \]

\[ m_2 = \text{Gaussian peak scaling factor } (0 \leq m_2 \leq 1) \text{ (unitless)} \]

\[ m_4 = \text{Peak width term (degrees } 2\theta) \]

The \( FWHM \) determined in Eq. (32) is then used to calculate a rough estimate of the volume-averaged crystallite size by use of the Scherrer equation in Eq. (33), which
assumes that Bragg peak broadening is due to finite crystallite size (< 150 nm) effects only [173].

\[
D = \frac{K \lambda}{B \cos \theta_B}
\]  

(33)

where: \(D\) = Volume-averaged crystallite size (nm)

\(K\) = Shape factor, 0.94 for spherical crystallites (unitless)

\(B\) = Full-width at half the maximum intensity (FWHM) of Bragg reflection (radians 2\(\theta\))

\(\theta_B\) = Bragg angle (radians \(\theta\))

The Philips PANalytical X’Pert Pro diffractometer employed in this study is set up in the \(\theta/2\theta\) configuration, as illustrated in Figure 29 – the incident x-ray beam rotates around the sample at an angle \(\theta\) while the x-ray detector rotates at an angle 2\(\theta\).

![Figure 29: Powder x-ray diffractometry in the \(\theta/2\theta\) configuration.](image)

The incident x-ray beam is generated by bombarding a Cu anode with electrons, dislodging inner-shell electrons and thereby emitting Cu-K\(_\alpha\) and Cu-K\(_\beta\) x-rays. The K\(_\beta\) component of the emitted x-rays is removed by passing the x-rays through a Ni
monochromator (the absorption edge of Ni lies between the wavelengths of Cu-K\(_\alpha\) and Cu-K\(_\beta\) radiation [174]), so that the beam directed onto the sample surface consists of only Cu-K\(_{\alpha1}\) and Cu-K\(_{\alpha2}\) radiation. An algorithm in the data processing software removes the K\(_{\alpha2}\) contribution from the diffracted x-rays, leaving only the K\(_{\alpha1}\) contribution (the wavelength of Cu-K\(_{\alpha1}\) x-rays is 1.54056 Å [127]).

4.3.3 Characterization of Mn-based metallic nanocomposite microstructure

A material’s microstructural character has a significant impact on its magnetic properties [64]. The microstructure and surface features of the samples studied in this work will be examined with scanning electron microscopy (SEM). The SEM and EDX techniques are both carried out with the same electron microscope (discussed in Section 4.3.1), but the two techniques rely on different interactions between the specimen and the electron beam. While EDX utilizes characteristic x-ray emissions to determine the sample composition, SEM takes advantage of secondary electron (SE) emissions, which result from scattering of outer-shell specimen electrons by the primary incident beam electrons [170].

An image of the specimen’s microstructure is developed from these SE emissions, which occur throughout the entire interaction volume but only escape from a thin layer that is typically within 50-500 Å of the sample surface due to their low energy (Figure 27a) [175]. A SE detector can sense the angle and intensity of the SE emissions to construct a two-dimensional image of the sample’s surface features [170]. Surface images of samples studied in this work are collected using electron beams with
accelerating voltages \((E_0)\) in the range \(~3-12\) keV and working distances between \(8-15\) mm.

4.4 **Investigation & analysis of magnetic response of Mn-based nanocomposites**

A material’s magnetic character provides information about the ordering of its electron spins – magnetic properties may be intrinsic and therefore structure-insensitive or extrinsic and depend on the structure of the material, as detailed in the basic discussion of magnetism in Section 2.2. The magnetic character of samples in this study will be investigated with superconducting quantum interference device (SQUID) magnetometry and vibrating sample magnetometry (VSM) as a function of temperature \((T)\) and applied field \((H)\) under field-cooled (FC) and zero-field-cooled (ZFC) conditions. Correlations between the magnetism and the structure will be developed to enhance understanding of the origins of the magnetic properties. All magnetic measurements will be corrected for the high-field linear susceptibility. The shape of the hysteresis \((M-H)\) curves measured by these techniques at a variety of temperatures will be decomposed to determine the relative contribution of each magnetic component to the total magnetization.

4.4.1 **Characterization of the bulk magnetic response by superconducting quantum interference device (SQUID) magnetometry**

The volume-averaged magnetic moment of a material may be probed with the ultrasensitive SQUID magnetometry technique [37]. Figure 30 illustrates schematically the operating principles behind a typical SQUID magnetometer, which has three primary parts – a superconducting magnet consisting of a solenoid wrapped in a superconducting wire, a superconducting detection coil, and a flux-voltage transformer [165].
Figure 30: Basic configuration of a SQUID magnetometer. The sample’s magnetic moment induces changes in current through the pickup coils.

An electric current passes through the superconducting wire to produce a strong uniform longitudinal magnetic field $H$ in the positive and negative directions. The interaction between the coils and the magnetic moment of the sample induces currents in the pick-up coils of the SQUID magnetometer that are proportional to the total sample flux as the specimen is stepped vertically through the coils [165]. This current induces a secondary magnetic flux in a secondary coil, separate from the specimen. The secondary magnetic flux is converted to a dc voltage proportional to the amount of flux through the primary coil. A voltage ($V$) vs. position ($z$) plot is collected as the sample is scanned through the coils and is used to determine the $z$-component of sample moment as a function of variations in $H$ and $T$.

The Quantum Design MPMS-XL5 SQUID magnetometer employed to investigate the magnetic response of materials in this study operates in the applied field range $-50 \text{kOe} \leq H \leq 50 \text{kOe}$, the temperature range $1.8 \text{K} \leq T \leq 400 \text{K}$, and is sensitive to magnetic moments as small as $10^{-8} \text{ emu}$ [176]. In this thesis work, the magnetic moment of
samples is measured as a function of temperature and applied field. The specimens are cooled from 300 K to 10 K in cooling fields of $H_{\text{cool}} = 0$ kOe (the ZFC condition) or $H_{\text{cool}} = 1$ kOe (the FC condition) and the magnetic moment $m$ is measured under a constant probe field upon increasing temperature $T$. After ZFC and FC magnetic moment ($m$) vs. $T$ measurements are collected, the magnetic response is investigated as a function of $H$ by cooling the samples from 300 K to 10 K in fields of $H_{\text{cool}} = 0$ kOe (the ZFC condition) or $H_{\text{cool}} = 50$ kOe (the FC condition) and measuring the sample moment $m$ as $H$ is swept from 50 kOe to -50 kOe at a constant temperature $T$. Once this hysteresis loop is collected, the material is heated to collect hysteresis loops at higher temperatures.

4.4.2 Determination of the magnetic character of Mn-based nanocomposites through vibrating sample magnetometry (VSM)

The volume-averaged magnetic response of a material may also be probed by using vibrating sample magnetometry (VSM). Figure 31 illustrates schematically the basic operating principles of a VSM – a nonmagnetic rod vibrates the specimen in a set of pickup coils, and the oscillating magnetic flux from the sample induces in the pickup coils an alternating magnetic field with a magnitude proportional to the magnetic moment of the sample [40].

The Quantum Design VersaLab VSM is employed to investigate the magnetic response of materials in this study. This apparatus operates in the applied field range of $-30$ kOe $\leq H \leq 30$ kOe, in the temperature range $50$ K $\leq T \leq 1000$ K, and is sensitive to magnetic moments as small as $10^{-6}$ emu [177]. While not as sensitive as the SQUID magnetometer from Section 4.4.1 – the sensitivity of the VSM is two orders of magnitude
less than that of the SQUID magnetometer – the VSM has an averaging time of 1 sec for much faster measurements (a measurement typically takes 4 sec in the SQUID magnetometer used in this study) [176, 177]. Magnetic data collection on the VSM will be carried out in a fashion identical to that outlined for the SQUID magnetometer in Section 4.4.1, albeit within the $H$ and $T$ ranges of the VersaLab instrument.

![Basic vibrating sample magnetometer configuration.](image)

**Figure 31: Basic vibrating sample magnetometer configuration.**

### 4.4.3 Decomposition of multiphase demagnetization curves to determine the relative contributions of each component of the total magnetization

The measured magnetization of a sample is the sum of contributions from all magnetic components which constitute the system [178]. Each individual component in turn has unique magnetic properties, such as the saturation magnetization ($M_s$), the intrinsic coercivity ($H_c$), and the remanent magnetization ($M_r$). The linear high-field magnetic susceptibility ($\chi_{\text{linear}}$) will be subtracted from hysteretic measurements to isolate the nonlinear contributions to the magnetic response of the materials in this study. An empirical equation for describing the shapes of ferromagnetic (FM) demagnetization $M$-$H$ curves [179] (shown below in Eq. (34)) will then be used to decompose multiphase demagnetization curves, and to characterize such properties for each magnetic component.
or magnetic phase. The sigmoidal shape of a typical demagnetization curve for a FM material may be described by a modified inverse tangent function, \( i.e. M = A \tan^{-1}(kH) \), where \( M \) is the total magnetization, \( A \) is a proportionality constant, \( k \) is some unknown factor, and \( H \) is the applied magnetic field. The proportionality constant \( A \) limits the magnetization to a value equal to the saturation magnetization \( (M_s) \), while the factor \( k \) determines both the intrinsic coercivity \( (H_{ci}) \) and the magnetic remanence \( (M_r) \).

\[
M(H) = \sum_{i=1}^{n} \frac{2M_s^{(i)}}{\pi} \tan^{-1} \left[ \left( \frac{H \pm H_{ci}^{(i)}}{H_{ci}^{(i)}} \right) \tan \left( \frac{\pi S^{(i)}}{2} \right) \right]
\]  

(34)

where:

- \( M = \) Total nonlinear magnetization (emu/g)
- \( H = \) Applied magnetic field (Oe)
- \( n = \) Number of contributions to the total magnetization (unitless)
- \( i = \) Index denoting each individual contribution
- \( M_s^{(i)} = \) Saturation magnetization of component \( (i) \) (emu/g)
- \( H_{ci}^{(i)} = \) Coercivity of component \( (i) \) (Oe)
- \( S^{(i)} = \) Squareness of demagnetization curve of component \( (i) \) \( (i.e. M_r^{(i)}/M_s^{(i)}) \) (unitless)

In principle, the summation in Eq. (34) can be performed over all FM phases present in the sample. It is important to note that Eq. (34) is not derived from first principles, but rather is derived empirically based solely on approximation of the shape of a FM demagnetization curve. The relative contribution of each constituent magnetic
phase to the total magnetization \( x_i \) will be determined by calculating the fraction its saturation magnetization contributes to the total saturation magnetization, i.e. \( x^{(i)} = \frac{M_{s}^{(i)}}{M_{s}^{(tot)}} \).

4.5 Investigation of the thermal character of magnetic and structural transformations in Mn-based nanostructured alloys

Calorimetry, the science of measuring the evolution or absorption of heat from a material, is used to investigate the thermal character of chemical reactions or physical changes [180]. Heat treatment can cause such physical changes to the magnetic and structural properties of samples in this study as a result of relaxation and diffusion, and may result in phase transformations in samples of certain compositions [159]. The calorimetry technique will be carried out using a differential scanning calorimeter (DSC) to probe relaxation, grain growth, and phase transformations as a function of \( T \) in the Mn-based nanostructured alloys studied in this thesis work.

In a DSC, the sample material and an inert reference material with known thermal properties are each placed in pans and inserted into the calorimeter furnace. The furnace temperature \( T \) is raised at a constant rate as the sample and reference pans are both conductively heated. If the specimen undergoes a physical change or has a different heat capacity than the reference material at temperature \( T \), different amounts of heat flow to the sample pan and to the reference pan [181]. The DSC quantifies the heat flow difference between the sample and reference pans at temperature \( T \), allowing direct determination of the heat capacity of the specimen and the thermal character of any physical change with a latent heat associated with it. First-order magnetic and structural
phase transformations evolve latent heat, thus causing a peak in the heat flow difference at $T$ – the direction of a peak depends on whether a transformation is endothermic or exothermic. The plot of differential heat flow vs. $T$ in Figure 32 shows peaks associated with typical phase transformations often observed in data obtained from a DSC, such as heat capacity changes, crystallization and recovery, and fusion.

![Figure 32: Typical features of a DSC curve. Exothermic transitions in the positive direction (up), endothermic in the negative direction (down).](image)

In the work described in this proposal, thermal measurements are carried out on a Netzsch STA449-F3 Jupiter® simultaneous TG-DTA/DSC apparatus, which operates in the temperature range $-210 \, ^\circ\text{C} < T < 1200 \, ^\circ\text{C}$, with an empty Al$_2$O$_3$ crucible as the reference pan. Samples are placed in an Al$_2$O$_3$ crucible and heated to approximately 700 $^\circ\text{C}$ at rates of 5-20 $^\circ\text{C/minute}$ under an Ar atmosphere (Medtech Gases, 99.995% purity), then cooled back to room temperature at ~7-10 $^\circ\text{C/minute}$ using evaporated liquid N$_2$. Data are collected in two heating-cooling cycles to test for whether a transformation process is reversible or irreversible. The DSC controls heating rates more precisely than it controls
cooling rates so quantitative information about observed transformation processes will be derived from the heating curves only.

Multiple phase transformations may occur at near-identical temperatures, resulting in superposition of multiple DSC peaks. The contribution of each individual phase to the total DSC peak signal will be determined using a Gaussian fitting method similar to that used for decomposition of multiphase Bragg reflections in x-ray diffraction patterns (Eq. (30) in Section 4.3.2). Here, \( m_1 \) = DSC background signal (units of mW/mg), \( m_2 \) = DSC peak scaling factor (units of mW/mg), \( m_3 \) = temperature at maximum of DSC peak (units of °C), and \( m_4 \) = DSC peak width factor (units of °C). Kissinger analysis will be used to determine the activation energy of each phase transformation (Eq. (35)) [182, 183].

\[
\ln \left( \frac{\phi}{T_p^2} \right) = -\frac{E_a}{R} \left( \frac{1}{T_p} \right) + A
\]

(35)

where:
- \( \Phi \) = Heating rate (K/sec)
- \( T_p \) = temperature at the maximum of the transition peak (K)
- \( E_a \) = activation energy (J/mol)
- \( R \) = ideal gas constant (8.314 J/mol·K)
- \( A \) = constant (unitless)

Kissinger analysis assumes that a phase transformation follows first-order transformation kinetics (i.e. absorbs or emits latent heat), has only a single rate-limiting step, and that the rate constant \( k \) follows an Arrhenius dependence on temperature. The
activation energy $E_a$ will be calculated from the linear slope of the plot of $\ln \left( \frac{\phi}{T_p^2} \right)$ vs. $1/T_p$. It may be important to note that Eq. (35) has been shown to be accurate within 2% for most other transformation kinetics as well, given large values of $E_a/RT_p > 10$ [183, 184].

4.6 **Summary of experimental techniques used to investigate the magnetic and structural character of Mn-based nanocomposites**

In summary, in this work the differential scanning calorimetry (DSC), superconducting quantum interference device (SQUID) magnetometry, vibrating sample magnetometry (VSM), x-ray diffraction (XRD), scanning electron microscope energy-dispersive x-ray spectroscopy (EDX), and scanning electron microscopy (SEM) techniques will be used to elucidate the relationships between the atomic and microscopic structure and the magnetic character of nanostructured Mn-based alloys. Developing correlations between these attributes is anticipated to enable tailoring of the magnetic and structural properties of these alloys.
5.0 EXPERIMENTAL DESIGN

The overarching goal of this thesis work is to gain a fundamental understanding of the magnetic and structural conditions underlying exchange bias ($H_{ex}$) and magnetic remanence ($M_r$) enhancement in nanostructured bulk magnetic systems comprised of ferromagnetic (FM) and antiferromagnetic (AF) phases. In this thesis nanostructured specimens of Fe/MnX ($X = $ Cu, Al, etc.) will be synthesized and studied as model FM/AF nanocomposite systems, with Fe as the FM component and MnX as the AF component. An intimate mixture of the AF nanostructured Mn-based metallic component and nanosized regions of the FM matrix is anticipated to exhibit FM/AF exchange coupling and thereby augmented values of the magnetic remanence ($M_r$), coercivity ($H_c$), and maximum energy product ($BH_{max}$), the figure of merit in permanent magnetic materials [7].

A thorough fundamental understanding of the AF Mn-based component must be obtained prior to investigation of the more complex FM/AF nanocomposite containing Fe, including comprehension of the magnetic and structural attributes of these alloys and attainment of knowledge to allow control of their structural character. The specific objectives of this thesis work are thus threefold:

1. Synthesize, characterize, and understand correlations between magnetic and structural properties in bulk binary MnX ($X = $ Cu, Al, etc.) alloys with AF character.

2. Design and control structure of nanostructured MnX alloys on the nanoscopic and microscopic scales.
3. Implement MnX binary alloys with AF character into more complex Fe/MnX FM/AF nanocomposite systems and investigate how to promote exchange coupling across interfaces between the AF component and FM matrix, in order to achieve enhanced $H_c$, $M_r$, and $(BH)_{max}$.

Completion of these research objectives is anticipated to fulfill the overarching research goal – to understand the conditions underlying exchange bias and remanence enhancement in bulk FM/AF nanocomposites, and to apply this understanding to tailor the functional magnetic behavior. Work to date represents initial steps towards fulfillment of this overall research goal. Nanostructured Mn-based metallic alloys have been synthesized by plasma arc-melting and subsequent rapid solidification processing to retain metastable nanostructured states at room temperature. Samples have been characterized with magnetic and structural probes and subject to post-synthesis processing techniques, such as heat treatment and mechanical milling, to promote formation of and exchange coupling across intimate interphase interfaces. Preliminary attempts have been made to implant the nanostructured MnX alloys in a FM Fe-rich matrix phase – Fe/CuMn alloys of two compositions have been synthesized by rapid solidification and the magnetic and structural character of the as-quenched ribbons has been measured (Section 6.3). Further work for implantation of the nanostructured MnX alloys in a FM Fe-rich matrix and formation of intimate interphase interfaces between the AF MnX component and the FM matrix will be described in the recommendations for future work in Section 8.0.
The rationale for thesis experiments carried out to date is discussed in Section 5.1. Section 5.2 discusses each specific research objective and what is needed to satisfy each. Experimental designs and techniques are discussed in Section 5.3.

5.1 **Rationale for thesis experiments**

The ultimate goal of this thesis work is the clarification of exchange bias and magnetic remanence enhancement produced in bulk nanocomposite magnetic materials consisting of ferromagnetic (FM) and antiferromagnetic (AF) components. Model FM and AF components for study should ideally be relatively abundant, low in cost, and resistant to corrosion [1, 12]. The accompanying subsections will discuss, firstly, the motivation for using nanostructured FM and AF components (Section 5.1.1). The rationale for selection of various fabrication and processing techniques to foster interphase mixing between nanoscaled FM and AF phases is detailed in Section 5.1.2. Section 5.1.3 provides a justification for selection of the model FM/AF nanocomposite system used for study.

5.1.1 **Motivation for nanostructuring in ferromagnetic/antiferromagnetic (FM/AF) material systems**

Interphase quantum mechanical exchange interactions in materials containing an intimate mixture of ferromagnetic (FM) and antiferromagnetic (AF) components enact a unidirectional exchange anisotropy on the interfacial magnetic moments [5, 6]. The orientations of magnetic moments at the interface do not play a significant role in the orientation of the total magnetization if the average size of the FM regions is much greater than the exchange length ($l_{ex}$), given in Eq. (10) in Section 3.1.1.1 [1, 8, 39, 55,
The exchange length $l_{\text{ex}}$ is typically on the order of a few nanometers and is actually similar in magnitude to the domain wall width ($\delta_w$) in ferromagnetic materials [63, 64]. Appreciable exchange anisotropy will therefore not be observed in FM/AF composites with coarse-grained FM components, rendering fine FM regions necessary for investigations of the nature of exchange anisotropy in bulk systems.

In Kneller and Hawig’s seminal report on the optimization of hard magnetic properties in exchange-spring magnets (discussed in Section 3.1.2.2), they assumed that the ideal size of the AF regions was comparable to that of the FM regions [8]. It has been shown that an optimal microstructure which simultaneously maximizes coercivity and magnetization contains between about 10 vol. % and 50 vol. % of the AF component, depending on the microstructural geometry of the system. Synthesized nanocomposites should therefore be of approximate nominal composition $(\text{FM})_{100-x}(\text{AF})_x$, where $x = 10$-$50$, assuming similar densities and average molecular weight for the FM and AF components.

### 5.1.2 Selection of synthesis and post-synthesis processing techniques to foster interphase mixing

The exchange anisotropy phenomenon manifests in materials consisting of intimately-mixed regions of ferromagnetic (FM) and antiferromagnetic (AF) components of sufficiently small size, as discussed in Section 5.1.1 and Section 3.1.2.3 [1, 5, 7, 8, 42]. Materials studied in this thesis must therefore be carefully fabricated and manipulated by metallurgical methods to promote formation of interfaces between nanoscopic regions of FM and AF phases. The following subsections present a discussion of the rationale for
selection of optimal synthesis and post-synthesis processing techniques to foster mixing between the FM and AF phases.

5.1.2.1 Selection of synthesis techniques to promote formation of metastable nanostructured states

For reasons discussed in Section 5.1.1, the techniques used to synthesize bulk ferromagnetic/antiferromagnetic (FM/AF) composite solids must promote the formation of nanoscopic FM and AF regions. Development of fine grains or particles, however, is an energy-intensive process as illustrated in the plot of the change in Gibbs free energy $\Delta G$ vs. particle radius $r$ in Figure 33 [185]. In the absence of other effects, addition of atoms inside the particle volume reduces the free energy of the particle by an amount proportional to $r^3$, whereas addition of atoms to the surface raises the free energy of the particle by an amount proportional to $r^2$ [31, 159].

![Figure 33: Plot of Gibbs free energy $\Delta G$ vs. particle radius $r$. The surface/interfacial energy contribution raises $\Delta G$ proportionally to $r^2$, while the volume energy contribution lowers $\Delta G$ proportionally to $r^3$ [185].](image-url)
Fine-grained solid phases are thus generally thermodynamically unstable due to the reduction of free energy conferred by particle growth [159]. Retention of nanostructured phases requires local equilibrium (i.e. metastability). Metastable states, identified as local energy minima accessed through provision of sufficient energy to overcome an activation energy barrier as shown in the typical thermodynamic state diagram (Figure 34), may include nanostructured or fine-grained particles, metastable phases, and non-equilibrium alloy compositions [159, 160, 186]. Rapidly quenching a liquid material into the solid state permits access to highly metastable states which may exhibit intriguing magnetic and structural properties not otherwise observed [37, 40, 186]. Melt spinning (Section 4.1.2) is one such rapid solidification processing technique often used for synthesis of bulk solid glasses and amorphous alloys [31, 160]. In this thesis work melt-spinning will be employed for the fabrication of bulk ferromagnetic/antiferromagnetic (FM/AF) composite systems to access and retain metastable nanostructured states at room temperature.

![Figure 34: Thermodynamic state diagram (free energy vs. thermodynamic state). Metastable states are local energy minima accessed through provision of sufficient activation energy ($E_a$).](image)
5.1.2.2 Progression of metastable nanostructured states

Examination of the progression of magnetic and structural properties over several metastable states can provide important information about the stability of the system. Thermal energy will be used as the activation energy in this thesis work to induce progression of the ferromagnetic/antiferromagnetic (FM/AF) nanocomposite systems from the metastable as-solidified state to additional metastable states through grain growth, relaxation, and other diffusive processes [159]. Treatment at elevated temperatures may result in magnetic or structural phase transformations in the FM/AF nanocomposite systems under investigation. Calorimetric measurements will be carried out to investigate the thermal character, reversibility, kinetics, and energy requirements of any magnetic or structural phase transformations in the annealing range studied which may affect the magnetic and structural properties [159].

5.1.2.3 Post-synthesis processing to foster formation of intimate interfaces between ferromagnetic (FM) and antiferromagnetic (AF) components

The exchange bias phenomenon manifests in materials consisting of a nanoscale mixture of ferromagnetic (FM) and antiferromagnetic (AF) components [1, 5-7, 42]. It was noted in Section 5.1.2.1 that rapid solidification is anticipated to promote development of metastable nanostructured states in the bulk FM/AF composites under investigation. The microstructure and nanostructure of the nanocomposites’ studied in this thesis work will be manipulated by metallurgical means to foster formation of and exchange coupling across intimate FM/AF interfaces. To this end, mechanical milling
(discussed in Section 4.1.3) will be used to develop FM/AF interfaces via pulverization of FM/AF nanocomposite specimens into fine powders.

5.1.3 Selection of model ferromagnetic/antiferromagnetic (FM/AF) nanocomposite systems

Any investigations of magnetic and structural behaviors of exchange-biased bulk ferromagnetic/antiferromagnetic (FM/AF) nanocomposite systems require, first, selection of model materials to study. Ideal model material systems are anticipated to exhibit the exchange anisotropy phenomenon (defined in Section 2.2.6) when fabricated appropriately to obtain an intimate mixture of nanostructured FM and AF components, as discussed Sections 3.1.2.3 and 5.1.1. Model FM/AF nanocomposites should also consist of materials which are easily obtainable, low in cost, easy to process, nontoxic, and corrosion resistant [1]. Fe will be selected as a model FM component due to its low cost and elemental abundance, high saturation magnetization ($M_s$) $\sim 220$ emu/g at room temperature, and high Curie temperature ($T_C$) $\sim 770 \, ^\circ C$ (Table 3) [37, 39, 40, 102].

As noted in Section 3.2.1, low-cost MnX ($X = $ Cu, Al, etc.) binary alloys have been reported to exhibit AF character, and both Cu and Al are immiscible in Fe, which permits the eventual synthesis of Fe/MnX FM/AF magnetic nanocomposites. It has also been observed that the AF character of these MnX alloys can be manipulated by simply modifying their Mn content [10, 14, 51, 82, 107]. The Mn-based alloys Cu-Mn and Al-Mn are thus selected as model AF components in this thesis work – the predominantly-AF character of Mn-rich Cu-Mn alloys and near-equiaatomic $\varepsilon$-phase Al-Mn alloys is described in Sections 3.2.1.1 and 3.2.1.2, respectively [10, 11, 110, 149, 187].
Selection of Cu-Mn alloys as model antiferromagnetic (AF) components

Hysteresis loops collected from atomically-disordered quenched Cu-Mn alloys with low Mn content (~ 15-30 at. % Mn) have been observed to be displaced significantly from the origin at 4.2 K (Figure 17a, Section 3.2.1.1) [9, 110, 114]. The loop shift was attributed to the exchange bias ($H_{ex}$) phenomenon, wherein a unidirectional exchange anisotropy is conveyed by quantum mechanical exchange interactions between magnetic moments at the interface between FM and AF magnetic phases (Section 3.1.1.4). It has been hypothesized that the type of interatomic exchange coupling between Mn atoms depended on the Mn-Mn interatomic distance in these quenched Cu-Mn alloys – nearest-neighbor Mn atomic pairs were thought to be antiferromagnetically exchange-coupled to one another and next-nearest-neighbor Mn atoms were thought to be ferromagnetically exchange-coupled to one another [110, 114]. Since Mn content largely determines the Mn-Mn interatomic distance, the large $H_{ex}$ values were attributed to exchange interactions between AF Mn-rich assemblies and FM Mn-poor assemblies which occur as a result of localized random fluctuations in Mn content.

The magnetic phase diagram for quenched Cu-Mn alloys (Figure 18a, b, and c) highlights the dependence of the alloys’ ferromagnetic (FM) or antiferromagnetic (AF) character and the magnetic ordering temperatures on the Mn content of the alloy [14, 82, 108, 114]. Cu-Mn alloys exhibit spin glass-like behavior (defined in Section 3.2.1.1) over the entire composition range below a temperature $T \sim 200$ K (Figure 18) [9, 14, 82]. Mn-rich Cu-Mn alloys containing more than approximately 72 at. % Mn exhibit long-range AF order; the Néel temperature ($T_N$, defined in Section 2.2.3) of an antiferromagnetic Cu-Mn alloy with approximate composition Cu$_{30}$Mn$_{70}$ is near room
temperature, while more concentrated Cu-Mn alloys near 80 at. % Mn display higher values of $T_N$ up to $\sim 484$ K [82]. As the Mn concentration of the alloy increases, so too does the value of $T_N$. The first Cu-Mn alloy specimen synthesized, characterized, and investigated in this thesis work will be of nominal composition Cu$_{30}$Mn$_{70}$, with further experiments coming on Cu-Mn alloys with higher Mn content.

Selection of Al-Mn alloys as model antiferromagnetic (AF) components

Lasjaunias, Godinho, and Berger reported magnetic spin glass-like behavior in Mn-poor Al-Mn alloys similar to that observed in Mn-poor Cu-Mn alloys (Section 3.2.1.2) [188]. Park et al., Wyslocki et al., and Jiménez-Villacorta et al. demonstrated the AF character of the near-equatomic hexagonal $\varepsilon$-AlMn phase at low temperatures, with Jiménez-Villacorta et al. also reporting a large $H_{cx}$ shift $\sim10$ kOe in major field-cooled (FC) hysteresis loops collected at 10 K (Figure 23b) [10, 11]. The first Al-Mn alloy specimen synthesized and investigated in this thesis work will be of nominal composition Al$_{45}$Mn$_{55}$.

Other investigators note the appearance of a metastable FM $\tau$-AlMn phase with a chemically-ordered face-centered-tetragonal $L1_0$-type unit cell (Figure 19b) upon heat treatment of quenched $\varepsilon$-AlMn alloys at temperatures between 400 °C and 800 °C [15, 16, 19, 20, 29, 150]. This $L1_0$-structured $\tau$-AlMn phase is reported as having FM character with relatively high values of the coercivity ($H_c$), magnetic remanence ($M_r$) and saturation magnetization ($M_s$). In addition to investigation of the antiferromagnetic (AF) character of rapidly-solidified $\varepsilon$-AlMn specimens, the $\varepsilon \rightarrow \tau$ transformation in such melt-spun alloys should also be thoroughly characterized and understood using magnetic and
structural probes. Heat treatment conditions should be selected so as to examine the evolution of the magnetic properties with the sensitive magnetic measurements techniques available after the Al45Mn55 ribbons are annealed in temperatures near the onset of the $\varepsilon \rightarrow \tau$ transformation near 400 °C.

5.2 Research objectives

This thesis work centers upon the clarification of exchange bias ($H_{ex}$) and magnetic remanence enhancement in bulk ferromagnetic/antiferromagnetic (FM/AF) nanostructured magnetic systems. Exchange anisotropy manifests only in materials with intimate interfaces between nanoscopic FM and AF regions (as discussed in Sections 5.1.1 and 5.1.2) but can potentially enhance the magnetic remanence ($M_r$), coercivity ($H_c$), and maximum energy product ($BH_{max}$), the figure of merit in permanent magnetic materials [7, 152].

Nanostructured specimens of Fe/MnX (X = Cu, Al, etc.) alloys will be synthesized by plasma arc-melting (Section 4.1.1) and subsequent rapid solidification processing (Section 4.1.2) and studied as model exchange-biased FM/AF nanocomposite systems, with Fe as a model FM component and binary MnX alloys as model AF components, to facilitate achievement of the overarching thesis goal. The magnetic and structural properties of the Fe/MnX alloys will be investigated to develop relationships between their magnetic and structural character on the nanoscopic and microscopic scales. Additional post-synthesis processing and metallurgical manipulation techniques such as thermal annealing and mechanical milling will be employed to foster formation of and exchange coupling across interfaces between nanoscopic regions of the AF Mn-
based component and the FM Fe-rich matrix. The ability to design and control the structure of the FM/AF nanocomposites on the microscopic and nanoscopic scales is anticipated to enable tailoring of the functional magnetic response.

Prior to investigation of the ferromagnetic/antiferromagnetic (FM/AF) Fe/MnX (X = Cu, Al, etc.) nanocomposite systems it is necessary to develop a fundamental understanding of the magnetic and structural behaviors of the less complex AF Mn-based portion, the binary MnX alloys. These preliminary requirements lead to three research objectives whose fulfillment will be a step towards clarification of $H_{ex}$ and $M_r$ enhancement in FM/AF nanocomposite systems. The goals of each research aim are summarized in the following subsections. Experimental designs and techniques that have been used to satisfy each objective will be outlined in Section 5.3. Experiments for fulfillment of the third and final research objective to implant the MnX alloys in a FM Fe-rich matrix will be discussed in the recommended future work section, in Section 8.0.

5.2.1 Aim 1: Synthesize, characterize and understand correlations between magnetic and structural properties in bulk binary MnX (X = Cu, Al, etc.) alloys with antiferromagnetic (AF) character

It is important to synthesize and thoroughly investigate and understand the magnetic and structural attributes of the less complex antiferromagnetic (AF) binary metallic MnX (X = Cu, Al, etc.) alloys prior to investigation of the same in the more complex exchange-biased ferromagnetic/antiferromagnetic (FM/AF) Fe/MnX nanocomposite systems. MnX alloy specimens will be synthesized by plasma arc-
melting and subsequent rapid solidification via melt-spinning in order to access and retain metastable nanostructured states at room temperature (Section 5.1.2).

Subsequent thermal annealing treatments will be used to induce progressive structural changes in the as-quenched MnX ribbons on the nanoscopic and microscopic scales through grain growth, relaxation and diffusion, and the thermal evolution of the magnetic and structural properties will be investigated [31, 159]. Annealing treatments may result in phase transformations which can significantly alter the magnetic and structural behavior of the MnX alloy specimens. Calorimetric studies will be used to evaluate the thermal character of such phase transformations. Information gathered from magnetic, structural, and thermal probes will be combined to develop correlations between these attributes, which is anticipated to enable control of the functional magnetic response of bulk Mn-based alloys with antiferromagnetic (AF) character.

5.2.2 Aim 2: Design and control structure of nanostructured MnX (X = Cu, Al, etc.) alloys on the nanoscopic and microscopic scales

The ultimate goal of this thesis is clarification of the conditions underlying exchange bias and remanence enhancement in ferromagnetic/antiferromagnetic (FM/AF) nanocomposite systems. Nanostructured Fe/MnX (X = Cu, Al, etc.) are employed as model FM/AF materials for study, with Fe as the FM component and MnX as the AF component, as discussed in Section 5.1.3. The first research objective (Section 5.2.1) was focused on the synthesis and thorough characterization and understanding of relationships between the magnetic and structural properties of the AF binary Mn-based portion prior to implementation in the FM/AF nanocomposite systems.
The second research objective centers around controlling the structure of the composites on the nanoscopic and microscopic scales to foster formation of and exchange coupling across interfaces between the AF MnX portion and the FM Fe-rich matrix. Rapid solidification synthesis and thermal annealing may be inadequate in this regard, rendering additional metallurgical manipulation of the microstructure necessary. To this end, cryogenic mechanical milling will be used to improve interphase mixing between the AF MnX alloys and the FM Fe-rich matrix. Mechanical milling parameters, such as the grinding crucible and media, milling speed, and milling time intervals, are detailed in Section 4.1.3 for both planetary and cryogenic milling. Prior to investigation of the effect of mechanical milling on the magnetic and structural character of the FM/AF Fe/MnX (X = Cu, Al, etc.) nanocomposite as a whole it is again necessary to develop a fundamental understanding of its effect on the less complex AF portion, the Mn-based binary MnX alloy. The structural properties will be characterized on the nanoscopic and microscopic scales using the techniques detailed in Section 4.3, and these data will be correlated to understand how to best control the micro- and nanostructure of the MnX specimens.

5.2.3 Aim 3: Implement MnX (X = Cu, Al, etc.) binary alloys with antiferromagnetic character into more complex Fe/MnX ferromagnetic/antiferromagnetic (FM/AF) nanocomposite systems, and investigate how to promote exchange coupling across interfaces between the AF component and FM matrix in order to achieve enhanced coercivity ($H_c$), magnetic remanence ($M_r$), and maximum energy product ($BH_{max}$).

The overarching goal of this thesis is, again, the elucidation of exchange bias and remanence enhancement in ferromagnetic/antiferromagnetic (FM/AF) nanocomposite
systems. Nanostructured ternary Fe/MnX (X = Cu, Al, etc.) alloys are selected as model systems for study, with Fe as the FM component and binary MnX alloys as the AF portion. The two previous research aims focused on the synthesis, metallurgical manipulation, and thorough characterization and investigation of the AF MnX portion on the nanoscopic and microscopic scales. This final objective further expands on the first two research aims – after developing a thorough understanding of the magnetic and structural attributes of the AF MnX portion, the less-complex Mn-based binary alloys will be implemented into more complex FM/AF Fe/MnX ternary alloys. This objective will be satisfied through in-depth investigations of how to foster FM/AF exchange coupling to convey enhanced coercivity ($H_c$), remanence ($M_r$), and maximum energy product ($BH_{max}$) in bulk FM/AF nanocomposite systems. By then employing the knowledge gained from fulfillment of the two previous objectives (Sections 5.2.1 and 5.2.2), the respective effects of the AF MnX component and the FM Fe-rich matrix on the magnetic and structural character of the system can be isolated and understood. These Fe/MnX nanocomposites are anticipated to exhibit FM/AF exchange coupling and thereby enhanced values of the magnetic remanence ($M_r$), coercivity ($H_c$), and maximum energy product ($BH_{max}$), the figure of merit in permanent magnetic materials [7]. Once the magnetic and structural features of the Fe/MnX (X = Cu, Al, etc.) ternary composites are understood, similarities to behaviors reported for other similar nanocomposites can be drawn to establish properties which are general to many FM/AF nanocomposite systems, culminating in achievement of the overarching research goal.
5.3 Proposed design of experiments and experimental conditions

The goal of this thesis work is to understand exchange bias ($H_{ex}$) and magnetic remanence ($M_r$) enhancement in nanocomposite systems consisting of ferromagnetic (FM) and antiferromagnetic (AF) components. Nanostructured alloys of the form Fe/MnX (X = Cu, Al, etc.) are used as model materials for study, with MnX as the AF component and Fe as the FM component. The first research objective is the synthesis, characterization, and understanding of the magnetic and structural properties of the nanostructured MnX binary alloys (Section 5.2.1). The second, related goal is to manipulate the structure of the MnX alloys on the nanoscopic and microscopic scales (Section 5.2.2). The third and final research objective will be implantation of the AF MnX binary alloys into more composite Fe/MnX FM/AF nanocomposite systems (Section 5.2.3).

The following subsections discuss experimental designs for fulfillment of the three research goals described in Section 5.2 – fabrication, characterization, and understanding of the magnetic and structural properties of MnX alloys, design and control of their microstructure on the nanoscopic and microscopic scales, and implantation of the MnX binary alloys in more complex Fe/MnX systems. The synthesis and post-synthesis processing of the pure, nanostructured MnX alloys is outlined in Section 5.3.1. Section 5.3.2 describes the experiments and techniques employed for the design and processing of the Fe/MnX composite samples – a majority of these investigations are recommended as future work (Section 8.0). Section 5.3.3 contains a discussion of the magnetic, structural, and thermal characterization of both the pure and composite MnX and Fe/MnX samples.
5.3.1 Fabrication and post-synthesis processing of pure samples: nanostructured 
MnX (X = Cu, Al, etc.) binary alloys

Nanostructured MnX (X = Cu, Al, etc.) binary metallic alloys of various compositions and corresponding magnetic character will be synthesized using plasma arc-melting, followed by rapid solidification via melt spinning (Sections 4.1.1 and 4.1.2). The alloy specimens will be subject to thermal annealing treatments to induce progressive structural changes, and will then be mechanically milled to manipulate and control the microstructure such that nanoscopic interfaces with a ferromagnetic matrix are possible.

5.3.1.1 Synthesis of MnX (X = Cu, Al, etc.) binary alloys

After formation of a homogeneous slug of MnX binary alloy using plasma arc-melting (Section 4.1.1), rapid solidification via melt spinning (Section 4.1.2) will be used to access and retain metastable nanostructured states at room temperature. The first alloy specimens synthesized for completion of this research objective are of compositions Al_{45}Mn_{55} and Cu_{30}Mn_{70}. As the research proceeds, it will be necessary to synthesize nanostructured Cu-Mn and Al-Mn alloys of two additional compositions (shown in Table 5) to evaluate the impact of Mn content on the magnetic and structural character of these rapidly-solidified alloys, measured using the magnetic and structural probes detailed in Sections 4.3 and 4.4.
Table 5: Cu-Mn and Al-Mn alloy compositions to synthesize by rapid solidification via melt-spinning and investigate with magnetic and structural probes.

<table>
<thead>
<tr>
<th>Alloy compositions to synthesize and investigate (at. % Mn)</th>
<th>Cu-Mn alloys</th>
<th>Al-Mn alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition 1</td>
<td>70 at. % Mn</td>
<td>55 at. % Mn</td>
</tr>
<tr>
<td>Composition 2</td>
<td>80 at. % Mn</td>
<td>50 at. % Mn</td>
</tr>
<tr>
<td>Composition 3</td>
<td>90 at. % Mn</td>
<td>60 at. % Mn</td>
</tr>
</tbody>
</table>

5.3.1.2 Progressive changes to the structure of MnX (X= Cu, Al, etc.) alloys

Moderate-temperature isochronal thermal annealing treatments will be employed to induce the progression of the rapidly-solidified MnX (X = Cu, Al, etc.) alloys over a range of metastable states through grain growth, relaxation, and diffusive processes (Section 5.1.2.2). Investigation of the magnetic and structural character in the various metastable states can provide important information about the stability of the system. Prior to heat treatment, nanostructured MnX (X = Cu, Al, etc.) alloy specimens studied in this thesis work will be sealed in vitreous silica tubes under a vacuum pressure of $P \sim 1 \times 10^{-5}$ Torr to minimize oxidation and sample contamination (Section 4.2.1). Samples will be annealed isochronally in 30-minute intervals under moderate temperatures conditions from 200 °C to 500 °C. Heat treatment conditions for each Mn-based binary alloy system are listed in Table 6.
Table 6: Proposed annealing conditions for Cu-Mn and Al-Mn alloys of the compositions listed in Table 5. Heat treatment will be carried out isochronally in 30-minute intervals.

<table>
<thead>
<tr>
<th>Proposed heat treatment temperatures (°C)</th>
<th>Cu-Mn alloys</th>
<th>Al-Mn alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Annealing treatment #1</strong></td>
<td>200 °C</td>
<td>200 °C</td>
</tr>
<tr>
<td><strong>Annealing treatment #2</strong></td>
<td>300 °C</td>
<td>250 °C</td>
</tr>
<tr>
<td><strong>Annealing treatment #3</strong></td>
<td>400 °C</td>
<td>300 °C</td>
</tr>
<tr>
<td><strong>Annealing treatment #4</strong></td>
<td>450 °C</td>
<td>350 °C</td>
</tr>
<tr>
<td><strong>Annealing treatment #5</strong></td>
<td>500 °C</td>
<td>400 °C</td>
</tr>
</tbody>
</table>

Alloy specimens will be characterized with the magnetic and structural probes described in Sections 4.3 and 4.4 after each annealing treatment to observe the thermal evolution of the magnetic and structural behaviors. Data obtained using these techniques will be compared to those collected from the as-solidified MnX binary alloys, then thoroughly studied and understood to evaluate the influence of progressive structural changes on the magnetic response.

5.3.1.3 Formation of intimate interphase interfaces in MnX (X = Cu, Al, etc.) alloys

In this thesis work, interfaces between the antiferromagnetic (AF) Mn-based alloy and ferromagnetic (FM) Fe-rich matrix will be developed through pulverization of the composites into fine, nano-sized powders via mechanical milling (Section 4.1.3). Prior to investigation of the effect of mechanical milling on the complex FM/AF nanocomposite system, it is critical to first understand its impact on the AF portion. To this end, specimens of the as-solidified binary MnX (X = Cu, Al, etc.) alloys will be used as
precursors for mechanical milling. Samples will be milled under cryogenic conditions for total times of 10 minutes, 20 minutes, 40 minutes, and 90 minutes. It is expected that longer milling times will give increasingly small powder particles with greater degrees of crystallographic disorder and higher defect densities [160]. The milled powders will then be characterized and studied with magnetic and structural probes (Sections 4.3 and 4.4) to clarify the effect of milling time and treatment on the crystal structure, particle size, and microstructure, all of which are anticipated to affect the magnetic behavior of the system. Comprehension of the effect of pulverization on these attributes is anticipated to lead to the ability to design and control the microstructure of the antiferromagnetic (AF) bulk MnX binary alloys, and potentially enable formation of and exchange-coupling across intimate interfaces with the FM Fe-rich matrix.

5.3.2 Fabrication and post-synthesis processing of composite samples: Fe/MnX (X = Cu, Al, etc.) nanocomposites

After careful synthesis, processing, and characterization of the less-complex MnX (X = Cu, Al, etc.) binary alloy specimens, Fe/MnX magnetic nanocomposites will be fabricated and processed in a similar manner to evaluate the magnetic and structural properties pertinent to exchange bias and remanence enhancement in bulk ferromagnetic/antiferromagnetic nanocomposite systems.

5.3.2.1 Synthesis of Fe/MnX (X = Cu, Al, etc.) nanocomposite samples

It was established in Section 5.1.1 that the ratio of ferromagnetic (FM) component to antiferromagnetic (AF) component in FM/AF nanocomposite systems is one of the primary factors that determines the magnetic and structural character – composites with
high FM content will possess larger saturation magnetization ($M_s$) values, while composites with higher AF content may possess much higher coercivity ($H_c$) values. Balancing these competing attributes is critical in fabrication of materials with optimal exchange bias ($H_{ex}$) and maximum energy product ($BH_{max}$). Nanostructured Fe/MnX (X = Cu, Al, etc.) composites with various Fe:MnX (i.e. FM/AF) compositional ratios will therefore be synthesized using plasma arc-melting and subsequent rapid solidification via melt-spinning to access and retain metastable nanostructured states (Table 7). The as-solidified Fe/MnX specimens will then be characterized with magnetic and structural probes (Sections 4.3 and 4.4) to evaluate the magnetic response and the nanoscopic and microscopic structural behavior.

### Table 7: Fe/MnX (X = Cu, Al, etc.) compositions to synthesize by rapid solidification via melt-spinning and investigate with magnetic and structural probes.

<table>
<thead>
<tr>
<th>FM:AF (Fe:MnX) compositions to investigate (at. %)</th>
<th>Fe-Cu-Mn alloys</th>
<th>Fe-Al-Mn alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition 1</strong></td>
<td>Fe$<em>{90}$(Cu$</em>{30}$Mn$<em>{70}$)$</em>{10}$</td>
<td>Fe$<em>{90}$(Al$</em>{45}$Mn$<em>{55}$)$</em>{10}$</td>
</tr>
<tr>
<td><strong>Composition 2</strong></td>
<td>Fe$<em>{90}$(Cu$</em>{10}$Mn$<em>{90}$)$</em>{10}$</td>
<td>Fe$<em>{50}$(Al$</em>{45}$Mn$<em>{55}$)$</em>{50}$</td>
</tr>
<tr>
<td><strong>Composition 3</strong></td>
<td>Fe$<em>{50}$(Cu$</em>{30}$Mn$<em>{70}$)$</em>{50}$</td>
<td>Fe$<em>{70}$(Al$</em>{45}$Mn$<em>{55}$)$</em>{30}$</td>
</tr>
</tbody>
</table>

To simplify analysis of the magnetic and structural data collected on the Fe/MnX ternary alloys, knowledge obtained from identical experiments on the less complex AF Mn-based binary alloy portion (Sections 5.2.1 and 5.2.2) may be effectively “subtracted out” to isolate the role of the FM Fe matrix. In this manner the origins of the magnetic and structural behaviors present in FM/AF nanocomposites, including exchange bias and
remanence enhancement, will be better understood. Elucidation of these relationships is anticipated to enable tailoring of the functional magnetic response.

5.3.2.2 Progression of metastable states in Fe/MnX (X = Cu, Al, etc.) nanocomposites

After synthesis of Fe/MnX composite samples of various compositions, the as-solidified specimens will be sealed in thin vitreous silica tubes under a vacuum pressure of $P \sim 1 \times 10^{-6}$ Torr to minimize oxygen contamination. Sealed samples will be subject to heat treatment under identical temperature conditions to those given for the MnX pure samples (Section 0) to induce progression over a range of metastable states via grain growth, relaxation, and diffusion. Annealed Fe/MnX specimens will then be characterized with magnetic and structural probes (Sections 4.3 and 4.4) to evaluate the effect of structural changes on the alloys’ magnetic response. Calorimetric studies will also be carried out to evaluate the thermal character of any magnetic or structural phase transformations in the range of annealing temperatures investigated. Correlations between the magnetic and structural character of the nanostructured bulk Fe/MnX ternary alloys may be developed in this manner.

5.3.2.3 Formation of intimate ferromagnetic/antiferromagnetic (FM/AF) interfaces in Fe/MnX (X = Cu, Al, etc.) nanocomposite samples

It is important to recall the optimal microstructural geometry and size for the FM and AF regions is on the nanometric scale (Section 3.1.2.3) [1, 8]. Interfaces between nanoscopic regions of the ferromagnetic (FM) Fe-rich matrix and the antiferromagnetic (AF) MnX component will be created by pulverization of the Fe/MnX nanocomposite
systems into a fine, nano-sized powder via cryogenic mechanical milling, or cryomilling (Section 4.1.3). Cryomilling of Fe/MnX composite samples will be carried out for one Fe:MnX (i.e. FM:AF) compositional ratio over a range of milling times identical to those used for pulverization of the MnX alloys (Section 5.3.1.3) into fine nano-sized powder particles. Longer milling times are anticipated to decrease the particle size and thereby change the magnetic response of the composite. Mechanically-milled powders will then be characterized using the magnetic and structural probes described in Sections 4.3 and 4.4 after each milling interval. Also of interest is the effect of mechanical milling precursor on the magnetic and structural properties of the Fe/MnX powders; annealed specimens of rapidly-solidified Fe/MnX, and separate granules of pure Fe and MnX nanostructures will each be used as milling precursors, again for a single Fe:MnX compositional ratio (Table 8).

**Table 8: Different Fe/MnX (X = Cu, Al, etc.) precursors to use for mechanical milling.**

<table>
<thead>
<tr>
<th>Fe/MnX precursors for mechanical milling to synthesize and investigate</th>
<th>Fe$<em>{50}$(Cu$</em>{30}$Mn$<em>{70}$)$</em>{50}$</th>
<th>Fe$<em>{50}$(Al$</em>{45}$Mn$<em>{55}$)$</em>{50}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Precursor 1</strong></td>
<td>Annealed at 450 °C</td>
<td>Annealed at 350 °C</td>
</tr>
<tr>
<td><strong>Precursor 2</strong></td>
<td>50 at. % Fe powder + 50 at. % rapidly-solidified Cu$<em>{30}$Mn$</em>{70}$</td>
<td>50 at. % Fe powder + 50 at. % rapidly-solidified Al$<em>{45}$Mn$</em>{55}$</td>
</tr>
</tbody>
</table>
5.3.3 Magnetic, structural, and thermal characterization of pure and composite samples

Pure and nanocomposite MnX and Fe/MnX (X = Cu, Al, etc.) samples are fabricated by the methods in Sections 5.3.1 and 5.3.2. The following subsections describe experiments to determine the magnetic, thermal, and structural character of the as-fabricated, annealed, and mechanically milled pure and composite samples on the nano- and microscopic scales.

5.3.3.1 Structural and compositional characterization experiments

A material’s crystal structure determines important intrinsic magnetic properties such as its saturation magnetization ($M_s$) and magnetic ordering temperature [39]. The crystal structure of the studied alloys is investigated by x-ray diffraction (XRD) measurements carried out in the $\theta/2\theta$ configuration (Section 4.3.2). The diffracted x-ray intensity is measured over the diffraction angle range 20-90 $^\circ$2$\theta$ in 0.02 $^\circ$2$\theta$ intervals, dwelling 5-seconds at each point to simultaneously maximize the diffracted x-ray intensity the detector senses and minimize noise in the measurements. Since Bragg reflections from multiple crystallographic phases may overlap to form a single peak, the relative contribution of each phase to the Bragg peak will be estimated using the Gaussian fit method of Eq. (30). Fit parameters will be used to determine the unit cell lattice dimensions and the crystallite size of each phase by Eq. (32) and Eq. (33) to understand the effect of heat treatment on the nanoscopic structure of each phase. The crystal structure of the side of the melt-spun ribbon that solidifies in contact with the Cu wheel (i.e. wheel side) and the side of the ribbon that solidifies in contact with the inert
atmosphere (i.e. free side) will each be examined by XRD to determine the effect of higher vs. lower quench rates on the crystal structure.

A material’s microstructural character has a significant impact on its important extrinsic technical magnetic properties, such as its magnetic susceptibility ($\chi$) and coercivity ($H_c$) [64]. The microstructural character of the as-synthesized Mn-based melt-spun ribbons will be investigated on both the free and wheel sides of the melt-spun ribbons using scanning electron microscopy (SEM), as discussed in Sections 4.3.1 and 4.3.3. Longitudinal SEM images of the microstructure of the melt-spun ribbon specimens will be obtained from the wheel side and the free side to highlight the effect of quench rate on microstructure. Microstructural images of polished ribbon cross-sections will also be collected to gather information about the dynamics of the melt-spinning process. The volume-averaged chemical composition of both the free- and wheel-sides of the as-solidified alloy specimens will then be verified using EDX technique (Section 4.3.1).

5.3.3.2 Characterization of the magnetic response of pure and composite samples

The thermal annealing treatment experiments discussed in Sections 0 and 5.3.2.2 are anticipated to induce progressive changes to the structure of the pure MnX (X = Cu, Al, etc.) binary alloy specimens and the Fe/MnX nanocomposite specimens, respectively, which may affect the alloys’ magnetic response. After careful examination of the nano- and micrometric structural character of the pure and composite ferromagnetic/antiferromagnetic (FM/AF) samples (Section 5.3.3.1), the magnetic response of the as-synthesized and annealed samples will be characterized and studied.
Elucidation of correlations between the magnetic and structural attributes of the alloys studied is anticipated to enable tailoring of the magnetic response through manipulation of the structure on the nanoscopic and microscopic scales.

The magnetic response will be investigated as a function of temperature ($T$) and applied field ($H$) using the superconducting quantum interference device (SQUID) magnetometry and vibrating sample magnetometry (VSM) techniques, detailed in Sections 4.4.1 and 4.4.2, respectively. The magnetization ($M$) will be measured as a function of temperature ($T$) and applied field ($H$) to obtain information about important intrinsic and extrinsic magnetic properties (defined in Section 2.2.2), such as the magnetic anisotropy and its origins, the magnetic reversal mechanism, the coercivity ($H_c$) and intrinsic coercivity ($H_{ci}$), magnetic remanence ($M_r$), magnetic susceptibility ($\chi$), and saturation magnetization ($M_s$). Proposed magnetic measurement conditions are shown in Table 9.

**Table 9: Proposed conditions for magnetization ($M$) vs. temperature ($T$) and $M$ vs. applied field ($H$) measurements.**

<table>
<thead>
<tr>
<th>$M$ vs. $T$ measurement conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cooling field</strong> ($H_{cool}$) (kOe)</td>
</tr>
<tr>
<td>0 kOe</td>
</tr>
<tr>
<td>1 kOe</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$M$ vs. $H$ measurement conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cooling field</strong> ($H_{cool}$) (kOe)</td>
</tr>
<tr>
<td>0 kOe</td>
</tr>
<tr>
<td>50 kOe</td>
</tr>
</tbody>
</table>
The hysteresis loops will then be decomposed by the method of Eq. (34) in Section 4.4.3 to determine the character of each magnetic phase and the relative contribution of each phase to the total magnetization. These results will then be correlated to those obtained from structural characterization experiments (Section 5.3.3.1) to clarify the influence of progressive changes to the nano- and microscopic structure of nanostructured MnX and Fe/MnX alloys on their magnetic response.

5.3.3.3 Investigation of the thermal character of magnetic and structural phase transformations

The differential scanning calorimetry (DSC) technique will be employed to investigate the thermal character of any phase transformations which may have occurred as a result of heat treatment of the studied pure and composite alloys. Calorimetric measurements, conditions of which have been described in Section 4.5, will be carried out over two heating and cooling cycles to evaluate the reversibility of the transformation. A Gaussian fitting method described in Section 4.5 will be used to determine the contribution of each phase transition to the DSC peak, and the activation energy of each transformation will be determined using Kissinger analysis in Eq. (35).

Finally, once the thermal, magnetic, and structural attributes of the Fe/MnX (X = Cu, Al, etc.) ternary alloys are understood, similarities to behaviors reported for other similar nanocomposites may be drawn to establish properties which are general to many FM/AF nanocomposite systems. The thesis investigations of the magnetic and structural attributes of nanostructured Fe/MnX specimens will thus shed light on the conditions
underlying exchange bias in bulk FM/AF systems, culminating in achievement of the overarching research goal.
6.0 RESULTS AND ANALYSIS

The goal of this thesis work is to understand and test the conditions underlying exchange bias and magnetic remanence enhancement in bulk nanocomposite systems consisting of ferromagnetic (FM) and antiferromagnetic (AF) components. Fe/MnX (X = Cu, Al, etc.) alloys are used as model FM/AF nanocomposites, with Fe as the model FM component and MnX as the model AF component. This goal will be achieved through fulfillment of three more specific research objectives (Section 5.2):

1. Synthesize, characterize, and understand correlations between magnetic and structural properties in bulk binary MnX (X = Cu, Al, etc.) alloys with AF character.
2. Design and control structure of nanostructured MnX alloys on the nanoscopic and microscopic scales.
3. Implement MnX binary alloys with AF character into more complex Fe/MnX FM/AF nanocomposite systems and investigate how to promote exchange coupling across interfaces between the AF component and FM matrix, in order to achieve enhanced values of coercivity ($H_c$), magnetic remanence ($M_r$), and maximum energy product ($\langle BH\rangle_{\text{max}}$).

The first research aim has been partially satisfied by work to date using the experimental strategies and techniques detailed in Section 5.3. Bulk specimens of binary MnX alloys with nominal compositions Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$ have been synthesized by plasma arc-melting followed by rapid solidification via melt-spinning, in order to promote formation of metastable nanostructured states. The as-solidified MnX
specimens have been characterized and studied with magnetic, structural, and thermal probes (Sections 4.3, 4.4, and 4.5). Subsequent isochronal thermal annealing treatments have been used to induce progressive changes in the as-solidified alloys’ crystal structure and microstructure, and the evolution of their magnetic and structural character has been investigated.

Some progress has been made towards the second research objective of controlling the structure of the binary Mn-based metallic alloys on the micro- and nanometric length scales as well. In addition to modification of the structure through thermal annealing, the microstructure and nanostructure of a rapidly-solidified Cu_{30}Mn_{70} specimen has been manipulated using the mechanical milling technique at cryogenic conditions (Section 4.1.3), and its effect on the magnetic and structural character of the Mn-based binary alloy Cu_{30}Mn_{70} has been investigated. Cryomilling has been employed to foster formation of and exchange coupling across intimate interfaces between the AF MnX alloy and the FM Fe-rich matrix. During the course of this research, some work towards fulfillment of the third and final research objective (i.e. implantation of the binary MnX (X = Cu, Al, etc.) alloys in a FM Fe-rich matrix and investigation of FM/AF exchange coupling) has also been carried out. Ribbons of nominal composition Fe_{90}(Cu_{30}Mn_{70})_{10} and Fe_{90}(Cu_{10}Mn_{90})_{10} have been synthesized by rapid solidification via melt-spinning. The as-solidified ribbons have been characterized by magnetic and structural probes.

The following sections presents results of characterization experiments for the binary MnX alloys and ternary Fe/MnX alloys synthesized to date. Section 6.1 presents the compositional, structural, and magnetic properties of melt-spun Cu_{30}Mn_{70} in the as-
quenched state, after heat treatment, and after mechanical milling. Section 6.2 shows compositional, structural, magnetic, and thermal character data collected from melt-spun Al_{45}Mn_{55} ribbons in the as-quenched state and after subsequent annealing treatments. Section 6.3 presents structural and magnetic character data obtained from as-quenched Fe_{90}(Cu_{30}Mn_{70})_{10} and Fe_{90}(Cu_{10}Mn_{90})_{10} ribbons. The findings are summarized in Section 6.4. These data will be interpreted and discussed in Chapter 7.0.

6.1 Cu_{30}Mn_{70}: Magnetic and structural character

The first two objectives of this thesis work are to synthesize and investigate the magnetic and structural character of nanostructured binary MnX (X = Cu, Al, etc.) alloys, and then to design and control their structure on multiple length scales, prior to carrying out the same in Fe/MnX composite systems. The crystal structure and composition of a magnetic material determine its important intrinsic magnetic properties (Section 2.2.2) including its saturation magnetization ($M_s$), magnetocrystalline anisotropy field ($H_k$) and constant ($K_1$), and its Curie or Néel temperature ($T_C$ or $T_N$) [37]. The microstructure and geometry of the material significantly affect its technical (extrinsic) magnetic properties such as magnetic susceptibility ($\chi$), magnetic remanence ($M_r$), coercivity ($H_c$), and exchange bias field ($H_{ex}$) [1, 7, 166, 167]. Development of correlations between the magnetic and structural behavior of the MnX alloys is therefore anticipated to lead to the ability to tailor the functional magnetic properties. Here a Cu_{30}Mn_{70} alloy specimen is synthesized and subject to post-synthesis processing techniques including thermal annealing and mechanical milling to control the structure on multiple length scales. The alloy is then characterized by compositional, structural, and magnetic probes.
6.1.1 Cu$_{30}$Mn$_{70}$ melt-spun ribbons: Structural and compositional character

*Overview:* Ductile, continuous ribbons of thickness ~35 μm and nominal composition Cu$_{30}$Mn$_{70}$ were synthesized by plasma arc-melting and subsequent rapid solidification via melt spinning (Section 4.1.2). The composition, microstructure, and crystal structure of the as-quenched specimens were examined using the techniques in Section 4.3. X-ray diffraction (XRD) analysis of the as-spun ribbons revealed the presence of two face-centered-cubic (*fcc*) phases with slightly different lattice parameters on both the free and wheel sides; the unit cell volume of the *fcc* phase with smaller lattice dimensions is approximately ~0.6 % lower than that of the *fcc* phase with larger lattice dimensions. Diffraction measurements of the evolution of the crystal structure with 30-minute annealing treatments in the temperature range $200 \, ^\circ\text{C} \leq T_{\text{anneal}} \leq 450 \, ^\circ\text{C}$ showed a homogenization of the *fcc* phase lattice parameter to $a \sim 3.731 \pm 0.012 \, \text{Å}$ and showed the appearance of a second complex cubic phase with unit cell volume $V \sim 704.0 \pm 2.8 \, \text{Å}^3$. Ribbons annealed at $T \sim 450 \, ^\circ\text{C}$ were mechanically milled at cryogenic temperatures for times of 10-40 minutes, and the morphology and crystal structure of the cryomilled powder was characterized as a function of milling time; Scherrer analysis of the XRD data showed a decrease in the crystallite size from ~23 nm to ~13 nm.

6.1.1.1 Cu$_{30}$Mn$_{70}$: Structural and compositional character in the as-quenched ribbons

The volume-averaged chemical composition of as-solidified Cu$_{30}$Mn$_{70}$ was verified using scanning electron microscope energy-dispersive spectroscopy (EDX) analysis (Figure 35c) (Section 4.3.1); the free side contained approximately $72 \pm 1 \, \text{at.\% Mn}$ while the wheel side contained about $70 \pm 1 \, \text{at.\% Mn}$, highlighting slight Mn
segregation as a function of cooling rate. The free side of melt-spun ribbons is cooled at a slower rate than the wheel side, so higher cooling rates decreased the Mn content of the Cu$_{30}$Mn$_{70}$ alloy. Scanning electron microscopy (SEM) (Section 4.3.3) examinations of the microstructural character of the as-quenched ribbons reveal a lamellar-like morphology (~0.5-1 μm lamellae) on the free side and a granular morphology (~1-3 μm grain diameter) on the wheel side (Figure 35a and b). The 0.1-0.2 μm dark spots in (b) are believed to be due to some type of inhomogeneity. The origins of the respective microstructures are pending further investigation.

Figure 35: SEM images showing morphology of (a) free and (b) wheel sides of as-spun Cu$_{30}$Mn$_{70}$ ribbons. (c) EDX analysis showed that the free side contained 71.6 ± 0.3 at. % Mn; wheel side was found to contain 70.4 ± 0.2 at. % Mn, accentuating the effect of cooling rate on composition.

X-ray diffraction (XRD) analysis of the crystal structure revealed a well-crystallized phase with face-centered-cubic (fcc) structure on both sides of as-quenched Cu$_{30}$Mn$_{70}$ ribbons (Figure 36a). Magnification of the (111) Bragg reflection (Figure 36b) showed a double peak structure, consistent with the presence of two phases with slightly different lattice parameters, denoted as fcc-1 and fcc-2. Additionally, on the free side of the ribbons, the relative intensity of the (111) Bragg reflection of the fcc-1 phase was found to be nearly twice as large as that of the fcc-2 phase, and vice-versa on the wheel side (Figure 36b), highlighting the dependence of the relative amounts of each fcc phase on quench rate.
The XRD patterns in Figure 36a have been analyzed using the fitting method in Eq. (30) to isolate the Bragg peaks of each constituent phase (Figure 36b), and a least-squares cell parameter program has been used to calculate the unit cell dimensions of each fcc phase [171]. The Scherrer formula in Eq. (33) has been used to approximate the average crystallite size ($D$). Table 10 summarizes the calculated unit cell dimensions for the fcc-1 and fcc-2 phases on the free and wheel sides of the Cu$_{30}$Mn$_{70}$ melt-spun ribbons. In summary, it has been found that the free side and the wheel side contain essentially the same two fcc phases with slightly different lattice parameters – the free side contains more of the fcc-1 phase with larger unit cell dimensions of approximately $a = 3.750 \pm 0.002$ Å, while the majority fcc-2 phase on the wheel side possesses slightly smaller unit cell dimensions of approximately $a = 3.740 \pm 0.012$ Å. On the free side of the ribbons, the crystallite size $D$ of both the fcc-1 and fcc-2 phases are markedly different at approximately ~50 and ~20 nm, respectively, whereas on the wheel side, the calculated $D$ values of ~35 nm are nearly identical for both phases.
Table 10: Lattice constants and structural parameters of fcc phases in as-spun Cu$_{30}$Mn$_{70}$ ribbons on the free and wheel sides.

<table>
<thead>
<tr>
<th>Side</th>
<th>Phase</th>
<th>$a$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free side</td>
<td>fcc-1</td>
<td>3.750 ± 0.002</td>
<td>52.73 ± 0.08</td>
<td>~49 ± 5</td>
</tr>
<tr>
<td></td>
<td>fcc-2</td>
<td>3.744 ± 0.006</td>
<td>52.48 ± 0.25</td>
<td>~21 ± 5</td>
</tr>
<tr>
<td>Wheel side</td>
<td>fcc-1</td>
<td>3.748 ± 0.004</td>
<td>52.65 ± 0.17</td>
<td>~35 ± 5</td>
</tr>
<tr>
<td></td>
<td>fcc-2</td>
<td>3.740 ± 0.012</td>
<td>52.31 ± 0.50</td>
<td>~38 ± 5</td>
</tr>
</tbody>
</table>

6.1.1.2 Cu$_{30}$Mn$_{70}$: Effect of annealing temperature on crystal structure

Heat treatment is used to induce progressive structural changes and modify the magnetic response of alloys studied in this work. Cu$_{30}$Mn$_{70}$ ribbons annealed 30 minutes at $T_{\text{anneal}} \sim 450$ °C became embrittled. Diffraction measurements could not be obtained from both the free and wheel sides of the ribbons after embrittlement; the ribbons were ground with a mortar and pestle to permit collection of diffraction data. As annealing proceeded it was found that all Bragg peaks associated with the fcc-1 and fcc-2 phases moved to slightly higher values of $2\theta$, reaching a smaller unit cell lattice parameter $a$, and the relative intensities of and the separation between the fcc-1 and fcc-2 Bragg reflections along the $2\theta$-axis decreased, resulting in the fcc-1 and fcc-2 Bragg peaks merging. Additionally, several Bragg peaks appeared which indexed to a complex cubic phase (Figure 37a and b).
The x-ray diffraction (XRD) results shown in Figure 37 are consistent with a decrease and homogenization of the lattice dimensions of the two \( fcc-1 \) and \( fcc-2 \) phases upon annealing; Table 11 summarizes the effect of heat treatment at \( T \sim 450 \) °C on the calculated structural parameters for both \( fcc \) phases. These results indicate that as annealing proceeds from room temperature to \( T \sim 450 \) °C the lattice parameters decrease and homogenize to \( 3.731 \pm 0.012 \) Å and the crystallite size \( (D) \) changes to a median value of \( \sim30 \) nm, nearly halfway between the original sizes of 50 and 20 nm. The unit cell dimensions of the complex cubic phase are calculated as \( a = 8.896 \pm 0.012 \) Å and \( V = 704.0 \pm 2.8 \) Å\(^3\). The relative intensities of the (111) Bragg reflections of the \( fcc \) phases decrease simultaneously with an increase in the relative intensities of the (411) Bragg peaks associated with the complex cubic phase, reflecting formation of the complex cubic phase at the expense of the \( fcc \) phases after \( \text{Cu}_{30}\text{Mn}_{70} \) ribbons are annealed at \( T \sim 450 \) °C.
Table 11: Lattice constants and structural parameters of fcc phases in as-spun Cu$_{30}$Mn$_{70}$ ribbons (free side) and in Cu$_{30}$Mn$_{70}$ ribbons after annealing 30 minutes at $T \sim 450 \, ^\circ\text{C}$.

<table>
<thead>
<tr>
<th>$T_{\text{anneal}}$</th>
<th>Phase</th>
<th>$a$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-spun Free side</td>
<td>fcc-1</td>
<td>3.750 ± 0.002</td>
<td>52.73 ± 0.08</td>
<td>~49 ± 5</td>
</tr>
<tr>
<td></td>
<td>fcc-2</td>
<td>3.744 ± 0.006</td>
<td>52.48 ± 0.25</td>
<td>~21 ± 5</td>
</tr>
<tr>
<td>450 °C Powder</td>
<td>fcc-1 &amp; fcc-2</td>
<td>3.731 ± 0.012</td>
<td>51.94 ± 0.13</td>
<td>~30 ± 5</td>
</tr>
</tbody>
</table>

6.1.1.3 Cu$_{30}$Mn$_{70}$: Effect of cryomilling time on crystal structure and microstructure

Mechanical milling under cryogenic conditions, or cryomilling, was employed to manipulate the structure of specimens studied in this thesis work on the microscopic and nanoscopic scales and to promote formation of interphase interfaces, in partial fulfillment of the second research objective described in Section 5.2.2. Cu$_{30}$Mn$_{70}$ ribbons, embrittled after annealing at $T \sim 450 \, ^\circ\text{C}$ for 30 minutes, were used as cryomilling precursors for total milling times from 10-90 minutes. Cryomilling parameters and procedures used are described in Section 4.1.3. SEM examinations of the microstructure of Cu$_{30}$Mn$_{70}$ powder after cryomilling for 90-minutes revealed rough flake-like particles approximately 10-25 μm in size (Figure 38a and b). Diffraction analysis of the cryomilled ribbons showed that no new Bragg reflections corresponding to additional phases appeared over the range of milling times investigated (Figure 38c). All Bragg peaks associated with the face-centered-cubic (fcc) and complex cubic phases were found to remain at essentially the same positions on the $2\theta$-axis and retain the same relative intensities. Each Bragg reflection is broadened and the signal-to-noise ratio declines as milling proceeds, pointing to a decrease in crystallographic ordering with longer milling times. It is important to
note that the signal-to-noise ratio was too poor to permit resolution of multiple phases in the \textit{fcc} (111) Bragg reflection after cryomilling for only 10 minutes.

Figure 38: (a) and (b) SEM images of pulverized Cu\textsubscript{30}Mn\textsubscript{70} ribbons after cryomilling for 90 minutes; ribbons annealed at 450 °C used as precursor. Particles are flake-like and \~{}10-25 μm in size. (c) XRD examination as a function of milling time ($t_{\text{mill}}$) from 0-90 minutes.

Figure 39 illustrates the effect of milling time on the lattice parameter of the \textit{fcc} phase in the Cu\textsubscript{30}Mn\textsubscript{70} powders and on the crystallite size ($D$), calculated using the Scherrer formula in Eq. (33). It was found that the average unit cell lattice parameter ($a$) remained essentially constant (at \~{}3.74 Å), while $D$ decreased with milling time, dropping approximately 40 % after 20 minutes of cryomilling from \~{}23 nm to \~{}13 nm.
6.1.2 Cu₃₀Mn₇₀ melt-spun ribbons: Magnetic response

Overview: The structure of a material determines its technical, or extrinsic magnetic response (Section 2.2.2) [1]. Melt-spun Cu₃₀Mn₇₀ ribbons have been sealed in vitreous silica tubes and the magnetic response of the alloy has been characterized using a superconducting quantum interference device (SQUID) magnetometer as a function of temperature \(T, 10 \text{ K} \leq T \leq 400 \text{ K}\) and as a function of applied field \((H, -50 \text{ kOe} \leq H \leq 50 \text{ kOe})\) (Section 4.4.1). Results obtained from the as-solidified ribbons via SQUID magnetometry are correlated to the structural character on the nanoscopic and microscopic scales to enable tailoring of the functional magnetic properties. The alloy samples sealed in vitreous silica tubes were then isochronally annealed in 30-minute intervals in the nominal temperature range \(200 \text{ °C} \leq T_{\text{anneal}} \leq 450 \text{ °C}\), and the magnetic character was measured after each heat treatment step in order to examine the progressive evolution of the magnetic response. Ribbons annealed at nominally 450 °C were cryomilled for 10-40 minutes to manipulate the micro- and nanostructure, and the
evolution of the magnetic response with heat treatment and mechanical milling has been observed.

Field-cooled (FC, 50 kOe) magnetization loops collected from the as-quenched Cu$_{30}$Mn$_{70}$ ribbons at $T = 10$ K were found to be anhysteretic in nature and displayed a uniaxial shift of $\sim 10$ kOe – that decreased with increasing temperature – along the field axis. A single contribution to the magnetic signal with very high coercivity of $\sim 166$ kOe was observed in the as-solidified state. Upon annealing at $T \sim 200$-$450 \, ^\circ$C, hysteresis appeared, the magnetization ($M$) increased, and an additional lower-coercivity contribution to the magnetization grew at the expense of the high-coercivity contribution. Mechanical milling caused significant increases in $M$ and a concomitant decline in the hysteresis shift.

6.1.2.1 Cu$_{30}$Mn$_{70}$: Magnetic response in the as-quenched state

The field-cooled (FC) and zero-field-cooled (ZFC) magnetization ($M$) vs. temperature ($T$) curves obtained from the as-spun Cu$_{30}$Mn$_{70}$ ribbons with a measuring field of 1 kOe superimposed to reach a peak at a temperature of $T_{\text{peak}} \sim 125$ K (Figure 40a). The ZFC and FC hysteresis loops collected at 10 K were closed (i.e. anhysteretic), linear, and parallel to one another (Figure 40c), where the ZFC magnetization loop was centered at the origin but the FC magnetization loop was found to be displaced from the origin by a large shift of roughly $\sim 10$ kOe along the negative field ($H$) axis.
Figure 40: (a) FC and ZFC $M$ vs. $T$ curves obtained from as-spun Cu$_{30}$Mn$_{70}$. 
(b) $\chi_{\text{linear}}$ vs. $T$. (c) FC and ZFC magnetization loops collected at 10 K from as-quenched ribbons.

It was also observed that the FC hysteresis loop shift decreased as $T$ increased and disappeared when $T > T_{\text{peak}}$, as illustrated in Figure 41a. Hysteresis loops obtained from as-solidified Cu$_{30}$Mn$_{70}$ ribbons remained mostly linear over the entire temperature range studied (10-300 K). Figure 40b illustrates the effect of $T$ on the magnitude of the high-field linear susceptibility ($\chi_{\text{linear}}$); much like the behavior of the ZFC magnetization $M_{\text{ZFC}}$, $\chi_{\text{linear}}$ reached a peak in the range $T \sim 100$-200 K. The linear portion of the magnetic susceptibility $\chi_{\text{linear}}$ was removed from the magnetization loops to examine the nonlinear adjusted contributions to the total magnetization, as described in Section 4.4 (Figure 41b). The adjusted magnetization (*i.e.* the hysteretic portion) was found to be essentially
constant at 10 K and did not cross the field ($H$) axis. The vertical shift of the nonlinear portion and the horizontal shift of the total magnetization loop each declined concurrently with increasing $T$, as the magnetization loops became increasingly symmetric about the origin (Figure 41a and b), reflecting increasing magnetic reversibility with increasing temperature.

![Figure 41: (a) Effect of $T$ on FC hysteresis loop obtained from as-solidified Cu$_{30}$Mn$_{70}$ ribbons. (b) Magnetization loops collected from as-quenched ribbons, adjusted for linear susceptibility contribution.](image)

6.1.2.2 Cu$_{30}$Mn$_{70}$: Effect of heat treatment on magnetic response

Melt-spun Cu$_{30}$Mn$_{70}$ have been isochronally heat treated for 30 minutes in the approximate temperature range $200 \, ^\circ\!C \leq T_{\text{anneal}} \leq 450 \, ^\circ\!C$ to induce progressive structural changes at the nanoscopic and microscopic scales. Similar to the behavior observed in the as-quenched state, the ZFC and FC branches of the magnetization ($M$) vs. temperature ($T$) curve converged for $T > T_{\text{peak}}$ (Figure 42a). The total magnetization $M$ and $T_{\text{peak}}$ each increased with heat treatment (Figure 42a). As annealing proceeded, the linear high-field magnetic susceptibility ($\chi_{\text{linear}}$) also increased over the entire temperature range while retaining its $M_{\text{ZFC}}$-like peak behavior with a maximum around $T_{\text{peak}}$ (Figure 42b).
Figure 42: Thermal evolution of (a) $\chi$ vs. $T$ curves and (b) High-field linear magnetic susceptibility, from total magnetization loops obtained from Cu$_{30}$Mn$_{70}$ ribbons. Both the total and linear susceptibility come to a peak between 100 K and 150 K.

Upon annealing at 200 °C for 30 minutes the total field-cooled (FC) magnetization loops (Figure 43a) became open and very slightly sigmoidal-shaped, in contrast to the entirely linear behavior of the total FC magnetization loop in the as-quenched ribbons at 10 K. The magnitude of the shift of the total FC magnetization loops at 10 K was observed to oscillate in a sinusoidal-like pattern around approximately $\sim$ 10 kOe with increasing annealing temperature ($T_{\text{anneal}}$), as shown in Figure 43b; the shift of magnetization loops collected at 50 K decreased steadily towards $\sim$ 0 kOe with increasing $T_{\text{anneal}}$. 
Figure 43: (a) Total FC magnetization loops obtained at 10 K. (b) Shift of the total hysteresis loops vs. $T_{\text{anneal}}$ at 10 K and 50 K. (c) $\chi_{\text{linear}}$-adjusted portion of the magnetization loops collected from as-spun and annealed ribbons at 10 K. (d) Decomposition of the $\chi_{\text{linear}}$-adjusted demagnetization curve at 10 K after annealing at $T \sim 200$ °C, in accordance with the method of (34), as an illustrative example.

The $\chi_{\text{linear}}$-adjusted portion of the magnetization loops (i.e. the hysteretic portion) collected at 10 K from the as-solidified and annealed ribbons is shown in Figure 43c. The nonlinear contribution remained highly asymmetric about the origin with annealing in the temperature range $T_{\text{anneal}} \sim 200$-450 °C, but became increasingly symmetric about the field ($H$) axis with increasing $T_{\text{anneal}}$ until eventually crossing the $H$ axis after heat treatment at $T \sim 450$ °C. The significant asymmetry about the field axis of the adjusted magnetization loops collected at 10 K highlights the inability of the material to obtain
magnetic saturation in the negative direction even in large applied reverse fields of $H = -50$ kOe, especially in the as-solidified ribbons.

The nature of the large magnetic reversal fields has been investigated through decomposition of the $\chi_{\text{linear}}$-adjusted demagnetization curves (the hysteretic portion) measured at 10 K from the as-quenched and annealed Cu$_{30}$Mn$_{70}$ ribbons, done in accordance with the method of Eq. (34) in Section 4.4.3 [179], in order to determine the relative contributions of each constituent magnetic phase. As an illustrative example, Figure 43d shows this decomposition analysis technique applied to the demagnetization curve obtained at 10 K from Cu$_{30}$Mn$_{70}$ ribbons annealed 30 minutes at $T \sim 200$ °C. Analysis of the decomposition fitting reveals two contributions to the $\chi_{\text{linear}}$-adjusted portion of the magnetization at 10 K – a “softer” magnetic phase, denoted as phase-1, which has lower saturation magnetization ($M_s$) and intrinsic coercivity ($H_{ci}$) values $\sim 4$-25 kOe but approximately the same magnetic remanence ratio (i.e. squareness, $S$), and an “ultrahard” magnetic phase, denoted as phase-2, that possesses higher $M_s$ and much larger $H_{ci} \sim 56$-166 kOe values. Table 12 summarizes the effect of annealing temperature on the magnetic character calculated for both constituent magnetic phases.
Table 12: Magnetic character of each contribution to the hysteretic demagnetization curves obtained from Cu$_{30}$Mn$_{70}$ ribbons at $T = 10$ K for different $T_{\text{anneal}}$, from the method in Eq. (34).

<table>
<thead>
<tr>
<th>$T_{\text{anneal}}$ (°C)</th>
<th>$M_s$ (emu/g)</th>
<th>$H_{ci}$ (kOe)</th>
<th>$S$ ($M_r/M_s$)</th>
<th>$M_{s,(i)}/M_{s,(tot)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Magnetic Phase-1 at $T = 10$ K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 °C</td>
<td>0.001</td>
<td>4.50</td>
<td>0.750</td>
<td>0.010</td>
</tr>
<tr>
<td>200 °C</td>
<td>0.049</td>
<td>14.4</td>
<td>0.787</td>
<td>0.256</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.073</td>
<td>10.1</td>
<td>0.794</td>
<td>0.317</td>
</tr>
<tr>
<td>450 °C</td>
<td>0.085</td>
<td>23.1</td>
<td>0.868</td>
<td>0.490</td>
</tr>
<tr>
<td><strong>Magnetic Phase-2 at $T = 10$ K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 °C</td>
<td>0.122</td>
<td>166</td>
<td>0.842</td>
<td>0.990</td>
</tr>
<tr>
<td>200 °C</td>
<td>0.142</td>
<td>62.3</td>
<td>0.946</td>
<td>0.744</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.157</td>
<td>61.3</td>
<td>0.901</td>
<td>0.683</td>
</tr>
<tr>
<td>450 °C</td>
<td>0.088</td>
<td>56.1</td>
<td>0.857</td>
<td>0.510</td>
</tr>
</tbody>
</table>

The ultrahard phase-2 was found to dominate the magnetic response in the as-solidified ribbons. As annealing proceeded the calculated value of $M_s$ for magnetic phase-1 rose, $H_{ci}$ of the phase-2 declined, and the relative fractional contribution of the softer magnetic phase-1 to the total magnetization (i.e. $M_{s,(i)}/M_{s,(tot)}$) increased at the expense of that of the ultrahard phase-2. The relative fractional contributions of phase-1 and phase-2 to the adjusted magnetization were found to be roughly equal after 30 minutes of heat treatment at $T \sim 450$ °C. Neither magnetic phase-1 nor phase-2 were observed in magnetization loops collected at temperatures above the $\chi_{ZFC}$ peak temperature $T_{\text{peak}}$. The effect of thermal annealing treatment on the saturation magnetization ($M_s$) and relative fractional contribution to the adjusted magnetization is illustrated graphically in Figure 44.
These data showed that the FC demagnetization curve collected from the as-solidified Cu$_{30}$Mn$_{70}$ ribbons at $T = 10$ K consist of two magnetic phases – an ultrahard portion with intrinsic coercivity $H_{ci} \sim 166$ kOe and a much more magnetically-soft portion with $H_{ci} \sim 4.5$ kOe. As annealing proceeds, the magnetic contribution from the more magnetically-soft phase-1 grows at the expense of that of the ultrahard magnetic phase-2.

6.1.2.3 Cu$_{30}$Mn$_{70}$: Effect of cryomilling time on magnetic response

Cryogenic milling, or cryomilling (Section 4.1.3), has been employed as a means of manipulating the structure of the Mn-based alloys studied in this thesis work on the microscopic and nanoscopic scales to promote formation of and exchange-coupling across intimate interfaces between ferromagnetic (FM) and antiferromagnetic (AF) phases. Cu$_{30}$Mn$_{70}$ ribbons fabricated by rapid solidification via melt-spinning have been
cryomilled for total milling times between 0-40 minutes. The magnetic response of the cryomilled powder has been measured by SQUID magnetometry after each milling interval as a function of temperature in the range $10 \, \text{K} \leq T \leq 400 \, \text{K}$ and as a function of applied field in the range $-50 \, \text{kOe} \leq H \leq 50 \, \text{kOe}$. Magnetic measurements of cryomilled Cu$_{30}$Mn$_{70}$ powders showed that as milling proceeded the magnetization ($M$) increased significantly and the field-cooled (FC) and zero-field-cooled (ZFC) branches cease to converge above a peak temperature ($T_{\text{peak}}$) (Figure 45a). For improved clarity, Figure 45b and Figure 45c, respectively, display magnifications of the $M$ vs. $T$ data collected over the 0-10 minute and 25-40 minute milling intervals. Figure 45d displays the high-field linear magnetic susceptibility ($\chi_{\text{linear}}$) vs. $T$ curves collected at different cryomilling times; as milling proceeded there was very little change in the shape or placement of the peak in $\chi_{\text{linear}}$, but $\chi_{\text{linear}}$ appeared to increase by a constant value over the entire temperature range after each milling interval. Additionally, a small bump appeared in the FC and ZFC $\chi$ vs. $T$ curve obtained from Cu$_{30}$Mn$_{70}$ ribbons cryomilled for only 10 minutes, pointing to the appearance of an additional magnetic phase.

It was found that the peak in $\chi_{\text{ZFC}}$ grew increasingly small with longer milling times, eventually becoming essentially constant over the entire temperature range investigated after milling for 25 minutes or longer. The displacement of the total magnetization loops along the field $H$ axis at 10 K was found to decrease significantly with even short cryomilling times (Figure 45e), dropping to ~ 4.8 kOe after 10 minutes of milling and ~ 0.4 kOe after 25 minutes of cryomilling. After removal of the linear contribution to the susceptibility $\chi_{\text{linear}}$, an additional magnetic phase was observed in the low-$H$ region of the adjusted magnetization loops after cryomilling for 10 minutes, with
further cryomilling exaggerating the sigmoidal-shape of the nonlinear loops. It is interesting to note that the magnetic character changed little between 25 and 40 minutes of milling, except for a small increase in $\chi_{\text{linear}}$ (Figure 45c, d, e, f). In summary, these results show that cryomilling caused a significant increase in the magnetization ($M$) that was constant over the entire temperature range studied, introduced an additional phase whose magnetization response can be seen in the low-field region of Figure 45f, and caused a rapid deterioration of the hysteresis shift at 10 K.
Figure 45: Effect of cryomilling time (10-40 minutes) on (a), (b), and (c) FC and ZFC $\chi$ vs. $T$ curves. (d) $\chi_{\text{linear}}$ vs. $T$ curves obtained from cryomilled Cu$_{30}$Mn$_{70}$ powders. (e) $M$ vs. $H$ loops collected at 10 K as a function of cryomilling time. (f) $\chi_{\text{linear}}$-adjusted $M$ vs. $H$ loops collected at 10 K.
6.2  **Al$_{45}$Mn$_{55}$: Magnetic, structural, and thermal characterization**

Comprehension of relationships between the magnetic and structural behavior of MnX (X = Cu, Al, etc.) alloys is expected to enable tailoring of the alloys’ functional intrinsic and extrinsic magnetic properties. Al$_{45}$Mn$_{55}$ ribbons have been fabricated by rapid solidification via melt spinning and, after sealing the as-solidified ribbons in thin vitreous silica tubes at a vacuum pressure of $P \approx 1 \times 10^6$ Torr to minimize oxygen contamination during measurement, their magnetic and thermal properties have been characterized. The compositional and structural character of the as-spun ribbons has been examined on both the free and wheel sides of the ribbons to evaluate the effect of cooling rate on the Mn content, morphology, and crystal structure. Ribbons were subsequently isochronally heat treated for 30 minutes in the nominal temperature range $200 \, ^\circ C \leq T_{\text{anneal}} \leq 400 \, ^\circ C$ to manipulate their structure on the nanoscopic and microscopic scales, and the magnetic response and structural character were measured after each heat treatment. The following subsections present the compositional, structural, magnetic, and thermal character results obtained from melt-spun Al$_{45}$Mn$_{55}$.

6.2.1  **Al$_{45}$Mn$_{55}$: Structural and compositional character**

*Overview:* Melt-spun Al$_{45}$Mn$_{55}$ ribbons were observed to be shiny, brittle, and approximately 50 $\mu$m thick and 1-5 cm in length. The volume-averaged chemical composition and microstructure of the as-solidified ribbons were examined using energy-dispersive x-ray spectroscopy (EDX) and scanning electron microscopy (SEM), respectively (Section 4.3). The thermal evolution of the crystal structure has been investigated after isochronal 30-minute heat treatments in the temperature range $200 \, ^\circ C \leq
$T_{\text{anneal}} \leq 400 \, ^\circ\text{C}$ using x-ray diffraction (XRD) measurements. The as-quenched ribbons were found to consist of two majority hexagonal phases with slightly different unit cell dimensions on the order of $a \sim 2.7$ Å and $c \sim 4.4$ Å. After the Al$_{45}$Mn$_{55}$ ribbons were heat treated 30 minutes at $T_{\text{anneal}} \sim 345 \, ^\circ\text{C}$, diffraction data showed the growth of a crystallographic phase with a chemically-ordered face-centered-tetragonal (fct) unit cell structure ($a \sim 2.77$ Å, $c \sim 3.56$ Å) at the expense of the hcp phases.

### 6.2.1.1 Al$_{45}$Mn$_{55}$: Structural and compositional character of the as-solidified ribbons

Scanning electron microscope energy-dispersive x-ray spectroscopy (EDX) analysis of the volume-averaged chemical composition of as-quenched Al$_{45}$Mn$_{55}$ ribbons (Figure 46) revealed that the free side of the ribbons contained approximately $56 \pm 1$ at. % Mn and the wheel side contained about $54 \pm 1$ at. % Mn. These results highlight the effect of quench rate on chemical composition – the higher quench rate present on the wheel side of the ribbons results in a lower Mn content.

![Figure 46](image-url)

**Figure 46:** EDX spectra obtained from as-spun Al$_{45}$Mn$_{55}$ ribbons reveal that the free side contains $56 \pm 1$ at. % Mn and the wheel side contains $54 \pm 1$ at. % Mn.
X-ray diffraction (XRD) patterns collected on both sides of the as-solidified Al\textsubscript{45}Mn\textsubscript{55} ribbons (Figure 47a) revealed the presence of a majority phase with hexagonal (\textit{hcp}) structure, one minority rhombohedral phase, and one additional unidentified Bragg peak at \(\sim 82.5 \, ^\circ\theta\). Magnification of the (101) Bragg peak of the \textit{hcp} phase (Figure 47b) revealed a double peak structure, pointing to the coexistence of two \textit{hcp} phases with slightly different unit cell dimensions, denoted as \textit{hcp-1} and \textit{hcp-2}. It was found that the wheel side displayed much more evenly-distributed Bragg peak intensities between the \textit{hcp-1} and \textit{hcp-2} phases, whereas on the free side the intensities of the \textit{hcp-1} Bragg reflections far outweighed those of the \textit{hcp-2} Bragg peaks. Such a discrepancy in the relative intensities of the two phases accentuates the effect of cooling rate on the relative amounts of each hexagonal phase.

![Figure 47: (a) XRD patterns obtained from free & wheel sides of as-spun Al\textsubscript{45}Mn\textsubscript{55} ribbons, showing major \textit{hcp} Bragg peaks and those from additional phases. (b) Magnification of (a) to emphasize double peak structure.](image)

The diffraction patterns collected from both the free and wheel sides of the as-solidified ribbons have been analyzed using the fitting method described in Eq. (30) to determine the Bragg angles of each constituent crystallographic phase. The unit cell
dimensions of each phase are calculated using the least-squares cell parameter program described in Section 4.3.2 [171]. The calculated values of the hexagonal unit cell lattice parameters \((a\) and \(c\)) and unit cell volumes \((V)\) of the two \(hcp\) phases observed in the as-quenched ribbons are shown in Table 13. The crystallite size \((D)\) approximated using the Scherrer formula in Eq. (33) is also shown – \(D \sim 60\) nm for the \(hcp\) phase with larger unit cell dimensions and \(D \sim 30\) nm for the \(hcp\) phase with smaller unit cell dimensions. These analyses suggest that the unit cell lattice dimensions of the \(hcp-1\) phase were slightly larger than those of the \(hcp-2\) phase, while both phases possessed essentially identical \(c/a\) ratios of \(\sim 1.62\).

**Table 13: Structural parameters calculated for the \(hcp-1\) and \(hcp-2\) phases on both sides of the as-solidified \(Al_{45}Mn_{55}\) ribbons.**

<table>
<thead>
<tr>
<th>Side</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(c/a) ratio</th>
<th>(V) (Å(^3))</th>
<th>(\langle D\rangle) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free</td>
<td>(hcp-1)</td>
<td>2.702 ± 0.005</td>
<td>4.371 ± 0.005</td>
<td>1.618 ± 0.004</td>
<td>82.91 ± 0.32</td>
</tr>
<tr>
<td></td>
<td>(hcp-2)</td>
<td>2.699 ± 0.008</td>
<td>4.340 ± 0.011</td>
<td>1.608 ± 0.006</td>
<td>82.14 ± 0.53</td>
</tr>
<tr>
<td>Wheel</td>
<td>(hcp-1)</td>
<td>2.702 ± 0.005</td>
<td>4.372 ± 0.005</td>
<td>1.618 ± 0.004</td>
<td>82.93 ± 0.32</td>
</tr>
<tr>
<td></td>
<td>(hcp-2)</td>
<td>2.696 ± 0.007</td>
<td>4.361 ± 0.009</td>
<td>1.618 ± 0.005</td>
<td>82.35 ± 0.46</td>
</tr>
</tbody>
</table>

These data showed that essentially the same two nanostructured \(hcp\) phases with slightly different lattice constants are present on both the free and wheel sides of the as-spun \(Al_{45}Mn_{55}\) ribbons. The free side contains more of the larger \(hcp-1\) phase while the majority phase on the wheel side of the ribbons is the smaller \(hcp-2\) phase.

**6.2.1.2 \(Al_{45}Mn_{55}\): Effect of heat treatment on structural and compositional character**

Rapidly-solidified \(Al_{45}Mn_{55}\) ribbons were annealed isochronally in 30 minute intervals in the temperature range \(200\) °C < \(T\) < \(350\) °C as a means of inducing progressive structural changes – the crystal structure was examined by XRD analysis.
after each heat treatment. It was found that as annealing proceeded the relative intensities of all Bragg peaks associated with the \textit{hcp} phases decreased and the separation along the 2\(\theta\)-axis between the \textit{hcp-1} and \textit{hcp-2} Bragg reflections decreased, as shown in Figure 47a and emphasized in Figure 47b. Heat treatment at 345 °C for 30 minutes resulted in a large decrease in the relative intensities of all Bragg peaks associated with the \textit{hcp} phases, an order-of-magnitude increase in the relative intensity of the Bragg reflection associated with the (211) reflection of a tetragonal phase, and in the appearance of several additional Bragg peaks corresponding to a face-centered-tetragonal (\textit{fct}) phase.

The Bragg reflections unique to the \textit{hcp} phase were best fitted as the sum of two Gaussian distributions, per the method in Eq. (30) for evaluation of the contribution of each constituent phase to its associated Bragg peak. Table 14 summarizes the effect of heat treatment on the calculated unit cell dimensions for the \textit{hcp-1} and \textit{hcp-2} phases.

![Figure 48](image-url)  

**Figure 48:** (a) Evolution of XRD patterns collected from \(\text{Al}_{45}\text{Mn}_{55}\) ribbons with annealing treatment. (b) Magnification of a selected region of (a) showing double peak structure.
Table 14: Effect of annealing treatment on structural parameters calculated for the hexagonal phases (hcp-1 and hcp-2) observed in melt-spun Al₄₅Mn₅₅ ribbons. Unit cell dimensions of the fct phase observed after annealing at 345 °C for 30 minutes are shown at bottom of table.

<table>
<thead>
<tr>
<th>T_{anneal}</th>
<th>phase</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a ratio</th>
<th>V (Å³)</th>
<th>〈D〉 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22 °C</td>
<td>hcp-1</td>
<td>2.702 ± 0.005</td>
<td>4.371 ± 0.005</td>
<td>1.618 ± 0.004</td>
<td>82.91 ± 0.32</td>
<td>~60 ± 5</td>
</tr>
<tr>
<td>295 °C</td>
<td>hcp-1</td>
<td>2.707 ± 0.005</td>
<td>4.377 ± 0.006</td>
<td>1.614 ± 0.004</td>
<td>83.33 ± 0.33</td>
<td>~50 ± 5</td>
</tr>
<tr>
<td>345 °C</td>
<td>hcp-1</td>
<td>2.702 ± 0.005</td>
<td>4.371 ± 0.006</td>
<td>1.615 ± 0.004</td>
<td>82.91 ± 0.33</td>
<td>~45 ± 10</td>
</tr>
<tr>
<td>22 °C</td>
<td>hcp-2</td>
<td>2.699 ± 0.008</td>
<td>4.340 ± 0.011</td>
<td>1.608 ± 0.006</td>
<td>82.14 ± 0.53</td>
<td>~30 ± 5</td>
</tr>
<tr>
<td>295 °C</td>
<td>hcp-2</td>
<td>2.700 ± 0.007</td>
<td>4.372 ± 0.009</td>
<td>1.619 ± 0.005</td>
<td>82.62 ± 0.46</td>
<td>~25 ± 5</td>
</tr>
<tr>
<td>345 °C</td>
<td>hcp-2</td>
<td>2.694 ± 0.006</td>
<td>4.363 ± 0.007</td>
<td>1.620 ± 0.004</td>
<td>82.27 ± 0.39</td>
<td>~45 ± 10</td>
</tr>
<tr>
<td>345 °C</td>
<td>fct</td>
<td>2.769 ± 0.002</td>
<td>3.559 ± 0.005</td>
<td>1.285 ± 0.002</td>
<td>27.29 ± 0.06</td>
<td>~20 ± 5</td>
</tr>
</tbody>
</table>

Figure 49a and b illustrate graphically the effect of heat treatment temperature on the calculated structural attributes of the hcp-1 and hcp-2 phases, respectively. It is clear that the unit cell volume of the hcp-2 phase (Figure 49b) is slightly smaller than that of the hcp-1 phase (Figure 49a), but otherwise the structural parameters of both hcp phases remain constant with annealing treatment (within error).

Figure 49: Calculated values of a, c, and V for the hcp AlMn phases as a function of annealing temperature in Al₄₅Mn₅₅ ribbons.
6.2.2 \textbf{Al}_{45}\text{Mn}_{55}: Magnetic response}

\textit{Overview:} A material’s composition, crystal structure, and microstructure strongly affect its technical magnetic properties such as its magnetic susceptibility ($\chi$), magnetic remanence ($M_r$), coercivity ($H_c$), and exchange bias field ($H_{ex}$) [1, 7, 166, 167]. The magnetic response of rapidly-solidified \text{Al}_{45}\text{Mn}_{55} ribbons has been characterized with the techniques detailed in Section 4.4. The magnetic behaviors of \text{Al}_{45}\text{Mn}_{55} are related back to the structural properties to develop the ability to tailor the alloy’s functional magnetic properties, discussed in Section 2.2.2. After magnetic and structural characterization of the as-solidified samples, the alloy specimens have been isochronally annealed in 30-minute intervals in the temperature range $200 \, ^\circ\text{C} \leq T_{\text{anneal}} \leq 400 \, ^\circ\text{C}$ to evaluate the effect of progressive structural changes on the magnetic response.

Field-cooled (FC) hysteresis loops were shifted approximately $\sim13$ kOe along the field axis at 10 K. FC demagnetization curves collected from the as-solidified ribbons at 10 K were observed to consist of two phases – one (\textit{phase-1}) with higher magnetization and much higher intrinsic coercivity $\sim19$ kOe that contributed approximately 92 \% of the total magnetization ($M$), and one (\textit{phase-2}) with lower magnetization and much lower intrinsic coercivity $\sim1.2$ kOe that contributed only $\sim8$ \% of the total $M$. While the magnetization of \textit{phase-1} increases at annealing temperatures as low as $T > 150 \, ^\circ\text{C}$, it is clear that the lower-coercivity magnetic \textit{phase-2} grows at the expense of the higher-coercivity \textit{phase-1} after annealing at $T > 275 \, ^\circ\text{C}$. After annealing at 345 \, ^\circ\text{C}, \textit{phase-2} accounts for approximately 91\% of the magnetization at 10 K (and 100\% of the magnetization at 300 K) and possesses a saturation magnetization $M_s \sim 17.1$ emu/g and intrinsic coercivity $H_{ci} \sim 2.4$ kOe.
6.2.2.1 $\text{Al}_{45}\text{Mn}_{55}$: Magnetic response of the as-quenched ribbons

The field-cooled (FC) and zero-field-cooled (ZFC) magnetization ($M$) vs. temperature ($T$) curves of the as-quenched Al$_{45}$Mn$_{55}$ ribbons (Figure 50a) have been found to superimpose to reach a peak at $T_{\text{peak}} = 95$ K [10]. The ZFC hysteresis loop obtained from the as-spun ribbons at 10 K (Figure 50c) was observed to be centered at the origin while the FC loop displayed a large shift of ~13 kOe along the negative applied field ($H$) axis, which decreased rapidly with increasing $T$ and eventually disappeared entirely for $T > T_{\text{peak}} = 95$ K (Figure 50d). The evolution of the linear high-field magnetic susceptibility ($\chi_{\text{linear}}$) with temperature is shown in Figure 50b – it has been found that $\chi_{\text{linear}}$ rises to a peak between 50 K and 100 K, much like the behavior observed for the ZFC magnetization. The total magnetization loops have been adjusted for $\chi_{\text{linear}}$ as described in Section 4.4.3. It was observed that the adjusted magnetization loops obtained at 10 K consisted of two distinct magnetic phases – one that exhibits a rectangular magnetization loop and a prominent shift of ~13 kOe along the $H$ axis, and another which appears in the low-field region. The contribution of the shifted rectangular portion decreased with increasing $T$ and vanished above $T_{\text{peak}}$ in both the total and $\chi_{\text{linear}}$-adjusted magnetization loops (Figure 50d and e).
Figure 50: (a) FC and ZFC $M$ vs. $T$ curves obtained from as-spun Al$_{45}$Mn$_{55}$. (b) $\chi_{\text{linear}}$ vs. $T$ curves. (c) FC & ZFC hysteresis loops at 10 K. (d) FC $M$ vs. $H$ loops at 10-300 K. (e) FC $M$ vs. $H$ loops adjusted for the high-field linear susceptibility contribution.
6.2.2.2 $\text{Al}_{45}\text{Mn}_{55}$: Effect of heat treatment on the magnetic response

Rapidly-solidified $\text{Al}_{45}\text{Mn}_{55}$ ribbons have been heat treated in the temperature range $100 \, ^{\circ}\text{C} < T < 350 \, ^{\circ}\text{C}$ to cause progressive structural changes on the microscopic and nanoscopic scales which affect the magnetic response. After each annealing treatment magnetic measurements were collected as a function of temperature ($T$) in the range $10 \, \text{K} < T < 400 \, \text{K}$ and a function of applied field ($H$) in the range $-50 \, \text{kOe} < H < 50 \, \text{kOe}$ using a superconducting quantum interference device (SQUID) magnetometer. It was found that the linear high-field magnetic susceptibility ($\chi_{\text{linear}}$) increased steadily with heat treatment at both $10 \, \text{K}$ and $300 \, \text{K}$ (Figure 51b), while the magnetization ($M$) at $10 \, \text{K}$ and the hysteresis shift increased and decreased, respectively, with annealing treatment at $295 \, ^{\circ}\text{C}$ and $345 \, ^{\circ}\text{C}$ (Figure 51c). The magnetization of the unshifted hysteresis loops collected at $300 \, \text{K}$ also increased with annealing (Figure 51d). Further heat treatment at $345 \, ^{\circ}\text{C}$ caused $M$ to rise nearly two orders of magnitude and changed the $M_{\text{ZFC}}$ vs. $T$ curve from a peak shape to a concave-down shape (Figure 51a).
Figure 51: Thermal evolution of (a) $M$ vs. $T$ curve and (b) $\chi_{\text{linear}}$ vs. $T_{\text{anneal}}$, obtained from magnetization loops from Al$_{45}$Mn$_{55}$ at 10 K. (c) FC linear-adjusted hysteresis loops at 10 K. Inset: Full-scale view to emphasize high $M$ values after annealing at 345 °C. (d) FC linear-adjusted hysteresis loops collected at 300 K.

Figure 52 graphically summarizes the effect of annealing in the temperature range $T \sim 100$-350 °C on the saturation magnetization ($M_s$), intrinsic coercivity ($H_{ci}$), and the shift of the $\chi_{\text{linear}}$-corrected magnetization loops collected at 10 K along the field axis (Figure 51c). Heat treatment at $T < 150$ °C was observed to cause little change in the values of $M_s$, $H_{ci}$, and the FC magnetization loop shift. For $T_{\text{anneal}} > 150$ °C, $M_s$ rose with increasing annealing temperature, while $H_{ci}$ and the loop shift both began to decline gradually. Both $H_{ci}$ and the shift slowly declined with annealing. In contrast, $H_{ci}$ increases towards a limiting value (~1.8 kOe) with heat treatment at 300 K. Further
annealing at $T \sim 345 \, ^\circ C$ for 30 minutes caused a sharp order-of-magnitude rise in the value of $M_s$ to about 20 emu/g, and a concomitant precipitous decline in both $H_{ci}$ and the FC loop shift at 10 K.

![Figure 52: Thermal evolution of $M_s$, $H_{ci}$, and the FC hysteresis loop shift at 10 K.](image)

The method in Eq. (34) has been used to decompose the FC demagnetization curves collected at 10 K from the as-spun and annealed melt-spun ribbons (Figure 51c) and to evaluate the relative contribution of each constituent magnetic phase [179]. The demagnetization curve decomposition analysis revealed the presence of two contributions to the total magnetization at 10 K, resulting in a two-stage demagnetization curve in the second quadrant. The first contribution, denoted as phase-1, was found to possess higher saturation magnetization ($M_s$) values and higher intrinsic coercivity ($H_{ci}$) values in the as-solidified ribbons, while the second contribution to the $\chi_{\text{linear}}$-corrected magnetization was found to possess lower $M_s$ values and lower $H_{ci}$ values in the as-quenched ribbons. As an illustrative example, Figure 53a shows this demagnetization curve decomposition...
The magnetic properties of both magnetic phase-1 and phase-2 were found to be essentially constant at 10 K with heat treatment at \( T < 150 \) °C (Figure 53b, c, and d). After annealing at low temperatures of only \( T > 150 \) °C the calculated values of \( M_{s,1} \) began to steadily increase (Figure 53c) and \( H_{ci,1} \) began to steadily decrease (Figure 53d).
After annealing at $T > 250 \, ^\circ\text{C}$ for 30 minutes the values of $M_s$ calculated for phase-2 began to change, while the intrinsic coercivity of phase-2 remained constant within error. The relative fractional contribution of phase-2 to the total magnetization at 10 K, given by $(M_s^{\text{phase-2}}/M_s^{\text{total}})$, was observed to steadily increase for $T_{\text{anneal}} \geq 275 \, ^\circ\text{C}$, and increased precipitously to about 91 % upon further annealing at 345 °C (Figure 54). In contrast, it has been determined that the fractional contribution of phase-1 to the total magnetization at 10 K declined steadily when $T_{\text{anneal}} \geq 275 \, ^\circ\text{C}$ and dropped sharply to approximately 9 % after heat treatment at 345 °C. These results suggest that magnetic phase-2 began to grow at the expense of the high-$H_{\text{ci}}$ phase-1 when the melt-spun Al$_{45}$Mn$_{55}$ ribbons were annealed at $T_{\text{anneal}} \geq 275 \, ^\circ\text{C}$, and that the transformation proceeded much more rapidly as $T_{\text{anneal}}$ rose to 345 °C.

![Figure 54: Effect of annealing treatment on relative fractional contribution to the linear-adjusted magnetization at 10 K, from decomposition of demagnetization curves collected from Cu$_{30}$Mn$_{70}$ ribbons in accordance with method of Eq. (34).](image-url)
Table 15 summarizes the effect of heat treatment on the values calculated for the saturation magnetization ($M_s$), intrinsic coercivity ($H_{ci}$), squareness or remanence ratio ($S$), and fractional contribution to the total magnetization ($M_s^{(i)}/M_s^{(total)}$) for each constituent magnetic phase at 10 K after heat treatment at several temperatures. Table 16 summarizes similarly the results of the decomposition analysis method of (34) as applied to the demagnetization curves collected at 300 K, as a function of annealing temperature; the FC demagnetization curves obtained at 300 K were found to consist only of a single magnetic phase.

Table 15: Magnetic character of each magnetic phase (phase-1 & phase-2) contributing to the total demagnetization curves obtained from Al$_{45}$Mn$_{55}$ ribbons at $T = 10$ K for different $T_{anneal}$ determined using method in Eq. (34).

<table>
<thead>
<tr>
<th>$T_{anneal}$ (°C)</th>
<th>$M_s$ (emu/g)</th>
<th>$H_{ci}$ (kOe)</th>
<th>$S$ ($M_r/M_s$)</th>
<th>$M_s^{(i)}/M_s^{(total)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Magnetic Phase-1 at T = 10 K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 °C</td>
<td>2.22 ± 0.04</td>
<td>19.6 ± 0.1</td>
<td>0.96 ± 0.01</td>
<td>0.92 ± 0.03</td>
</tr>
<tr>
<td>98 °C</td>
<td>2.23 ± 0.04</td>
<td>19.5 ± 0.1</td>
<td>0.96 ± 0.01</td>
<td>0.94 ± 0.02</td>
</tr>
<tr>
<td>149 °C</td>
<td>2.22 ± 0.03</td>
<td>19.2 ± 0.1</td>
<td>0.96 ± 0.01</td>
<td>0.95 ± 0.02</td>
</tr>
<tr>
<td>200 °C</td>
<td>2.30 ± 0.03</td>
<td>18.1 ± 0.2</td>
<td>0.95 ± 0.00</td>
<td>0.94 ± 0.02</td>
</tr>
<tr>
<td>250 °C</td>
<td>2.33 ± 0.02</td>
<td>17.6 ± 0.2</td>
<td>0.95 ± 0.00</td>
<td>0.94 ± 0.01</td>
</tr>
<tr>
<td>275 °C</td>
<td>2.34 ± 0.03</td>
<td>17.3 ± 0.2</td>
<td>0.96 ± 0.00</td>
<td>0.91 ± 0.02</td>
</tr>
<tr>
<td>295 °C</td>
<td>2.36 ± 0.03</td>
<td>16.6 ± 0.2</td>
<td>0.96 ± 0.00</td>
<td>0.86 ± 0.02</td>
</tr>
<tr>
<td>321 °C</td>
<td>2.37 ± 0.03</td>
<td>16.6 ± 0.2</td>
<td>0.96 ± 0.00</td>
<td>0.86 ± 0.02</td>
</tr>
<tr>
<td>345 °C</td>
<td>1.60 ± 0.36</td>
<td>12.3 ± 2.1</td>
<td>0.94 ± 0.06</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td><strong>Magnetic Phase-2 at T = 10 K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 °C</td>
<td>0.18 ± 0.04</td>
<td>1.2 ± 1.7</td>
<td>0.15 ± 0.17</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>98 °C</td>
<td>0.14 ± 0.00</td>
<td>1.1 ± 1.8</td>
<td>0.16 ± 0.22</td>
<td>0.06 ± 0.00</td>
</tr>
<tr>
<td>149 °C</td>
<td>0.12 ± 0.03</td>
<td>0.8 ± 1.0</td>
<td>0.19 ± 0.21</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>200 °C</td>
<td>0.14 ± 0.03</td>
<td>0.8 ± 1.2</td>
<td>0.14 ± 0.18</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td>250 °C</td>
<td>0.14 ± 0.03</td>
<td>0.8 ± 1.1</td>
<td>0.14 ± 0.18</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td>275 °C</td>
<td>0.24 ± 0.04</td>
<td>1.3 ± 1.2</td>
<td>0.17 ± 0.12</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>295 °C</td>
<td>0.38 ± 0.04</td>
<td>2.2 ± 0.7</td>
<td>0.32 ± 0.06</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td>321 °C</td>
<td>0.39 ± 0.04</td>
<td>2.2 ± 0.7</td>
<td>0.32 ± 0.06</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td>345 °C</td>
<td>17.14 ± 0.04</td>
<td>2.4 ± 0.1</td>
<td>0.38 ± 0.01</td>
<td>0.91 ± 0.52</td>
</tr>
</tbody>
</table>
Table 16: Magnetic character of the total demagnetization curves collected at 300 K for different annealing conditions.

<table>
<thead>
<tr>
<th>$T_{\text{anneal}}$ (°C)</th>
<th>$M_s$ (emu/g)</th>
<th>$H_{ci}$ (kOe)</th>
<th>$S$ ($M_r/M_s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One phase at $T = 300$ K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 °C</td>
<td>$0.11 \pm 0.00$</td>
<td>$1.2 \pm 0.1$</td>
<td>$0.14 \pm 0.02$</td>
</tr>
<tr>
<td>230 °C</td>
<td>$0.08 \pm 0.00$</td>
<td>$1.4 \pm 0.1$</td>
<td>$0.23 \pm 0.02$</td>
</tr>
<tr>
<td>250 °C</td>
<td>$0.09 \pm 0.00$</td>
<td>$1.4 \pm 0.1$</td>
<td>$0.24 \pm 0.02$</td>
</tr>
<tr>
<td>275 °C</td>
<td>$0.12 \pm 0.00$</td>
<td>$1.5 \pm 0.1$</td>
<td>$0.26 \pm 0.02$</td>
</tr>
<tr>
<td>295 °C</td>
<td>$0.28 \pm 0.00$</td>
<td>$1.6 \pm 0.1$</td>
<td>$0.27 \pm 0.01$</td>
</tr>
<tr>
<td>321 °C</td>
<td>$0.31 \pm 0.00$</td>
<td>$1.6 \pm 0.1$</td>
<td>$0.24 \pm 0.01$</td>
</tr>
<tr>
<td>345 °C</td>
<td>$17.64 \pm 0.16$</td>
<td>$1.8 \pm 0.1$</td>
<td>$0.28 \pm 0.01$</td>
</tr>
</tbody>
</table>

In the as-spun state the higher-magnetization phase (phase-1) contributes approximately 92 % of the total magnetization and displays a large intrinsic coercivity $H_{ci,1} \sim 19.6$ kOe and squareness (or magnetic remanence ratio, $M_r/M_s$) of $S_1 \sim 0.96$. In contrast, it was determined that the lower-magnetization phase (phase-2) accounted for only about 8 % of the total magnetization and possessed significantly lower values of $H_{ci,2} \sim 1.2$ kOe and $S_2 \sim 0.15$ at 10 K. The $M_s$ values calculated from the demagnetization curves collected at 300 K were slightly smaller than that calculated for phase-2 at 10 K, but the calculated $H_{ci}$ and $S$ values were found to be essentially identical to those of magnetic phase-2 at 10 K. These results suggest that phase-2, the magnetic signature of which grows after annealing at $T \sim 275$ °C for 30 minutes, is responsible for the sigmoidal-shaped hysteresis at 300 K, while phase-1 is absent at this temperature.

6.2.3 Al$_{45}$Mn$_{55}$: Thermal character of observed phase transformations

*Overview:* Differential scanning calorimetry (DSC) has been used to determine the thermal character of any phase transformations which may have occurred as a result of annealing in the temperature range $100$ °C < $T$ < $345$ °C, causing physical changes to the
alloy and affecting the magnetic character. Calorimetric measurements collected from as-quenched Al45Mn55 ribbons (Figure 55) displayed a strong peak from an exothermic transformation in the approximate temperature range 300-500 °C on the initial heating curve only, suggesting an irreversible nature. It was found that the peaks grew in intensity and shifted towards higher temperatures as the heating rate (Φ) increased. Close examination of the DSC exotherms obtained at lower heating rates (5 K/min ≤ Φ ≤ 15 K/min) revealed a multiple peak structure, consistent with the occurrence of multiple phase transformations at similar temperatures (emphasized in the inset of Figure 55a). These results show two phase transitions comprise each DSC exotherm – one at higher temperatures and one at lower temperatures.

Figure 55: (a) DSC curves (initial heating step) obtained from Al45Mn55 ribbons at heating rates of 5-20 K/min. Inset: Magnification of the DSC exotherm collected at 5 K/min to emphasize double peak structure. (b) Kissinger analysis carried out on the DSC exotherms, determined using the fitting method detailed in Section 4.5.

The multiphase DSC exotherms collected at heating rates of Φ = 5-20 K/min have been analyzed by the fitting method detailed in Section 4.5 in order to determine the number of phase transformations contributing to the exotherm and the temperature of
each transformation. The peak at lower temperature ($T$) was observed to be much smaller in magnitude and area than the peak at higher temperature, and it was determined that the DSC exotherms were best fitted as the sum of two Gaussian distributions with maxima in the range $\sim$340-370 °C and $\sim$400-425 °C (shown in the inset of Figure 55a). The maxima were used as the peak temperatures in Kissinger’s analysis (Eq. (35) in Section 4.5) for evaluation of the activation energy of each constituent phase transformation. Kissinger analysis of the DSC exotherms with maxima in the range $\sim$340-370 °C and $\sim$400-425 °C show that the activation energy ($E_a$) calculated for the smaller, low temperature portion of the DSC exotherms is approximately $E_a \sim 128 \pm 11$ kJ/mol; $E_a$ calculated for the major transformation peak at higher temperatures is about $E_a \sim 155 \pm 10$ kJ/mol (Figure 55b).

6.3 $\text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{70})_{10}$ and $\text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10}$: Magnetic and structural character

The overarching goal of this thesis work is to implant the antiferromagnetic (AF) MnX (X = Cu, Al, etc.) alloys described in Sections 3.2.1.1 and 3.2.1.2 in a ferromagnetic (FM) Fe-rich matrix phase to produce an exchange-biased permanent magnetic nanocomposite. It is desired to clarify the origins and conditions underlying exchange bias ($H_{ex}$) and magnetic remanence ($M_r$) enhancement in bulk FM/AF magnetic nanocomposite systems. Some work has been accomplished in this regard – ribbons of nominal composition $\text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10}$ and $\text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10}$ have been fabricated by rapid solidification via melt-spinning, and preliminary analysis of the magnetic and structural character of the as-solidified specimens has been carried out. Further, more thorough study is recommended for future work to better understand both systems (Section 8.2).
6.3.1  \( \text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10} \) and \( \text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10} \): Structural character of as-spun ribbons

**Overview:** The crystal structure of as-solidified \( \text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10} \) and \( \text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10} \) ribbons (Figure 56a) have been characterized by x-ray diffraction (XRD) measurements. The XRD data showed two Bragg peaks, including the majority peak at approximately \( 44.8 \degree2\theta \), associated with a crystallographic phase with body-centered-cubic (bcc) structured unit cells. Several additional Bragg reflections contributed by an unidentified phase were also observed in both \( \text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10} \) and \( \text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10} \) ribbons. It is important to note that the volume-averaged compositional character of either alloy has not been verified by scanning electron microscope energy-dispersive x-ray spectroscopy (EDX) (Section 4.3.1).

**Figure 56:** (a) XRD patterns collected from as-solidified \( \text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10} \) and \( \text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10} \) ribbons. (b) Magnified view of bcc (110) Bragg reflection of both alloys.

Magnification of the (110) Bragg reflections from the bcc phases (Figure 56b) observed in both Fe(CuMn) alloys revealed a triple-peak structure in the \( \text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10} \) as-spun ribbons and a double peak structure in the \( \text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10} \) as-
solidified ribbons, consistent with the presence of three and two \textit{bcc} phases with slightly different unit cell dimensions in the Fe\textsubscript{90}(Cu\textsubscript{30}Mn\textsubscript{70})\textsubscript{10} and Fe\textsubscript{90}(Cu\textsubscript{10}Mn\textsubscript{90})\textsubscript{10} as-quenched ribbons, respectively. However, the signal-to-noise ratio observed for the (200) Bragg peaks from the \textit{bcc} phases was too poor to permit resolution of more than a single Bragg peak. Lattice dimensions have therefore only been calculated for a single \textit{bcc} phase in each alloy, using the least-squares cell parameter program described in Section 4.3.2. Both as-spun Fe\textsubscript{90}(Cu\textsubscript{30}Mn\textsubscript{70})\textsubscript{10} and Fe\textsubscript{90}(Cu\textsubscript{10}Mn\textsubscript{90})\textsubscript{10} ribbons were found to contain a \textit{bcc} structural phase with unit cell lattice parameter \(a \sim 2.858 \pm 0.003 \text{ Å}\) and unit cell volume \(V \sim 23.34 \pm 0.07 \text{ Å}^3\).

6.3.2 \textbf{Fe\textsubscript{90}(Cu\textsubscript{30}Mn\textsubscript{70})\textsubscript{10} and Fe\textsubscript{90}(Cu\textsubscript{10}Mn\textsubscript{90})\textsubscript{10}: Magnetic response in as-quenched state}

\textit{Overview:} The magnetic response of rapidly-solidified Fe\textsubscript{90}(Cu\textsubscript{30}Mn\textsubscript{70})\textsubscript{10} and Fe\textsubscript{90}(Cu\textsubscript{10}Mn\textsubscript{90})\textsubscript{10} melt-spun alloys has been investigated as a function of temperature \((T, 10 \text{ K} \leq T \leq 350 \text{ K})\) and applied field \((H, -50 \text{ kOe} \leq H \leq 50 \text{ kOe})\) using superconducting quantum interference device (SQUID) magnetometry, discussed in Section 4.4.1. Figure 57a shows field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibility \((\chi)\) vs. \(T\) curves collected under a probe field of 1 kOe. The FC and ZFC \(\chi\) vs. \(T\) curves were observed to be concave-down functions of \(T\) over nearly the entire temperature range. It has been determined that the as-solidified Fe\textsubscript{90}(Cu\textsubscript{10}Mn\textsubscript{90})\textsubscript{10} possesses a susceptibility about 60 % higher than that of the as-quenched Fe\textsubscript{90}(Cu\textsubscript{30}Mn\textsubscript{70})\textsubscript{10} ribbons, highlighting the effect of Mn content on the magnetic character. The FC and ZFC \(\chi\) vs. \(T\) curves were identical over the entire temperature range in the Fe(CuMn) alloy with higher Mn content. The FC and ZFC susceptibility were not equal in the Fe\textsubscript{90}(Cu\textsubscript{30}Mn\textsubscript{70})\textsubscript{10} alloy,
which nominally contains around 20 at. % less Mn. At high $T$ the $\chi_{\text{ZFC}}$ vs. $T$ curve obtained from the Fe$_{90}$(Cu$_{30}$Mn$_{70}$)$_{10}$ as-solidified ribbons displayed a small hook-shaped portion where $\chi$ began to increase.

![Figure 57: (a) FC and ZFC $\chi$ vs. $T$ curves obtained from as-spun Fe$_{90}$(Cu$_{30}$Mn$_{70}$)$_{10}$ and Fe$_{90}$(Cu$_{10}$Mn$_{90}$)$_{10}$ ribbons. (b) FC hysteresis loops collected from as-solidified ribbons at 10 K.](image)

The FC magnetization loops collected at 10 K on as-spun Fe$_{90}$(Cu$_{30}$Mn$_{70}$)$_{10}$ and Fe$_{90}$(Cu$_{10}$Mn$_{90}$)$_{10}$ ribbons (Figure 57b) were found to be symmetric about the origin and sigmoidal-shaped. Both alloys possessed very high saturation magnetization ($M_s$) values of $\sim 185$ emu/g but very low coercivity ($H_c$) values of $\sim 100$ Oe. It was also observed that the field required to obtain complete magnetic saturation is much higher in the $\sim 7$ at. % Mn alloy; the saturating field in Fe$_{90}$(Cu$_{10}$Mn$_{90}$)$_{10}$ is $\sim 2$ kOe, whereas the saturating field in Fe$_{90}$(Cu$_{30}$Mn$_{70}$)$_{10}$ is $\sim 30$ kOe.
6.4 **Summary of magnetic, structural, and thermal character data obtained from**

\( \text{Cu}_{30}\text{Mn}_{70}, \text{Al}_{45}\text{Mn}_{55}, \text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10} \) and \( \text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10} \) melt-spun ribbons

In summary, two binary MnX (X = Cu, Al, etc.) alloy specimens of composition \( \text{Cu}_{30}\text{Mn}_{70}, \text{Al}_{45}\text{Mn}_{55}, \text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10} \) and \( \text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10} \) have been fabricated by rapid solidification via melt spinning and their structural, magnetic, and thermal behavior has been observed. The effect of structural modification via thermal annealing in the temperature ranges \( T \sim 200-450 \) °C and \( T \sim 100-350 \) °C on the crystal structure, microstructure, and magnetic response of \( \text{Cu}_{30}\text{Mn}_{70} \) and \( \text{Al}_{45}\text{Mn}_{55}, \) respectively, has also been investigated. After \( \text{Cu}_{30}\text{Mn}_{70} \) melt-spun ribbons were embrittled by annealing 30-minutes at \( T \sim 450 \) °C, they were subject to cryogenic mechanical milling for 10-40 minutes as a means of manipulating the nanoscopic and microscopic structure and the influence of milling time has been examined. The thermal character of the exothermic phase transformation in \( \text{Al}_{45}\text{Mn}_{55} \) alloys around \( \sim 300-500 \) °C has been measured and analyzed. Understanding relationships between these behaviors is anticipated to enable tailoring of the functional magnetic response of such alloys.

X-ray diffraction (XRD) analysis of as-solidified \( \text{Cu}_{30}\text{Mn}_{70} \) ribbons revealed the presence of two face-centered-cubic (\textit{fcc}) phases with slightly different lattice parameters on both the free and wheel sides, on the order of \( a \sim 3.74-3.75 \) Å. Field-cooled (FC, 50 kOe) hysteresis loops collected from the as-spun ribbons were anhysteretic and shifted along the field axis by \( \sim 10 \) kOe at \( T = 10 \) K. The unit cell lattice parameters of the \textit{fcc} phases decreased and homogenized to \( a \sim 3.731 \pm 0.012 \) Å and a secondary complex cubic phase with \( a \sim 8.896 \pm 0.012 \) Å appeared after 30 minutes of heat treatment \( T \sim \)
450 °C. Decomposition of the FC demagnetization curves revealed two contributions to
the total magnetization at 10 K – an ultrahard phase with intrinsic coercivity $H_{ci} \sim 55-166$
kOe and a softer phase with $H_{ci} \sim 5-25$ kOe. The softer phase grew at the expense of the
ultrahard phase with annealing in the temperature range $T \sim 200-450$ °C. Structural
analysis showed that cryomilling minimally modified the lattice parameter of the $fcc$
phases but caused a deterioration of crystallographic order, a reduction of the crystallite
size from ~23 nm to ~13 nm, a significant increase in the magnetization ($M$), a
simultaneous decline in the hysteresis shift, and the appearance of a small amount of
some additional magnetic impurity.

Diffraction measurements revealed that as-solidified Al$_{45}$Mn$_{55}$ ribbons consisted
of two majority hexagonal phases with slightly different unit cell dimensions on the order
of $a \sim 2.7$ Å and $c \sim 4.4$ Å. Field-cooled (FC) hysteresis loops collected from the as-
quenched ribbons were shifted approximately ~13 kOe along the field axis at 10 K and
consisted of two phases – one with higher $M_s$ and $H_{ci} \sim 19$ kOe ($phase-1$) that contributed
approximately 92 % of the total magnetization, and one with lower $M_s$ and $H_{ci} \sim 1.2$ kOe
($phase-2$) that contributed only ~8 % of the total $M$. The magnetic contribution of $phase-
1$ began to increase after heat treatment $T > 150$ °C, while that of $phase-2$ began to grow
at the expense of the higher-coercivity $phase-1$ after annealing at $T > 275$ °C. Heat
treatment of the Al$_{45}$Mn$_{55}$ ribbons at $T_{anneal} \sim 345$ °C caused the growth of a phase with a
tetragonal unit cell structure ($a \sim 2.77$ Å, $c \sim 3.56$ Å) at the expense of the $hcp$ phases.
Concomitantly, the magnetic contribution of $phase-2$ increased from ~8 % of the total
magnetization to approximately 91% at 10 K (and 100% at 300 K); $M_s$ of phase-2
increased from ~0.4 emu/g to ~17.1 emu/g, while the calculated intrinsic coercivity
increased only slightly from $H_{ci} \sim 1.2 \pm 1.7$ to $H_{ci} \sim 2.4 \pm 0.1$ kOe. The differential scanning calorimetry (DSC) curves collected from the as-solidified ribbons showed the presence of an irreversible exothermic transformation in the temperature range ~300-500 °C. Kissinger analysis of the biphasic DSC exotherms with maxima in the range ~340-370 °C and ~400-425 °C show that the activation energy ($E_a$) calculated for the smaller, low temperature portion of the DSC exotherms is approximately $E_a \sim 128 \pm 11$ kJ/mol; $E_a$ calculated for the major transformation peak at higher temperatures is about $E_a \sim 155 \pm 10$ kJ/mol.

Both as-spun Fe$_{90}$(Cu$_{30}$Mn$_{70}$)$_{10}$ and Fe$_{90}$(Cu$_{10}$Mn$_{90}$)$_{10}$ ribbons were found to contain a bcc structural phase with unit cell lattice parameter $a \sim 2.858 \pm 0.003$ Å and unit cell volume $V \sim 23.34 \pm 0.07$ Å$^3$. Several Bragg peaks associated with unidentified phases were also present. Both alloys possessed very high saturation magnetization ($M_s$) values of ~185 emu/g but very low coercivity ($H_c$) values of ~100 Oe. It was also observed that the field required to obtain complete magnetic saturation is much higher in the ~7 at. % Mn alloy; the saturating field in Fe$_{90}$(Cu$_{10}$Mn$_{90}$)$_{10}$ is ~2 kOe, whereas the saturating field in Fe$_{90}$(Cu$_{30}$Mn$_{70}$)$_{10}$ is ~30 kOe.
7.0 DISCUSSION OF RESULTS

The overarching goal of this research is to comprehend exchange bias ($H_{ex}$) and magnetic remanence ($M_r$) enhancement in bulk ferromagnetic/antiferromagnetic (FM/AF) nanocomposite systems. Fe/MnX (X = Cu, Al, etc.) is employed as a model FM/AF system for study, with Fe as the FM component and MnX as the AF component; specific research objectives are described in Section 5.2. This thesis work has been centered on elucidation of the magnetic, structural, and thermal character of the model nanostructured AF portion – rapidly-solidified MnX alloys with compositions Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$. Post-synthesis processing techniques – thermal annealing and mechanical milling – were used to modify the structure of the MnX alloys on the nanometric and micrometric scales and the evolution of their magnetic and structural character has been observed. Development of correlations between each of these attributes is anticipated to lead to the ability to control the technical magnetic response of these alloys, which may lead to new processing pathways for engineering of advanced permanent magnetic materials.

Experimental data obtained from the MnX alloys with magnetic (Section 4.4.1), structural (Section 4.3), and thermal probes (Section 4.5) were presented and analyzed in Section 6.0. Both of the MnX binary alloys synthesized to date – melt-spun Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$ ribbons – were found to consist of two majority structural phases with slightly different lattice dimensions, and exhibited significant shifts of ~10-13 kOe in their respective field-cooled (FC) magnetization loops collected at $T = 10$ K. Interpretations of these results suggest that the large hysteresis shifts are actually manifestations of the exchange bias ($H_{ex}$) phenomenon (Section 3.1.2.3), attributed to nanoscopic variations in local Mn concentration that result in a structural and
corresponding magnetic phase separation into AF Mn-rich regions and FM Mn-poor regions. Exchange interactions between these regions are believed to cause the significant $H_{\text{ex}}$ shift at low temperatures. Additionally, the transformation of the hexagonal $\varepsilon$-AlMn phase to the tetragonal $L1_0$-structured $\tau$-AlMn phase, reported to possess robust permanent magnetic character, has been observed after heat treatment for 30 minutes at $T_{\text{anneal}} \geq 275$ °C, which is nearly 100 °C lower than literature values [11, 12, 17-21, 23, 27-30]. The magnetic, structural, and thermal character data obtained from melt-spun Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$ ribbons are discussed in more detail and more thoroughly examined in Sections 7.1 and 7.2. Section 7.3 presents preliminary interpretations of data collected to date from melt-spun Fe$_{90}$(Cu$_{30}$Mn$_{70}$)$_{10}$ and Fe$_{90}$(Cu$_{10}$Mn$_{90}$)$_{10}$ ribbons. Finally, Section 7.4 discusses relationships between the magnetic and structural character general to exchange-biased MnX (X = Cu, Al, etc.) alloys.

7.1 Cu$_{30}$Mn$_{70}$: Discussion of magnetic and structural data obtained from melt-spun ribbons

*Overview:* The first two objectives of this thesis research were to first synthesize and investigate the magnetic and structural character of nanostructured binary MnX (X = Cu, Al, etc.) alloys, and then to design and control their structure on multiple length scales prior to carrying out the same in Fe/MnX nanocomposite systems (Section 5.2). Since the structure and composition of a material significantly affect its functional magnetic character, development of relationships between these behaviors is expected to enable manipulation of the magnetic response [1, 39]. To this end, a MnX alloy of nominal composition Cu$_{30}$Mn$_{70}$ has been synthesized by rapid solidification via melt-
spinning and subsequently subjected to post-synthesis processing techniques including thermal annealing and mechanical milling, in order to control the structure on multiple length scales. The volume-averaged chemical composition has been verified within ± 1 at. % by scanning electron microscope energy-dispersive x-ray spectroscopy (EDX) analysis (Section 4.3.1).

X-ray diffraction (XRD) measurements revealed the presence of two face-centered-cubic (fcc) phases of slightly different lattice parameter in the as-solidified ribbons (Table 10), coincident with a large exchange bias ($H_{ex}$) shift of ~10 kOe in the field-cooled magnetization loop collected at $T = 10$ K (Figure 40c). Decomposition of the demagnetization curves in accordance with the method of Eq. (34) showed the occurrence of two contributions to the magnetization at 10 K – an ultrahard magnetic phase-2 and a softer magnetic phase-1 – which evolved with annealing treatment (Table 12, Figure 43d, Figure 44).

7.1.1 Cu$_{30}$Mn$_{70}$: Structural character of rapidly-solidified ribbons

Structural and compositional data obtained from Cu$_{30}$Mn$_{70}$ melt-spun ribbons are shown in Section 6.1.1. X-ray diffraction (XRD) analysis of both the free and wheel sides of the as-quenched Cu$_{30}$Mn$_{70}$ ribbons (Figure 36) revealed the presence of two well-crystallized face-centered-cubic (fcc) phases, identified as the $\gamma$-CuMn phase in the Cu-Mn binary equilibrium phase diagram (Figure 13), that possessed slightly different unit cell lattice parameters ($a$) and unit cell volumes ($V$). The calculated unit cell dimensions for both phases, denoted as $fcc-1$ and $fcc-2$, are shown in Table 10.
It is hypothesized that the fcc-1 and fcc-2 phases present in the as-solidified ribbons possess slightly different unit cell dimensions due to variations in Mn content, as reported by Turchanin et al. [128]. Mn atoms (atomic diameter ~ 2.80 Å) substitute for Cu atoms (atomic diameter ~ 2.56 Å) in the fcc lattice because, while it is known that Mn and Cu display complete mutual solid solubility in the γ-CuMn phase regime, Mn atoms are too large to fit inside the fcc Cu interstitial sites – the tetrahedral interstitial sites are ~ 0.3 Å wide and the octahedral sites are ~ 0.5 Å wide [189]. The unit cell dimensions of γ-CuMn alloys likely increase as the Mn content rises because the atomic diameter of Mn is slightly greater than that of Cu [121]. The empirically-derived plot of the γ-CuMn lattice parameter against the Mn content in the fcc phase shown in Figure 58 confirms this hypothesis.

![Figure 58: Dependence of unit cell lattice parameter (a) of the quenched fcc γ-CuMn phase on Mn content [121].](image)

The unit cell dimensions calculated for the fcc phases (Table 10) are used in conjunction with the empirical formula for the γ-CuMn unit cell lattice parameter as a function of composition (Eq. (26), developed by Cowlam et al. [117]) for determination of the Mn content in the fcc unit cell (Table 17). It is estimated that, on the free side, the fcc-1 phase is enriched in Mn and contains ~ 82-86 at. % Mn in the as-solidified state; on
the wheel side, the \textit{fcc-1} phase contains \~82-89 at. \% Mn. The \textit{fcc-2} phase likely possesses markedly lower Mn content and is estimated to contain about 40-49 at. \% Mn on the free side, and \~35-51 at. \% Mn on the wheel side. It is important to note that, based on Figure 58, very small changes to or errors in the calculated unit cell lattice parameters of the quenched-in $\gamma$-CuMn phase may correspond to significantly different estimations of the Mn content of the \textit{fcc} unit cell.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{Side} & \textbf{Phase} & \textbf{$a$ (Å)} & \textbf{$x_{\text{Mn}}$ (at. \% Mn)} \\
\hline
Free side & \textit{fcc-1} & 3.750 ± 0.002 & 82-86 at. \% \\
 & \textit{fcc-2} & 3.744 ± 0.006 & 40-49 at. \% \\
\hline
Wheel side & \textit{fcc-1} & 3.748 ± 0.004 & 82-89 at. \% \\
 & \textit{fcc-2} & 3.740 ± 0.012 & 35-51 at. \% \\
\hline
\end{tabular}
\caption{Composition of the \textit{fcc} $\gamma$-CuMn unit cell in the as-solidified Cu$_{30}$Mn$_{70}$ melt-spun ribbons, calculated using the empirically-derived Eq. (26), developed by Cowlam \textit{et al.} [117].}
\end{table}

These results suggest a disproportionation of Mn content into two distinct compositionally-variant nanostructured regions on both the slower-cooling free side and the more rapidly-quenched wheel side. The higher relative intensity of the Bragg peaks associated with the \textit{fcc-1} phase on the free side points to a preponderance of the Mn-rich \textit{fcc-1} $\gamma$-CuMn phase regions and a lesser amount of Mn-poor \textit{fcc-2} phase regions. Conversely, the wheel side contains a higher amount of the Mn-poor \textit{fcc-2} regions than the Mn-rich \textit{fcc-1} regions. Energy-dispersive x-ray spectroscopy (EDX) analysis of the volume-average chemical composition confirmed a higher Mn content on the free side.
than on the wheel side (Figure 35), accentuating the effect of quench rate on the distribution of Mn concentration in the alloy.

Diffraction measurements were then carried out after the as-solidified ribbons were annealed for 30 minutes at $T \sim 450 \, ^\circ\text{C}$ (Figure 37a and b). The lattice dimensions of the two $fcc-1$ and $fcc-2$ phases were found to decrease and become homogenized to approximately $a \sim 3.731 \pm 0.012 \, \text{Å}$ with annealing (Table 11). Additionally, several prominent Bragg reflections appeared which corresponded to a complex cubic phase, identified as the $\alpha$-Mn equilibrium phase (Figure 13) with $a = 8.896 \pm 0.012 \, \text{Å}$ and $V = 704.0 \pm 2.8 \, \text{Å}^3$, approximately 0.6 % lower than the literature value of 708.277 Å$^3$ (Section 3.2.1.1) [121, 190]. The ~0.6 % reduction in the volume of the $\alpha$-Mn phase is likely due to either lattice strain or a small amount of Cu substitution (~1-2 atoms of Cu substituted for Mn atoms per unit cell).

Upon annealing at $T \sim 450 \, ^\circ\text{C}$ it seems that the Mn content in the $\gamma$-CuMn unit cell declined – based on Eq. (26), it declined from ~80-90 at. % Mn in the $fcc-1$ phase and ~40-50 at. % Mn in the $fcc-2$ phase to between 30-45 at. % in both phases. It is hypothesized that aging caused diffusion of Mn throughout the matrix, homogenizing somewhat the previously-segregated Mn content in the $\gamma$-CuMn phases and permitting some growth of the equilibrium $\alpha$-Mn phase – which mostly contains Mn due to minimal solubility of Cu in this phase [128] – at the expense of the metastable $fcc \gamma$-phases.

Cryogenic milling (Section 4.1.3) was employed to manipulate the microstructure of the rapidly-solidified Cu$_{30}$Mn$_{70}$ ribbons on the microscopic and nanoscopic scales and to promote formation of intimate interphase interfaces. Cu$_{30}$Mn$_{70}$ ribbons annealed at $T \sim$
450 °C were used as milling precursors. Diffraction analysis showed that the lattice parameters of the fcc phases were unaffected by milling and remained relatively constant at $a \sim 3.74$ Å (Figure 38c). Longer milling times caused the fcc Bragg peaks to broaden and the average crystallite size ($D$) to decrease from $D \sim 23$ nm to $D \sim 13$ nm, signaling a reduction in crystallographic order (Figure 39).

### 7.1.2 Cu$_{30}$Mn$_{70}$: Discussion of the magnetic response of melt-spun ribbons

The magnetic properties of melt-spun Cu$_{30}$Mn$_{70}$ have been characterized as a function of applied field ($H$, -50 kOe $\leq H \leq$ 50 kOe) and temperature ($T$, 10 K $\leq T \leq$ 350 K) in the as-spun state and after heat treatment in the temperature range 200 °C $\leq T_{\text{anneal}} \leq$ 450 °C using superconducting quantum interference device (SQUID) magnetometry (Section 4.4.1). The zero-field-cooled (ZFC) and field-cooled (FC) branches of the magnetization ($M$) vs. $T$ curve were found to superimpose above the peak temperature $T_{\text{peak}} = 125$ K in the as-quenched ribbons (Figure 40a), which is characteristic of materials that exhibit magnetic blocking behavior at low temperature (defined in Section 3.1.2.1) [39, 81]. Ribbons field-cooled through the blocking temperature ($T_B$) displayed a significant shift of the magnetization loop along the field ($H$) axis, as large as $\sim$10 kOe at 10 K (Figure 41a). The observed hysteresis shift is diagnostic of the exchange bias ($H_{\text{ex}}$) phenomenon (Section 3.1.2.3), wherein quantum mechanical exchange interactions between adjacent nano-sized ferromagnetic (FM) and antiferromagnetic (AF) phases convey a unidirectional anisotropy that shifts the major hysteresis loop along the $H$ axis [5, 39, 42].
Magnetization loops collected from rapidly-solidified Cu$_{30}$Mn$_{70}$ after field-cooling through $T_B$ were found to consist of both linear and nonlinear (i.e. anhysteretic and hysteretic) portions. The linear contribution to the magnetic susceptibility ($\chi_{\text{linear}}$), shown in Figure 40b, was very small in magnitude ($\sim 10^{-5} \, \text{emu/g-Oe}$) and reached a peak at approximately 120 K, similar to the behavior of $M_{ZFC}$. These characteristics suggest $\chi_{\text{linear}}$ is actually the magnetic signal from an AF phase with Néel temperature $T_N \sim T_B$; at high temperatures ($T > T_B$) this phase is paramagnetic and $\chi_{\text{linear}}$ rises as $T$ falls, but $\chi_{\text{linear}}$ begins to decrease as AF ordering sets in at $T < T_B \sim T_N$.

The nonlinear hysteretic portion of the magnetization loops obtained at 10 K (Figure 43c) were observed to be highly asymmetric about not only the magnetization ($M$) axis but also about the field ($H$) axis, signifying that magnetic saturation (and complete magnetization reversal) was not obtained in both the positive and negative directions. The nonlinear hysteresis loop collected from the as-solidified ribbons was flattened to a constant value of $M$ because a large majority of the magnetic moments were unable to reverse and lower the net magnetization of the alloy, even in a large negative field of -50 kOe [50].

The nature of the large magnetic reversal fields was investigated through decomposition of the descending-field branches of the nonlinear FC loops obtained from the as-spun and annealed ribbons in accordance with the method of Eq. (34) (Figure 43d) [179]. This analysis revealed two contributions to the nonlinear magnetization at 10 K – a “softer” magnetic phase, denoted as phase-1, which has lower saturation magnetization ($M_s$) and lower intrinsic coercivity ($H_{ci}$) $\sim 4-25$ kOe values, and an “ultrahard” magnetic phase, denoted as phase-2, that possesses higher $M_s$ and much larger $H_{ci} \sim 56-166$ kOe
values. The effect of annealing temperature on the attributes of both magnetic phases is summarized in Table 12. The ultrahard phase-2 entirely dominates the magnetic response in the as-solidified ribbons (~99% of the hysteretic magnetization). As annealing proceeded in the range $200 \, ^{\circ}C < T < 450 \, ^{\circ}C$, the antiferromagnetic (AF) character of both phase-1 and phase-2 decreased, and it was found that phase-1 grew at the expense of phase-2 (Figure 44). Neither magnetic phase were observed in magnetization loops collected at $T > T_B = 125 \, K$.

The demagnetization curve calculated for the ultrahard phase-2 in the as-spun Cu$_{30}$Mn$_{70}$ ribbons at 10 K was found to be essentially constant over the entire range of applied fields due to its large $H_{ci}$ values, indicating that magnetic saturation was not approached in the negative direction due to incomplete magnetization reversal (Table 12). The demagnetization curve calculated for the lower-$H_{ci}$ phase-1 was symmetric about the $H$-axis, indicating magnetic saturation and complete magnetization reversal was attained in both directions. Since the total nonlinear hysteresis loops were themselves minor magnetization loops, it may be inferred that phase-2 is responsible for the large magnetic reversal fields. The growth of the softer magnetic phase-1 appears responsible for the appearance of the sigmoidal-shaped nonlinear magnetization loop with heat treatment at $T > 200 \, ^{\circ}C$.

The microstructure and nanostructure of rapidly-solidified Cu$_{30}$Mn$_{70}$ ribbons was modified by cryogenic milling (Section 4.1.3) for 10-40 minutes and the effect of cryomilling on the alloy's magnetic response has been investigated. Magnetic measurements (Figure 45) show that cryogenic milling caused the exchange coupling present at 10 K in the as-quenched and annealed ribbons to deteriorate rapidly. These
data indicate that cryomilling may have conveyed a significant number of structural
defects into the alloy, which in turn may have caused the ferromagnetic/antiferromagnetic
(FM/AF) interfacial contact to become increasingly nonideal with longer milling times,
leading to a reduced strength of the FM/AF exchange coupling.

Cryogenic mechanical milling also introduced a secondary FM impurity which
appeared in the low-field region of the nonlinear hysteresis loops collected after milling
for just 10 minutes (Figure 45b). The amount of this FM impurity, believed to be small
steel flakes that chipped off of the magnetized impactor rod during its rapid oscillations,
appears to increase as milling progresses. Assuming the FM impurity has a saturation
magnetization ($M_s$) identical to that of pure $\alpha$-Fe ($M_s \sim 220$ emu/g at 10 K) (Table 3)
[102], the impurity comprises approximately 0.1 wt. % of the powder after 40 minutes of
milling.

7.1.3 $\text{Cu}_{30}\text{Mn}_{70}$ melt-spun ribbons: Correlations between magnetic and structural
caracter

X-ray diffraction analysis of melt-spun $\text{Cu}_{30}\text{Mn}_{70}$ ribbons revealed
disproportionation of Mn content across two distinct phases (Figure 36b). Magnetic
measurements showed a significant hysteresis loop shift $\sim 10$ kOe along the field ($H$)
axis. In Kouvel’s seminal reports on the magnetic character of water-quenched CuMn
and related Mn-based alloys, he also observed shifted magnetization loops but only found
a single randomly atomically-disordered phase (Sections 3.2.1.1) [9, 110, 114]. These
results suggest that the significant shift of $\sim 10$ kOe at 10 K, attributed to the exchange
bias ($H_{\text{ex}}$) effect, in rapidly-solidified $\text{Cu}_{30}\text{Mn}_{70}$ ribbons is due to nanoscopic fluctuations
in local Mn content which causes a structural and magnetic phase separation into nano-sized regions of a Mn-rich cubic $\gamma$-CuMn phase and a Mn-poor $\gamma$-CuMn phase.

Areas with higher Mn content are more statistically likely to contain a greater number of Mn-Mn nearest-neighbor atomic pairs where antiferromagnetic (AF) exchange-coupling correlations force neighboring spins into an antiparallel alignment, whereas regions depleted in Mn are more statistically likely to consist of a greater number of Mn-Mn next-nearest-neighbor pairs where ferromagnetic (FM) interatomic exchange coupling is more prevalent [14, 51, 82, 110, 111]. Exchange interactions between the primarily-AF Mn-rich regions and the FM Mn-poor regions are thought to result in the large $H_{ex}$ shift – the ultrahard magnetic phase-2 is ascribed to the AF Mn-rich regions while the softer magnetic phase-1 is believed to be the magnetic signature of the effectively-FM Mn-poor regions. Figure 59 illustrates schematically this phenomenological model proposed to explain the observation of the large exchange bias at low temperatures; Mn-rich regions are shown in darker shades of grey and increasingly Mn-poor regions shown in lighter shades of grey. Exchange coupling at the interface between the two regions is thought to cause the observed unidirectional exchange anisotropy.

It is important to note that the shift of ~10 kOe is not the actual $H_{ex}$ field – $H_{ex}$ is defined as the shift of the major magnetization loop along the H axis (Section 3.1.2.3) [5, 6]. Since complete reversal is never obtained in the magnetization loops collected from melt-spun Cu$_{30}$Mn$_{70}$ ribbons in this study, the shift is likely not equal to the true exchange bias $H_{ex}$. As such, the unidirectional magnetic anisotropy energy and the magnetic anisotropy field cannot be determined.
Figure 59: Schematic illustration of the hypothesized microstructure and magnetic order of the fcc $\gamma$-CuMn phase at $T < T_B$ in Cu$_{30}$Mn$_{70}$ as-quenched ribbons (top) and annealed ribbons (bottom). Exchange interactions between the predominantly-AF Mn-rich regions and the effectively-FM Mn-deficient regions are thought to cause the large $H_{ex}$ [51].

Heat treatment at $T \sim 450$ °C for 30 minutes caused the lattice parameters of the two $\gamma$-CuMn phases to grow closer together, suggesting a diffusional homogenization of Mn content throughout the matrix. This hypothesis is corroborated by the decrease in the $\gamma$-phase unit cell dimensions, simultaneous with the formation of the $\alpha$-Mn phase; the solubility of Cu in the $\alpha$-Mn phase is reportedly negligible (Section 3.2.1.1) [128]. These data point to growth of the Mn-poor regions at the expense of the Mn-rich regions and a decline of the Mn content across the $\gamma$-CuMn phase, leading to a decrease in the number of Mn-Mn nearest-neighbor AF exchange correlations and the resultant decreased $H_{ex}$ and $H_{ci}$ values, and to the increased magnetization ($M$) values observed (Figure 43).
7.2 **Al\textsubscript{45}Mn\textsubscript{55}: Discussion of the magnetic, structural, and thermal character of rapidly-solidified ribbons**

*Overview:* This thesis work is centered around the synthesis and magnetic and structural characterization and analysis of nanostructured MnX (X = Cu, Al, etc.) binary alloys and the design and control of their nanoscopic and microscopic structure, as discussed in Section 5.2. Comprehension of relationships between these alloys’ magnetic and structural behavior is expected to enable regulation of their functional magnetic properties. To this end, nanostructured specimens of Al\textsubscript{45}Mn\textsubscript{55} have been fabricated by rapid solidification via melt spinning then subjected to post-synthesis thermal annealing treatment in the approximate temperature range \(100 \degree C \leq T_{\text{anneal}} \leq 350 \degree C\) to induce progressive structural changes on the microscopic and nanoscopic scales. The alloys’ compositional, structural, magnetic, and thermal properties have been characterized in the as-solidified state and as a function of annealing using the techniques described in Sections 4.3.1, 4.3.2, 4.4.1, and 4.5, respectively.

X-ray diffraction (XRD) analysis revealed the as-spun Al\textsubscript{45}Mn\textsubscript{55} ribbons consisted of two hexagonal (hcp) \(\varepsilon\)-AlMn phases (Figure 47), denoted as \(hcp-1\) and \(hcp-2\), that contributed a prominent exchange bias \(H_{\text{ex}} \sim 13\) kOe at 10 K (Figure 50c and d, and Figure 51c). Analysis of the field-cooled (FC) demagnetization curves obtained from the as-solidified and annealed ribbons with Eq. (34) indicated that the antiferromagnetic (AF) character of the \(\varepsilon\)-AlMn phases decreased upon annealing at \(T > 150 \degree C\). Treatment at \(T_{\text{anneal}} \geq 275 \degree C\) caused the nucleation of the ferromagnetic (FM) tetragonal \(L1_0\)-type \(\tau\)-AlMn phase at the expense of the parent \(\varepsilon\)-phases. Upon heat treatment at \(T \sim 345 \degree C\),
the τ-phase comprised approximately 18 wt. % of the ribbons, based on a reported saturation magnetization ($M_s$) value of $M_s \sim 98$ emu/g [10, 11].

7.2.1 Al$_{45}$Mn$_{55}$: Structural properties of melt-spun as-quenched and annealed ribbons

The crystal structure of the rapidly-solidified Al$_{45}$Mn$_{55}$ ribbons has been analyzed by x-ray diffraction (XRD). Diffraction data were analyzed using the fitting method described in Eq. (30) to determine the Bragg angles of each constituent crystallographic phase and its respective contribution to the diffraction pattern. The unit cell dimensions of each phase were calculated using the least-squares cell parameter program described in Section 4.3.2 [171]. It was found that as-solidified Al$_{45}$Mn$_{55}$ ribbons contained two majority nanostructured hexagonal phases (hcp-1 and hcp-2) (Figure 47a and b), identified as the metastable ε-AlMn phase in the Al-Mn binary equilibrium phase diagram (Figure 19a), which possessed slightly different unit cell dimensions ($a$ and $c$) and unit cell volumes ($V$) as a result of variations in local Mn content. The unit cell volume calculated for the larger hcp-1 ε-AlMn phase, $V \sim 82.91 \pm 0.32$ Å$^3$ (Table 13), is approximately 0.7 % above the literature value $V \sim 82.32$ Å$^3$ [15, 21], pointing to a small amount of excess Mn incorporation in the hcp-1 unit cell (i.e. $x_{Mn} > 55$ at. %). In contrast, the unit cell volume calculated for the hcp-2 phase is ∼0.2 % below the literature value, suggesting that the Mn content of this phase is slightly lower than the 55 at. % Mn commonly reported for ε-AlMn alloys.

As annealing proceeded in the temperature range $100 \text{ °C} \leq T_{\text{anneal}} \leq 350 \text{ °C}$ the unit cell dimensions of hcp-1 and hcp-2 became slightly closer to one another (Table 14).
Upon heat treatment at \( T \approx 345 \, ^\circ C \), the relative intensities of Bragg reflections associated with the \( \varepsilon \)-phase decreased significantly and Bragg peaks grew that were associated with a phase with tetragonal structure. The (001) Bragg reflection at \( \sim 24.36 \, ^\circ 2\theta \), the (100) Bragg peak at \( \sim 32.33 \, ^\circ 2\theta \), and the (110) reflection at \( \sim 46.36 \, ^\circ 2\theta \) are each superlattice peaks, pointing to a degree of chemical ordering. This chemically-ordered face-centered-tetragonal (\( fct \)) phase is identified as the \( L1_0 \)-structured \( \tau \)-AlMn phase (shown in Figure 20). Indeed, the unit cell dimensions calculated for this \( fct \) phase (bottom of Table 14) are in good agreement with literature values for the \( L1_0 \)-type \( \tau \)-phase (Section 3.2.1.2) \([12, 15]\). These results signify growth of the \( L1_0 \)-type \( \tau \)-phase at the expense of the \( hcp \) \( \varepsilon \)-phases.

### 7.2.2 \( \text{Al}_{45}\text{Mn}_{55} \): Discussion of the magnetic response of the melt-spun ribbons

The magnetic response of rapidly-solidified \( \text{Al}_{45}\text{Mn}_{55} \) ribbons has been characterized as a function of thermal annealing treatment in the temperature range \( 100 \, ^\circ C \leq T_{\text{anneal}} \leq 350 \, ^\circ C \) using superconducting quantum interference device (SQUID) magnetometry (Section 4.4.1). The zero-field-cooled (ZFC) and field-cooled (FC) magnetization \( M \) vs. \( T \) curves were found to superimpose above a peak temperature \( T_{\text{peak}} = 95 \, K \) in the as-solidified state (Figure 50a). Such behavior is typical of systems that display some type of magnetic blocking interaction at low temperature (Section 3.1.2.1) \([39, 82]\). Major FC magnetization loops collected from the as-spun ribbons at 10 K displayed a prominent shift of \( \sim 12-13 \, kOe \) along the field \( (H) \) axis (Figure 50b), consistent with manifestation of the exchange bias \( (H_{\text{ex}}) \) phenomenon (Section 3.1.2.3), which conveys a unidirectional anisotropy as a result of quantum mechanical exchange...
interactions between adjacent nano-sized ferromagnetic (FM) and antiferromagnetic (AF) phases [5, 39, 42].

Decomposition of the demagnetization curves collected from melt-spun Al_{45}Mn_{55} ribbons at 10 K, in accordance with the method of Eq. (34), revealed two contributions to the magnetization (Figure 50d), as noted in Section 6.2.2.2. Magnetic properties of magnetic phase-1 and magnetic phase-2 calculated in this manner are shown in Table 15 (values at 10 K) and Table 16 (values at 300 K). The coercivity and magnetization values calculated for phase-2 change minimally between 10 K and 300 K, suggesting that phase-2 is a ferromagnetic (FM) phase with a Curie temperature (T_c) of at least 300 K; the steady concave-down shape of the M vs. T plot from 10 K < T < 400 K raises this estimate to T_c > 400 K. The plot of the relative contribution of each phase to the total magnetization vs. annealing temperature in Figure 54 shows that the FM phase-2 began to grow at the expense of the high-H_{ci} magnetic phase-1 when the rapidly-solidified Al_{45}Mn_{55} ribbons were annealed at T_{anneal} ≥ 275 °C, and that the transformation proceeded much more rapidly for T_{anneal} ≥ 345 °C.

### 7.2.3 Al_{48}Mn_{55}: Discussion of the thermal character of the phase transformation in rapidly-solidified ribbons

An irreversible exothermic phase transformation was observed in the temperature range 300-500 °C in differential scanning calorimetry (DSC) measurements carried out on melt-spun Al_{48}Mn_{55} ribbons (Figure 55a) (Section 6.2.3). The multiphase DSC exotherms collected at heating rates of 5-20 K/min were analyzed by fitting each peak as the sum of multiple Gaussian distributions (Section 4.5) to determine the number of
phase transformations contributing to the peak and the temperature of each transformation. It was determined that the DSC peaks were best fit as the sum of two Gaussian distributions with maxima in the range ~340-370 °C and ~400-425 °C (shown in the inset of Figure 55a), pointing to either the presence of two concurrent, separate phase transitions in this temperature range or to the incidence of a single two-stage transformation.

Kissinger analysis, shown in Eq. (35), has been used to determine the activation energy ($E_a$) of the phase transformation responsible for each portion of the DSC exotherm (Figure 55b). The activation energy was of the low temperature ($T$) portion of the transformation was calculated as $E_a \sim 128 \pm 11$ kJ/mol, while the activation energy calculated for the higher $T$ transformation was calculated as $E_a \sim 155 \pm 10$ kJ/mol (Figure 55b). The peak at lower $T$ was observed to be much smaller in magnitude and area than the higher-$T$ peak. It is hypothesized that the biphasic DSC exotherms are due to two separate occurrences of the same transformation; the low-$T$ peak is from some small degree of nucleation of a new structural phase, while the high-$T$ peak is from the majority of the irreversible transformation from the parent phase to the new phase.

7.2.4 Al$_{45}$Mn$_{55}$: Correlations between structure, thermal character, and magnetic response

Interpretations of data collected to date suggest that the magnetic behavior of the hexagonal ($hcp$) $\varepsilon$-AlMn phases in rapidly-solidified Al$_{45}$Mn$_{55}$ closely mimics that of the face-centered-cubic $\gamma$-CuMn Cu$_{30}$Mn$_{70}$ alloy discussed in Section 7.1.3 (Figure 59). The large exchange bias ($H_{ex}$) shift $~13$ kOe observed at 10 K in as-spun Al$_{45}$Mn$_{55}$ ribbons is
attributed to nanoscopic fluctuations in local Mn content which cause a structural and corresponding magnetic phase separation into nano-sized regions of an antiferromagnetic (AF) Mn-rich hcp \( \varepsilon \)-AlMn phase and a ferromagnetic (FM) Mn-poor \( \varepsilon \)-AlMn phase. The so-called magnetic phase-1 discussed in Section 7.2.2 is ascribed to the magnetic response of these exchange-coupled FM/AF \( \varepsilon \)-AlMn regions. As noted in Section 7.1.3, similar behavior has also been reported for water-quenched CuMn and AgMn alloys which contain random distributions of Mn atoms, rather than nano-sized regions with distinctly different Mn content as observed in this work [9, 110, 114]. A phenomenological model is proposed to account for the observation of exchange anisotropy at low temperatures in the AlMn system similar to that proposed for rapidly-solidified Cu\(_{30}\)Mn\(_{70}\) alloys (Figure 59), whereby the AF Mn-rich \( \varepsilon \)-AlMn regions are intimately mated with and exchange-coupled to the FM Mn-deficient \( \varepsilon \)-AlMn regions. Exchange coupling at the interface between the two regions is thought to cause the observed unidirectional exchange anisotropy (Figure 60).

In the as-solidified ribbons the so-called phase-1 was found to account for approximately 92 % of the total magnetization at 10 K. The simultaneous decay of the \( H_{\text{ex}} \) shift at 10 K and increase in the magnetization of phase-1 after annealing the ribbons at \( T_{\text{anneal}} \geq 150 \) °C suggests a deterioration of the AF character of the \( \varepsilon \)-AlMn phases. The decline of AF character is likely a result of homogenization of Mn content across the two hcp phases via diffusion of Mn atoms throughout the material – reduced Mn concentration conveys a lower number of antiferromagnetically-coupled Mn-Mn nearest-neighbor atomic pairs [14, 51].
Figure 60: Schematic illustration of the hypothesized microstructure and magnetic order of the hcp ε-AlMn phases at \( T < T_B \) in Al\(_{45}\)Mn\(_{55}\) as-quenched ribbons (top) and ribbons annealed at \( T_{\text{anneal}} \geq 275 \, ^\circ\text{C} \) (bottom). Exchange interactions between the predominantly-AF Mn-rich regions and the effectively-FM Mn-deficient regions are thought to cause the large \( H_{\text{ex}} \) [51], and as annealing proceeds, Mn homogenizes throughout the ε-AlMn phase. The strongly ferromagnetic \( L_1\text{ }_0\)-type τ-phase is believed to nucleate at the grain boundaries of the parent ε-phases.

As annealing proceeded to \( T_{\text{anneal}} \geq 275 \, ^\circ\text{C} \), the saturation magnetization \( (M_s) \) and the relative fraction of the total magnetization contributed by phase-1 \( (x_1) \) at 10 K began to decrease from \( x_1 \sim 94 \% \) and that of phase-2 \( (x_2) \) began to increase from \( x_2 \sim 6 \% \) to \( x_2 \sim 14 \% \) (Figure 53c and Figure 54). The relative fraction of the total magnetization...
contributed by phase-2 then rose precipitously to $x_2 \sim 91\%$ of the total magnetization upon further heat treatment at $T_{\text{anneal}} \sim 345 \, ^\circ C$ (Table 15). Here, magnetic measurements also revealed a sharp order-of-magnitude increase in $M_s$ (Figure 51c) and diffraction measurements showed the growth of the tetragonal $L1_0$-ordered $\tau$-AlMn phase at the expense of the hexagonal $\varepsilon$-AlMn phases. Indeed, the coercivity ($H_c$) values calculated for the FM phase-2 ($\sim 1.2 \pm 1.7 \, kOe$ to $2.2 \pm 0.7 \, kOe$, as shown in Table 15 and Table 16) are in line with literature values reported for the FM tetragonal $L1_0$-type $\tau$-AlMn phase ($H_c \sim 1.5$-3.0 $kOe$) [10, 12]. These results suggest the formation of small nuclei of the FM $\tau$-AlMn phase (phase-2) at the expense of the hexagonal $\varepsilon$-AlMn phases (phase-1), and thus the onset of the $\varepsilon \rightarrow \tau$ transformation at $T_{\text{anneal}} \sim 275 \, ^\circ C$. Nucleation of the $\tau$-phase occurs to a much greater extent after annealing at $T_{\text{anneal}} \sim 345 \, ^\circ C$. Based on a reported saturation magnetization $M_s \sim 98 \, \text{emu/g}$ in the $L1_0$-type $\tau$-phase [10] and the $M_s$ values calculated for magnetic phase-2 at 300 K a function of annealing temperature (Table 16), the FM $\tau$-AlMn phase comprises about $\sim 0.1 \, \%$ in the as-quenched state, $\sim 0.3 \, \%$ after the ribbons were annealed at $T_{\text{anneal}} \sim 275 \, ^\circ C$, and approximately 18 $\%$ of the ribbons after heat treatment at $T_{\text{anneal}} \sim 345 \, ^\circ C$ (Figure 61). The bottom portion of Figure 60 illustrates graphically the hypothesized nucleation of the FM $\tau$-phase upon 30 minutes of heat treatment at $T_{\text{anneal}} \sim 275 \, ^\circ C$. 
Calorimetric measurements confirmed the presence of a multi-stage irreversible exothermic transformation in this temperature range (Figure 55), signifying the onset of the $\varepsilon \rightarrow \tau$ transformation at a temperature approximately 100 °C lower than in previous works [15, 17, 19, 29]. Furthermore, Kissinger analysis revealed that the activation energy ($E_a$) of the majority high-temperature portion of the $\varepsilon \rightarrow \tau$ transformation was $E_a \sim 155 \pm 10$ kJ/mol, identical within error to the previous value of 154.4 kJ/mol reported by Yanar et al. for the activation energy of the transformation in oil-quenched Al$_{45}$Mn$_{55}$ ingots (Section 3.2.1.2) [29]. However, the additional low-temperature transformation observed in the calorimetric measurements possessed a calculated activation energy of $E_a \sim 128 \pm 11$ kJ/mol, approximately 20% lower than the value calculated by Yanar et al. These results suggest that rapid solidification imparted more defect centers and thereby an increased number of low-energy heterogeneous nucleation sites that promoted
nucleation of the τ-phase at a much lower temperature; the appearance of a DSC
exotherm at lower temperatures is likely due to nucleation of the FM $L1_0$-type τ-AlMn
phase at these lower-energy nucleation centers.

7.3 $\text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10}$ and $\text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10}$: Discussion of magnetic and
structural character data obtained from rapidly-solidified ribbons

Fe(CuMn) alloy specimens of nominal compositions $\text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10}$ and
$\text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10}$ were fabricated by rapid solidification via melt-spinning (Section 4.1.2)
to attempt to realize exchange bias in bulk ferromagnetic/antiferromagnetic (FM/AF)
magnetic nanocomposite systems. Preliminary magnetic and structural characterization
data were reported in Section 6.3. X-ray diffraction (XRD) patterns revealed the as-
quenched ribbons contained several prominent and as-yet unidentified Bragg peaks
(Figure 56), likely due to some Fe-oxide phase, and a majority body-centered-cubic ($bcc$)
phase, identified as $\alpha$-Fe. The calculated unit cell lattice parameter ($a$) $\sim 2.860 \pm 0.006$ Å
and unit cell volume ($V$) $\sim 23.39 \pm 0.15$ Å$^3$ are in good agreement with literature values
for pure $\alpha$-Fe ($a \sim 2.8606$ Å, $V \sim 23.41$ Å$^3$) [122].

Magnetic measurements (Figure 57) showed the magnetic response was
dominated by a strongly ferromagnetic phase with Curie temperature ($T_c$) above 350 K.
Magnetization loops were symmetric about the origin and showed no exchange bias ($H_{ex}$)
shift in either alloy. Hysteresis measurements revealed a saturation magnetization ($M_s$)
value of $\sim 185$ emu/g in both $\text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10}$ and $\text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10}$ as-quenched
ribbons at 10 K; the magnetic saturating field of $\sim 30$ kOe was larger in rapidly-solidified
$\text{Fe}_{90}(\text{Cu}_{30}\text{Mn}_{70})_{10}$ than the $\sim 2$ kOe saturating field in $\text{Fe}_{90}(\text{Cu}_{10}\text{Mn}_{90})_{10}$, reflecting a
greater magnetic anisotropy field in the ribbons with lower Mn content. If it is assumed that the \(\alpha\)-Fe phase observed in the XRD pattern is the only phase that contributes to the magnetization, then based on the \(M_s\) value of \(\sim 221.9\) emu/g reported for \(\alpha\)-Fe at 0 K \cite{102} the alloys contain about 85 wt. % pure \(\alpha\)-Fe. These results suggest that attainment of exchange bias in melt-spun Fe/CuMn ribbons has been unsuccessful to date. In future work, rigorous investigations of the magnetic and structural properties of these ternary alloys should be carried out to ascertain how to better promote formation of and exchange-coupling across FM/AF interfaces. These experiments will be further detailed in Section 8.0.

7.4 **Summary of relationships between the magnetic and structural characteristics of exchange-biased MnX (X = Cu, Al, etc.) alloys**

In the course of this thesis work, two nanostructured MnX (X = Cu, Al ,etc.) alloys of composition Cu\(_{30}\)Mn\(_{70}\) and Al\(_{45}\)Mn\(_{55}\) were synthesized by rapid solidification via melt-spinning for use as model antiferromagnetic components in exchange-biased ferromagnetic/antiferromagnetic (FM/AF) permanent magnetic nanocomposites of the form Fe/MnX. Both as-solidified MnX alloys contained two distinct majority chemically-disordered structural phases that possessed identical crystallographic structures but slightly different unit cell dimensions – in the case of Cu\(_{30}\)Mn\(_{70}\), the as-spun ribbons contained two face-centered-cubic (fcc) \(\gamma\)-CuMn phases with unit cell lattice parameter \(a \sim 3.74-3.75\) Å, whereas as-spun Al\(_{45}\)Mn\(_{55}\) consisted of two hexagonal (hcp) \(\varepsilon\)-AlMn phases with unit cell dimensions \(a \sim 2.37\) Å and \(c \sim 4.34-4.37\) Å. The variations in unit cell dimensions were ascribed to rapid-solidification-induced “solute trapping” \cite{186} which caused nanoscopic modulations in local Mn content; the two fcc phases
present in as-quenched Cu$_{30}$Mn$_{70}$ were thought to consist of ~80-90 at. % Mn and ~35-50 at. % Mn, respectively, while melt-spun Al$_{45}$Mn$_{55}$ retained hcp phases with Mn content slightly above and below 55 at. % Mn.

Below their respective magnetic blocking temperatures ($T_B$) – $T_B$ ~ 125 K in as-spun Cu$_{30}$Mn$_{70}$, $T_B$ ~ 95 K in as-spun Al$_{45}$Mn$_{55}$ – the as-quenched MnX alloys possessed low magnetization $M \sim 10^{-1}$-$10^0$ emu/g and their respective field-cooled (FC) magnetization loops collected at 10 K displayed prominent shifts of ~10-13 kOe along the field axis. The shifts were diagnostic of the exchange bias ($H_{ex}$) phenomenon, whereby quantum mechanical exchange interactions across intimate FM/AF interfaces confer a unidirectional anisotropy that results in a displacement of the major FC hysteresis loop along the $H$ axis. The effective magnetic anisotropy energy in rapidly-solidified Cu$_{30}$Mn$_{70}$, in fact, was sufficiently high that very little magnetization reversal occurred in a reverse field of -50 kOe.

The as-solidified MnX alloys were subsequently heat treated for 30 minutes at low-to-moderate temperatures up to $T_{anneal}$ ~ 450 °C to induce progressive structural changes and their magnetic and structural properties were measured in each interval. It was found that the lattice parameters of both phases homogenized and decreased and a secondary phase appeared upon annealing; in the case of Cu$_{30}$Mn$_{70}$ the complex cubic $\alpha$-Mn phase appeared after annealing at $T_{anneal}$ ~ 450 °C, while in the case of Al$_{45}$Mn$_{55}$ melt-spun ribbons, the ferromagnetic (FM) tetragonal $L1_0$-type $\tau$-AlMn phase nucleated from the parent hcp $\epsilon$-AlMn phases upon heat treatment at $T_{anneal}$ ≥ 275 °C. The $L1_0$-ordered $\tau$-AlMn phase has been reported to exhibit attractive permanent magnetic character due to a high magnetocrystalline anisotropy energy $K_1 \sim 10^7$-$10^8$
erg/cm\(^3\) and moderate maximum energy product values \((BH)_{\text{max}} \sim 2-7\) MGOe [2, 3, 10-12, 15-27]. Previous researchers have postulated a compositionally-invariant nucleation and growth mechanism \((i.e.\) a massive transformation) for the \(\varepsilon \rightarrow \tau\) transformation, wherein the \(\tau\)-phase nucleates almost exclusively at the \(\varepsilon\)-phase grain boundaries due to the high interfacial energy at these sites [29, 30]. The onset of the \(\varepsilon \rightarrow \tau\) transformation at 275 °C in this thesis work, which represents a nearly 100 °C reduction over previously-reported values for the transition temperature [12, 17, 19, 20, 29], is therefore thought to be a result of an enhanced density of high-energy defects and grain boundary interfaces that act as heterogeneous nucleation centers for \(L_{10}\)-type \(\tau\)-AlMn in rapidly-solidified \(\text{Al}_{45}\text{Mn}_{55}\) ribbons. Based on a saturation magnetization \(M_s \sim 98\) emu/g reported for the pure \(\tau\)-phase [11] and analyses of the magnetic measurements, it was found that the FM \(\tau\)-phase comprised about \(\sim 0.1\) wt. % of the as-solidified \(\text{Al}_{45}\text{Mn}_{55}\) ribbons, \(\sim 0.3\) wt. % after the ribbons were annealed at \(T_{\text{anneal}} \sim 275\) °C, and \(\sim 18\) wt. % of the ribbons after heat treatment at \(T_{\text{anneal}} \sim 345\) °C (Figure 61).

A phenomenological model was proposed to account for the observation of the prominent \(H_{ex} \sim 10-13\) kOe in the \(\text{Cu}_{30}\text{Mn}_{70}\) and \(\text{Al}_{45}\text{Mn}_{55}\) specimens at 10 K; Mn-Mn nearest-neighbor atomic pairs were hypothesized to be antiferromagnetically-coupled to one another, while Mn-Mn next-nearest-neighbor pairs were postulated to be ferromagnetically exchange-coupled to one another, in order to minimize the interatomic exchange interaction energy in the material. Areas of the \(\gamma\)-CuMn and \(\varepsilon\)-AlMn phases containing high concentrations of Mn atoms are therefore statistically-likely to contain a preponderance of AF coupling between nearest-neighbor pairs. As the Mn content in majority phases decreases with heat treatment, the average distance between Mn atoms
also decreases, and consequently the extent of AF coupling decreases and the number of FM correlations increases. Since structural probes revealed distinct segregation into two compositionally-variant regions, it is suggested that the Mn-rich regions were predominantly-AF and the Mn-poor regions were effectively AF. Quantum mechanical exchange interactions between these regions are believed to contribute significantly to the observed exchange anisotropy in Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$, as shown in Figure 59 and Figure 60, respectively. The crystallographic coherency between the constituent FM and AF regions is thought to play a significant role in this regard [1, 7]; the respective lattice parameters of the two fcc and hcp phases in the Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$ ribbons were within approximately 0.5% of one another, rendering an enhanced propensity for ideal or nearly-ideal FM/AF interfacial contact. It is suggested that interatomic exchange coupling between Mn-enriched clusters and Mn-deficient clusters within each region also contributed to the large exchange bias, a la Kouvel’s model for randomly-disordered Cu-Mn and Ag-Mn alloys [9, 110, 114]. As annealing proceeded, data collected from magnetic and structural probes reflected the growth of the Mn-poor regions at the expense of the Mn-rich regions, as Mn content was homogenized via diffusion throughout the matrix, resulting in a reduction AF character and the observed increase in the magnetization and reduction in exchange bias.
8.0 CONCLUSIONS AND RECOMMENDATIONS

First observed by Meiklejohn and Bean in Co/CoO core/shell nanoparticles [42], the exchange bias ($H_{ex}$) phenomenon is the uniaxial shift of the major magnetic hysteresis loop along the applied field ($H$) axis as a result of a unidirectional anisotropy conveyed by quantum-mechanical exchange interactions between nanostructured ferromagnetic (FM) and antiferromagnetic (AF) phases. The $H_{ex}$ shift effectively augments the intrinsic coercivity ($H_c$), magnetic remanence ($M_r$), and maximum energy product ($BH_{max}$) of a material and renders improved permanent magnetic character. Exchange anisotropy has been studied extensively in thin film systems, as can be seen in the review articles by Berkowitz and Nogués [5, 6], due to the relative ease of controlling the FM/AF interface and the fact that modern devices like spin-valves [100] generally employ exchange-biased magnetic thin films. Investigations of the $H_{ex}$ effect in bulk nanocomposite systems for use in rare-earth-free permanent magnet applications, however, are exceedingly scarce [1, 7].

This thesis work attempts to address such deficiencies in the literature by taking initial steps towards clarification of the underpinnings of the $H_{ex}$ and $M_r$ enhancement phenomenon in bulk FM/AF magnetic nanocomposite systems. Fe/MnX ($X = \text{Cu, Al, etc.}$) alloys have been selected as model nanostructured FM/AF composite systems for study, using an Fe-rich matrix as the model FM component and MnX alloys as the model AF component. Nanostructured specimens of Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$ have been synthesized by rapid solidification via melt-spinning and subsequently subjected to post-synthesis processing techniques – thermal annealing and cryogenic milling – to evaluate the effect of micro- and nanostructural manipulation on the magnetic response.
Elucidation of these relationships is anticipated to enable tailoring of the functional magnetic properties.

Two major conclusions may be drawn from this thesis work. Firstly, the prominent shifts along the field axis of ~10-13 kOe exhibited by field-cooled (FC, 50 kOe) magnetization loops at 10 K in melt-spun specimens of Cu$_{30}$Mn$_{70}$ and Al$_{45}$Mn$_{55}$ are attributed to the exchange bias ($H_{ex}$) effect, signaling the presence of exchange-coupled ferromagnetic (FM) and antiferromagnetic (AF) phases. A phenomenological model has been proposed that accounts for the observation of significant unidirectional exchange anisotropy in both MnX ($X = \text{Cu, Al, etc.}$) alloys studied. As-quenched MnX ribbons were each found to consist of two majority nanostructured phases – face-centered-cubic (fcc) $\gamma$-CuMn phases and hexagonal (hcp) $\varepsilon$-AlMn phases, respectively – with slightly different unit cell dimensions. The majority phases with larger unit cell dimensions are thought to possess enriched Mn content, whereas the majority phases with smaller unit cell dimensions are thought to be deficient in Mn; similar disproportionation of Mn content between two structurally-similar phases was reported by Turchanin et al. in tempered $\gamma$-CuMn alloys [128]. The Mn-Mn interatomic exchange interaction is believed to exhibit a competitive nature, whereby Mn-Mn nearest-neighbor pairs and Mn-Mn next-nearest-neighbor pairs interact by AF and FM interatomic exchange, respectively. The large $H_{ex}$ shifts ~ 10-13 kOe observed in both MnX alloys in this work at 10 K are thus ascribed to quantum mechanical exchange interactions across intimate interfaces between nanoscopic AF Mn-rich regions and effectively-FM Mn-deficient regions, conferred by nanometric modulations in Mn content as a result of rapid solidification.
Analyses of demagnetization curves collected from rapidly-solidified Al$_{45}$Mn$_{55}$ at 10 K and 300 K, done in accordance with Eq. (34), led to the second conclusion that may be drawn from this work: rapid solidification of the Al$_{45}$Mn$_{55}$ alloy via melt-spinning enabled the nucleation of the ferromagnetic (FM) tetragonal $L1_0$-type $\tau$-AlMn phase after heat treatment at approximately 275 °C, nearly 100 °C lower than previously reported nucleation temperatures for the $\tau$-phase [12, 17, 19, 20, 29]. Based on the saturation magnetization $M_s \sim 98$ emu/g reported for the $L1_0$-type $\tau$-phase [10, 11], it was found that the FM $\tau$-AlMn phase composed approximately $\sim 0.1$ wt. % of the as-spun Al$_{45}$Mn$_{55}$ ribbons. The amount of $L1_0$-ordered $\tau$-phase grew to $\sim 0.3$ wt. % after the ribbons were annealed at $T_{\text{anneal}} \sim 275$ °C, and $\sim 18$ wt. % after heat treatment at $T_{\text{anneal}} \sim 345$ °C.

The reduction of the $\varepsilon \rightarrow \tau$ transformation temperature observed in this thesis work suggests that melt-spinning may have increased the number of heterogeneous nucleation sites in the parent $\text{A}_3$-type $hcp$ $\varepsilon$-phase. The enhanced number of high-energy nucleation sites and defect centers likely increased the driving force for $\tau$-AlMn nucleation and growth, conveying a reduced activation energy for the $\varepsilon \rightarrow \tau$ transition. Indeed, the activation energy at the initial stages of the massive transformation of the $hcp$ $\varepsilon$-AlMn phase to the $L1_0$-ordered $\tau$-phase was calculated as $128 \pm 11$ kJ/mol from calorimetric data, constituting an $\sim 18\%$ reduction over the value of 154.4 kJ/mol determined by Yanar et al. [29]. Continued clarification of these results may enable further reduction of the $\varepsilon \rightarrow \tau$ transformation temperature, which could have profound implications on the development of fabrication, processing techniques and strategies, and engineering of rare-earth-free alternative permanent magnetic materials.
The following sections recommend future work to build on these conclusions and further elucidate the mechanisms of exchange bias and remanence enhancement in bulk three-dimensional nanocomposite systems for alternative permanent magnet applications. Section 8.1 suggests experiments that may be useful for development of correlations between the magnetic and structural character of the binary MnX (X = Cu, Al, etc.) alloys studied in this thesis work. Section 8.2 sets forth recommendations for investigations of the magnetic and structural behaviors of Fe/MnX nanocomposites.

8.1 **Recommended future investigations of the magnetic, structural, and thermal character of MnX (X = Cu, Al, etc.) binary alloys**

The exchange bias ($H_{ex}$) field is defined as the uniaxial shift of the major field-cooled (FC) magnetization loop along the field ($H$) axis, wherein the hysteresis loop is asymmetric about the origin but symmetric about the field axis (Section 3.1.2.2). Field-cooled (50 kOe) magnetization loops obtained from rapidly-solidified Cu$_{30}$Mn$_{70}$ ribbons in the as-quenched state and after 30-minute annealing treatments in the temperature range $200 \, ^\circ C < T_{\text{anneal}} < 450 \, ^\circ C$ were observed to be strongly asymmetric about the field ($H$) axis at $T = 10 \, K$ (Figure 43c, Sections 6.1.2.1 and 6.1.2.2), signifying an inability to obtain magnetic saturation (and complete magnetization reversal) in the positive and negative directions. The observed loop shift thus is likely not equivalent to the true value of the $H_{ex}$ shift. Further heat treatment of the Cu$_{30}$Mn$_{70}$ ribbons (using the annealing conditions given in Table 6, Section 0) may sufficiently lower the magnetic reversal fields to permit determination of the true $H_{ex}$ field, true intrinsic coercivity ($H_{ci}$), and the magnetic anisotropy energy barrier of each constituent magnetic phase (Table 12). The magnetic anisotropy energy barrier is of particular interest for the evaluation of the
average magnetically-blocked particle size (Eq. (21), Section 3.1.2.1) [81, 191], and for determination of the optimal AF size and geometry, per Kneller [8].

Preliminary Curie-Weiss analysis (Eq. (27), Section 3.2.1.1) of the magnetic susceptibility (χ) vs. T curves obtained from melt-spun Cu₃₀Mn₇₀ ribbons has been carried out; some future work should be dedicated to discussion and interpretation of these data. While the observed morphologies of the free- and wheel-side surfaces of the as-solidified Cu₃₀Mn₇₀ ribbons were unremarkable (Figure 35a and b), electron microscopy examination of the cross-section of the ribbons should be carried out to gain deeper insight into the rapid solidification dynamics and kinetics, and to shed light on the concentration distribution of magnetic manganese atoms.

Cu-Mn and Al-Mn alloys of different compositions (shown in Table 5 & Section 5.3.1.1), or even other Mn-based binary alloys like IrMn or AgMn, should be synthesized to evaluate the effect of variations of Mn content on the magnetic and structural character. An additional shape anisotropy energy and improved exchange coupling between the FM Fe-rich matrix and the predominantly-AF MnX alloys may be induced by alignment of the magnetic domains via heat treatment in an applied magnetic field (Section 3.1.1.3) [192]. Augmentation of the magnetic anisotropy energy barrier is expected to improve the utility of MnX (X = Cu, Al, etc.) alloys as antiferromagnetic (AF) components in exchange-biased nanocomposites.
8.2 Recommended future investigations of the magnetic, structural, and thermal character of Fe/MnX (X = Cu, Al, etc.) nanocomposites

After gaining a deeper understanding of the magnetic and structural character of the antiferromagnetic (AF) MnX (X = Cu, Al, etc.) binary alloys, they should be carefully implanted in a ferromagnetic/antiferromagnetic (FM/AF) nanocomposite of the form Fe/MnX, and the materials should be processed to foster formation of intimate nanoscale interfaces between the two phase (see Sections 5.1.2.3, 5.2.3, and 5.3.2). Elucidation of correlations between the magnetic and structural features of these new, more complex FM/AF nanocomposites should be developed to enable engineering of the permanent magnetic character.

To date, alloys of composition Fe$_{90}$(Cu$_{30}$Mn$_{70}$)$_{10}$ and Fe$_{90}$(Cu$_{10}$Mn$_{90}$)$_{10}$ have been synthesized by rapid solidification via melt-spinning. Preliminary interpretations of the magnetic and structural attributes of these systems (Section 6.3) indicate that initial attempts to obtain FM/AF exchange coupling in a single processing step have been unsuccessful. Rapid solidification of an alloy with lower Fe content may promote more pronounced separation between the Cu-Mn and Fe phases – Table 7 in Section 5.3.2.1 gives desired compositions to investigate. Additionally, the MnX alloys should be cryomilled with Fe powder to attempt to cold-work the two components together and develop intimate interphase interfaces (Table 8, Section 5.3.2).
### 9.0 NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(BH)_{\text{max}}$</td>
<td>Maximum energy product, GOe</td>
</tr>
<tr>
<td>$a$</td>
<td>Unit cell $a$ lattice parameter, Å</td>
</tr>
<tr>
<td>$A$</td>
<td>Exchange stiffness parameter, erg/cm</td>
</tr>
<tr>
<td>AF</td>
<td>Antiferromagnetic</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>$b$</td>
<td>Unit cell $b$ lattice parameter, Å</td>
</tr>
<tr>
<td>$B$</td>
<td>Full-width at half the maximum intensity of a Bragg peak, radians $2\theta$</td>
</tr>
<tr>
<td>$B$</td>
<td>Magnetic flux, G</td>
</tr>
<tr>
<td>BN</td>
<td>Boron nitride</td>
</tr>
<tr>
<td>BPR</td>
<td>Ball-to-powder weight ratio, unitless</td>
</tr>
<tr>
<td>$c$</td>
<td>Unit cell $c$ lattice parameter, Å</td>
</tr>
<tr>
<td>$d$</td>
<td>Interplanar spacing in the unit cell, Å</td>
</tr>
<tr>
<td>$D$</td>
<td>Volume-averaged Scherrer crystallite size, nm</td>
</tr>
<tr>
<td>$D_b$</td>
<td>Critical size for observation of magnetic blocking behavior, cm</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>$D_{\text{sd}}$</td>
<td>Critical size for observation of single-domain behavior, cm</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Electron beam accelerating voltage, keV</td>
</tr>
<tr>
<td>$E_{\text{anisotropy}}$</td>
<td>Uniaxial magnetic anisotropy energy barrier per unit volume, erg/cm$^3$</td>
</tr>
<tr>
<td>$E_B$</td>
<td>Energy barrier to spontaneous magnetization reversals, erg</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Critical excitation energy, keV</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive x-ray spectroscopy</td>
</tr>
</tbody>
</table>
\( E_{\text{ex}} \)  Unidirectional exchange anisotropy energy density, erg/cm²
\( E_{\text{exchange}} \)  Interatomic exchange coupling energy, erg
\( E_{\text{me}} \)  Uniaxial magnetocrystalline anisotropy energy density, erg/cm³
\( E_{\text{me}} \)  Uniaxial magnetoelastic anisotropy energy density, erg/cm³
\( E_{\text{shape}} \)  Shape anisotropy energy density, erg/cm³
\( E_{\text{surface}} \)  Surface anisotropy energy density, erg/cm²
FC  Field-cooled
\textit{fcc}  Face-centered cubic unit cell
\textit{fct}  Face-centered tetragonal unit cell
FM  Ferromagnetic
FWHM  Full width at half the maximum intensity of a Bragg peak, radians \( 2\theta \)
\( G \)  Gibbs free energy, J
\( h \)  Planck’s constant, \( 1.626 \times 10^{-27} \) erg · sec
\( H \)  Applied external magnetic field, Oe
\( H_c \)  Magnetic coercive field, Oe
\( H_{\text{ci}} \)  Intrinsic magnetic coercive field, Oe
\( H_{\text{cool}} \)  Magnetic field applied during cooling, Oe
\( hcp \)  Hexagonal close-packed unit cell
\( H_d \)  Demagnetizing field, Oe
\( H_{\text{ex}} \)  Exchange bias field, Oe
\( H_{\text{meas}} \)  Magnetic field applied during \( M \) vs. \( T \) measurements, Oe
\( J_{\text{ex}} \)  Interatomic exchange integral, erg
\( K \)  Shape factor for Scherrer equation, unitless
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1, K_2$</td>
<td>First and second order magnetocrystalline anisotropy constants, erg/cm$^3$</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant, $1.38 \times 10^{-16}$ erg/K</td>
</tr>
<tr>
<td>$K_{\text{eff}}$</td>
<td>Effective uniaxial anisotropy constant, erg/cm$^3$</td>
</tr>
<tr>
<td>$K_{\text{ex}}$</td>
<td>Unidirectional exchange anisotropy constant, erg/cm$^2$</td>
</tr>
<tr>
<td>$l_{\text{ex}}$</td>
<td>Exchange length, nm</td>
</tr>
<tr>
<td>$M$</td>
<td>Magnetization, emu/g</td>
</tr>
<tr>
<td>MFM</td>
<td>Magnetic force microscopy</td>
</tr>
<tr>
<td>$M_r$</td>
<td>Remanent magnetization, emu/g</td>
</tr>
<tr>
<td>$M_s$</td>
<td>Saturation magnetization, emu/g</td>
</tr>
<tr>
<td>$N_d$</td>
<td>Demagnetization factor, unitless ($0 \leq N_d \leq 4\pi$)</td>
</tr>
<tr>
<td>NRL</td>
<td>Naval Research Laboratory</td>
</tr>
<tr>
<td>NSLS</td>
<td>National Synchrotron Light Source</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>$S$</td>
<td>Squareness of hysteresis loop = $M_r/M_s$, unitless</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>$S_{ij}$</td>
<td>Spin angular momentum vector of atom $i$ or atom $j$, unitless</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting quantum interference device magnetometry</td>
</tr>
<tr>
<td>$T$</td>
<td>System temperature, K</td>
</tr>
<tr>
<td>$T_{\text{anneal}}$</td>
<td>Annealing temperature, °C</td>
</tr>
<tr>
<td>$T_b$</td>
<td>Blocking temperature, K</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Curie temperature, K</td>
</tr>
<tr>
<td>$T_N$</td>
<td>Néel temperature, K</td>
</tr>
<tr>
<td>$V$</td>
<td>Crystallographic unit cell volume, Å$^3$</td>
</tr>
</tbody>
</table>
VSM  Vibrating sample magnetometry

\( x \)  Depth of electron beam penetration, \( \mu m \)

XRD  X-ray diffraction

\( y \)  Width of electron beam interaction volume, \( \mu m \)

ZFC  Zero-field-cooled

Greek characters

\( 2\theta \)  Angle of detector arm, degrees

\( \delta_w \)  Domain wall width, nm

\( \theta \)  Angle between the magnetization and the easy axis, degrees

\( \theta \)  Angle of incident radiation, degrees

\( \kappa \)  Magnetic hardness parameter, unitless

\( \lambda \)  Wavelength of x-ray radiation, nm

\( \lambda_{si} \)  Isotropic magnetostriction, unitless

\( \mu \)  Magnetic moment, emu or \( \mu_B \)

\( \mu_0 \)  Permeability of free space, 1 or \( 4\pi \times 10^{-7} \) T/(A/m)

\( \mu_B \)  Bohr magneton, \( 9.274 \times 10^{-21} \) erg/G or emu

\( \rho \)  Sample density, g/cm\(^3\)

\( \sigma \)  Applied compressive or tensile stress, dyne/cm\(^2\)

\( \tau \)  Relaxation time between magnetization flips, seconds

\( \tau_0 \)  Attempt time, \( \sim 1 \times 10^{-9} \) seconds

\( \phi \)  Angle between electron spin magnetic moments, degrees
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi$</td>
<td>Magnetic susceptibility, $M/H$, emu/g·Oe or unitless</td>
</tr>
<tr>
<td>$\chi_0$</td>
<td>Temperature-independent susceptibility, $M/H$, emu/g·Oe or unitless</td>
</tr>
</tbody>
</table>


93. OSullivan, J., X. L. Rao, J. M. D. Coey, Magnetic coupling of the composite mixtures Sm$_2$Co$_{17}$/Sm$_2$Fe$_{17}$N$_3$ and Sm$_2$Co$_{17}$/Fe, Journal of Applied Physics, 81 (8), 5124-5126, 1997.


190. Ibid., *PDF #65-3159-Mn, alpha-Mn structure*.
