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Leveraging Anisotropy to Enhance Multiferroic Transduction

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Leveraging Anisotropy to Enhance Multiferroic Transduction

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Mechanical Engineering

by

Kyle Peter Wetzlar

2015
ABSTRACT OF THE DISSERTATION

Leveraging Anisotropy to Enhance Multiferroic Transduction

by

Kyle Peter Wetzlar

Doctor of Philosophy in Mechanical Engineering

University of California, Los Angeles, 2015

Professor Gregory P. Carman, Chair

Multiferroic coupling has recently been shown to provide an effective and efficient means to transduce energy between various physical regimes and unlike the majority of transduction mechanisms actually improves at reduced length scales. The work presented herein explores the effects of anisotropic energy application to further enhance the coupled behavior of such systems and enable applications such as thermal energy harvesting, electrically small antennas, energy efficient memory, and microscale actuators. Four types of anisotropy are presented: magnetocrystalline, electroelastic, magnetoelastic and shape, which are utilized in joint and competing fashions to deterministically control magnetic and electric states at micro and nanoscales. First, a study is performed to determine the most efficient and energy dense way to transduce thermal energy into magnetic energy by leveraging single domain magnetic states and the
temperature dependence of magnetocrystalline anisotropy. A numeric case study is performed which shows that gadolinium and neodymium cobalt are capable of 30% and 22% relative efficiencies, respectively, which is a significant improvement over the state of the art thermoelectric efficiency of 15%. Second, design and testing of an electrically small multiferroic receiver antenna is performed to show the efficient transduction of EM radiation in the HF and VHF frequency spectrums to electrical power in structures which are five orders of magnitude smaller than the wavelength in free-space. A multi-step finite element framework is used to design and simulate an array of magnetostrictive resonator elements which can generate a coherent surface acoustic wave in a piezoelectric substrate. An optimization scheme is used to design systems capable of transmission coefficients on the order of -4.7 dB. Lastly, a method of directly observing the deterministic control of magnetic states as a function of electric field through the use of Lorentz transmission electron microscopy is presented. Here, magnetoelastic anisotropy is leveraged to reversibly modulate magnetic domain states in a controlled fashion. These results provides significant evidence of the viability of anisotropy enhanced multiferroic transduction to enable future works in energy harvesting, magnetoelectrics and microscale actuators.
The dissertation of Kyle Peter Wetzlar is approved.

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Ph'nglui mglw'nafh Cthulhu R'lyeh wgah'nagl fhtagn
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**Kyle P. Wetzlar**, “Leveraging Anisotropy to Enhance Multiferroic Transduction” Sandia National Lab Invited Speaker, Albuquerque, NM (Feb 2015)

**Kyle P. Wetzler**, “Leveraging Anisotropy to Enhance Multiferroic Transduction” Naval Research Lab Invited Speaker, Washington, DC (Jan 2015)


Chapter 1: INTRODUCTION

1.1 The Future of Multiferroic Devices

Multiferroic materials, especially those which can be structured at the nanoscale, have obtained significant interest due to their wide array of potential applications in electronic systems. The intrinsic coupling that characterizes this material class can permit an efficient and often power dense solution to transducing energy across the four major physical regimes: electrical, magnetic, mechanical and thermal. Of pertinent interest, and those which will be discussed in the main body of this document, are the dynamic phenomena and anisotropic effects which can be leveraged to develop multiphysical transducers such as thermal energy harvesters, electronically small antennas, electrically driven micromechanical actuators and highly efficient memory solutions. Firstly, however, a history of multiferroics and a breakdown of the requisite phenomenological formulations that describe the transduction behaviors are presented.

1.2 The Structure of this Body of Work

This work is divided into six chapters which are organized by theme. The first chapter provides descriptions of the material systems used throughout this body of work as well as a primer in the concepts that are most pertinent to the application spaces being explored. The following three chapters are delineated by the type of multiferroic coupling that governs the primary anisotropic phenomenon which enables the application space at hand. Chapter 2 examines thermomagnetic energy harvesting with two case studies that elucidate the benefits of designed nanoscale systems and of order-to-order transformations which leverage the temperature dependence of magnetocrystalline anisotropy, respectively. Chapter 3 discusses dynamic magnetoelectric
coupling and a method to design and optimize multiferroic receiving antennas utilizing anisotropic surface acoustic wave generation. Chapter 4 provides a methodology for examining the modulation of magnetic domain structures with electrically controlled anisotropic strains and illustrates a means to actualize strain mediated memory and electrically controlled micromotors. Each of these chapters contains a synopsis, a literature review corresponding to the type of coupling presented, a problem statement, my contributions to the greater body of knowledge and a conclusion which contextualizes that work. Chapter 5 summarizes the body of work in aggregate and provides a path to advance the work presented herein. Finally, the work is concluded with a list of the works referenced through this document.

1.3 Multiferroic Composites

The term “multiferroic” was originally coined by Schmid is 1994\(^1\) to establish a definition of materials which exhibited multiple ferroic orderings simultaneously. The four primary order parameters are ferroelectricity, ferromagnetism, ferroelasticity and ferrotoroidicity, however when Schmid established the multiferroic definition, only the first 3 were considered. In this work he broke down the various crystal classes, namely the boracite and perovskite families, to establish the symmetries required for materials to behave in accordance with the first 3 ferroic orders, but given the difficulty to design materials of that nature, a practical focus was given to the subclass of purely intrinsic magnetoelectric materials. An interesting observation was that while materials can intrinsically exhibit all of the ferroic orderings, for all known compounds and alloys that show this behavior, they do so at the cost of coupling efficiency with each added ordering\(^2\). Namely, that materials with fewer coupled order parameters exhibit more efficient coupling than those with more.
Materials which exhibit multiferroic coupling can be further divided into two classes: single phase and composite systems. The former saw its inception in the 1960’s with a case study on cryogenic Nickel-Iodine Boracite\(^3\) and continued to be a hot area of study throughout the 60’s and 70’s with a large focus on nonlinear magnetoelectricity\(^4\)–\(^6\). This area fell out of favor for the next two decades as the materials that were being developed provided to inefficient a coupling to be feasible in their proposed application spaces. This changed in the early 2000’s when epitaxially grown Bismuth Ferrite\(^7\) (BiFeO\(_3\)) and Terbium Manganate\(^8\) (TbMnO\(_3\)) were shown to provide large magnetoelectric polarization and magnetization changes when subject to fields of the other ferroic order. An even more effective coupling was discovered in composite multiferroics; material systems typically comprised of ferroelectric and ferromagnetic materials that are mechanically coupled to one another. Study on this type of material system began with Ryu\(^9\) on bulk composites of Lead Zirconate Titanate (PZT) and Nickel Ferrite (NiCo\(_{0.02}\)Cu\(_{0.02}\)Mn\(_{0.01}\)Fe\(_{1.8}\)O) where nearly an order of magnitude improvement was shown over single phase materials. This work has led to many advancements toward the enhancement of efficient coupling\(^10\), especially in the regime of nanostructured composites\(^11\), where much like their purely mechanical counterparts are beginning to be specifically designed to leverage anisotropic behavior. The work presented throughout this document will focus on 3 aspects of such anisotropy to refine transduction capabilities in the energy harvesting, antenna and actuator application spaces. The following sections will overview the specifics of the ferromagnetic and ferroelectric material classes to provide context for how this will be accomplished.
1.3.1 Magnetic Materials

Matter exhibits magnetic properties in one of four forms. Diamagnetism, the most common class, encompasses materials which exhibit no spontaneous magnetization and are generally considered to be non-magnetic. Materials which fall into this class have a permeability less than that of freespace and are therefore slightly repelled by magnetic fields, but typically require extremely large fields for the effect to be significant. Paramagnetism can be thought of as the polar opposite of diamagnetism, and is generalized as materials which have a slightly higher permittivity than freespace and no spontaneous magnetization. They will be attracted to either pole of a permanently magnetized media when in close proximity but will lose their magnetic moment almost immediately upon removal. Antiferromagnetic materials are those that maintain constituents which are spontaneously magnetizable, but whose magnetic moments completely cancel one another out. Under small applied fields these media will appear non-magnetic in the same sense as para or diamagnets, but as the field is increased to moderate or large levels the magnetization will appear to jump as the spins are all forced to align with the field. As the field is reduced, the moments return to an orientation in which they cancel each other out such that to external magnetic remenance remains. The final class of magnetic materials are ferromagnets. In these materials the electron’s spins act in a cooperative fashion, known as ferromagnetic exchange, such that they have a very large permeability and see a large magnetization increase in the presence of an applied magnetic field which saturates ($M_s$) once all of the spins are aligned. See Figure 1 (Left) for a comparison of magnetization behavior as a function of applied field for ferro and paramagnets. After being in the presence of a magnetic field, these ferromagnets retain a portion of their magnetization called remnant magnetization ($M_r$). While most consider materials
to exist in one of these classes exclusively, the type of magnetism that a material exhibits is actually temperature dependent.

Figure 1: (Left) Illustration of magnetization vs applied magnetic field for ferro and paramagnetic materials. (Right) Visualization of the magnetic Curie temperature when a magnetic media transitions from a ferromagnet into a paramagnet.

Magnetic susceptibility is a term used to describe how magnetizable a magnetic media is, and is defined as the slope of a magnetization vs magnetic field curve (MH loop). From the MH loop in Figure 1 (Left) the initial ferromagnetic slope, and thus the susceptibility, can be seen as being much larger than for the paramagnet. Figure 1 (Right) illustrates how a ferromagnetic material has the largest susceptibility at absolute zero and sees a reduction in its susceptibility as it is heated until it reaches zero at a temperature known the Curie point (T$_C$). Beyond this temperature the material becomes paramagnetic and no longer exhibits a remnant magnetization as the magnetic exchange energy, which forces the spins to behave coherently, reduces to zero. This phase transformation is entirely reversible and once the material has its temperature reduced below T$_C$ it will once again behave ferromagnetically. Antiferromagnetic materials have a similar phase transition at their Néel temperature (T$_N$) above which they transition into either ferro or paramagnetic behavior depending on the material in question. These phenomena will be used as the basis for transducing thermal into electrical energy in Chapter 2.
Magnetic materials are also subject to a number of directionally dependent anisotropy energies depending on the mechanical loading conditions that they are subject to, their crystal structure, and their geometric shape. Figure 2 illustrates these three directionally dependent energies and provides the equations which govern them. Figure 2 (a) shows how the difference in applied external strain (Δε) reorients the magnetic spins to align with one another up to a saturation value (λs) and that the energy is proportional to that product and the materials modulus of elasticity (E). Figure 2 (b) provides the 4th order expansion of magnetocrystalline anisotropy and illustrates the easy axes associated with hexagonal and cubic crystals. In this formulation, the magnetocrystalline coefficients (K1 and K2) are phenomenologically measured as functions of temperature and the magnetization direction (θ) is measured from the Z-axis. For hexagonal crystals there are two possible easy directions, one along the C-axis (shown in green and blue) and one along the basal plane (shown as the crossed axes). By comparison, cubic crystals have 7 possibly easy axis directions: one along each face and one along each corner. Figure 2 (c) illustrates the effect that geometric shape has on the magnetization state. Simply put, the magnetization wants to lie along the longest axis of the material and is averse to lying in the shorter directions. The rank three demagnetization tensor (N) is populated depending on the shape¹² and has a norm of one. Considering various combinations of these directionally dependent energy terms will be shown to be instrumental in designing optimized multiferroic systems. Chapter 2:
1.3.2 Piezoelectric Materials

Figure 3: Piezoelectric material behavior. (a) Polarization of a ferroelectric crystal. (b) Ferroelectric hysteresis loop. (c) Strain-electric field behavior of a ferroelectric crystal.

Piezoelectric materials are those which exhibit a mechanical response under the application of an applied field, or experience an electric potential change as a function of applied strain. A subclass of these materials are ferroelectric crystals which exhibit a remnant polarization after the application of a strain or applied field and can be considered the electrical analog of ferromagnets. This type of behavior necessitates non-centrosymmetric materials and is most often seen in perovskite crystals wherein the central ion “polarizes” along a specific crystal direction to deform from a cubic lattice into an orthorhombic, rhombohedral or tetragonal orientation. Figure 3(a) illustrates this behavior for a perovskite crystal polarized into a tetragonal state. As these materials are polarized a PV (Polarization vs Voltage) hysteresis loop can be measured such as the one seen in Figure 3(b). As the polarization is reversed across the coercive voltage, the central ion “pops” across the central axis of the crystal and the strain state reverses to form the “butterfly curve” seen in Figure 3(c). It should also be noticed that the crystal doesn’t experience strain isotropically, and that there is a sort of electromechanical Poisson’s effect that occurs as the crystal is polarized. Such a phenomenon will be used in conjunction with the magnetic anisotropies to yield deterministic control of magnetic states as a function of applied electric field.
Beyond their bulk material behaviors, ferromagnetic materials have unique characteristics as they are scaled down into the nanoscale. When interrogating the mesoscale magnetic properties, an observation can be made of a domain structure inside of which magnetic spins are aligned. To minimize the total magnetic energy, these domains form closure paths such that adjacent domains attempt to cancel out stray flux that would otherwise exit the material. There is, however, an energy cost to these domain walls that is length scale dependent and as the magnetic material is reduced beneath a critical length it is no longer energetically favorable to form said walls; this size is known as the single domain limit and is illustrated in Figure 4. The benefit to this type of behavior is that the remnant magnetization is nearly equal to the saturation value. If the size is reduced further, there is a second critical point, shown in Figure 4(a), where the thermal fluctuations overcome the stability of the magnetic anisotropy and the material no longer maintains a remnant field or experiences a coercivity. For the purpose of this work, it will be important to stay above this superparamagnetic critical length, which for Ni is around 10 nm. Figure 4(b) illuminates the domain structure for a 300x100x25 nm single domain Ni element, seen with a single north and
south pole, and a 60 nm Ni thin film comprised of a maze like structure of domain walls. Whereas
the latter can experience some domain wall modulation, especially at critical thicknesses as further
examined in Chapter 4, the former single domain elements can achieve as much as a full and
reversible 90° rotation under the anisotropic application of magnetic field or, more interestingly,
electrically modulated ferroelectric strain. Additionally, such deterministic rotation can occur with
precise temperature variation. Control of these forms of magnetic rotation will form the basis of
the energy transduction techniques presented in Chapters 2 and 4.
Chapter 2: TRANSDUCTION OF THERMAL ENERGY INTO ELECTRICAL ENERGY

2.1 Synopsis

A method of enhancing the efficiency and energy density of thermomagnetic energy transduction by minimizing entropic loss is presented. An analysis of the thermomagnetic efficiency of elemental ferromagnets is presented which provides an argument that more ordered systems can produce larger efficiencies. This methodology is expanded to explore the temperature dependent rotation of magnetization direction in textured and monolithic ferromagnetic crystals. A new method of comparing the energy transduction by examining the variation in magnetic entropy is presented. Here it was shown that the spin reorientation transition in NdCo$_5$ can provide upwards of 2MJ/m$^3$ of magnetic energy at a relative efficiency of 22% for energy harvesting applications and that tailored crystalline nanostructures can be tuned by their shape to modify their optimal operating regime as a thermal sensor.

2.2 Literature Review

Thermal energy, a ubiquitous and abundant potential resource, goes mostly unharnessed for lack of an efficient harvesting methodology. The largest body of research on thermal energy harvesting focuses on thermoelectrics utilizing the Seebeck effect$^{16}$, where a thermal gradient is converted into an electric voltage. This effect was first discovered in 1821 and recent research has
primarily focused on finding new materials with larger thermoelectric figures of merit, a term directly related to efficiency. To date however, the relative efficiencies are below 20% of the Carnot limit\textsuperscript{17,18} and become significantly worse for temperature gradients less than 100 K which makes their use impractical for the majority of thermal energy harvesting applications. Therefore, there is a need to find new transduction mechanisms capable of converting waste heat into electrical energy more efficiently than presently possible.

An alternative, and substantially less explored field, is that of thermomagnetics. Thermomagnetic transduction involves thermally inducing a magnetic phase transition and harnessing it as electrical energy. Figure 5 shows a concept for a thermomagnetic generator operating about the magnetic phase transition that occurs in ferromagnets when operated about their Curie point ($T_c$). The second order Curie magnetic phase transition was initially investigated in an analytical paper by Brillouin and Iskenderian in 1948\textsuperscript{19}. Their model suggested that, for ferromagnetic materials operating about their Curie temperature, a maximum relative efficiency of 55% Carnot is possible; a value substantially larger than current Seebeck devices. In 1959, Elliot et al. experimentally evaluated bulk gadolinium (Gd) as a material suitable for harvesting thermomagnetic energy at room temperature\textsuperscript{20}. However, power density calculations from Elliot's thermomagnetic generator failed to produce significant power outputs. In 1965, a manganese-copper ferrite alloy with a room temperature $T_c$ was studied by Murakami\textsuperscript{21}, however the efficiency of this material was not reported. An analytical model using resonating magnetic fields was proposed by Rosengsweig\textsuperscript{22} in 1967; here calculations suggested that large magnetic fields are required to obtain high efficiencies. One of the main issues was the lack of sufficiently strong permanent magnets to overcome bulk scale demagnetization effects and the degradation of the ferromagnetic exchange length near the Curie temperature.
Following the development of high remanence rare earth magnets, in the 1980’s Kirol et al. analytically proposed a regenerative thermomagnetic cycle using a combination of Ho$_{69}$Fe$_{91}$ at cryogenic temperatures, Gd near room temperature, and Fe far above ambient$^{23}$. Figure 5 illustrates Kirol’s design for a thermomagnetic generator. This regenerative thermomagnetic approach suggested a maximum relative efficiency of 75%; a substantial improvement over Seebeck devices or Brillouin’s original proposition. Utilizing this methodology, Solomon et al. designed and analytically evaluated a similar regeneration cycle using Y$_2$Fe$_{17}$ in 1991$^{24}$. Y$_2$Fe$_{17}$ was chosen since its Curie temperature could be varied with iron content and yield a harvesting approach over a broader temperature range. While interesting, these regenerative approaches were not experimentally verified and thus the reported efficiencies have yet to be empirically quantified.
Ujihara in 2007 proposed a different thermomagnetic approach using a strain mediated multiferroic mechanism to transduce thermomagnetic energy into electrical energy\textsuperscript{25}. The multiferroic was operated about its Curie point and strain coupled to a ferroelectric material. Figure 6 provides the layout for such a design. This approach bypasses the need for coils to harvest the energy and allows the thermomagnetic generator to operate at the micro/nano-scale where resistive losses dominate current driven systems. He postulated that micro/nanoscale systems have the potential to operate at substantially higher frequencies due to increased surface to volume ratio allowing faster heating and cooling times thus generating substantially higher power outputs. It should be noted however, that Uhihara’s experimental study focused on power output and did not report the efficiency of the multiferroic. Another multiferroic methodology was proposed by Song et al.\textsuperscript{26}, who postulates improved efficiency from use of magnetic first order transformations in Ni\textsubscript{44}Co\textsubscript{6}Mn\textsubscript{40}Sn\textsubscript{10}. This transformation between a ferromagnetic austenite phase and an antiferromagnetic martensite phase was predicted to have a relative efficiency of approximately
30% when operating in an Ericsson cycle with a 1 T magnetic bias field. However such a technique has yet to be experimentally verified.

Recently, experiments carried out by Hsu and myself on poly-crystalline Gd\textsuperscript{27}, operating about its Curie Point, showed a relative efficiency of 10%. However, analytic computation by Hsu et al. showed that nanoscale, single domain, Gd elements could be used to increase relative efficiencies to 30% of Carnot. An additional benefit of single domain elements is that they maintain a remnant saturation magnetization and thus would not require a bias field for cyclic operation. The increased efficiency and simplified cycle provide compelling reasons to reduce the scale of thermomagnetic generators to the micro/nano scale. The work which performed in this study will be covered in greater depth in the following section.

The thermomagnetic energy harvesting approach appears to be a viable alternative to conventional thermoelectrics with regard to efficient thermal energy transduction, especially with regard to applications of relatively small temperature differentials. It has been shown, by leveraging multiferroic composites and numerically tailoring the ferromagnetic systems to the environments of interest, that these systems do experimentally exhibit large energy densities and efficiencies which equal or exceed their thermoelectric counterparts. Significant benefits could be derived by reducing the overall scale of these generators but additional studies are needed to provide information about operating single domain elements about their Curie temperature.

In all the above research the focus was on either first or second order phase transformations near the Curie point. In a slightly different approach Ohkoshi in 1977 focused on the magnetic phase transformation that occurs near magnetic spin reorientation to harvest waste heat\textsuperscript{28}. Spin reorientation exploits a temperature induced change in magnetic easy axis that can be converted
to electrical energy and benefits from the cooperative motion of spins rather than the randomization that occurs at Curie temperature. The spin reorientation phenomenon was first observed by Houghton and Weyhmann\textsuperscript{29} in 1968 and then analytically evaluated later that year by Horner and Varma\textsuperscript{15}, who theorized that certain materials could make a spontaneous ordered to ordered transition due to the temperature dependence of magnetocrystalline anisotropy. In 1977 Ohkoshi was the first and, to the author’s knowledge, only paper to suggest using this spin reorientation phenomenon to harvest thermal energy\textsuperscript{30}. In these experiments, bulk single crystal NdCo5 was experimentally reported to have a relative efficiency of 9% of Carnot. While the results were promising for an initial concept, an analytical design suggesting the efficiency and potential energy transducible was unavailable. This type of order-to-order transition will be the primary focus of the present work to be discussed later in the manuscript.

In addition to the experimental thermomagnetic work, a number of analytical models have been applied to both thermomagnetics as well as the more studied area of magnetocalorics. Srivastava and Song\textsuperscript{31} analyzed the first order phase transformation present in Ni\textsubscript{44}Co\textsubscript{6}Mn\textsubscript{40}Sn\textsubscript{10} using a free energy formulation in order to maximize the potential energy output by calculating entropy densities. Kvirikadze and Zviadadze\textsuperscript{32} utilize a similar energy formulation but focus on a system Hamiltonian and expand their analysis to 2nd order phase transformations about the Curie point. Bulgrin et al. analyzed the experimental work done by Ujihara, describing a methodology to optimize the multiferroic transduction from thermal to electrical energy through a ferromagnetic medium\textsuperscript{33}.

While all of the previous modeling efforts do an admirable job elucidating different aspects of thermomagnetic harvesting, none provide the means to compare the effectiveness of the different
modes of thermomagnetic transduction. A model that is capable of comparing and contrasting different approaches is needed for this field to continue. This comparison is begun by comparing the conversion efficiencies for different ferromagnetic materials in a study conducted by Chin-Jui Hsu, Samuel Sandoval and myself.

2.3 Thermomagnetic Conversion Efficiencies for Ferromagnetic Materials

2.3.1 Defining the Thermomagnetic Power Cycle

An idealized thermomagnetic cycle is illustrated in Figure 7 along with a plot of magnetization as a function of magnetic field (M-H plot) for two different temperatures (i.e. $T_{\text{cold}}$ and $T_{\text{hot}}$). The four illustrations shown in Figure 7 contain a magnetic flux source, namely a permanently magnetized hard ferromagnet to create the magnetic field, a “cold” heat sink, a “hot” heat source, and a material which is either ferromagnetic at $T = T_{\text{cold}}$ or non-ferromagnetic at $T =$
The non-ferromagnetic state represents a paramagnet when operating about the Curie point, and antiferromagnetic when transitioning about a Néel temperature. The processes shown in Figure 7 can be described as follows: Initially at (1), the temperature of the material is above \( T_c \) (at \( T_{hot} \)) and is thus non-ferromagnetic. By bringing the material into thermal contact with a cold reservoir, the temperature drops to \( T_{cold} \) (\( T_{cold} < T_c \)) and the ferromagnetic material becomes ferromagnetic at (2). During this process, the material is subjected to a magnetic field which increases the magnetization of the material to (3) as shown in the M-H plot. At this same time, the material is brought into thermal contact with the hot reservoir, and therefore, the temperature again increases to \( T_{hot} \) at (4) and the material becomes non-ferromagnetic and returns to the cold side and thus completing the cycle returning to (1).

When a material is magnetized and demagnetized as illustrated in Figure 7, the maximum available energy can be calculated by using the area method\(^{34} \). The same principal is used to analyze a thermomagnetic cycle here, but the difference is that the magnetization and demagnetization process in a thermomagnetic cycle involves an additional heat exchange process. In a thermomagnetic cycle, the net magnetic energy available, \( W_{out} \), from a ferromagnetic material is defined\(^{35} \) by the area enclosed (i.e. the bounded area 1234 in Figure 7) and is mathematically expressed as (in cgs unit: erg/cm\(^3\)):

\[
W_{out} = - \frac{1}{4\pi} \oint_{cycle} H dB = - \frac{1}{4\pi} \oint_{cycle} (HdH + 4\pi HdM(T,H))
\]

(2.1)

where \( B \) is magnetic induction, \( H \) is magnetic field, and \( M \) is magnetization. Since the integral of the HdH term is zero in a complete cycle, Equation (2.1) reduces to:
\[ W_{\text{out}} = - \oint_{\text{cycle}} HdM(T, H) \]  

By following the first law of thermodynamics (i.e. energy conservation), the heat input in a thermomagnetic cycle is defined\(^{35}\) as follows:

\[ Q_m = Q_{\text{out}} + W_{\text{out}} = \rho \int_{T_{\text{cold}}}^{T_{\text{hot}}} C_p(T) dT + T \int dS_m + W_{\text{out}} \approx \rho \int_{T_{\text{cold}}}^{T_{\text{hot}}} C_p(T) dT \]  

where \( \rho \) is the density, \( C_p \) is the specific heat for the material, \( S_m \) is the magnetic entropy. For relatively small \( H \), the integral of \( C_p \) term is much larger than the other two terms and thus the equation can be further simplified as shown in Equation (2.3). A justification of this approximation is discussed in the results section. The absolute efficiency, \( \eta_{\text{abs}} \), in one cycle is then defined as the ratio of the energy produced, the net magnetic energy available, to the heat input into the system\(^{19,35}\):

\[ \eta_{\text{abs}} = \left| \frac{W_{\text{out}}}{Q_{\text{in}}} \right| = \frac{\oint_{\text{cycle}} HdM(T, H)}{\rho \int_{T_{\text{cold}}}^{T_{\text{hot}}} C_p(T) dT + T \int dS_m + \oint_{\text{cycle}} HdM(T, H) \approx \frac{\oint_{\text{cycle}} HdM(T, H)}{\rho \int_{T_{\text{cold}}}^{T_{\text{hot}}} C_p(T) dT} \]  

\( \eta_{\text{abs}} \) can be compared to the efficiency of a Carnot cycle (\( \eta_{\text{Carnot}} \)) operating between the same two temperatures where \( \eta_{\text{Carnot}} \) represents the maximum efficiency of any heat engine and is a function of only \( T_{\text{hot}} \) and \( T_{\text{cold}} \). The relative efficiency, expressed as a percentage of Carnot, \( \eta_{\text{rel}} \), may now be defined as

\[ \eta_{\text{rel}} = \frac{\eta_{\text{abs}}}{\eta_{\text{Carnot}}} = \frac{\eta_{\text{abs}}}{1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}} = \frac{\eta_{\text{abs}}}{\Delta T} \frac{T_{\text{hot}}}{T_{\text{hot}}} \]
2.3.2 Theory and Analysis

Figure 8: Isothermal magnetization curves of polycrystalline Gd. The gray area represents the net available magnetic energy ($W_{\text{out}}$) in a thermomagnetic cycle defined by Equation 2 (for $T_{\text{cold}} = 273$ K, $\Delta T = 50$ K, and $H_{\text{app}} = 3000$ Oe).

The analysis presented in the previous section can be used along with experimental data available in the literature to determine relative efficiency $\eta_{\text{rel}}$ for a wide range of ferromagnetic materials to assess the efficiency of thermomagnetic generation compared to other approaches. To outline the procedure used to evaluate available thermomagnetic materials, polycrystalline Gd was utilized as an example working body in the defined thermomagnetic cycle. Figure 8 shows the $M$-$H$ plot for a $\sim 1$ mm$^3$ polycrystalline Gd sample (99.9% purity from Kurt J. Lesker Company). The isothermal magnetization curves shown in Figure 8 were measured at six different temperatures using SQUID (Superconducting Quantum Interference Device from Quantum Design). Reported $T_c$ values for Gd range from 287-295 K$^{36}$ and are dependent on experimental technique and the
definition used (i.e. rather than variations with material characteristics). By using the Arrott plot technique\textsuperscript{37}, $T_c$ was found to be approximately 288K for this polycrystalline Gd sample.

![Graph showing heat capacity of polycrystalline Gd as a function of temperature. The gray area represents the heat input ($Q_{in}$) in a thermomagnetic cycle defined by Equation 3 (for $T_{cold} = 273$ K and $\Delta T = 50$ K).](image)

**Figure 9:** Heat capacity of polycrystalline Gd as a function of temperature. The gray area represents the heat input ($Q_{in}$) in a thermomagnetic cycle defined by Equation 3 (for $T_{cold} = 273$ K and $\Delta T = 50$ K).

Calculations of Gd’s thermomagnetic efficiencies are illustrated for a temperature difference of $\Delta T = 50$ K, with $T_{cold} = 273$ K (i.e. $T_{hot} = 323$ K). The applied magnetic field ($H_{app}$) chosen for this calculation is 3000 Oe which is comparable to the field level of an NdFeB permanent magnet at its surface. This field level is relatively small and thus the approximation present in Equation (2.4) is used for the calculation (with errors < 1%). As shown in Figure 8, when Gd is at $T_{cold} = 273$ K, with the applied field $H_{app} = 3000$ Oe, the magnetization $M_{cold} = 620$ Oe. As the Gd is heated to $T_{hot} = 323$ K the magnetization at the same $H_{app}$ drops to $M_{hot} = 48$ Oe. Using Equation (2.2) and integrating around the thermomagnetic cycle, the net magnetic energy ($W_{out}$) per unit volume for this cycle is $1.06 \times 10^6$ erg/cm$^3$. The heat input ($Q_{in}$) required in this cycle can be calculated using a $C_p$-T plot. Figure 9 shows a $C_p$-T plot of the polycrystalline Gd
used in this study and measured with DSC (Differential Scanning Calorimeter from PerkinElmer). $C_p$ is known to be a function of temperature and it behaves abnormally near the temperature where the magnetic phase transformation occurs (i.e. a maximum value of $C_p$ appears in the vicinity of $T_c$). By integrating $C_p(T)$ over the temperature span from $T_{\text{cold}} = 273 \text{ K}$ to $T_{\text{hot}} = 323 \text{ K}$ as defined by Equation (2.3), $Q_{\text{in}}$ is found to be $1.09 \times 10^9 \text{ erg/cm}^3$. Therefore, for this particular thermomagnetic cycle, the absolute efficiency is $\eta_{\text{abs}} = 0.097\%$ which corresponds to a relative efficiency of $\eta_{\text{rel}} = 0.63\%$ when compared to the Carnot limit. This process illustrates how the efficiencies of a wide range of materials may be calculated.

![Figure 10: Heat input components at various applied fields](image)

Figure 10: Heat input components at various applied fields
The relative efficiency $\eta_{rel}$ can also be calculated for larger values of $H_{app}$, namely those generated by superconducting coils\textsuperscript{35,38}. However, the efficiency at high magnetic fields requires inclusion of magnetic entropy $S_m$ and $W_{out}$ terms into $Q_{in}$ (see Equation (2.3)). Figure 10 shows a plot of $\eta_{rel}$ (see Equation (2.5)) calculated without the approximation as well as the three components in $Q_{in}$ (i.e. the integral of $TdS_m$ and $C_pdT$, and $W_{out}$) as a function of applied magnetic field for a thermomagnetic cycle of $T_{cold} = 290$ K and $\Delta T = 10$ K. In Fig. 4-6, the data points for $H_{app} = 20, 50, \text{and } 80$ kOe are obtained from Solomon [9] while the data points for $H_{app} = 3$ kOe are calculated based on the results presented in Figure 8 and Figure 9. Figure 10 shows that $\eta_{rel}$ increases substantially from a low value of 4.7% to 53.5% as $H_{app}$ increases. This clearly indicates that larger magnetic fields produce higher efficiencies as suggested in the literature\textsuperscript{22,24,35}. Figure 10 also shows that the $S_m$ component as well as $W_{out}$ is negligible in $Q_{in}$ at lower magnetic fields (i.e. $H_{app} < 20$ kOe). In this study, a relatively low magnetic field, $H_{app} = 3$ kOe, was chosen to compare materials based on available hard magnetic materials (i.e. $H_{app} = 3$ kOe is approximately the maximum available). However, it should be noted that larger efficiencies are possible by applying larger $H_{app}$, but producing large $H_{app}$ could also degrade efficiencies because a magnetic source typically requires power.
Figure 11: Relative efficiency of a thermomagnetic generator using polycrystalline Gd (H_{app} = 3000 Oe). The temperature of each entry represents T_{cold}.

Efficiencies can now be calculated for Gd operating at different temperature ranges and some results are shown in Figure 11. Here, one can observe the variation of \( \eta_{\text{rel}} \) as a function of \( \Delta T \) calculated for six different T_{cold} (i.e. 273, 278, 283, 288, 293, and 298 K). The results show that a large \( \Delta T \) reduces \( \eta_{\text{rel}} \), regardless of T_{cold}, and thus, the highest \( \eta_{\text{rel}} \) is found for the smallest \( \Delta T \).

Therefore, minimizing the thermal excursion generally maximizes the efficiency for the thermomagnetic energy harvesting. For a \( \Delta T = 5 \) K, the highest efficiency is for T_{cold} = 288 K rather than one of the extreme temperatures (i.e. 273 or 298 K). The reason for this optimum is that the magnetization changes the most dramatically at 288 K for the given \( \Delta T = 5 \) K. That is, for colder temperatures (T_{cold} < 288 K), the material is ferromagnetic and the change in magnetization for a \( \Delta T = 5 \) K is relatively small which provides a relatively small work output. Likewise for
higher temperatures ($T_{\text{cold}} > 288$ K), the material is paramagnetic and once again the magnetization change as well as the output work for $\Delta T = 5$ K is small. This result can also be explained by the temperature dependence of spontaneous magnetization predicted by Weiss theory using Brillouin function$^{34}$ where the sharpest change of magnetization happens at the temperature closer to $T_c$ (i.e. the slope $\Delta M/\Delta T \to \infty$ at $T_c$) and thus the largest work output per $\Delta T$ should be near $T_c$.

Table 1: Thermal magnetic properties and efficiencies of ferromagnetic materials

<table>
<thead>
<tr>
<th>Elements</th>
<th>$T_c$ [K]</th>
<th>Magnetic phase transition</th>
<th>Crystal Structures</th>
<th>$M_{\text{cold}}$ [emu/cm$^3$] ($T_{\text{cold}}$ [K], $H_\text{app}$ [Oe])</th>
<th>Max.$^c C_p$ [J/mol.K]</th>
<th>$\eta_{\text{Carnot}}$ [%]</th>
<th>$\eta_{\text{rel}}$ [%]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1394</td>
<td>F-P$^e$</td>
<td>Poly</td>
<td>139 (1389, 3000)</td>
<td>54.2</td>
<td>0.36</td>
<td>2</td>
<td>39,40</td>
</tr>
<tr>
<td>Fe</td>
<td>1044</td>
<td>F-P</td>
<td>Poly</td>
<td>288 (1039, 3000$^b$)</td>
<td>72.5</td>
<td>0.49</td>
<td>3.4</td>
<td>41,42</td>
</tr>
<tr>
<td>Ni</td>
<td>630</td>
<td>F-P</td>
<td>Poly</td>
<td>76 (630, 3000)</td>
<td>42.5</td>
<td>0.79</td>
<td>3.4</td>
<td>41</td>
</tr>
<tr>
<td>Gd</td>
<td>288</td>
<td>F-P</td>
<td>Poly, Single</td>
<td>375 (288, 3000)</td>
<td>52.4</td>
<td>1.71</td>
<td>11.4</td>
<td>36</td>
</tr>
<tr>
<td>Tb</td>
<td>221</td>
<td>F-A$^f$</td>
<td>Poly, Single</td>
<td>1176 (221, 3000)</td>
<td>148</td>
<td>2.21</td>
<td>17.5</td>
<td>43-45</td>
</tr>
<tr>
<td>Dy</td>
<td>89</td>
<td>F-A</td>
<td>Poly, Single</td>
<td>1028 (89, 3000)</td>
<td>70.8</td>
<td>5.32</td>
<td>7.5</td>
<td>46-48</td>
</tr>
<tr>
<td>Ho</td>
<td>20</td>
<td>F-A</td>
<td>Poly, Single</td>
<td>1594 (15, 3000)</td>
<td>16.5</td>
<td>25</td>
<td>16.2</td>
<td>49-51</td>
</tr>
<tr>
<td>Er</td>
<td>20</td>
<td>F-A</td>
<td>Poly, Single</td>
<td>678 (20, 3000)</td>
<td>20.8</td>
<td>20</td>
<td>3.5$^f$</td>
<td>52-56</td>
</tr>
</tbody>
</table>

a. $H_{\text{app}} = 3$ kOe and $\Delta T = 5$ are assumed for all the calculations. Optimistic isothermal magnetization data were chosen from interpolation.

b. For single crystal, only the magnetizations along the easy axis were considered.

c. $C_p(T)$ anomaly appeared in the vicinity of $T_c$

d. $M_{\text{cold}}$ at 3000Oe was calculated from linear interpolation.

e. Ferromagnetic to paramagnetic transition at $T_c$

f. Ferromagnetic to antiferromagnetic transition at $T_c$

g. Calculated based on interpolation using limited isothermal magnetization data for polycrystalline Er.
h. $\eta_{\text{rel}} = 3.4\%$ if using the isothermal magnetization data shown by Gama and Foglio$^{53}$.

Based on the results shown in Figure 11, $\eta_{\text{rel}}$ for a wide range of ferromagnetic materials are further evaluated. Table 1 shows $\eta_{\text{rel}}$ as well as the corresponding $\eta_{\text{Carnot}}$ calculated for eight
ferromagnetic elements (Co, Fe, Ni, Gd, Tb, Dy, Ho, and Er) in a thermomagnetic cycle based on \( \Delta T = 5 \) and \( H_{\text{app}} = 3000 \) Oe as described previously. These elements are arranged in the table from the highest to lowest \( T_c \). The fifth column reflects which case is presented. Among the elements analyzed, Co, Fe, and Ni are 3d transitional elements (which have incomplete 3d electron shells) and the remainder are rare earth elements (which have incomplete 4f electron shells)\(^{57}\). Furthermore, Gd is the only element which has a \( T_c \) in the range of room temperature. All of the elements studied are ferromagnetic below \( T_c \), but not all of them are paramagnetic above \( T_c \). Here, Tb, Dy, Ho, and Er have ferro-to-antiferromagnetic phase transition across \( T_c \) as shown in the third column.

In Table 1, all the data used including \( T_c \), \( M_{\text{cold}} \), and the peak \( C_p \) values were obtained from experimental data reported in the literature (except for Gd shown in Figure 8 and Figure 9). For elements with experimental data available, the \( \eta_{\text{rel}} \) was calculated for both single and polycrystalline structures. For single crystal materials, the isothermal magnetization curves were measured along the easy axis of the material. In general, for both single and polycrystalline cases, interpolations were used to obtain isothermal magnetization curves for the different temperatures used in the efficiency calculations. Any error introduced due to interpolation should not significantly alter the calculated \( \eta_{\text{rel}} \). However, significant discrepancies were found to exist in the isothermal magnetization curves of single crystal Er measured along the easy axis. Feron (see Coqblin\(^{52}\)) showed that single crystal Er can be fully saturated at fields as small as ~1 kOe at 20 K while Gama and Foglio\(^{53}\) showed that 15 kOe is required to saturate single crystal Er at the same temperature. In Table 1, two sets of \( \eta_{\text{rel}} \) for single crystal Er are presented based on both of these experimental data\(^{52,53}\). As for polycrystalline Er, the M-H data are more consistent\(^{54,55}\), however, only limited isothermal magnetization data are available in the literature.
Additional comments concerning the construction of Table 1 are warranted. First, for $Q_{in}$ calculations, the same $C_p$-T plot was used for both single and polycrystalline structures. It was previously reported\textsuperscript{36} that the $C_p$ as a function of temperature shows insignificant differences between single and polycrystalline structures. Second, the $\eta_{\text{Carnot}}$ of each element is also displayed in the table as well. The increase of $\eta_{\text{Carnot}}$ observed in the table as $T_c$ decreases corresponds to the definition of $\eta_{\text{Carnot}}$ (see Equation (2.5)), which suggests that the total thermal efficiency of a thermomagnetic device is superior in cryogenic environments, a comment that is true for all heat engines. Third and finally, the calculations for $W_{out}$ in this study neglected magnetic hysteresis effects. Only the $H$ increasing section of the isothermal magnetization curves were used (i.e. as contrasted with $H$ decreasing). In general, hysteresis may arise in the rare earth elements (e.g. see Rhodes\textsuperscript{49}) which have a ferro-to-antiferromagnetic phase transition. However, if this hysteresis is accounted for in calculations, it may result in a net increase in $\eta_{\text{rel}}$ due to the increased $W_{out}$ produced by a larger remanence ($M_r$) in $H$ decreasing curves as compared to $H$ increasing curves. Therefore, the data presented in Table 1 for rare earth elements (Dy, Er, Ho, and Tb) may be a conservative estimate of efficiency.

2.3.3 Discussion of Results

As can be seen in Table 1, 3d elements generally have a lower $\eta_{\text{rel}}$ then rare earth elements. Our results show that polycrystalline Co, Fe, and Ni (and maybe Er) have a $\eta_{\text{rel}} < 5\%$ while polycrystalline Gd, Tb, Dy, and Ho have more than twice that value ($\eta_{\text{rel}} = 7.5\text{-}17.5\%$). While not shown in the table, the 3d elements can also achieve similar efficiencies as the rare earth elements if the magnetic field is increased. For example, if Fe is operated with $H_{\text{app}} = 5$ kOe, an increase of $\eta_{\text{rel}} = 10\%$ is reached; while for Co, an applied field of 7 kOe produces an increased $\eta_{\text{rel}} = 11\%$. These results, which correspond to the results shown in Figure 10, help explain the obstacles
reported in the early development of thermomagnetic generation in the 1950s. That is, researchers could not find magnets capable of generating sufficient fields to saturate the ferromagnetic materials and thus could not produce high power outputs. However, one thing worth noting is that increases of $\eta_{rel}$ as $H_{app}$ increases may be limited for materials that have an antiferromagnetic state above $T_c$ (e.g. rare earth elements). This is because these materials are typically saturated at relatively small magnetic fields in the antiferromagnetic state as compared to materials in the paramagnetic state. The saturation in the antiferromagnetic state also saturates $W_{out}$, and therefore, maximizes $\eta_{rel}$ at lower $H_{app}$ values.

Additionally, single crystalline elements typically have a higher $\eta_{rel}$ than polycrystalline elements for the same thermomagnetic cycle. For example, $\eta_{rel}$ of polycrystalline Gd is 11.4% while for single crystal it is 20.5%. This observation is a result of a larger magnetization value (i.e. a higher susceptibility) for a single crystalline ferromagnetic material, when the field is applied along the easy axis, as compared to a polycrystal at the same applied field. The larger magnetization value present in single crystalline materials is attributed to magnetocrystalline anisotropy which reduces the energy barrier when a magnetic field is applied in the easy direction, and therefore, the spins can be aligned more easily along this direction. In a thermomagnetic cycle, increasing $M_{cold}$ directly increases $W_{out}$ (i.e. the bounded area in the M-H plot), and thus increases efficiency for single crystal materials aligned along their easy axis.

As noted previously, the rare earth elements (Gd, Dy, Ho, and Tb) produce substantially higher $\eta_{rel}$ for the chosen thermomagnetic cycle compared with 3d elements (note that Er is an outlier as mentioned before). Here, Dy, Ho, and Tb transform from a ferromagnetic to antiferromagnetic phase at $T_c$ and this transition is an order-to-order phase transformation. In sharp contrast, the 3d elements undergo an order-to-disorder phase transformation (i.e. ferromagnetic to
paramagnetic). The increased efficiency in order-to-order transition suggested by Table 1 is partially due to the lower $T_c$ of rare earth elements producing a larger $M_{\text{cold}}$ when compared to the $M_{\text{cold}}$ of 3d elements. However, an important additional distinction for order-to-order transitions is that the change in magnetization ($M_{\text{cold}}/M_{\text{hot}}$) is much larger than order-to-disorder transitions. For example, for the thermomagnetic cycle used in this study, it was observed that the magnetization of Gd (order-to-disorder phase transformation) decreased by ~36% from $T_{\text{cold}}$ to $T_{\text{hot}}$; whereas rare earth elements with order-to-order phase transformation decreased by ~60% for the same $\Delta T$. Therefore, one explanation for the increased $\eta_{\text{rel}}$ in order-to-order phase transformations is that a relatively larger amount of magnetic energy is lost to entropy during the transition to a disordered state as compared to an ordered state. In fact, one paper by Ohkoshi and Kobayashi$^{58}$ suggested a similar order-to-order transition but one which relied on spin-reorientation as the mechanism for thermomagnetic generation in 1977. In their work, the thermal dependence of the magnetocrystalline anisotropy constants was used to change the spontaneous magnetization from one crystal axis to another and thus produce a net change of magnetization along one crystal axis. However, a discussion on the relative merits of this approach in the thermomagnetic energy harvesting efficiency was absent in their study.
The results in Table 1 also suggest that it is difficult to achieve $\eta_{rel} \sim 55\%$ as predicted in theory\textsuperscript{19}. While such findings may seem discouraging, potential solutions are possible. Since both single crystals and order-to-order transitions show relatively higher $\eta_{rel}$, it is inferred that the thermomagnetic energy harvesting efficiency can be improved by eliminating “randomness”. Here, the randomness is defined by either structural or magnetic disorder in ferromagnetic materials. Consider an example of a single domain, where all the spins are aligned in one direction (i.e. a well ordered magnetic state). Figure 12 shows the illustration of an isothermal magnetization curve representative of single domain Gd as well as actual magnetization curves of polycrystalline Gd measured at 283 and 288 K with SQUID. From a macroscopic view, the single domain is a completely uniform magnetization state achieved by eliminating domain walls (i.e. eliminating randomness). Therefore, it also has nearly 100% remanence at zero applied field, such that $M_{cold}$
= M_s at any field, where M_s is spontaneous or saturation magnetization. The theoretical M_s of Gd at 283 K calculated using Brillouin function is assumed to be the magnetization of single domain Gd at zero applied field, and the magnetization of single domain Gd at 5 kOe is assumed to be the same as polycrystalline Gd. In Figure 12, the W_{out} of single domain Gd is calculated to be $6.92 \times 10^5$ erg/cm$^3$ while in contrast the W_{out} of polycrystalline Gd is $2.42 \times 10^5$ erg/cm$^3$. For this case, $\eta_{rel} = 30.4\%$ is calculated for single domain Gd, which is nearly three times larger than polycrystalline $\eta_{rel} = 10.6\%$, and begins approaching the values previously calculated from theory.

2.3.4 Concluding Remarks

In this section, an efficiency analysis on eight ferromagnetic elements for thermomagnetic energy harvesting using a magnetic field of 3 kOe representative of NdFeB permanent magnets is conducted. Results show that the theoretical maximum efficiency of a thermomagnetic generation is difficult to achieve using conventional approaches associated with ferromagnetic materials. While larger magnetic fields increase $\eta_{rel}$, further power consumption is required to generate these larger magnetic fields and this may be an issue. In general, superior efficiencies are observed when a more uniform magnetization state is present, such as single crystals or order-to-order phase transitions, as compared to more random structures such as polycrystalline or order-to-disorder phase transitions. It is further suggested that by eliminating domain walls, the spin configuration can reach a more ordered state, especially at small magnetic field ($H_{app} \sim 0$), while still retaining fairly high magnetization values. This suggests that the $\eta_{rel}$ of single domains produce substantially higher efficiencies as compared to multi-domain structures. With these notions in mind, the focus was shifted to single domain elements which experience spin reorientation transitions.
2.4 A Unifying Metric for Comparing Thermomagnetic Transduction Utilizing Magnetic Entropy

2.4.1 Introduction

While all of the previous modeling efforts do an admirable job elucidating different aspects of thermomagnetic harvesting, none provide the means to compare the effectiveness of the different modes of thermomagnetic transduction. A model that is capable of comparing and contrasting different approaches is needed for this field to continue. The objective of this section is to present a method to compare the thermal to magnetic transduction efficiencies for different thermomagnetic systems. A free energy formulation is derived to examine the temperature dependence of the saturation magnetization and the magnetocrystalline anisotropy. This allows for a direct comparison between operating about a spin reorientation transition methods and the alternative ferromagnetic to paramagnetic transformation at the Curie point. A case study is performed comparing Gd, operating about its Curie point, to Gd, operating about its spin reorientation temperature. Another case study on NdCo$_5$ operating about its spin reorientation temperature, using experimentally derived values of the materials temperature dependent magnetic properties is presented. Analysis suggests that choosing the appropriate material and operating about its spin orientation produces considerable efficiencies (~22%) as well as large harvestable energy densities (~2.6 MJ/m$^3$); an order of magnitude larger than Gd single domains operating about their curie point (~100 kJ/m$^3$).
2.4.2 Theory

The following analytical development uses thermodynamic energy principles to predict the conversion of thermal energy into magnetic energy for a single crystal and single domain ferromagnetic material. The following formulation is for hexagonal crystals but is sufficiently general that it can be expanded to other crystalline structures. Beginning with internal energy $U$:

$$dU = \delta Q + \delta W$$

(2.6)

And expanding the change in heat, $\delta Q = T \delta S$, assuming the heat generation processes are reversible, and work, $\delta W = H dB$, where the magnetic flux $B$ is represented as $B = \mu_o (H + M)$, yields:

$$dU = T dS + \mu_o (HdH + HdM)$$

(2.7)

Here $T$ is temperature, $S$ is entropy, $\mu_o$ is the permeability of free space, $H$ is applied magnetic field, and $M$ is the material’s magnetization. Next the entropy is separated into a lattice and a magnetic component.

$$dU = T d\left(S_{lat} + S_{mag}\right) + \mu_o (HdH + HdM)$$

(2.8)

Under the assumption that the magnetic contribution to the specific heat is much smaller than the thermal component, the lattice component of the entropy can be converted to specific heat at constant pressure by utilizing the relation $TdS_{lat} = C_p dT$, using this conversion the internal energy becomes:

$$dU = C_p dT + TdS_{mag} + \mu_o (HdH + HdM)$$

(2.9)
In this analysis, temperature (T) and the applied magnetic field (H) are the preferred independent variables; therefore, Equation (2.9) is converted from internal energy (U) to free energy (F), with the following Legendre transformation:

\[ dF = d\left( U - TS_{mag} - \frac{\mu_0}{2} H^2 - \mu_0 HM \right) = C_p dT - S_{mag} dT - \mu_0 MdH \] 

(2.10)

If the magnetic terms are considered to be completely decoupled from the lattice expansion, a modified free energy term \( dE_{mag} \) which only considers the magnetic components can be formulated by dropping the specific heat \( (C_p) \) term:

\[ dE_{mag} = -S_{mag} dT - \mu_0 MdH \] 

(2.11)

From the modified free energy it can be seen that the magnetic entropy \( (S_{mag}) \) and the magnetization \( (M) \) can be computed by the following total differentials:

\[ S_{mag} = -\frac{dE_{mag}}{dT} \quad \mu_0 M = -\frac{dE_{mag}}{dH} \] 

(2.12)

For this analysis, the applied magnetic field and magnetization are represented in spherical coordinates with reference to the hexagonal crystal convention shown in Figure 1:

![Figure 13: Hexagonal crystal orientation and angles associated with the vectors of magnetization (M) and magnetic field (H)](image)

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From Figure 13, the applied magnetic field vector (H) and the resulting magnetization vector (M) contain two sets of angles to describe their direction in spherical coordinates. Here $\alpha$ and $\theta$ correspond to the polar angles measured from the C-axis of the crystal, whereas $\beta$ and $\phi$ correspond to the azimuthal angles measured from the A-axis. The unit vectors for the magnetic field, $\hat{\alpha}$, and the magnetization, $\hat{\theta}$, are as follows:

$$\hat{\alpha} = \langle \sin(\alpha) \cos(\beta), \sin(\alpha) \sin(\beta), \cos(\alpha) \rangle$$

(2.13)

$$\hat{\theta} = \langle \sin(\theta) \cos(\phi), \sin(\theta) \sin(\phi), \cos(\theta) \rangle$$

(2.14)

In a magnetic system, the free energy can be broken down into the magnetocrystalline anisotropy energy ($E_{\text{MCA}}$), the magnetostatic energy ($E_{\text{MS}}$), and the demagnetization energy ($E_{\text{DM}}$) as general functions of the temperature ($T$) and magnetic field ($H$):

$$E_{\text{mag}}[T, H] = E_{\text{MCA}}[T, H] + E_{\text{MS}}[T, H] + E_{\text{DM}}[T, H]$$

(2.15)

For a hexagonal crystal structure the magnetocrystalline anisotropy energy in spherical coordinates uses magnetocrystalline anisotropy constants $K_1$, $K_2$, and $K_4$, which are also dependent on temperature:

$$E_{\text{MCA}}[T, H] = K_1[T] \sin(\theta[T, H])^2 + K_2[T] \sin(3\theta[T, H])^4$$

$$+ K_4[T] \sin(\theta[T, H])^6 \cos(6\phi[T, H])$$

(2.16)

The magnetostatic energy due to the applied field in spherical coordinates is as follows, where $M_s$ is the generalized temperature dependent saturation magnetization, which could change according to the Curie-Weiss Law for a second order transformation or a magnetic phase change, as shown by Song$^{26}$.
\[ E_{MS} [T, \hat{H}] = -M_s [T] \hat{\theta}[T, \hat{H}] \cdot H \hat{\alpha}[T, \hat{H}] \]

\[ = -M_s H^* \begin{pmatrix} \sin(\theta) \sin(\alpha) \cos(\phi) \cos(\beta) \\ +\sin(\theta) \sin(\alpha) \sin(\phi) \sin(\beta) \\ +\cos(\theta) \cos(\alpha) \end{pmatrix} \] (2.17)

The demagnetization energy of the magnetic structure, assuming an ellipsoidal geometry, becomes the following:

\[ E_{DM} [T, \hat{H}] = -M_s^2 (T) \left( \hat{\theta} \cdot \hat{N} \hat{\theta} \right) \] (2.18)

\[ M_s^2 (T) \begin{pmatrix} A * \sin(\theta[T, \hat{H}])^2 \cos(\phi[T, \hat{H}])^2 \\ +B * \sin(\theta[T, \hat{H}])^2 \sin(\phi[T, \hat{H}])^2 \\ +C * \cos(\theta[T, \hat{H}])^2 \end{pmatrix} \] (2.19)

where \( \hat{N} \) represents a diagonal matrix, with demagnetization factors \( A, B, C \) along the coordinate axes of the magnetic element.

The magnetic entropy is calculated by differentiating the magnetic free energy with respect to temperature:

\[ -S_{mag} = \frac{E_{mag}}{dT} = \frac{dE_{MCA}}{dT} + \frac{dE_{MS}}{dT} + \frac{dE_{DM}}{dT} \] (2.20)

This leads to the following magnetic entropy:

\[ -S_{mag} = K_1 \sin(\theta)^2 + 2K_1 \sin(\theta) \cos(\theta) \theta' + K_2 \sin(\theta)^4 \\
+4K_3 \sin(\theta)^3 \cos(\theta) \theta' + K_4 \sin(\theta)^6 \cos(6\phi) \\
+6K_4 \sin(\theta)^5 \cos(6\phi) \cos(\theta) \theta' \\
-6K_4 \sin(\theta)^6 \sin(6\phi) \phi' - M_s^2 H \hat{\theta} \cdot \hat{\alpha} - M_s^2 H \hat{\theta} \cdot \hat{\alpha} \\
-2M_s^2 \hat{\theta} \cdot \hat{N} \hat{\theta} - M_s^2 \hat{\theta} \cdot \hat{N} \hat{\theta} - M_s^2 \hat{\theta} \cdot \hat{N} \hat{\theta} \] (2.21)
Where all of the material parameters are functions of temperature, and primes denote a differentiation of a material parameter with respect to temperature.

The vectors $\hat{\gamma}$ and $\hat{\delta}$ are defined from the chain rule:

$$
\hat{\theta} = \frac{d\hat{\theta}}{dT} = \frac{d\hat{\theta}}{d\theta} \frac{d\theta}{dT} + \frac{d\hat{\theta}}{d\phi} \frac{d\phi}{dT} = \hat{\gamma}' + \hat{\delta}'
$$

(2.22)

So that $\hat{\gamma} = (\cos(\theta)\cos(\phi), \cos(\theta)\sin(\phi), -\sin(\theta))$ and $\hat{\delta} = (-\sin(\theta)\sin(\phi), \sin(\theta)\cos(\phi), 0)$ are the temperature derivatives of the field vectors.

Collapsing and combining terms leads to entropy:

$$
S_{mag} = -\left( K_1 + K_2 \sin^2(\theta) + K_4 \sin^4(\theta) \cos(6\phi) \right) \sin^2(\theta)
+ M_s \hat{\theta} \cdot \left( H\hat{\alpha} + 2M_s \hat{N} \cdot \hat{\theta} \right)
- 2 \left( K_1 + 2K_2 \sin^2(\theta) - 3K_4 \sin^4(\theta) \cos(6\phi) \right) \sin(\theta) \cos(\theta) \theta'
+ M_s \left( H\hat{\alpha} + 2M_s \hat{N} \cdot \hat{\theta} \right) \cdot \hat{\gamma}' + M_s \left( H\hat{\alpha} + 2M_s \hat{N} \cdot \hat{\theta} \right) \cdot \hat{\delta}'
+ 6K_4 \sin(\theta)^6 \sin(6\phi) \phi'
$$

(2.23)

Returning to the total free energy differential in Equation 5 and knowing that lattice expansion due to specific heat change cannot be harvested magnetically leads to the calculation of magnetic work done as:

$$
\Delta W = W_2 - W_1 = \Delta S_{mag} \Delta T - \mu_o \left( M [T_1] - M [T_2] \right) \Delta H
$$

(2.24)

In the case that the magnitude of the magnetization due to the temperature change is negligible, such as in the case of spin reorientation, and the applied field remains constant, then the change in work becomes:

$$
\Delta W = \Delta S_{mag} \Delta T
$$

(2.25)
This work represents the total energy transduced from the thermal into the magnetic regime. In order to determine the transduction efficiency between these two states, it is necessary to calculate the amount of heat (Q$_{in}$) flowing into the system to produce a temperature change (ΔT). This is given as:

\[ \Delta Q_{in} = \Delta Q_{out} + \Delta W \]  \hspace{1cm} (2.26)

Using conservation of energy and knowing that all of the temperature dependent magnetic components are included in ΔW, the additional amount of thermal energy (ΔQ$_{out}$) to return the system to its initial temperature is contained in the lattice component:

\[ \Delta Q_{out} = \int_{T_1}^{T_2} C_p(T) \, dT \]  \hspace{1cm} (2.27)

The total thermal energy required to increase the system temperature from the cold temperature $T_1$ to the hot temperature $T_2$ is then determined by plugging Equations (2.25) and (2.27) into Equation (2.26):

\[ \Delta Q_{in} = \int_{T_1}^{T_2} C_p(T) \, dT + \Delta S_{mag} \Delta T - \mu_o (M [T_1] - M [T_2]) \Delta H \]  \hspace{1cm} (2.28)

From Equations (2.25) and (2.28), the total absolute thermal to magnetic transduction efficiency ($\eta_{abs}$) is:

\[ \eta_{abs} = \frac{\Delta W}{\Delta Q_{in}} \]  \hspace{1cm} (2.29)

Using the canonical definition of Carnot efficiency ($\eta_c$):

\[ \eta_c = \frac{\Delta T}{T_2} \]  \hspace{1cm} (2.30)

The relative efficiency ($\eta_{rel}$) can be calculated from Equations (24) and (25) as:
This formulation provides an approach to compare the transduction of thermal to magnetic energy with a metric that is consistent across the various transformation mechanisms. It can be seen that a larger change in magnetic entropy relative to the change in specific heat will yield a larger relative efficiency.

2.4.3 Results and Discussion

In order to compute the energy outputs and efficiencies of the selected test materials, Gd and NdCo₅, the thermodynamic energy formulation was coded into Mathematica to facilitate a numerical solution for each process in the thermodynamic cycle. This was accomplished by first obtaining the saturation magnetization (Mₛ), heat capacity (Cₚ), and magnetocrystalline anisotropy coefficients (K’s) as functions of the temperature from the literature²⁸⁻⁶¹ and fitting each set with a spline for continuous differentiability. The calculation also necessitates a declaration of the external independent parameters: applied field (Ĥ), initial and final temperatures (T₁ and T₂), and the shape of the magnetic element via the demagnetization factors (N̂). For simplicity, only elliptical elements were considered in this study using the formulation conceived by Osborn¹²; however, demagnetization factors for other shapes exist in the literature and can be used in their place. In order to visualize how these parameters affect the magnetic energy profile of a system, 3D energy plots were generated. By minimizing the magnetic energy, Equation (2.15), with respect to magnetization direction in spherical coordinates (θ̂), i.e.
for a given temperature and applied magnetic field, the direction of magnetization can be determined. Repeating this calculation as a function of T allows us to track the magnetization vector as a function of temperature. The energy difference between initial and final states of the system can then be determined and used to estimate the efficiency of a thermal cycle.

Figure 14: Energy surfaces for NdCo$_5$ shown with the applied field vector (H) in green and the resulting magnetization vector (M) in red. The black and blue arrows correspond to the C and B axes of the hexagonal crystal, respectively. The position of M is determined from minimization of the energy function as a function of magnetization direction angles. Left – The energy surface of a NdCos sphere at T = 255K with a 100 Oe field applied at $\alpha = 45^\circ$ and $\beta = 45^\circ$. Right – The energy surface of NdCos at T = 286K with the same applied field parameters. It should be noted that the blue and red colors represent the negative and positive relative energies, respectively.

With hexagonal, six fold, crystal symmetry, global minimization has the potential to return six magnetization vectors which are all equivalent in the absence of a symmetry breaking magnetic or demagnetization field. Figure 14 provides two examples of the energy surfaces for NdCo$_5$ above
and below the spin reorientation transition temperature. It is apparent that NdCo₅ has an energy surface with six symmetrical energy wells, with blue surfaces corresponding to a negative total energy value and red to a positive value; negative energy values are a result of the magnetocrystalline parameters, which are normalized to 0 at not at absolute zero, but rather at Tₑ, where magnetic cohesion disappears.

Multiple energy minimums can cause numerical issues since the magnetization vector for the material element is non-unique. In a continuum sense however, the magnetization is expected to transition continuously from one state to the next as the independent parameters of the system change, for example as temperature is increased. To address numerical issues due to non-unique solutions, we broke the energy minimization routine into two parts. The algorithm was initiated by computing a global energy minimum at the prescribed initial temperature and selecting a specific magnetization state. From there a local energy minimization scheme, in conjunction with the global minima computed at the temperature extremes, were used to compute local minima at differential temperatures across the prescribed interval to track the shortest path to connect the global minimum. This methodology guaranteed a continuous transition of magnetization vectors for all possible input parameters.
Figure 15: Magnetization angle for NdCo$_5$ as it transitions through its spin-reorientation zone, as defined between $T_L$ and $T_H$

Figure 15 illustrates how the axial angle and energy surfaces vary with temperature for a perfect single domain sphere of NdCo$_5$ transitioning through its spin reorientation region. Below the SR region, as seen in the top left inset, the six energy minima lay in the basal plane with preferences at the vertexes of the hexagonal crystal. As the temperature increases beyond 260 K, the middle inset shows two easy cones of six fold symmetry remaining of the original surface which begin to collapse toward the C-axis as the temperature is further increased. It can also be seen that energy maxima nucleate along the B-plane beyond 260 K and continue to grow as the temperature is swept to 286 K. As the temperature is increased beyond the SR region, the energy minima collapse completely to the C-axis and the entire basal plane becomes energetically unfavorable where it can be seen to contain six maxima along the edges of the hex crystal in the right most inset. Simply put, the easy axis rotates from 90 degrees below 260 K to 0 degrees above 286 K. With
magnetization direction as a function of temperature computed, it was then possible to calculate the thermomagnetic work potential and efficiency of this transition.

<table>
<thead>
<tr>
<th>Material</th>
<th>Transition</th>
<th>$T_L$ [K]</th>
<th>$T_H$ [K]</th>
<th>$Q_{in}$ [J/m$^3$]</th>
<th>$W_{out}$ [J/m$^3$]</th>
<th>$\eta_{abs}$</th>
<th>$\eta_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>SR</td>
<td>219</td>
<td>243</td>
<td>4.67 E7</td>
<td>10.2 E5</td>
<td>0.02%</td>
<td>0.01%</td>
</tr>
<tr>
<td></td>
<td>Curie</td>
<td>283</td>
<td>288</td>
<td>1.31 E7</td>
<td>6.83 E5</td>
<td>0.52%</td>
<td>30.4%</td>
</tr>
<tr>
<td>NdCo$_5$</td>
<td>SR</td>
<td>255</td>
<td>286</td>
<td>1.04 E8</td>
<td>2.57 E6</td>
<td>2.4%</td>
<td>22.2%</td>
</tr>
<tr>
<td>Bi$_2$Te$_3$ (Ref-18)</td>
<td>TE</td>
<td>303</td>
<td>553</td>
<td>-</td>
<td>-</td>
<td>7.2%</td>
<td>15.9%</td>
</tr>
</tbody>
</table>

The work and efficiencies were computed for Gd’s spin reorientation, Gd’s Curie point operation, and NdCo$_5$’s spin reorientation by using Equations 21 through 27 and their numerically computed magnetization states. In these calculations, the applied magnetic field was 100 Oe at $\alpha$ and $\beta$ equal to 45$^\circ$ to guarantee that the spin reorientation always occurred along the same plane. The operating temperatures were chosen to maximize the relative efficiency ($\eta_{rel}$), our prescribed figure of merit. These results were compiled in Table 2. For Gd it can be seen that operating about its SR temperature actually results in a significant reduction in performance as compared to operating about its Curie point: 30.4% relative efficiency for Curie to 0.01% relative efficiency for spin reorientation. NdCo$_5$, on the other hand, showed an order of magnitude increase in work density, as well as an increase in absolute efficiency as compared to either Gd example. It should be noted, however, that the relative efficiency for NdCo$_5$ was about 8% smaller than the efficiency for Gd operating about its Curie point transition. This is reasonable as the operating temperature differential is approximately 6 times larger for NdCo$_5$ ($\Delta T$=31 K) than Gd ($\Delta T$=5 K) about its $T_c$ which significantly reduces the ratio of the absolute efficiency to the Carnot limit. For comparison the most efficient thermoelectric generator is included for the information that is available in the literature$^{16,18}$. While the absolute efficiency is superior of Bi$_2$Te$_3$ its operating temperature
differential is 250 K which yields a relative efficiency half as large as the calculated thermomagnetic efficiency of Gd.

The validity of the calculations was checked by determining which term dominated Equation 15 across the operating temperature differential and compared its magnitude of change to the reported experimental results\textsuperscript{27,58,59}. When the materials operate about their SR zones, the magnitude of their magnetostatic energy is approximately constant, and the majority of the temperature induced variation occurs in the magnetocrystalline parameters, where the energy densities are on the same order as the calculated work. For operation about the Curie point, the magnetocrystalline terms reduce to zero, such that only the magnitude of magnetization changes with temperature. For Gd, the method described herein was compared against Hsu et al\textsuperscript{27}, where the work was computed from the area between M-H loops, and was seen to yield identical results.

An interesting observation was made regarding the stability of the spin reorientation transitions of the two materials under the application of externally applied anisotropy fields. NdCo\textsubscript{5} experiences almost no variation in the shape of its energy surface for any simulated elliptical profile and sees its axial angle of magnetization ($\theta$) shift by only about 1° when the geometry is swept from a perfect sphere to either an oblate or prolate spheroid with aspect ratio 100:1. This behavior is a consequence of the fact that the magnitude of the magnetocrystalline terms are orders of magnitude larger than the demagnetization values associated with the geometric fractions of saturated magnetization. Practically, this means that, so long as nanostructures of NdCo\textsubscript{5} can be deposited epitaxially and below the critical size at which domain formation becomes energetically unfavorable, the overall tolerances and defects associated with lithographic patterning should have negligible effects on the expected thermomagnetic behavior.
Figure 16: Gd energy surfaces at the beginning (220 K) and end (260 K) of the unbiased spin reorientation transition. Left: Oblate spheroids with an aspect ratio of 2:1. Middle: Perfect spheres, Right: Prolate spheroids with an aspect ratio of 1:2.

By comparison, a definite lack of stability was observed in Gd, which exhibits a relatively weak magnitude of total magnetocrystalline anisotropy near its spin reorientation transition. It was determined that the magnetization angle at any given temperature could be modified significantly by geometric alteration. Figure 16 shows how sweeping a spheroid of Gd from an oblate spheroid of aspect ratio 2:1 to a prolate spheroid of aspect ratio 1:2 prevents the spin reorientation transition across the temperature range that it is expected to occur for an unbiased geometry, albeit in different ways. For the oblate spheroid, an easy plane of energy minima forms on the basal plane of the hexagonal crystal and the magnetization does not start to rotate off of the basal plane until
approximately 275 K and does not finish its reorientation until nearly 295 K. Conversely, prolate geometries which bias the C-axis of the hexagonal crystal drive the spin reorientation to a lower temperature with start and end temperatures of approximately 180 K and 240 K, respectively. Thus, unlike operation about the Curie point, materials exhibiting a spin reorientation transition can be tuned to the necessities of the application space by controlling external anisotropy fields such as the shape controlled demagnetization, applied magnetic field, or magnetoelastic stresses, when these fields are on the same order as the magnetocrystalline anisotropy.

2.4.4 Concluding Remarks

An energy formulation was developed to predict the thermal and geometric effects on the magnetic landscape of single domain ferromagnetic elements. From this formulation, it was shown that magnetic entropy can serve as a unifying metric for calculating the work output and efficiencies of thermomagnetic materials, even as they undergo different types of transitions. It can be seen that crystals which have magnetocrystalline anisotropic energy densities that are an order of magnitude larger than their magnetostatic terms can significantly outperform materials which are thermomagnetic cycled about their Curie point. This work identified NdCo$_5$ as having an energy density of 2.57 E6 J/m$^3$, an order of magnitude improvement over single domain Gd operating about its Curie point, while still maintaining a relative efficiency of 22.2%, which is only approximately 8% lower than Gd. The theory also shows that with a full consideration of the 3-D energy surfaces and magnetic anisotropies, spin reorientation transitions can be tuned for various temperature regimes to provide unique adaptability to the application space and environment of operation.
2.5 Fabrication of NdCo5 films to Enable Spin-Reorientation Harvesting

2.5.1 Background and Initial effort on Textured Gd

The effort which was originally intended to produce single domain Gd elements for a harvesting apparatus operating about the Curie point led to some interesting observations of the effects of magnetocrystalline anisotropy and how to texture films to maximize its effect. This effort was initiated by attempting to evaporate Gd using the CHA Industries Solution Evaporator available at UCLA’s Integrated Systems Nanofabrication Cleanroom (ISNM). Even though these samples were capped with about 10 nm of self-passivating platinum (Pt), the magnetization values present in the literature were unable to be achieved. It was determined that this was due to the fact that the cryopump used to maintain the vacuum was only rated for $5 \times 10^{-7}$ Torr, which was insufficient to prevent oxidation from occurring in Gd during the evaporation process. As evaporation systems are also unable to produce crystalline films, the approach was modified to utilize an ultra-high vacuum (UHV) sputtering system. The Denton UHV sputtering system was capable of achieving $5 \times 10^{-8}$ Torr and was run in DC sputtering mode in an Argon (Ar) atmosphere with a pressure of $10^{-3}$ Torr with a flow rate of 20 SCCM. The 99.9% pure Gd target was sputtered at 30 W and a deposition rate of ~1 Å/s to a thickness of 25 nm and was then capped with 20 nm of Pt before breaking vacuum.
The sputtered film was examined by x-ray diffraction (XRD) to test for crystallinity and superconducting quantum interference device (SQUID) magnetometry to examine how the magnetization changed with temperature using the zero-field cooling/field cooling (ZFC-FC) technique. These results are presented in Figure 17. It can be seen from the XRD intensity plot that the Gd film showed a high degree of crystallinity with a sharp peak in the [002] direction, corresponding to the C-axis direction of the hexagonal crystal. The ZFC-FC measurement was taken in the in-plane orientation using a SQUID and showed a distinct hump between 220 and 260 K, indicating that the magnetic moment rotated into the direction of measurement. This anomaly is consistent with measurements for single crystal Gd\textsuperscript{62,63} and shows that the film was deposited with sufficient epitaxy to achieve spin reorientation, which is an interesting distinction between this work and the previously published work by Berger et al\textsuperscript{63} wherein no temperature dependent magnetic rotation occurred. Their explanation was that sufficiently thin films exhibit such a large shape anisotropy that rotation into the out of plane direction should be entirely energetically unfavorable. It was believed that grain boundaries observed in their film acted as effective defects.
which interfered with the long range order required to produce spin reorientation, but that the large degree of epitaxy observed in our films facilitated the spin reorientation response.

Figure 18: Arrott plot for 25 nm sputtered Gd thin film deposited under UHV

Figure 18 presents the Arrott plot consisting of $M^2$ vs $H/H$ values obtained from the isothermal magnetization data of our epitaxial Gd thin films. The curves are generated from measurements conducted at five different temperatures. The Curie temperature is canonically defined from an Arrott plot as the temperate whose curve, when extrapolated, intersects the origin. For this Gd film, it was found that the saturation magnetizations measured at the lower temperatures are similar to those presented by Dan’Kov et al\textsuperscript{36}; however, the measured values became disparate at higher temperatures. The Arrott plot from the sputtered film shows that the Curie temperature is
approximately 278 K, representing a roughly 15 K shift from the bulk critical point at ~298 K, which was verified from the available evaporation source ingot. In the literature, shifts in the Curie temperature were also observed in various epitaxial and sputtered Gd films. The change of $T_c$ in the sample was attributed to internal stresses which were introduced during the sputtering process. This process of shifting $T_c$ is an interesting one because it shows that by modifying the crystalline and magnetic ordering of a material, in this case by depositing a very thin film epitaxially and altering the anisotropy conditions, it is possible to tune the thermomagnetic behavior.

![Figure 19: Left - Isothermal magnetization curves of Gd nanobar array. Right – (a) TEM image of Gd nanobar, (b) Diffraction pattern of nanobar cross-section, (c) HRTEM of nanobar, (d) Select area FFT image with FCC zone, (e) HRTEM image of nanobar, (f) Selected area FFT image of HCP zone.](image)

When the same deposition process was used in combination with a lift-off procedure to produce nano-structures, in an attempt to create single domain elements, the saturation magnetization and coercivity results proved unsatisfactory. These results can be seen on the left side of Figure 19.
From the M-H curves it was observed that the saturation at 53 K is less than 500 emu/cm$^3$, when it should be closer to 2000 emu/cm$^3$, and has a coercivity of less than 500 Oe. This most probably indicates a non-uniform crystallinity. It was also expected that, due to the magnetocrystalline anisotropy change across the spin reorientation transition, there would be a change from easy to hard axis as the temperature was increased, however that was not observed in the nanostructures. Given these disparities, the nanobars were examined under a high resolution transmission electron microscope (HRTEM), Figure 19 Right, where it was noticed that the Pt capping layer failed to coat the sidewalls after lift-off, leading to a dramatic reduction in the amount of ferromagnetic material present by oxidation, and that different regions of the bars had different crystal structures; the cubic (FCC) zone seen in subset (d) produces significantly less magnetocrystalline anisotropy than the hexagonal (HCP) zone in subset (f).

The reduction in saturation magnetization along with the absence of shape anisotropy induced single domains in the Gd nanobars can be attributed to oxidation as well as non-uniform morphologies in the films crystallinity. The presented results show that the crystallographic ordering, and uniformity of the film has a substantial impact on the magnetic anisotropy and magnetic moment of Gd nanostructures. Utilizing these realization were turned out efforts to the fabrication of NdCo$_5$ which should show a significant increase in Spin-Reorientation while having more stability in its microstructure.

2.5.2 Fabrication of NdCo$_5$

This section focuses on sputter deposition of thin film epitaxial NdCo$_5$. While this was attempted, the stated objective of creating an epitaxial thin film of NdCo$_5$ was not actualized. However, great strides were made which narrowed the selection space and provide a direction for further research
in this arena. Unlike elemental gadolinium, NdCo\textsubscript{5} is a bimetallic compound which requires precise stoichiometric control to achieve the desired magnetic properties. In the literature epitaxial thin films have been produced by pulsed laser deposition (PLD) using co-deposited single element targets\textsuperscript{59}, however this method was unavailable to us and would prove cost and time prohibitive in the event of desired scale-up. Thus an attempt was made to epitaxially deposit this material by a process of co-sputtering and annealing. That process is discussed presently.

![EDS results of Nd-Co deposition on Si substrate. Inset shows co-sputtering configuration.](image)

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<th>Weight % Error</th>
<th>Atom %</th>
<th>Atom % Error</th>
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Figure 20: EDS results of Nd-Co deposition on Si substrate. Inset shows co-sputtering configuration.

Neodymium and cobalt targets of 99.9% purity were obtained from the Kurt J. Lesker Company and calibrated into our Denton UHV sputtering system. Figure 20 shows the co-sputtering configuration and the initial attempt to deposit the material on a silicon substrate. The parameters of deposition were an Ar pressure and flow rate of 2.5 mTorr at 20 SCCM, sputtering
powers of 280 and 42 Watts for Nd and Co respectively, a pre-sputter time of 360 sec, and a target to substrate distance of 5cm. After depositing the 100 nm film, the composition was examined using electron diffraction spectroscopy (EDS) to provide the atomic percentage of each element present. Stoichiometric NdCo$_5$ should be 16.67% Nd and 83.33% Co, but the initial attempt showed approximately 5% more Nd content than desired.

![XRD:](image)

**Figure 21: XRD results of recrystallization study on original Nd-Co deposition**

Even with this disparity measurements were performed to create a baseline for recrystallization temperatures. This work included measuring the XRD response following annealing the sample in atmosphere at temperatures ranging between 500° and 850° C. The results are presented in Figure 21. The data shows that the sample became crystalline once annealed above 750° C. While a moderate peak presented itself along the (002) C-axis direction, the largest peak was in a cubic (101) direction. This can be partially attributed to compositional variation, but it was suspected that the cubic Si substrate provided the greatest contributing factor and one that would not produce epitaxial NdCo$_5$ structures. However, these results indicate that temperatures above 750° C are required to crystallize the deposited films.
Figure 22: Left – EDS of 100 nm of NdCo$_5$ film on sapphire. Right – XRD of 100 nm NdCo$_5$ film on sapphire.

In subsequent runs sapphire substrates, being a hexagonal crystal with lattice parameters within 4% of the desired NdCo$_5$ crystallography, were used to deposit the NdCo$_5$ film. This substrate choice was predicted to produce conditions from which an epitaxial film could be produced if the deposition and crystallization rate could be adequately controlled. During deposition on this substrate a parametric study was conducted wherein the driving power to the plasma sources was proportionally modified to tune the NdCo composition. Figure 22 provides the EDS and XRD results for a NdCo$_5$ sample once the appropriate deposition parameters were. From the EDS results, large peaks appeared corresponding to the aluminum and oxygen present in the substrate, however it can be seen that after subtracting out the counts due to the substrate that the desired NdCo$_5$ composition was obtained (i.e. see circled composition in Figure 22). The XRD study in Figure 22 right was conducted on a both bare sapphire wafer and the unannealed film sample which showed very strong agreement between the lattice structures of the two materials, indicating that film was apparently epitaxial deposited without post deposition annealing. This result suggested that the deposition energy was sufficient to at least partially crystalize the film as a crystalline structure is observed in the XRD.
Using the unannealed sample that appeared to be epitaxial deposited shown in Figure 22, the NdCo$_5$ film magnetic response was measured using SQUID at temperatures below (240) and above (298 and 350) the SR zone. The results are presented in Figure 23. The magnetization curves were taken in the out-of-plane (C-axis) direction. It was expected that the M-H loops would show a hard axis at less than 250 K, which would then transition to an easier axis, with a larger coercivity, above 280 K. Here it is important to also point out that the overall coercivity was only 200 Oe, much lower than the expected 2500 Oe at 350 K in a single crystal. The smaller coercive field was originally attributed to the lack of a fully crystalline material; it was hypothesized that the materials contained both amorphous and crystalline regions through the thickness of the film producing a softer magnetic structure. To resolve the amorphous/crystalline problem the films a portion of the sample was annealed at 850 $^\circ$ C. However, upon magnetic measurements of the annealed sample and subsequent measurements on composition, it was found that the Nd content of the annealed portion dropped substantially. The remaining thin film contained only trace Nd content. At this stage it was determined that, like Gd, Nd is highly reactive and a capping layer would be necessary to prevent loss of Nd content during heat treatments.

Figure 23: Magnetization curves of 100 nm of NdCo$_5$ on sapphire
During the next set of depositions 10 nm of Ti was sputtered over the top of the NdCo₅ in-situ, before breaking vacuum. Ti was chosen because of its self-passivating oxide layer. The argon flow rate was reduced from 20 SCCM to 12 SCCM in an attempt to slow the deposition rate and attain a higher ordering of the NdCo₅ crystals. Figure 24 shows the magnetization curves for the Ti capped sample. Using the same experimental procedure in the SQUID with additional measurements performed at colder temperatures, a spin reorientation appears to be present between 200 and 350 K. While this temperature differential is much larger than expected, it showed that this deposition method had promise to achieve the desired effect. Additionally, it was hypothesized that the lower coercivity value, 100 Oe compared to the predicted 2500 Oe, was due to internal stresses and could be rectified by annealing the sample to relax the crystal lattice.
This sample was subsequently annealed to 850 °C, for 1 hour, in a tube furnace under a reducing environment, 90% argon with 10% hydrogen to prevent oxidation. Figure 25 shows the results of the repeated magnetization curves after annealing and subsequent XRD. It can be seen that the annealing increased the coercivity from approximately 80 to nearly 250 Oe, which was attributed to a reduction in film stress and potential relaxation of the crystals into a more ordered state. Unfortunately, the reorientation observed before annealing was absent. The XRD appears to indicate that post annealing relaxes a portion of deposited film into a cubic form, with a notable peak forming in the (110) direction as well as the hexagonal (002). Additionally, WDS results showed that the Ti capping layer was depleting the Nd during the annealing process. To prevent this reaction in subsequent depositions, future runs were capped with tantalum (Ta), a material which is much more stable and less reactive at high temperatures.
Figure 26: Left – XRD results for Ta capped NdCo$_5$ after 2 hour anneal at 1000$^\circ$ C for 2 hours; Right – ZFC-FC results for the same sample between 100 and 350 K.

Figure 26 shows the crystallography and temperature dependent magnetization results for one of the stoichiometric NdCo$_5$ samples capped in Ta after a 2 hour anneal at 1000$^\circ$ C. The XRD plot shows peak counts very similar to the Ti coated sample in Figure 25, indicating that the sample crystallized during the annealing process. A WDS stoichiometry study (not shown) indicated NdCo$_5$ composition had been achieved. That is, the values are close to those shown in Figure 14 left, both before and after annealing. Given the compositional and crystallographic success on this sample, the samples were examined for their magnetization as a function of temperature using ZFC-FC and a valley was observed at 250 K during the field cooling portion of the experiment. This anomaly in the in-plane magnetization measurements suggests that the magnetization is rotating into the direction of measurement at this temperature, matching the theoretical prediction. However, the magnitude of this change was only approximately 5 emu/cc, at an applied field of 50 Oe. It was postulated that the magnitude was smaller than originally anticipated due to the fact that this film appeared to be polycrystalline rather than textured. The less than fully crystallized regions contributed less to magnetization rotation due to being less thermomagnetically coupled. Magnetization loops at constant temperatures were performed to confirm the hypothesized lack of global easy axis rotation.
The results in Figure 27 confirmed our suspicions that while the sample was noticeably crystalized, that the uniformity of the crystallization was not epitaxial. This can be observed in the small coercivity values, approximately 100 Oe instead of the expected 2500 Oe, and absence of a hard-axis curve for the measurements at 298 and 350 K. It was hypothesized that in order to achieve the required crystal epitaxy through the thickness of the film, to obtain spin reorientation, it would be necessary to heat the substrate at or above 850 during the co-sputtering processes; an ability that I did not have access to for this study. Additionally, field alignment was attempted, an application of 3000 Oe along the C-axis, during two different annealing processes: vacuum annealing at 750° C for 2 hours, the max that our cryo-pump could handle, and tube furnace annealing at 1000 ° C for 1 hour under the reducing environment. Neither of these methods significantly improved the crystal uniformity or magnetic properties.
Figure 28: Cross sectional TEM micrographs of Terfenol-D thin films crystallized by (a) substrate heating and (b) post annealing.

While it is believed that sputter deposition can be used to successfully deposit epitaxial thin film NdCo$_5$, it is posited that in-situ substrate heating at 850° C is required with both minimal Ar pressure and under UHV. Figure 28 illustrates the disparity in crystallization methods for a different rare earth intermetallic compound, Terfenol-D, but the crystallization process is understood to be similar. In this tangential effort, it was seen that when the Terfenol-D film was crystallized via substrate heating during sputter deposition, as seen in Figure 28(a), that after the first 20-30 nm of polycrystalline grown that the subsequent grains began to grow in a textured fashion. This phenomenon is characterized by the striated grain pattern on the right side of Terfenol-D film. By comparison, when Terfenol-D films are crystallized by post annealing, Figure 28(b), a more homogenous polycrystalline film is produced. This non-oriented polycrystalline morphology is understood to suppress the Spin-Reorientation process. While the post annealing method is useful to uniformly grow randomly oriented crystals from an amorphous film with very low film stress, it is believed that the substrate heating method provides sufficient mobility in-situ for the co-sputtered material to nucleate textured crystal growth, and remain contaminant and oxide free as UHV is never broken. While epitaxial thin films exhibiting the Spin-Reorientation
response this was not successfully achieved, it is believed that his study has laid the ground work for future work in this area.

2.5.3 Concluding Remarks

Stoichiometric, crystalline, NdCo$_5$ was successfully produced via co-sputtering. While post annealing in an UHF environment led to complete recrystallization, the orientation of said crystals were not aligned in an epitaxial fashion. It was shown that NdCo$_5$ is highly reactive, even in a crystallized state, and that proper encapsulation is necessary to prevent oxidation and contamination. Given the disparity in crystallographic growth observed in Terfenol-D, it is believed that substrate heating during the sputter deposition process, as opposed to post-annealing, can yield the epitaxial growth required to achieve spin reorientation.
Chapter 3: **TRANSUDING EM RADIATION INTO ELECTRO-ACOUSTIC POWER**

3.1 **Synopsis**

A multiferroic antenna was designed using a finite element model (FEM) in COMSOL Multiphysics, then optimized by incorporating a particle swarm optimization (PSO) scheme in MATLAB. Antennas were designed to operate at various center frequencies ranging from HF to VHF and show that, by leveraging multiferroic coupling effects, the size of a receiving structure could be orders of magnitude smaller than a typical conducting dipole antenna. The multiferroic receiving structure consists of an array of ferromagnetic nickel (Ni) resonating structures which are strategically placed on a ferroelectric lithium niobate (LiNbO3) substrate to elicit a coherent electromechanical surface acoustic wave (SAW) which transduces the incoming electromagnetic (EM) signal to interdigitated electrodes (IDE’s) where the signal can be processed. By converting the an EM wave, travelling at the speed of light in free space, into a coupled electromechanical wave, operating at the speed of sound in the substrate, the effective wavelength is reduced by approximately 5 orders of magnitude. The specifics of how this phenomenon is leveraged will be covered in the forthcoming chapter.
3.2 Literature Review

![Experimental setup and results for a Magnetoelectric phase shifter](image)

Figure 29: Experimental setup and results for a Magnetoelectric phase shifter\textsuperscript{66}.

Dynamic magnetoelectric effects have been explored in the literature since the 70’s. Ganguly in 1975 showed that a SAW delay line consisting of a magnetoelastic Ni film deposited between two sets of IDE’s could be used to shift the electroacoustic response under the application of a static magnetic field\textsuperscript{66}. The setup and results of said system are presented in Figure 29. In this work it was shown that the coupling behavior is highly dependent on the frequency of SAW wave as well as the magnitude of the applied biasing field. The first harmonic SAW response of LiNbO\textsubscript{3} at 70 MHz was observed first to achieve a maximal phase shift of 14 degrees when a 1200 G field was applied in the propagation direction. By comparison when the same field was applied to the 3\textsuperscript{rd} harmonic SAW at 210 MHz, the phase shift increased to 80 degrees. This experiment showed that the greatest change in the electroacoustic propagation velocity occurred when the applied magnetic field generated a magnetoelastic anisotropy induced compressive state in the Ni. This compressive loading effectively increased the “stiffness” of the Ni and therefore created a mechanical impedance mismatch in the path of the coupled wave. Additional work was performed in this area for stronger magnetoelastic materials\textsuperscript{67,68}, and with regard to additional damping.
criteria. This notion of magneto-electro-mechanical coupling in the MHz regime formed the basis for continued study in this area.

In an approach more closely related to antenna design, Mindlin formulated a mechanism for EM radiation from a piezoelectric media. Contrary to previous reports by Tiersten, who concluded that vibrations in a dielectric could not launch an EM wave due to “trapped energy” associated with a purely reactive mode, Mindlin derived a method for examining the Eigen space of AT-cut quartz to determine whether a propagation mode were possible. In this study Mindlin isolated a thickness-shear mode for a plate resonator that should idealistically output \( 25 \times 10^3 \varepsilon_0^2 \) W/cm\(^2\) such that for 10 µε the total power radiated was predicted to be 25µW/cm\(^2\). A method of practically creating an electrode pattern to generate the requisite loading conditions has yet to be realized.

Utilizing the efficient transduction of the thickness-shear mode, advancements were made in the realm of resonator based magnetoelectric sensors. Srinivasin performed a case study on single phase and composite multiferroic thin films with the goal of enabling high sensitivity DC magnetometers, tunable microwave devices and miniature antennas. Loss mechanisms associated with leakage and eddy currents are identified to be associated with the highly conductive ferromagnetic materials that make up the multiferroic composites especially at higher frequencies. Solutions to remedy these loses are layering techniques such as molecular beam epitaxy (MBE) or pulsed laser deposition (PLD) which can deposit alternating layers of material below the thickness at which eddy currents are prevalent and a consideration of magnetoelastic oxides which have significantly smaller conductivities.
Following that conclusion, Vopsaroiu developed a hexaferrite based multiferroic composite for the detection of static magnetic fields. The benefit of selecting a hexaferrite as the ferromagnetic material was shown to be two fold. First the conductivity is minimized to prevent leakage and eddy current loses. Second the coercivity of this class of material is very low, nearly behaving superparamagnetically. This minimal hysteresis is ideal for sensitive, low field, magnetometers, as the detection characteristics are nearly linear. The multiferroic plate structure described in this work operates on the bulk acoustic wave (BAW) principle under combined variable DC magnetic field loading and small constant AC magnetic perturbation. Reported was a perfectly linear magnetoelectric voltage generation in the mV regime for DC magnetic field signals ranging from -2000 to 2000 Oe. This design showed excellent promise as a magnetoelectric transducer but further advances are necessary to accommodate operation at high frequency.

Multiferroic transduction at microwave frequencies was reported by Pettiford in a study on yttrium iron garnet (YIG) deposited on PZT. The bimorph structure presented in this work was operated as band-reject filter at 10MHz and a pass band filter at 1-7 GHz. Throughout the experiments shown, the ferromagnetic resonance (FMR) characteristics of the YIG were modulated under the application of an applied DC magnetic field. These changes in the high frequency magnetic response of the YIG also affect the acoustic wave response and its mechanical coupling behavior with the PZT. By optimizing the volume ratios of the ferromagnetic to ferroelectric material and utilizing a DC bias to anisotropically bias the bimorph, the transmission coefficient the device was shown to achieve a peak attenuation of 60 dB in its filter responses. Employing the coupling methodologies presented in this literature review and exploiting symmetry breaking anisotropic biasing, it will be posited in the following section that an electrically small antenna can be designed to efficiently transduce EM radiation in the HF and UHF ranges.
3.3 HF/VHF Multiferroic Receiving Antennas a Method of Actualization

3.3.1 Problem Introduction

The ability to significantly reduce the scale of antenna structures is a point of interest for many application spaces. A few primary examples include the reduction of VHF aircraft antennas such that they no longer carry significant aerodynamics footprints and HF antennas for implantable medical devices which would not see significant reduction in performance due to the proximity of water. It is believed that such a phenomenon can be accomplished by utilizing the intrinsic coupling inherent in multiferroic heterostructures to design antenna structures which are 4 to 5 orders of magnitude smaller than a typical dipole antenna.

![Diagram of multiferroic SAW receiving antenna](image)

**Figure 30: Philosophical approach governing the operating of a multiferroic SAW receiving antenna**

The philosophical approach to designing a multiferroic receiving antenna based in surface acoustic wave architecture is illustrated in Figure 30. The multiferroic heterostructure shown in the figure is comprised of 3 main parts. First are the magnetoelectric resonators; these ferromagnetic structures are designed to transduce incoming EM radiation into an acoustic wave. A large array of these ferromagnetic structures, which are designed to operate in a coherent resonant mode, serve to maximize the energy transduction from the magnetic to the mechanical regime and are seen as...
the blue rectangles on the left of the figure. The second component is the ferroelectric substrate seen in beige stretching the length of the figure. This material’s primary role is to serve as the medium to with which the mechanical oscillations in the magnetoelectric resonators are converted into a coupled electromechanical wave. Ideally this substrate is mechanically impedance matched to the resonator bed and maintains low mechanical damping and dielectric loss characteristics such that it can propagate a coupled wave with maximal amplitude for a significant distance. The third component is the interdigitated electrode (IDE), shown in gold on the right side of Figure 30, and output circuitry. The IDE structure transduces the electrical component of the traveling electromechanical wave into a signal which can be rectified by the circuitry to retrieve the information stored in the initial EM wave. It is paramount that the electrodes be specifically designed to harness the maximum voltage potential seen in the traveling wave oscillations and that the circuitry have the proper load impedance such that phase loss and signal reflection don’t wash out the signal transduction process completely. Using the notion that the size of resonant antenna structures are a prototypically bound to functions of the wave length; if an EM wave at the frequency of interest can be transduced from air into our heterostructure, then the corresponding size constraint is reduced by the ratio of the acoustic velocity in the materials over the speed of light in air. This serves as a 5 orders of magnitude reduction in scale and permits multiferroic structures to be significantly smaller than their purely electrical counterparts.

The following section will delve into how these phenomena are harnessed, the proper material choices to maximize the response, and how such a heterostructure can be designed, and fabricated. Studies were performed on structures designed for 18 and 150 MHz respectively. Descriptions of the modeling, optimization, fabrication and testing of the 18 MHz system utilizing
Ni and LiNbO$_3$ will be covered first. The work pertaining to the 150 MHz systems comparing Ni and FeGaB ferromagnetic materials will follow.

### 3.3.2 Theory and Modeling

Table 3: SAW materials for various wave types and their velocities$^{35}$

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</tbody>
</table>

In order to maximize the electroacoustic response the appropriate ferroelectric substrate needed to be selected. Table 3 provides a list of different materials typically used in different acoustic devices. Upon examining the different available materials and wave modes, the Rayleigh surface acoustic wave type was chosen as the nature of such waves is the most conducive to long distance, lossless propagation$^{76}$. Of those materials listed, LiNbO$_3$ has shown to have orders of magnitude stronger piezoelectric coupling, with sheer mode coefficients equal to 3.7 C/m$^2$ vs 0.04 C/m$^2$ for quartz, and was thusly chosen. From a mechanical impedance standpoint, it was known that propagation velocity, and thus the mechanical stiffness of the ferroelectric substrate relative
to a chosen magnetostrictive material, needed to be matched to maximize the coupling between the two materials. However, because of the highly coupled, anisotropic nature of these crystals, it would be necessary to determine which of the two crystal cuts would provide the optimal anisotropic propagation properties from their full tensoral properties.

Figure 31: (Left) Crystallographic orientation of LiNbO$_3$ trigonal crystals. Stiffness, piezoelectric and dielectric properties of the YZ cut (Middle) and YX-128° cut (Right) varieties. Insets of the two properties list show visualizations of electromechanical waves generated by uniform radial displacements within 100 mm wafers.

Figure 31 provides a diagram of the LiNbO$_3$ trigonal crystal as well as the full 3-D set of electromechanical properties for the two crystal cuts which exhibit Rayleigh wave propagation. The notation used to describe these crystals is as follows: the first axis direction indicates that the indicated wave type is designed to propagate, the second axis denotes the crystal axis which points normal to the wafer of material. For the YX-128° cut, for example, this means that the Rayleigh wave mode propagates best along the Y-axis and that the normal direction of the wafer is a 128° Euler rotation from the Z-axis toward the X-axis with the angle of rotation θ shown in Figure 31 left. To visualize the difference in electromechanical propagation behavior between the two crystal cuts, a FEM model was designed where 100 mm diameter wafers of the two cuts
were actuated by a uniform radial displacement as seen in the lower portions of Figure 31 mid and right. In these models, the deformation fringes show the mechanical displacement and the color scheme represents the voltage potential with red/yellow equaling positive values and teal/blue equaling negative. If one examines the fringe pattern in the Y direction (vertical), the YX-128° cut can be seen to have a more coherent electrical potential oscillation.

![Figure 32: Cross-sections of the YZ cut (left) and YX-128° cut (right) crystals in the Y direction.](image)

Cross-sections of simulated wafers cut in the Y direction are illustrated in Figure 32. These images specifically illuminate the differences in the potential coherency between the two cuts as the wave propagates from the center of the wafers. The degree of coherence is of extreme importance for our multiferroic SAW antenna, as electroacoustic waves generated by the magnetoeelastic resonators will need to be inherently coherent in order to design an electrode structure to detect the oscillation. If the two images in Figure 32 are compared with the notion of electrode placement in mind, it should be expected that the YX-128° cut would be much easier to design a differential electrode structure for. Interdigitated structures placed at the repeating intervals of surface peaks and valleys which could span the width of the cross section would allow for the electromechanical wave to be extracted as an electrical signal. By comparison, the “twisted” behavior seen by the YZ cut would require a diagonal electrode structure across its width to maximize the signal output and thus would be more susceptible to losses associated
with effects such as group delay or mixed mode propagation. Thus YX-128° cut was selected as the substrate of choice for the subsequent modeling and prototyping effort.

Table 4: Magnetostrictive materials suitable for high frequency magnetomechanical transduction

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_e$ (ppm)</th>
<th>$q_{33}$ (ppm Oe$^{-1}$)</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>-32</td>
<td>-0.17</td>
<td>200</td>
</tr>
<tr>
<td>CoFeB</td>
<td>-110</td>
<td>-5.00</td>
<td>160</td>
</tr>
<tr>
<td>FeGaB</td>
<td>70</td>
<td>7.00</td>
<td>65</td>
</tr>
<tr>
<td>Metglas</td>
<td>-110</td>
<td>-8.00</td>
<td>100</td>
</tr>
</tbody>
</table>

After selecting the ideal substrate material, it was necessary to down select from the available magnetostrictive materials which could be deposited on the chosen substrate. Table 4 outlines the materials which have been characterized for their dynamic responses. For maximum performance it’s ideal to maximize the piezomagnetic coupling coefficient $q_{33}$ which indicates the amount of strain generated as a function of magnetic field and match the elastic modulus to the substrate material to minimize the mechanical impedance mismatch. It was recognized that while Ni has an order of magnitude smaller piezomagnetic coupling coefficient than the other magnetoelastic materials, it is perfectly stiffness matched to LiNbO$_3$. When combining that fact with the ease of deposition both in nanoscale thickness via evaporation and sputtering, or at the microscale via electroplating, an initial effort was focused on Nickel. A case study focusing on FeGaB will be explored as an alternative later in a later section.
With an initial set of characteristic materials chosen, a finite element model (FEM) was developed to design the ideal heterostructure capable of transducing EM radiation into an acoustic signal. Like most FEM formulations, certain assumptions need to be made to generate a system of solutions which are stable, convergent and solvable in a reasonable amount of time. In order to accomplish this the ferroelectric and ferromagnetic behaviors were approximated as linearly piezoelectric and piezomagnetic for the LiNbO$_3$ and Ni respectively. The piezomagnetic Ni was treated as polycrystalline and multidomain with an isotropic saturation magnetostriction coefficient at -32 ppm, a relative permeability of 20 and all other properties defined by COMSOL’s built in material coefficients. The LiNbO$_3$ was treated with a full trigonal tensors defined in the Stress-Charge constitutive form with coefficient values provided in the literature by Weis and Gaylord. The surrounding air, gold (Au) IDE’s and SiO$_2$ isolation layer were treated as fully isotropic media and had all of their coefficients defined by COMSOL’s material library. Figure 33 shows the geometric layout of the modeled system. The geometry was broken up into two separate models and three different studies for numerical stability. Geometry 1 shows the quarter symmetry model of a representative model for the quasi-infinite array of Ni resonators on the LiNbO$_3$ substrate. Geometry 2 provides the extension of the substrate wherein the electromechanical wave is transduced into an electrical signal by the IDE structure and into a load circuit.
To couple an incoming electromagnetic wave into a multiferroic SAW structure and determine the outgoing electrical signal across IDE’s it was necessary include three physics packages: Electromagetic Waves Frequency Domain (EMW), Piezoelectric Devices (PZD), and Electrical Circuits (Cir). The EMW module defines the full set of Maxwell’s equations in frequency domain and is used to establish the incoming EM wave as a sinusoidal plane wave. This approximation is valid due to the fact that the piezomagnetic resonators are about 5 orders of magnitude smaller than the wavelength of the EM wave and thus the phase of said EM wave should be nearly constant over an aperture encompassing even a very large array of Ni elements. The EM wave is generated by a surface current of magnitude 1 A/m established at the upper Z boundary of the surrounding air and enforced by perfect electric conductors (PEC) and perfect magnetic conductors (PMC) placed on the short and long axis of the Ni resonator respectively. The lower Z boundary is also defined with a PEC to be congruent with it being defined as a ground plane in the PZD and Cir physics modules.

The PZD physics package is then used to define the piezomagnetic and resulting piezoelectric effects in the two separate geometries. The first encompasses the transduction of the EMW to the resonator bed. Here the Ni element and insulating SiO2 layer are set as both linear elastic and electrical materials. Within the linear elastic sub-module, an initial strain is defined for the Ni as a function of the magnetic field extracted from the EMW module to provide the piezomagnetic coupling. LiNbO3 is defined as a piezoelectric material in a fully anisotropic stress-charge form. The negative Z boundary is defined as fixed and grounded based on the constraints of the proposed testing apparatus and all boundaries in the XY plane are given symmetry and zero charge conditions to approximate a quasi-infinite array of Ni elements. A general extrusion mapping function is applied to a domain one quarter of the X spacing parameter from the positive
X symmetry boundary. This general extrusion is a general coupling operator used to feed displacement and voltage potentials from each node of the first geometrical component to the second which are handled in separate studies to accommodate computational performance. The second geometry contains an extended LiNbO₃ element and Au traces which make up the IDE’s. Within the second PZD physics the incoming negative X surface is given prescribed displacement and voltage conditions which are fed from the general extrusion coupling operator. Odd IDE’s are defined as terminal 1 with even IDE’s as terminal 2 and are pushed forward into the Cir physics module with a 1000 Ohm resistor placed between them to measure the outgoing voltage. The load resistance was chosen to maximize the power transfer to the circuit. The positive and negative Y surfaces are given symmetry and zero charge conditions to approximate their quasi-infinite nature and the bottom surface is grounded and fixed to match the conditions of geometry 1. Finally the positive X direction is terminated with a perfectly matched layer (PML) to prevent any reflection of the electromechanical wave off the positive X boundary which would interfere with the incoming wave. As the actual LiNbO₃ substrate wafer that this model simulates is several wavelengths larger in length than the array and IDE system, approximating the trailing surface in this fashion makes sense from both an elastodynamics and computational throughput standpoint.

The EMW solution is computed for geometry one first, using an iterative solver of either a biconjugate gradient stabilization (BiCStab) or fast generalized minimal residual algorithm (FGRES) numerical method to compute and feed forward the magnetic field in frequency domain. With the magnetic field calculated, its solution is fed into a second study for geometry 1 which solves the coupled piezomagnetic-piezoelectric physics. The resulting displacements and piezoelectric voltage are then pushed forward into a third study which solves the combined piezoelectric-circuit model for geometry 2 and provides the voltage output from the circuit model.
Figure 34: Visualization of the Particle Swarm Optimization Scheme\textsuperscript{79}. Inset (a) shows how each particle agent’s position is updated based on 3 weighting factors. Inset (b) provides a schematic of how the particles trace out a nonlinear parameter space and use their social interaction to attempt to reach a global optimum.

With the FEM model in place, an optimization scheme was developed in Matlab to serve as a wrapper and run a large series of Comsol FEM simulations. Particle swarm optimization (PSO) was identified as an ideal method to interrogate the large number of geometric variables that are used to define the multiferroic heterostructure. PSO is a meta-heuristic algorithm which can search any n-dimensional space that has a defined scalar output. An illustration of how PSO functions is shown in Figure 34. Each particle or agent is initialized with a random position and velocity...
defined in the n-dimensional parameter space. Following the evaluation of the scalar optimization function, Equation (3.1) is used to calculate each particle's velocity:

\[ v(n+1) = w \cdot v(n) + c_1 \cdot \text{rand} \in [0,1] \cdot (P_{\text{best}} - x(n)) + c_2 \cdot \text{rand} \in [0,1] \cdot (G_{\text{best}} - x(n)) \]  

(3.1)

In this formulation, \( w \) is the inertial weight which biases the calculated velocity as a proportion of previous velocity, \( c_1 \) is the cognitive weight which biases the agent’s velocity based on its personal best solution, and \( c_2 \) is the social weight which biases the function with respect to global best calculated for all agents. The cognitive and social weights are each multiplied by a random number between 0 and 1 to more effectively navigate local maxima and avoid getting “stuck” on parameter boundaries. The values of these weighting functions were chosen to match Robinson’s recommendations. The position of each particle is then updated by Equation (3.2).

\[ x(n+1) = x(n) + \Delta T \cdot v(n+1) \]  

(3.2)

Here \( \Delta T \) is the time step which was held constant at a value of 1 in our simulations. Consideration was then given how the boundaries of the parameter space would be handled.

![Diagram](image.png)

Figure 35: Options for parameter space boundary conditions.
Figure 35 outlines the three options for boundary conditions that a canonically used in PSO schemes. Absorbing walls nullify the component of velocity in the “direction of the boundary” effectively serving a perfect damping condition. This method is most suitable for small roughing parameter sets in which accumulation on a boundary indicates that the parameter space should be shifted in the direction of agglomeration. Reflecting walls invert the component of velocity in the “direction of the boundary”. This method is ideal when using a large rough parameter set whose bounds are heavily dictated by external constrains and where solutions are preferred away from the perimeters. Invisible walls impose no change in velocity when a particle passes out-of-bounds but also do not evaluate the optimization function outside of the parameter set. This method is most suitable for small parameter sets where a large number of particles are used to finely evaluate the parameter space. If a particle drifts out-of-bounds, this method relies on the social weighting function \((c_2)\) to effectively “pull” the particle back into the desired space. For this study the invisible walls boundary condition was modified such that if a particle passes out-of-bounds, then in addition to not solving the optimization function, the velocity function of Equation (3.1) is modified to set the inertial weight equal to zero. This served to reduce the number of time steps required to bring particles back into the parameter space and therefore reduce the number of total iterations required to converge to a solution even if the \(G_{\text{best}}\) was located near a boundary.

With the boundary conditions of the optimization scheme determined, it was necessary to determine appropriate termination conditions to halt the scheme in the event of convergence or gross divergence. Three termination conditions were set: a global residual error of 0.1%, a local residual error of 0.01% and an iteration limit of 100 time steps. The global error check results when all of the particle agents converge on the global defined best solutions. The local error check accommodates the situation where multiple meta-stable solutions occur with similar overall
magnitudes and is set to a higher tolerance to give an additional bias to the potential of finding a global maximum. The iteration limit is put in to stop the scheme if the results are divergent so that the scheme doesn’t have to be manually terminated. Once these conditions were input, case studies were performed for the two frequencies of interest.

### 3.3.3 HF 18 MHz Modeling and Evaluation

<table>
<thead>
<tr>
<th>Parameter Space for the 18MHz Ferromagnetic Resonator Bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Res Length</td>
</tr>
<tr>
<td>Lower Bound</td>
</tr>
<tr>
<td>Upper Bound</td>
</tr>
</tbody>
</table>

Figure 36: Schematic planar view of the quarter symmetry ferromagnetic resonator and surrounding piezoelectric substrate.

The effort to develop a multiferroic antenna was begun in the HF band at 18 MHz. This frequency was chosen with aerospace applications in mind as the characteristic length of electric dipole antennas at 18 MHz is approximately 16.5 meters, where a five order of magnitude reduction would prove invaluable if said antenna could prove viably mountable on an aircraft. The ferromagnetic resonator bed was chosen to be a rectangular array of rectangular elements. Figure
36 illustrates a planar schematic of the quarter symmetry implementation of the resonator array in Comsol. Since the goal is to generate a coherent electroacoustic surface wave which propagates over the surface of the piezoelectric substrate, we heuristically decided that a pure-bending mode would transfer the maximal strain from the magnetically actuated resonators. A parameters space which was hypothesized to encompass such a mode was developed for the array as seen in Table 5. The parameters of interest are the resonator length, width and height, as well as the x and y spacing between elements. All of the parameters except for the resonator height were defined as functions of the wavelength of the electroacoustic wave in the piezoelectric media except for the resonator height, which was defined explicitly to accommodate fabrication constraints. An early decision was made to attempt to maximize the magnetic material and thus aim for resonator thicknesses above 1 µm. For this reason electroplating was chosen as the deposition method, whose minimum reliable thickness was experimentally shown to be 4µm. This parameter set was input into the optimization function with output voltage across the IDT’s chosen as the scalar optimizing output and run to convergence.

Figure 37: Optimization results for the 18 MHz design. (a) Electric potential results for geometry 1, the quarter symmetry component shown on the general extrusion surface. Boxed results highlight solutions with the most
coherent potential in the upper third of the model. (b) Electric potential results for geometry 2, the extended piezoelectric element. The colored boxes match their counterparts from geometry 1.

Figure 37 shows the results of the first optimization solution for the 18 MHz antenna. In this study 10 particles were used and the personal best for each agent is displayed in Figure 37(a). From these results, the solutions with the most coherent electrical potentials are shown boxed. The solutions boxed in green was returned as the global best, returning the highest peak voltage across the IDT’s at 2.3 µV. The next best solution was returned by the solution boxed in purple with a voltage of 1.2 µV. Figure 37(b) shows the electrical potential results of geometry 2 for the two best solutions. Here a mostly coherent electroacoustic wave can be seen to propagate along the surface with a regular pattern of peaks and valleys. Using the parameter values of the global best solutions, fabrication of the device was initiated.

Figure 38: An Optical Image of the final nickel resonator structures electroplated onto a lithium niobate substrate
The array of nickel resonators shown in Figure 38 is fabricated on four inch diameter YX-128° cut lithium niobate wafers (Atom Optics) which have been optically polished on both sides to a final 500μm thickness. The XY plane of the lithium niobate crystal is aligned perpendicular to the flat of the wafer. The wafers are poled perpendicular to the direction of propagation during the growth process.

Table 6: Deposition parameters use to fabricate the seed layer for the electroplated nickel bed

<table>
<thead>
<tr>
<th>#</th>
<th>Material</th>
<th>Rate (A/s)</th>
<th>Thickness (nm)</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silicon Dioxide</td>
<td>1</td>
<td>20</td>
<td>Electrical isolation from the substrate</td>
</tr>
<tr>
<td>2</td>
<td>Titanium</td>
<td>1</td>
<td>20</td>
<td>Adhesion</td>
</tr>
<tr>
<td>3</td>
<td>Copper</td>
<td>3</td>
<td>100</td>
<td>Seed layer for electroplating</td>
</tr>
<tr>
<td>4</td>
<td>Titanium</td>
<td>1</td>
<td>20</td>
<td>Oxidation prevention</td>
</tr>
</tbody>
</table>

Fabrication begins with wafer inscription using a diamond scribe on the back of each wafer for identification during processing. A dielectric and metal stack is evaporated on the top surface of the wafer using an electron beam evaporation system (CHA Industries). This multi-layered system of materials acts as the seed layer for the nickel electrodeposition step and to electrically isolate the nickel resonators from the substrate. Table 6 lists the materials used to create the seed layer for the electroplating listed in the order they are deposited as well as outlining the deposition rate and a brief description of each layer.
Figure 39: Optical image of the patterned photoresist. Lighter areas are openings to the underlying titanium capping layer. Dimensions are annotated in the image.

After evaporation a negative tone photoresist, KMPR 1005, is spun onto the wafers. This photolithography step defines a through mask plating mold used in the growth of the nickel elements. The dimensions of the nickel resonators are determined from simulation results and shown in Figure 39 for a patterned photomask. The resist is spun to a film thickness of roughly 7 μm to accommodate the resonator design height of 6.4 μm without the occurrence of mushrooming at the top of the nickel element.

Following resist patterning the wafers is ready for electroplating. To expose the underlying copper plating seed, the titanium capping layer must be removed from the seed stack. Removal of the titanium is performed in a 1% hydrofluoric acid etching solution. Confirmation of etch completion is done visually. The plating solution is a commercially available, ready to use nickel plating bath of a Watt’s composition (Technics HT-2). The bath is maintained at 55°C with a
hotplate and an in-situ thermocouple. A constant current power supply is held at a current density of 5 mA/cm² during deposition. The total deposition time to achieve 6.4 μm is 64 minutes for a deposition rate of 100 nm/min at the selected current density. In the event of over-plating and mushrooming from the top of the plating mold, the excess film thickness is polished down with a chemical-mechanical polishing (CMP) system. Generally processed wafers do not require polishing, however, from previous testing the CMP parameters are: 1 PSI sample to plate pressure, 30 rpm plate speed, 100 nm alumina slurry. This results in a material removal rate of 1 μm/min for the electroplated nickel film.

Figure 40: Optical image of electrodeposited nickel resonators on the lithium niobate substrate. The plated nickel thickness was measured at 6.5μm by profilometry measurements.

The plating mold is removed with a commercial photoresist stripper (AZ 300T) at 80º C for 30 minutes. This exposes the underlying seed layer which covers the remainder of the wafer. This remaining seed layer is removed with a dilute hydrofluoric acid etch to remove the top titanium
capping layer followed by an APS 100 copper etch for the copper seed layer and another hydrofluoric acid etch to remove the final titanium adhesion layer and silicon dioxide isolation layer. Figure 40 shows the completed nickel resonators after the seed stack has been removed from the surface of the lithium niobate.

Figure 40: (Left) Final patterned transducer electrodes after liftoff of evaporated gold over a KMPR 1005 photomask. Dimensions are shown for the width and pitch of the IDT electrodes. (Right) Optical image of a completed sample showing the gold IDT electrodes and the electroplated nickel resonator array.

A second lithography step using KMPR 1005 is performed to define the IDT patterns used for device measurement. This negative tone photomask is used as a liftoff layer through which a conductive material is evaporated onto the surface of the lithium niobate at patterned openings in the film. Metallization of the IDT structures is completed by electron beam evaporation of titanium and gold of 20 nm and 100 nm respectively. An optical image of the completed electrode patterns is shown in Figure 41(Left) along with dimensions for the IDT pitch and finger width. The photoresist and undesired metal is removed using a commercial photoresist stripper (AZ 300T) heated to 80°C for ~12 hours. Figure 41(Right) shows an optical image of a completed test device with both gold IDT and nickel resonator patterns deposited on the surface of a lithium niobate wafer.
Figure 42: Left image shows a sample used in VNA based testing. SMA connectors are bonded in a single ended method directly to the IDT patterns. The sample shown to the right uses an amplifier and RF detector connected to one of the IDT patterns for testing with a lock-in amplifier.

Completed four inch wafers are diced into 40x70 mm plates containing the two sets of interdigitated transducer (IDT) patterns and nickel resonator elements. The sample dies are glued to carriers printed on Rogers Corp. 5880 RT/duroid substrates using commercial single part epoxy (E6000). A compliant, soluble adhesive is chosen for bonding to prevent excessive strain on the bottom surface of the die during curing and to allow for ease of die removal. Two carrier layouts are used which connect the IDT patterns to different testing systems. A direct connection layout used for testing devices with a network analyzer is shown in the left image of Figure 42. This connection method uses edge mounted SMA connectors soldered to CPW transmission lines. These transmission lines are connected using wire bonding to the IDT pads in a single ended (G-S) arrangement. A board layout for lock-in measurements is shown in the right image of Figure 42. The right IDT is directly connected to a surface mount SMA connector via a CPW transmission line. The opposing IDT is connected to an RF differential amplifier (AD8350-15). The output of the amplifier is converted to single ended operation and passed into an RF power detector (ADL5501) with the low-pass cutoff frequency set to a default of 100 KHz. The power detector
output is connected to an edge mounted SMA connector. A 5 volt linear voltage regulator (UA78M05) provides power to the amplifier and RF detector.

![Diagram of connections used in the acoustic send/receive test of an 18MHz antenna device using a lock-in technique.]

Figure 43: Block diagram of the connections used in the acoustic send/receive test of an 18MHz antenna device using a lock-in technique.

A simplified block diagram of the sample connections for this test is shown in Figure 43. Two testing methods are used to characterize the IDT to IDT transmission spectra of the antenna device as well as free space IDT coupling. A vector network analyzer (Agilent N5247A) is used to measure the S12 transmission response by connecting ports one and two to the IDT patterns on each die. This allows for the measurement of a full set of scatter parameters. The frequency is measured over a 10-50 MHz range using a coupled port power of -5 dBm. A second lock-in method is used by converting the output response at a receiver IDT into a DC representation of the RF RMS power of the signal and demodulating the power response with a lock-in amplifier. This technique can yield extremely high sensitivity measurements down to $10^{-12}$ volt range in the correct test environment. An excitation IDT is directly connected to a Stanford Research Systems SG382
RF source. The source frequency is swept from 10-50 MHz at a port power of -5 dBm. This source also provides a 10 KHz modulation signal for the lock-in reference by using 100 percent amplitude modulation of the RF output. The RF detector output on the receiving IDT is connected to an EG&G 7220 DSP Lock-In Amplifier. The lock-in preamplifier provides 20 dB of gain for a full scale sensitivity of 5 mV. The time constant of the internal filter is fixed to 50 ms. The frequency sweep is divided into 800 points where a lock-in measurement magnitude is performed at each point.

![Figure 44: S12 transmission spectra for an IDT to IDT test of an antenna sample with nickel resonators using a vector network analyzer measurement. The repeating peaks indicate a sub-resonant oscillation below the measurement range of the analyzer (10 MHz) with a harmonic spacing of about 7 MHz. The 18 MHz center frequency of the IDT structures occurs at the same frequency as one of the low frequency upper harmonics by coincidence. This large noise in the]
system is superimposed onto the desired acoustic response detected at the port 2 IDT. Testing of the measurement system components indicates the IDT pattern is likely the source of the unwanted noise in the device response. This resonance can occur from the inductive and capacitive reactive components of the IDT acting as an electrical oscillator or if the electrodes are exciting acoustic modes in the lithium niobate substrate not accounted for in the device design. Because the IDT pattern itself is the source of this resonant noise, the desired response is difficult to decouple from the system without re-designing the electrodes to either suppress these oscillations or to shift the operating frequency of the device. Tests using the IDT patterns in a differential measurement mode show that while not completely removed from the response the system noise can be made much smaller than the desired signal.

Figure 45: Linear transmission magnitude in an acoustic send/receive test using a lock-in technique of samples with nickel resonator elements.

Figure 45 shows the IDT to IDT transmission spectra for an antenna device with nickel resonators measured using a lock-in method. This measurement also shows the presence of strong
resonant noise in the system but the response at the operating frequency of the IDT pattern is greatly magnified. This shows that an acoustic wave is indeed propagating from one IDT to another across the surface of the device. The decrease in the magnitude of the noise components also points to a change in the way signal is being measured from the IDT pattern. The receiving electrodes in this test system are operated differentially by an RF amplifier instead of the single ended approach used by the transmitting electrode and the electrodes used in the VNA based measurements. The unbalanced design of the IDTs, chosen to simplify the carrier board and connector arrangement, is likely the cause of the unwanted system oscillations. Future tests with single ended IDT connections should be performed using a balun to eliminate such noise. Additionally future revisions of the antenna device should be made with balanced IDT patterns or with an integrated system for making unbalanced to balanced conversions.

Figure 46: Scatter parameters of a reference IDT (port 1) and a loop antenna (port 2) tuned to 18MHz.
The magnitude of electromagnetic coupling into the IDT from a resonant transmitter is also studied. The test is performed using a 1/10th wavelength (at 18 MHz) copper loop antenna and a reference device connected to a network analyzer. The reference device is identical to the antenna sample shown in the left image of figure 1 without the resonating nickel structures. This sample allows the study of isolated IDT electrodes on the surface of lithium niobate without a magneto-elastic contribution to the signal. The loop is held roughly 1.8 m from the ground to the loop center and 1 m away from the reference sample. The loop is tuned to 17.5 MHz using a variable air gap capacitor. Figure 46 shows the scatter parameters measured for the loop antenna and reference sample system. The reflection coefficient for the loop shows a -12 dB dip at the set frequency indicating efficient energy transfer from the loop to the surrounding environment. The transmission spectra show an approximate 12 dB response at 17.5 MHz indicating the existence of electromagnetic coupling between the IDT pattern and the loop antenna. This coupling can occur directly into the conductive electrode patterns or through an excitation of the intrinsic polarization in the ferroelectric substrate. Electromagnetic coupling into the IDT pattern can be problematic for frequency domain testing as the desired magneto-elastic contribution can be a similar order of magnitude which will lead to ambiguity in the output signal. To decouple the EM contribution reference patterns can be used as correction standards to calibrate the test system.

Time resolved measurements can also be used to decouple the acoustic and electromagnetic contributions to the output. In this method the acoustic wave time of arrival is roughly $10^3$ slower than the electromagnetic wave. This known velocity ratio and the propagation distance of the SAW can be used to window the frequency domain measurement to contain only acoustic components. Additionally a field modulation approach similar to cavity based ferromagnetic resonance test systems can be used which fix the frequency of the electromagnetic transmitter and modulate a
strong DC magnetic bias field applied to the sample. This type of measurement leverages the near zero magnetostrictive strains produced in the resonators at low and saturated magnetization states to remove the electromagnetic noise and achieve measurement contrast to purely magnetically generated signals. The latter measurement system is currently being explored to study the magnitude of electromagnetic coupling into the nickel resonator elements at VHF frequencies. In order to design a multiferroic structure that could be properly tested in this apparatus, the focus of this effort was shifted to developing the FEM for 150 MHz.

3.3.4 VHF 150 MHz Modeling and Evaluation

Modeling of an antenna structure to operate at the VHF frequency of 150 MHz was initiated by scaling the parameter space in Table 5 to the corresponding wavelength. As this frequency yields a dimensional space approximately an order of magnitude smaller than the 18 MHz system, the deposition method to be used in the fabrication of the resonators was changed from electroplating to sputtering. This necessitated that the bounds of the resonator thickness be modified to the limits of sputtering, or between 50 and 900 nm. Upon reflecting on the results of the 18 MHz optimization run, it was observed in the results shown in Figure 37 that a large portion of the electroacoustic energy was being lost to the bulk of the substrate, as seen by bright spots beneath the first 1/3 of the substrate depth. It was thus decided that a better metric to optimize these structures was the efficiency between how much electrical power is being delivered to a load in the circuit model relative to how much EM power is impinging on the resonator bed.
Figure 47: Effective transmission coefficient (S12) value for the second optimization run which used power as the optimization target. The inset shows the potential solution for the combined geometry.

The global best solution to the first optimization run for the 150 MHz design can be seen in Figure 47. Here an effective transmission coefficient (S12) is presented which compares the power across a lumped impatience load in the outgoing circuit model to the power of the incident EM wave in the Maxwell formulation. Additionally, the inset shows the electric potential wave generated at the center frequency. It can be seen that the majority of the electroacoustic energy is confined at the surface in a highly coherent and repeating fashion. A parametric sweep was used to determine the ideal load impedance for the 8 electrodes which make up the modeled IDE and a value of 100 K Ohms was used to determine the full frequency response shown in Figure 47. A large characteristic impedance being required to yield an appreciable power makes physical sense as piezoelectric media are strong dielectrics that generate very little current but large voltages when mechanically actuated. From the efficiency vs frequency plot, a very narrow peak can be found at the center frequency with a gain of -16 dB and a half-peak width of approximately 5 MHz or 3% bandwidth. Systems such as these, which rely on a mechanical resonance phenomenon, are
prototypically narrow bandwidth, but it is hypothesized that by combining structures which resonate at near frequencies the bandwidth can be increased at the cost of gain.

![Figure 48: Comparison of transmission efficiency for various electrode numbers shown with and without mechanical considerations.](image)

After the initial optimization on the resonator array at 150 MHz frequency was performed, the model was adapted to discern the optimal number IDE’s necessary to capture the maximal amount of coherent energy from the electroacoustic wave. To accomplish this, a 2D projection of the extended piezoelectric model was developed to permit the inclusion of air above the IDE elements and significantly increase the extended member’s length without sacrificing computation time. The number of electrodes was bounded between 12 and 48 and run once with the Au electrodes included as a purely electrical material, where only its conductivity was considered, and once with its full mechanical properties. Figure 48 shows the results of the study. The data appears to indicate that when the mechanics of the electrode elements are not considered that there is very little change in the electrical response of the electroacoustic wave. A test was also performed without air to show identical results and allayed the worry that when air was considered that there would be a significant capacitive effect between the positive and negative electrodes that would
heavily modify the optimal impedance of the load circuit. When the mechanics of the electrodes were considered, there was a noticeable drop in efficiency seen between 18 and 36 electrodes. The reason for this appeared to be a small amount of Bragg interference occurring which lead to a small group delay induced phase separation. Beyond 36 electrodes, this effect becomes mitigated by having additional terminals to pull additional signal out of the system. This methodology was then applied to the 3D configuration to discern if modifications needed to be made to further optimize the structure.

Figure 49: Parametric study of optimal load impedance for the 3D piezoelectric extension for 24 electrodes with and without mechanical coupling.

The full 3D extended piezoelectric structure was modified to include 24 electrodes, the largest number that could be computed due to memory constraints. Like the 2D test run previously, the electrodes were considered both with and without their mechanical contribution to the system. Figure 49 shows that the optimized impedance of the load circuit changed dramatically from the 100 KOhm optimum at 8 IDE’s discussed previously in the first optimization test. The inclusion of the mechanical effect of the IDE’s also significantly altered the electrical response compared to
when it was discounted. Utilizing these findings, a second optimization was performed for 24 electrodes which included the mechanical effects of the electrodes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>150 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>1.55 λ</td>
</tr>
<tr>
<td>Width</td>
<td>λ</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.45 λ</td>
</tr>
<tr>
<td>Y-Space</td>
<td>0.65 λ</td>
</tr>
</tbody>
</table>

Figure 50: Effective transmission coefficient (S12) as a function of frequency for the 2nd optimization run that included 24 IDE’s and a 5000 Ohm circuit impedance. Solutions for both the full 3D model and the 2D projection are shown for comparison. The insets show the resonator parameters and the potential solution for the combined geometry at the center frequency.

The second optimization run was performed with the same bounds on the ferromagnetic resonator space as the initial run, but was modified to include 24 IDE elements and a circuit impedance of 5000 Ohm. Figure 50 shows the frequency response of the global best result of the optimization and the insets show the optimized resonator geometry and the potential wave solution of the combined geometry at the center frequency. From the lower inset of Figure 50, the electromechanical wave is seen to maintain a strong coherence with the majority of the wave confined to the surface. The frequency response shown in Figure 50 is significantly different than the result of the first optimization shown in Figure 47. The peak gain increased from -16 dB to -8.6 dB and the shape of the center peak is much broader having a half-peak width of approximately
20 MHz. Additionally, a note should be made that while the amplitude of the 2D solution is lower than the 3D solution, the trend is very similar and if computational time or memory constraints were an issue that it could be used with in the optimization scheme with only a small reduction in accuracy. Given the promising results of the solution presented for Ni, consideration was once again given to Table 4 to determine if superior performance can be derived from choosing a material with a larger piezomagnetic coefficient.

![Figure 51: Effective transmission coefficient (S12) is a function of frequency for FeGaB with 24 IDE’s and 5000 Ohm circuit impedance. Solutions for both the full 3D model and the 2D projection are shown for comparison. The inset shows the potential solution for the combined geometry at the center frequency.](image)

For maximum contrast with the Ni solution seen in Figure 50, FeGaB was selected to determine how the geometry optimized for negatively magnetostrictive Ni would behave for a positively magnetostrictive material. Figure 51 shows the results for replacing the Ni elements with FeGaB of the same geometry. From the frequency response it can be seen that the amplitude at the center frequency increased to -4.7 dB at the cost of some bandwidth. The explanation for
this effect is twofold: FeGaB has a piezomagnetic coupling coefficient that is an order of magnitude larger than Ni, from which one would expect a higher transduction efficiency, and that FeGaB has a mechanical stiffness only 33% of LiNbO$_3$ which increases the mechanical impedance between the resonators and the substrate. While initially surprising that such a large disparity in ferromagnetic properties yielded such a similar transmission response, it was determined that the magnetomechanical resonance response is one that is almost entirely governed by the shape anisotropy and the relative spacing of the resonators. The geometric parameters listed in the inset of Figure 50 have been shown to yield a pure 2$^{nd}$ order bending response for both positive and negative magnetostrictive materials with promising results for each optimized system.

### 3.3.5 Concluding Remarks

Multiferroic antenna structures were designed for devices operating in the HF and VHF frequency band. A multi-step finite element framework was used to design and simulate an array of magnetostrictive resonator elements which were shown to generate a coherent 18 MHz acoustic plane waves on the surface of a piezoelectric substrate. Using a set of optimized dimensions for this array of resonators, a set of prototype wafers were fabricated using thin film processing techniques. A variety of radio frequency tests were performed to characterize the operation of the system components and testing is in progress to examine the performance of these prototype devices as radio receivers. The novel acoustic wave design of this magnetoelectric antenna allowed for a significant decrease in the size of existing antenna systems operating in this frequency range.

To permit future lab bench testing, when an anechoic chamber isn’t available, the center frequency was shifted to 150 MHz within the VHF band. Further optimization was performed to elucidate the effects that capacitive buildup, mechanical mismatch, and ferromagnetic coupling
parameters had on the frequency response of such SAW designs. It was shown that the resonance and coupling behavior was nearly entire due to geometric considerations and that anisotropic electromechanical effects play a large role in the performance of these structures. Future work on this area could be to expand the physics to include loss characteristics, nonlinear coupling behavior, and explore other potentially interesting resonator geometries. The potential for these new and compact antennas to expand the accessibility of long wavelength radio bands in a portable package is of great importance in both military and civilian communication applications and it is believed that a solid foundation has been lain to continue this work.
Chapter 4: **Strain Coupled Multiferroic Heterostructures**

4.1 Synopsis

The effects of shape and magnetoelastic anisotropy on the magnetic domain state of thin films and nanostructure are presented in this chapter. Thin films deposited at a thickness near the critical thickness at which the domain state transitions from Bloch wall dominance to Néel wall dominance is modulated under the application of ferroelectric strains. These transitions provide that the externally observed magnetic behavior can be deterministically controlled by an applied electric field. Following that, the magnetic domain states of various ferromagnetic nanostructures are explored under anisotropy conditions. By controlling the ratios of the applications of magnetoelastic, shape and magnetostatic energies, the domain configurations of these structures can be highly controlled. Transmission electron microscopy operating in the Lorentz mode will interrogate a number of structures to determine the amount of magnetoelastic anisotropy change that arises from strain transferred between a ferroelectric and ferromagnetic media. A coupled low shape anisotropy disk – ring structure will be shown to achieve full 90 degree rotation in its magnetic domain under the application of electric field induced anisotropic strain. This behavior shows a promising path forward to developing new types of strain mediated magnetic memory and efficient multiferroic micromotors.

4.2 Literature Review

It has been shown that the magnetization behavior of nanoscale magnetic materials is significantly different than bulkscale phenomenon. In thin film geometries, where the out-of-plane
dimension is significantly smaller than the in-plane dimensions, the demagnetization energy is dramatically larger in-plane. With respect to measurements of M-H curves, a large anisotropy field would be required to saturate the magnetization in the hard out-of-plane direction. Practically, this means that the magnetization has a strong preference to lie in an in-plane direction.

Beneath a certain thickness, even Bloch walls, which have an out-of-plane component, become energetically unfavorable and in their place planar Néel walls form to separate the domains and minimize the magnetostatic energy\(^8\). Figure 52 illustrates the critical thickness of domain wall transition for an idealized material similar to nickel. It can be seen that at 40 nm the energy required to form a Bloch becomes greater than that of a Néel wall. Experimental verifications of Ni have shown that if the film is greater than 100 nm in thickness the domain pattern is entirely separated by 180° Block walls\(^8\). Magnetic force microscopy images (MFM) show that these divisions are delineated into a regular series of “stripes”. Once the thickness is reduced beyond 35 nm, no out of plane magnetization is observed by the probe\(^8\). For this reason, interrogation methods which are capable of observing magnetic phenomena beyond the surface of the material, such as Lorentz TEM, will be examined later in this chapter.
The major benefit of nanoscale magnetic materials is that they can be strongly mechanically coupled to ferroelectric substrates to form robust composite multiferroic heterostructures which appear magnetoelectric. In the last decade, a significant body of work on the subject was accomplished on electrically controlled magnetic phenomena\textsuperscript{82–97}. These studies ranged from domain wall motion in Ni/PZT composites\textsuperscript{82}, to the electrical modification of planar anisotropy in Ni\textsuperscript{83,85,86} and FePt\textsuperscript{96} thin films when linearly strained by LiNbO\textsubscript{3}\textsuperscript{83}, PZN-PT\textsuperscript{96} and PMN-PT\textsuperscript{98}, and most interestingly the giant electric field induced magnetic reorientation of Ni by driving PMN-PT across its ferroelectric coercivity\textsuperscript{85,86}. These latter experiment by Wu et al. will be examined more closely for its relevance to the new body of work presented herein.

Wu established that many stable magnetic configurations could be achieved in magnetoelastic nanostructures by leveraging the anisotropic ferroelectric strains available in PMN-PT single crystals. This ferroelectrically driven anisotropic strain is capable of inducing magnetoelastic anisotropy and potentially instigating magnetic rotation. Figure 53 left shows the strain response measured along the (100) direction of the PMN-PT crystal as it was actuated by out of plane
electric fields ranging from ± 0.4 MV/m. The canonical butterfly loop behavior is observed for the full bi-polar loop (shown in black), but more interestingly a partial reversing field loop is depicted (green) which shows that stopping at -0.14 MV/m before a full polarization reversal yields a remnant strain of 1250 ppm when the field is returned back to 0 MV/m. Inspecting the full in-plane anisotropic response, shown in Figure 53, it can be seen that if the crystal is oscillated between ±0.14 MV/m that not only is a significant anisotropic strain difference produced (1400 ppm), but that the sweep results in two stable remnant strains of opposite polarity. Utilizing this behavior, multiferroic composites, created by depositing ferromagnetic nanostructures onto the partially depoled PMN-PT, could see large, stable, and reversible changes to its magnetic anisotropy state.

Figure 54: Normalized Kerr rotation hysteresis curves (M-H) measured along the in-plane principle axes of a 35nm Ni film subject to the anisotropic strain states of a partially depoled PMN-PT substrate. The different colored curves correspond to points B-E in Figure 53 Right. [Wu et al. (2011)]

To experimentally observe the effect that PMN-PT’s anisotropic strain behavior could yield on a magnetoelastic material, a 35 nm Nickel film was deposited on a partially de-poled substrate. A magneto optic Kerr effect (MOKE) study was performed by Wu, et al. on the multiferroic heterostructure under in-situ applied electric fields. Initially the PMN-PT crystal was partially repolarized under the application of +0.14MV/m and measurements were made to
interrogate the magnetization loops of the Ni along the X (01-1) and Y (100) axes of the substrate, shown as the black curves of the two plots respectively. Under these conditions the X-axis appears to be a hard axis, while the Y-axis is substantially easier. This is the expected behavior as Ni is a negatively magnetostrictive material from which applied strains create an anisotropy field with energy wells along the compressive direction and energy maxima along the axis of tension. The electric field was then reduced to 0 MV/m, and the magnetic anisotropy is maintained (red curves) because the strain difference is remnant in the PMN-PT. From there the electric field is reversed to -0.14MV/m causing the ferroelectric crystal to now develop tension in the Y-axis and compression along the X-axis. Under these strain conditions the easy and hard axes of the Ni also reverse, as seen in green. Once again the applied electric field is reduced to 0 MV/m and as expected the magnetic configuration is maintained. These experiments show that stable magnetic configurations can be created and maintained under the application and release of electric field, and illuminates why PMN-PT was selected as the substrate in the present work.

Control of ferromagnetic thin film properties by ferroelectric actuation isn’t limited to easy-hard axis manipulation, but as was shown by Hsu and Hockel, the energy landscape governing the type of domain wall formation can also altered via strain. In contrast to Wu’s work on (011) PMN-PT, Hsu and Hockel utilized the isotropic planar tensions and compressions generated in (001) PMN-PT to eliminate the stripe domain pattern observed in 60 nm Ni films as otherwise seen by MFM. This apparent removal of the domain walls occurs as the ferroelectrically induced magnetoelastic anisotropy quenches the out-of-plane component of the exchange energy and thusly forces a transition from Bloch wall dominated flux closure to a Néel wall governed system. The specifics of this experiment will be explored in some detail to elucidate one effect of electrically driven anisotropy control of magnetic domains.
In their test, 60nm of polycrystalline Ni was deposited onto a pre-poled single crystal sample of PMN-PT (001) that was 500 μm thick. The substrate was poled prior to deposition to prevent a remnant strain condition upon the release of the electric field. During the experiment the electric field was swept by voltage control from 0 to 0.8 MV/m, the saturating field of the substrate. Figure 55a shows the bi-directional planar strain vs. electrical field curves for the PMN-PT substrate. At the strain states labeled I-IV, the magnetic topology of the deposited Ni film was interrogated using AFM/MFM as shown in Figure 55b. From the AFM images it should be noted that throughout the electric field sweep that there is almost no change in ferroelectric domain structure and that the height difference is approximately ±2 nm, which indicates that the electromechanical response is entirely piezoelectric. When inspecting the MFM images it can be observed that before an electric field is applied (Figure 55b-I) there is a typical stripe domain pattern, indicating that the domain walls are of the Bloch wall configuration. As the field is increased to 0.4 MV/m, as seen in Figure 55b-II, the contrast of the domain walls reduces significantly. Once the field reaches the saturation strain of the PMN-PT at 0.8 MV/m, denoted in Figure 55b-III, the domain pattern has almost no out of plane component. Once the electric field
is removed (Figure 55b-IV), the pattern returns with the same contrast at which it began, but with a slightly different configuration, pointed out by the white arrows. This irreversible component of the magnetization component was explained by pinning effects due to the underlying ferroelectric domain wall configuration. It was also noted that when the same test parameters were applied to a 100 nm thick Ni film, no change was observed in the domain pattern. This experiment showed two very important results: firstly, when operating near a critical thickness of a magnetic film that the domain wall configuration can be reversibly altered by the application of a strain field and secondly that even under the application of significant strains, the magnetic domains can become pinned by geometric and ferroelectric domains. Further questions remain which could not be resolved by the testing mechanisms applied in this study, namely what occurs to the magnetic domains of films which are beneath the Néel wall critical thickness and how geometric effects alter the strain induced behavior of magnetic nanostructures. These questions will be answered by the experiments performed in the present work.

4.3 Electrically Controlled Reversible and Hysteretic Domain Wall Evolution in Ni/PMN-PT Heterostructure Observed by Lorentz TEM.

4.3.1 Problem Introduction

Magnetoelectric strain-coupled heterostructures are of significant technological interest, particularly for the development of electrically controlled magnetic memory devices such as MRAM\textsuperscript{10,99,100} and more recently in the design of micro and nanoscale magnetic actuators. In these devices the magnetic phase is controlled electrically by a piezoelectric substrate, with interfacial strain playing the role of magneto-electric energy transduction. Of particular interest is the energy transduction between ferroelectric and magnetic domains and the reorientation that occurs at or
near their interfaces. While the existence of magnetoelastic coupling in magnetolectric composites has been widely established\textsuperscript{101,102} direct observations of piezoelectrically induced magnetic domain wall motion, especially at the nanoscale, are largely absent. That is, the vast majority of reports focus on macroscopic measurements via SQUID or VSM systems rather than direct observations of domain movements. Measurements of magnetic domain wall evolution in response to a ferroelectric domain state are critical for understanding the role of strain anisotropy, strain gradients, and pinning sites. Of additional interest is being able to discern what occurs in structures that are beneath the critical thickness in which out of plane magnetic moments become energetically unfavorable. Finally, observations of magnetoelastically-induced Barkhausen jumps are needed to provide application oriented information to reduce device level magnetic noise, which has recently been associated with irreversible domain wall motion\textsuperscript{103,104}. Direct domain wall observations at the nanoscale, particularly in magnetolectric heterostructures, requires imaging techniques with enhanced spatial resolution and unique magnetic sensing capabilities. In this study, Lorentz Transmission Electron Microscopy (TEM) is used to observe electrically-induced magnetic domain wall motion, at room temperature, on a Ni / PMN-PT (011) heterostructure with a back-etched electron transparent observation window. The domain motion is classified as reversible for unipolar electric fields or hysteretic for 180 degree ferroelectric reorientations with several sudden magnetoelastically induced Barkhausen jumps. Magnetization gradients are observed in the nickel film and these are shown with COMSOL finite element simulations to be caused by mechanical strain gradients throughout observation window. This work represents the first direct observation of magnetic domain movement using Lorentz-TEM of a magnetolectric strain-coupled heterostructure consisting of a bulk single crystal piezoelectric substrate.
Many techniques currently exist to observe domain wall motion in magnetoelectric composites such as MFM\textsuperscript{84}, MOKE\textsuperscript{91}, and PEEM\textsuperscript{105}. While some of these techniques are simple, inexpensive, and accessible, others such as PEEM are less accessible. In addition, MFM risks perturbing the magnetization of the sample during measurement while PEEM and MOKE are surface sensitive and/or lack spatial resolution. In contrast, Lorentz TEM has the advantage of a few nanometers spatial resolution and high sensitivity to the in-plane magnetization making the technique ideal to study domain walls such as Néel walls, which are expected in nickel thin films below 60nm\textsuperscript{106}. Lorentz imaging in Fresnel mode can be classically understood through the deflection of the electron beam due to the Lorentz force as it passes through a magnetic sample. In the Fresnel method, the image is defocused so that the object plane is no longer in the same plane as the specimen. Depending on the local orientation of the magnetization, the beam deflection direction will vary leading to either enhanced or decreased intensity at areas of varying magnetization (i.e. domain walls). It should be noted that the required defocusing decreases the overall resolution of the technique in comparison to standard bright field TEM and can obscure structural information such as grain boundaries. However, it remains one of the highest resolution magnetic imaging techniques available, with a limit of only a few nanometers\textsuperscript{107}. Sample preparation is critical to achieve such high resolution imaging. In particular, the sample must be transparent to electrons and thus the thickness must be less than 100 nm. Fabrication techniques have been demonstrated previously by Brintlinger et al. for magnetoelectric Lorentz TEM samples\textsuperscript{108} however the limited sample viewing area and the reduced strain output of the thin film piezoelectric in that work made the magnetoelastic origin of the observed magnetic domain evolution unclear. In the present work this issues has been circumvented by utilizing a transparent TEM permeable sample fabricated from a bulk piezoelectric/magnetic thin film heterostructures.
to avoid substrate clamping issues. This substantially increases the strain magnitude, observable area, and strain uniformity necessary for a robust multiferroic domain coupling study.

4.3.2 Experimental Setup

![Sample preparation and geometry details. a.) SEM micrograph of sample backside showing FIB milled observation window. b.) SEM micrograph of observation window edge. The window thickness is approximately 100nm. c.) Experimental diffraction pattern image of the PMN-PT (011) substrate with crystallographic axes indexed. d.) TEM Lorentz image of observation window with relevant crystallographic axes indexed.](image)

Figure 56: Sample preparation and geometry details. a.) SEM micrograph of sample backside showing FIB milled observation window. b.) SEM micrograph of observation window edge. The window thickness is approximately 100nm. c.) Experimental diffraction pattern image of the PMN-PT (011) substrate with crystallographic axes indexed. d.) TEM Lorentz image of observation window with relevant crystallographic axes indexed.

A 35 nm thick polycrystalline nickel film was deposited by evaporation onto a 0.5 mm thick PMN-PT (011) single crystal (Atom Optics, Shanghai) with top and bottom face 50 nm thick Pt electrodes. The planar dimensions of the bulk substrate are approximately 10 mm x 10 mm. The sample is cleaved in two separate pieces to create a reentrant side wall with an overhanging film edge as shown schematically in Figure 56a (side view) and with SEM in Figure 56b. Focused ion beam milling with a Ga+ beam source at a 30 kV energy level was used to etch the PMN-PT substrate and release the Ni/Pt multilayer from the backside. After the preliminary bulk ablation of the PMN-PT substrate, currents as low as 1nA were used for high precision milling as well as
to minimize collateral damage to the Ni/Pt film. The end result was an electron-transparent observation window roughly 10 x 10 μm. This observation window is seen edge-on in Figure 56c revealing a thickness of approximately 100 nm (35 nm of Ni with some Pt and residual PMN-PT). It should be noted that the thickness of the membrane is non uniform as indicated by the uneven SEM contrast in Figure 56b. Near the edge of the membrane the thickness is approximately 65nm, but this thickness increases to approximately 100 nm near the center of the membrane. All TEM images were taken using a JEOL 2100F-LM microscope with a specially designed objective pole piece that eliminates the residual Oersted field on the samples. To establish the crystallographic axes of the PMN-PT substrate, necessary for linking the strain direction to changes in magnetic structure, the sample’s diffraction pattern was analyzed (Figure 56d). The diffuse ring pattern corresponds to the polycrystalline Ni film; diffraction spots to the single crystal PMN-PT substrate. The real space crystallographic axes of the sample was determined by correcting the intrinsic optical rotation of the microscope between diffraction and imaging mode and is shown in the bright field image in Figure 56e.
Figure 57: (left) Piezoelectric strain data for the PMN-PT (011) substrate used in this study with specific strain states (A-H) referenced in the main text. Measured by T. Wu et al.98 (right) Schematics of strain states in the observation window at different electric fields.

Single crystal PMN-PT is a popular piezoelectric material in the literature because it has significant and reproducible electric field/strain behavior. The (011) crystal cut has recently received attention because it has large anisotropic in-plane remnant poling strain, considerable linear anisotropic piezoestrain, and a large non-linear jumping strain during 180 degree ferroelectric polarization reversal. Figure 57 shows a plot of the strain in each in-plane axis (see Figure 56e) as well as the anisotropic strain (i.e. $\Delta \varepsilon = \varepsilon_y - \varepsilon_x$) vs. electric field as originally measured by Wu et al.98 The a-h labels in Figure 57 refer to specific strain states/electric fields at which Lorentz images were captured. The magnetoelastic anisotropy in a magnetic film at a given electric field is related to the strain anisotropy by $K_{me} = \frac{3}{2} \lambda_s E (\Delta \varepsilon)$. Here $\lambda_s$ is Ni saturation magnetostriction coefficient (-32 ppm) and $E$ is the Young’s modulus of nickel (200x10^9 Pa). The applied electric field creates magnetoelastic anisotropy in the Ni film and reorients the magnetization of the film through rotation, growth, or de-pinning/jumping mechanisms. The
amount of magnetization reorientation is related to the magnitude and direction of the applied strain anisotropy, therefore quantification of the strain for this magnetoelastic study is essential.

**Figure 58:** (a-c) Strain gradients in the nickel thin film at various voltages as calculated by COMSOL simulations. Color bar corresponds to strain anisotropy \( \Delta \varepsilon = \varepsilon_y - \varepsilon_x \). White and black arrows schematically show strain distribution and magnetization direction, respectively.

A finite elements model was developed using COMSOL Multiphysics to approximate the non-linear electric fields and strain gradients observed around the complex geometry of the 10 x 10 \( \mu \)m Ni thin film window. The PMN-PT was modeled as a 0.5 x 0.5 x 0.5 mm element using the piezoelectric module with full anisotropic tensor quantities for stiffness, permittivity and piezoelectric coupling. A 3.5\(^{\circ}\) slope was removed from one (100) edge to form the overhanging cleaved edge and a 10 x 10 \( \mu \)m slot was cut vertically from the center of the cleaved edge to form the observation window. The materials coefficients were derived from experimental strain gauge measurements\(^{98}\). The Ni film on the top surface of the PMN-PT was approximated by a linear shell element and given isotropic material values to approximate the polycrystalline nature E-beam evaporated Ni. Electric fields between -0.16 and 0.32 MV m\(^{-1}\) were applied to the model to match experimental conditions. Figure 58a-c shows a series of calculated strain states corresponding to electric fields a, b, and c in Figure 57. The color plot corresponds to the local strain anisotropy.
$\Delta \varepsilon = \varepsilon_y - \varepsilon_x$ with colors on the red end of the spectrum indicating a larger strain anisotropy. Shown schematically with white and black arrows are the strain distribution and local magnetization direction, respectively. A “saddle”-shaped strain gradient is visible at all voltages, caused by the significant poling induced remnant compression along the (01-1) axis. As shown in Figure 58b and c, the strain gradient within this saddle becomes more pronounced as the electric field is increased. This effect of strain gradient on the local magnetization will be discussed in detail in the next section.
4.3.3 Experimental Results

![Image of experimental results]

Figure 59: (a-d) Uni-polar piezoelectric strain on Nickel thin film/ PMN-PT (011) heterostructure observed with Lorentz TEM corresponding to strain states a-d in Figure 29, respectively. Magnetization of domains are indicated with arrows. (a.) 0 V before applied voltage. (b.) 80V (.16 MV m⁻¹) (c.)160 V (.32 MV m⁻¹). (d.) 0 V.

The magnetic thin film’s response to a unipolar linearly increasing piezostrain is shown in Figure 59 a-d. The light grey rectangular region in in Figure 59 is the boundary of the observation window. This region contains a thin membrane of Ni/Pt and trace amounts of PMN-PT, which appear as irregular spotting in the observation window. The edge of the sample is along the lower portion of the image while the vast majority of the substrate continues in all directions above, left, and right of the observation window. The sample is poled prior to imaging in in Figure 59a,
therefore a substantial poling anisotropic strain of about 1300ppm (point a in Figure 57 and Figure 59a) is already present in the film, with compression in the x direction ((01-1) axis) and tension in the y direction (100). As can be seen in Figure 59a, the sharp white and black contrast is visible extending parallel to the (100) axis and originating at the junction between the observation window and the bulk substrate along the top of the image. This contrast results from rapidly changing magnetization consistent with the presence of Néel walls. From a classical perspective, the Lorentz force due to the interaction of the beam with the sample’s magnetic structure causes local deflections of the beam. At discontinuities in the magnetization (i.e. domain boundaries), this results in either increased or decreased intensity. Furthermore, weak line contrast is observed in the area, known as ripple contrast, representing a slow change of local magnetization.

Magnetization ripples result from the competing interactions of the random crystalline anisotropies due to the multiple grain orientations and the exchange interaction between neighboring grains. Based on the ripple contrast the local magnetization directions can be determined on either side of the domain walls. These directions are marked with arrows in Figure 59a. As the voltage is increased to 0.16 MV/m, the tensile strain along the y axis (100) decreases to approximately 0 ppm (point b in Figure 57 and Figure 59b) and the strain along the x (01-1) does not change significantly. This represents a roughly 200 ppm change in anisotropic strain equivalent to 1.9 kJ/m³ of magnetoelastic anisotropy in the film. Looking at Figure 59b, little changes occur in the domain wall configuration as contrasted to Figure 59a, but a ripple pattern begins to form over the entire substrate. The ripple patterns run along the x (01-1) axis, indicating that the local magnetization is aligned perpendicular to these ripples (i.e. along the y (100) axis). This magnetization reorientation arises due to the relative increased compression (i.e. magnetoelastic anisotropy increased) along the (100) and nickel’s negative magnetostriction (see Figure 57b). Comparing in Figure 59b with
the COMSOL simulation in Figure 59b, the change in magnetization may be explained by the increased strain gradient in the film relative to the 0 MV/m case. In Figure 59c, 0.32 MV/m is applied to the substrate equivalent to 150 ppm of compressive strain along the (100) axis (point c in Figure 57 and Figure 59c) and 4 kJ/m³ of change in the film’s magnetoelastic anisotropy relative to the 0 MV/m state. The domain walls that were immobile in Figure 59b have now de-pinned and a significant Barkhausen jump is visible. Two of the domain walls have combined forming a long chain extending along the (100) direction indicating that magnetization (and domain wall alignment) along the compressive strain direction (100) is preferred. The long white domain wall in Figure 31c is intersected by a dark domain wall which runs along the (01-1) forming a cross tie domain wall at their intersection. The presence of the cross tie in Figure 59c further confirms the prevalence of Néel walls in this film with flux closure predominantly within the plane of the film, though it is unclear which of the intersecting domain walls is the primary Néel wall and which is the crossing Bloch line. Interestingly, the domain walls appear to originate at or near imperfections in the film (i.e. the irregular dark spots) which may serve as magnetostatic pinning sites. It is unclear whether these film imperfections are a result of the FIB milling process, which may introduce substrate debris and damage the film, or the sample fabrication process (i.e. the metal evaporation,) which may introduce film impurities. The ripple patterns from Figure 59b are now broader and more defined; extending in a curving trajectory along the (01-1) implying that a nonlinear strain gradient exists due to the geometry of the observation window. The larger component of magnetization ripples along the (100) direction implies that the magnetization is now reorienting toward the (01-1) axis. Interestingly, the curving trajectory of the magnetization in Figure 59c corresponds well with the finite element simulated strain gradient in Figure 59c. The most significant effect is observed in the center of the window region and this is shown by the
simulations to also have the highest strain gradient. Upon removal of the electric field in Figure 59d, the ripple patterns disappear completely and the domain walls return to their original locations (contrast with in Figure 59a) indicating that domain wall motion in the unipolar linear regime is a reversible process. At least two additional unipolar electric field cycles were applied to the sample and the domain wall motion in each successive test was reproducible and reversible. The one-to-one correspondence between strain state and magnetization evolution is further evidence of the strong coupling between ferroelectricity and magnetization in this magnetoelectric heterostructure.

Figure 60: (a, d-h) Reversing electrical polarization procedure on magnetoelectric heterostructure observed in Lorentz TEM corresponding to strain states a, d-h in Figure 29, respectively. (a.) 0 MV/m the substrate is prepoled with a positive electric field. (d.) -0.08 MV/m just prior to the coercive field of the PMN-PT. (e.) -0.16 MV/m just after passing the coercive field. (f.) -0.32 MV/m. (g.) -0.16 MV/m. (h.) 0 MV/m.

The heterostructure’s response to a bipolar electric field is described next. Figure 60a, d-h is a series of Lorentz TEM images for the heterostructure under six different electric fields (i.e. a
to d to e to f to g to h in Figure 57). Going from Figure 60a (point a in Figure 57) to Figure 60b (just prior to the coercive field, -0.08 MV/m, point d in Figure 57) there is little change in strain state from the PMN-PT and a corresponding lack of magnetic change in Lorentz TEM. The electric field is next decreased to just below the coercive field (-0.08MV/m point d in Figure 57) in Figure 60d and there is little change in the magnetic image, attributed to a relatively small change in strain state. As the field decreases below the electric coercive field (-0.16MV/m, point e in Figure 57), the strain anisotropy (i.e. $\Delta\varepsilon=\varepsilon_y - \varepsilon_x$) drops by 1300 ppm with a decrease in compression along the x axis, as schematically shown in Figure 57 point e. Figure 60e reveals at this strain state that two domain walls (indicated by yellow arrow) have vanished and that the film’s magnetization state is more uniformly aligned with the (100) compressive direction. The fact that a significant electrically-induced magnetic domain evolution occurred near a large strain jump is further evidence that the observed spin rearrangement is magnetoelastic in origin. As the voltage is decreased to -0.32 MV/m (point f in Figure 57), Figure 60f reveals a ripple pattern emerging and crossing domain walls similar to those previously seen in Figure 59c. The anisotropic strain states and magnetoelastic anisotropy produced in Figure 60c and Figure 60f are nearly identical as shown by comparing Figure 57, point’s c and f. This further supports the argument that these magnetic evolutions are due to magnetoelastic anisotropy and not merely ferroelectric switching behavior. Reducing the voltage to -0.16 MV/m (point g in Figure 57) causes the domain walls to relax in Figure 59g; however two walls remain pinned at an imperfection which is labeled with an arrow. A comparison between Figure 60e and Figure 60g (points e and g in Figure 57) reveals that although both images were taken at the same electric field, the domain wall configuration is different indicating an irreversible magnetic domain evolution produced by a hysteretic ferroelectric states in the PMN-PT. Reducing the electric field completely to 0 MV/m in Figure
60h, the magnetic domain walls relax further and return to the same strain state as in Figure 60a. Comparing the domain wall pattern in Figure 60a and Figure 60h indicates that two domain walls have vanished during the ferroelectric polarity reversal, demonstrating hysteretic magnetic irreversibility.

4.3.4 Concluding Remarks

In this chapter magnetic domain structures have been measured as a function of electric field in a bulk ferroelectric substrate coupled with a nanostructured ferromagnetic thin film. Unipolar electric fields applied linearly increased the magnetoelastic anisotropy in the nickel thin film and caused reversible magnetic domain wall motion and local spin arrangement. However, bipolar electric fields caused a hysteretic polarization reversal in the ferroelectric substrate resulting in non-reversible magnetic domain wall evolutions and Barkhausen jumps in the magnetic film. COMSOL finite element simulations demonstrate that the observed local spin arrangement follows a saddle-shaped mechanical strain gradient. Domain wall stabilization and pinning sites resulting from film defects were shown to play a critical role in the domain wall reversal behavior. These pinning sites could play a significant role in stabilizing devices based on magnetoelastic coupling and warrant further study. The observation of subtle domain wall phenomena in this study was made possible by the combination of a unique sample structure and Lorentz microscopy which has high sensitivity to in-plane magnetization and excellent spatial resolution. Furthermore, this data provides an important approach to begin more systematic measurements on magnetic reorientation with an electric field necessary for applications such as MRAM and magnetic actuators. This study also paves the way for the examination of ferromagnetic nanostructures such as rings and disks as their approach their single domain limits.
4.4 Electrically Controlled Domain Wall Evolution in Nickel Nanostructures Deposited on PMN-PT Observed by Lorentz TEM

4.4.1 Problem Statement

Patterned ferromagnetic nanostructures whose magnetic state may be modulated via magnetic field have been studied extensively for applications in non-volatile data storage and memory. However, little work has been done to utilize the same phenomenon using magnetomechanical actuation at the nanoscale. While attractive features of single domain magnetic elements include the stability and predictability of magnetic states, these characteristics simultaneously inhibit magnetic manipulation for recording or actuation. For example, in bi-stable single domain nanostructures the large shape anisotropy requires a relatively large external energy to switch the magnetization\(^48\) (i.e., high strength magnetic field). Therefore, geometries and external mechanisms which can actuate these structures and easily switch magnetization directions with low power need to be investigated. Several approaches to lower the energy barrier between magnetic states have been attempted using low geometric ratios and/or magnetic meta-stabilities and switching mechanism which include current injection\(^112\), voltage-induced magnetic anisotropy\(^113\), and magnetoelastic strain\(^81\). More recently, the ring geometry has been studied for both its unique metastable “onion” magnetization state, and its stable “vortex” state, for encoding a bit of information in chirality\(^114\). Reorientation of the onion magnetization state is accomplished by either applying a magnetic field\(^115-117\) or injecting current\(^118,119\). Both of these reorientation mechanisms result in either an onion to vortex transition or a partial rotation of the onion’s vortex-type domain wall. These methods are considered impractical due either to large energy requirements, in the case of applied field, or cumbersome wiring arrangements, in the
case of current injection. Furthermore, neither of these two methods are capable of achieving coherent rotation of the onion state (onion to reverse onion transition), though this has been proposed\textsuperscript{120}. Therefore, other ring switching approaches warrant study.

More recently, researchers\textsuperscript{83,102,121,122} have suggested using mechanical and electric field induced strain as magnetic switching mechanism through the generation of magnetoelastic (ME) anisotropy in magnetoelectric heterostructures. Hockel et al. pioneered such a study on ring structures using MFM\textsuperscript{123}. ME anisotropy (e.g., $K_{\text{ME}} = (3/2)\lambda_s E |\varepsilon_y - \varepsilon_x|$) is a function of the material’s magnetostriction constant $\lambda_s$, Young’s modulus $E$, and induced strain anisotropy $\varepsilon_y - \varepsilon_x$. The KME is used to overcome other energies, such as shape anisotropy and defect pinning, to reorient the magnetization direction. The induced anisotropic strain is generated electrically by combining a ferroelectric with a magnetostrictive material to form a magnetoelectric heterostructure or laminate\textsuperscript{9}. One ferroelectric material that has been studied to produce anisotropic strains is a single crystal PMN-PT cut with the (011) axis oriented out-of-plane. This particular cut produces tensile and compressive strains in two orthogonal in-plane axes (01-1 and 100) as well as providing a memory effect from the remnant strain states\textsuperscript{124}. Magnetoelectric heterostructures of this type are simple in design, requiring only electrodes on the piezoelectric member to achieve magnetic reorientation. While a few papers exist in the literature investigating magnetoelectric nanobar structures\textsuperscript{102}, their application to low-write-energy memory and actuators is limited by the requirement of overcoming the Gibbs free energies associated with the shape anisotropy of these geometries.

The study of a strain mediated multiferroic control of ring structures has really only taken shape in the past several years. Hockel’s initial study consisted of observations of 35 nm and 10 nm thick Ni ring structures with inner/outer dimensions of 350/500, 700/1000 and 1400/2000 nm
respectively\textsuperscript{123}. The investigation showed that in structures where an onion state could be initialized by an external magnetic field, the transverse or vortex walls which separated the two domains could be coherently rotated with strain. It was seen that while onion states could be repeatedly generated in all 6 geometric configurations that only the rings with 2000 nm outer diameters could be rotated consistently and coherently. Additionally, a detailed account was made to illuminate that the vortex walls associated with thicker rings were more easily moved under the application of strain (ie. under lower values) than the transverse walls prevalent in the 10 nm structures. Building on Hockel’s findings Cui developed a method to actuate single magnetic nanostructures\textsuperscript{125} and Sohn conducted a parametric study of Ni ring geometries with 2 and 3 um outer diameters, with between 200 and 650nm annular widths, and having thicknesses between 15 and 45 nm\textsuperscript{126}. In the latter experiments repeatable 45 degree rotation was observed in the 2 um, 300nm annular width, for 15 and 30 nm thick structures. The goal however, is to obtain full 90 degree rotation and better understand the magnetization dynamics that occur for low anisotropy magnetic structures as they are actuated. To accomplish this, a Lorentz TEM study will be presented to explore ferroelectric actuation of various Ni nanostructures deposited on FIB milled PMN-PT as an extension of the study presented in the previous subchapter.

![Magnetization Phase diagrams for various ring geometries. (a-b) Permalloy Rings, (c-d) Cobalt Rings [Laufenberg et al. 127 (2007)]](image)

Figure 61: Magnetization Phase diagrams for various ring geometries. (a-b) Permalloy Rings, (c-d) Cobalt Rings [Laufenberg et al. 127 (2007)]
Figure 61 shows magnetic phase diagrams of permalloy and cobalt rings outlining geometries which exhibit transverse and vortex walls separating their onion domains in both experimental and simulated studies. It was observed that vortex walls were more prevalent at larger annular widths and for thicker structures. The calculated phase boundaries were computed as a balance of stray field and exchange energy using the following equations:

$$\Delta E_{\text{stray}} = -\frac{1}{8} \mu_0 M_s^2 t^2 W$$  \hspace{1cm} (4.1)

$$\Delta E_{\text{ex}} = 2\pi A \ln\left(\frac{r_{\text{max}}}{r_{\text{min}}}\right)$$  \hspace{1cm} (4.2)

Where \(t\) = thickness, \(W\) = annular width, and \(A\) = exchange stiffness. From these equations a critical thickness can be solved for, under the assumption of small \(r\)’s, as:

$$t = \frac{16\pi A}{\mu_0 M_s^2 W}$$  \hspace{1cm} (4.3)

Using this formulation and available experiments, a phase diagram was compiled for Ni rings.
Figure 62: Phase diagram of Ni ring magnetization states as functions of annular width and deposition thickness. The solid blue and dashed black lines indicates the calculated and observed phase boundaries respectively. Red dots indicate previous experimental work. Blue dots indicate the experimental points to be evaluated in the current body of work.

Figure 62 illustrates the type of domain wall expected for Ni rings of various geometries both calculated by Equation (4.3) (blue line) and by experiments\textsuperscript{126,128} (red dots). The study presented here attempts to examine 20 nm thick Ni structures with annular widths ranging from 100 to 700 nm (blue dots), as well as solid disks and squares, to discern the apparent domain wall structure present and whether those structures can have their magnetization state deterministically modulated by 90 degrees with anisotropic ferroelectric strain provided by single crystal PMN-PT(011). In this work, observations are made by Lorentz TEM made possible by a collaboration with Brookhaven National Lab and corroborated by LLG modeling.
4.4.2 Experimental Setup

![Electron beam lithography pattern](image)

**Figure 63:** Electron beam lithography pattern used to define the ring and landau square geometry of Ni structures on the PMN-PT substrate

In order to characterize the Ni structures by Lorentz TEM, it was necessary to fabricate an electron transparent window on the ferroelectric PMN-PT substrate where the structures would be suspended by the top metal electrode. The technique to accomplish this is a modified version of the one outlined in Hockel et al. as well as Section 4.3.2. In this experiment 50 nm Pt electrodes were deposited by E-beam evaporation over the top and bottom surfaces of a 0.5 mm thick PMN-PT (011) single crystal (TRS Technologies) that is approximately 10 x 10 mm in the planar dimensions. Following electrode deposition, a PMMA/MMA double layer photoresist is spin coated over the top surface to facilitate electron beam lithography and provide easy lift-off of the unwanted metalization. A Vistec EBPG 5000+ES Electron Beam writer was utilized to pattern the resist according to Figure 65. The ring geometries were chosen to fill the gap in the phase diagram illustrated in Figure 62 and discern whether a full 90 degree magnetization rotation could be accomplished via applied strain for any of these geometries. In addition to the ring geometries, three different sized squares were chosen to verify the strain transfer from the PMN-PT, through
the Pt electrode, to the Ni structures. The patterned array was deposited 8 units (denoted in Red) wide and across the length of the 10 x 10 mm PMN-PT substrate along the (100) Y-direction, which matches the previous setup as is illustrated in Figure 56a. Following patterning, the resist is developed in a Methyl isobutyl ketone (MIBK)/Isopropanol 3:1 solution, and polycrystalline Ni is evaporated with a 3 nm Ti adhesion layer to form the ferromagnetic nanostructures. The excess metal coating the polymer layer was then removed by lift-off, etching away the PMMA/MMA in a 24 hour bath of N-methyl-2-pyrrolindone and rinsed in acetone. Finally the structures were cleaned with acetone, methanol, and isopropanol for 10 seconds each to remove any organic matter or residue to the surfaces.

Figure 64: SEM images of the PMN-PT substrate and deposited nanostructures post FIB milling. (a) Wide angle shot to illustrate the depth of the roughing cut relative to the window. (b) Close-up isometric view of electron transparent viewing window. (c) Top-down-view of patterned viewing window. (d) Front-on of window view to measure the overall thickness of the window and structures.
After the Ni array was deposited on the electroded, PMN-PT surface, the viewing window needed to be milled out to obtain an electron transparent region to view the magnetic structures. The patterned sample was cleaved across its width, the (01-1) direction of the crystal transverse to the long axis of the pattern, to create the reentrant side wall with an overhanging top edge. Focused ion beam (FIB) milling with Ga+ ions at a 30 kV energy level was performed to ablate the PMN-PT sidewall and release the Pt electrode containing the Ni nanostructures. Initially, bulk etching was performed at 5 µA with the ion beam rastering into the face of the cleaved surface no closer than 5 µm from the upper Pt electrode. Following bulk ablation, the beam current was reduced to as low as 1nA to perform high precision milling on the underside of the observation window to reduce its thickness to less than 100 nm and minimize collateral damage to the Pt electrode. Figure 64(a-b) shows isometric views of the final results of the FIB milling process using SEM. The 100 µm deep roughing cut, which can be seen in Figure 64a, is performed to guarantee minimal tilt is required by the TEM sample holder in the event that the slope of reentrant side wall is less than 2 degrees. The zoomed in picture depicted in Figure 64b shows that the film was reduced below the critical thickness to enable electron transparency, as the Ni structures are clearly visible through the thickness of the observation window, as well as the microstructural changes to the PMN-PT sidewall between two different beam currents. Comparing this sample to one which cracked during the milling process (not shown in this manuscript), it was posited that large roughness and sharp edges of ferroelectric material have a tendency to initiate cracks as charges build in these regions of high field concentration when observed by high resolution SEM. The observation window was approximately 18 x 22 µm in area as can be seen in the top-down view in Figure 64c. A larger window to match the proposed 30 x 30 µm window was unfeasible as attempts increase its area in other samples (not shown) led to bowing of the milled membrane which made uniform thinning
impossible without tearing the near the edges. Figure 64d shows a front-on view of the observation window and illustrates the variation between the thickest regions, where Ni structures are present, and the thinnest regions which saw a small amount of non-uniform milling. With the viewing window milled from the cleaved sample which had an overhanging top edge, the other half which cleaved with a negative sloping reentrant face was utilized to measure the ferroelectric response of the PMN-PT crystal.

![Anisotropic strain vs. electric field plot](image)

**Figure 65:** Anisotropic strain vs. electric field plot of the PMN-PT substrate marked-up with arrows depicting the hysteretic applied field path and letters indicating the electric field values at which magnetic measurements were taken.

Figure 65 illuminates the magnitude of anisotropic planar strain between the (100) and (01-1) axis as a function of applied electric field measured for the same crystal used to fabricate the TEM observation window. In one dimensionalized terms positive values indicate an effective tensile strain along the (100) direction and negative values indicate a compressive strain. As indicated in the previous study, the (011) crystal cut has recently received attention because it has large anisotropic in-plane remnant poling strain, considerable linear anisotropic piezostrain, and a large
non-linear jumping strain during 180 degree ferroelectric polarization reversal. This exact behavior is observed in the crystal examined in Figure 65. For the purpose of the following experiments the ferroelectric crystal was initialized by saturating it with a -0.8 MV/m electric field and returning the field to 0 MV/m to settle the remnant anisotropic strain at -1200 ppm as demarcated by point (a). The field was then increased and held at its coercive field value of +0.16 MV/m whereby the sign of the strain anisotropy changes and the strain increases to +800 ppm at point (b). A further increase of electric field repolarizes the material in the positive out-of-plane direction and the strain anisotropy once again flips to a negative value, this time falling to -600 ppm before linearly increasing to 0 ppm at +0.43 MV/m at point (c). After the crystal is fully saturated at +0.8MV/m, the strain anisotropy linearly decreases to the remnant value of -1200 ppm at point (d) when the field is removed. This process is then exactly mirrored as a negative field is applied through the coercivity at point (d) (-0.16 MV/m) and once again through -0.43MV/m at point (f) to negative saturation. This strain-electric field path was shown to be repeatable over many cycles and forms the basis for the anisotropic strain application to the Ni nanostructures.
4.4.3 Results

Figure 66: TEM images of the viewing window. (a) Standard in-focus Fresnel mode showing the electron transparency of the viewing window with certain structures highlighted by colored circles. (b) 2 um Ni square (shown previously highlighted in red) observed under Lorentz defocus with white arrows showing asymmetrical domain formation. (c) 1 um Ni square (highlighted in green) showing Landau configuration of Néel domain pattern at -0.43 MV/m of electric field. (d) 1 um square after electric field is swept to -0.16 MV/m. (e) 1 um square at +0.16MV/m. (f) 1um square at +0.43 MV/m returned to the Landau configuration.

The TEM study was initiated by verifying the electron transparency of the observation window. Figure 66a shows a standard TEM micrograph of the viewing area. The well-known phenomena of Landau state formation was utilized in the magnetic squares to experimentally discern whether strain was being effectively transferred to the magnetic media by observing the separation and elongation of the central vortex as electric fields were applied to the ferroelectric as demarcated by the letters in Figure 65. The first square studied was 2 um in side length, circled in red in Figure 66a, and done so at -0.43 MV/m after negative field saturation such that it was experiencing no
anisotropic strain. As can be seen in Figure 66b, the Néel wall pattern did not form the canonical Landau state at the deposition thickness of 20 nm. Under the same -0.43 MV/m applied field, the objective was positioned over the 1 um square as seen in Figure 66c (its location in the pattern is circled in green in Figure 66a). Here it was confirmed that the formation of the Landau state, which can be seen as 4 in-plane domains separated by four 90 degree Néel walls and containing a vortex at its center. The inset of this, and the following 3, images depicts the directions of the magnetic domains with red arrows as well as the location of the domain walls with dotted white lines. As the electric field is reduced to -0.16MV/m, the anisotropic strain reduced linearly to approximately -800 ppm and it can be seen that the vortex core of the Landau state begins to broaden in Figure 66d with the domains associated with the larger value of compressive strain begin to grow. Continuing the electric field reduction to 0 MV/m, the remnant strain anisotropy of -1300 ppm is reached and the vortex core completely separated into a 180 degree Néel wall. After the field was increased through the positive coercive field value and to the point of positive electric field where the anisotropy is minimized, point (C) of Figure 65, the 180 degree wall collapses back into a single vortex core and the canonical Landau state reemerges. This procedure shows that the strain transfer to the Ni elements has both hysteretic and reversible components which can be leveraged to generate cyclic operation of stable magnetic configurations. In order to determine exactly how much of the strain energy was transferred to the Ni elements, the elongation of the vortex core into a 180 degree domain wall was compared to an LLG numeric simulation which mapped the magnitude of effective magnetic anisotropy required to achieve the same effect.
Figure 67: LLG simulation of 1μm Ni square depicted with a magnetization vector applied to each finite element (top) and with a simulated Lorentz TEM contrast (bottom). (a-b) No applied anisotropy field. (c-d) 5 kJ/m$^3$ of applied anisotropy energy in the X direction from left to right. (e-f) 10 kJ/m$^3$ of anisotropy field applied in the X direction.

Figure 67 illustrates the results of an LLG micromagnetic simulation on 1 μm Ni square. In these studies the magnetization state was initialized in a random configuration and left to settle into an equilibrium position before a uniform, uniaxial magnetic anisotropy was applied to simulate the effects of applied strain. The top row of images shows the discrete magnetic moments applied to the finite elements to illuminate the approximate directions of the local spin states. The bottom row provides the simulated contrast that would be expected when viewing the magnetic configurations of the corresponding image in the top row under Lorentz TEM. The uniaxial anisotropy ($K_1$) was ramped up until the length of the 180 degree domain wall matched the values
observed by the experimental results seen in Figure 66(d and e). Using the formulation for effective uniaxial magnetoelastic anisotropy:

\[ K_{ME} = \frac{3}{2} \lambda_J E(\Delta\varepsilon) \]  

(4.4)

the expected anisotropy was calculated from the strain differences measured from the PMN-PT crystal in Figure 65. For the Ni square under the application of -0.16 MV/m (Figure 66d) and the corresponding strain measured in Figure 65 at -800 ppm, the resulting magnetoelastic anisotropy is calculated at 7680 J/m³. At the remnant strain value of -1200 ppm under 0 MV/m (Figure 66e), the corresponding anisotropy is calculated at 12480 J/m³. Both of these calculations assume that the etched out Pt window experiences the same strain as the Pt over the bulk PMN-PT and that there is perfect strain transfer to the entire Ni structure by the electrode. It is understood however, that due to shear lag and mechanical impedance disparities between the three materials, that such as optimistic anisotropy is unfeasible. To obtain values of the strain (\(\Delta\varepsilon\)) experienced by the Ni structures observed under TEM, anisotropy energies from the LLG simulations which matched the observed domain states, and Equation (4.4) were utilized. For the results of Figure 66d and Figure 66e the strain was calculated at -536 ppm from 5150 J/m³ and -815 ppm from 7820 J/m³ respectively. These results were approximately 66% of the strain values measured from the PMN-PT in Figure 65 and are very reasonable given a 15% stiffness mismatch between Pt and Ni as well as the expectation that the etched out observation window would see marginally less strain than if it had PMN-PT beneath it to be electrically actuated. Thus a 66% correction factor will be applied to the effective anisotropic strain values for the remainder of the study.
Figure 68: Measurement of domain wall thickness and energy for a 2 μm Ni ring. (a) Domain structure under no application of electric field. (b) Domain structure when field is applied up to the anisotropy free value of 0.43 MV/m. Insets show the TEM images from which the measurements were taken, marked up with red arrows to show magnetization and blue line to show where the measurement of the domain wall was made.

Following the determination of the quantity of strain being transferred to the Ni elements, a characterization of ring elements was performed. The study was initiated by interrogating the full disk, which can be seen circled in yellow in Figure 66a. As stated in the experimental setup, the PMN-PT was saturated with a -0.8 MV/m electric field and then returned to 0 MV/m to observe the remnant magnetic configuration in the disk. Figure 68(a) illustrates the magnetic state present under remnant strain conditions. From the inset it can be seen that there is a 180 degree Néel wall running down the middle of the disk which truncates at a vortex core, which can be seen as the brighter white dot at the top left of the wall. The red arrows indicate the approximate directions of the magnetic spins near the wall and it can be seen that there is a sort of “pseudo-vortex state” present in disks of this geometry. Here, the magnetization forms a circular pattern around the perimeter of the structure but instead of a single vortex core at the center, a similar pattern to the 1 μm square can be seen when the remnant strain is applied to the Landau configuration, wherein the vortex is “stretched” into a 180 degree Néel wall. The graph presented in Figure 68a shows the measured width and intensity of the Néel wall, measured across the blue line shown in the inset. Under remnant strain, the wall appears to be approximately 250 nm wide using its half-peak width.
and have an arbitrary intensity of 800. As the field was increased to the point of zero anisotropy at +0.43 MV/m as seen in Figure 68b, it was observed that the domain wall “straightened” considerably and that the magnetic circulation about the domain wall was significantly less dispersive. The line scan across the domain wall indicates that the width of the wall reduced slightly to approximately 200 nm as measured from its half-peak width, and that the intensity saw a significant increase to 900. From this it can be seen that the 180 degree Néel wall is significantly more stable in the disk geometry than in the square, but that its characteristics can still be modified under the application of strain.

Figure 69: Lorentz TEM images of a Ni disk which did not lift off its ring structure. The letters (a-f) correspond to the strain states observed in the PMN-PT substrate under electric field application as seen in Figure 65. The insets depict the magnetization states with red arrows and domain walls as a white dotted line.
Given that what appeared to be a second full disk was visible in the observation window, an attempt was made to corroborate the effect of domain wall modification which was seen previously. In a much more interesting scenario, it was found that this disk was not actually a disk, but a 200 nm annular width ring that a 20 nm thick disk redeposited onto. Figure 69 shows the effects of actuating this structure with strain. In this figure the letters demarking the applied electric field align exactly with the letters shown in the strain-electric field plot as seen in Figure 65. Throughout this set of experiments the PMN-PT was initialized by saturating it at -0.8 MV/m. Figure 69a shows this stacked geometry at remnant strain. Here it can be seen that a 180 degree Néel wall bisects the disk from bottom left to top right and contains a vortex near its center. The inset at the top right corner provides a schematic drawing of the domain wall configuration shown as a dotted white line and the approximate magnetization directions provided with red arrows. As the ferroelectric was swept to its positive coercive field value of 0.18 MV/m, the sign of the strain anisotropy switched from negative to positive, and the domain wall can be seen to have rotated by 90 degrees in Figure 69b. After repolarizing the PMN-PT crystal in the positive direction by increasing the field beyond the coercivity, the strain anisotropy becomes negatively signed again and the Néel wall rotates back to its original position up through the zero anisotropy mark as observed in Figure 69c. As the field was increased to positive saturation at 0.8 MV/m the anisotropy once again flips sign to become positive and the Néel wall rotated by 90 degrees (not shown) to match the orientation seen in Figure 69b. After positive saturation the field is once again reduced to 0 MV/m. Here the strain anisotropy reduces to -1300 ppm in a linear fashion and as the field passes through point (c) on Figure 65 the domain wall rotates back to its original position as seen in Figure 69d. Continuing to sweep the field negative pushes the ferroelectric through its negative coercivity at -0.18 MV/m and domain state rotates again to align the majority of its
magnetic moments in the compressive direction, 90 degrees from where it began as seen in Figure 69e. Finally as the strain anisotropy becomes negative one last time beyond -0.2 MV/m the rotation is reversed and up until the zero anisotropy point of -0.42 MV/m the strain matches the image in Figure 69f.

From the cyclic results presented in Figure 69, a number of very interesting phenomena can be inferred in this stacked system. The one-to-one evolution of the magnetic state as a function of electric field provides strong evidence that the magnetoelectric heterostructure is strongly coupled. It was posited that in order for this reversible rotation to occur that the ring portion of the structure, which is in contact with the strained Pt film, its magnetic state must be an onion state that can have its pseudo-poles easily modulated under the application of changing magnetic anisotropy. As the upper disk sees only a single vortex state at its center and no out of plane magnetic moments at its edges, it can be inferred that the onion state domains are separated by a transverse wall and not a vortex wall. This is in agreement with what previous experiments would have predicted for the geometry in question and not the calculations based on Equation (4.3), seen in Figure 62. Thus it was believed that phase diagram boundaries which were generated by PEEM and MFM are a correct representation of the magnetic states corresponding to this range of ring geometries. Most interesting is the repeatable nature of the 90 degree rotation of the disks magnetic domain. This rotation closely approximates a rotational magnetic actuator system, similar to a stator (the ring) and rotor (the disk) which are adhered by magnetic and van der Waals forces. If a low friction bearing could be designed such that the disk could freely rotate and electrodes were positioned to deterministically rotate the onion state present in the ring, this could serve as a prototype micromotor controlled entirely by electric field control of multiferroic anisotropy; the first of its kind.
4.4.4 Concluding Remarks

Within this section it has been shown that direct measurements of magnetoelastic nanostructures under the application of electric field induced anisotropic strains. The observation of subtle domain wall phenomena in this study was made possible by the combination of a unique sample structure, high resolution deposition techniques, and Lorentz microscopy which has high sensitivity to in-plane magnetization and excellent spatial resolution. An observation was made that square structures of Ni less than 1.5 µm were required to form a Landau state and that the vortex core could be modulated under the application of anisotropic strains. Observations of the application of magnetoelastic anisotropy also showed that approximately 66% of the strain energy of a PMN-PT substrate can be transduced to an under etched observation window which is viewable under Lorentz TEM. Additionally, it was shown that the width and intensity of Néel walls present in magnetic nanostructures could be stabilized or diminished depending on their direction when anisotropic strains are applied. The experimental curve delineating the vortex to transverse wall onion phases was confirmed by the TEM study and the data provides an approach to further characterize the magnitude of magnetoelastic anisotropy required to rotate elements in different areas of the phase diagram. Most importantly, it was determined that electric field controlled strains could be utilized to deterministically rotate a magnetic heterostructure, consisting of a disk and ring, by a full 90 degrees when the sign of strain anisotropy is reversed. This observation provides the basis for electrically controlled strain mediated memory, rotational magnetic actuations at the nanoscale, and substantiates the foundation for magnetic micromotors.
Chapter 5: CONCLUSION

In the present work the leveraging of anisotropic material behavior was demonstrated to play a significant role in the design of efficient and energy dense transduction mechanisms between various physical regimes. A commonality between the structures presented herein is the mechanical coupling between ferromagnetic and ferrelectric materials to form multiferroic composites. These composite structures were shown to have unique and interesting behavior as functions of temperature, scale, and strain state. While it had been shown previously that these quantities had considerable effects on multiferroic transduction, the additional understanding of anisotropic crystalline, mechanical and domain configurations permit deterministic control of magnetization behavior and allow for optimal coupling into other ferroic media.

Chapter 2 explored the specifics of magnetocrystalline anisotropy as means to increase the energy density and efficiency of thermomagnetic transduction. Here it was shown that the multiferroic transduction of thermal to magnetic energy is enhanced by more highly ordered phase transformations. A case study was performed on order-to-order transitions consisting of the temperature dependent rotation of magnetization direction in textured and monolithic ferromagnetic crystals. A unifying metric of comparing the energy transduction by examining the variation in magnetic entropy is presented. Here it was shown that the spin reorientation transition in NdCo$_5$ can provide upwards of 2MJ/m$^3$ of magnetic energy at a relative efficiency of 22% for energy harvesting applications and that tailored crystalline nanostructures can be tuned by their shape to modify their optimal operating regime.

In Chapter 3 an archetype for an electrically small antenna structure was designed to reduce the requisite length scale by 5 orders of magnitude by utilizing magnetolectric coupling through
anisotropic electroacoustic SAW propagation. A multi-step finite element framework was developed to design and simulate an array of magnetostrictive resonator elements which can generate coherent electroacoustic waves on the surface of piezoelectric substrates. It was shown that the SAW generation and propagations was highly dependent on the mechanical anisotropy of the ferroelectric crystal and the shape anisotropy of the ferromagnetic resonator. Studies were performed for antennas in the HF and VHF range at 18 and 150 MHz, respectively. With the proper anisotropic control, efficiencies as high as -4.7 dB at the center frequency were predicted.

Chapter 4 showed the direct measurement of magnetic domain modulation as a function of electric field for films and nanostructures. Observations of the application of magnetoelastic anisotropy showed that approximately 66% of the strain energy from a ferroelectric substrate can be reliably transduced to ferromagnetic structures deposited on their surface. Under the application of this electrically induced anisotropic strain it was shown that the width and intensity of Néel walls present in magnetic nanostructures could be stabilized or diminished depending on the direction of application. Most importantly, it was determined that electric field controlled strains could be utilized to deterministically rotate a magnetic heterostructure, consisting of a disk and ring, by a full 90 degrees when the sign of strain anisotropy is reversed. This observation provides the basis for electrically controlled strain mediated memory, rotational magnetic actuations at the nanoscale, and substantiates the foundation for magnetic micromotors.
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