ABSTRACT

ALVANDI-TABRIZI, YOUNESS. Electric Control of Magnetization in Biferroic Heterostructures with Patterned Interfaces: A Phase-Field Micromagnetic Study (Under the direction of Dr. Justin Schwartz and Dr. Thomas Dow).

Magnetoelectric coupling in biferroic composite films with ferroelectric and ferromagnetic phases enables control of dielectric polarization via magnetic field or manipulating the magnetization via electric field. The coupling of the ferroic orders is usually strain-mediated and orders-of-magnitude stronger than that in rarely existing single-phase biferroic systems. Potential for practical applications are thereby much higher. Yet, there are fundamental challenges in fully exploiting the emergent properties. In this project, a new design framework based on using patterned interfaces between the constituents is studied with the goal of enhancing electrically induced reconfigurability of the magnetic hysteresis in biferroic heterostructures.

A three-dimensional continuum based micromagnetic model is developed to simulate the magnetization process and strain-mediated magnetoelectric coupling. The model employs the Landau–Lifshitz–Gilbert equation along with mechanical equilibrium and Gauss’ Law for magnetism to calculate the temporal and spatial distributions of the magnetic moments. Thus, this approach falls within the category of phase-field methods used for non-conserved systems. Finite element method is used to solve the partial differential equations in fully coupled fashion while using a different discretization method for each equation.

To perform a quantitate verification of the model, the magnetization process in polycrystalline thin films with different crystallographic texturing and substrate-induced strain is computed. The obtained results are compared with a set of experimental measurements of sol-gel deposited NiFe₂O₄ thin films. The model demonstrate how the magnetization process is altered by adopting different microstructural orientations and the presence of substrate-induced strain.
A comprehensive parametric study is then conducted to analyze the influence of material and geometric variations on the hysteretic behavior of thin films with periodically-ordered nanostructures. Material parameters are magnetostriction coefficient, magnetocrystalline anisotropy constant, and saturation magnetization. Geometric parameters are feature shape, size, spacing, and inclusion of a base layer. The results indicate that patterning could drastically change the magnetization process. Depending on the selection of material and geometric parameters, and the application of mechanical strain, remanence and coercivity may either increase or decrease. Such behavior is explained by considering magnetic anisotropy of different physical origins.

Finally, the magnetization process in biferroic heterostructures of NiFe$_2$O$_4$ and PbTiO$_3$ is simulated. Composite thin films with flat, stripe-patterned, and square-patterned interfaces are considered. The results show that the interfacial patterning dramatically improves the magnetoelectric coupling and hence the electrically induced reconfigurability of the magnetic properties. This is attributed to the elimination of the so-called substrate clamping effect and increase in interfacial surface area.
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Electric Control of Magnetization in Biferroic Heterostructures with Patterned Interfaces: A Phase-Field Micromagnetic Study

by
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DEDICATION

To my mom for her noble heart; and my dad for always having my back.
BIOGRAPHY

Youness was born in April 16\textsuperscript{th}, 1983 in Tabriz, Iran. He went to his hometown university, University of Tabriz, to study mechanical engineering where he received his undergraduate degree in 2007 and his master’s degree in 2010. After working in industry for a while, he attended NC State University in 2013 to pursue his PhD in the same field. He earned his doctoral degree in mechanical engineering in 2018. His research interest include experimental characterization and computational modeling of engineering materials for understanding processing-structure-property relationships. While doing research, he was involved in teaching multiple courses during which he was recognized by Graduate Student Association for Excellence in Classroom Teaching. Youness is also interested in running marathons, cycling, reading, watching movies and playing/listening to music.
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Chapter 1 Introduction

1.1 Motivations

Multiferroic materials exhibit multiple ferroic orders simultaneously. Biferroic magnetoelectric systems are the widely used class of these materials that poses ferromagnetic and ferroelectric order coupling. The magnetoelectric coupling enables controlling dielectric-polarization via applying magnetic field or manipulating material magnetization through application of electric field. The coexistence of ferroelectric and ferromagnetic orders was studied in both single-phase materials with direct coupling between the two ferroic orders [1,2] and composite materials with strain-mediated coupling [3,4]. The room temperature response obtained in strain-mediated coupling is orders-of-magnitude higher than that in single-phase materials, and thus potential for applications is higher. Progress has been sporadic, however, due to the complexity of the composite materials design, especially at small scales.

The most critical parameters impacting magnetoelectric composite performance are interfacial integrity and geometry [3]. Two common design approaches are based on using vertical interfaces in nano-pillars of one phase embedded in a film matrix of another phase or using horizontal interfaces by depositing alternating layers of each phase [5]. To achieve coupling in the layered structure, the in-plane strain should be utilized which is impacted by clamping imposed by the substrate [4,6]. This substrate clamping effect hinders the magnetoelectric coupling in layered structures. By contrast, the coupling in nano-pillar structures uses out-of-plane strain which is not affected by the substrate clamping. The vertical interfaces in these structures, however, span the entire thickness of the film resulting in current leakage problems [7]. An ideal system for achieving high magnetoelectric coupling thereby would be one containing vertical interfaces that are not continuous along the film thickness. A laminated structure with patterned interfaces would serve this purpose. The patterning introduces three-dimensional interfaces, some of which are vertical,
consistent with the ideal geometry for magnetoelectric coupling. In addition, the leakage problem is eliminated due to its layered structure.

1.2 Overview

This dissertation presents a three-dimensional phase-field micromagnetic model to realize the new design framework based on using patterned interface for layered biferroic heterostructure. The model is sought to be an experimentally verifiable design tool for optimizing the material and geometric parameters in patterned films. The focus is on the electric control of magnetization with the aim of achieving electrically induced reconfigurability of magnetic properties. In Chapter 1, motivations for researching this topic and the structure of the dissertation are discussed. Chapter 2 provides a brief overview of the definitions, concepts, background, and applications of strain-mediated magnetoelectric coupling along with the physical origins of ferromagnetism and ferroelectricity. The phase-field micromagnetic formulation used for developing the model in the proceeding chapters are explained in Chapter 3. An experimental verification of the model is presented in Chapter 4 where the role of crystallographic texturing and substrate-induced strain in the magnetization behavior of NiFe$_2$O$_4$ and CoFe$_2$O$_4$ thin films is studied. Chapter 5 utilizes this model to perform a comprehensive parametric study on the magnetization process in magnetic films with periodically ordered surface features. Chapter 6 builds on Chapter 5 to analyses the efficacy of the proposed design framework in improving the strain-mediated magnetoelectric coupling and thus electrically induced reconfigurability of the magnetic properties in NiFe$_2$O$_4$-PbTiO$_3$ composite film system.
Chapter 2 Magnetoelectric biferroic materials

2.1 Introduction

The focus in the field of material science over the past decades was on the invention of new class of materials known as functional materials. A material is generally considered to be functional if it poses certain physical properties that can be utilized for particular applications. One new class of functional materials is multiferroic magnetoelectric heterostructures. These materials are developed in response to the growing demand for miniaturization and power saving in electronic devices. The aim of this chapter is to provide a brief review of the concept of multiferroicity and magnetoelectric coupling with a focus on magnetoelectric biferroic composites.

2.2 Definitions and concepts

Ferroic materials are defined as materials that when undergo below a transition temperature show spontaneous long-range ordering of a macroscopic physical property [1]. As showing in Figure 2.1, this ordering leads to formation of domain structure which can be switched historically by the application of an external field. Ferroic materials are categorized as ferromagnetic, ferroelectric, ferroelastic and ferrotoroidic materials. There are also antiferroic materials in which the ordering is cancelled out; examples are antiferromagnetic and antiferroelectric materials.

Figure 2.1 a) Schematic illustration of ferroic ordering for ferroelectric and ferromagnetic materials, b) historical switching of domain structure (after [1])
The following definitions are given to describe each class of ferroic materials [8].

- **Ferroelectricity** is observed in materials that exhibit stable spontaneous polarization which can be switched by the application of an electric field.

- **Antiferroelectricity** is observed in materials that form order dipole moments but cancel each other completely within each crystallographic unit cell. The macroscopic net polarization is zero.

- **Ferromagnetism** is attributed to a material that experience stable spontaneous magnetization that can be switched by the application of a magnetic field.

- **Antiferromagnetism** is seen in materials that have ordered magnetic moments but they cancel each other completely within each magnetic unit cell. The macroscopic net magnetization is zero.

- **Ferrimagnetism** is incomplete antiferromagnetic cancellation in a way that there is a net magnetization that, similar to ferromagnetic materials, can be switched by the application of a magnetic field.

- **Ferroelasticity** results in spontaneous deformation that is stable and can be switched by the application of a stress field.

- **Ferrotoroidicity** is observed in materials that possess a stable and spontaneous order parameter that is taken to be the curl of a magnetization or polarization. By analogy with other ferroic materials, this order parameter needs to be switchable.

The phenomenon of multiferroicity is attributed to a material that exhibit multiple ferroic or antiferroic ordering simultaneously [9–11]. The most well-known class of multiferroic materials is actually biferroic, possessing ferroelectric and ferromagnetic ordering.
Magnetoelectric coupling is an independent concept that describes controlling dielectric-polarization via applying magnetic field or manipulating material magnetization through application of electric field. This phenomenon is not exclusive to multiferroics and may exist among other class of materials such as paramagnetic ferroelectrics. Figure 2.2 shows the relationship between multiferroic and magnetoelectric materials and the area that these two overlap.

![Figure 2.2](image)

Figure 2.2 The relationship between multiferroic and magnetoelectric materials [8].

The magnetoelectric (ME) biferroic materials are referred to materials that exhibit coupling between the co-existing ferroelectric and ferromagnetic ordering. This notion was originally studied in single-phase materials with direct coupling between the two ferroic orders [1,8]. The room temperature response obtained in such materials, however, is not high enough for most technological applications due to having either low permittivity or low permeability [3]. The alternative approach is to utilize the magnetoelastic and electromechanical coupling in magnetostrictive\(^1\) and piezoelectric\(^2\) materials to make synthetic biferroic heterostructures. The

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\(^1\) Magnetostriction describes a change in strain as a quadratic function of applied magnetic field, or change in magnetization as a quadratic function of applied stress [8].

\(^2\) Piezoelectricity describes a change in strain as a linear function of applied electric field, or change in polarization as a linear function of applied stress [8].
strain transfer across the interface of the two phases will allow the coupling of ferromagnetic and ferroelectric orders (Figure 2.3).

![Figure 2.3 Schematic illustration of strain mediated ME coupling [3].](image)

ME biferroic heterostructures have been made in the form of bulk composites as well as composite films [3,5,12,13]. The response obtained through strain-mediated coupling is orders-of-magnitude higher than in single-phase materials, and thus the potential for applications is enhanced greatly.

### 2.3 Historical background

The history of ME biferroicity starts in 1894 when Pierre Curie stated that “The applications of symmetry conditions provide us that a body with an asymmetric molecule gets electrically polarized when placed in a magnetic field…. And perhaps magnetically when placed in an electric field” [14]. The concept of symmetry was used to predict the existence of the ME effect in certain crystals [15,16]. However, the predictions were not confirmed experimentally until 1960 when ME effect was observed for the first times in Cr$_2$O$_3$. This was followed by thousands
of papers reporting the observation of ME effect in many single crystal and polycrystalline materials [14].

The chart in Figure 2.4 summarizes the evolution of multiferroic magnetoelectricity ever since the prediction of the concept by Pierre Curie. The main applications, advantages and/or disadvantages, research emphasis or challenges of each generation are also included in this figure [17].

![Figure 2.4](image)

Figure 2.4 Evolution on the development of ME materials: from single-phase compounds to multi-phase ferromagnetic/ferroelectric composites and from bulk laminates to micro-/nano-thin films [17].

As mentioned previously, ME biferroicity in single phase materials is mostly observed at low temperatures. Bismuth ferrite (BiFeO₃) is one of the few materials that shows room temperature ME biferroicity [8]. The coupled orders, however, are ferroelectricity and antiferromagnetism. In other words, it exhibits magnetically switchable electric polarization, but the net magnetization is zero. This antiferromagnetic behavior is a big shortcoming from technological point of view.

The idea of strain mediated ME coupling was first proposed in 1972 by van Suchtelen [7,10]. Later on, researchers at Philips Laboratories in the Netherlands started to fabricate first ME composites. They employed unidirectional solidification approach to prepare ceramic composites
of BaTiO$_3$-CoFe$_2$O$_4$. The obtained ME coefficient was hundreds of times larger than that of single-phase multiferroics [10]. However, since the unidirectional solidification method is very costly, this new field of ME composite went dormant for the next 20 years. In early 1990s, the conventional sintering process was used to prepare more cost-effective ME composites. Since then numerous efforts have gone into developing new fabrication methods in order to improving the ME coupling and increase the ME coefficient. Along with the progress in processing methods, analytical models were developed to predict and study the mechanisms that result in ME effect [18]. This expedited the advancement in experimental techniques.

2.4 The origin of ferromagnetism

2.4.1 Diamagnetic and paramagnetic materials

Magnetization is the manifestation of the electric charges in motion [19]. On this basis, electrons orbiting the nucleus in atom and electrons spinning themselves will produce magnetic moment. The magnetic moment due to electron spin is parallel to the axis of the spin and the magnetic moment due to electron orbital motion is normal to the plane of the orbit. The vector field that explains the density of the magnetic moments is called magnetization.

The magnetic moment of an atom is vector sum of spin and orbital magnetic moments of all electrons in atom. There are two possible scenarios:

1. There is no unpaired electrons in the outer orbital shell and as a result the magnetic moments of electrons are canceled and the net magnetic moment of the atom is zero.

2. There are unpaired electrons in the outer orbital shell and as a result the magnetic moments of the electrons are only partially canceled and the net magnetic moment of the atom is non-zero.
The former leads to definition of diamagnetic materials. Electrons which fill closed shell in an atom orient their spin and orbital magnetic moment in a way that the atomic magnetic moment is zero. Monoatomic rare gases such as helium (He), or polyatomic gases such nitrogen (N₂) are good examples.

Although, the net magnetization of diamagnetic materials is zero, application of the applied field induces negative magnetic moments in the opposite direction. A repulsive force builds up in the atom resisting the magnetic field to lower the amount of current orbiting around the nucleus by reducing the electron speed. This translates into the negative magnetization. This effect which is called diamagnetic effect is not exclusive to diamagnetic materials. But since it is very week, it can only be detected in diamagnetic materials. For this reason, the magnetic susceptibility, which is the measure of the amount of magnetic moments induced in a material by application of the magnetic field, is negative in diamagnetic materials.

Paramagnetic materials are consisted of the atoms in which there exist unpaired electrons in the outer orbital and hence the magnetic moments of the electrons is only partially cancelled out. In the absence of a magnetic field, thermal agitations tend to distribute the atomic moment randomly. As a result, the material as a whole has zero net magnetization. By the application of the magnetic field, the atomic moments orient themselves along the field resulting in magnetization along the field direction. That means the magnetic susceptibility in paramagnetic materials is positive. As soon as the magnetic field is removed, thermal agitations push the material to go back to its disordered state with zero net magnetization. The effect of thermal agitations decreases as the temperatures goes down and hence the magnetic field required to bring order to the magnetic moments becomes smaller. Oxygen gas (O₂) is a good example of paramagnetic material.
2.4.2 Ferromagnetic materials

In some paramagnetic materials, such as iron, nickel and cobalt, the interatomic distance is so small that below a certain temperature known as Curie temperature, the magnetic moments of the electrons in each atom is coupled to the magnetic moments of the electrons in neighboring atoms. When the atoms get closer to each other they start to exchange the electrons that orbit their outer shell. Such exchange interaction is stronger between atoms of iron, nickel and cobalt and develops a force between the unpaired electrons in 3d shell aligning their spin in the same direction. As a result, the net magnetic moment of atom is much larger than the regular paramagnetic materials.

This strong net magnetic moment and interaction between them result in parallel alignment of magnetic moments in the material even in the absence of magnetic field (see Figure 2.5a). This is called spontaneous magnetization and the materials that show this behavior are classified as ferromagnetic materials.

The regions of the material in which the magnetic moments are aligned parallel to each other are called domains. In order to reduce the free energy of the system, there should be more than one domain in materials that are larger than a critical size. The magnetization vector in each domain is usually normal or antiparallel to the magnetization vector in the neighboring domains. These domain are separated by domain walls.

Under the application of the magnetic field, the domains that are aligned close the field direction increase in size and those that are aligned far from the field direction reduce in size. This process involves domain wall motion which is very sensitive to the presence of defects in the crystal structure. By increasing the applied field all domain walls go away and material becomes a monodomain with magnetization along the field direction.
The important characteristic of ferromagnetic materials is the hysteretic losses during the magnetization process. When a ferromagnetic material is cooled down from Curie temperature, domain structures will form with a magnetization in each domain equal to the maximum possible amount of the magnetization that can be reached. This is known as saturation magnetization. Usually, the domain structure forms in a way that the net magnetization of the material is zero. As it is shown in see Figure 2.5b, by applying an external field, the net magnetization increases non-linearly until it reaches to its saturation level. Removing the field, the material does not go back to its original un-magnetized state, rather it holds a non-zero net magnetization which is called remanent magnetization. In order to reduce the net magnetization to zero, a negative external field should be applied which is known as coercive field.

2.4.3 Antiferromagnetic and ferrimagnetic materials

It should be emphasized that the interatomic distance is the only contributor for ferromagnetic behavior and it goes away when the temperature reaches the Curie temperature. Above this temperature a ferromagnetic material becomes paramagnet. In some materials such as Mn, the interatomic spacing is so small that the exchange interaction between atoms results in alignment of electron spins in opposite directions (see Figure 2.5a). This phenomenon, which is called antiferromagnetism, results in complete cancelation of magnetic moments and hence produces zero net magnetization.

There is another phenomenon observed in compounds known as ferrimagnetism which is similar to antiferromagnetism but results in partial cancelation of the magnetic moments of each constituents due to their special crystal structure.
2.4.4 Magnetostriction

Depending on the crystal structure, in most materials the magnetic moment due to electron’s spin is much stronger than that due to electron’s orbital motion. Accordingly, in most calculations the orbital magnetic moment is ignored. For some materials, such as ferromagnets, the strength of the orbital magnetic moment is not negligible and hence its presence is very important because the interaction between the magnetic moment due to electron’s spin with that due to electron’s orbital motion results in spin-orbit coupling. Since the orbital motion of the electron is dictated by the lattice structure, the spin-orbit coupling links the electronic magnetic moment to crystal structure. In other words, changing the orientation of the magnetic moments will result in deformation in lattice structure. This links the mechanical strain and magnetization in ferromagnetic materials and is called magnetostriction.
2.5 The origin of ferroelectricity

2.5.1 Dielectric and paraelectric materials

A dielectric material is an electrical insulator in which electrical dipole moments can be induced by the application of electric field. The vector field that expresses the density of induced electrical dipole moments is called polarization. One of the important properties of dielectric materials is dielectric constant $K$, also known as relative permittivity, which is the measure of the materials ability to store charge. In most dielectric materials the polarization achieved is linearly proportional to the applied field and the dielectric constant is the constant of the proportionality.

There are four main mechanisms for polarization in dielectric materials [20].

1. Electronic polarization
2. Ionic polarization
3. Orientational polarization
4. Spontaneous polarization

Electronic polarization occurs in all materials and arises from field induced changes in symmetrical distribution of electron cloud around each atom. Ionic polarization takes place in materials made of two or more different kinds of atoms that share their valence electrons and form an ion. Similar to electronic polarization, the ionic polarization is induced by the application of electric field. Both of these polarization mechanism seek lower potential energy by elastically displacing the valence electron clouds from their original thermal equilibrium state to a new equilibrium state. The new equilibrium state is only slightly dependent on thermal agitations.

Orientational polarization occurs in materials that possess permanent dipoles. These are the materials that have ionic bonding in which the negative and positive charge centroids do not coincide. One good example is water (H$_2$O). The directions of these permanent dipole moments
are randomly distributed in the material and hence the net polarization is equal to zero. An electric field will cause them to change their orientations which results in the rotation of the molecule. This process that is called orientational polarization is strongly temperature dependent. After the electric field is removed the ordered orientations go back to their disordered state resulting in zero net polarization. This temporary polarization of the material in the presence of electric field is called paraelectricity and is analogous to the concept of paramagnetism.

As paramagnetism corresponds to positive magnetic susceptibility, paraelectricity corresponds to positive electric susceptibility. It should be noted that there is no counterpart to diamagnetization in dielectric materials and unlike diamagnetic materials that have negative magnetic susceptibility, the electric susceptibility in dielectric materials is not negative.

2.5.2 Pyroelectric and piezoelectric materials

The formation and rotation of electrical dipole moments is coupled with the lattice structure in crystals. The lattice structure is also linked to thermal agitations and mechanical strain. As a result, the formation and rotation of the electrical dipole moments is coupled to temperature field and strain field. The coupling of the dipole moments with temperature is expressed with pyroelectric effect and its coupling with strain is expressed by piezoelectric effect.

2.5.3 Ferroelectric materials

In pyroelectric materials, the permanent dipole moments are present only below a critical temperature, also known as Curie temperature. Above this temperature the centroid of negative charges coincides with the centroid of the positive charges and no electric dipole moment form. At and below this critical temperature, the crystal undergoes a phase transformation that results in different centroids for positive and negative charges and hence leads to development of permanent
electrical dipole moments. The dipole moment in each unit cell is coupled with the dipole moments of the neighboring unit cells so that they tend to be aligned parallel. This process is called spontaneous polarization.

The chain of unit cells with coupled dipole moments will form a domain of ordered dipole moments. This is similar to formation of magnetic domains in ferromagnetic materials. However, the spontaneous polarization is the characteristic of pyroelectric materials and is not exclusive to ferroelectric materials. Ferroelectricity, requires the spontaneous polarization to be reversible by the application of external electric field. The difference between pyroelectricity and ferroelectricity is shown in Figure 2.6.

![Figure 2.6 Schematic representation of the fundamental polarization mechanisms and crystal symmetry in dielectric materials](image)

The prefix ferro- is derived from ferum, which means iron in Latin. This prefix is more relevant for ferromagnetics because iron is a good example of ferromagnetic materials. But there
is no iron atom in ferroelectric materials. In fact, ferroelectricity is discovered much later than ferromagnetism. Thus, the prefix ferro- in ferroelectricity implies similarity in characteristics to ferromagnetism.

Just like the ferromagnetic materials, ferroelectric materials show hysteretic behavior with saturation polarization, remanent polarization and coercive field. In similar sense, there are materials that show antiferroelectric behavior (see Figure 2.6).

2.5.4 Crystal symmetry

It can be imagine that materials exhibiting ferroelectric behavior must have crystalline order. In fact all ferroelectric materials are either single crystals or polycrystalline solids composed of crystallites. On a similar basis, all the mechanisms for polarization of dielectric materials mentioned above can be explained by the symmetry in crystalline structure.

According to the symmetry elements of translational position and orientation, there are 230 space groups. Ignoring translational reputation, these 230 space groups are reduced to 32 point groups that are based on orientation only. These 32 point groups are subdivisions of seven basic crystal systems. In the order of the lowest symmetry to the highest symmetry, these seven basic crystalline structures are triclinic, monoclinic, orthorhombic, tetragonal, trigonal (rhombohedral), hexagonal, and cubic [22].

Piezoelectric behavior requires possessing no center of symmetry because all the components of the piezoelectric tensor are zero for centrosymmetric crystals. Accordingly, the piezoelectric effect may only exist in non-centrosymmetric point groups. There are 11 point groups that have center of symmetry. One of the non-centrosymmetric point groups exhibit other combined symmetry elements that results in the cancellation of the piezoelectric charges. Hence, the remaining 20 point groups show piezoelectric behavior. 10 classes of these 20 point groups
possess unique polar axis that can be spontaneously polarized. These 10 classes show piezoelectric and pyroelectric behavior at the same time. There is only one subgroup within this 10 point groups that is capable of reversing the spontaneous polarization along the polar axis. This is the only symmetry that fulfils the requirement for ferroelectricity.

### 2.6 ME biferroic heterostructures

#### 2.6.1 Strain mediated ME coupling

ME biferroic composites that are made by combining ferromagnetic and ferroelectric materials possess very strong ME coupling which is several orders of magnitude higher than that in single compounds and is sustainable at room temperature [5].

Strain mediated ME coupling in biferroic composites is an extrinsic effect; a product tensor property that results from cross interaction of magnetostrictive effect in ferromagnetic phase and piezoelectric effect in ferroelectric phase [5]. As schematically shown in Figure 2.7, when a magnetic field is applied to a composite, the magnetic phase changes its shape magnetostrictively. The strain is then passed along to the ferroelectric phase resulting in electric polarization (converse piezoelectric effect). This process is called as direct ME effect (Figure 2.7a). The inverse process is referred to as converse ME effect (Figure 2.7b). In this case electric field is applied which results in deformation of ferroelectric phase due to piezoelectric effect. As the strain is transferred to the ferromagnetic phase, the magnetostriction effect alters the magnetization.
Figure 2.7 Schematic illustration of strain-mediated ME effect in a composite system consisting of a magnetic layer (purple) and ferroelectric layer (pink) [5].

2.6.2 Connectivity schemes

Advances in thin-film growth techniques have enabled development of nano-structured multiferroic composites. Experiments show that such materials could exhibit more promising ME effect compared to their bulk counterparts [3,5,7,10,23]. Unlike the bulk counterparts where the connectivity between the two phases are not very strong\(^1\), the two phases in nano-structured films are directly connected in atomic level [5,8]. This implies stronger coupling between the phases. In addition, larger electric field can be comfortably applied to thin-films as they require smaller bias voltages [3]. Moreover, the small scale nature of these materials allows more precise control over parameters during fabrication process which enable tuning of the properties toward targeted behavior [5].

---

\(^1\) Connectivity between the phases in bulk composites is usually achieved via polymeric resins or sintering the phases [10].
The ME composites are generally classified based on connectivity of the phases that constitute the material. The classification follows the notation of Newnham [24] in which the design is referred to as \( x-y \) where \( x \) is the dimension of the connectivity in the first phase and \( y \) is the dimension of the connectivity in the second phase. The most widely employed designs are shown in Figure 2.8.

![Diagram](image)

**Figure 2.8** Schematic illustration of three kinds of ME composite nanostructures with common connectivity schemes. (a) 0-0 non-continuous inclusions embedded in a continuous matrix (3), (b) 2-2 horizontal laminated layers of ferroelectric and ferromagnetic materials, and (c) 1-3 vertical pillars of one phase embedded in a matrix of another phase [5].

The ME coupling in film composites is highly affected by the constraint imposed by the substrate. The mechanical clamping of the substrate reduces the flexibility of the film to deform under electric/magnetic field and drastically reduces the ME coupling [3,5,7,10,14]. The 2-2 configuration is more affected as in-plane deformation is needed in order to transfer the strain between layers. As a consequence, this configuration is expected to have a weak ME coupling at nano-scale which is exactly the opposite of what is observed in large-scale [7]. The strain transfer in 1-3 systems, on the other hand, is not limited to in-plane deformation and could be achieved via out-of-plane deformation as well [7]. As a result, 1-3 systems show reduced substrate clamping effect which should lead to more efficient ME coupling. However, since the vertical structures in these films are continuous along the thickness and because the ferromagnetic phase usually has lower resistivity than ferroelectric phase, ferromagnetic phase forms a short circuit. The leakage problem affects the piezoelectric functionality of the ferroelectric phase and hence weakens the
overall ME coupling [7,10] If the leakage problem is eliminated, larger interfacial surface area in these systems leads to even more enhanced ME coupling that can exceed the values reported for balk composites [2,3].

Since the ferromagnetic phases are not connected to the electrodes in the laminated structure, the leakage problem does not exist in 2-2 systems. Moreover, the fabrication process for 2-2 systems are much easier which makes these design configuration even more desired.

2.6.3 ME coefficient

The figure of merit that quantifies the coupling strength between the electric and magnetic field in synthetic biferroic ME materials is ME coefficient which is a product tensor property [7,10]. Direct ME coefficient ($\alpha_{direct}$) measures the efficacy of controlling the electric polarization through the applied magnetic field.

$$\alpha_{direct} = \frac{\partial P}{\partial H}$$ (2.1)

The direct ME voltage coefficient ($\alpha_E$), which is the ratio of output electric field produced to the applied magnetic field, is another metric.

$$\alpha_E = \frac{\partial E}{\partial H}$$ (2.2)

Electric field control of magnetization is quantified by the converse ME coefficient ($\alpha_{converse}$) that measures the appearance of the magnetization upon applying electric field.

$$\alpha_{converse} = \frac{\partial M}{\partial E}$$ (2.3)

The ME coefficient is directly related to the elastic coupling within the piezoelectric and magnetostrictive phases as well as the interfacial coupling between them [4]. On this basis, the parameters affecting the performance of biferroic ME films fall into two main categories:
1) Parameters related to constituents of the composite and their independent performance.

2) Parameters related to connectivity and interfacial bonding, including the interfacial geometry and the presence of intermediate layers.

2.6.4 Material selection

The parameters that should be considered for selecting constituents of biferroic ME heterostructures include electric permittivity, magnetic permeability, ordering temperatures, remanent polarization, remanent magnetization, coercive electric field, coercive magnetic field, dielectric losses, electrical resistivity, and piezoelectric and magnetostrictive constants [3]. In addition, the conditions required to synthesize the phases with the desired textures and to process the integrated composite must be factored.

It should be noted that the ultimate purpose of design plays a significant role in determining what parameters should be considered, whether it is designed for magnetic control of polarization or electric control of magnetization. Figure 2.9 summarizes the best values of ME coefficient obtained for different combinations of materials in bulk and film-based ME composites having 0-3, 1-3, and 2-2 connectivity [4].

Figure 2.9 Reported values of off-resonance ME voltage coefficients for various material systems: (a) bulk and (b) film-based ME composites [3].
Various piezoelectric and magnetostrictive phases have been used for construction of ME composites. Some of these materials are listed in Table 2.1. Among the piezoelectric materials, PZT-based ceramics have been widely employed to fabricate the ME composites due to their low cost, high piezoelectric response, and flexibility in modifying the composition. For the magnetostrictive phase, terfenol-D with high magnetostriction and metglass (amorphous Fe-alloy) with high magnetic permeability have been the most used materials [3].

Table 2.1 List of well-known piezoelectric and magnetostrictive materials used as constituents of ME composites. The list is taken from [3].

<table>
<thead>
<tr>
<th>Piezoelectric Phase</th>
<th>Magnetostrictive Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lead-based:</strong></td>
<td><strong>Metals:</strong></td>
</tr>
<tr>
<td>Pb(Zr,Ti)O₃ (PZT)</td>
<td>Fe, Co, Ni</td>
</tr>
<tr>
<td>Pb(Mg₁₀/₃Nb₂₀/₃)O₃-PbTiO₃ (PMN-PT)</td>
<td>FeNi-based</td>
</tr>
<tr>
<td>Pb(Zn₁₀/₃Nb₂₀/₃)O₃-PbTiO₃ (PZN-PT)</td>
<td>FeCo-based</td>
</tr>
<tr>
<td>Pb(Mg₁₀/₃Nb₂₀/₃)₁₋ₓ(Zrₓ,Ti₁₋ₓ)₁₋ₓO₃ (PMN-PZT)</td>
<td>CoNi-based</td>
</tr>
<tr>
<td>Pb(In₁₀/₃Nb₂₀/₃)O₃-Pb(Mg₁₀/₃Nb₂₀/₃)O₃-PbTiO₃ (PIN-PMN-PT)</td>
<td>NizMnGa</td>
</tr>
<tr>
<td><strong>Lead-free:</strong></td>
<td><strong>Alloys:</strong></td>
</tr>
<tr>
<td>BaTiO₃ (BTO)-based</td>
<td>Permendur (FeCoV)</td>
</tr>
<tr>
<td>(K₀.₅Na₀.₅)NbO₃ (KNN)-based</td>
<td>Galfenol (FeGa), FeGaB</td>
</tr>
<tr>
<td>Na₀.₅Bi₀.₅TiO₃ (NBT)-based</td>
<td>Samfenol (SmFe₂)</td>
</tr>
<tr>
<td><strong>Others:</strong></td>
<td><strong>Ceramics:</strong></td>
</tr>
<tr>
<td>AlN</td>
<td>Terfenol-D (Tb₁₋ₓDyₓFe₂)</td>
</tr>
<tr>
<td>ZnO</td>
<td>Fe-based metallic glasses (FeBSi, FeBSiC, FeCoB, FeCoSi, FeCoSiB, FeCuNbSiB)</td>
</tr>
<tr>
<td>(Sr, Ba)Nb₂O₅</td>
<td></td>
</tr>
<tr>
<td>Ba₁₋ₓSrₓTiO₃ (BSTO)</td>
<td></td>
</tr>
<tr>
<td>Bi₁₋ₓSrₓTiO₃ (BST)</td>
<td></td>
</tr>
<tr>
<td>La₂Ga₅SiO₁₄ (LGS)</td>
<td></td>
</tr>
<tr>
<td>La₂Ga₅Ta₀.₅O₁₄ (LGT)</td>
<td></td>
</tr>
<tr>
<td>Polyurethane (PU)</td>
<td></td>
</tr>
<tr>
<td>Polyvinylidene difluoride (PVDF)</td>
<td></td>
</tr>
</tbody>
</table>

It has been widely accepted that the only contributor to ME effect in bulk composites is strain coupling [10]. However, the mechanisms responsible for ME effect in nano-structured composites are still under investigation. Better understanding of the ME coupling in these materials requires considering the basic characteristic of films such as residual stress/strain resulting from lattice mismatch or differences in coefficient of thermal expansion. In addition to
this, the effect of spontaneous polarization/magnetization should also be taken into account as the obtained domain structure is relatively comparable to the size scale of the films [5,23].

In addition to the strain mediated coupling, studies have reported two other mechanisms that contribute to the converse ME effect; charge-mediated and exchange-bias mediated ME effects [7].

In the laminated heterostructures containing ultrathin ferromagnetic films, an electric field could result in the accumulation of spin-polarized electrons or holes at the interface. The change in the number of free carriers produces a change in the surface magnetization and the surface magnetocrystalline anisotropy [7].

The exchange bias, resulting from the exchange coupling between the uncompensated interfacial spins of the antiferromagnetic and the spins of the ferromagnetic layer, has also been employed for electric field control of the magnetic properties in the ferromagnetic films [7].

2.7 Applications

The potential applications of different ME composite depend on the type of the ME coupling. The most popular proposed applications are magnetic sensors, electric sensors, biomedical applications, magnetoelectric recording, energy harvesters, magnetic antenna, high-frequency inductors, and high-frequency signal processing devices [1,3,7,10,25]. The main advantages of using multiferroic magnetoelectricity for these applications are design miniaturization, lowering power consumption and improving performance speed [7].

2.8 Modeling of ME behavior in biferroic films

2.8.1 Green’s function method

Early attempts to model biferroic ME films were based on the Green’s function approach which was used successfully for bulk composites [26,27]. These models, however, were not
capable of simulating the complexity of ferroelectric and ferromagnetic domain structures. Since
the relative sizes of the films are very close the domain sizes, any assumption that neglects domain
structure effects is intrinsically inaccurate. An alternative approach is the phase-field method
which has been proven to be a powerful tool for studying the ferroelectric and ferromagnetic
ordering [28–30].

2.8.2 Phase-field methods

Many problems in materials science, including ferroelectric and ferromagnetic behavior,
are heterogeneous in nature at the mesoscale and involve the formation and evolution of domains.
Phase-field methods, which are based on deriving an evolution equation from thermodynamics
that predicts the transition of the domains, effectively capture the spatial and temporal evolution
of the interfaces in such problems [28–30]. The evolution equation consists of variables, generally
known as order parameters, which are constant within the domains and continuous across the
interfaces. Additional field equations are coupled with the evolution equation to derive the
constitutive relationships that describe the desired physical behavior. Determining the distribution
of the order parameters by solving these equations enables understanding the mechanisms behind
domain structure formation and evolution, and predicting its behavior under different condition.
Phase-field methods have been used previously to model ferroelectric [28,31–36] and
ferromagnetic [37–43] behavior. They have also been used to model biferroic coupling in ME
composite films by combining the equations of the ferroelectric and ferromagnetic models [44–
46].
Chapter 3 Phase-field micromagnetics: a continuum thermodynamics formulation

3.1 Free energy functional

The free energy functional for phase-field micromagnetic modeling is a state function for magnetization derived from continuum thermodynamics and crystal symmetry considerations. Assuming the temperature is constant and well below the Curie temperature it can be written as:

\[ h = h(\varepsilon_{ij}, H_i, m_i, m_{ij}) \]  \hspace{1cm} (3.1)

where the primary field variables are the strain field tensor \( \varepsilon_{ij} \), magnetic field vector \( H_i \), magnetization unit vector (also known as direction cosines) \( m_i \), and its gradient \( m_{ij} \). Standard index notation with summation convention over repeated indices is used throughout this document. The indices are running over the range of 1-3. The comma in the subscript denotes partial differentiation with respect to spatial coordinate \( x_i \).

Under the assumption of linear kinematics, the strain tensor in a material body can be calculated from mechanical displacement \( u_i \).

\[ \varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) \]  \hspace{1cm} (3.2)

The magnetic field and magnetization unit vector are related to the magnetic field \( B_i \), via

\[ B_i = \mu_0(H_i + M_s m_i) \]  \hspace{1cm} (3.3)

\( \mu_0 \) is the permeability of the free space and \( M_s \) is the saturation magnetization. The magnetic field can be expressed as the gradient of the magnetic scalar potential \( \phi \).

\[ H_i = -\phi_{,i} \]  \hspace{1cm} (3.4)

Assuming constant saturation magnetization

\[ m_i = \frac{M_i}{M_s} \]  \hspace{1cm} (3.5)
where $M_i$ are the components of the magnetization field vector. The modulus of the magnetization vector is assumed to be constant and equal to the saturation magnetization. Therefore, it is more convenient to use the magnetization unit vector as the primary order parameter.

The total free energy density functional for phase-field micromagnetics modeling consists of contributions from magnetocrystalline anisotropy energy $h_{\text{aniso}}$, exchange energy $h_{\text{exch}}$, elastic energy $h_{\text{elastic}}$, and magnetostatic energy $h_{\text{magnetostatic}}$. The competition between these four energy terms defines the magnetic state of the material:

$$h = h_{\text{aniso}} + h_{\text{exch}} + h_{\text{elastic}} + h_{\text{magnetostatic}}$$ (3.6)

The magnetocrystalline anisotropy energy arises because the magnetization process depends on the crystallographic directions. Ignoring the higher order terms, the magnetocrystalline anisotropy energy for cubic symmetry is

$$h_{\text{aniso}} = K_1(m_1^2m_2^2 + m_1^2m_3^2 + m_2^2m_3^2) + K_2(m_1^2m_2^2m_3^2)$$ (3.7)

Here $K_1$ and $K_2$ are denoted as the first and second anisotropy constants. Depending on their sign and magnitude, Eq. (3.7) creates energy wells that favor certain magnetization directions.

The exchange energy or gradient energy is related to the inhomogeneous distribution of the magnetization and originates from a short-range interaction between magnetic moments while tending to keep them parallel. The mathematical expression is defined as the square of the spatial gradient of the magnetization directions:

$$h_{\text{exch}} = A_{\text{exch}}(m_{1,1}^2 + m_{1,2}^2 + m_{1,3}^2 + m_{2,1}^2 + m_{2,2}^2 + m_{2,3}^2 + m_{3,1}^2 + m_{3,2}^2 + m_{3,3}^2)$$ (3.8)

where $A_{\text{exch}}$ is the exchange stiffness constant.

The elastic energy arises from deformations due to the effect of inhomogeneous magnetostriction. The compatibility of the strain field requires that the magnetostrictive strains be
accompanied by elastic strains. The resultant elastic energy contains a positive term for pure elastic strains and a negative term for quasi-plastic magnetostrictive strains [47].

\[ h_{\text{elastic}} = \frac{1}{2} C_{ijkl} (\varepsilon_{ij} - \varepsilon^m_{ij})(\varepsilon_{kl} - \varepsilon^m_{kl}) = \frac{1}{2} C_{ijkl} e_{ij} e_{kl} \]  

(3.9)

where \( C_{ijkl} \) is the fourth order elastic stiffness tensor, \( \varepsilon_{ij} \) is the pure elastic strain, \( \varepsilon^m_{ij} \) is the magnetostrictive strain, and \( e_{ij} = \varepsilon_{ij} - \varepsilon^m_{ij} \). The magnetostrictive strain is a function of magnetostriction constants and components of the magnetization unit vector. In the case of a cubic crystal it is given by:

\[
\varepsilon^m_{ij} = \begin{bmatrix}
\frac{3}{2} \lambda_{100} \left( m_1^2 - \frac{1}{3} \right) & \frac{3}{2} \lambda_{111} m_1 m_2 & \frac{3}{2} \lambda_{111} m_1 m_3 \\
\frac{3}{2} \lambda_{111} m_2 m_1 & \frac{3}{2} \lambda_{100} \left( m_2^2 - \frac{1}{3} \right) & \frac{3}{2} \lambda_{111} m_2 m_3 \\
\frac{3}{2} \lambda_{111} m_3 m_1 & \frac{3}{2} \lambda_{111} m_3 m_2 & \frac{3}{2} \lambda_{100} \left( m_3^2 - \frac{1}{3} \right)
\end{bmatrix}
\]

(3.10)

where \( \lambda_{100} \) and \( \lambda_{111} \) are magnetostriction constants corresponding to the displacement due to saturation along \(<100>\) and \(<111>\) directions, respectively. Given the symmetry in crystal classes, most elements of the stiffness tensor are zero. For a cubic crystal, only three independent elastic constants are needed. Using the Voigt notation, Eq. (3.9) can be re-written as

\[
h_{\text{elastic}} = \frac{1}{2} c_{11}(e_{11}^2 + e_{22}^2 + e_{33}^2) + c_{12}(e_{11}e_{22} + e_{22}e_{33} + e_{11}e_{33}) \\
+ c_{44}(e_{12}^2 + e_{21}^2 + e_{23}^2 + e_{32}^2 + e_{13}^2 + e_{31}^2)
\]

(3.11)

Substituting Eq. (3.10) into Eq. (3.11) and neglecting the higher order terms yield the following polynomial expressions for elastic energy.
\[ h_{\text{elastic}} = \frac{1}{2} c_{11}(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + c_{12}(\varepsilon_{11}\varepsilon_{22} + \varepsilon_{22}\varepsilon_{33} + \varepsilon_{11}\varepsilon_{33}) \]

\[ + c_{44}(\varepsilon_{12}^2 + \varepsilon_{21}^2 + \varepsilon_{23}^2 + \varepsilon_{32}^2 + \varepsilon_{13}^2 + \varepsilon_{31}^2) \]

\[ - \frac{3}{2} \lambda_{100}(c_{11} - c_{12})(\varepsilon_{11}m_1^2 + \varepsilon_{22}m_2^2 + \varepsilon_{33}m_3^2) \]

\[ - 3\lambda_{111}c_{44}(\varepsilon_{12}m_1m_2 + \varepsilon_{21}m_2m_1 + \varepsilon_{23}m_2m_3 + \varepsilon_{32}m_3m_2 + \varepsilon_{13}m_1m_3 \]

\[ + \varepsilon_{31}m_3m_1) \]

The energy landscape associated with the self-demagnetization field and external field is called the magnetostatic interaction energy. The demagnetization field energy is the result of the interaction of the magnetization with the magnetic field generated by the magnetic body itself. The competition between the long-range magnetostatic energy and short-range exchange energy forms the magnetic domain structure. It should be noted that the magnetostatic energy includes both the energy stored in the material as well as in the free space.

\[ h_{\text{magnetostatic}} = -\mu_0 M_S(H_1m_1 + H_2m_2 + H_3m_3) - \frac{1}{2}\mu_0(H_1^2 + H_2^2 + H_3^2) \]

Summing the above energy terms, the total magnetic free energy density functional for a cubic crystal is obtained.

### 3.2 Field equations

The field equation for the stress field equilibrium is based on the conservation of linear and angular momentum. Assuming small deformations and neglecting the body forces, the quasi-static mechanical equilibrium in a material body takes the following form for Cauchy stress tensor \( \sigma_{ij} \)

\[ \sigma_{ij,j} = 0 \]

The magnetic field in the material body (and also in the free space) is governed by Gauss' Law for magnetism which ensures the solenoidality of the magnetic induction:

\[ B_{i,i} = 0 \]
The stress and magnetic field induction can be calculated using derivatives of the free energy density functional with respect to the strain and magnetic field, respectively,

\[ \sigma_{ij} = \frac{\partial h}{\partial \varepsilon_{ij}} \]  
\[ B_i = -\frac{\partial h}{\partial H_i} \]  

Substituting Eq. (3.16) into (3.14) and Eq. (3.17) into Eq. (3.15), the final form of the field equations are written as

\[ \frac{\partial}{\partial x_j} \left( \frac{\partial h}{\partial \varepsilon_{ij}} \right) = 0 \]  
\[ \frac{\partial}{\partial x_i} \left( \frac{\partial h}{\partial H_i} \right) = 0 \]  

### 3.3 Evolution equation

The evolution equation that is mostly used in phase-field micromagnetics is the LLG equation. The evolution equation in this study is derived following a similar approach proposed by Landis [38]. In his work, the configurational micro-forces are incorporated into the balance law of angular momentum and the second law of thermodynamics is used to derive two evolution equations for magnetic domain and martensite twin structures of ferromagnetic shape memory alloys. Here, only the magnetic part is needed and hence the magnetization unit vector \( m_i \) is employed as the sole order parameter. See [38] for more details. Removing the martensitic parts and using the magnetization unit vector instead of the magnetization vector as the order parameter, the evolution equation becomes:

\[ \frac{1}{\gamma_0 \varepsilon_{ijk}} \frac{\partial m_j}{\partial t} m_k + \beta_{ij} \frac{\partial m_j}{\partial t} - \frac{1}{M_s} \frac{\partial}{\partial x_j} \left( \frac{\partial h}{\partial m_i} \right) = -\frac{1}{M_s} \frac{\partial h}{\partial m_i} \]  

(3.20)
where $\gamma_0 = 1.76 \times 10^{11}$ T$^{-1}$s$^{-1}$ is the gyromagnetic ratio for an electron spin, $\epsilon_{ijk}$ is the permutation tensor, and $\beta_{ij}$ is the viscosity tensor. The viscosity tensor is a diagonal matrix with constant positive elements and is related to Gilbert’s damping parameter $\eta$ through Rayleigh dissipation functional [48]:

$$\beta_{ij} = \eta \delta_{ij} = \frac{\alpha}{\gamma_0} \delta_{ij}$$  \hspace{1cm} (3.21)

Here, $\delta_{ij}$ is Kronecker delta and $\alpha$ is the same dimensionless damping coefficient that appears in the LLG equation. It can be easily shown that Eq. (3.20) without the first term is similar to the Allen-Cahn equation if one computes the functional derivatives as described in [49]. In fact, some studies have used Eq. (3.20) without the first term for micromagnetic modeling [40]. Although, it is computationally simpler to remove the first term, implementation for micromagnetics may not predict an accurate time history or even a final equilibrium state.

Eq. (3.18), (3.19), and (3.20) together form a series of partial differential equations (PDEs) that explain the governing physics of phase-field micromagnetics.

### 3.4 Crystallographic orientations

To model polycrystalline materials, a different coordinate system must be used so that the directions of the free energy minima match the crystallographic easy-axis dictated by magnetoelastic and magnetocrystalline anisotropy within each grain. In other words, the free energy functional has to be transformed from a global coordinate system to a local crystallographic coordinate system. The Euler angles are used to transform the coordinates:

$$0 < \varphi < 2\pi$$  \hspace{1cm} (3.22)

$$0 < \theta < \pi$$  \hspace{1cm} (3.23)

$$0 < \psi < 2\pi$$  \hspace{1cm} (3.24)
Figure 3.1 Schematic illustration of the three consecutive rotation described by Eqs. (3.25)-(3.27) that relate the global coordinates \((x_1, x_2, x_3)\) to the local coordinates \((x_{1''}, x_{2''}, x_{3''})\).

As shown in Figure 3.1, angles \(\varphi\), \(\theta\), and \(\psi\) are three consecutive counter clockwise rotations with respect to \(x_3\), \(x_1'\), and \(x_3''\) axes described by three rotation matrices.

\[
R_{x_3}(\varphi) = \begin{bmatrix}
\cos(\varphi) & \sin(\varphi) & 0 \\
-\sin(\varphi) & \cos(\varphi) & 0 \\
0 & 0 & 1
\end{bmatrix} \tag{3.25}
\]

\[
R_{x_1'}(\theta) = \begin{bmatrix}
1 & 0 & 0 \\
0 & \cos(\theta) & \sin(\theta) \\
0 & -\sin(\theta) & \cos(\theta)
\end{bmatrix} \tag{3.26}
\]

\[
R_{x_3''}(\psi) = \begin{bmatrix}
\cos(\psi) & \sin(\psi) & 0 \\
-\sin(\psi) & \cos(\psi) & 0 \\
0 & 0 & 1
\end{bmatrix} \tag{3.27}
\]

Matrix multiplication of above three matrices results in a general rotational matrix that can be used to describe any crystal orientation within grains:

\[
R(\varphi, \theta, \psi) = R_{x_3''}(\psi)R_{x_1'}(\theta)R_{x_3}(\varphi) \tag{3.28}
\]

To describe the free energy density functional in the local coordinate system, the independent field variables in Eq. (3.1) must be transformed from to the local coordinates using

\[
\epsilon_{ij}^{local} = R_{im}R_{nj}\epsilon_{mn}^{global} \tag{3.29}
\]

\[
H_{i}^{local} = R_{ij}H_{j}^{global} \tag{3.30}
\]
\[ m_{i}^{local} = R_{ij} m_{j}^{global} \]  
\[ m_{i,j}^{local} = R_{im} R_{nj} m_{m,n}^{global} \]  

The expression of the free energy functional in the local coordinate system can be obtained by substituting the above transformed dependent variables into Eq. (3.1).

\[ h^{local} = h^{local}(\varepsilon_{ij}^{local}, H_{i}^{local}, m_{i}^{local}, m_{i,j}^{local}) \]  

Using this expression of the free energy density functional in Eqs. (3.18), (3.19), and (3.20) yields the partial derivatives in the local coordinate system:

\[
\left( \frac{\partial h}{\partial \varepsilon_{ij}} \right)^{local} = \frac{\partial h^{local}(\varepsilon_{ij}^{local}, m_{i}^{local}, m_{i,j}^{local}, H_{i}^{local})}{\partial \varepsilon_{ij}^{local}} 
\]  
(3.34)

\[
\left( \frac{\partial h}{\partial H_{i}} \right)^{local} = \frac{\partial h^{local}(\varepsilon_{ij}^{local}, m_{i}^{local}, m_{i,j}^{local}, H_{i}^{local})}{\partial H_{i}^{local}} 
\]  
(3.35)

\[
\left( \frac{\partial h}{\partial m_{i}} \right)^{local} = \frac{\partial h^{local}(\varepsilon_{ij}^{local}, m_{i}^{local}, m_{i,j}^{local}, H_{i}^{local})}{\partial m_{i}^{local}} 
\]  
(3.36)

\[
\left( \frac{\partial h}{\partial m_{i,j}} \right)^{local} = \frac{\partial h^{local}(\varepsilon_{ij}^{local}, m_{i}^{local}, m_{i,j}^{local}, H_{i}^{local})}{\partial m_{i,j}^{local}} 
\]  
(3.37)

Finally, the partial derivatives of the free energy functional expressed in the local coordinates should be transformed back to the global coordinate system using the transpose of the rotational matrix in Eq. (3.28):

\[
\left( \frac{\partial h}{\partial \varepsilon_{ij}} \right)^{global} = R_{im} R_{nj} \left( \frac{\partial h}{\partial \varepsilon_{mn}} \right)^{local} 
\]  
(3.38)

\[
\left( \frac{\partial h}{\partial H_{i}} \right)^{global} = R_{ij} \left( \frac{\partial h}{\partial H_{j}} \right)^{local} 
\]  
(3.39)

\[
\left( \frac{\partial h}{\partial m_{i}} \right)^{global} = R_{ij} \left( \frac{\partial h}{\partial m_{j}} \right)^{local} 
\]  
(3.40)
\[
\left( \frac{\partial h}{\partial m_{i,j}} \right)^{global} = R_{im}R_{nj}\left( \frac{\partial h}{\partial m_{m,n}} \right)^{local}
\]  

(3.41)

The details of finite element implementation of these formulations are presented in the proceeding chapters.
Chapter 4 On the influence of crystallographic texturing and substrate-induced strain: experimental verification

4.1 Abstract

A three-dimensional continuum based micromagnetic model is developed to simulate the magnetization process in polycrystalline thin films and address the influence of crystallographic texturing, grain size and the substrate-induced strain on the spontaneous domain structure and hysteresis curves of NiFe$_2$O$_4$ and CoFe$_2$O$_4$ thin films. The model employs the Landau–Lifshitz–Gilbert equation along with mechanical equilibrium and Gauss’ Law for magnetism to calculate the temporal and spatial distributions of the magnetic moments. Thus, this approach falls within the category of phase-field methods used for non-conserved systems. The finite element method is used to solve the partial differential equations in fully coupled fashion while using a different discretization method for each equation. The results demonstrate how the magnetization process is altered by adopting different microstructural orientations revealing stronger sensitivity in CoFe$_2$O$_4$ thin films than in NiFe$_2$O$_4$ thin films. Moreover, it is shown that the substrate-induced compressive strain favors in-plane magnetization, whereas the tensile strain switches the easy axis from the in-plane to the out-of-plane direction. The validity of the model is verified by comparing the results with recently published experimental data for sol-gel deposited NiFe$_2$O$_4$ thin films.

4.2 Introduction

Since its introduction in the 1960s [50], the continuum theory of micromagnetics has been widely used to capture the complex magnetization processes in various material systems at the meso-scale. The computational micromagnetics is based on discretizing the continuum magnetic media into sub-micrometer cells and using an equation of motion for magnetic medium within those cells. Gauss' Law for magnetism is then used to explain the magnetostatic interactions of the magnetic moments with each other and with external magnetic field. Modern micromagnetics uses
the Landau–Lifshitz–Gilbert (LLG) equation first developed in 1935 [51], and later modified by Gilbert in 1956 [48], as the equation of motion. It also uses the balance law of linear momentum to account for the inhomogeneous local stress distribution caused by the elastic incompatibility of the magnetostrictive strain [37].

Micromagnetic modeling, even without consideration of magnetoelastic coupling, falls into the class of phase-field modeling used over the past two decades to solve similar problems involving mobile sharp interfaces [29,52]. The LLG equation takes the same role as the evolution equation in phase-field methods and predicts the evolution of the interfaces, i.e. the motion of the magnetic domain walls. In fact, the LLG equation can be classified as an Allen-Cahn type equation used for predicting the kinetics of non-conserved fields [29].

The magnetization field vector with its constant magnitude is the order parameter of the evolution equation in micromagnetics. It orients itself uniformly within the magnetic domains and continuously changes its direction across the domain walls. Similar to other phase-field models, a free energy functional couples the order parameter to other field variables such as strain and magnetic field. This is a polynomial functional describing the total energy of the system; an integral representation of the magnetization vector, its derivatives, and other field variables that are all functions of geometry, material properties, temperature, etc.

The LLG equation in phase-field micromagnetics is accompanied by two other fundamental balance law equations for stress and magnetic field. Incorporating the free energy functional into these equations leads to set of equations that describe the temporal and spatial distribution of the magnetization vector for a given magneto-mechanical boundary condition.

Phase-field micromagnetics has been employed in various studies of ferro/ferri-magnetic materials including thin films [37,40,41,53]. Due to its meso-scale and multiphysics nature,
micromagnetic simulations are computationally expensive and hence most simulations are restricted to nanostructures or two-dimensional cases. With the improvement in the computational resources, more sophisticated problems have been simulated recently which include strain-mediated switching [54–56], electrically induced magnetization [44,57], ferromagnetic shape-memory alloys [58,59], exchange coupling [60], and more [42]. At the same time, new numerical techniques are being adopted to lower the computational cost and expand the horizon to larger scales [43].

Although the crystallography of the magnetic films are known to have significant effect on the magnetic behavior of the films, it has received little attention from the micromagnetics community and most studies are limited to monocrystalline films. In the few cases considering polycrystallinity, the simulation was simplified [61–63] or the focus was only on the final equilibrium domain structure rather than the hysteretic behavior [64]. Similarly, the literature suffers from the lack of a comprehensive study on the effect of substrate-induced strain. In the few available studies concerned with the substrate-induced strain, the hysteresis behavior was not included [39,65].

The purpose of this study is to develop a three-dimensional phase-field micromagnetic model to analyze the magnetic behavior of polycrystalline thin films. The model utilizes the formulation proposed by Landis [38] (see Chapter 3) and incorporates it into finite element code COMSOL Multiphysics. The goal is to develop a comprehensive design tool for predicting the effect of crystallographic texturing, grain size, and substrate-induced strain on the spontaneous and hysteretic behavior in thin films. Nickel ferrite (NiFe$_2$O$_4$) and cobalt ferrite (CoFe$_2$O$_4$) are selected for this study due to their range of interesting physical properties such as room temperature ferrimagnetism and small gap insulation. To evaluate the validity of the model, the
obtained results are compared with recently published experimental data for sol-gel deposited NiFe$_2$O$_4$ films [66,67].

4.3 Finite element model

Substituting the previously derived energy expressions in Chapter 3 into the field equations (Eqs. (3.18) and (3.19)) and the evolution equation (Eq. (3.20)) and performing the reverse transformation to the global coordinates yields seven non-linear partial differential equations with unknowns for mechanical displacement components ($u_1$, $u_2$, and $u_3$), magnetization direction components ($m_1$, $m_2$, and $m_3$), and magnetic scalar potential ($\phi$). To solve these equations numerically, the finite element method (FEM) was employed via COMSOL Multiphysics that features a mathematical module for defining custom partial differential equations [68]. The finite element mesh is shown in Figure 4.1. Different solution domains and discretization methods are used for each equation, significantly reducing the computational time and allowing adjustments to the solution domain and mesh for each equation. For instance, Eq. (3.19) necessitates extending the simulation domain to the free space surrounding the magnetic body to ensure the normal component of the magnetic flux is continuous across the interface [69]. Inclusion of the free space in the solution domain of the Eqs. (3.18) and (3.20), however, is not needed and would add unnecessary computational effort. The minimum size of the free space above which the results are not affected was determined via preliminary trial and error simulations.

Figure 4.1 also shows the grain structure which is modeled by constructing a separate geometry with tessellation of truncated octahedrons and defining different values of Euler angles within each grain. Separating the geometry of the grain structure from simulation domains used for solving the equations allows the use of regular cubic elements in the mesh. It should also be noted studying the effect of grain boundary thickness was not within the scope of the present work; grain boundaries are assumed to be very thin. The grain boundary thickness could be readily
included if the free energy functional constants within the grain boundaries were known. Also note that a defect-free microstructure is assumed within each grain.

![Finite element domain and mesh](image)

Figure 4.1 Finite element domain and mesh for a) Eq. (3.18), b) Eq. (3.19), c) Eq. (3.20), and d) the grain structure.

The material constants in the free energy functional are of different orders of magnitude, so achieving numerical convergence in COMSOL Multiphysics is difficult. Accordingly, the normalization scheme summarized below is used to reduce the differences in the orders of magnitude:

\[
\begin{align*}
A_{\text{exch}}^* &= \frac{A_{\text{exch}}}{A_{\text{exch}}} \\
x^* &= \frac{x}{l_{\text{exch}}} \\
c_{ijkl}^* &= c_{ijkl} \frac{l_{\text{exch}}^2}{A_{\text{exch}}} \\
k_1^* &= k_1 \frac{l_{\text{exch}}^2}{A_{\text{exch}}} \\
k_2^* &= k_2 \frac{l_{\text{exch}}^2}{A_{\text{exch}}} \\
\phi^* &= \phi \frac{\mu_0}{A_{\text{exch}}} \\
M_i^* &= M_l \frac{\mu_0 l_{\text{exch}}}{A_{\text{exch}}} \\
H_i^* &= H_l \frac{\mu_0 l_{\text{exch}}}{A_{\text{exch}}} \\
B_i^* &= B_l \frac{l_{\text{exch}}}{\sqrt{\mu_0 A_{\text{exch}}}} \\
t^* &= t \frac{\gamma_0 \sqrt{\mu_0 A_{\text{exch}}}}{l_{\text{exch}}} \\
h^* &= h \frac{l_{\text{exch}}}{A_{\text{exch}}} \\
\end{align*}
\] (4.1)
In this notation, the starred parameters are normalized dimensionless parameters. \( l_{\text{exch}} \) is the exchange length; a characteristic length scale of ferromagnetic materials below which magnetization reversal occurs by quasi-uniform rotation rather than a nucleation process [70];

\[
l_{\text{exch}} = \sqrt{\frac{A_{\text{exch}}}{\mu_0 M_s^2}}
\]

(4.2)

The maximum element size in micromagnetic simulations should not exceed the exchange length value. In addition, same element size must be used in all directions to avoid artificial gradient energy distribution.

The real value of \( \alpha \) in Eq. (3.21) is difficult to obtain experimentally and usually has a nonlinear dependence upon magnetization. To facilitate the computational process in this study, \( \alpha = 1 \) is used. Selection of a correct value is only important when the simulation must be in real time; within the scope of this study it has no effects [69].

To ensure that the magnitude of the magnetization vector is constant, the following domain constraint is applied to the entire magnetic body:

\[
m_1^2 + m_2^2 + m_3^2 = 1
\]

(4.3)

Without this constraint, which is not enforced by the LLG equation, the magnitude of the magnetization vector collapses to zero. There are other techniques to handle this constraint, such as using additional term in the free energy functional [38,40] or expressing the magnetization field vector in spherical coordinate system [41]. The point-wise constraint in COMSOL Multiphysics [68] makes it easier to implement the constraint numerically without adding complexities to the computational process.

The boundary conditions are illustrated in Figure 4.2. The substrate is represented by applying a mechanical constraint at the bottom of the film.
where $\hat{\varepsilon}_{11}$ and $\hat{\varepsilon}_{22}$ are prescribed planar strain values induced by the substrate due to lattice mismatch or differences in the coefficients of thermal expansion. In this study, isotropic planar strains are applied, i.e. $\hat{\varepsilon}_{11} = \hat{\varepsilon}_{22}$. All other surfaces of the film are assumed traction free by applying following natural boundary condition:

$$\sigma_{ij}n_j = 0$$

where $n_j$ are the components of a unit vector normal to the surface. The external magnetic field is applied by constraining the magnetic potential on a pair of two opposing surfaces at the outer boundary of the free-space region:

$$\phi = 0$$
$$\phi = \hat{\phi}$$

where $\phi$ is the prescribed value of the magnetic scalar potential. Selection of the two surface pairs determines whether the applied field is in-plane or out-of-plane (see Figure 4.2). All other surfaces on the free space outer boundary are assumed to have zero magnetic flux:

$$\frac{\partial h}{\partial H_i} n_i = 0$$

Finally, all film surfaces are assumed to have zero flux of magnetization gradient:

$$\frac{\partial h}{\partial m_{i,j}} n_j = 0$$
Eq. (3.20) requires an initial condition for the magnetization unit vector. A pseudorandom number generator is used to generate three random numbers $P_1$, $P_2$, and $P_3$, with uniform distribution between -1 and 1. The following relations were then used to generate the initial values for the components of the magnetization unit vectors $\hat{m}_1$, $\hat{m}_2$, $\hat{m}_3$. This is necessary to make sure the initial condition follows the requirement for the magnetization field vector to have a constant magnitude:

\begin{align*}
\hat{m}_1 &= \frac{P_1}{\sqrt{P_1^2 + P_2^2 + P_3^2}} \\
\hat{m}_2 &= \frac{P_2}{\sqrt{P_1^2 + P_2^2 + P_3^2}} \\
\hat{m}_3 &= \frac{P_3}{\sqrt{P_1^2 + P_2^2 + P_3^2}}
\end{align*}

(4.12) (4.13) (4.14)

4.4 Materials

NiFe$_2$O$_4$ (NFO) and CoFe$_2$O$_4$ (CFO) are insulating magnetic oxides with cubic inverse spinel structure that possess high Curie temperature, high saturation magnetization, and high thermal and chemical stability. The combination of these properties makes them attractive for a wide variety of low and high frequency applications [71].
Similar to other inverse spinel ferrites, half of the trivalent iron cations in NFO and CFO occupy the tetrahedral sites and the remaining half along with divalent cations (nickel or cobalt) reside on the octahedral sites. The antiferromagnetic coupling between the iron cations in tetrahedral sites and those in octahedral sites result in partial cancelation of the magnetic moments and hence Néel-type ferrimagnetism \[72\].

Despite having identical crystal structure, the origin of the magnetocrystalline anisotropy in NFO and CFO is different. Like other inverse spinel ferrites, NFO has a negative magnetocrystalline anisotropy constant which results in \(\langle 111 \rangle\) as the easy-axis and \(\langle 100 \rangle\) as the hard-axis. In contrast, CFO exhibits hard magnetic behavior with positive and a much larger magnetocrystalline anisotropy constant which leads to \(\langle 100 \rangle\) as the easy-axis and \(\langle 111 \rangle\) as the hard-axis. CFO also shows a magnetostriction constant which is an order of magnitude higher than that of NFO. These differences make NFO and CFO interesting choices for analyzing the effect of crystallographic texturing and substrate-induced strain in magnetic thin films.

The NFO and CFO material constants for the free energy functional, along with their corresponding normalized values, are listed in Table 4.1. These parameters are extracted from either single crystal measurements or first principal calculations \[73–77\]. The normalized values are computed using Eq. (4.1).
Table 4.1 Material constants in the free energy functional adopted from [73–77] and their corresponding normalized values computed using Eq. (4.1).

<table>
<thead>
<tr>
<th>Material</th>
<th>Original</th>
<th>Normalized</th>
<th>Original</th>
<th>Normalized</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe$_2$O$_4$</td>
<td></td>
<td></td>
<td>CoFe$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>$c_{11}$</td>
<td>$2.73 \times 10^{11}$ Pa</td>
<td>$5.962 \times 10^{6}$ Pa</td>
<td>$2.86 \times 10^{11}$ Pa</td>
<td>$3.716 \times 10^{6}$ Pa</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>$1.61 \times 10^{11}$ Pa</td>
<td>$3.508 \times 10^{6}$ Pa</td>
<td>$1.73 \times 10^{11}$ Pa</td>
<td>$2.248 \times 10^{6}$ Pa</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>$8.23 \times 10^{10}$ Pa</td>
<td>$1.797 \times 10^{6}$ Pa</td>
<td>$9.70 \times 10^{10}$ Pa</td>
<td>$1.260 \times 10^{6}$ Pa</td>
</tr>
<tr>
<td>$\lambda_{100}$</td>
<td>$-4.59 \times 10^{-5}$</td>
<td>$-4.59 \times 10^{-5}$</td>
<td>$-5.90 \times 10^{-4}$</td>
<td>$-5.90 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\lambda_{111}$</td>
<td>$-2.16 \times 10^{-5}$</td>
<td>$-2.16 \times 10^{-5}$</td>
<td>$1.20 \times 10^{-4}$</td>
<td>$1.20 \times 10^{-4}$</td>
</tr>
<tr>
<td>$K_1$</td>
<td>$-6.93 \times 10^3$ Jm$^{-3}$</td>
<td>$-1.51 \times 10^2$</td>
<td>$1.00 \times 10^5$ Jm$^{-3}$</td>
<td>$12.99 \times 10^1$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>$-0.43 \times 10^3$ Jm$^{-3}$</td>
<td>$-93.88 \times 10^{-4}$</td>
<td>0.0 Jm$^{-3}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$M_s$</td>
<td>$2.7 \times 10^8$ Am$^{-1}$</td>
<td>1.414</td>
<td>$3.5 \times 10^8$ Am$^{-1}$</td>
<td>1.414</td>
</tr>
<tr>
<td>$A_{\text{exch}}$</td>
<td>$1.0 \times 10^{-11}$ Jm$^{-1}$</td>
<td>1</td>
<td>$0.7 \times 10^{-11}$ Jm$^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>$4\pi \times 10^{-7}$ Hm$^{-1}$</td>
<td>1</td>
<td>$4\pi \times 10^{-7}$ Hm$^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>$1.76 \times 10^4$ T$^{-1}$s$^{-1}$</td>
<td>1</td>
<td>$1.76 \times 10^4$ T$^{-1}$s$^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>$14.776 \times 10^{-9}$ m</td>
<td>1</td>
<td>$9.536 \times 10^{-9}$ m</td>
<td>1</td>
</tr>
</tbody>
</table>

4.5 Results and discussion

4.5.1 Spontaneous magnetization

The spontaneous magnetization is simulated by initializing the magnetic moments at each nodal point to arbitrary random orientations and then allowing them to relax in the absence of external magnetic field. The simulation continues until the free energy reaches its minimum value and the domain structure becomes stable. Figure 4.3 shows the initial and final states for randomly-oriented unstrained NFO and CFO films. The arrows represent the directions of the magnetization vectors and different colors denote the values of the $m_1$ component of the magnetization. Random texturing is achieved by assigning random values for Euler angles using a random function with uniform distribution within the ranges defined in Eqs. (3.22), (3.23), and (3.24). The film dimensions are $850 \times 850 \times 75$ nm$^3$ and $550 \times 550 \times 50$ nm$^3$ for NFO and CFO, respectively.

Due to stronger demagnetization effect in the out-of-plane direction and resultant shape anisotropy, the equilibrium spontaneous magnetization in both NFO and CFO films is planar.
Unlike CFO, the spontaneous domain structure for NFO is symmetric with no preferred planar direction. This is believed to be due to lower exchange stiffness constant in CFO which was verified by running a dummy simulation with artificially increased exchange stiffness constant.

Changing the seeding in the random function that controls the initial condition almost always results in the same final magnetization state for NFO. The domain structure in CFO, however, is sensitive to the initial state. In other words, there are multiple local minima for the energy functional of CFO.

Figure 4.3 (a) Random initial condition for the magnetization unit vector and equilibrium spontaneous domain structure for unstrained randomly-textured (b) NFO, and (c) CFO films. The arrows point to the directions of the magnetization vectors and different colors denote the values of \( m_1 \) component of the magnetization. The film dimensions are 850 × 850 × 75 nm³ and 550 × 550 × 50 μm³ for NFO and CFO, respectively.
4.5.2 Crystallographic texturing

To study the effect of crystallography texturing, four cases are selected: randomly-oriented, (100)-textured, (111)-textured, and (110)-textured films. In all cases, the substrate-induced strain is set to zero. The Euler angles for randomly-oriented films are defined as explained in the previous section. For other textured films, a random function with normal distribution and standard deviation of 0.05 rad is used. The mean values of the Euler angles are listed in Table 4.2. The standard deviation of 0.05 rad results in slightly different values for each grain and leads to a textured polycrystalline microstructure. Otherwise the films would be monocrystalline. The corresponding stereographic projection of the crystal orientations are shown in Figure 4.4.

Table 4.2 Mean values of the Euler angles (in radian) for producing different crystallographic texturing.

<table>
<thead>
<tr>
<th>Euler angles</th>
<th>(100)-textured</th>
<th>(111)-textured</th>
<th>(110)-textured</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varphi$</td>
<td>0</td>
<td>$\frac{3\pi}{4}$</td>
<td>$\frac{\pi}{4}$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>0</td>
<td>$\frac{\pi}{2} - \sin^{-1}\left(\frac{1}{\sqrt{3}}\right)$</td>
<td>$\frac{\pi}{2}$</td>
</tr>
<tr>
<td>$\psi$</td>
<td>0</td>
<td>0</td>
<td>$\sin^{-1}\left(\frac{1}{\sqrt{3}}\right)$</td>
</tr>
</tbody>
</table>

Figure 4.4 Schematic representation of the polycrystalline film and stereographic projections of the crystal orientations.

No criterion is applied to control the degree of misalignment between the grains. The side length of the base octahedron is set equal to 2.7 times the exchange length. For NFO this is about
40 nm which is equal to the grain size reported in recently published studies [66,67] that will be compared with the modeling results obtained here.

Figure 4.5 shows the spontaneous domain structure for CFO films with different texturing. The interfaces between magnetic domains are marked by dark surfaces. The crystallographic texturing effect on the spontaneous domain structure is more evident in CFO whose magnetocrystalline anisotropy constant is two orders of magnitude larger than that of NFO. In fact, different crystallographic texturing in NFO results in similar domain structure (that was shown in Figure 4.3b) with slightly different wall thickness. Therefore, only the results for CFO are reported in here.

Each type of texturing results in a different spontaneous domain structure. The shape of the domains and transition of the magnetization vector at the interfaces are affected by the magnetocrystalline anisotropy and its competition with the magnetic anisotropy due to the demagnetization effect (shape anisotropy).

For the randomly-oriented film in Figure 4.5a, the magnetocrystalline anisotropy dictated by the crystal orientations is different from one grain to another. As a result, the spontaneous domain structure tends to follow the pattern of the grain structure. Figure 4.5b demonstrates the spontaneous domain structure of (100)-textured film. All domains have sharp interfaces with 90° transitioning. The easy-axis in CFO is along \( \langle 100 \rangle \) directions, favoring 90° domain walls. Combination of high magnetocrystalline anisotropy and low exchange stiffness constant allows the formation of the sharp interfaces. Moreover, shape anisotropy suppresses any out-of-plane magnetization.

In (111) and (110)-textured films in Figure 4.5c and d, the easy-axis direction dictated by the magnetocrystalline anisotropy differs from that dictated by the shape anisotropy. Because of
strong magnetocrystalline coupling in CFO, the magnetization vectors overcome the
demagnetization effect and exhibit an out-of-plane component. Similar to other cases, only 90°
domain walls are present.

Figure 4.5 Spontaneous domain structure of unstrained CFO films with (a) randomly-oriented, (b) (100)
textured, (c) (111)-textured, and (d) (110)-textured microstructure. The arrows represent the
magnetization vectors and different colors denote the values of $m_1$ component of the magnetization. The
interfaces between magnetic domains are marked by dark surfaces. The film dimensions are 550 × 550 ×
50 nm$^3$.

The hysteresis curves were obtained by magnetizing the films directly from their random
initial condition with zero net magnetization up to saturation and subsequently demagnetizing
them back to zero net magnetization and then magnetizing again in the opposite direction. The
magnetic field is applied by sweeping the values of the magnetic scalar potential. For a given value
of magnetic scalar potential, the simulation continues until equilibrium is achieved. To save
computational time, a stop condition that detects the steady state net magnetization is imposed at
each step. No significant changes occur when the simulation is allowed to continue beyond this

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termination point. Despite the lack of symmetry in the microstructure, the computed hysteresis curves for the size scale used in this study are found to be symmetric with respect to the magnetization direction for both NFO and CFO. Therefore, to further reduce the computation time, only half of the hysteresis curve is computed. When plotting the results, the additive inverse values were copied from the computed values from the previous step to form the full curve.

Hysteresis plots for in-plane and out-of-plane magnetization are shown in Figure 4.6 and Figure 4.7 for NFO and CFO, respectively. Random orientation of the crystal structure removes the effect of the magnetocrystalline anisotropy. Hence, larger magnetocrystalline anisotropy constant should increase the difference between textured and randomly oriented films.

In-plane magnetization curves of the NFO film shown in Figure 4.6a reveal a small difference between the four differently textured films. For in-plane magnetization of the (1\(\bar{1}0\))-textured film, the easy-axis is aligned along the external field direction while for the (100)-textured film, the hard-axis is aligned in that direction. Therefore, the (1\(\bar{1}0\))-textured film is expected to give the highest coercivity and largest remanent magnetization. The trend is opposite for the in-plane magnetization of the CFO film depicted in Figure 4.7a. The easy-axis for NFO is the hard-axis for CFO and vice versa. Therefore, the (100)-textured film is expected to give the highest coercivity and largest remanent magnetization. Because of higher magnetocrystalline anisotropy the difference is more significant than that observed for NFO.
As discussed previously, the shape anisotropy is dominant for unstrained films and hence the out-of-plane magnetization is not expected to be hysteretic. This trend does not change for NFO when adopting different crystallographic texturing (see Figure 4.6b). Even for the (111)-textured film, where the magnetocrystalline easy-axis is parallel to the external field direction, the effect is negligible. In CFO, however, the stronger magnetocrystalline coupling leads to hysteresis loop formation when the magnetocrystalline easy-axis and the external field point in the same direction. This occurs in the (100)-textured CFO film as plotted in Figure 4.7b.
Figure 4.7 (a) In-plane and (b) out-of-plane magnetization hysteresis curves of unstrained randomly-oriented, (100)-textured, (111)-textured, and (110)-textured CFO films.

Figure 4.8 shows the effect of the grain size on the hysteresis behavior of the CFO film. CFO is selected because it exhibited stronger texture dependency. While the out-of-plane magnetization do not reveal any significant difference when reducing the grain size from 50 nm to 25 nm, the in-plane coercivity exhibits a remarkable decrease. This would be unexpected because smaller grains increase the coercivity due to the larger grain boundary density increasing the domain wall pinning. In this model, however, the effects of grain boundaries are not considered, so the reduction in coercivity with smaller grains is simply due to the increased number of grains,
which increases the randomness of the crystal orientations and eliminates the overall magnetocrystalline anisotropy.

![Diagram](image)

Figure 4.8 (a) In-plane and (b) out-of-plane magnetization hysteresis curves of unstrained randomly-oriented CFO films with grain sizes of 25 and 50 nm.

For the results presented in this section, the effect of crystal orientations is isolated from other parameters, whereas in the experimental studies, the texturing is achieved by changing the substrate or other processing parameters which also brings about other effects such as different residual strain or grain size, etc.
4.5.3 Substrate-induced strain effect

Substrate-induced strain is a general term that covers strain due to mismatch in lattice constants and coefficients of thermal expansion, as well as defects in the film-substrate interface. The resulting strain is anisotropic and non-uniform. For the sake of simplicity, however, the substrate-induced strain in this study is restricted to isotropic and uniform strain which is only present in epitaxial growth.

To study the effect of substrate-induced strain, spontaneous domain structures as well as the hysteresis curves were calculated for five biaxial strain values of -0.50%, -0.25%, 0.00%, 0.25%, and 0.50%. As NFO and CFO exhibit similar trend, only the results for NFO are reported here. Random crystal orientation is considered in this section to eliminate the overall magnetocrystalline anisotropy effect.

The effect of substrate-induced strain on the spontaneous domain structure is shown in Figure 4.9; different colors denote the values of the out-of-plane component of the magnetization $m_3$. While the compressive strains only cause minor differences in NFO, the tensile strain brings a major change in the spontaneous domain structure. For the compressive and zero strain values, the spontaneous magnetization is planar and only 90° domain walls exist. These domain walls become sharper as the compressive strain increases. When the substrate-induced strain is tensile, the magnetization vectors align along the out-of-plane direction and the transition from one domain to another occurs through 180° domain walls.
Figure 4.9 Spontaneous domain structure of NFO for a biaxial substrate-induced strain values of (a) - 0.50%, (b) -0.25%, (c) 0.00%, (d) 0.25%, and (e) 0.50%. The arrows represent the magnetization vectors and different colors denote the values of $m_3$ component of the magnetization. The film dimensions are $850 \times 850 \times 75 \text{nm}^3$.

The hysteresis curves are plotted in Figure 4.10 for different substrate-induced strain values. The in-plane magnetization curves shown in Figure 4.10a reveal that when the strain is compressive, the remanent magnetization stays relatively unchanged with respect to the unstrained film but the coercivity field increases. Tensile strain increases the coercivity field as well but also reduces the remanent magnetization. The tensile strain of 0.50% seems to make the in-plane magnetization harder compared to other strain values.

Figure 4.10b shows that the effect of substrate-induced strain is more pronounced on the out-of-plane magnetization. As explained in the previous section, due to shape anisotropy effect, the out-of-plane direction is a hard-axis for magnetization of NFO films. Therefore, the
magnetization curves are expected not to show a hysteresis loop. This is the case for compressive and zero substrate-induced strains. While the compressive strain only changes the slope of the curve, the tensile strain drastically changes the shape of the hysteresis curve and results in loop formation. When the tensile strain value is 0.50%, the out-of-plane coercivity is 250% larger than that for the in-plane magnetization with the same substrate-induced strain. This indicates that the magnetic easy-axis for this strain is in the out-of-plane direction.

Figure 4.10 (a) In-plane and (b) out-of-plane magnetization hysteresis curves of NFO films with biaxial substrate-induced strain values of -0.50%, -0.25%, 0.00%, 0.25%, and 0.50%.
In the absence of overall magnetocrystalline anisotropy, the magnetization easy-axis is determined by cooperation or competition between the shape anisotropy and magnetoelastic (strain-induced) anisotropy. In the case of compressive strain, they act cooperatively and hence the easy-axis due to shape anisotropy is parallel to that resulting from magnetoelastic anisotropy. This results in a planar easy-axis and hence larger coercivity and remanent magnetization. When the strain is tensile, the magnetoelastic anisotropy becomes dominant and tends to reorient the magnetization easy-axis along the out-of-plane direction. As a result, the spontaneous domain structures seen in Figure 4.9d and e form, the in-plane magnetization exhibits larger coercivity, and the out-of-plane magnetization starts to show hysteretic behavior.

4.5.4 Comparison with experimental data

Two sets of previously published experimental data are selected for comparison to the results obtained here: polycrystalline NFO films deposited using chemical solution deposition on silicon substrates [66] and on platinized silicon substrates [67]. The former produced randomly oriented microstructures, whereas the latter resulted in (111)-textured films. The film thickness and average grain size in both cases are around 110 nm and 40 nm, respectively. A comparison of the results are shown in Figure 4.11 for in-plane magnetization of a randomly-textured film, in-plane magnetization of a (111)-textured film, and out-of-plane magnetization of a (111)-textured film.

The in-plane hysteresis curves of randomly oriented films plotted in Figure 4.11a reveals relatively good agreement between the experimental data and modeling results when a substrate-induced strain of 0.50% is applied. Similarly, the in-plane and out-of-plane hysteresis curves of (111)-textured film depicted in Figure 4.11b and c indicate that the best matching is achieved only when the strain is around 0.50%.
Figure 4.11 Comparison of the modeling results with experimental data for (a) in-plane magnetizing of randomly-oriented NFO film [66], (b) in-plane magnetizing of (111)-textured NFO film [67], and (c) out-of-plane magnetization of (111)-textured NFO film [67].
As discussed previously, the out-of-plane magnetization in unstrained NFO films is not hysteretic due to weak magnetocrystalline coupling and a strong demagnetization effect (see Figure 4.6b); hysteretic behavior only appears when the substrate-induced strain is applied. Therefore, the hysteresis seen in the experimental data is likely due the presence of strain at the film-substrate interface; the existence of such strain, however, is not discussed in [66,67].

The polycrystalline nature of the films, especially when there is no planar texturing which is the case for both experimentally reported films considered here [66,67], eliminates the overall effect of lattice constant mismatch even if there is a coherent grain boundary at the film-substrate interface. The difference in the coefficients of thermal expansion, however, is likely to produce such strain. The room temperature coefficient of thermal expansion in NFO and Si are $10.7 \times 10^{-6}$ and $2.555 \times 10^{-6}$ K$^{-1}$, respectively [78,79]. According to [66,67], the annealing temperatures for both randomly-oriented and (111)-textured films is 750 °C. The mismatch in the coefficient of thermal expansion could result in residual strains up to 0.6% after annealing to this temperature and during the cooling process. Another source of strain in the experimental data could be lattice distortion due to oxygen vacancies [80]. Therefore, a tensile strain of 0.50% is reasonable.

The small discrepancy seen in Figure 4.11 could be due to the fact that the domain wall pinning at grain boundaries is not included in this study. Moreover, the crystal structure within the grains are considered to be defect free which is not the case in the experimental samples.

4.6 Conclusion

A detailed procedure for developing a phase-field micromagnetic model for polycrystalline films is presented. It is demonstrated that the developed model is able to capture the unique features of the spontaneous magnetization as well as the magnetic hysteresis curve. This provides a comprehensive tool for analyzing the role of crystallographic texturing and substrate-induced strain on the magnetic behavior of NFO and CFO films. The influence of crystallographic texturing
in CFO is shown to be so high that it overcomes the out-of-plane demagnetization effect. The spontaneous and hysteretic behavior in NFO films, however, exhibit less sensitivity to changes in microstructural orientations. Application of substrate-induced strain leads to reorientation of the magnetic easy-axis and drastic changes in the magnetization behavior. 90° domain walls become sharper when the strain is compressive and are replaced by 180° domain walls when the strain is tensile. Reorientation of the magnetic easy axis due to tensile strain manifests itself in the formation of the hysteresis loop in out-of-plane magnetization. Comparison of the modeling results with experimental data for NFO confirms the validity of the model in capturing the magnetization process in polycrystalline thin films. Furthermore, the modeling results indicate the presence of substrate-induced tensile strain that results in hysteretic behavior in out-of-plane direction. The results obtained in this study provide an insightful understanding of the magnetization process in magnetic films which then can be used for developing complex systems such as multiferroic heterostructures.
Chapter 5 On the hysteretic behavior of periodically ordered magnetic nanostructures

5.1 Abstract

A parametric study of the effects of geometric and material variations on the magnetization reversal process in magnetic thin films with periodic surface features is performed using three-dimensional phase-field micromagnetic model. Material parameters are magnetostriction coefficient, magnetocrystalline anisotropy constant, and saturation magnetization. Geometric parameters are feature shape, size, spacing, and inclusion of a base layer. The model employs an expression of the free energy functional that relates magnetic moments to mechanical strain and magnetic field. The Landau–Lifshitz–Gilbert (LLG) equation is used along with mechanical equilibrium and Gauss’ law for magnetism to minimize the free energy functional and predict the temporal and spatial evolution of the magnetic moments. The results indicate that patterning drastically changes the magnetization process. Depending on the selection of material and geometric parameters, and the application of mechanical strain, remanence and coercivity may either increase or decrease. Such behavior is explained by considering magnetic anisotropy of different physical origins.

5.2 Introduction

Enhancing the magnetic permeability and improving the ferromagnetic resonance frequency are two crucial factors in designing magnetic films for high frequency applications and microwave technologies [81]. Enhancements are achieved to a certain extent in continuous films by controlling growth parameters, compositional adjustments, crystallographic texturing, mechanical strain, multilayer coupling, post-deposition treatments, etc. An emerging alternative approach is patterning the films by introducing periodically ordered high aspect ratio features via lithographic fabrication [82–85]. Features such as stripes sitting atop a bare substrate or another magnetic layer add an in-plane uniaxial magnetic anisotropy to the film altering the domain
structure and reversal mechanism. The existence of this uniaxial anisotropy is essential for increasing the ferromagnetic resonance frequency \([81,86]\) and improving the permeability. Furthermore, patterning suppresses eddy current losses \([81]\).

Patterning magnetic media into arrays of nanostructured elements such as dots, rings and anti-dots is used in high density data recording where each individual element acts as a single domain storing one bit of data \([84,87]\). Precise fabrication of such structures with uniaxial magnetic anisotropy enables deterministic domain switching and ensures stable magnetic states.

Experimental studies aiming to explain the magnetic behavior of patterned films have been reported \([88–90]\). These studies, however, suffer from the existence of microstructural and geometrical variations introduced during fabrication processes \([84,91]\). Due to existence of such variations that are of the fundamental importance for the magnetization reversal of small-scale elements, it is not possible to draw clear conclusions from the experimental data. Moreover, most patterned systems are affected by complex interactions between magnetic entities, further complicating the experimental studies. Such problems are easily avoided in micromagnetic analysis.

In addition to the limitations associated with experimental studies, the role of design variables such as geometric and material parameters on the performance that should be expected from the patterned films are not fully understood. There are also contradicting reports in the literature demanding explanation. For instance, the induced shape anisotropy in patterned films is expected to widen the coercivity field when the magnetic field is applied along the stripes’ longer axis \([92]\). There are, however, experimental studies that show the opposite results \([93,94]\).

The objective of this work is to perform a comprehensive parametric study on the role of geometric and material parameters on the magnetization behavior in magnetic thin films with
periodic structures. The goal is to gain a deeper insight on the influence of these parameters and how it can be utilized to design magnetic films for a range of applications.

A phase-field micromagnetic model that was developed in Chapter 3 and experimentally verified in Chapter 4 is employed. The model uses an expression of the free energy functional that relates the magnetic moments to mechanical strain and magnetic field. The Landau–Lifshitz–Gilbert (LLG) equation [48,51] is then used to calculate the temporal and spatial distribution of magnetization. In addition, the model accounts for mechanical equilibrium and Gauss’ law for magnetism. The LLG equation takes the same role as the evolution equation in phase-field methods and predicts the evolution of the interfaces, i.e. the motion of the magnetic domain walls [29,52]. In fact, the LLG equation can be classified as an Allen-Cahn type equation used for predicting the kinetics of non-conserved fields [29].

Three material parameters that are considered to be most important in determining the magnetic behavior of films are selected: magnetostriction coefficient, magnetocrystalline anisotropy constant, and saturation magnetization. The influence of geometric parameters were investigated by considering stripe and square patterning with varying feature size and spacing.

5.3 Finite element model

The details of the finite element model is similar to that of Chapter 4. One difference is that a single crystal magnetic material model is considered in this chapter and variations in the crystallographic orientations are not included. Mesh is also different because of using different geometries (see Figure 5.1).
5.4 Material and geometric parameters

5.4.1 Material parameters

Variations of magnetostriction coefficient ($\lambda_{100}$), first order magnetocrystalline anisotropy constant ($K_I$), and saturation magnetization ($M_s$) are considered. These material parameters are known to have direct effect on the magnetization behavior and can be controlled through manufacturing process and material selection. The material configurations with these variations do not represent real materials; instead they are selected so as to cover the range at which each constant varies across different ferri/ferromagnetic materials.

$\lambda_{100}$ takes two values for magnetic materials with low magnetostriction (e.g. permalloy) and high magnetostriction (e.g. terfenol-D). $K_I$ takes three values: a negative value to represent materials with low magnetocrystalline anisotropy and $<111>$ easy axis (e.g. iron), a positive value for materials with low magnetocrystalline anisotropy and $<100>$ easy axis (e.g. nickel ferrite), and a large positive value to represent materials with large magnetocrystalline anisotropy and $<100>$ as the easy axis (e.g. cobalt ferrite). Finally, $M_s$ takes two values for materials with low saturation magnetization (e.g. nickel ferrite) and high saturation magnetization (e.g. iron).
Table 5.1 Naming convention and material parameters combinations along with other constants in the free energy functional of Eqs. (3.18)-(3.20).

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<th>$c_{44}$ (Pa)</th>
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Table 5.2 Normalized values of material constants in Table 5.1 calculated following the same normalization scheme proposed in [95].

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<td>1.414</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

63
Combination of these variations result in 12 distinct virtual magnetic materials. Table 5.1 lists the naming convention used for each combination alongside the corresponding values for all material constants in Eqs. (3.18)-(3.20). To facilitate numerical convergence, these numbers are normalized following the same normalization scheme proposed in Chapter 4; these are shown in Table 5.2. Variations in elastic constants are not considered in this parametric study. A fixed value is selected for each elastic constant by averaging the values of the elastic constants of ceramic and metallic ferri/ferromagnetic materials available in the literature; terfenol-D, galfenol, permalloy, iron, nickel, nickel ferrite, cobalt ferrite.

5.4.2 Geometric parameters

The role of geometrical variations are studied by considering stripe and square patterns; these are defined and summarized in Figure 5.2, and Table 5.3 and Table 5.4. Selection of these geometric parameters enables understanding the influence of feature shape, feature width, feature spacing, and base layer on the magnetization behavior of magnetic films with periodic features.

### Table 5.3 Normalized values of geometric parameters for stripe-patterned films.

<table>
<thead>
<tr>
<th>Naming convention</th>
<th>Shape</th>
<th>(w^*)</th>
<th>(l^*)</th>
<th>(d^*)</th>
<th>(s^*)</th>
<th>(t^*)</th>
<th>(b^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STR (d=4) (s=4) (b=0)</td>
<td>Stripe</td>
<td>64</td>
<td>64</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>STR (d=8) (s=8) (b=0)</td>
<td>Stripe</td>
<td>same</td>
<td>same</td>
<td>8</td>
<td>8</td>
<td>same</td>
<td>0</td>
</tr>
<tr>
<td>STR (d=16) (s=16) (b=0)</td>
<td>Stripe</td>
<td>same</td>
<td>same</td>
<td>16</td>
<td>16</td>
<td>same</td>
<td>0</td>
</tr>
<tr>
<td>STR (d=8) (s=2.67) (b=0)</td>
<td>Stripe</td>
<td>same</td>
<td>same</td>
<td>8</td>
<td>2.67</td>
<td>same</td>
<td>0</td>
</tr>
<tr>
<td>STR (d=8) (s=24) (b=0)</td>
<td>Stripe</td>
<td>same</td>
<td>same</td>
<td>8</td>
<td>24</td>
<td>same</td>
<td>0</td>
</tr>
<tr>
<td>STR (d=8) (s=8) (b=1)</td>
<td>Stripe</td>
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<td>same</td>
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<td>8</td>
<td>same</td>
<td>1</td>
</tr>
<tr>
<td>STR (d=8) (s=8) (b=2)</td>
<td>Stripe</td>
<td>same</td>
<td>same</td>
<td>8</td>
<td>8</td>
<td>same</td>
<td>2</td>
</tr>
</tbody>
</table>

### Table 5.4 Normalized values of geometric parameters for square-patterned films.

<table>
<thead>
<tr>
<th>Naming convention</th>
<th>Shape</th>
<th>(w^*)</th>
<th>(l^*)</th>
<th>(d^*)</th>
<th>(s^*)</th>
<th>(t^*)</th>
<th>(b^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQR (d=4) (s=4) (b=0)</td>
<td>Square</td>
<td>64</td>
<td>64</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>SQR (d=8) (s=8) (b=0)</td>
<td>Square</td>
<td>same</td>
<td>same</td>
<td>8</td>
<td>8</td>
<td>same</td>
<td>0</td>
</tr>
<tr>
<td>SQR (d=16) (s=16) (b=0)</td>
<td>Square</td>
<td>same</td>
<td>same</td>
<td>16</td>
<td>16</td>
<td>same</td>
<td>0</td>
</tr>
<tr>
<td>SQR (d=8) (s=2.67) (b=0)</td>
<td>Square</td>
<td>same</td>
<td>same</td>
<td>8</td>
<td>2.67</td>
<td>same</td>
<td>0</td>
</tr>
<tr>
<td>SQR (d=8) (s=24) (b=0)</td>
<td>Square</td>
<td>same</td>
<td>same</td>
<td>8</td>
<td>24</td>
<td>same</td>
<td>0</td>
</tr>
</tbody>
</table>
Note that changing the saturation magnetization alters the exchange length $l_0$ used to normalize the dimensions. In this parametric study, however, the normalized dimensions are kept the same for all material combinations. Although changing the saturation magnetization alters the actual size of the films, the comparison carried out for the magnetization behavior in these films is valid by virtue of using normalized dimensions.

![Patterned nanostructures with different geometric parameters](image)

**Figure 5.2** Patterned nanostructures with different geometric parameters.

### 5.5 Results

5.5.1 The role of material parameters

The role of material parameters on the switching behavior of magnetic films with stripe patterns is studied by comparing the magnetization curves for patterned and unpatterned films. The in-plane and out-of-plane hysteresis curves computed for the material configurations given in Table 5.1 are plotted in Figure 5.3 and Figure 5.4. The patterned film has the geometric configuration of STR $d^8 s^8 b^0$. The in-plane curves are calculated by applying the magnetic field along the stripes’ longer axes.
Figure 5.3 Comparison of in-plane magnetization curves of striped and unpatterned thin films for different material parameters and 0.00% biaxial strain.

Figure 5.3 and Figure 5.4 reveal that the shape of the hysteresis behavior is highly sensitive to the selection of material parameters, and in particular $K_I$ and $M_s$. In the absence of mechanical strain, $\lambda_{100}$ exhibits a minimal role in the magnetization reversal process. While the hysteresis curves of patterned and unpatterned films remain unchanged relative to one another, switching to higher $\lambda_{100}$ reduces slightly the hysteresis when $K_I$ is positive and $M_s$ is minimum.

At lower $M_s$, altering $K_I$ significantly changes the zero field (remanent) magnetization and coercivity field for both in-plane and out-of-plane magnetization (Figure 5.3a, b and Figure 5.4a, b). Positive $K_I$ produces rectangular hysteresis loops in which the coercivity field increases by increasing the $K_I$. With negative $K_I$, the hysteresis loop becomes narrower, leading to smaller
remanent magnetization and coercivity. The difference between the patterned and reference film is negligible. Only in some cases ($\lambda^{(1)}_{100} K_1^{(1)} M_s^{(1)}$ and $\lambda^{(2)}_{100} K_1^{(1)} M_s^{(1)}$ for in-plane magnetization, and $\lambda^{(1)}_{100} K_1^{(2)} M_s^{(1)}$ and $\lambda^{(2)}_{100} K_1^{(2)} M_s^{(1)}$ for out-of-plane magnetization) does patterning increase slightly the coercivity field.

Figure 5.4 Comparison of out-of-plane magnetization curves of striped and unpatterned thin films for different material parameters and 0.00% biaxial strain.

Switching to higher $M_s$, altering $K_I$ produces negligible variation in both in-plane and out-of-plane magnetization (Figure 5.3c, d and Figure 5.4c, d). The influence of patterning, however, becomes more significant for in-plane magnetization (Figure 5.3c). In this case the stripe patterning results in wider hysteresis loop with much larger coercivity (about a factor of four
compared to the unpatterned reference film). At higher $M_s$, the out-of-plane magnetization does not show hysteretic behavior (Figure 5.4c, and Figure 5.4d). The striping effect is insignificant and only changes the slope of the curve.

5.5.2 The role of mechanical strain

To understand how mechanical strain changes the influence of patterning on the magnetization switching, the hysteresis curves are calculated while a compressive biaxial strain of 0.1% is applied at the bottom surface of the films. The results are shown in Figure 5.5 for in-plane and out-of-plane magnetization of STR $d=8$ $s=8$ $b=0$ and the reference unpatterned film.

![Diagram](image)

**Figure 5.5** Comparison of in-plane and out-of-plane magnetization curves of striped and unpatterned thin films for different material parameters and 0.10% biaxial strain.
The preliminary calculations show that, the lower value of $\lambda_{100}$ is not high enough to produce effective coupling between the applied mechanical strain and magnetic moments. Therefore, for the sake of brevity, only the results for maximum $\lambda_{100}$ are presented.

According to Figure 5.5, applying a compressive biaxial strain when $M_s$ is minimum, the in-plane hysteresis curve becomes narrower (Figure 5.5a). This indicates that magnetization becomes harder along the in-plane direction. In contrast, the out-of-plane magnetization results in wider hysteresis loops, demonstrating easier magnetization in that direction (Figure 5.5c). More interestingly, unlike the zero-strain magnetization that demonstrated larger coercivity field for patterned films, strained patterned films exhibit smaller coercivity when $M_s$ is minimized.

When $M_s$ is maximum, the in-plane magnetization exhibit similar trend as unstrained films with slightly tighter hysteresis loops (Figure 5.5b). In this case, the magnetoelastic anisotropy is insufficient to assist with the formation of out-of-plane hysteresis loop for unpatterned films (Figure 5.5d). In patterned films, however, applying mechanical strain produces double hysteresis loop.

5.5.3 The role of geometric parameters

The role of geometric parameters in stripe patterning are studied by considering different width, spacing, and the inclusion of a base layer. The results are shown in Figure 5.6 for the geometric parameters listed in Table 5.3. As magnetostriction exhibited marginal effect on the magnetization process, this section is devoted to the influence of magnetocrystalline anisotropy and saturation magnetization. Note that only half of the hysteresis curves are displayed.

One could understand the effect of stripe aspect ratio by only considering the results for films in which the spacing-to-width ratio is constant: STR $d=4$ $s=4$ $b=0$, STR $d=8$ $s=8$ $b=0$, and STR $d=16$ $s=16$ $b=0$. In addition, the influence of spacing-to-width ratio is studied by only considering the
stripes in which their widths are constant: STR $d=8$ $s=2.67$ $b=0$, STR $d=8$ $s=8$ $b=0$, and STR $d=8$ $s=24$ $b=0$.

Finally, the magnetization curves in Figure 5.6 enable an understanding of the role of adding a base layer: STR $d=8$ $s=8$ $b=0$, STR $d=8$ $s=8$ $b=1$, and STR $d=8$ $s=8$ $b=2$.

Figure 5.6 Comparison of in-plane magnetization curves of stripe patterning with different geometric parameters: (a) $\lambda_{100}^{(2)} K_{1}^{(1)} M_{s}^{(1)}$, (b) $\lambda_{100}^{(2)} K_{1}^{(1)} M_{s}^{(2)}$, (c) $\lambda_{100}^{(2)} K_{1}^{(1)} M_{s}^{(1)}$, (d) $\lambda_{100}^{(2)} K_{1}^{(2)} M_{s}^{(1)}$, (e) $\lambda_{100}^{(2)} K_{1}^{(2)} M_{s}^{(2)}$, and (f) $\lambda_{100}^{(2)} K_{1}^{(2)} M_{s}^{(2)}$. 
Figure 5.6a, c, and e reveal that when $M_s$ is at its minimum, while switching the values of $K_I$ reshapes the hysteresis curves significantly, stripe patterning results in either a similar or slightly different magnetization process compared to the unpatterned film.

Compared to unpatterned films, narrow stripes (STR $d=4$ $s=4$ $b=0$ and STR $d=8$ $s=8$ $b=0$) and stripes with larger spacing (STR $d=8$ $s=24$ $b=0$) exhibit higher coercivity for $K_I=1\times10^4$ (Figure 5.6a). Wider stripes (STR $d=16$ $s=16$ $b=0$) and stripes with smaller spacing (STR $d=8$ $s=2.67$ $b=0$) show similar curves. The addition of the base layer (STR $d=8$ $s=8$ $b=1$ and STR $d=8$ $s=8$ $b=2$), however, leads to a narrower loop with smaller coercivity.

For $K_I = -1\times10^4$ (Figure 5.6c), patterning yields the same magnetization curves as an unpatterned film; altering the geometric parameters has no effect.

When $K_I = 1\times10^5$ (Figure 5.6e), all geometric parameters return larger coercivity fields except those with wider stripes (STR $d=16$ $s=16$ $b=0$) and stripes with smaller spacing (STR $d=8$ $s=2.67$ $b=0$). While the patterned film with a thin base layer (STR $d=8$ $s=8$ $b=1$) also yields larger coercivity, that with a thicker base layer (STR $d=8$ $s=8$ $b=2$) does shows no effect.

As shown in Figure 5.6b, d, and f, the effect of using different geometric parameters in stripe patterning becomes more significant when $M_s$ is maximized. The narrower the stripes, the larger coercivity field. This is stronger when the spacing-to-width ratio is also higher (e.g. STR $d=8$ $s=24$ $b=0$). At certain geometric parameters (e.g. STR $d=4$ $s=4$ $b=0$, STR $d=8$ $s=2.67$ $b=0$, STR $d=8$ $s=8$ $b=1$, and STR $d=8$ $s=8$ $b=2$), the hysteresis curve shows two or even three steps, indicating multi-step reversal. In addition, as the stripe width increases or the spacing-to-width ratio decreases, the shape of the hysteresis curves becomes similar to that of the unpatterned reference film. Inclusion of the base layer results in a similar effect; thicker base layer (i.e. STR $d=8$ $s=8$ $b=2$) exhibits a hysteresis behavior more similar to that of the unpatterned film.
The influence of geometric parameters on the magnetic behavior of patterned films with square features are seen in Figure 5.7 for the geometric parameters listed in Table 5.4. Square features are selected to eliminate the uniaxial magnetic shape anisotropy existing in stripe features and to enable studying the role of other contributing factors such as magnetostatic interactions between the features.

Figure 5.7 Comparison of in-plane magnetization curves of square patterning with different geometric parameters: (a) $\lambda^{(2)}_{100} K^{(1)}_1 M^{(1)}_s$, (b) $\lambda^{(2)}_{100} K^{(1)}_1 M^{(2)}_s$, (c) $\lambda^{(2)}_{100} K^{(1)}_1 M^{(1)}_s$, (d) $\lambda^{(2)}_{100} K^{(1)}_1 M^{(2)}_s$, (e) $\lambda^{(2)}_{100} K^{(2)}_1 M^{(1)}_s$, and (f) $\lambda^{(2)}_{100} K^{(2)}_1 M^{(2)}_s$. 
As shown in Figure 5.7a, c, and e, the behavior of square patterns is similar to stripe patterns when \( M_s \) is minimum; the shape of the magnetization curve changes by varying \( K_I \) but the effect of patterning is minimal. As with stripe patterns, the influence of square patterning is more visible when \( M_s \) is at its maximum. Figure 5.7b and d reveal that for lower values of \( K_I \) (regardless of its sign), larger spacing (SQR \( d=8 \) \( s=24 \) \( b=0 \)) or larger width (SQR \( d=16 \) \( s=16 \) \( b=0 \)) produce larger coercivity field. Whereas smaller features (SQR \( d=4 \) \( s=4 \) \( b=0 \) and SQR \( d=8 \) \( s=8 \) \( b=0 \)) and smaller spacing (SQR \( d=8 \) \( s=2.67 \) \( b=0 \)) lead to much smaller coercivity and remanent magnetization, even smaller than the unpatterned reference film. The trend is opposite when \( K_I \) is maximum (Figure 5.7f); smaller features yield larger coercivity and larger features return smaller coercivity. SQR \( d=8 \) \( s=2.67 \) \( b=0 \) also exhibits two-step switching.

To better understand the magnetization process and how selection of the geometric parameters controls the magnetic switching in patterned films, the distribution of the stray field around the magnetic elements after removing the applied field is displayed in Figure 5.8 for \( \lambda_{100}^{(2)} K_1^{(1)} M_s^{(2)} \). This material configuration is selected because the geometric parameters have stronger effect when \( M_s \) is at its maximum. The results for the unpatterned film is included for comparison. These contour plots correspond to the remanent magnetization stage in the magnetization curves plotted in Figure 5.6b and b for stripe and square patterns with fixed width and varying spacing. When the magnetic elements are closer to each other, the distribution of the stray field around the elements is similar to that of the unpatterned film. It seems that the magnetic elements form a single unit magnet with only one pair of south-north poles. For SQR \( d=8 \) \( s=2.67 \) \( b=0 \), switching starts even before removing the field and, as a result, multiple pairs of poles are formed. When the features are placed at a greater distance from each other they act separately, creating isolated pairs of south-north poles.
Figure 5.8 Distribution of the stray field after removing the applied field for $\lambda_{100}^{(2)} K_1^{(1)} M_s^{(2)}$.

The interaction between elements is also studied by looking at the spontaneous domain structure. This is shown in Figure 5.9 for stripe- and square-patterned films with fixed width and varying spacing. Similar to Figure 5.8, the material configuration are limited to $\lambda_{100}^{(2)} K_1^{(1)} M_s^{(2)}$. The arrows represent the directions of the magnetization vectors and different colors denote the values of the $m_i$ component of the magnetization. The unpatterned reference film shows a planar symmetric domain structure with no preferred direction. The results for patterned films are drastically different; stripe patterning creates magnetic domains with clear preferred orientation parallel to the stripe main-axis. The stripe-patterned film with a thin base layer (STR $d=8$ $s=8$ $b=1$) shows similar behavior, but the effect of patterning becomes weaker for thicker base layer (STR $d=8$ $s=8$ $b=2$). Square patterning results in a single domain for each element but with clustered domains over multiple elements. The clustering goes away as the spacing between the element increases (SQR $d=8$ $s=24$ $b=0$).
5.6 Discussion

Magnetic anisotropy is the primary controlling factor in the magnetization reversal process in thin films. The source of magnetic anisotropies can be the competition or cooperation of magnetocrystalline anisotropy, geometric anisotropy, magnetoelastic coupling, and magnetostatic interactions; selection of material and geometric parameters determines which of these factors prevails and governs the overall magnetic anisotropy. Coercivity, remanence, and the shape of the hysteresis curve are dictated by the strength of the overall magnetic anisotropy and the direction of the applied field relative to the magnetic easy-axis.

Magnetic anisotropy due to shape of a magnetic body originates from inherently self-demagnetizing action inside the material that is referred to as a demagnetizing field [96]. This field is proportional to the demagnetizing coefficient (a geometric factor) and the magnitude of the
saturation magnetization [19]. For a given geometry, lower saturation magnetization results in smaller demagnetizing field and hence weakens the shape anisotropy. This is why, for the geometric parameters selected for this study, patterning does not exhibit a significant difference in the magnetization process when material configurations with low saturation magnetization are used (Figure 5.3a, b and Figure 5.4a, b). For such low saturation magnetization, a much higher aspect ratio geometry is required to achieve the desired shape anisotropy and a larger influence from patterning. In contrast, when larger saturation magnetization is selected, the patterning becomes effective in controlling the in-plane magnetic behavior of the films (Figure 5.3c and d). Owing to the same reason, the out-of-plane magnetization becomes harder leading to the absence of hysteresis and no effect from patterning (Figure 5.4c and d).

The magnetocrystalline anisotropy acts like a magnetic field pushing the magnetic moments to be aligned along the crystallographic easy-axis. The field is called the anisotropy field and is directly related to the magnetocrystalline anisotropy constant and inversely proportional to the saturation magnetization [19,90]. While increased saturation magnetization boosts the demagnetizing field and resultant shape anisotropy, the inverse proportionality of the anisotropy field to \( M_s \) makes magnetocrystalline anisotropy essentially ineffective. This explains why switching the values of the magnetocrystalline anisotropy constant while the saturation magnetization is maximized does not significantly alter the magnetization curves (Figure 5.3c, d and Figure 5.4c, d).

Magnetoelastic anisotropy results from the application of mechanical strain via magnetoelastic coupling. Magnetoelastic anisotropy depends on the magnetostriction coefficient and also varies inversely with saturation magnetization [19,90]. With positive magnetostriction coefficient, a compressive biaxial strain favors magnetization along the direction perpendicular to
the plane of the strain. The effect is stronger when the saturation magnetization is minimum. The combination of shape anisotropy and magnetostriction anisotropy lowers coercivity for patterned films compared to unpatterned films (Figure 5.5a and c) for in-plane direction and generates double hysteresis loops for out-of-plane direction (Figure 5.5d).

The periodic elements in patterned films interact with one another magnetostatically [85,89,97,98] generating another form of magnetic anisotropy called interaction anisotropy. The extent to which this interaction plays a role in the magnetization reversal process depends on the magnitude of the saturation magnetization and the spacing between the elements [19]. In patterned films with smaller saturation magnetization or larger spacing, the interaction is insufficient to drive changes in the magnetization process. When the saturation magnetization is higher and the magnetic elements are closer, however, the magnetostatic interplay becomes sufficient to prevail over other factors and thus change the remanence and coercivity.

With high magnetostatic interaction, the periodically ordered magnetic elements behave collectively, forming a single unit magnet comparable to an unpatterned film with one pair of south and north poles [91] (Figure 5.8). The spontaneous domain structure shows magnetic clustering over several elements due to this magnetostatic interplay (SQR d=8 s=2.76 b=0 and SQR d=8 s=8 b=0 in Figure 5.9). They also exhibit a similar demagnetizing trend as in unpatterned films. Like shape anisotropy, interaction anisotropy is stronger when the saturation magnetization is higher. Nonetheless, it eliminates the effect of shape anisotropy causing the magnetization curves to be more like those of the unpatterned films. Interaction anisotropy becomes weaker when the magnetocrystalline anisotropy increases [91], making the shape anisotropy the dominant controlling factor and the hysteresis increases (SQR d=8 s=2.76 b=0 and SQR d=8 s=8 b=0 in Figure 5.7f).
To better understand the effect of interaction anisotropy, the evolution of the domain structure during the application of the external field is studied for $\lambda_{100}^{(2)} K_1^{(1)} M_s^{(2)}$. The snap shots of magnetic domain structure right at the remanence and coercivity are shown in Figure 5.10. Only patterned films with the smallest spacing-to-width ratio (STR $d=8$ $s=2.76$ $b=0$ SQR $d=8$ $s=2.76$ $b=0$) are considered to focus on the effect of interactions between magnetic elements. The effect of interaction anisotropy is clearly visible in the snap shots. Each element in the square patterning is so small that they can only act as single domains. Under the pressure of the collective demagnetizing field some of the elements begin switching before the magnetic field is removed leading to much smaller net remanent magnetization and coercivity.

![Figure 5.10 Snap-shots of the domain structure at remanence and coercivity for $\lambda_{100}^{(2)} K_1^{(1)} M_s^{(2)}$.](image)

When the magnetostatic interactions are sufficient, the reversal in each element occurs sequentially with short pauses between each sequence while the applied field continues to increase [89]. This is reflected in the appearance of steps in the magnetization curves in Figure 5.6 and
Figure 5.7. In addition to magnetostatic interactions, domain wall pinning in stripe patterns with a base layer is also responsible for multi-step switching.

Depending on which anisotropy becomes the dominant controlling factor, patterning can result in both wider and narrower hysteresis curves. This implies that patterning can be used for achieving desired properties sought for a wide variety of applications.

5.7 Conclusion

A phase-field micromagnetic model was used to perform a comprehensive parametric study on the role of material and geometric parameters on the hysteresis behavior of patterned films. The combined effects of four magnetic anisotropies of different physical origins determines the magnetization reversal process; shape, magnetocrystalline, magnetoelastic anisotropy, and interaction anisotropies. The reversal process in magnetic films with low saturation magnetization is mainly governed by the magnetocrystalline anisotropy and is not influenced by the selection of geometric parameters owing to weaker demagnetizing field. For the case of high saturation magnetization, the magnetocrystalline anisotropy field becomes so small that it eliminates the influence of magnetocrystalline anisotropy. The demagnetizing field increases, however, driving stronger shape anisotropy. As a result, the geometric parameters become highly influential in determining the hysteresis behavior. High-aspect-ratio stripes yield larger coercivity and remanence. In the presence of biaxial strain, magnetoelastic anisotropy reverses the effect of shape anisotropy and results in smaller coercivity for even high-aspect ratio stripe patterning. When placed in adequate distance relative to each other and with high saturation magnetization, magnetostatic interactions between the elements begin playing a stronger role. This leads to smaller remanence and coercivity and emerging of multi-step switching. The results reported in this study can be utilized by device designers to select materials and geometric variables for desired functionalities and applications.
6.1 Abstract

A new design framework based on using patterned interfaces is proposed to improve strain-mediated magnetoelectric coupling in layered biferroic heterostructures. The focus is on the electric control of magnetization with the aim of realizing electrically induced reconfigurability of magnetic properties. A three-dimensional phase-field micromagnetic model with finite element method is employed to simulate the magnetization process in biferroic heterostructures of NiFe$_2$O$_4$ and PbTiO$_3$. Composite thin films with flat, stripe-patterned, and square-patterned interfaces are considered. The results show that the interfacial patterning dramatically improves the magnetoelectric coupling and hence the electrically induced reconfigurability of the magnetic properties. This is attributed to the elimination of the so-called substrate clamping effect, different interfacial strain profile, and increase in interfacial surface area.

6.2 Introduction

Multiferroicity, the simultaneous existence of multiple ferroic or antiferroic orders in one material system, was hypothesized in 1894 and observed experimentally as a combination of ferroelectric and ferromagnetic behavior in 1950s [1,15]. Interest in multiferroic materials, however, has only become significant in the past fifteen years [3]. Furthermore, although truly multiferroic materials have been postulated, research has been focused on materials with two ferroic behaviors, hence we refer to such materials as biferroic. Magnetoelectric (ME) coupling in biferroic systems enables controlling dielectric-polarization via applying magnetic field or manipulating material magnetization through application of electric field. Single phase ME materials are rare, however, and have a room temperature response that is too small for most technological applications due to having either low permittivity or low permeability [3,8,99].
The alternative approach is to utilize the magnetoelastic and electromechanical coupling in magnetostrictive and piezoelectric materials to make synthetic biferroic heterostructures. The strain transfer across the interface of the two phases will allow the coupling of ferromagnetic and ferroelectric orders. Such heterostructures have been made in the form of bulk composites as well as composite films. The response obtained through strain-mediated coupling is orders-of-magnitude higher than in single-phase materials, and thus the potential for applications is enhanced greatly [3,7,10,23]. Progress has been sporadic, however, due to the complexity of the composite materials design, especially at small scales.

Among the critical parameters impacting ME composite performance is interfacial connectivity between the constituents [3,23]. Two successful approaches are shown in Figure 6.1a and Figure 6.1b: nano-pillars of one phase embedded in a film matrix of the other phase and laminated structure of layered phases. Each of these connectivity schemes has advantages and challenges. On one hand, the in-plane strain coupling in a layered structure is impacted by the constraint imposed by the substrate [4,6]. On the other hand, the vertical interfaces of the nano-pillars span the entire thickness of the film, resulting in current leakage problems [7]. Since the out-of-plane strain coupling is not affected by substrate clamping [13], one could expect the highest ME coupling for the vertical interfaces if the leakage problem is resolved. An ideal system for achieving high ME coupling through strain thereby would be one containing vertical interfaces that are not continuous along the film thickness direction. Accordingly, in this study a new design principle based on using patterned interface in layered structure is proposed (see Figure 6.1c). The patterning introduces three-dimensional interfaces, some of which are vertical, consistent with the ideal geometry for ME coupling. The layered structure also eliminates the leakage problem.
The goal of this study is to employ a three-dimensional meso-scale model to analyze the efficacy of this new design for improving strain-mediated ME coupling. The scope of the project is narrowed to electric control of magnetization with the goal of achieving reconfigurable magnetic properties in thin films. The model employs an expression of free energy functional that relates magnetic moments to strain and magnetic field. In addition, energy terms associated with electro-elastic coupling are added. The Landau–Lifshitz–Gilbert equation is used to predict the evolution of the magnetic moments. The model utilizes the formulations proposed in [36,38] and incorporates them into finite element code COMSOL Multiphysics.

The materials selected are nickel ferrite (NFO) and lead titanate (PTO) as magnetostrictive and piezoelectric materials, respectively. The influence of electric polarization in the PTO phase on the magnetization reversal process in the NFO phase is studied. ME heterostructures with flat, stripe-patterned, and square-patterned interfaces are considered.

6.3 Model development

6.3.1 Ferromagnetic phase

The modeling of the ferromagnetic phase is based on the formulation presented in Chapter 3.
6.3.2 Ferroelectric phase

In ferroelectric modeling, electric polarization $P_i$ is treated as the primary order parameter [28,36,100]. The free energy functional for ferroelectric modeling contains all the dielectric, elastic and piezoelectric information of the material. It is consisted of expressions for Landau energy, elastic energy, gradient energy, and electrostatic energy. Time-dependent Ginsburg-Landau (TDGL) equation is used as the evolution equation to minimize the free energy functional and calculate the distribution of the electric polarization [36]. In analogy to phase-field micromagnetic modeling, the evolution equation is accompanied by mechanical equilibrium and Gauss’ theorem.

Since the focus of this study is only on the magnetization switching process and electrically induced variations in magnetic properties, the electric polarization in this study is assumed to be uniform and not affected by the magnetization process. In other words, electric polarization is not treated as unknown. This simplification enables reduction of the ferroelectric modeling to electro-mechanical modeling and discarding the complexities associated with time-dependent Ginsburg-Landau (TDGL) equation and Gauss' Theorem. In addition, only energy terms associated with electro-elastic coupling need to be considered and other energy terms are excluded.

The elastic energy density for ferroelectric material contains a positive term for pure elastic strains and a negative term for electrostrictive strains caused by electric polarization.

$$h^{FE\ elastic}_{\text{cubic}} = \frac{1}{2}C_{ijkl}(\varepsilon_{ij} - \varepsilon_{ij}^e)(\varepsilon_{kl} - \varepsilon_{kl}^e) = \frac{1}{2}C_{ijkl}e_{ij}e_{kl}$$

(6.1)

where $C_{ijkl}$ is the fourth order elastic stiffness tensor, $\varepsilon_{ij}$ is the pure elastic strain, $\varepsilon_{ij}^e$ is the electrostrictive strain, and $e_{ij} = \varepsilon_{kl} - \varepsilon_{ij}^e$. The electrostrictive strain is a function of electrostriction constants and components of the electric polarization. In the case of quadratic electrostriction it is given by:
\[ \varepsilon_{ij}^e = \begin{bmatrix} Q_{11}P_1^2 + Q_{12}(P_2^2 + P_3^2) & Q_{44}P_1P_2 & Q_{44}P_1P_3 \\ Q_{44}P_1P_2 & Q_{11}P_2^2 + Q_{12}(P_1^2 + P_3^2) & Q_{44}P_2P_3 \\ Q_{44}P_1P_3 & Q_{44}P_2P_3 & Q_{11}P_3^2 + Q_{12}(P_1^2 + P_2^2) \end{bmatrix} \] (6.2)

Here \( Q_{ij} \) are electrostrictive coefficients. Given the symmetry in crystal classes, most elements of the stiffness tensor are zero. For unpolarized paraelectric cubic crystal, only three independent elastic constants are needed. Using the Voigt notation, Eq. (6.1) can be re-written as

\[ h_{cubic}^{FE \text{ elastic}} = \frac{1}{2} c_{11}(e_{11}^2 + e_{22}^2 + e_{33}^2) + c_{12}(e_{11}e_{22} + e_{22}e_{33} + e_{11}e_{33}) \]

\[ + c_{44}(e_{12}^2 + e_{21}^2 + e_{32}^2 + e_{31}^2) + \frac{1}{2} q_11(e_{11}P_1^2 + e_{22}P_2^2 + e_{33}P_3^2) \]

\[ - \frac{1}{2} q'_{11} \left(e_{11}(P_2^2 + P_3^2) + e_{22}(P_1^2 + P_3^2) + e_{33}(P_1^2 + P_2^2)\right) \]

\[ - q_{44}((e_{12} + e_{21})P_1P_2 - (e_{23} + e_{32})P_2P_3 - (e_{13} + e_{31})P_1P_3) \]

\[ + a_{11}'(p_4^4 + p_2^4 + p_3^4) + a_{12}'(p_2^2p_2^2 + p_2^2p_3^2 + p_1^2p_3^2) \]

where

\[ q_{11} = 2(c_{11}Q_{11} + 2c_{12}Q_{12}) \] (6.5)

\[ q'_{11} = 2(c_{12}Q_{11} + c_{11}Q_{12} + c_{12}Q_{12}) \] (6.6)

\[ q_{44} = 2c_{44}Q_{44} \] (6.7)

\[ a_{11}' = \frac{1}{2} c_{11}Q_{11}^2 + 2c_{12}Q_{11}Q_{12} + c_{11}Q_{12}^2 + c_{12}Q_{12}^2 \] (6.8)

\[ a_{12}' = c_{12}Q_{11}^2 + 2c_{11}Q_{11}Q_{12} + 2c_{12}Q_{11}Q_{12} + c_{11}Q_{12}^2 + 3c_{12}Q_{12}^2 + 2c_{44}Q_{44}^2 \] (6.9)

Calculating \( e_{ij} = \varepsilon_{kl} - \varepsilon_{ij}^e \) using (6.2) and substituting it into Eq. (6.3) yield the following polynomial expressions for elastic energy of the paraelectric phase with cubic symmetry. The higher order terms are neglected.
In formulating of ferroelectric free energy functional, one must account for the symmetry breakdown in the vicinity of the Curie temperature; unpolarized high-symmetry paraelectric phase transformation to polarized low-symmetry ferroelectric phase. This has important implications on the elastic energy where tetragonal symmetry replaces cubic symmetry. To consider the tetragonal symmetry, the following mathematical expression proposed in [101] is adopted to extend the expression of the elastic energy in (6.4).

\[
\begin{align*}
  h_{\text{extension \ II}}^{FE} &= \frac{1}{2} g_{11}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) \\
  &\quad + \frac{1}{2} g'_{11}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) + \varepsilon_{21}(P_2^4 + P_3^4) + \varepsilon_{33}(P_1^4 + P_2^4) \\
  &\quad + g_{44}(\varepsilon_{12}P_1^4 + \varepsilon_{21}P_2^4 + \varepsilon_{22}P_3^4) + \varepsilon_{12}(P_2^4 + P_3^4) + \varepsilon_{23}(P_2^4 + P_3^4) + \varepsilon_{33}(P_1^4 + P_2^4) \\
  &\quad + \varepsilon_{32}(P_3^4 + P_2^4) + \varepsilon_{13}(P_3^4 + P_1^4) + \varepsilon_{23}(P_3^4 + P_1^4) + \varepsilon_{31}(P_3^4 + P_1^4) \\
  h_{\text{extension \ III}}^{FE} &= \frac{1}{2} h_{11}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) + \frac{1}{2} h'_{11}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) \\
  &\quad + h_{12}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) + \varepsilon_{11}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) \\
  &\quad + \varepsilon_{12}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) + \varepsilon_{13}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) \\
  &\quad + \varepsilon_{21}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) + \varepsilon_{23}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) \\
  &\quad + \varepsilon_{31}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) + \varepsilon_{32}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) \\
  &\quad + \varepsilon_{12}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) + \varepsilon_{13}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) \\
  &\quad + \varepsilon_{21}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) + \varepsilon_{23}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) \\
  &\quad + \varepsilon_{31}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4) + \varepsilon_{32}(\varepsilon_{11}P_1^4 + \varepsilon_{22}P_2^4 + \varepsilon_{33}P_3^4)
\end{align*}
\]
Here $f_{ij}, f_{ij}', g_{ij}, g_{ij}', h_{ij}$, and $h_{ij}'$ take the role of elastic coefficients and provide additional degree of freedom that allows elastic behavior of tetragonal polarized phase. In the absence of electric polarization, the extended part becomes zero and the elastic energy reduces to elastic behavior of cubic paraelectric phase. The total elastic energy density of ferroelectric material can be written by adding Eqs. (6.4), (6.10), (6.11) and (6.12).

$$h_{FE\text{ elastic}} = h_{cubic}^{FE \text{ elastic}} + h_{extension I}^{FE \text{ elastic}} + h_{extension II}^{FE \text{ elastic}} + h_{extension III}^{FE \text{ elastic}}$$

(6.13)

6.3.3 Finite element implementation

The details of the finite element model is similar to that of Chapter 4. One difference is that a single crystal magnetic material model is considered in this chapter and variations in the crystallographic orientations are not included. Mesh is also different because of using different geometries (see Figure 6.2).

In addition to the normalization scheme presented in Eq. (4.1), the above normalization method is used for material constants in Eq. (6.4), (6.10), (6.11), and (6.12). To make sure that physical properties are in the same scale, the same normalization scheme must be used for both ferromagnetic and ferroelectric constants.

$$q_{ij}^* = q_{ij} \frac{p_0^{2l_2} A_{exch}}{A_{exch}}$$  \quad  $$q_{ij}'^* = q_{ij}' \frac{p_0^{2l_2} A_{exch}}{A_{exch}}$$  \quad  $$q_{ij}'' = q_{ij} \frac{p_0^{4l_2} A_{exch}}{A_{exch}}$$  \quad  $$q_{ij}''' = q_{ij}' \frac{p_0^{4l_2} A_{exch}}{A_{exch}}$$

$$f_{ij}^* = f_{ij} \frac{p_0^{2l_2} A_{exch}}{A_{exch}}$$  \quad  $$f_{ij}'^* = f_{ij}' \frac{p_0^{2l_2} A_{exch}}{A_{exch}}$$  \quad  $$g_{ij}^* = g_{ij} \frac{p_0^{4l_2} A_{exch}}{A_{exch}}$$  \quad  $$g_{ij}'^* = g_{ij}' \frac{p_0^{4l_2} A_{exch}}{A_{exch}}$$

$$h_{ij}^* = h_{ij} \frac{p_0^{4l_2} A_{exch}}{A_{exch}}$$  \quad  $$h_{ij}'^* = h_{ij}' \frac{p_0^{4l_2} A_{exch}}{A_{exch}}$$

(6.14)
As explained in the previous section the components of the electric polarization \((P_1, P_2,\) and \(P_3\)) are not treated as unknowns and assumed to be uniform and constant in the ferroelectric material.

\[
P_1 = \hat{P}_1 \\
P_2 = \hat{P}_2 \\
P_3 = \hat{P}_3
\]  

(6.15) \hspace{1cm} (6.16) \hspace{1cm} (6.17)

where \(\hat{P}_1, \hat{P}_2,\) and \(\hat{P}_3\) are prescribed values of electric polarization along spatial coordinates \(x_1, x_2,\) and \(x_3.\)

Figure 6.2 Finite element domain and mesh for a) Eq. (3.20), b) Eq. (3.18), and c) Eq. (3.19).

6.4 Considered materials and geometry

NiFe\(_2\)O\(_4\) (NFO) which is a ferrimagnetic insulating oxide is selected as the magnetic material. The hysteretic properties of polycrystalline NFO thin films was studied Chapter 4 where the computed hysteresis curves were verified with experimental measurements [95]. NFO has a negative magnetocrystalline anisotropy constant which results in \(\langle 111 \rangle\) as the easy-axis and \(\langle 100 \rangle\)
as the hard-axis. In addition, NFO has relatively small saturation magnetization compared to other ferri-/ferromagnetic materials. This makes magnetoelastic anisotropy to become more effective for controlling the magnetization behavior. On this basis, NFO is ideal for studying strain-mediated ME coupling.

PbTiO$_3$ (PTO) is chosen as the ferroelectric material. At its polarized phase, it exhibits a tetragonal structure with relatively large electro-mechanical coupling. This makes it a good candidate for making biferroic heterostructures. In fact PTO has been used with NFO and other ferrites for making ME composites [6,102].

The material constants in the free energy functional along with their corresponding normalized values are listed in Table 6.1 for NFO and PTO, respectively. These parameters are extracted from either single crystal measurements or first principal calculations [73–76,103]. The normalized values are computed using Eqs. (4.1) and (6.14).

Table 6.1 Material constants for NiFe$_2$O$_4$ adopted from [73–76] and their corresponding normalized values computed using Eq. (4.1).

<table>
<thead>
<tr>
<th></th>
<th>NiFe$_2$O$_4$</th>
<th>Normalized</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{11}$</td>
<td>$2.73 \times 10^{11}$ Kg m$^{-1}$s$^{-2}$</td>
<td>$5.962 \times 10^6$</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>$1.61 \times 10^{11}$ Kg m$^{-1}$s$^{-2}$</td>
<td>$3.508 \times 10^6$</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>$8.23 \times 10^{10}$ Kg m$^{-1}$s$^{-2}$</td>
<td>$1.797 \times 10^6$</td>
</tr>
<tr>
<td>$\lambda_{100}$</td>
<td>$-4.59 \times 10^{-5}$</td>
<td>$-4.59 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\lambda_{111}$</td>
<td>$-2.16 \times 10^{-5}$</td>
<td>$-2.16 \times 10^{-5}$</td>
</tr>
<tr>
<td>$K_1$</td>
<td>$-6.93 \times 10^{1}$ Kg m$^{-1}$s$^{-2}$</td>
<td>$-15.13 \times 10^2$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>$-0.43 \times 10^{1}$ Kg m$^{-1}$s$^{-2}$</td>
<td>$-93.88 \times 10^4$</td>
</tr>
<tr>
<td>$M_s$</td>
<td>$2.7 \times 10^5$ A m$^{-1}$</td>
<td>1.414</td>
</tr>
<tr>
<td>$A_{exch}$</td>
<td>$1.0 \times 10^{-11}$ Kg m s$^{-2}$</td>
<td>1</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>$4\pi \times 10^{-7}$ Kg m A$^{-2}$s$^{-2}$</td>
<td>1</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>$1.76 \times 10^{11}$ Kg A$^{-1}$s$^{-2}$</td>
<td>1</td>
</tr>
<tr>
<td>$l_e$</td>
<td>$14.776 \times 10^{-9}$ m</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 6.2 Material constants for PbTiO$_3$ adopted from [103] and their corresponding normalized values computed using Eq. (6.14).

<table>
<thead>
<tr>
<th>PbTiO$_3$</th>
<th>Original</th>
<th>Normalized</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{11}$</td>
<td>$3.42 \times 10^{11}$ Kg m$^{-1}$ s$^{-2}$</td>
<td>$7.467 \times 10^6$</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>$1.31 \times 10^{11}$ Kg m$^{-1}$ s$^{-2}$</td>
<td>$2.860 \times 10^6$</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>$5.40 \times 10^{10}$ Kg m$^{-1}$ s$^{-2}$</td>
<td>$1.179 \times 10^6$</td>
</tr>
<tr>
<td>$q_{11}$</td>
<td>$9.630 \times 10^9$ Kg m$^{-3}$ A$^{-2}$ s$^{-4}$</td>
<td>$1.172 \times 10^5$</td>
</tr>
<tr>
<td>$q'_{11}$</td>
<td>$1.187 \times 10^{10}$ Kg m$^{-3}$ A$^{-2}$ s$^{-4}$</td>
<td>$2.007 \times 10^5$</td>
</tr>
<tr>
<td>$q_{44}$</td>
<td>$1.520 \times 10^9$ Kg m$^{-3}$ A$^{-2}$ s$^{-4}$</td>
<td>$2.570 \times 10^4$</td>
</tr>
<tr>
<td>$a'_{11}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$a'_{12}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$f_{11}$</td>
<td>$-6.402 \times 10^{10}$ Kg m$^{-3}$ A$^{-2}$ s$^{-4}$</td>
<td>$-1.082 \times 10^7$</td>
</tr>
<tr>
<td>$f'_{11}$</td>
<td>$-1.472 \times 10^{10}$ Kg m$^{-3}$ A$^{-2}$ s$^{-4}$</td>
<td>$-2.489 \times 10^6$</td>
</tr>
<tr>
<td>$f_{12}$</td>
<td>$-1.111 \times 10^{11}$ Kg m$^{-3}$ A$^{-2}$ s$^{-4}$</td>
<td>$-1.878 \times 10^6$</td>
</tr>
<tr>
<td>$f'_{12}$</td>
<td>$-3.099 \times 10^{10}$ Kg m$^{-3}$ A$^{-2}$ s$^{-4}$</td>
<td>$-5.239 \times 10^5$</td>
</tr>
<tr>
<td>$f_{44}$</td>
<td>$-5.555 \times 10^{10}$ Kg m$^{-3}$ A$^{-2}$ s$^{-4}$</td>
<td>$-9.392 \times 10^5$</td>
</tr>
<tr>
<td>$f'_{44}$</td>
<td>$-1.292 \times 10^9$ Kg m$^{-3}$ A$^{-2}$ s$^{-4}$</td>
<td>$-2.183 \times 10^4$</td>
</tr>
<tr>
<td>$g_{11}$</td>
<td>$7.580 \times 10^7$ Kg m$^{-7}$ A$^{-4}$ s$^{-6}$</td>
<td>$9.924 \times 10^2$</td>
</tr>
<tr>
<td>$g'_{11}$</td>
<td>$1.294 \times 10^{10}$ Kg m$^{-7}$ A$^{-4}$ s$^{-6}$</td>
<td>$1.694 \times 10^6$</td>
</tr>
<tr>
<td>$g_{44}$</td>
<td>$2.553 \times 10^8$ Kg m$^{-7}$ A$^{-4}$ s$^{-6}$</td>
<td>$3.342 \times 10^3$</td>
</tr>
<tr>
<td>$h_{11}$</td>
<td>$4.134 \times 10^{11}$ Kg m$^{-7}$ A$^{-4}$ s$^{-6}$</td>
<td>$5.412 \times 10^6$</td>
</tr>
<tr>
<td>$h'_{11}$</td>
<td>$9.505 \times 10^{10}$ Kg m$^{-7}$ A$^{-4}$ s$^{-6}$</td>
<td>$1.244 \times 10^6$</td>
</tr>
<tr>
<td>$h_{12}$</td>
<td>$7.170 \times 10^{10}$ Kg m$^{-7}$ A$^{-4}$ s$^{-6}$</td>
<td>$9.387 \times 10^5$</td>
</tr>
<tr>
<td>$h'_{12}$</td>
<td>$2.001 \times 10^{10}$ Kg m$^{-7}$ A$^{-4}$ s$^{-6}$</td>
<td>$2.620 \times 10^5$</td>
</tr>
<tr>
<td>$h_{44}$</td>
<td>$3.585 \times 10^{10}$ Kg m$^{-7}$ A$^{-4}$ s$^{-6}$</td>
<td>$4.694 \times 10^5$</td>
</tr>
<tr>
<td>$h'_{44}$</td>
<td>$8.340 \times 10^8$ Kg m$^{-7}$ A$^{-4}$ s$^{-6}$</td>
<td>$1.092 \times 10^4$</td>
</tr>
<tr>
<td>$P_0$</td>
<td>$0.88$ A s m$^{-2}$</td>
<td>$1$</td>
</tr>
</tbody>
</table>

The geometries of biferroic heterostructures considered in this study are shown in Figure 6.3. There are two general groups shown in this figure; a) NFO layer laminated between the substrate and PTO layer (Sub-NFO-PTO), and b) PTO layer laminated between the substrate and NFO layer (Sub-PTO-NFO). For each group, there is a laminated heterostructure with 1) flat interface, 2) stripe-patterned interface, and 3) square-patterned interface.
Figure 6.3 Considered geometries for biferroic heterostructures; laminated films with a) flat interface, b) stripe patterns, c) square patterns.

6.5 Results and discussions

Results demonstrated in this section are devoted to the effect of polarization direction on the magnetic hysteresis curves. Full polarization saturation in the desired direction is introduced into the ferroelectric phase before applying the magnetic field. There are three polarization directions; in the plane of the film parallel to the in-plane magnetization direction (IP∥), in the plane of the film perpendicular to the in-plane magnetization direction (IP⊥), and normal to the plane of the film along the out-of-plane magnetization direction (OP). In addition, an unpolarized case is included in which the components of the polarization vector are set to zero.

The magnetic hysteresis curves are computed by magnetizing the films directly from their random initial condition with zero net magnetization up to saturation and subsequently demagnetizing them back to zero net magnetization and then magnetizing again in the opposite
direction. For the stripe patterning, the in-plane magnetization is calculated along the stripes’ main axis direction.

6.5.1 Magnetization in unpolarized composite films

To evaluate the extent to which geometrical patterning plays a role in modifying the hysteresis curves, the magnetization curves for unpolarized films are shown in this section. This is necessary before analyzing the results for the influence of electric polarization on the magnetization process in composite films with different interfacial patterning.

The hysteresis curves are shown in Figure 6.4 for in-plane and out-of-plane magnetization. As it can be seen, the overall difference in the magnetization curves is negligible indicating minimal effect from patterning when the PTO phase is unpolarized. The in-plane magnetization exhibits slightly wider loop for stripe-patterning and narrower loop for square patterning (only in Sub-PTO-NFO). This is expected as stripes introduce uniaxial shape anisotropy into the film favoring in-plane magnetization along stripes’ main axis. Out-of-plane magnetization does not yield hysteresis loop for any of the cases. The only notable difference is sharper magnetization for square patterning in the case of Sub-PTO-NFO (Figure 6.4d).

The minor effect of patterning observed in unpolarized PTO-NFO composite films is in agreement with the results reported in Chapter 5 on the influence of material and geometric parameters on the magnetization reversal process in thin films with periodically ordered surface features. NFO has relatively small saturation magnetization compared to other ferri-/ferromagnetic materials. This eliminates the effect of self-demagnetizing action within the magnetic layer that is responsible for producing the magnetic shape-anisotropy. As a consequence, NFO is expected to show small effect from surface patterning. On this basis, the effect of patterning reported in the proceeding section is mainly due to ME coupling rather than the magnetic shape anisotropy.
Figure 6.4 Comparison of in-plane and out-of-plane magnetization curves in unpolarized biferroic heterostructures with different interfacial patterning: a\textsubscript{1}) Sub-NFO-PTO (in-plane magnetization), a\textsubscript{2}) Sub-PTO-NFO (in-plane magnetization), b\textsubscript{1}) Sub-NFO-PTO (out-of-plane magnetization), b\textsubscript{2}) Sub-PTO-NFO (out-of-plane magnetization).

6.5.2 Magnetization in polarized composite films

The influence of electric polarization on the in-plane magnetization curves are shown in Figure 6.5 for biferroic composite films with flat, stripe-patterned, and square-patterned interfaces. It can be seen that switching the polarization direction in the PTO phase has a negligible effect on the magnetization process in NFO phase when a flat interface is used. In composite films with patterned interface, however, much stronger ME coupling is observed; switching the direction of electric polarization results in thoroughly different hysteresis curves for both stripe- and square-patterned interfaces. The effect is more robust when the NFO layer goes on the top of the PTO layer.
Figure 6.5 Comparison of in-plane magnetization curves in biferroic heterostructures with ferroelectric layer polarized in different directions; a) Sub-NFO-PTO with flat interface, a2) Sub-PTO-NFO with flat interface, b) Sub-NFO-PTO with stripe-patterned interface, b2) Sub-PTO-NFO with stripe-patterned interface, c) Sub-NFO-PTO with square-patterned interface, and c2) Sub-PTO-NFO with square-patterned interface.

According to Figure 6.5a1 and Figure 6.5a2, the hysteresis parameter that seems to be mostly affected by the polarization in unpatterned films is the remanent (zero-field) magnetization
which is higher for IP\perp polarization and lower for IP\parallel polarization. For the case of Sub-PTO-NFO, IP\parallel polarization also returns a narrower hysteresis curve with a smaller coercivity.

Figure 6.5b\textsubscript{1} and Figure 6.5b\textsubscript{2} demonstrate that with stripe patterning, coercivity ranges from about 25% of that in unpatterned case for IP\parallel polarization to about 225% for OP polarization. The saturation magnetization field increase and the remanent magnetization decrease for IP\parallel and IP\perp polarization. It is also noted that OP polarization results in two-step switching behavior for both Sub-NFO-PTO and Sub-PTO-NFO cases.

Figure 6.5c\textsubscript{1} and Figure 6.5c\textsubscript{2} reveal that the range at which the coercivity can be extended magnetoelectrically is significantly higher when square-patterning is used; IP\parallel polarization yields a wide hysteresis loop with coercivity field up to 6 times higher than unpolarized case.

The influence of electric polarization on the out-of-plane magnetization curves are shown in Figure 6.6 for biferroic heterostructures with flat, stripe-patterned, and square-patterned interfaces. Stronger demagnetization field along the film thickness suppresses out-of-plane magnetization and prevents the formation of hysteresis loop in that direction for unpolarized films. Polarizing the PTO phase does not result in a significant difference for composite films with flat interface. Only for the case of polarized Sub-NFO-PTO films, small hysteresis loops emerges (Figure 6.6a).

Suppression of the out-of-plane magnetization weakens in films with stripe- and square-patterned interfaces and thus larger hysteresis loops are observed. This is more evident in square-patterned films when the films are polarized in the plane of the film (Figure 6.6c\textsubscript{1} and Figure 6.6c\textsubscript{2}). Due to in-plane symmetry in films with flat and square-patterned interfaces, IP\parallel and IP\perp polarization return similar magnetization curves. For stripe-patterned interface, IP\parallel results in widest hysteresis loop with largest coercivity and remanent magnetization.
Figure 6.6 Comparison of out-of-plane magnetization curves in biferroic heterostructures with ferroelectric layer polarized in different directions; a₁) Sub-NFO-PTO with flat interface, a₂) Sub-PTO-NFO with flat interface, b₁) Sub-NFO-PTO with stripe-patterned interface, b₂) Sub-PTO-NFO with stripe-patterned interface, c₁) Sub-NFO-PTO with square-patterned interface, and c₂) Sub-PTO-NFO with square-patterned interface.
6.5.3 Interfacial strain in polarized composite films

The contour plots in Figure 6.7 and Figure 6.8 show the interfacial strain values along the polarization directions for Sub-NFO-PTO and Sub-PTO-NFO composite films, respectively. The difference between these interfaces is clearly evident in these figures.

The piezoelectric effect in the PTO phase results in tensile straining of the PTO layer in the polarization direction. The strain computed at the interface, however, depends on the shape of the interface and can be tensile or compressive. The magnetoelastic anisotropy induced in the NFO layer depends on the sign and magnitude of the transferred strain. A compressive strain in the plane of NFO film assists in-plane magnetization, whereas a tensile strain facilitates out-of-plane magnetization [95].

According to Figure 6.7 and Figure 6.8 the strain in the areas far from the edges is minimum for the flat interface. This amount of strain is not sufficient for altering the magnetization process in NFO layer. As a result, negligible difference is observed in the hysteresis curves calculated for composite film with flat interface when polarized in different directions.

For the composite film with stripe-patterned interface, IP∥ polarization generates almost same amount of strain as it does in flat interface (Figure 6.7a2 and Figure 6.8a2). The interfacial area, however, is about 60% larger compared to flat interface. This means larger volume of the NFO layer experiences the transferred strain leading to higher magnetoelastic anisotropy.

IP⊥ polarization generates a much more complex strain profile at the stripe-patterned interface. With IP⊥ polarization, the PTO stripes expand in the transverse direction placing the NFO stripes in compression (Figure 6.7b2 and Figure 6.8b2). The compressive strain is so high that it introduces a uniaxial in-plane anisotropy along the transverse direction. As a consequence the magnetization parallel to the stripes becomes harder leading to smaller coercivity and remanent
magnetization for the hysteresis curves computed in this direction. Similar behavior is observed for composite films with square-patterned interface when polarized along $\text{IP} \parallel$ and $\text{IP} \perp$ directions (Figure 6.7a₃, Figure 6.7b₃, Figure 6.8a₃, and Figure 6.8b₃). The difference is that $\text{IP} \parallel$ polarization generates compressive strain parallel to the magnetization direction leading to much wider hysteresis loop. $\text{IP} \perp$ polarization, however, generates compressive strain in the transverse direction. This results in narrower in-plane magnetization curves. Moreover, the volume fraction of the PTO phase is larger for the square patterning leading to smaller mechanical constrain from NFO and hence larger piezoelectric strain.

![Diagram showing interfacial strain along the polarization directions for Sub-NFO-PTO composite films.](image)

Figure 6.7 Interfacial strain along the polarization directions for Sub-NFO-PTO composite films.
Owing to the vertical parts in the stripe and square patterning, the out-of-plane polarization yields much larger strain values at the interface compared to flat interface (Figure 6.7c2, Figure 6.7c3, Figure 6.8c2, and Figure 6.8c3). This out-of-plane strain is tensile which helps the in-plane magnetization in NFO layer. The transferred strain is so high that it results in two-step switching behavior in these films.

Owing to substrate clamping effect, the amount of strain at the PTO-NFO interface is smaller when PTO is placed at the bottom layer. Yet, since NFO at the top is less affected by the substrate clamping, it can deform easily showing stronger ME coupling for Sub-PTO-NFO. In contrast, when NFO is placed at the bottom, the amount of strain at the interface is larger but this strain is not as effective in modifying the magnetization process because substrate clamping directly affects the NFO layer. The difference is reflected in the magnetization curves plotted in Figure 6.5 and Figure 6.6.
Figure 6.7 and Figure 6.8, confirms the in-plane symmetry for flat and square-patterned interfaces when the polarization is in the plane of the film.

6.6 Conclusion

A phase-field micromagnetic model was used to study the influence of interfacial patterning on the electric control of magnetization in biferroic heterostructures of NiFe₂O₄ and PbTiO₃. Magnetic hysteresis curves in composite films with flat, stripe-patterned and square-patterned interfaces are computed. The obtained results indicate that patterning could significantly improve the strain-mediated ME coupling by eliminating the substrate clamping effect and changing the interfacial strain profile. In addition, larger volume of magnetic layer is exposed to the piezoelectric strain contributing to more effective strain transfer. As a result of stronger ME coupling, the hysteresis in the magnetic layer is shown to be highly sensitive to the direction of the polarization in ferroelectric layer. This implies that one could successfully reconfigure the magnetic properties to desired values sought for a wide variety of applications by altering the direction of the bias electric field.
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Appendix A: Wolfram Mathematica program for implementation of phase-field micromagnetics

Remove["Global`*"]

(*Coordinate transformation*)

Tr1 = {{Cos[p], Sin[p], 0}, {-Sin[p], Cos[p], 0}, {0, 0, 1}}
Tr2 = {{1, 0, 0}, {0, Cos[q], Sin[q]}, {0, -Sin[q], Cos[q]}}
Tr3 = {{Cos[r], Sin[r], 0}, {-Sin[r], Cos[r], 0}, {0, 0, 1}}

Tij = {{T11, T12, T13}, {T21, T22, T23}, {T31, T32, T33}} = Tr3.Tr2.Tr1

(*Strain tensor transformation*)

eij = {{e11, e12, e13}, {e21, e22, e23}, {e31, e32, e33}} = {{u1x, (u1y + u2x)/2, (u1z + u3x)/2}, {(u1y + u2x)/2, u2y, (u2z + u3y)/2}, {(u1z + u3x)/2, (u2z + u3y)/2, u3z}}


(*Elastic stiffness tensor*)

cij = {{c11, c12, c12, 0, 0, 0}, {c12, c11, c12, 0, 0, 0}, {c12, c12, c11, 0, 0, 0}, {0, 0, 0, c44, 0, 0}, {0, 0, 0, 0, c44, 0}, {0, 0, 0, 0, 0, c44}}
(*Magnetization vector transformation*)

\[
\mathbf{m}_i = \begin{pmatrix} m_1 \\ m_2 \\ m_3 \end{pmatrix}, \quad \mathbf{m}_{ti} = \begin{pmatrix} m_{t1} \\ m_{t2} \\ m_{t3} \end{pmatrix} = \text{Transpose}[T_{ij}] \cdot \mathbf{m}_i
\]

(*Magnetic vector transformation*)

\[
\mathbf{H}_i = \begin{pmatrix} H_1 \\ H_2 \\ H_3 \end{pmatrix}, \quad \mathbf{H}_{ti} = \begin{pmatrix} H_{t1} \\ H_{t2} \\ H_{t3} \end{pmatrix} = \text{Transpose}[T_{ij}] \cdot \mathbf{H}_i
\]

(*Mechanical Equilibrium*)

\[
\begin{pmatrix} s_1, s_2, s_3, s_4, s_5, s_6 \end{pmatrix} = \mathbf{c}_{ij} \cdot \begin{pmatrix} \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3, \mathbf{e}_4, \\
\mathbf{e}_5, \mathbf{e}_6 \end{pmatrix}, \quad \begin{pmatrix} s_{11}, s_{12}, s_{13}, s_{22}, s_{23}, s_{33} \end{pmatrix} = \begin{pmatrix} s_1 - (3/2) \lambda_{100} (c_{11} - c_{12}) m_{t1}^2, \\
(3/2) \lambda_{100} (c_{11} - c_{12}) m_{t2}^2, \\
(3/2) \lambda_{100} (c_{11} - c_{12}) m_{t3}^2, \\
3 \lambda_{111} c_{44} m_{t2} m_{t3}, \\
3 \lambda_{111} c_{44} m_{t1} m_{t3}, \\
3 \lambda_{111} c_{44} m_{t1} m_{t2} \end{pmatrix}
\]

\[
\mathbf{st}_{ij} = \begin{pmatrix} s_{11}, s_{12}, s_{13}, s_{21}, s_{22}, s_{23}, s_{31}, s_{32}, s_{33} \end{pmatrix} = T_{ij} \cdot \begin{pmatrix} \mathbf{s}_{11}, \mathbf{s}_{12}, \mathbf{s}_{13}, \mathbf{s}_{22}, \mathbf{s}_{23}, \mathbf{s}_{33} \end{pmatrix} \cdot \text{Transpose}[T_{ij}]
\]

(*LLG*)

\[
\mathbf{d}_h = \begin{pmatrix} 2 K_1 m_{t1} (m_{t2}^2 + m_{t3}^2) + 2 K_2 m_{t1} m_{t2}^2 m_{t3}^2 - 3 \lambda_{100} (c_{11} - c_{12}) e_{t11} m_{t1} - 3 \lambda_{111} c_{44} (e_{t12} m_{t2} + e_{t21} m_{t2} + e_{t13} m_{t3} + e_{t31} m_{t3}) - \mu_0 M_s H_{t1}, \\
2 K_1 m_{t2} (m_{t1}^2 + m_{t3}^2) + 2 K_2 m_{t2} m_{t1}^2 m_{t3}^2 - 3 \lambda_{100} (c_{11} - c_{12}) e_{t22} m_{t2} - 3 \lambda_{111} c_{44} (e_{t21} m_{t1} + e_{t12} m_{t1} + e_{t23} m_{t3} + \mu_0 M_s H_{t2}, \\
2 K_1 m_{t3} (m_{t1}^2 + m_{t2}^2) + 2 K_2 m_{t3} m_{t1}^2 m_{t2}^2 - 3 \lambda_{100} (c_{11} - c_{12}) e_{t33} m_{t3} - 3 \lambda_{111} c_{44} (e_{t31} m_{t1} + e_{t13} m_{t1} + e_{t32} m_{t2} + \mu_0 M_s H_{t3}, \\
2 K_1 m_{t1} m_{t2} m_{t3} - 2 K_2 m_{t1} m_{t2} m_{t3} - 3 \lambda_{100} (c_{11} - c_{12}) e_{t12} m_{t2} + e_{t21} m_{t2} + e_{t13} m_{t3} + e_{t31} m_{t3} - \mu_0 M_s H_{t1}, \\
2 K_1 m_{t2} m_{t1} m_{t3} - 2 K_2 m_{t2} m_{t1} m_{t3} - 3 \lambda_{100} (c_{11} - c_{12}) e_{t21} m_{t1} + e_{t12} m_{t1} + e_{t23} m_{t3} + \mu_0 M_s H_{t2}, \\
2 K_1 m_{t3} m_{t1} m_{t2} - 2 K_2 m_{t3} m_{t1} m_{t2} - 3 \lambda_{100} (c_{11} - c_{12}) e_{t31} m_{t1} + e_{t13} m_{t1} + e_{t32} m_{t2} + \mu_0 M_s H_{t3}, \\
2 K_1 m_{t1} m_{t2} m_{t3} - 2 K_2 m_{t1} m_{t2} m_{t3} - 3 \lambda_{100} (c_{11} - c_{12}) e_{t12} m_{t2} + e_{t21} m_{t2} + e_{t13} m_{t3} + e_{t31} m_{t3} - \mu_0 M_s H_{t1}, \\
2 K_1 m_{t2} m_{t1} m_{t3} - 2 K_2 m_{t2} m_{t1} m_{t3} - 3 \lambda_{100} (c_{11} - c_{12}) e_{t21} m_{t1} + e_{t12} m_{t1} + e_{t23} m_{t3} + \mu_0 M_s H_{t2}, \\
2 K_1 m_{t3} m_{t1} m_{t2} - 2 K_2 m_{t3} m_{t1} m_{t2} - 3 \lambda_{100} (c_{11} - c_{12}) e_{t31} m_{t1} + e_{t13} m_{t1} + e_{t32} m_{t2} + \mu_0 M_s H_{t3} \end{pmatrix}
\]
et32*mt3) - mu0*Ms*Ht2}, {2 K1*mt3*(mt1^2 + mt2^2) + 2 K2*mt3*mt1^2*mt2^2 - 3
lambda100 (c11 - c12) et33*mt3 - 3 lambda111*c44 (et31*mt1 + et13*mt1 +
et23*mt2 + et32*mt2) - mu0*Ms*Ht3})

mij = {{m1x, m1y, m1z}, {m2x, m2y, m2z}, {m3x, m3y, m3z}}

{{mt1x, mt1y, mt1z}, {mt2x, mt2y, mt2z}, {mt3x, mt3y, mt3z}} =
Tij.Transpose[Tij].mij.Tij.Transpose[Tij]

(*Maxwell's Equation*)

Bi = {{B1}, (B2), (B3)} = (mu0 (Hi + Ms (mi)))

Bti = Tij.(mu0 (Hti + Ms (mti)))

(*Energy terms*)

h_anisotropy = K1*(mt1^2*mt2^2 + mt2^2*mt3^2 + mt1^2*mt3^2) +
K2*mt1^2*mt2^2*mt3^2

h_exchange = Ae*(mt1x^2 + mt1y^2 + mt1z^2 + mt2x^2 + mt2y^2 + mt2z^2 + mt3x^2 +
mt3y^2 + mt3z^2)

h_elastic = 0.5*c11*(et11^2 + et22^2 + et33^2) + c12*(et11*et22 + et22*et33 +
et11*et33) + c44*(et12^2 + et21^2 + et23^2 + et32^2 + et13^2 + et31^2)
h_{magnetoelastic} = -1.5*\lambda_{100} \((c_{11} - c_{12}) \(et_{11} \cdot mt_{1}^2 + et_{22} \cdot mt_{2}^2 + et_{33} \cdot mt_{3}^2\) - 3*\lambda_{111} \cdot c_{44} \((et_{12} \cdot mt_{1} \cdot mt_{2} + et_{21} \cdot mt_{2} \cdot mt_{1} + et_{23} \cdot mt_{2} \cdot mt_{3} + et_{32} \cdot mt_{3} \cdot mt_{2} + et_{13} \cdot mt_{1} \cdot mt_{3} + et_{31} \cdot mt_{3} \cdot mt_{1}\))

h_{stray} = -\mu_0 \cdot M_s \((H_{t1} \cdot mt_{1} + H_{t2} \cdot mt_{2} + H_{t3} \cdot mt_{3})\)

h_{Zeeman} = -0.5*\mu_0 \((H_{t1}^2 + H_{t2}^2 + H_{t3}^2)\)

\textit{(*COMSOL equations*)}

\texttt{MatrixForm[Tij]}
\texttt{MatrixForm[cij]}
\texttt{MatrixForm[stij]}
\texttt{MatrixForm[\{\{st_{11}\}, \{st_{22}\}, \{st_{33}\}, \{st_{23}\}, \{st_{13}\}, \{st_{12}\}\}]}
\texttt{MatrixForm[(-1) \cdot Tij.dh]}
\texttt{MatrixForm[\{\{Simplify[mt_{1x}]\}, \{Simplify[mt_{1y}]\}, \{Simplify[mt_{1z}]\}\}, \{\{Simplify[mt_{2x}]\}, \{Simplify[mt_{2y}]\}, \{Simplify[mt_{2z}]\}\}, \{\{Simplify[mt_{3x}]\}, \{Simplify[mt_{3y}]\}, \{Simplify[mt_{3z}]\}\}]

\texttt{MatrixForm[\{\{Simplify[mt_{1x}]\}, \{Simplify[mt_{1y}]\}, \{Simplify[mt_{1z}]\}, \{Simplify[mt_{2x}]\}, \{Simplify[mt_{2y}]\}, \{Simplify[mt_{2z}]\}, \{Simplify[mt_{3x}]\}, \{Simplify[mt_{3y}]\}, \{Simplify[mt_{3z}]\}\}]

\texttt{MatrixForm[B_{ti}]}
Appendix B: Wolfram Mathematica program for implementation of electro-elastic coupling

(*Energy terms*)

\[
\text{helastic} = c11*(\text{et11}^2 + \text{et22}^2 + \text{et33}^2)/2 + c12*(\text{et11}\text{et22} + \text{et22}\text{et33} + \text{et11}\text{et33}) + c44*(\text{et12}^2 + \text{et21}^2 + \text{et23}^2 + \text{et32}^2 + \text{et13}^2 + \text{et31}^2) - q11
\]

\[
(\text{et11}\text{Pt1}^2 + \text{et22}\text{Pt2}^2 + \text{et33}\text{Pt3}^2)/2 - qp11 (\text{et11} (\text{Pt2}^2 + \text{Pt3}^2) + \text{et22} (\text{Pt1}^2 + \text{Pt3}^2) + \text{et33} (\text{Pt1}^2 + \text{Pt2}^2))/2 - q44 (\text{et12}\text{Pt1}\text{Pt2} + \text{et21}\text{Pt2}\text{Pt1} + \text{et23}\text{Pt2}\text{Pt3} + \text{et32}\text{Pt3}\text{Pt2} + \text{et13}\text{Pt1}\text{Pt3} + \text{et31}\text{Pt1}\text{Pt3}) + ap11 (\text{Pt1}^4 + \text{Pt2}^4 + \text{Pt3}^4) + ap12 (\text{Pt1}^2\text{Pt2}^2 + \text{Pt2}^2\text{Pt3}^2 + \text{Pt1}^2\text{Pt3}^2)
\]

\[
\text{helasticextension1} = (f11\text{et11}^2/2 + fp11 (\text{et22}^2 + \text{et33}^2)/2 + f12
\]

\[
(\text{et11}\text{et22} + \text{et11}\text{et33}) + fp12\text{et22}\text{et33} + f44 (\text{et12}^2 + \text{et21}^2 + \text{et13}^2 + \text{et31}^2) + fp44 (\text{et23}^2 + \text{et32}^2)) \text{Pt1}^2 + (f11\text{et22}^2/2 + fp11 (\text{et11}^2 + \text{et33}^2)/2 + f12 (\text{et11}^2 + \text{et33}^2))/2 + f12 (\text{et11}\text{et22} + \text{et22}\text{et33}) + fp12\text{et11}\text{et33} + f44 (\text{et12}^2 + \text{et21}^2 + \text{et23}^2 + \text{et32}^2) + fp44 (\text{et13}^2 + \text{et31}^2) \text{Pt2}^2 + (f11\text{et33}^2/2 + fp11 (\text{et11}^2 + \text{et22}^2))/2 + f12 (\text{et11}\text{et33} + \text{et22}\text{et33}) + fp12\text{et11}\text{et22} + f44 (\text{et13}^2 + \text{et31}^2 + \text{et23}^2 + \text{et32}^2) + fp44 (\text{et12}^2 + \text{et21}^2)) \text{Pt3}^2
\]

\[
\text{helasticextension2} = g11 (\text{et11}\text{Pt1}^4 + \text{et22}\text{Pt2}^4 + \text{et33}\text{Pt3}^4)/2 + gp11
\]

\[
(\text{et11} (\text{Pt2}^4 + \text{Pt3}^4) + \text{et22} (\text{Pt1}^4 + \text{Pt3}^4) + \text{et33} (\text{Pt1}^4 + \text{Pt2}^4))/2 + g44
\]

\[
(\text{et12} (\text{Pt1}\text{Pt2}^3 + \text{Pt2}\text{Pt1}^3) + \text{et21} (\text{Pt2}\text{Pt1}^3 + \text{Pt1}\text{Pt2}^3) + \text{et23}
\]

\[
(\text{Pt2}\text{Pt3}^3 + \text{Pt3}\text{Pt2}^3) + \text{et32} (\text{Pt3}\text{Pt2}^3 + \text{Pt2}\text{Pt3}^3) + \text{et13} (\text{Pt1}\text{Pt3}^3 + \text{Pt3}\text{Pt1}^3) + \text{et31} (\text{Pt3}\text{Pt1}^3 + \text{Pt1}\text{Pt3}^3))
\]

\[
\text{helasticextension3} = h11 (\text{et11}\text{Pt1}^4 + \text{et22}\text{Pt2}^4 + \text{et33}\text{Pt3}^4)/2 + hp11 (\text{et22}\text{et33}\text{Pt1}^4 + \text{et11}\text{et33}\text{Pt2}^4 + \text{et11}\text{et22}\text{Pt3}^4)/2 + h12 ((\text{et11}\text{et22} + \text{et11}\text{et33}) \text{Pt1}^4 + (\text{et22}\text{et11} + \text{et22}\text{et33}) \text{Pt2}^4 +
\]

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\[(\text{et33} \cdot \text{et11} + \text{et33} \cdot \text{et22}) \cdot \text{Pt3}^4) + \text{hp12} \cdot (\text{et22} \cdot \text{et33} \cdot \text{Pt1}^4 + \text{et11} \cdot \text{et33} \cdot \text{Pt2}^4 + \text{et11} \cdot \text{et22} \cdot \text{Pt3}^4) + \text{h44} \cdot ((\text{et12}^2 + \text{et21}^2 + \text{et13}^2 + \text{et31}^2) \cdot \text{Pt1}^4 + (\text{et12}^2 + \text{et21}^2 + \text{et23}^2 + \text{et32}^2) \cdot \text{Pt2}^4 + (\text{et13}^2 + \text{et31}^2 + \text{et23}^2 + \text{et32}^2) \cdot \text{Pt3}^4) + \text{hp44} \cdot (\text{et23} \cdot \text{et32} \cdot \text{Pt1}^4 + \text{et13} \cdot \text{et31} \cdot \text{Pt2}^4 + \text{et12} \cdot \text{et21} \cdot \text{Pt3}^4)\]

(*Mechanical Equilibrium*)

\[\text{stij} = \{(\text{st11}, \text{st12}, \text{st13}), (\text{st21}, \text{st22}, \text{st23}), (\text{st31}, \text{st32}, \text{st33})\} = \{(\text{D[h, et11]}, \text{D[h, et12]}, \text{D[h, et13]}), (\text{D[h, et21]}, \text{D[h, et22]}, \text{D[h, et23]}), (\text{D[h, et31]}, \text{D[h, et32]}, \text{D[h, et33]})\}\]

\[\text{eij} = \{(\text{e11}, \text{e12}, \text{e13}), (\text{e21}, \text{e22}, \text{e23}), (\text{e31}, \text{e32}, \text{e33})\} = \{(\text{u1x}, (\text{u1y} + \text{u2x})/2, (\text{u1z} + \text{u3x})/2), ((\text{u1y} + \text{u2x})/2, \text{u2y}, (\text{u2z} + \text{u3y})/2), ((\text{u1z} + \text{u3x})/2, \text{u2z} + \text{u3y})/2, \text{u3z}\}\]

\[\{(\text{et11}, \text{et12}, \text{et13}), (\text{et21}, \text{et22}, \text{et23}), (\text{et31}, \text{et32}, \text{et33})\} = \text{Transpose[Tij].eij.Tij}\]

\[\text{sij} = \{(\text{s11}, \text{s12}, \text{s13}), (\text{s21}, \text{s22}, \text{s23}), (\text{s31}, \text{s32}, \text{s33})\} = \text{Tij.stij.Transpose[Tij]}\]

(*COMSOL equations*)

\[\text{MatrixForm[}\{(\text{s11}, \text{s12}, \text{s13}), (\text{s21}, \text{s22}, \text{s23}), (\text{s31}, \text{s32}, \text{s33})\}]\]
MatrixForm[{{Simplify[s11]}, {Simplify[s12]}, {Simplify[s13]},
{Simplify[s21]}, {Simplify[s22]}, {Simplify[s23]}, {Simplify[s31]},
{Simplify[s32]}, {Simplify[s33]}}]