

Magnetic and Elastic Properties of Magnetostrictive $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$

**A Dissertation Presented for
the Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

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Dedication

To my parents, for their endless love, support, and guidance. I owe more to you than I could ever hope to repay.

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First, I would like to thank Dr. Veerle Keppens for her guidance through these many years. She has helped with countless RUS fits, has read and improved more drafts of journal articles and dissertation-related documents than I feel comfortable thinking about, and has created a wonderful work environment in which I could learn and grow. I would also like to thank Dr. Claudia Rawn, Dr. Easo George, and Dr. Robert Compton for the time and effort they put into my dissertation and serving on my committee.

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Abstract

The $\text{Tb}_6[6 \text{ sub}]\text{Fe}_{1-x}[1-x \text{ sub}]\text{Co}_x[x \text{ sub}]\text{Bi}_2[2 \text{ sub}]$ ($x = 0, 0.125, 0.25$, and 0.375) family of compounds has been synthesized and investigated for magnetostrictive behavior using capacitance dilatometry. These measurements have been complemented by measurements of the elastic moduli using Resonant Ultrasound Spectroscopy (RUS), magnetization measurements (with a vibrating sample magnetometer (VSM)), as well as powder X-ray diffraction (XRD) and powder neutron diffraction measurements and heat capacity measurements.

Each of the compounds studied shows little magnetostriction at the Curie temperature but shows pronounced amounts of magnetostriction at temperatures below 100 K. Magnetostriction values of up to ~ 980 ppm have been discovered at low-temperatures. This increase of magnetostriction coincides with a structural transition at $T^* \sim 50$ K of hexagonal to triclinic (for $x = 0$) or monoclinic (for $x = 0.125, 0.25$, and 0.375) discovered using RUS and low-temperature XRD.

Our data show that the magnetic model of ferromagnetic terbium moments, with no contribution from iron, put forth in the literature is incomplete. Below the Curie temperature, from approximately 250 K to 50 K, there exists a ferrimagnetic ordering between the terbium and iron moments. Upon transitioning to the lower-symmetry structure below T^* , the magnetic moments of each of the three atomic sites cant away from the c-axis by differing amounts.

It is posited here that the large degrees of magnetostriction are due to the softening of the elastic moduli caused by the structural transition. Increasing the cobalt content leads to further elastic softening and magnetostriction although the structural

transition remains similar for each Co-doped compound. The difference in elastic softening and magnetostriction is therefore most likely due to the increased disorder caused by the cobalt atoms.

Key words: Magnetostriction; magnetoelastic coupling; elastic properties; Resonant Ultrasound Spectroscopy (RUS); powder neutron diffraction

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Introduction

Strongly magnetoelastic materials have the unique ability to transfer energy from the magnetic system to the elastic system, allowing for the generation of strain and applicable force from the application of a magnetic field. Conversely, magnetoelastic coupling allows for the change of magnetic properties such as permeability through the application of a stress (the Villari effect). One additional effect of this coupling between the two systems is the ability to change the elastic moduli with the application of a magnetic field, also known as the ΔE effect.

Although magnetostrictive effects have been known for over 150 years, the relatively small size of the effect limited applications until the Navy's research into magnetostrictive materials for the purpose of sonar resulted in the discovery of the novel material Terfenol-D ^[1]. Not only did Terfenol-D provide larger $\Delta l/l$ at lower magnetic fields than conventional materials, it also allowed for quicker response time and larger force production than other materials available at that time ^[1]. The surge in device development included research into using magnetostrictive materials for general applications such as sound and vibration sources, vibrational control, direct and nondirect motion control, material processing, and electromechanical converters ^[1]. More specific applications include sensors, actuators, transducers, medical applications and automotive accessories ^[2], among others. Ferromagnetic materials typically have magnetostriction values that range between 10 ppm and 2000 ppm.

It has been our aim to discover magnetostrictive properties in novel materials and to provide a better understanding of these properties. The materials studied in this research belong to the $Tb_6Fe_{1-x}Co_xBi_2$ family of compounds, which have been scarcely

studied and yet appear to be good candidates in which to find magnetoelastic behavior. Using measurement techniques such as vibrating sample magnetometry (VSM) to determine the magnetization and resonant ultrasound spectroscopy (RUS) to determine the elastic moduli, the two most important properties for magnetoelastic materials can be determined. Using these results in conjunction with powder neutron diffraction, it is our hope to provide insight in the magnetostriction properties of these materials, measured using capacitance dilatometry.

This dissertation consists of 4 chapters. In Chapter 1, we will provide a brief explanation of the physics behind magnetostriction, the development of magnetostrictive materials, and a review of the literatures on Tb_6FeBi_2 . In Chapter 2, the two main unique measurement techniques used in our lab, resonant ultrasound spectroscopy (RUS) and capacitance dilatometry will be reviewed. In Chapter 3, the results from a wide variety of measurement techniques applied to the $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ family of compounds will be presented and discussed. In Chapter 4, conclusions will be put forth for all of the research presented.

1. Literature Review

1.1 Magnetostriction

1.1.1 Physics

Giant magnetostriction is limited to a relatively small number of materials due to the requirement that there exists some degree of magnetoelasticity. As the name would imply, magnetoelasticity is the coupling of the magnetic and elastic systems of a material. Because all materials are elastic (even if scarcely), the limiting requirement is the existence of magnetism¹, which is caused by an imbalance in the magnetic moments of a material's electrons. While a detailed description of the underlying physics of magnetic materials is not necessary for the understanding of the research presented here, the methods by which magnetostriction manifests itself are quickly discussed to build a foundation which can allow for deeper analysis of results. As an applied magnetic field is increased, magnetostriction occurs first through the movement of magnetic domain walls and then subsequently through the rotation of those domains. For clarity, a magnetic domain is a volume of material in which the magnetic moments are all aligned parallel to one another. A brief description of how these two processes occur is what follows.

In cubic magnetic materials such as iron, each domain prefers to elongate in the direction its magnetization is pointing, usually along its “easy” axis. Figure 1 shows that the elongation of the closure domains (the triangular, horizontal domains) conflicts with

¹ While the compounds presented in this research are ferromagnetic and ferrimagnetic, it should be noted that paramagnetic materials such as $\text{Tb}_2\text{Ti}_2\text{O}_7$ also show very large amounts of magnetostriction^[3]. In these materials, magnetostriction is a consequence of strong spin-orbit coupling, and does not require the formation of magnetic domains.

the elongation of the vertical domains. This conflict brings about an elastic strain energy that increases as the material's dimensions change further in an applied magnetic field. The elastic strain energy is proportional to the volume of the closure domains, so increasing the number of closure domains, and therefore making them smaller, will decrease the elastic strain energy. By decreasing the elastic strain energy, the vertical domains are then more free to deform as they wish, resulting in elongation in the vertical direction and magnetostriction. Increasing the number of closure domains, however, also increases the number of vertical domains and domain walls, which not only increases the exchange energy due to the existence of more antiparallel domains but also increases the anisotropy energy due to the presence of more individual moments pointing along a direction other than an easy direction.

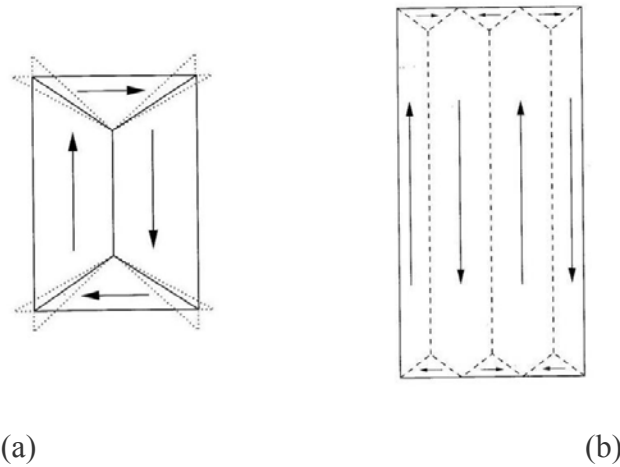


Figure 1: (a) The preferred deformation of the different kinds of domains due to magnetostriction and (b) a typical domain arrangement that minimizes the sum of all energy terms^[1]

The rotation of the domains involves anisotropy energy. Magnetocrystalline anisotropy involves the degree to which a material's lattice, electron orbitals, and the spin of its electrons are coupled. If a material has strong coupling, then it is difficult for

spins to rotate to align with an applied magnetic field because the entire electron orbital must also rotate. This difficulty is compounded because the orbitals are also strongly coupled to the rigid lattice. Materials such as rare earth metals have these strong couplings, but what distinguishes them from other materials that have weak coupling? What does this have to do with the physical manifestation of magnetostriction?

Electrons generate a magnetic moment (and thus contribute to the magnetic field) in two ways. The first – and most obvious – way is by orbiting the nucleus: a current or moving charge is a well-known source of magnetic field. In addition, electrons have a so-called “spin”, a quantum-mechanical contraption that is often pictured as the rotation of the electron about its own axis. The orbital magnetic moment μ_L and the spin magnetic moment μ_S , can be coupled, and it is the interaction between the two, whether they are added to one another or subtracted, that determines the total moment of the atom. By going against convention and imagining that the nucleus of an atom orbits a stationary electron, it has been determined that the spin-orbit interaction is proportional to Z^4 . The atomic-number dependence explains why elements such as hydrogen and helium have very weak spin-orbit coupling while heavier elements such as the rare earth metals have strong coupling.

Orbit-lattice coupling is linked to the structure of the material. Figure 2 shows a metal atom in an octahedral lattice (left) and in a tetrahedral lattice (right) of a transition metal oxide. Figure 3 shows the shape of different orbitals.

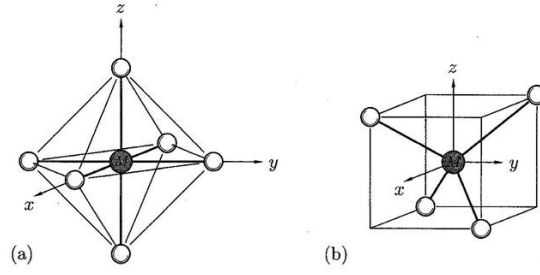


Figure 2: The location of a metal atom in a transition metal oxide with an (a) octahedral and (b) tetrahedral lattice ^[4]

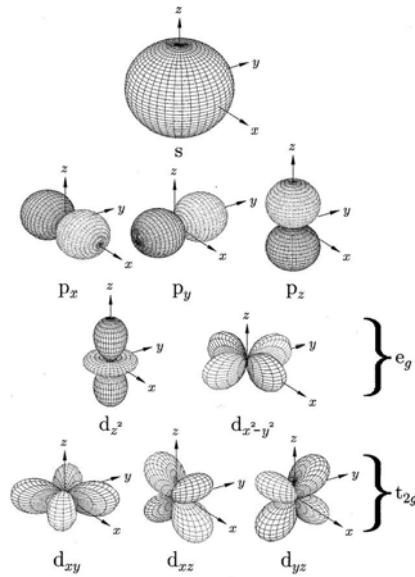


Figure 3: The different shapes of s, p, and d orbitals ^[4]

It is the Coulomb repulsion that dictates that the most favorable orbital is the one that will have minimal overlap with the orbitals produced by the other atoms on the lattice. Figure 4 shows a 2-D representation of the placement of orbitals discussed above. The top figure shows a preferred orientation while the bottom figure shows an orientation that is energetically less desirable. Assuming that the material has strong spin-orbit coupling as well as strong orbit-lattice coupling, a rotation of the electron spin moment (and by extension the magnetization) would result in a rotation of the orbital. If the

metal orbitals from the favorable configuration are forced to rotate, they are forced increasingly closer to the oxygen orbitals. As this happens, the orbitals begin to overlap and the Coulomb repulsion increases. It is this repulsion that provides resistance to the rotation of the magnetization. The orbitals can be forced to rotate to the configuration represented in the bottom figure by applying a strong enough field. If the Coulomb force is stronger than the force that keeps the lattice atoms stationary, the lattice atoms can shift away from the metal atom to reduce the Coulomb repulsion. It is this deformation of the lattice, caused by the rotation of orbitals, that results in magnetostriction.

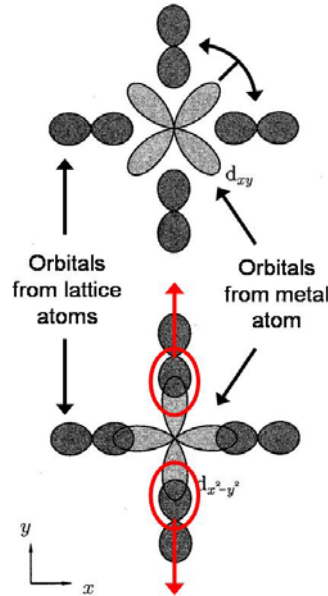


Figure 4: 2-D representation of orbital placement and rotation ^{modified from [4]}

With the basis of the rotational form of magnetostriction in place, the importance of the elastic moduli becomes clearer. High values of the elastic moduli indicate a stiffer material, or a material in which the atoms are held more rigidly in place. A material with such stiffer elastic moduli will better resist the movement of its atoms during the rotation of the orbitals, resulting in less magnetostriction than if the elastic moduli were lower.

1.1.2 Development of Magnetostrictive Materials

Multiple factors affect the applicability of a material system to a magnetostrictive device, some of which are the price, saturation magnetostriction, anisotropy, and transition temperature. Price is self explanatory; increased magnetostriction produces increased strain and force ^[2]; low anisotropy allows for saturation of the magnetostriction to occur at lower applied magnetic fields ^[5]; and transition temperatures above the natural operating temperature of the application negate the need for environmental temperature control (heating or cooling) ^[1].

Over the past 170 years or so, each of these factors has been optimized through a variety of methods. James Prescott Joule first discovered magnetostriction in iron in 1842 ^[6]. Iron, however, has magnetostriction on the order of 10^{-5} ^[1], small by today's standards. It was later found that rare earth elements such as terbium and dysprosium have magnetostriction values on the order of 10^{-3} but have large magnetic anisotropy ^[7]. While the magnetostriction of magnetic rare earth elements is obviously greatly improved over that of iron, the large magnetic anisotropy is detrimental as it requires large magnetic fields to obtain the improved magnetostriction ^[5]. The magnetic rare earths are also plagued with low transition temperatures (T_C of Tb $\sim$ 220 K, of Dy $\sim$ 89 K) ^[1]. The solution to these problems, it was found, was to create magnetostrictive compounds. The transition temperature of a rare earth can be raised by alloying with iron, which has a Curie temperature of 1044 K ^[1]. Terbium is typically used as the rare earth because, although gadolinium has a higher Curie temperature, the magnetostriction of terbium is approximately an order of magnitude larger than gadolinium ^[1]. Alloying terbium and iron appropriately results in the Laves phase $TbFe_2$, which has a Curie temperature of

711 K ^[1]. Another option is the alloying of dysprosium and iron, resulting in the Laves phase DyFe₂, which has a Curie temperature of 635 K ^[1]. These two Laves phases both have large anisotropies ^[5]. The anisotropies, however, are similar in magnitude and opposite in sign (indicating that the easy directions are different). Creating the pseudo-binary alloy Tb_{0.3}Dy_{0.7}Fe₂ (terfenol-D), which contains both Laves phases, maintains the high transition temperatures of the individual Laves phases while minimizing the anisotropy ^[5].

It should be noted that magnetic anisotropy in small amounts can be very beneficial. One example of this is grain-oriented Tb_{0.3}Dy_{0.7}Fe_{1.95} ^[8]. The small negative anisotropy constant K₁ results in the establishment of the <111> directions as the easy axes. A compressive stress applied along the [112] direction makes the moments populate the [$\bar{1}\bar{1}1$] and [$1\bar{1}\bar{1}$] directions, both of which are at right angles to the [112] direction. With the application of a 250 Oe magnetic field along the [112] direction, the magnetization aligned along the [$\bar{1}\bar{1}1$] and [$1\bar{1}\bar{1}$] directions will rotate towards [112], quickly reaching [111] (another easy direction) which is only 19.5° from [112] ^[8]. Too large of an anisotropy would require a larger magnetic field, but just enough anisotropy is needed to set <111> as the easy family of directions.

Admittedly, terfenol-D is an excellent magnetostrictive material. One of the only disadvantages is its high cost, but that has been reduced through increased production volume and automation of the fabrication process^[2]. The existence of terfenol-D does not mean that all research into new magnetostrictive materials need cease. Our research has involved the exploration of novel materials for magnetostriction, the optimization of the factors outlined above to improve magnetostriction and applicability, and the study of

the transitions occurring in these materials in hopes of finding new and interesting phenomena.

1.2 $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$

R_6TX_2 compounds (R = rare earth, T = Fe, Co, Ni, Mn, Ru, and X = Sb, Bi, Te) are known to crystallize in the Zr_6CoAs_2 -type hexagonal structure ^[9, 10] (unit cell shown in Figure 5), which is an ordered variant of the Fe_2P -type structure ^[11]. Whereas many of these compounds show ferromagnetic order, Tb_6FeBi_2 and Tb_6FeSb_2 are the most noteworthy, as their Curie temperatures (T_C) are only slightly below room temperature (T_C of $\text{Tb}_6\text{FeSb}_2 \sim 256 \text{ K}$ ^[12, 13] and of $\text{Tb}_6\text{FeBi}_2 \sim 250 \text{ K}$ ^[13, 14]). Other beneficial characteristics of the two systems are the presence of both terbium and iron (which produce terrific results in terfenol-D) and simple, straightforward synthesis ^[9, 12-14].

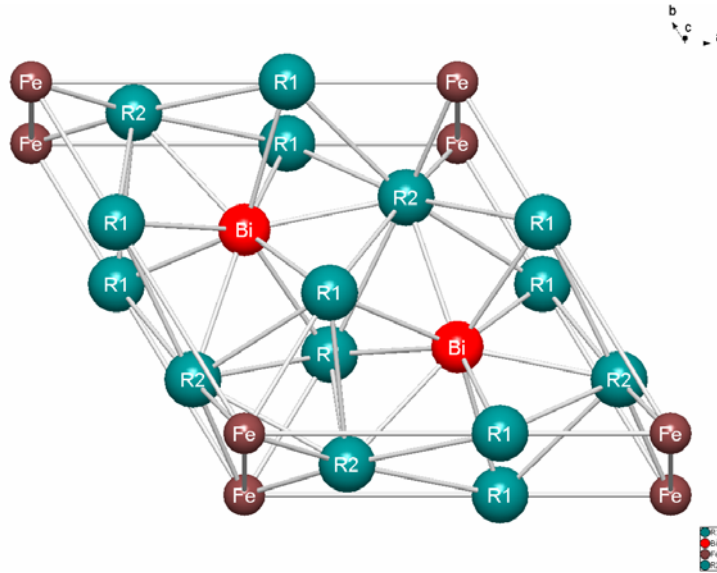


Figure 5: Unit cell of Tb_6FeBi_2 . R1 and R2 sit in different planes.

Probably the most important information (for our purposes) gathered from the literature are the results from neutron studies describing the atomic and magnetic structures of the parent compound ^[14]. At all temperatures these compounds are found to have hexagonal symmetry, with the unit cell comprised of two layers of atoms. One layer contains iron atoms and one set of terbium atoms. The second layer contains bismuth or antimony atoms and a second set of terbium atoms. Above the Curie temperature, the magnetic moments are not ordered, resulting in a unit cell as pictured in Figure 6(a). It is reported that at the Curie temperature, both sets of terbium moments undergo ferromagnetic collinear ordering along the c-axis, as shown in Figure 6(b), and transition to a ferromagnetic non-collinear structure at 60 K, where the moments are canted off of the c-axis by $\beta \sim 5.5^\circ$, shown in Figure 6(c) ^[14]. Figure 7 shows three neutron diffraction patterns, obtained above the Curie temperature (upper panel), between the two magnetic transitions (middle panel), and below the low-temperature transition (lower panel).

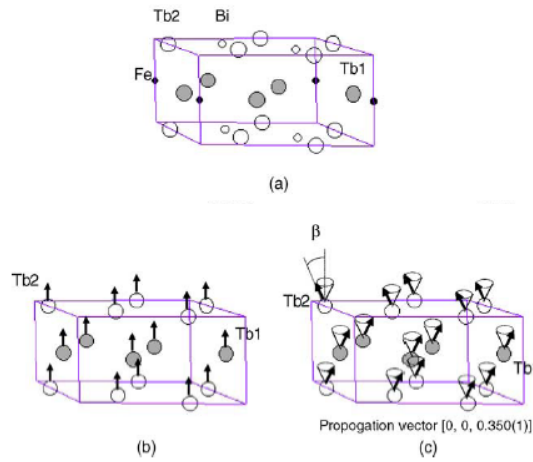


Figure 6: (a) The unit cell of Tb_6FeBi_2 . (b) The ferromagnetic collinear magnetic structure at 200 K and (c) the ferromagnetic non-collinear magnetic structure at 26 K. ^[14]

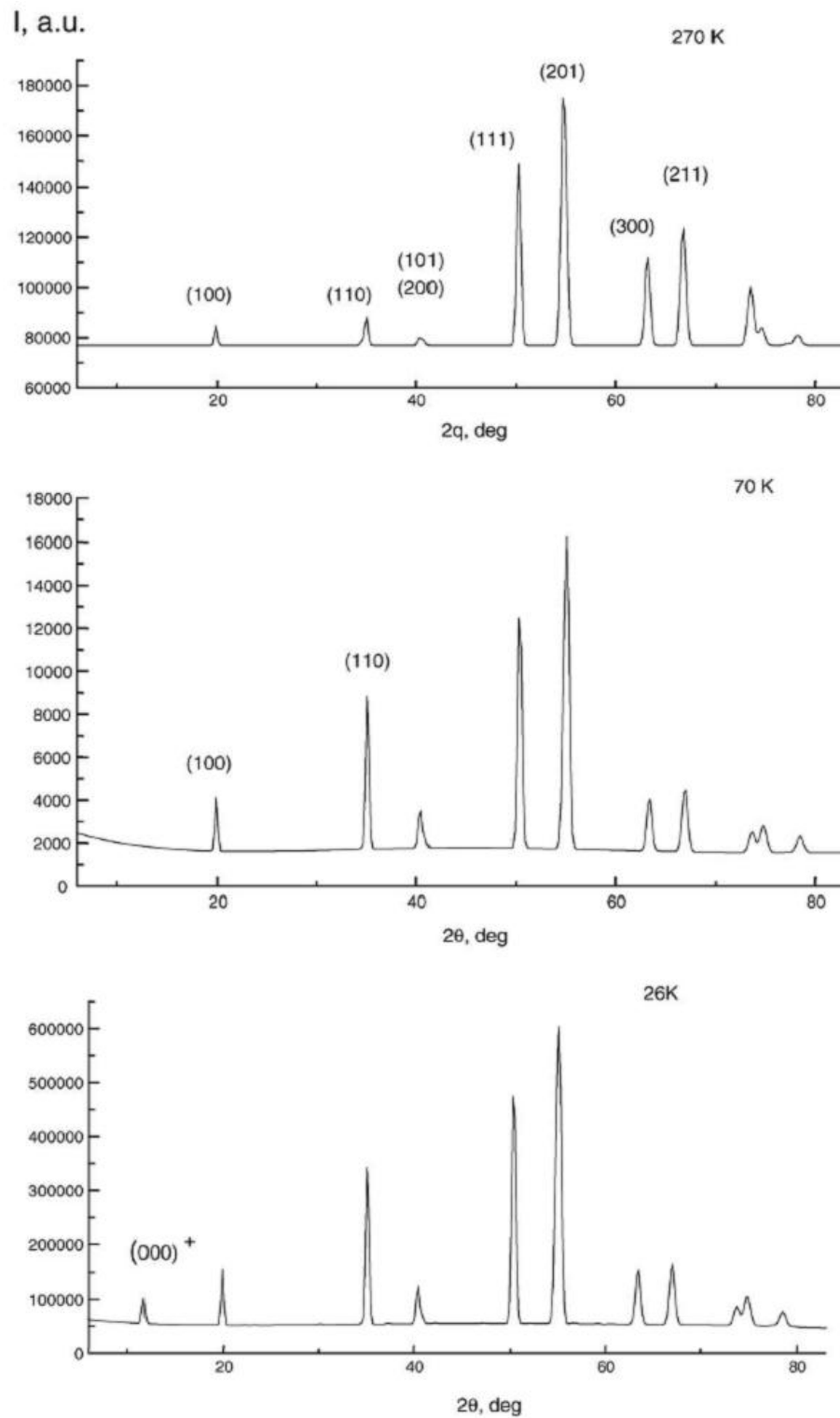


Figure 7: Neutron patterns at 270 K (above the Curie temperature), 70 K (between the two magnetic transition temperatures), and at 26 K (below the low-temperature magnetic transition temperature) ^[14]

While no such neutron study has been carried out for Tb_6FeSb_2 , studies of Ho_6FeSb_2 show a collinear canting of the holmium moments at 40 K and a ferromagnetic non-collinear ordering (different from that seen in Tb_6FeBi_2) at 22 K^[10]. Magnetization studies of Tb_6FeSb_2 have been carried out, the results of which are shown in Figure 8. The large increase of magnetization at ~ 256 K is due to the transition from a paramagnetic to a ferromagnetic configuration. It was our hypothesis that this would be the most likely place for any magnetostriction to occur because of the magnetization rotation at the transition. It is also reported that the magnetization of Tb_6FeSb_2 begins increasing again at low temperatures^[14].

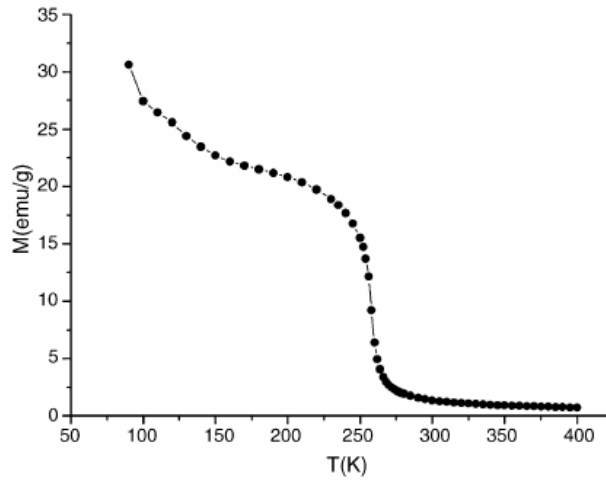


Figure 8: The magnetization of Tb_6FeSb_2 ^[12]

The magnetization and change of specific heat near the Curie temperature of both parent compounds has been reported by He et al.^[13]. Following the Landau theory of second-order phase transitions in conjunction with magnetization data, the following equation was used to fit the linear portion of H/M vs. M^2 curves at multiple temperatures around the Curie temperature^[13]:

$$\alpha + \beta M^2 = \frac{H}{M} \quad (1.1)$$

where α is the fitting parameter corresponding to the y-intercept of the linear portion of each curve and is different for each temperature, whereas β is the fitting parameter corresponding to the slope of the linear portion of each curve and remains relatively constant for all temperatures. The α parameter was then plotted as a function of temperature and once again the linear portion of the curve was fit, this time using the following equation:

$$\alpha = \alpha'(T - \Theta) \quad (1.2)$$

where α' is another fitting parameter, T is the temperature in Kelvin at which α was determined, and Θ is a fitting parameter corresponding to the Curie temperature. Θ was reported to be 244 and 252 K for Tb_6FeSb_2 and Tb_6FeBi_2 , respectively ^[13]. Finally, the change in heat capacity ΔC_p around the Curie temperature is determined using

$$\Delta C_p = \frac{(\alpha')^2 \Theta}{2\beta(\Theta)} \quad (1.3)$$

ΔC_p for Tb_6FeSb_2 and Tb_6FeBi_2 were reported to be 36.5 and 41.2 J kg⁻¹ K⁻¹, respectively.

There have been no reported studies involving the replacement of iron with cobalt in these families of materials. In some systems, doping with cobalt has been shown to raise the Curie temperature ^[15-18] (the T_C of cobalt is higher than that of iron ^[1]) and improve magnetostriction ^[19-21]. Unfortunately, cobalt doping serves to decrease magnetostriction in other systems ^[15, 18]. It was our hope that cobalt doping would improve both properties in the $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ and $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Sb}_2$ systems.

2. Experimental Details

2.1 Sample Synthesis

Polycrystalline ingots of each compound used in this study are synthesized by melting appropriate amounts of Tb, Co, Fe, and Bi using a plasma arc melter under Ar atmosphere. Excess Bi is added to compensate for the amount lost during melting. Each compound is arc-melted on a water-cooled copper hearth and flipped two additional times in order to ensure chemical homogeneity. The ingots are then wrapped in Ta foil, sealed in evacuated quartz tubes and annealed. The samples are annealed at 1100 K for seven days, followed by an additional five days of annealing at 773 K. Upon completion of the heat treatment, the samples are quenched in an ice water bath. X-ray diffraction analysis is used to confirm that the samples are single phase or contain little impurity or secondary phases.

2.2 Resonant Ultrasound Spectroscopy (RUS)

2.2.1 Development and Importance

Resonant ultrasound spectroscopy is a relatively new technique that is used to probe the resonances of a freely vibrating solid ^[22-25] of any crystal symmetry with the ultimate goal of determining the entire elastic tensor. While resonant ultrasound spectroscopy only really began to be developed in the 1960s, when computers were becoming more readily available, mechanical resonances have been used in the study of materials since the 19th century when flawed train wheels were detected by tapping on them and listening to the resulting sound. This allowed for detection of defects in the

wheels, as flawed wheels produce sound at a frequency different from that of a good wheel ^[23]. Gabriel Lamé and Horace Lamb solved the problem of calculating the resonant frequencies for cubes and spheres of isotropic, noncrystalline materials in 1880, which is a process critical to the determination of the elastic constants (as will be shown later). Such determination of the elastic constants did not take place until 84 years later. In 1964, Fraser and LeCraw developed a method of determining the elastic moduli of isotropic spheres using resonant frequencies and a single transducer ^[26]. This setup made use of the dual nature inherent in transducers, namely the ability to act as both a transmitter and receiver. The single transducer would first transmit mechanical waves to the spherical sample and then switch to behave as a receiver to detect the decay of the vibration^[26]. While the setup of their experiment differed slightly from that employed now in RUS, their experiment most likely marks the first RUS measurement and introduced the term resonant sphere technique (RST) ^[24]. The geophysics community realized the potential that this method had for determining the elastic moduli of Earth's constituent materials. In particular, Orson Anderson, Naohiro Soga, and Edward Schreiber improved RST, resulting in the measurements of the elastic moduli of spherical lunar samples in 1970 ^[24]. Anderson then tasked his student Harold Demarest with finding a way to make use of rectangular-parallelepiped samples ^[24]. With Demarest's success in 1971 came the birth of rectangular parallelepiped resonances, or RPR, which is used to this day ^[24, 27]. Finally, in 1988, Albert Migliori, John Sarrao, and William Visscher "rediscovered" RPR, introduced it to the general physics community, and worked to improve the technique through advancements of the hardware and software ^[23, 24]. It was Migliori who established that the phrase "resonant ultrasound spectroscopy"

refers to any technique that uses the ultrasonic resonant frequencies of a material to determine its elastic behavior ^[24]. The RUS technique used in the present research can be defined as the probe into the resonances of a freely vibrating solid.

The reasons that RUS is such a powerful and useful tool in analyzing the elastic properties of materials over other methods are numerous. While there are systems that can utilize larger samples, the system used in the research presented here works best with sample sizes on the order of a few cubic millimeters, thereby effectively reducing material costs. Another benefit is the ability to measure the entire elastic tensor in a single test.

Many advantages stem from the non-destructive nature of RUS. Once again, material costs are reduced since many tests can be run on a single sample. The ability to run multiple tests also removes the worry that variable sample quality will produce variable results if the elastic moduli are probed as a function of magnetic field or temperature. While wise research practices dictate that results from a single sample be confirmed with a second or third sample, the advantage is readily apparent.

Although there are certainly others, the last advantage mentioned here is the ability to detect the presence of phase transitions that occur as a function of temperature or applied magnetic field regardless of the ability to determine the elastic tensor. There exist situations involving material characteristics that prevent the quantitative determination of the elastic tensor, but the proportional relationship between the elastic moduli and a resonant frequency squared allows for a qualitative determination. The mathematics behind this relationship will be expounded upon later.

2.2.2 Principle

There are two ways in which RUS can be utilized, as shown in Figure 9. The direct procedure is to use known sample dimensions, density, and elastic tensor to calculate the resonant frequencies of a material. Conversely, the sample dimensions, density, and measured resonant frequencies can be used to calculate the elastic tensor in the inverse procedure. Because the inverse problem is typically solved using an iterative procedure involving the direct problem, what follows is a brief explanation of the mathematics behind the computation of the resonant frequencies, or the forward problem.

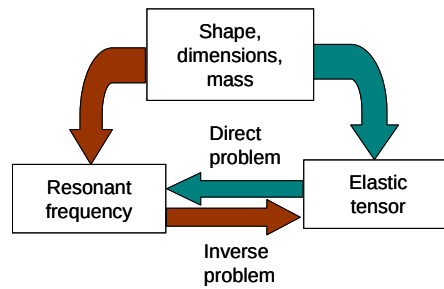


Figure 9: Principle of RUS

There have traditionally been two methods used in the determination of the resonant frequencies: finite-element model and energy minimization. The finite-element option involves balancing forces over a differential volume of the material and calculating the mechanical response, requiring not only knowledge of all of the relevant forces acting on that volume but also the possible modes of vibration for that volume. Energy minimization, on the other hand, simply looks for the minimum energy configuration, effectively bypassing the need for the user to know which vibrational modes are possible and reducing the risk of missing such a mode. For this reason, the energy minimization technique is typically used.

When a stress wave is introduced to a sample of material, a cube for example, there exist a number of possible normal vibrational modes at which the sample can elastically deform, some of which are shown in Figure 10. The determination of these modes of vibration along with the frequencies at which they occur (the natural or resonant frequencies) for a sample with known shape, density, and elastic moduli involves the solution at stationary points of the mechanical Lagrangian with free-surface boundary conditions ^[23]. This is the solution to the aforementioned forward problem, an iteration of which leads to the solution of the inverse problem (explained in greater detail later).

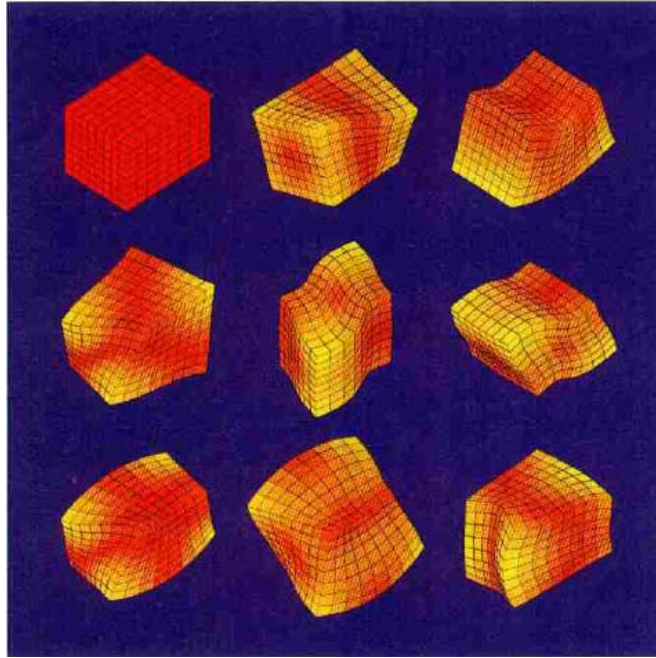


Figure 10: Potential normal modes of vibration for a cube ^[24]

Returning to the Lagrangian, its general form is given by

$$L = \int_V (KE - PE) dV \quad (2.1)$$

where KE and PE are the kinetic and potential energies, respectively. For an arbitrarily shaped elastic solid with volume V in a free surface S and with linear elastic tensor c_{ijkl} and density ρ , the kinetic energy is given by

$$KE = \frac{1}{2} \sum_i \rho \omega^2 u_i^2 \quad (2.2)$$

where ω is the angular frequency. The potential energy is

$$PE = \frac{1}{2} \sum_{i,j,k,l} C_{ijkl} \frac{\partial u_i}{\partial x_j} \frac{\partial u_k}{\partial x_l} \quad (2.3)$$

where u is the displacement vector and each subscript ranges from 1 to 3, corresponding to the x , y , and z directions.

By finding the minimum of the Lagrangian, which is also the equilibrium configuration of the system, the first step toward finding the stationary points of the Lagrangian is made. In order to find the way in which the Lagrangian changes with changing displacement vector, we let u vary arbitrarily in V and on S ($u_i \rightarrow u_i + \delta u_i$), resulting in the following equation:

$$L + \delta L = \int_V \left[\frac{1}{2} \sum_i \rho \omega^2 (u_i + \delta u_i)^2 - \sum_{i,j,k,l} C_{ijkl} \frac{\delta(u_i + \delta u_i)}{\delta x_j} \frac{\delta u_k}{\delta x_l} \right] dV \quad (2.4)$$

Keeping terms to first order in δu_i , we find

$$\delta L = \int_V \left[\sum_i \rho \omega^2 u_i \delta u_i - \sum_{i,j,k,l} C_{ijkl} \frac{\delta(\delta u_i)}{\delta x_j} \frac{\delta u_k}{\delta x_l} \right] dV \quad (2.5)$$

Integrating by parts gives

$$\delta L = \int_V \left(\sum_i \left[\rho \omega^2 u_i + \sum_{j,k,l} C_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l} \right] \delta u_i \right) dV - \int_S \left(\sum_i \left[\sum_{j,k,l} \vec{n}_j C_{ijkl} \frac{\partial u_k}{\partial x_l} \right] \delta u_i \right) dS \quad (2.6)$$

In order to determine the stationary Lagrangian, δL must logically equal zero. For this

to be the case, the terms in square brackets must also equal zero because δu_i is arbitrary in V and on S . The elastic wave equation is created when the first bracketed term is set to zero:

$$\rho \omega^2 u_i + \sum_{j,k,l} C_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l} = 0 \quad (2.7)$$

Setting the second bracketed term to zero and replacing the multiplication of the elastic tensor C_{ijkl} and the strain $\left(\frac{\partial u_k}{\partial x_l} \right)$ with the ij th component of the stress tensor σ_{ij} yields an expression of free-boundary conditions:

$$\sum_{j,k,l} \vec{n}_j C_{ijkl} \frac{\partial u_k}{\partial x_l} = \sum_j \vec{n}_j \sigma_{ij} = 0 \quad (2.8)$$

The set of u_i that satisfies these two conditions corresponds to ω being one of a discrete set of normal mode frequencies of free vibration of the system.

Using the Rayleigh-Ritz method, we expand the displacement vector in a complete set of functions $\{\Phi_\lambda\}$:

$$u_i = \sum_{\lambda} a_{i\lambda} \Phi_{\lambda} \quad (2.9)$$

where Φ_λ is a basis function that we set as powers of Cartesian coordinates, or

$$\Phi_{\lambda} = x^l y^m z^n \quad (2.10)$$

where $\lambda = (l,m,n)$ is the function label, a set of three nonnegative integers. Substituting Equation 2.9 in Equation 2.1 and changing it to a matrix equation gives

$$L = \frac{1}{2} \omega^2 \vec{a}^T E \vec{a} - \frac{1}{2} \vec{a}^T \Gamma \vec{a} \quad (2.11)$$

where $\vec{a}$ is a vector with elements a_i whose transpose is $\vec{a}^T$ and where matrices E and Γ

have elements

$$E_{\lambda i \lambda' i'} = \delta_{ii'} \int_V \Phi_{\lambda} \rho \Phi_{\lambda'} dV \quad (2.12)$$

and

$$\Gamma_{\lambda i \lambda' i'} = \sum_{j, j'} C_{iji' j'} \int_V \frac{\partial \Phi_{\lambda}}{\partial x_j} \frac{\partial \Phi_{\lambda'}}{\partial x_{j'}} dV \quad (2.13)$$

The order R of these two matrices is determined by the truncation condition

$$l + m + n < N \quad (2.14)$$

with

$$R = \frac{3(N+1)(N+2)(N+3)}{6} \quad (2.15)$$

The solutions of this free-vibration problem may be obtained by setting the derivatives of Equation 2.11 with respect to each of the R amplitudes $a_{i\lambda}$ equal to zero, yielding the eigenvalue equation

$$\omega^2 \overset{\leftrightarrow}{E} \vec{a} = \overset{\leftrightarrow}{\Gamma} \vec{a} \quad (2.16)$$

The eigenvalues of this equation are the resonant frequencies while the eigenvectors are the physical displacements of the solid when it is oscillating. Hiding in this equation is also the proof for the assertion put forth above that the qualitative behavior of the elastic moduli can be determined even if they can not be determined quantitatively. Such proof becomes evident once the angular frequency is replaced with the resonant frequency f and

Equation 2.13 is used in place of $\overset{\leftrightarrow}{\Gamma}$, as shown below

$$(2\pi f)^2 \overset{\leftrightarrow}{E} \vec{a} = \left(\sum_{j, j'} C_{iji' j'} \int_V \frac{\partial \Phi_{\lambda}}{\partial x_j} \frac{\partial \Phi_{\lambda'}}{\partial x_{j'}} dV \right) \vec{a} \Rightarrow f^2 \propto C \quad (2.17)$$

Now that the forward problem has been solved, it is a relatively simple matter to solve the inverse problem. Before the algorithm used for the final determination of the elastic tensor is discussed, a brief review of how resonant frequencies are measured and how the data appear will be covered. This information should give the reader a better understanding of how the algorithm works while sidestepping the fallacious impression that computers have reduced the process to a trivial matter.

2.2.3 Data collection and analysis

RUS involves placing either a parallelepiped or cylindrical sample between two piezoelectric transducers (Figure 11). A frequency generator creates an electromagnetic wave that is sent to one of the transducers, which then converts it into a mechanical wave. The mechanical wave travels through the sample and the material response is detected by the second transducer which then converts the mechanical wave back into an electrical signal. Finally, the electrical signal is sent to a lock-in amplifier. A typical resulting amplitude of the signal as a function of frequency is shown in Figure 12.



Figure 11: The RUS setup

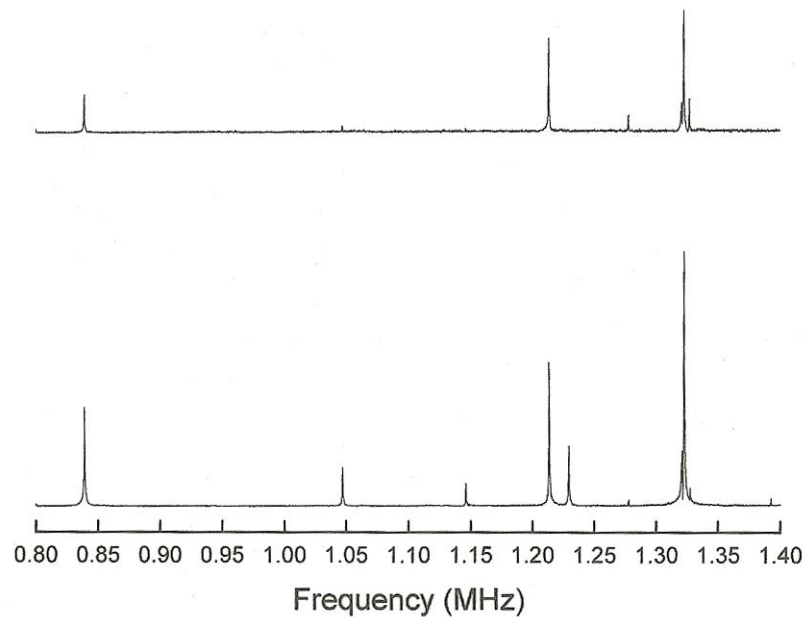


Figure 12: The same frequency spectrum measured with RUS and utilizing two different sample mounting techniques. The inability to detect some resonant frequencies (such as 1.15 MHz in the example shown here) with a particular mount illustrates one difficulty in data analysis ^[23]

One issue that arises with respect to locating peaks is related to the way in which the sample is mounted between the two transducers. Different mounts (i.e. face, edge, or corner) can result in different intensities for individual peaks, as shown in Figure 12. This can be understood by considering the contact points between the transducers and the sample as well as the way in which the different modes elastically deform (Figure 10). If the sample is mounted in such a way that a particular mode has a large degree of deformation (represented by yellow in Figure 10) at the contact point, the peak will be larger than if little deformation is present. Because the probability of missing a mode decreases by corner mounting, this is the preferred method. Corner mounting need not be used every time, however, because the roughness of the transducers and the ability to “face-mount” samples off-center help mitigate this issue. Mounting multiple ways and

collecting data can also help ensure that no mode is missed.

In order to begin the fitting procedure that determines the elastic tensor, the resonant frequencies or “peaks” need to be recorded. For polycrystalline samples, the first 20 resonances (as a minimum) need to be found; if even one resonance is skipped/missed, the entire following fitting procedure will fail. A general rule of thumb is that as the number of independent elastic moduli increases (symmetry decreases), the minimum number of resonances that should be found increases. This is because each vibrational mode and, by extension, each resonant frequency depends upon the moduli differently. If the sample is an orthorhombic single crystal with nine independent elastic moduli, many peaks (at least forty or fifty) are required to ensure that each modulus is well-represented by the measured peak list. When a modulus is well represented, the error in the final determination of that modulus is reduced. If the sample is polycrystalline with two independent elastic moduli, fewer peaks are typically required to achieve comparable moduli error.

The measured resonant frequencies are then entered into an analytical program (Rectangular Parallelepiped Resonance, or RPR, in our case) along with the sample dimensions, mass, and initial estimates for the elastic constants. The program uses the direct procedure described above to calculate the location of the resonant frequencies based upon the provided input for the elastic moduli. The calculated frequencies are then compared to the measured frequencies and the root mean square error is calculated as follows:

$$\sigma_{RMS} = 100 \times \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{g_i - f_i}{f_i} \right)^2} \% \quad (2.18)$$

where N is the number of frequencies measured, g_i is the measured frequency, and f_i is the calculated frequency. The results are refined through an iterative procedure. The input for elastic moduli is changed slightly by the program and a new error is calculated. If the error is improved, the program continues to change the moduli in a similar way; if the error is worsened, it changes the moduli another way. This continues until the program is unable to improve the fit in a significant manner. If the final RMS error is less than 0.5%, the elastic moduli determined by the program are tentatively accepted. At least one more sample is tested in order to confirm the result. If the error is larger than 0.5%, potential causes include sample problems (e.g. existence of a crack), missing or erroneously marked peaks, the use of too few peaks, or an initial elastic tensor estimate that was too different from the true tensor.

The RUS measurements on the polycrystalline samples yield both the shear modulus c_{44} and the longitudinal modulus c_{11} . Figure 13 shows a representative output file produced by the RPR program used to determine the elastic moduli from the resonant frequencies. The first line of the output file describes the sample being tested. The second line tells which moduli are independent. Because the samples studied for this research are polycrystalline, the longitudinal modulus c_{11} and the shear modulus c_{44} are the only two independent moduli. The fourth line informs of the order of the polynomial used in the fitting procedure as well as the user-input mass and the program-calculated density of the sample.

Tb6Fe0.875Co0.125Bi2-B1-s1-0.0478g-300.0K
 free moduli are c11, c44
 free dimensions are d1, d2, d3
 using 10 order polynomials mass= 0.0478 gm rho= 9.405 gm/cc

n	fex	fr	%err	wt	k	i	hf/d(moduli)
1	0.314173	0.309221	-1.58	0.00	4	1	0.00 1.00
2	0.343883	0.343762	-0.04	1.00	1	2	0.18 0.82
3	0.366889	0.366781	-0.03	1.00	7	2	0.18 0.82
4	0.533145	0.536954	0.71	1.00	5	1	0.15 0.85
5	0.584799	0.586056	0.21	1.00	8	2	0.06 0.94
6	0.608987	0.605855	-0.51	1.00	2	2	0.08 0.92
7	0.614948	0.611037	-0.64	1.00	3	2	0.01 0.99
8	0.737557	0.724464	-1.78	0.00	4	2	0.01 0.99
9	0.774218	0.763848	-1.34	0.00	3	3	0.06 0.94
10	0.816807	0.815959	-0.10	1.00	1	3	0.13 0.87
11	0.842318	0.849841	0.89	1.00	8	3	0.05 0.95
12	0.848782	0.851582	0.33	1.00	7	3	0.03 0.97
13	0.856023	0.857235	0.14	1.00	5	2	0.06 0.94
14	0.862176	0.861187	-0.11	1.00	2	3	0.08 0.92
15	0.872030	0.864577	-0.85	1.00	3	4	0.04 0.96
16	0.888614	0.887296	-0.15	1.00	6	2	0.06 0.94
17	0.908904	0.904516	-0.48	1.00	2	4	0.15 0.85
18	0.917907	0.914755	-0.34	1.00	4	3	0.04 0.96
19	0.922860	0.919621	-0.35	1.00	1	4	0.22 0.78
20	0.926761	0.932186	0.59	1.00	6	3	0.00 1.00
21	0.958018	0.962850	0.50	1.00	5	3	0.03 0.97
22	0.977832	0.972567	-0.54	1.00	4	4	0.08 0.92
23	1.001401	1.004136	0.27	1.00	6	4	0.01 0.99
24	1.006303	1.005982	-0.03	1.00	1	5	0.14 0.86
25	1.040440	1.037062	-0.32	1.00	8	4	0.15 0.85
26	1.040440	1.042148	0.16	1.00	7	4	0.29 0.71
27	1.072999	1.075758	0.26	1.00	5	4	0.31 0.69
28	1.089887	1.090577	0.06	1.00	6	5	0.28 0.72
29	1.089887	1.093550	0.34	1.00	5	5	0.09 0.91
30	1.108976	1.108798	-0.02	1.00	7	5	0.13 0.87

Bulk Modulus= 0.679

c11	c22	c33	c23	c13	c12	c44	c55	c66
1.1186	1.1186	1.1186	0.4597	0.4597	0.4597	0.3294	0.3294	0.3294

d1	d2	d3
0.12692	0.14596	0.27436

loop# 9 rms error= 0.4165 %, changed by 0.0000005 %

length of gradient vector= 0.000004 blamb= 0.000000

eigenvalues	eigenvectors
0.07850	1.00-0.04 0.00 0.00 0.00
74.54581	-0.04-1.00 0.02 0.00 0.07
802.37460	0.00 0.06-0.05-0.54 0.84
1694.72535	0.00 0.04 0.23 0.81 0.54
5659.45344	0.00-0.01-0.97 0.21 0.09

chisquare increased 2% by the following % changes in independent parameters

1.38	-0.17	0.05	-0.06	0.00
0.00	-0.15	0.04	0.02	0.00
0.00	0.00	-0.01	0.05	-0.11

Figure 13: A typical output file generated by the RPR program

The next block of text, from the letter “n” to the line numbered “30”, gives information regarding the resonant frequencies of the sample. The n column in this block gives the mode number. The f_{ex} and f_r columns contain the resonant frequencies experimentally determined and the resonant frequencies calculated by the program based upon given elastic moduli, respectively. It is the f_r column that is the solution to the direct problem described earlier. The $\%err$ column contains the percent difference between each experimental and calculated frequency. The wt column determines whether or not the resonant frequency is used in the determination of the moduli; 1.00 means that the frequency is used while 0.00 means that it is not. The k and i columns describe the symmetry and order of each mode, respectively. The last two columns, which fall under $df/d(moduli)$, reveal how each frequency is dependent upon each of the independent moduli. For instance, the location of the first resonant frequency is determined solely by c_{44} while the second frequency is determined by a combination of c_{11} and c_{44} .

Following the resonant frequency information is the bulk modulus, the elastic stiffnesses, the physical dimensions of the sample, the number of iterations the program completed, the rms error of the fit, the amount that the rms error changed following the last iteration, the eigenvalues, and the eigenvectors. The output file ends with information regarding the accuracy of results. The largest number in each column at the end of the output file gives the error bar for a variable solved for by the program. In order from left to right, the columns for this output file correspond to c_{11} , c_{44} , dimension 1, dimension 2, and dimension 3. At a single temperature, the dimensions are allowed to change to better improve the fit. The changes are typically very small, on the order of tenths of a percent, and are constraint such that the density remains constant. These

new, slightly altered dimensions are then used at every other temperature at which the sample is tested.

The elastic moduli of conventional solids, i.e. solids that do not display any thermodynamic irregularities, undergo a gradual stiffening with decreasing temperature (the so-called Varshni function) ^[28], as shown in Figure 14. Both magnetic and structural transitions are represented as deviations from this “Varshni” behavior. For this reason, RUS not only provides important information regarding the elastic behavior of the material but also probes for the existence of transitions and indicates where further study should be focused in the search for other interesting phenomena.

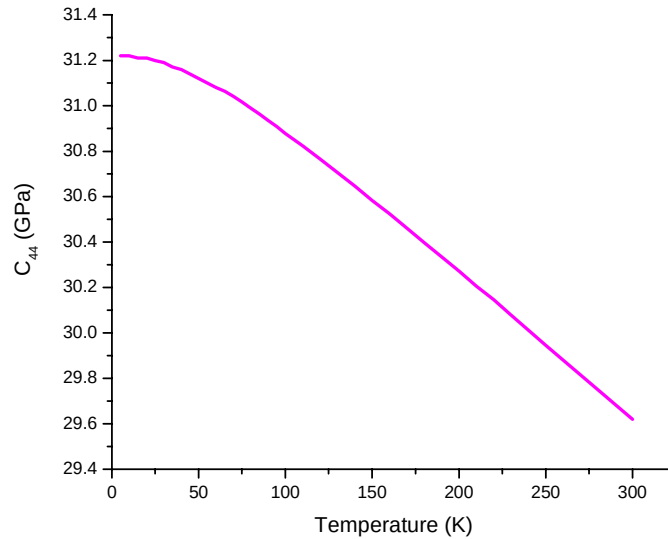


Figure 14: Typical Varshni behavior of a system with no thermodynamic irregularities

Difficulty also arises when analyzing the elastic moduli as a function of temperature. Figure 15 shows a frequency spectrum at 70 K and 30 K. The resonant frequencies for the spectrum at 70 K are quite simple to find while locating each of the

corresponding peaks in the 30 K spectrum is a daunting task, even if their approximate locations are already known. The occurrence of such a muddled spectrum occurs at times when the material is passing through a transition.

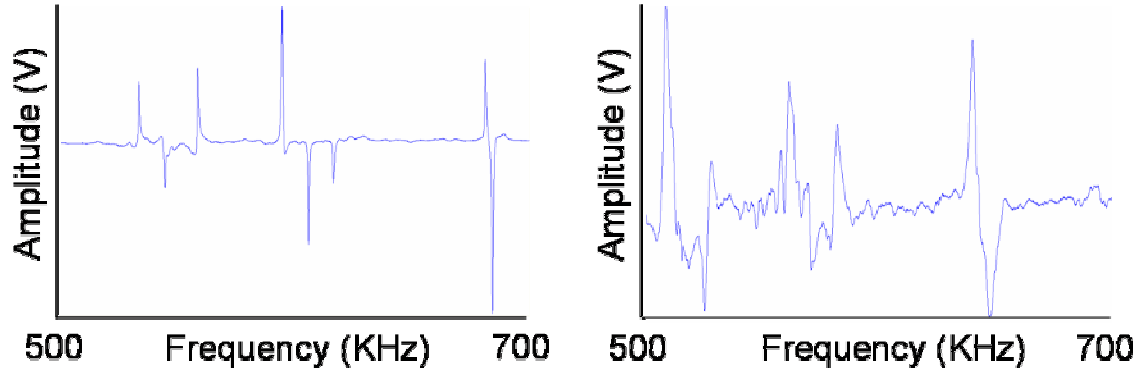


Figure 15: A partial spectrum of resonant frequencies at (Left) 70 K and (Right) 30 K

Fortunately, the relationship between f^2 and the elastic modulus can be used in such instances so that information regarding the elastic tensor is not completely lost in the most interesting temperature ranges. By finding a resonant frequency that is almost entirely dependent upon a single modulus (e.g. lines 1, 7, 8, 20, and 23 in Figure 13 above)) and ensuring that the behavior of that peak matches the behavior of the modulus at temperatures for which both can be well determined, very near approximations of the elastic moduli can be made in temperature ranges for which some resonances (and therefore the full elastic tensor) are nearly impossible to determine. Such a technique was employed in this research and will be referenced later.

2.3 Capacitance Dilatometry

There are multiple instruments/methods for the determination of length change, such as X-ray and neutron diffraction, extensometers, and capacitive dilatometers. X-ray and neutron diffraction have sensitivities on the order of 10^{-5} , extensometers are on the order of 10^{-7} , and capacitive dilatometers are on the order of 10^{-9} [29]. The diffraction techniques have the advantage of determining the change of each lattice parameter, which allows for the determination of the thermal expansion and magnetostriction in all three crystallographic directions for single crystals. They do not offer the high levels of sensitivity needed for such measurements, however. The method chosen for our research was capacitive dilatometry. Not all dilatometers based upon the measurement of capacitance are created equally. A popular design is to use parallel plates, but this typically results in large cell size. Not only does a large cell size hinder thermal stability, it prevents the cell from being incorporated into systems with limited space. The solution to this problem is to design the cell with tilted plates [30]. The dilatometer cell developed by Rotter et al. is shown in Figure 16 alongside the implementation of the cell in a multifunction probe made for our Physical Property Measurement System (PPMS). The magnetostriction both parallel and perpendicular to a magnetic field can be measured simply by rotating the cell 90° in the multifunction probe. Another benefit of this design is that the sample needs not be of any particular shape; the only restriction is that the bottom should be flat in order to provide a stable sample mount. The sample to be measured is placed between two capacitance plates and the capacitance is measured as a function of temperature or magnetic field. Any change in the dimensions of the sample is observed as a decrease (expansion) or increase (contraction) of the capacitance value.

The recorded capacitance is converted into a relative change in length $\Delta l/l$ using a series of inter-related equations.

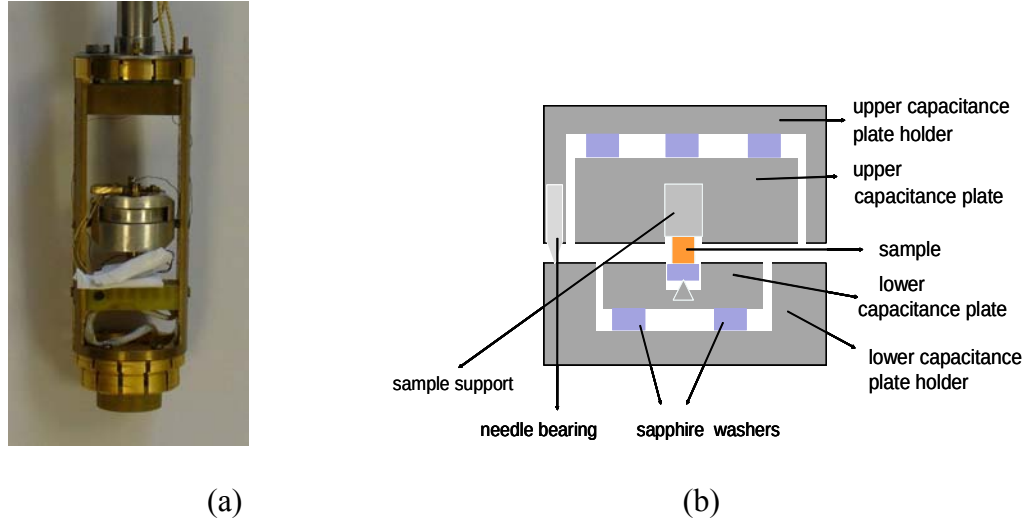


Figure 16: (a) The capacitance dilatometer cell inside the custom multifunction probe. (b) Schematic of capacitance dilatometer cell ^[30]

The mathematics behind magnetostriction measurements is based upon the geometry of the dilatometer cell, shown in part in Figure 16. It should be noted that Figure 17 is based upon a parallel plate dilatometer cell rather than a tilted plate cell for the purpose of simplifying the illustration. The following equations, however, apply to the tilted-plate cell in the determination of thermal expansion. It will be shown that the equations determining the magnetostriction are slightly altered thermal expansion equations.

$$\gamma_i = \frac{r_i}{b} \left[\frac{k(T)}{d(T)} - 1 \right] \quad (2.21)$$

where r_o and r_i are the radii of the outer and inner capacitance plates, b is the distance between the center of the capacitor and the pivot, and k the pivot distance given by

$$k(T) = k(T_o) \left[1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right] \quad (2.22)$$

where $k(T_o)$ is the pivot distance at $T_o = 300$ K and $\frac{\Delta l_{Ag-lit}}{l}(T)$ is the thermal expansion of silver obtained from literature.

Because the capacitance plates are also made of silver, the shape change due to thermal expansion must also be considered because it changes the capacitance. A_o and A_i , the areas of the outer and inner capacitance plates, are determined by πr^2 while their temperature dependence is determined by

$$A_o(T) = A_o(T_o) \left[1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right]^2 \quad (2.23)$$

$$A_i(T) = A_i(T_o) \left[1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right]^2 \quad (2.24)$$

From Figure 17, the following equation is set

$$d(T) + \Delta l_p = d_p(T) + \Delta l_{Sample} \quad (2.25)$$

where Δl_p and Δl_{Sample} are the changes in length of the capacitance plates and the sample, respectively, which are given by

$$\Delta l_p = \frac{\Delta l_{Ag-lit}}{l}(T) \cdot l_s \quad (2.26)$$

$$\Delta l_{Sample} = \frac{\Delta l_{Sample}}{l}(T) \cdot l_s \quad (2.27)$$

where l_s is the original length of the sample and $d_p(T)$ is the temperature dependence of the thickness of the spacer, given by

$$d_p(T) = d(T_o) \left(1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right) \quad (2.28)$$

Substituting Equations 2.26 through 2.28 into 2.23 and rearranging gives

$$d(T) - d(T_o) + \frac{\Delta l_{Ag-lit}}{l}(T) \cdot l_s = \frac{\Delta l_{Sample}}{l}(T) \cdot l_s + d(T_o) \frac{\Delta l_{Ag-lit}}{l}(T) \quad (2.29)$$

In order to eliminate the effects of silver expansion, the normalized gap $\hat{d}(T)$ is set as

$$\hat{d}(T) \equiv \frac{d(T)}{1 + \frac{\Delta l_{Ag-lit}}{l}(T)} \Rightarrow d(T) \equiv \hat{d}(T) \left(1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right) \quad (2.30)$$

By inserting a similar relation into Equations 2.23 and 2.24, the normalized areas of the

outer and inner plates $\hat{A}_o(T)$ and $\hat{A}_i(T)$ are given by

$$\hat{A}_o(T) \equiv \frac{A_o(T)}{1 + \frac{\Delta l_{Ag-lit}}{l}(T)} = A_o(T_o) \left(1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right) \quad (2.31)$$

$$\hat{A}_i(T) \equiv \frac{A_i(T)}{1 + \frac{\Delta l_{Ag-lit}}{l}(T)} = A_i(T_o) \left(1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right) \quad (2.32)$$

Applying Equation 2.30 and setting $d(T_o) = \hat{d}(T_o)$ at $T = T_o$, Equation 2.29 becomes

$$\hat{d}(T) \left(1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right) - \hat{d}(T_o) + \frac{\Delta l_{Ag-lit}}{l}(T) \cdot l_s = \frac{\Delta l_{Sample}}{l}(T) \cdot l_s + \hat{d}(T_o) \frac{\Delta l_{Ag-lit}}{l}(T) \quad (2.33)$$

Rearranging gives

$$\frac{\hat{d}(T) - \hat{d}(T_o)}{l_s} + \frac{\hat{d}(T) - \hat{d}(T_o)}{l_s} \frac{\Delta l_{Ag-lit}}{l}(T) + \frac{\Delta l_{Ag-lit}}{l}(T) = \frac{\Delta l_{Sample}}{l}(T) \quad (2.34)$$

Setting $\Delta \hat{d}_s(T) \equiv \hat{d}(T) - \hat{d}(T_o)$, rearranging and simplifying gives

$$\frac{\Delta l_{Sample}}{l}(T) = \frac{\Delta \hat{d}_s(T)}{l_s} \left(1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right) + \frac{\Delta l_{Ag-lit}}{l}(T) \quad (2.35)$$

Equation 2.35 is the equation used to calculate thermal expansion. To do so, however, the value of the gap change $\Delta \hat{d}_s(T)$ needs to be calculated from the capacitance change.

$\Delta \hat{d}_s(T)$ is calculated by rewriting Equations 2.19 to 2.21, 2.23, and 2.24 in terms of the normalized variables, giving the following set of equations:

$$\hat{d}(T) = \frac{2\varepsilon_o}{C(T)} \left[\hat{A}_o(T) \frac{1 - \sqrt{1 - \gamma_o^2}}{\gamma_o^2} - \hat{A}_i(T) \frac{1 - \sqrt{1 - \gamma_i^2}}{\gamma_i^2} \right] \quad (2.36a)$$

$$\gamma_o = \frac{r_o}{b} \left[\frac{k(T_o)}{\hat{d}(T)} - 1 \right] \quad (2.36b)$$

$$\gamma_i = \frac{r_i}{b} \left[\frac{k(T_o)}{\hat{d}(T)} - 1 \right] \quad (2.36c)$$

$$\hat{A}_o(T) = \pi r_o^2 \left(1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right) \quad (2.36d)$$

$$\hat{A}_i(T) = \pi r_i^2 \left(1 + \frac{\Delta l_{Ag-lit}}{l}(T) \right) \quad (2.36e)$$

Every variable on the right side of these equations is known except for the normalized

gap $\hat{d}(T)$. The set of equations is then solved by inserting some value for $\hat{d}(T)$ into the γ equations, calculating the γ and $\hat{A}(T)$ values, and inserting those values into equation 2.36a to calculate $\hat{d}(T)$. This new value of $\hat{d}(T)$ is compared to the original value of $\hat{d}(T)$ and if the difference is too large, then the new value is used in the calculation of equations 2.26b through 2.26e and the process starts again.

It was mentioned earlier that the calculation of magnetostriction is simply a variation of the calculation of the thermal expansion. This variation comes about by changing the temperature dependent variables to magnetic field dependent (i.e. $C(T) \rightarrow C(H)$). The importance of this modification is the fact that while silver does change shape with temperature, it does not with magnetic field. As such, all $\frac{\Delta l_{Ag-lit}}{l}(H)$ terms would become zero, changing Equation 2.35 to

$$\frac{\Delta l_{Sample}}{l}(H) = \frac{\Delta \hat{d}_s(H)}{l_s} \quad (2.33)$$

In order to map out the full magnetostrictive behavior of a given sample, magnetostriction measurements are usually repeated as a function of temperatures. Because of this, it would seem that the thermal expansion of the sample would have to be accounted for when changing temperatures by changing l_s each time the temperature is changed. Although this is theoretically correct, the change brought about by thermal expansion has such a small effect on the final magnetostriction value that it can be ignored.

2.4 X-Ray and Neutron Diffraction

For phase ID, a Philips Materials Research Diffractometer with a curved graphite crystal monochromator was utilized. Because the diffractometer uses a vertical stage, the sample was prepared from ground powders and mixed with a binding agent that did not contribute to the diffraction pattern. Cu K α 1 radiation, 45 kV, 40 mA, and a 0.4° divergent slit were used to collect diffraction data between 10-70° with a 0.02° step size for 50 minutes. X'Pert High Score Plus and PowderX^[31] were used for data analysis.

For structure determination, a PANalytical X'pert Pro MPD with an incident beam monochromator and X'cellerator detector in a θ -2 θ geometry was utilized. To extend the investigation to low temperatures, an Oxford PheniX cryostat was also used. A thin layer of N-grease was applied to a thermally conductive flat sample surface. The powdered sample was then poured onto and spread across the grease. Cu K α 1 radiation, 40 kV, 30 mA, and a 0.5° divergent slit were used to collect diffraction data between 20-100° with a step size of 0.017°. Fullprof was used for data analysis^[32].

Neutron powder diffraction measurements were carried out at the HB2A neutron powder diffractometer at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory, using the wavelengths $\lambda = 1.538 \text{ \AA}$ and $\lambda = 2.41 \text{ \AA}$ provided by a vertically focusing Ge(115) monochromator. For data collection, the detector array consisting of 44 ³He tubes was scanned in two segments to cover the total 2-theta range of 4-150° in steps of 0.05°. Overlapping detectors for a given step served to average the counting efficiency of each detector. More details about the HB2A instrument and data collection strategies can be found in Ref. [33]. Measurements were made on approximately 20 g of sample held in a cylindrical vanadium container in Debye-Scherrer geometry, loaded in a top-

loading closed cycle refrigerator (4-300 K).

3. Results

3.1 Room-Temperature X-Ray Diffraction

The first step after synthesizing a compound is to determine if the synthesis created the desired compound. Figure 18 shows the room temperature XRD patterns for all four compounds and confirms that the synthesis was successful. Using the patterns in Figure 18, the lattice parameters as a function of cobalt content were determined and are shown in Figure 19(a). As cobalt content increases, the lattice parameter a expands at a slower rate than c contracts, resulting in a slight volume decrease as shown in Figure 19(b). Proof of this change in lattice parameters can be found in the behavior of the two peaks marked with an arrow in Figure 18 and centered around 43° . In the $x = 0$ pattern, the peak on the left corresponds to the $(0\ 0\ 2)$ reflection while the peak on the right corresponds to the $(2\ 2\ 0)$ reflection. With increasing cobalt, the $(0\ 0\ 2)$ reflection shifts to larger 2θ values as c decreases while the $(2\ 2\ 0)$ reflection shifts to smaller 2θ values as a and b decrease. This movement continues until the two peaks merge and appear as one for $x = 0.375$.

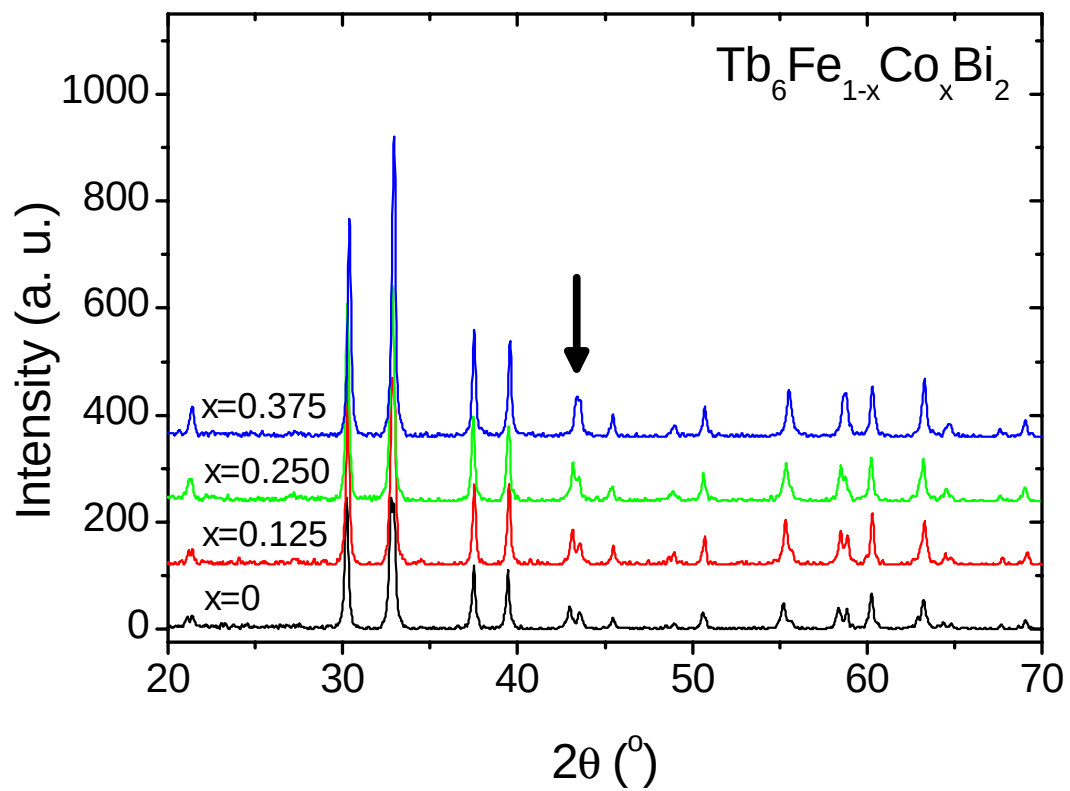


Figure 18: Room temperature XRD of each compound modified from [34]

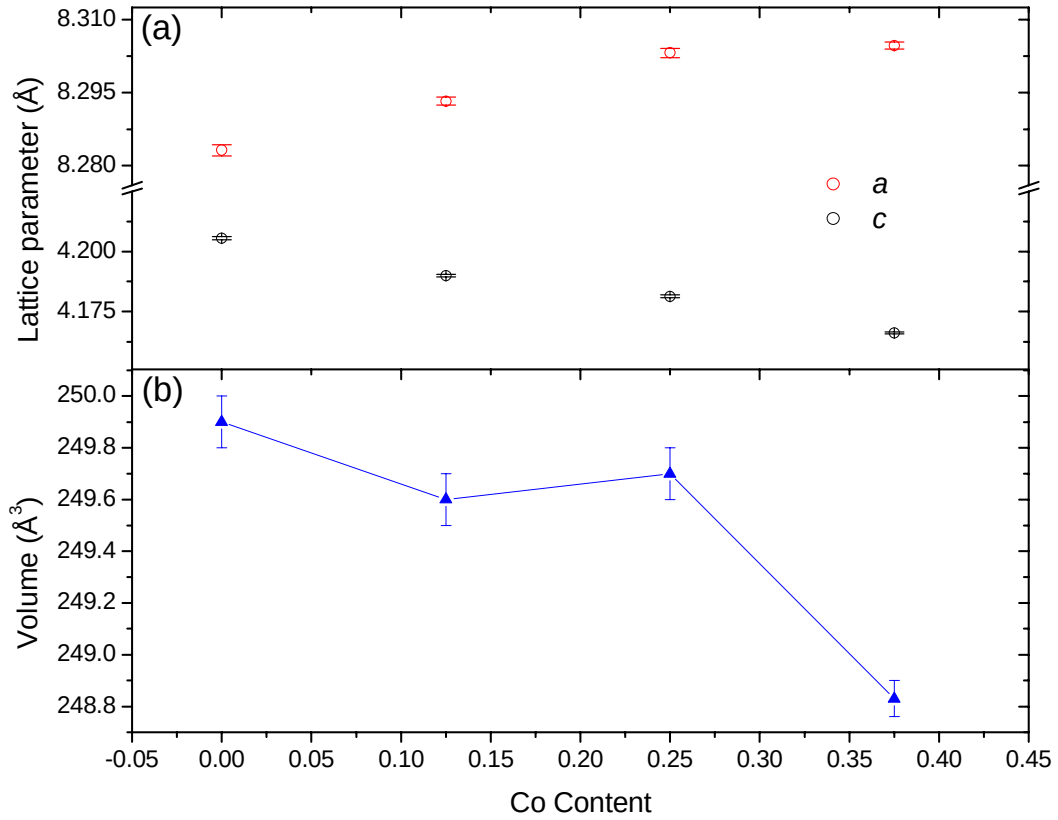


Figure 19: (a) Lattice parameters and (b) volume of each compound as determined by room-temperature XRD

3.2 Magnetization

3.2.1 Transition temperatures

Magnetization measurements were performed as a function of both temperature and magnetic field. The first set of results pertains to the magnetization with changing temperature (shown in Figure 20), from which magnetic transition temperatures can be obtained. The transition temperatures were determined as the intersection of two straight lines, one fit to the linear portion of the data at temperatures above the transition and the other fit to the linear portion of the increasing magnetization (examples of which are

shown for both T_{C1} and T_{C2}). As shown in the inset of Figure 20, both T_{C1} and T_{C2} decrease linearly with increasing cobalt content. T_{C1} ranges from 254 K ($x = 0$) to 240 K ($x = 0.375$) and T_{C2} ranges from 75 K ($x = 0$) to 61 K ($x = 0.375$).

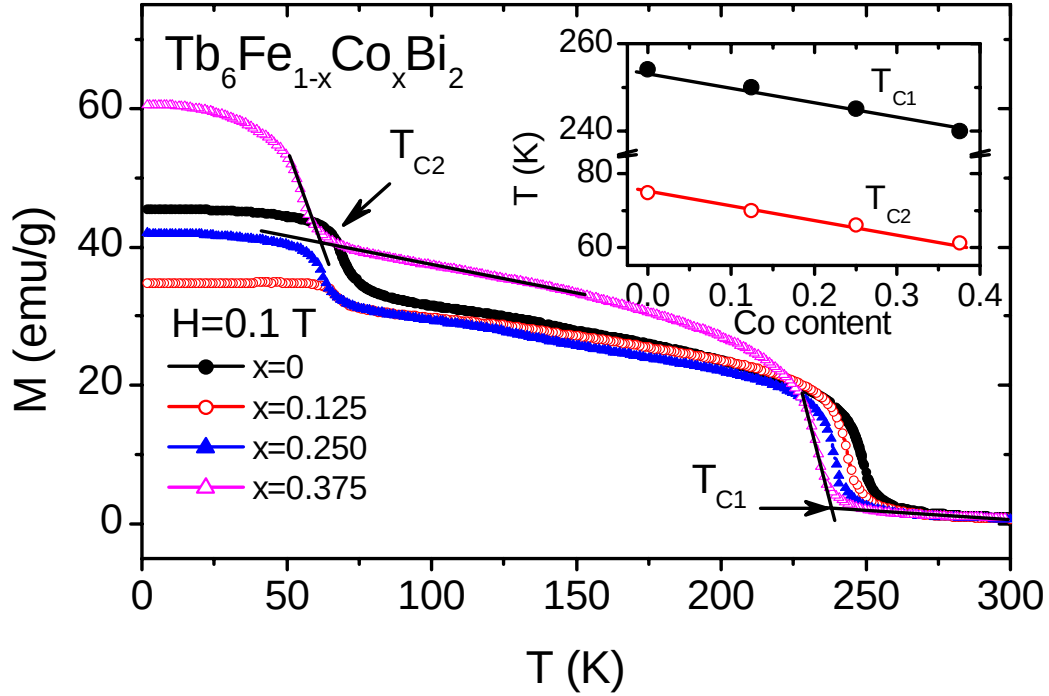


Figure 20: Magnetization as a function of temperature for each of the four compounds. Inset: Both magnetic transition temperatures as a function of cobalt content ^[34]

3.2.2 Shape Anisotropy

Unfortunately, difficulty occurred in determining a trend in magnetization quantitatively, most likely caused by shape anisotropy. A spherical sample of a material that has no magnetocrystalline anisotropy will magnetize equally regardless of direction. For shapes other than spheres, measurements made along a long dimension give magnetization values larger than those along shorter dimensions due to the demagnetizing field. The source of the demagnetizing field is shown in Figure 21 in

which a sample has been magnetized with a magnetic field applied from left to right and subsequently had the magnetic field removed. A north pole is formed at the right end, and a south pole at the left, and the fieldlines, radiating out from the north pole and ending at the south pole, constitute a field both outside and inside the magnet which acts from north to south and which therefore tends to demagnetize the magnet.

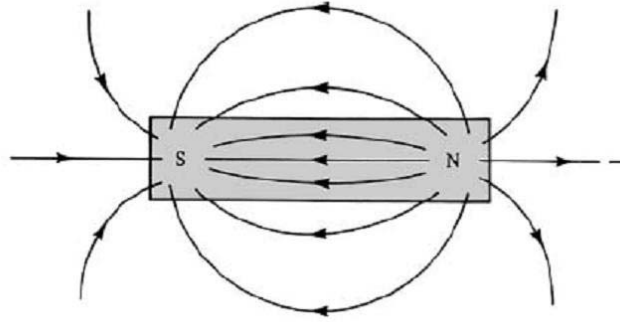


Figure 21: Magnetization of a bar magnet showing the occurrence of a demagnetizing field^[35]

Determining the demagnetizing field becomes very involved. For such shapes as rectangular parallelepipeds, the demagnetizing field is not uniform throughout because it is stronger at the poles, as indicated by Figure 21. Even in the case of a prolate spheroid with short dimension “a” and long dimension “c”, the demagnetizing field along c is given by

$$N_c = \frac{1}{(m^2 - 1)} \left[\frac{m}{\sqrt{m^2 - 1}} \ln(m + \sqrt{m^2 - 1}) - 1 \right] \quad (3.2)$$

where m is equal to c/a^[35]. Added complication comes when studying samples of other shapes because the susceptibility must also be considered. An equation similar to that of prolate spheroids that accounts for susceptibility does not exist currently for parallelepiped samples. Instead, tables have been made based upon certain ratios of

the dimensions and susceptibility values. Due to the time-constraining nature of building these tables, they are far from complete. Further discussion on demagnetizing fields can be found in Refs. [35, 36].

The possibility exists that the polycrystalline samples contain magnetocrystalline anisotropy that would also cause differing magnetization values depending upon the dimension along which the sample is magnetized. This magnetocrystalline anisotropy would exist if the sample were comprised of elongated grains rather than equiaxed grains. Optical microscopy was performed to determine whether the grains were equiaxed or elongated. A sample of $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Sb}_2$ was polished with a 1.0 micron slurry of Al_2O_3 and etched with a 2% Nital solution. The grain structure was investigated at a variety of surface locations and all grains appeared similar. As shown in Figure 21, the grains are equiaxed rather than elongated, indicating that texturing should not be the cause of the magnetization differences. It should be clarified that the straight lines seen in Figure 22 are artifacts of the polishing procedure. Also, some grains appear light while others appear dark because due to differing crystallographic orientations.

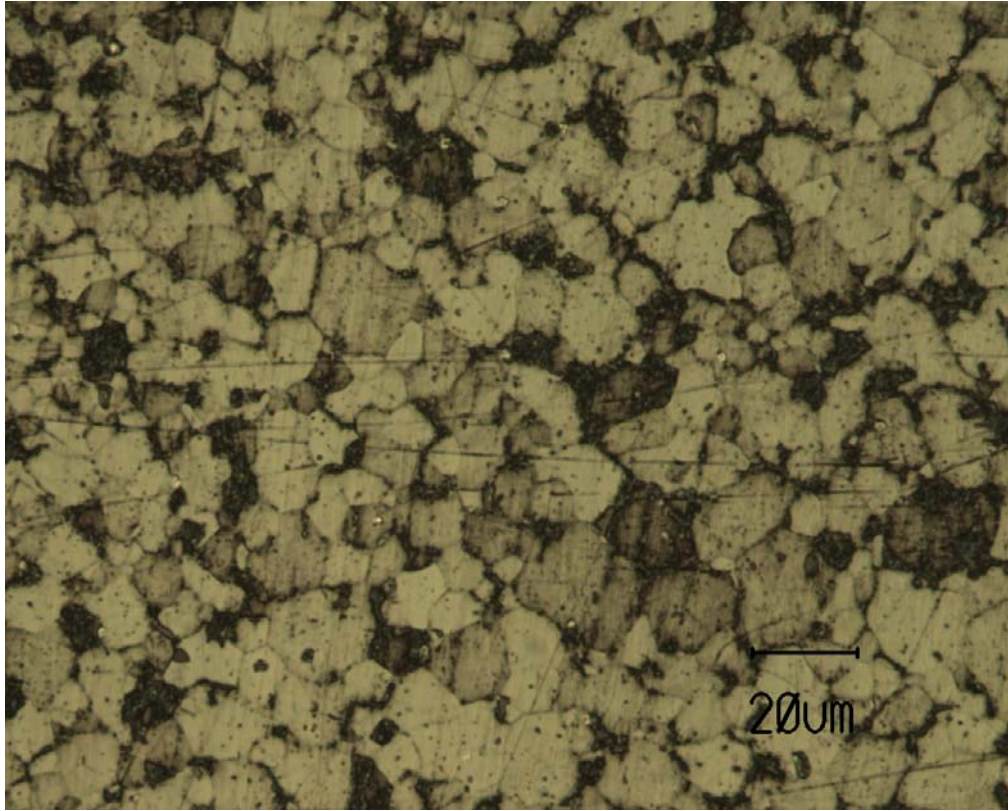


Figure 22: Optical microscopy of $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Sb}_2$ - 400X. Grains appear equiaxed.

With the possibility of magnetocrystalline anisotropy minimized, the next step was to perform magnetization measurements along three dimensions of different length. Upon completion, one dimension was polished to bring it nearly equal to the length of another, and new magnetization measurements were made. Theoretically, there are three possible outcomes to this test. If the reshaped dimension has no change of magnetization, it would indicate that the discrepancy is due to something other than shape, such as magnetocrystalline anisotropy. If the magnetizations of the two nearly identical dimensions become closer but there still exists some discrepancy, the issue could be related to both shape and magnetocrystalline anisotropy. Finally, if the magnetizations match after reshaping, the most likely explanation would be shape anisotropy.

Figure 23(a) shows the magnetization made along each of the three dimensions before reshaping while Figure 23(b) shows the magnetization measured along each of the three dimensions after the long dimension was reshaped. The result of the reshaping is that the magnetizations made along the nearly equal-length dimensions are also nearly equal. Therefore, the difference in the magnitude of the magnetic moments is most likely caused by shape anisotropy.

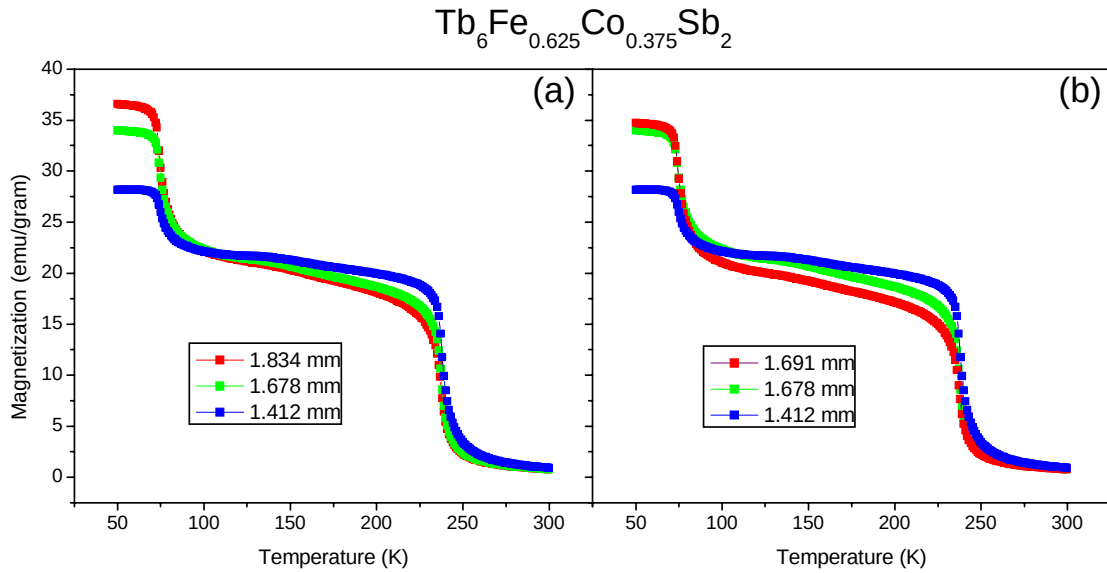


Figure 23: Magnetization measurements of a $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Sb}_2$ sample (a) with three different dimensions and (b) after the long dimension was polished to nearly match the middle dimension

3.2.3 Curie-Weiss Law

One method of determining if the theory of the magnetic behavior of each type of atom is accurate is to apply the Curie-Weiss law to magnetization data in the paramagnetic region which exists above the Curie temperature. Doing so gives the effective moment of the compound, which can then be compared to the theoretical value for whatever magnetic system is proposed. In the case of the materials studied here, the proposed system is an antiferromagnetic alignment between the terbium and iron

moments.

The Curie-Weiss law is given as

$$\chi = \frac{C}{T - \theta} \quad (3.2)$$

where T is the temperature (typically in Kelvin), θ is the Weiss temperature, and C the Curie constant given by

$$C = \frac{N\mu_{eff}^2}{3k_B} \quad (3.3)$$

where N is Avogadro's number, μ_{eff} is the effective moment, and k_B is Boltzmann's constant. If the inverse susceptibility is plotted as a function of temperature, as shown in Figure 24, then the slope of the line fitted to the linear portion is equal to $1/C$. Using Equation 3.3 and solving for μ_{eff} gives an effective moment of $\sim 8.65\mu_B$. The effective moments for three possible magnetic orderings are calculated using Equations 3.4 – 3.6,

$$\mu_{eff}^{\text{Ferromagnetic Tb}} = \mu_{eff-Tb} \quad (3.4)$$

$$\mu_{eff}^{\text{Ferromagnetic Tb/Fe}} = \sqrt{\left(\frac{6 * [\mu_{eff-Tb}]^2 + (1-x)[\mu_{eff-Fe}]^2 + (x)[\mu_{eff-Co}]^2}{7} \right)} \quad (3.5)$$

$$\mu_{eff}^{\text{Ferrimagnetic Tb/Fe}} = \sqrt{\left(\frac{6 * [\mu_{eff-Tb}]^2 - (1-x)[\mu_{eff-Fe}]^2 - (x)[\mu_{eff-Co}]^2}{7} \right)} \quad (3.6)$$

where the effective moment of terbium is taken as $9.3 \mu_B$, of iron is $2.2 \mu_B$, and of cobalt is $1.7 \mu_B$. Equation 3.4 assumes the magnetic order put forth by Morozkin^[14] in which only the terbium atoms carry a magnetic moment and align ferromagnetically. Equations 3.5 and 3.6 assume that the terbium and iron atoms both carry a magnetic moment and

that the moments of the two different atoms align parallel and antiparallel, respectively.

The result for each of the compounds and each magnetic model is given in Table 1.

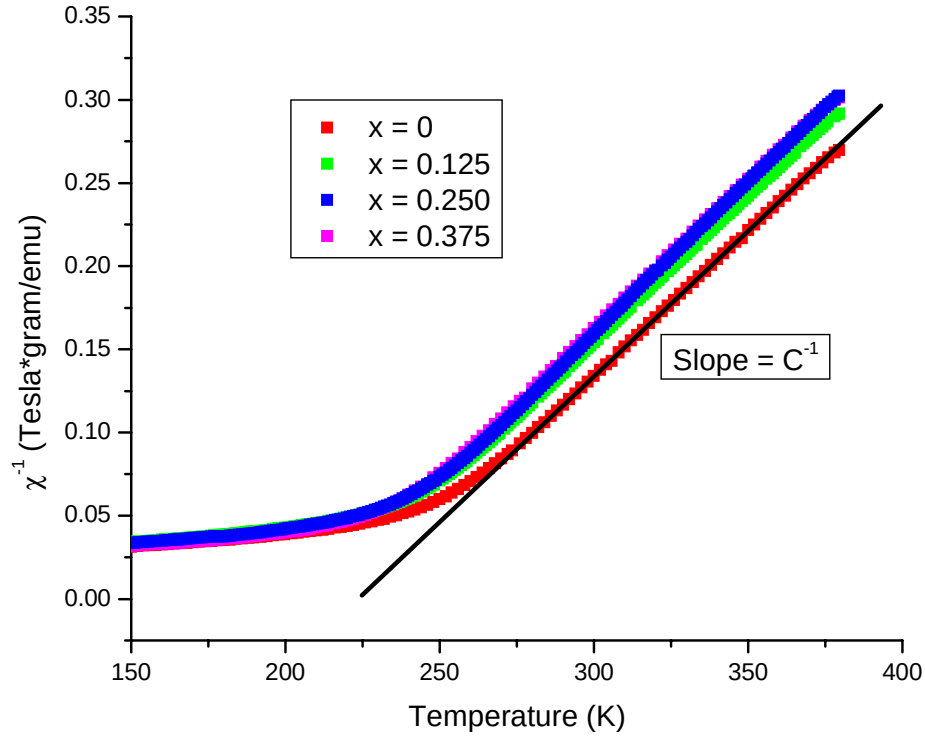


Figure 24: Curie-Weiss for each compound ^[34]

Table 1: Comparison of the experimental moment determined by Curie-Weiss law to the theoretical moment. Samples are specified for $x = 0.125$ to show the degree of sample-based difference. FoM = ferromagnetic, FiM = ferrimagnetic.

Composition	Sample	Experimental μ_{eff} (μ_B)	FoM - Tb μ_{eff} (μ_B)	% Δ	FoM - Tb/Fe μ_{eff} (μ_B)	% Δ	FiM - Tb/Fe μ_{eff} (μ_B)	% Δ
$x = 0$		8.56	9.3	8.0	8.650	1.0	8.570	0.1
$x = 0.125$	B1 - S1	8.48	9.3	8.8	8.649	2.0	8.572	1.1
	B2 - S1	8.39	9.3	9.8	8.649	3.0	8.572	2.1
	B2 - S3	8.36	9.3	10.1	8.649	3.3	8.572	2.5
$x = 0.25$		8.34	9.3	10.3	8.647	3.6	8.574	2.7
$x = 0.375$		8.44	9.3	9.3	8.645	2.4	8.576	1.6

As shown in Table 1, the differences between the experimentally determined moment and the moment calculated from the ferromagnetic terbium model proposed in literature range from approximately 8 to 10%, by far the largest disagreement of the three models. Maintaining the ferromagnetic model but adding a moment on the iron site greatly improves the agreement. The best agreement, however, is found for the ferrimagnetic model.

Unfortunately, the shape anisotropy also introduces some error in the determination of the effective magnetic moment. Table 1 shows that cobalt doping should theoretically have little effect on the effective moment of the compound. This, however, is not very well represented by the data. When measuring a sample with a smaller demagnetizing field, the measured magnetization will be larger as discussed above. This increased magnetization leads to a decrease of the inverse susceptibility (H/M), a decrease of the slope of the linear portion of the curve shown in Figure 24, and an increase in the Curie constant. Because everything other than the effective moment is a constant in the Curie constant, this results in an increase of the effective moment. It seems most logical to compare the largest value of the experimentally determined effective moment to the theoretical value because the theoretical value does not take into account a demagnetizing field. As such, the best theoretical value to be used as a comparison would be that of the parent compound which differs from the theoretical value by only 0.1%.

3.3 Elastic Moduli

Figure 25(a) shows the temperature-dependence of the shear modulus c_{44} and longitudinal modulus c_{11} for the parent compound Tb_6FeBi_2 . The main feature in Figure 25 is a dramatic softening of the moduli that sets in at the Curie temperature T_C (~ 250 K). Whereas the so-called ΔE effect is known to cause a softening of the elastic modulus of ferromagnets at T_C , which is lifted upon the application of a magnetic field,^[37] the observed drop in the moduli for Tb_6FeBi_2 is very uncharacteristic: it spans a large-temperature range, softening gradually until about 75 K, where it becomes much more pronounced, reaching a minimum at 40 K. It is tempting to link all of the softening to the magnetic transition reported in literature because no other transition is reported. Figure 25(b), however, shows that the softening of the elastic modulus becomes far more pronounced upon doping with Co: a decrease of approximately 35% from room temperature to the minimum of each curve is observed for $\text{Tb}_6\text{Fe}_{0.750}\text{Co}_{0.250}\text{Bi}_2$ and $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$. While the relatively smaller degree of softening found in the parent compound could possibly be explained using only the magnetic transition, it is very unlikely that this transition would cause the remarkable softening found in the cobalt-doped compounds could. This large degree of softening is a strong indication that there exists a low-temperature structural transition.

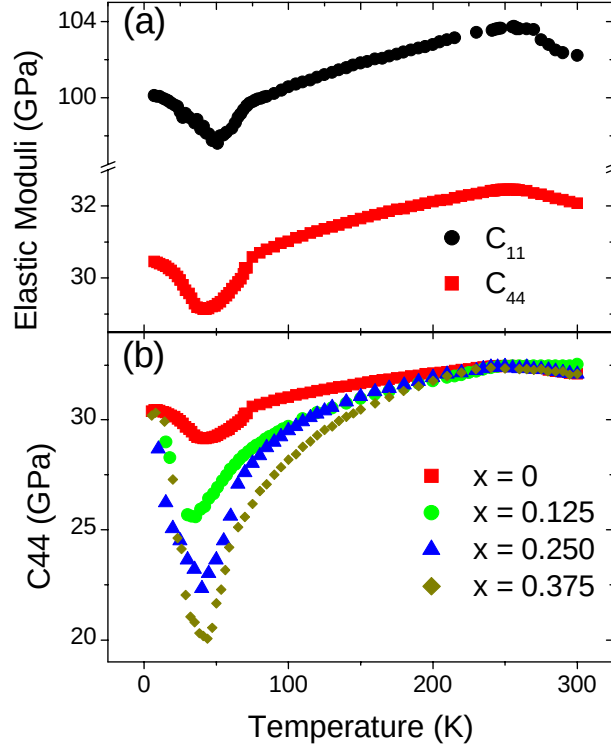


Figure 25: (a) Elastic moduli c_{11} and c_{44} versus temperature for parent compound Tb_6FeBi_2 ; (b) c_{44} versus temperature for $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$, as indicated.

Figure 26 shows the temperature-dependence of the elastic shear modulus in applied magnetic field. The longitudinal modulus was found to have the same qualitative behavior and is therefore not shown separately. Whereas the elastic response near the Curie temperature for both the parent and $\text{Tb}_6\text{Fe}_{0.750}\text{Co}_{0.250}\text{Bi}_2$ compounds is not noticeably affected by a magnetic field, the low-temperature softening is partially suppressed, indicating that application of a field counteracts the instability responsible for the softening.

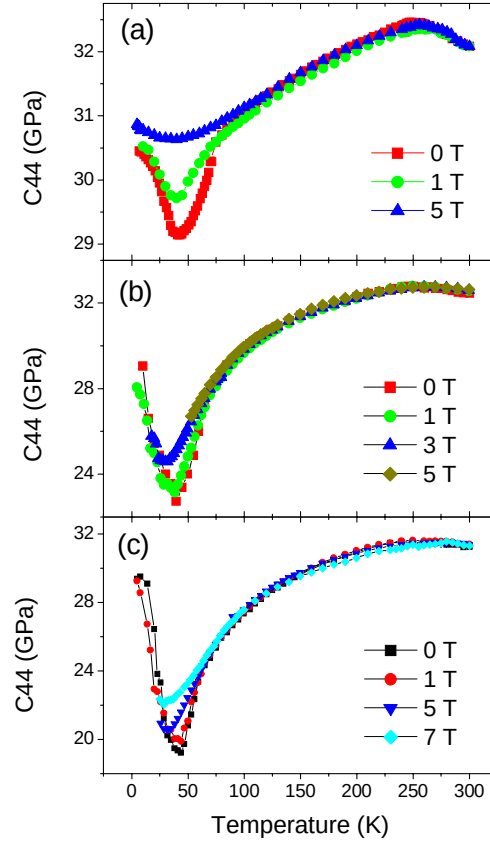


Figure 26: c_{44} versus temperature at various fields for polycrystalline samples of (a) Tb_6FeBi_2 , (b) $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Bi}_2$, and (c) $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$

3.4 Magnetostriction

Figures 27(a-f) show the magnetostriction of the four $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ compounds, $x = 0.000, 0.125, 0.250$, and 0.375 . It can be seen that regardless of composition, the magnetostriction, $\Delta l/l$, above 100 K ($\lambda_{\parallel \text{max}} @ 2\text{T} \sim 55$ ppm) is almost negligible compared to the several hundred ppm found at low temperatures ($T < 50$ K). Figures 27(b-e) show the dependence of magnetostriction on temperature for the different compositions. Qualitatively, the behavior is the same for each of the compounds; $\lambda_{\parallel}$ remains small

down to 70 K, turns negative between 60 K and 80 K, and rapidly increases in magnitude as the temperature is decreased below 60 K.

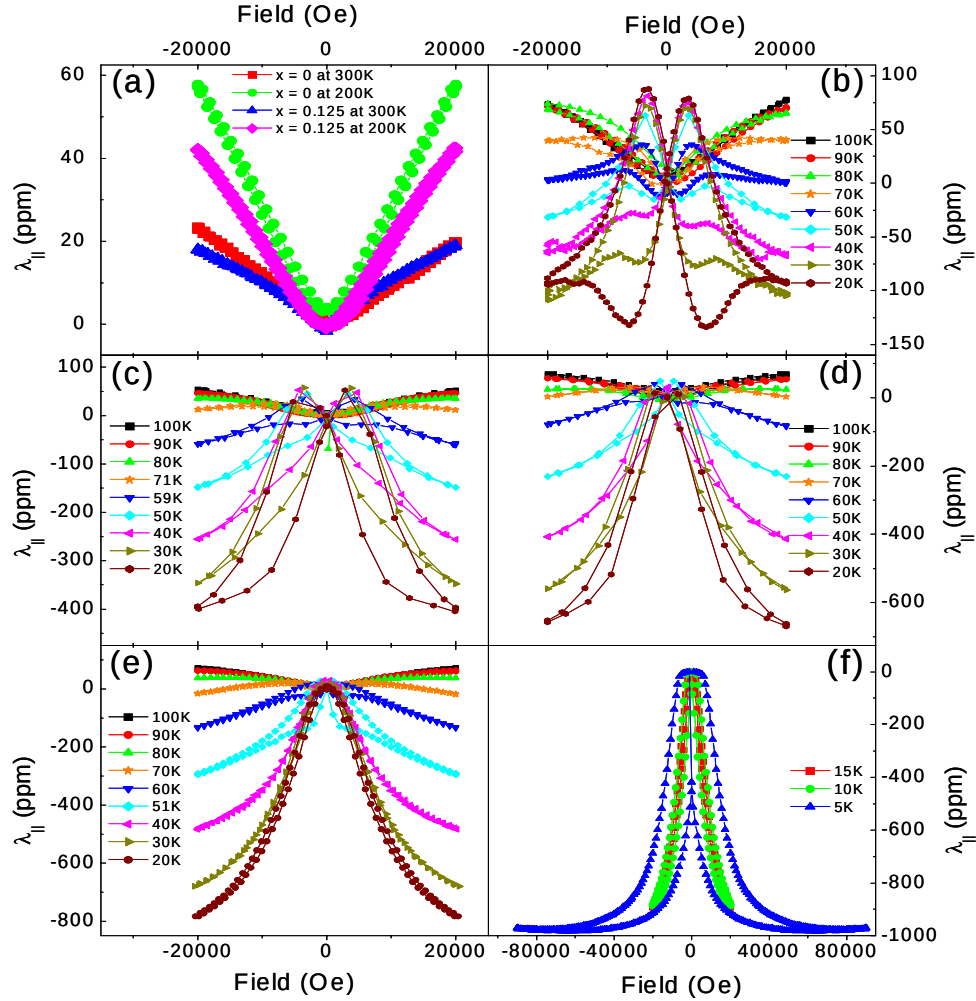


Figure 27: Magnetostriction $\lambda_{||}$ versus magnetic field for $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$. (a) Tb_6FeBi_2 and $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Bi}_2$ at $T \geq 200$ K. (b) Tb_6FeBi_2 , (c) $\text{Tb}_6\text{Fe}_{0.875}\text{Co}_{0.125}\text{Bi}_2$, (d) $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Bi}_2$, and (e) $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$ all at $T \leq 100$ K. (f) $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$ at $T \leq 15$ K with 5 K showing the saturation magnetization

The sign change of the slope at lower fields seen predominately in Figures 27 (b) and (c) can likely be explained using domain wall motion and rotation. Figure 28 is a two-dimensional representation of the domain behavior and magnetostriction changes as

a magnetic field is applied to a polycrystalline iron sample. At low applied fields, the 90° domain walls move in order to maximize the volume of the domains in which the magnetization is pointing along the easy direction most closely aligned with the applied magnetic field. This process is represented as a net expansion in our samples and can be clearly seen in Figure 27 (b) at low temperatures and fields below 5000 Oe. Once the sample is populated only with domains in which the moments are along an easy axis, magnetization rotation begins. To be clear, it is not the domain itself that rotates to align with the field; it is the individual moment of each atom that rotates. It is during the rotation of the magnetization that the majority of the magnetostriction occurs ^[35]. This process is most likely the cause of the decrease after the initial increase of magnetostriction.

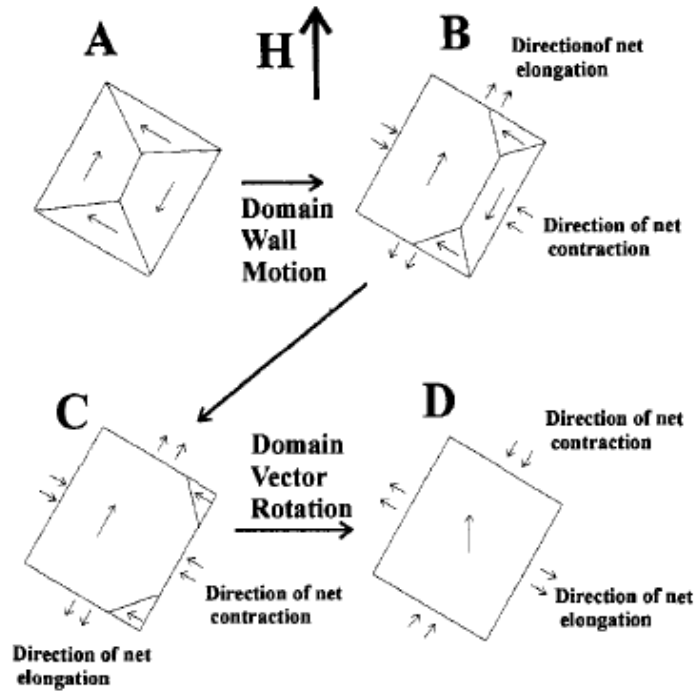


Figure 28: Domain behavior of a cubic material in a magnetic field. (a) Normal domain arrangement with no applied field. (b) and (c) Domain walls move to maximize those domains with magnetization aligned along an easy axis close to the applied field. (d) The magnetization rotates to align with the applied field. ^[38]

The changing behavior of the magnetostriction curves with decreasing temperature can also be explained through a consideration of the thermal energy and elastic moduli. Magnetization measurements from Section 3.2 show that as the thermal energy decreases, the magnetization increases due to an increase of magnetic order. Because the “force” exerted on a magnetization vector to align with an applied field is proportional to the magnitude of the magnetization, higher degrees of magnetic order brought about by less thermal energy should aid the magnetization in overcoming the magnetocrystalline anisotropy that is present. This increase of magnetization should then require smaller applied fields to force the rotation of the atomic orbitals, thereby explaining (in part) both the downward bend of the magnetostriction curves with

decreasing temperature as well as the shift toward lower temperatures at which the bend occurs.

The other factor that helps to explain these two occurrences is the softening of the elastic moduli, as seen in Section 3.3. The end result of softening moduli is the same as that of increasing magnetization, but the cause differs. As the moduli soften, there exists less of a hindrance to the rotation of the atomic orbital because less stress is needed to move the neighboring atom (i.e. to produce a strain). Less hindrance translates into a smaller magnetic field required to begin the magnetization rotation phase of the magnetostriction curve, causing the behavior of the magnetostriction curves described in the thermal energy discussion above.

The $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$ compound was tested down to 5 K and up to 9 T, the lowest temperature and highest magnetic field of the PPMS system. It was determined that the magnetostriction saturates at a value of approximately -980 ppm, at a magnetic field of 6T and a temperature of 5K. Also shown in Figure 27(f) is that the magnetostriction is essentially the same up to 2T for 5K, 10K, and 15K. Applying a magnetic field of 2T for any of the three temperatures produces a magnetostriction that is approximately 90% of saturation.

A significant difference between the three compositions is the magnitude of $\lambda_{\parallel}$ below 60K, shown in Figure 29. At 20K, the difference between $\lambda_{\parallel} @ 2\text{T}$ of Tb_6FeBi_2 and $\text{Tb}_6\text{Fe}_{0.875}\text{Co}_{0.125}\text{Bi}_2$ is 306 ppm (337%), between $\text{Tb}_6\text{Fe}_{0.875}\text{Co}_{0.125}\text{Bi}_2$ and $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Bi}_2$ is 264.4 ppm (65%), and between $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Bi}_2$ and $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$ is 205 ppm (31%). Overall, an increase of 775.4 ppm (852%) is brought about by doping the parent compound to produce $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$.

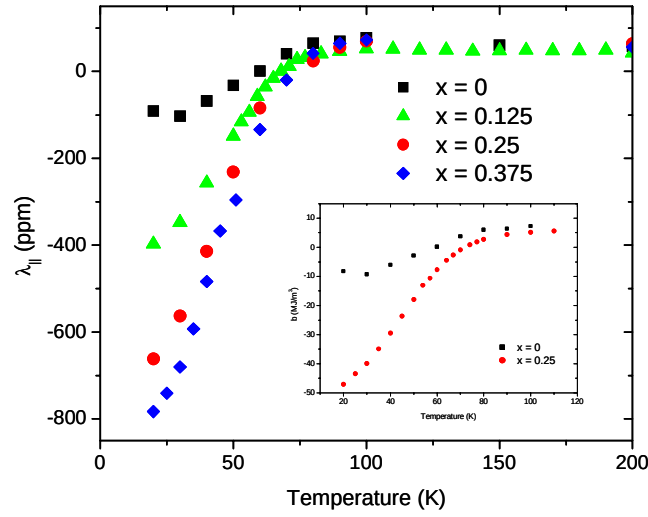


Figure 29: $\lambda_{||}$ at 20 kOe versus temperature for Tb_6FeBi_2 , $\text{Tb}_6\text{Fe}_{0.875}\text{Co}_{0.125}\text{Bi}_2$, $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Bi}_2$, and $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$. Inset: Magnetoelastic coupling versus temperature for Tb_6FeBi_2 and $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Bi}_2$.

It seems that it is not the new structure itself that causes the magnetostriction to increase so dramatically but the transition to the new structure. This is most easily demonstrated by comparing the magnetostriction values at 20 kOe of the cobalt-doped compounds. Each composition transitions to the same structure but the magnetostriction increases greatly with increased cobalt content. A similar finding is shown in the RUS Section 3.3, Figure 25(b). Although the low-temperature atomic structures are the same, the softening increases with increased cobalt content. It is most likely this increased softening that brings about the increased magnetostriction. Softening occurs in RUS because the atoms are in a period of transition and are more disordered. This movement and disorder cause the bonds between atoms to become weaker, thereby decreasing the elastic moduli. Disorder is further increased with the inclusion of cobalt because the cobalt atoms sit on the iron site in a disordered arrangement.

The capability of a material system to transfer energy from the magnetic to elastic systems (and vice versa) is defined as the magnetoelastic coupling. The importance of this coupling can be most easily seen by studying the total energy equation for a 2-D planar magnet, a schematic of which is shown in Figure 30. The total energy is comprised of the Zeeman, anisotropy, magnetoelastic, elastic, and stress energy terms and is given by the following equation

$$\begin{aligned}
 E_{Total} = & \overset{\text{Zeeman}}{-[HM_s\alpha_y]} - \overset{\text{Anisotropy}}{[K\alpha_x^2]} - \overset{\text{Magnetoelastic}}{[b(\epsilon_{xx}\alpha_x^2 + \epsilon_{yy}\alpha_y^2 + \epsilon_{xy}\alpha_x\alpha_y)]} \\
 & + \overset{\text{Elastic}}{\left[\frac{1}{2}C_{11}\epsilon_{xx}^2 + \frac{1}{2}C_{11}\epsilon_{yy}^2 + C_{12}\epsilon_{xx}\epsilon_{yy} + \frac{1}{2}\left(\frac{C_{11}-C_{12}}{2}\right)\epsilon_{xy}^2\right]} + \overset{\text{Stress}}{[\sigma\epsilon_{yy}]}
 \end{aligned} \tag{3.5}$$

where H is the applied magnetic field, M_s is the saturation magnetization, K is the anisotropy constant, α is a normalized component of the magnetization along the appropriate axis, b is the magnetoelastic coupling, ϵ is strain, C is the elastic stiffness, and σ is applied stress. If the magnetoelastic coupling were zero then the only terms that would be affected by applying a magnetic field are the Zeeman and anisotropy energies which have nothing to do with strain. Similarly, if a material with no magnetoelastic coupling is strained, the elastic and stress terms are affected but the magnetization is left unaffected. It is the presence of this magnetoelastic energy term that allows magnetostriction to occur. It is also reasonable that materials with larger magnetoelastic coupling have a greater capacity for magnetostriction due to the increased capability of energy to be transferred from the magnetic to elastic systems.

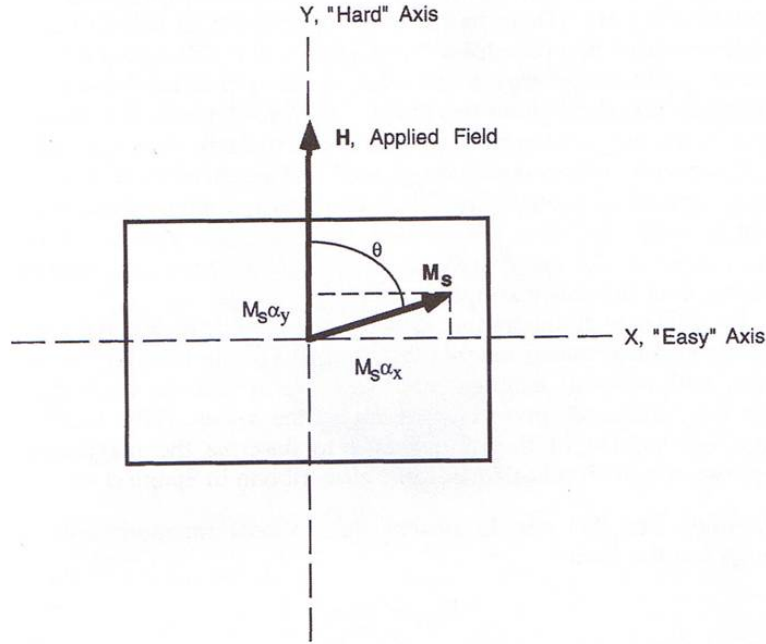


Figure 30: Schematic of a 2-D planar magnet

The elastic and magnetostrictive data presented above allow for an evaluation of the magnetoelastic coupling in these materials, using the following equation for polycrystalline materials:

$$b = \frac{\Delta l}{l} (C_{11} - C_{12}) \left(\alpha^2 - \frac{1}{3} \right)^{-1} = \frac{\Delta l}{l} (2 * C_{44}) \left(\alpha^2 - \frac{1}{3} \right)^{-1} \quad (3.6)$$

where b is the magnetoelastic coupling and α the cosine of the angle between the magnetization and measuring direction ^[1]. When the magnetization is saturated, $\alpha = 1$, and b can be determined accurately. However, as shown in Figures 27(b-e), the magnetostriction does not easily saturate for these compounds, which means that the magnetization does not saturate. Using $\alpha = 1$ and $\Delta l/l$ values at 20 kOe, the values for the magnetoelastic coupling, shown in the inset of Figure 29 for Tb_6FeBi_2 and $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Bi}_2$, are merely meant to provide underestimated approximates rather

than accurate absolute values. The magnetoelastic coupling reflects the composition dependence observed for $\lambda_{||}$, with cobalt-doped compounds having much larger coupling compared to the parent.

It is possible to get a more accurate value for the magnetoelastic coupling with the low temperature, high field magnetostriction data of $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$. The fact that high-field elastic constants could not be determined at very low temperatures for $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$ at first seems very problematic. While the degree of the softening during the low-temperature transitions is suppressed by a magnetic field, the moduli tend to stiffen to similar values regardless of the field applied when cooled to 5 K. This is because softening typically occurs as the material is going through a transition. Once the transition is complete, the moduli tend to stiffen to a value appropriate for the new structure. If a magnetic field does not change the end structure but only alters the transition process, then the elastic moduli for each field should be approximately the same at 5 K because the structure is the same. This is perhaps best illustrated by Figure 25(b). If a c_{44} value of 29.3 GPa is assumed, the magnetoelastic coupling becomes approximately -86 MJ/m^3 . Such large values for $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$ indicate that the large magnetostriction observed at low temperatures is caused by a combination of soft elastic moduli and large magnetoelastic coupling.

3.5 Heat Capacity

Heat capacity is defined as the amount of heat required to change the temperature of a system by a specified amount, typically 1 K. A system is able to store more or less energy when the degrees of freedom of that system increase or decrease, respectively.

When a system is able to store more energy, for example, more energy needs to be supplied to the system in order to increase the temperature.

A slight perspective shift allows for the conceptualization of heat capacity in a possibly easier way. Transitions such as the rearrangement of atoms or the rotation of spins require energy to complete. If a system is using more energy (when compared to a stable state) to undergo a transformation, extra energy is needed to compensate for the expended energy.

Regardless of the way in which the idea of heat capacity is approached, the relation between energy and temperature proves valuable in the study of phase transitions because both an increased capability to store energy and an increased need for energy are represented by an increase of the heat capacity. Because heat capacity is an intensive property, where doubling the volume would double the amount of heat needed to change the temperature, it is typically reported per mole or per gram, giving units of $\frac{J}{mol \cdot K}$ or

$$\frac{J}{g \cdot K}.$$

Figure 31 shows the heat capacity of each of the four compounds plotted together to illustrate the change brought about by cobalt-doping. There are two λ -type anomalies in heat capacity, one that peaks at ~ 70 K and another that peaks at ~ 250 K.

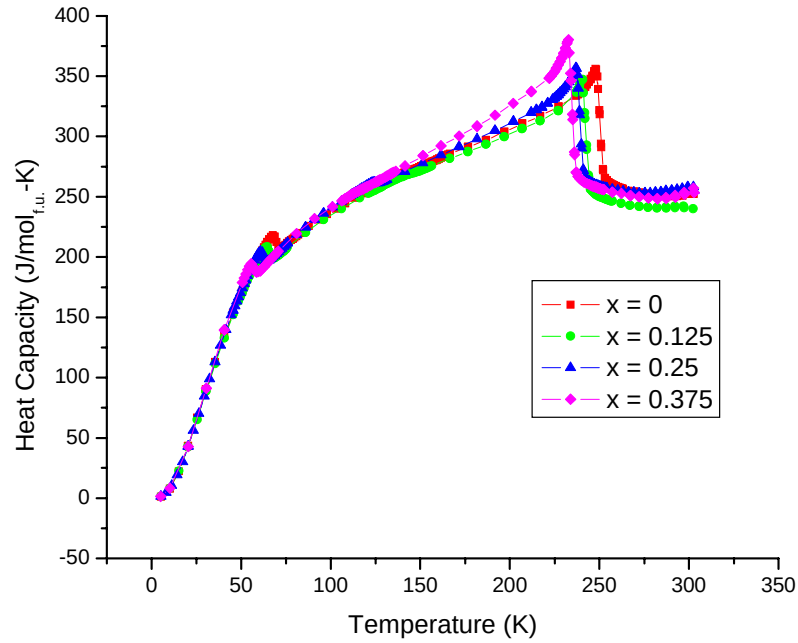


Figure 31: Heat capacity for each bismuth compound

Looking first at the high-temperature transition, the Curie temperatures determined by heat capacity closely match (both qualitatively and quantitatively) the Curie temperatures determined by magnetization measurements for each of the compositions. This comparison is shown in Table 2 with the Curie temperatures from heat capacity determined by selecting the temperature at which the slope begins to rapidly change upon cooling.

Table 2: Comparison of transition temperatures as determined by VSM, XRD, and heat capacity measurements

Composition	High Temperature			Low-Temperature	
	VSM	RUS	Heat Capacity	VSM	Heat Capacity
x = 0	254 K	~250 K	253 K	75 K	70 K
x = 0.125	250 K	~250 K	245 K	70 K	67 K
x = 0.25	245 K	~250 K	242 K	66 K	63 K
x = 0.375	240 K	~250 K	237 K	61 K	58 K

While the heat capacity measurements simply reaffirm what was already determined about the Curie temperature, they provide new insight to the low-temperature transitions. Based on the magnetization measurements and RUS data reported above, we naively assumed that the structural and magnetic low-temperature transitions occurred at different but close temperatures. However, the RUS data which were used to make such an assumption do not allow for a precise determination of the transition temperature. RUS has the temperature resolution needed but has two problems; the large softening of the moduli brought about by a structural change can often hide the smaller softening caused by magnetic transitions and (in the case of these materials) the onset of the softening is very gradual. Due to these issues, heat capacity measurements may give the best insight thus far into the temperatures of these transitions.

Table 2 also shows the comparison made of the low-temperature transition temperatures as determined by VSM and heat capacity measurements. The temperatures at which the transitions are estimated by the two measurement techniques are quite close. It is important to note that there is often some disagreement between results from different measurement techniques. Regardless of the exact transition temperatures, however, they occur at successively lower temperatures with the addition of cobalt. The lack of a second low-temperature anomaly in the heat capacity measurements would seem to indicate that there is either only a magnetic transition (without structural change) present or that the magnetic and structural transitions occur nearly simultaneously.

3.6 Low-Temperature X-ray Diffraction

In order to investigate the possible low-temperature structural transition that was indicated by RUS, XRD measurements were repeated as a function of temperature. Although Morozkin et al., the only group to have studied the parent compound at temperatures below 50 K with neutron data ^[14], make no mention of a structural change, our data clearly reveal a structural phase transition for both the parent and cobalt-doped compounds. Among the reflections revealing this structural change is the (3 0 0), which is shown in Figure 32 for the $x = 0, 0.25$ and 0.375 compounds. In the Co-doped compounds, the (3 0 0) peak clearly splits below 50 K. However, an entirely new peak appears for the parent compound below 40K, indicating that the parent compound undergoes a different structural transition than the cobalt-doped compounds. Tables 3 and 4, which provide information on not only the data collection but also the refinements, reveal that the structure above T_{C2} is $P-62m$ (hexagonal) for each compound while the low-temperature structure is $P1m1$ (monoclinic) for the all compounds, respectively. It is believed that the structure for the parent compound could be $P1$ (triclinic) due to the small differences seen in some reflections (like the (3 0 0) discussed above), but the structure could not be positively determined. As such, all parameters were refined using the $P1m1$ structure.

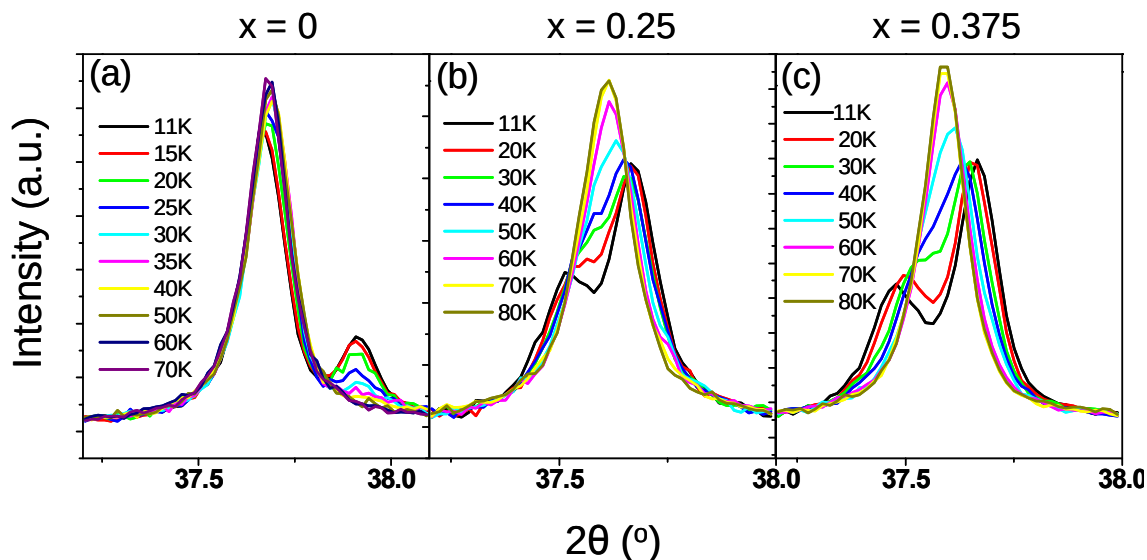


Figure 32: The temperature-dependent behavior of the (3 0 0) peak for (a) Tb_6FeBi_2 , (b) $\text{Tb}_6\text{Fe}_{0.75}\text{Co}_{0.25}\text{Bi}_2$, and (c) $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$

Table 3: XRD data collection parameters and refinement results for $x = 0$ and $x = 0.375$ compounds at 100 K

X-ray - Room Temperature		
	$x = 0$	$x = 0.375$
Powder diffraction data collection:		
Wavelength, Å	1.540598	1.540598
Scan range (degree 2θ)	20-100	20-100
Step size (degree 2θ)	0.017	0.017
Temperature, K	100 K	100 K
Phase		
$\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$	100 wt.%	92.6(6) wt.%
Tb_5CoBi_2	0 wt.%	7.4(4) wt.%
Refinement:		
R-Bragg	6.99	6.99
Goodness of fit, χ^2	0.778	0.83
Software	Fullprof	Fullprof
Variables	17	9
Crystal Data:		
Color	Grey	Grey
Crystal System	Hexagonal	Hexagonal
Space Group	$P-62m$	$P-62m$
a, b (Å)	8.2740(2)	8.2880(1)
c (Å)	4.2004(1)	4.1681(1)
Volume (Å ³)	249.03(1)	247.954(4)
Formula Weight	1427.358	1428.516
Calculated density (g/cm ³)	9.516	9.565

Table 4: XRD data collection parameters and refinement results for $x = 0$ and $x = 0.375$ compounds at 4 K

X-ray - Low Temperature		
	$x = 0$	$x = 0.375$
Powder diffraction data collection:		
Wavelength, Å	1.540598	1.540598
Scan range (degree 2θ)	20-100	20-100
Step size (degree 2θ)	0.017	0.017
Temperature, K	11 K	11 K
Phase		
Tb ₆ Fe _{1-x} Co _x Bi ₂	100 wt. %	93.0(3) wt. %
Tb ₅ CoBi ₂	0 wt. %	7.0(1) wt. %
Refinement:		
R-Bragg	11.6	6.99
Goodness of fit, χ^2	3.08	0.83
Software	Fullprof	Fullprof
Variables	17	9
Crystal Data:		
Color	Unknown	Unknown
Crystal System	Monoclinic*	Monoclinic
Space Group	<i>P1m1</i> *	<i>P1m1</i>
<i>a</i> (Å)	8.2351(7)	8.2970(3)
<i>b</i> (Å)	8.2816(6)	8.2987(3)
<i>c</i> (Å)	4.2082(3)	4.1672(1)
γ (°)	120.134(6)	120.313(1)
Volume (Å ³)	248.21(3)	247.70(1)
Formula Weight	1427.358	1428.516
Calculated density (g/cm ³)	9.548	9.575

* Possibly triclinic, could not be determined. Monoclinic model was used.

The low-temperature XRD also gives an approximate temperature at which the structural changes occur. The general rule of thumb for determining the temperature at which the transition begins is to choose the temperature corresponding to the first XRD peak that drops in intensity. For the cobalt-doped samples, that temperature would be between 50 K and 60 K. The approximate transition temperature is difficult to determine for the parent compound using the above method; instead, the temperature at which the small peak first appears can be used. Such a temperature is most likely between 35 K and

50 K. To be clear, this analysis of the transition temperature is not meant to give definitive temperatures but to provide a general idea as to where to look in other data for changes brought about by the structural transition.

3.7 Neutron Diffraction

While X-ray diffraction is the paramount technique to study structural changes, neutron diffraction has the advantage that it can also probe a material's magnetic structure (or changes thereof). Using the HB2A powder diffractometer at the HFIR facilities at ORNL, we were able to obtain neutron diffraction spectra for our samples at various temperatures. Figure 33 shows three spectra, one at a temperature above the reported Curie temperature, another between the Curie temperature and the low-temperature transitions, and the third below both the low-temperature structural and magnetic transitions for the $x = 0$ parent compound. Tables 5 and 6 summarize the data collection parameters as well as some of the crystal data. Further analysis of the neutron data will be separated into two parts, atomic and magnetic. Because the atomic structure determines what magnetic structures are possible, the atomic structure will be discussed first.

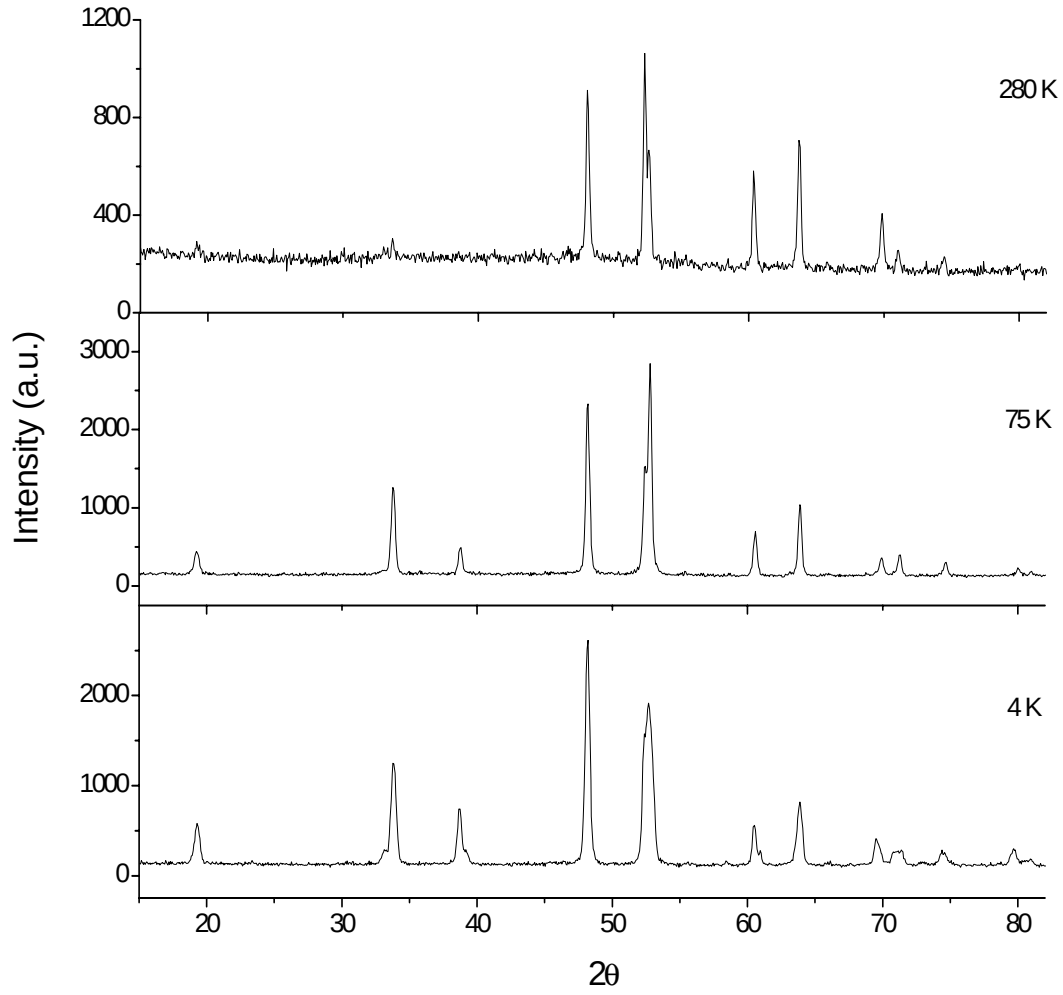


Figure 33: Neutron patterns of Tb_6FeBi_2 at 270 K (above the Curie temperature), 70 K (between the two magnetic transition temperatures), and at 26 K (below the low-temperature magnetic transition temperature)

Table 5: Powder neutron diffraction data collection parameters and refinement results for each compound above T_{C1}

	x = 0	x = 0.125	x = 0.250	x = 0.375
Powder diffraction data collection:				
Wavelength, Å	1.538, 2.41	2.41	2.41	1.538, 2.41
Scan range (degree 2θ)	5-127	8-130	5-127	5-127
Step size (degree 2θ)	0.075	0.075	0.075	0.075
Temperature, K	280 K	300 K	280 K	280 K
Phase	100 wt. %	100 wt. %	100 wt. %	100 wt. %
Refinement:				
<i>R-Bragg</i>				
1.538 Å Pattern	10.2	-	-	3.54
2.41 Å Pattern		14.4	13.6	
Goodness of fit, χ^2	2	1.31	3.5	1.54
Software	Fullprof	Fullprof	Fullprof	Fullprof
Variables	16	18	22	55 [†]
Crystal Data:				
Color	Gray	Gray	Gray	Gray
Crystal System	Hexagonal (60-300K)	Hexagonal (60-300K)	Hexagonal (60-300K)	Hexagonal (60-300K)
Space Group	<i>P</i> -62 <i>m</i>	<i>P</i> -62 <i>m</i>	<i>P</i> -62 <i>m</i>	<i>P</i> -62 <i>m</i>
Volume (Å ³)	250.27(1)	250.27(1)	249.17(1)	248.95(1)
Formula Weight	1427.358	1427.744	1428.13	1428.516
Calculated density (g/cm ³)	9.469	9.471	9.516	9.527

[†] 38 of the 55 are background variables

Table 6: Powder neutron diffraction data collection parameters and refinement results for each compound below T_{C2}

Neutron - Low Temperature				
	x = 0	x = 0.125	x = 0.250	x = 0.375
Powder diffraction data collection:				
Wavelength, Å	1.538, 2.41	1.538, 2.41	2.41	1.538, 2.41
Scan range (degree 2θ)	5-127	8-130	5-127	5-127
Step size (degree 2θ)	0.075	0.075	0.075	0.075
Temperature, K	4 K	4 K	4 K	4 K
Phase	100 wt. %	100 wt. %	100 wt. %	100 wt. %
Refinement:				
<i>R-Bragg</i>				
1.538 Å Pattern	6.92	4.54	-	7.15
2.41 Å Pattern	4.63	3.24	4.68	4.23
Goodness of fit, χ^2	4.93	1.2	3.44	4.39
Software	Fullprof	Fullprof	Fullprof	Fullprof
Variables	53	52	35	52
Crystal Data:				
Color	Unknown	Unknown	Unknown	Unknown
Crystal System	Monoclinic (4-60K)*	Monoclinic (4-60K)	Monoclinic (4-60K)	Monoclinic (4-60K)
Space Group	<i>P1m1</i> *	<i>P1m1</i>	<i>P1m1</i>	<i>P1m1</i>
Volume (Å ³)	248.12(2)	248.67(1)	247.70(1)	247.44(2)
Formula Weight	1427.358	1427.744	1428.13	1428.516
Calculated density (g/cm ³)	9.551	9.533	9.573	9.585

* Possibly triclinic, could not be determined. Monoclinic model was used.

3.7.1 Atomic Model

At 280 K and 100 K, our neutron spectra match closely with those put forth by Morozkin et al. ^[14]. As expected from the previous work, the data can be fitted with a hexagonal crystal structure for both temperatures. The unit cell information at temperatures above the Curie temperature is given in Table 7. Based solely upon the room-temperature data, there appears to be an expansion of a and contraction of c with the addition of cobalt, resulting in an overall decrease of volume. This behavior agrees with the XRD data previously collected at room temperature. The fitting factors are admittedly higher than desirable and are most likely due to low peak intensity as shown at 280K in Figure 33. The results do, however, closely match those found in literature for the parent compound, with the largest deviation of 0.5% occurring for the volume; all other parameters differ by less than 0.3% ^[14].

Table 7: Lattice parameters a and c , c/a , volume, and R-factor as determined by neutron diffraction above the Curie temperature

Composition	T (K)	a (Å)	c (Å)	c/a	V (Å ³)	R_F
$x = 0$	280	8.2892(1)	4.2058(1)	0.50738	250.3	10.2
$x = 0.125$	300	8.2991(2)	4.1957(1)	0.50556	250.3	14.4
$x = 0.25$	280	8.2956(2)	4.1809(1)	0.50399	249.2	13.6
$x = 0.375$	280	8.3002(2)	4.1726(1)	0.50270	249.0	8.08

As discussed in the low-temperature XRD section, below 100 K a structural change from hexagonal to monoclinic occurs that is not reported in literature. This structural change is seen in the neutron data as well. As is shown in Table 8, the deviation from hexagonal to monoclinic is subtle. The two parameters that can change for a transition from hexagonal to monoclinic to occur is the deviation of γ from 120°

and the deviation of a from b . The only compound for which a and b become noticeably different is the parent compound, which has a difference of 0.5%. While that may seem to be a very small difference, the variation between a and b for the cobalt-doped compounds does not exceed 0.02%. Conversely, γ increases with increasing cobalt content, reaching a maximum of 120.3° in the $x = 0.375$ compound.

Table 8: Lattice parameter data of the new low-temperature structure as determined by neutron powder diffraction

Composition	T (K)	A ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	c/a	γ ($^\circ$)	V ($\text{\AA}^3$)	R-Bragg	R _F
x = 0	4	8.2390(6)	8.2812(3)	4.2069(2)	0.5106	120.183(6)	248.1	4.63	2.93
x = 0.125	4	8.2829(4)	8.2844(4)	4.1917(1)	0.5061	120.186(1)	248.6	3.24	2.09
x = 0.25	4	8.2875(1)	8.2857(2)	4.1769(1)	0.5040	120.277(2)	247.7	4.68	2.54
x = 0.375	4	8.2937(4)	8.2930(4)	4.1681(1)	0.5026	120.331(1)	247.4	4.23	2.12

While the structural transition can be seen by looking at the pattern as a whole, the similarities and differences between the parent and doped compounds are easier to discuss by focusing on a single peak. Figures 34(a) and (b) show the (3 0 0) peak of the $x = 0$ and 0.375 compounds as determined by neutron diffraction, respectively. Figures 34(c) and (d) show the same peak for the same compounds, respectively, but as determined by XRD. As can be seen, the neutron data matches the XRD data very well. Approximate structural transition temperatures are determined to be between 30K and 40K for the parent compound and between 50 K and 60 K for the $x = 0.375$ compound. It should also be noted that the samples used for the XRD and neutron studies are different, indicating a reproducibility of results with respect to the structural transition.

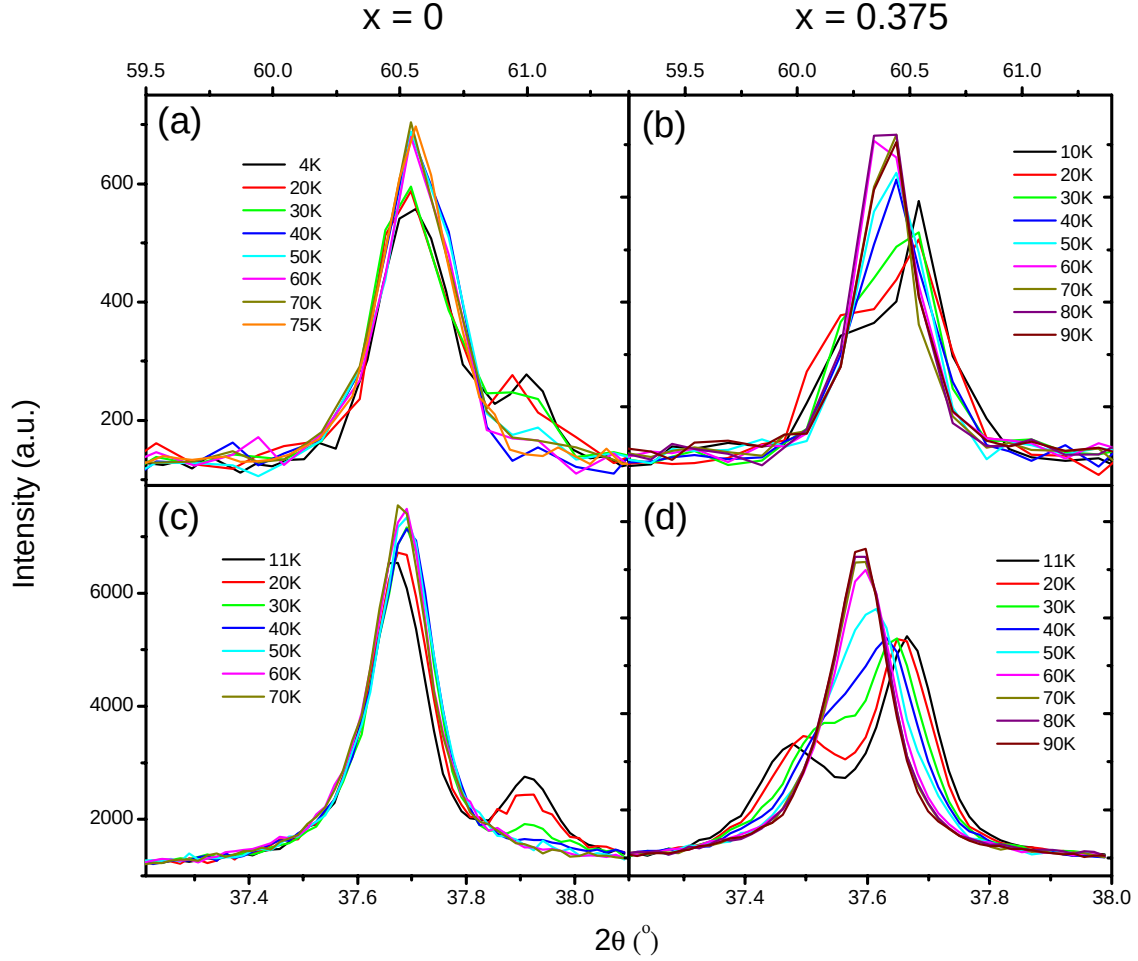


Figure 34: Neutron pattern of the (3 0 0) peak for (a) $x = 0$ and (b) $x = 0.375$. XRD pattern of the (3 0 0) peak for (c) $x = 0$ and (d) $x = 0.375$.

The difference in the structure between the doped and un-doped compounds observed with XRD is also present in the refinements of the neutron data. Figure 35 shows the lattice parameters a and b as a function of temperature for each of the four compounds. While the basal-plane lattice parameters of the cobalt-doped compounds remain nearly equal below the structural transition temperature, there is a pronounced separation for the parent compound. The first temperature at which this separation becomes prominent is 30 K, the same temperature at which the new peak first appears next to the (3 0 0) reflection in the raw data.

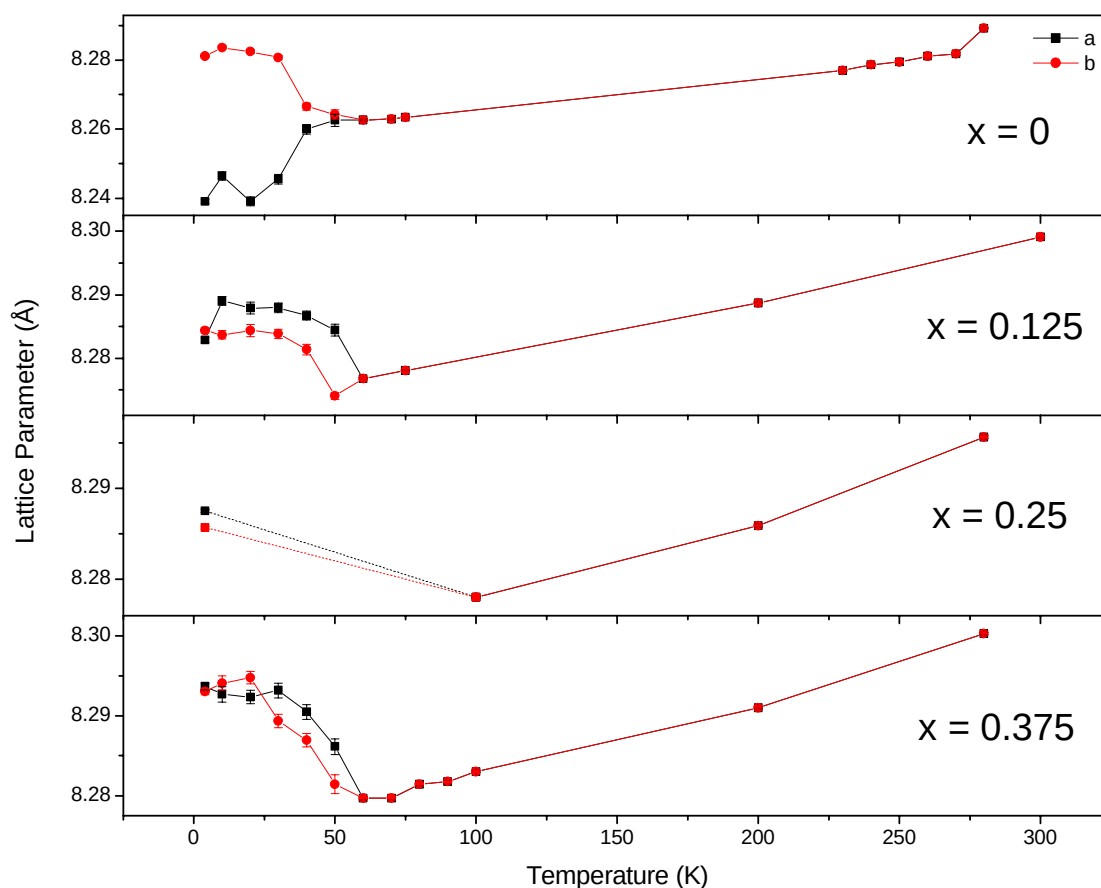


Figure 35: Lattice parameters for each of the four compounds, as listed. The hexagonal model was used from 300 K to 60 K while the monoclinic model was used at 50 K and below.

There is also a pronounced increase of the c parameter at 30 K for the parent compound (shown in Figure 36) that is not present in the cobalt-doped compositions. Each of the cobalt-doped compounds has similar behavior, a slight contraction along the c -axis with decreasing temperature from 300 K to 100 K, followed by a slight expansion coinciding with the structural transition. There is also an overall contraction along the c -axis with increased cobalt doping.

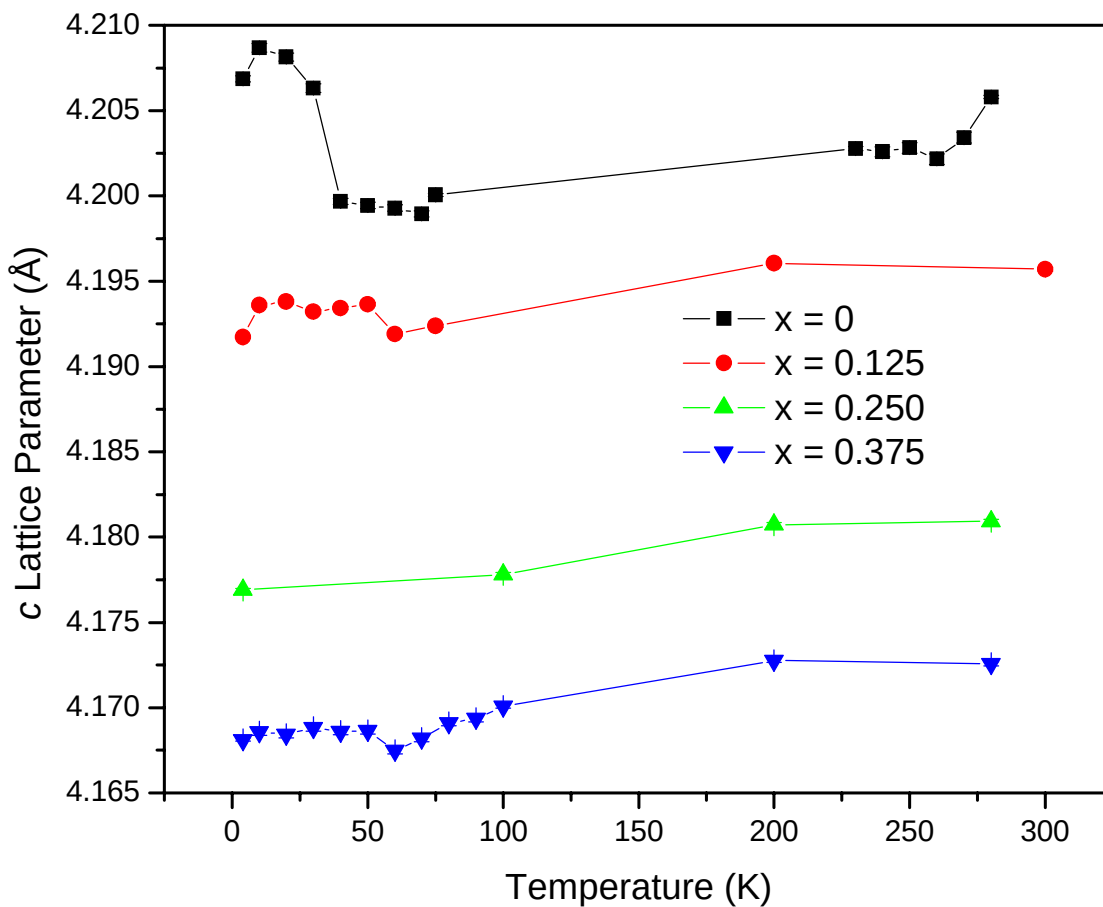


Figure 36: Lattice parameter c as a function of temperature for each of the four compounds

The angle β between the basal-plane axes increases with decreasing temperature for each of the compounds; this increase becomes larger as the doping exceeds $x = 0.125$. This behavior is shown in Figure 37.

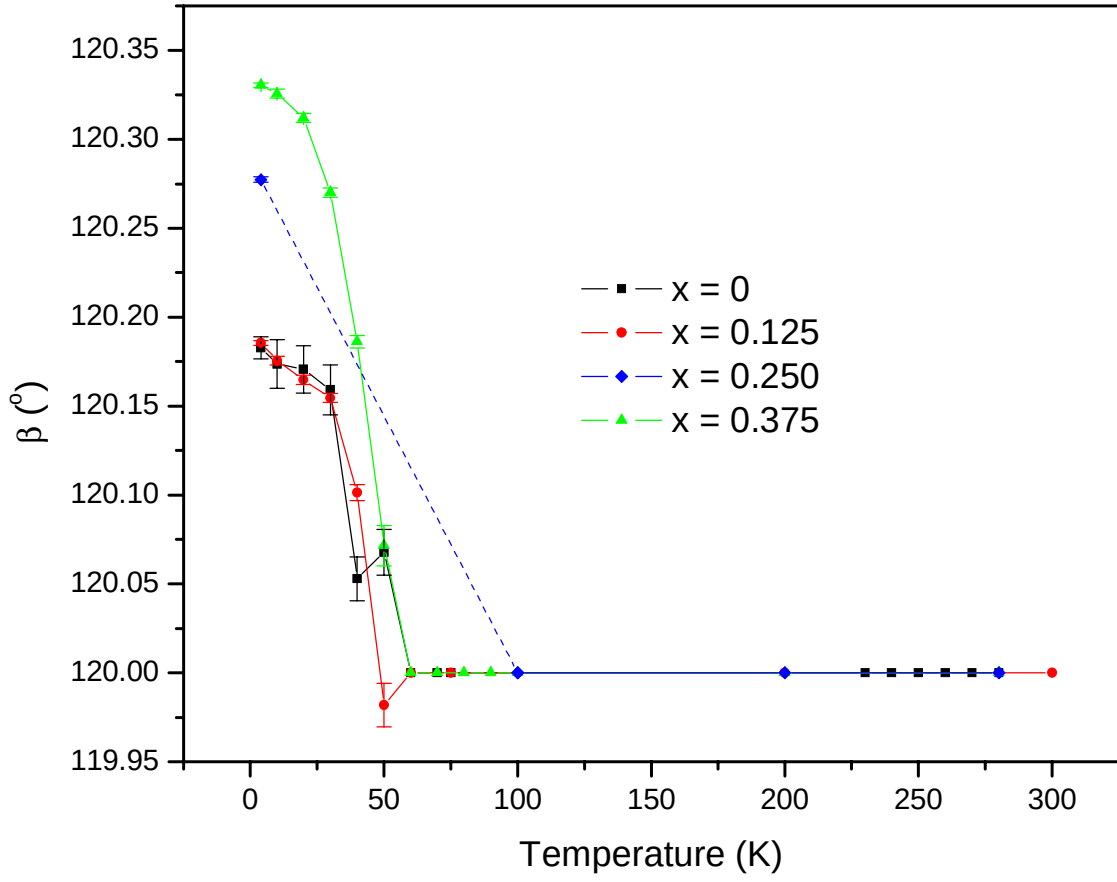


Figure 37: The angle between the a and b lattices for each of the compounds

Finally, the atom positions for each compound are given in Table 9. Although all compounds other than the parent contain cobalt, there is no mention of cobalt in Table 9. Because the cobalt atoms randomly replace the iron atoms, the iron and cobalt sites are treated as the same.

Table 9: Atom positions for each compound as determined by neutron diffraction

x = 0						
	x	y	z	x = 0.125	x	z
Tb1	0.235(7)	-0.008(8)	0	Tb1	0.241(6)	-0.011(5)
Tb2	-0.003(9)	0.225(9)	0	Tb2	0.011(6)	0.234(5)
Tb3	0.770(7)	0.751(7)	0	Tb3	0.778(7)	0.756(5)
Tb4	-0.018(8)	.577(7)	0.5	Tb4	-0.001(6)	0.597(4)
Tb5	0.626(8)	-0.007(8)	0.5	Tb5	0.606(6)	-0.017(5)
Tb6	0.423(8)	0.414(7)	0.5	Tb6	0.425(5)	0.402(4)
Fe1	0.00(1)	0.017(8)	0.5	Fe1	0.013(6)	-0.026(4)
Bi1	0.665(7)	0.31(1)	0	Bi1	0.681(9)	0.324(5)
Bi2	0.34203	0.6654	0	Bi2	0.34203	0.6654
x = 0.25						
	x	y	z	x = 0.375	x	z
Tb1	0.232(7)	0.000(9)	0	Tb1	0.247(5)	0.006(5)
Tb2	0.021(7)	0.27(1)	0	Tb2	0.005(5)	0.243(5)
Tb3	0.772(7)	0.779(9)	0	Tb3	0.783(5)	0.769(5)
Tb4	0.009(8)	0.63(1)	0.5	Tb4	0.008(5)	0.589(5)
Tb5	0.592(8)	0.01(1)	0.5	Tb5	0.625(5)	0.009(5)
Tb6	0.414(6)	0.40(1)	0.5	Tb6	0.405(5)	0.407(5)
Fe1	0.040(5)	0.018(8)	0.5	Fe1	0.045(4)	0.008(5)
Bi1	0.67316	0.34113	0	Bi1	0.682(7)	0.344(7)
Bi2	0.34203	0.6654	0	Bi2	0.34203	0.6654

3.7.2 Magnetic Model

In much the same way that the high-temperature data corroborates the hexagonal unit cell, so too is the paramagnetic model confirmed above ~ 250 K. However, below the Curie temperature, the refinement of our neutron diffraction data deviates from the study reported by Morozkin^[14]. While the ferromagnetic alignment of the terbium atoms agrees with [14], our neutron diffraction data indicate that there is a magnetic moment on the iron site that aligns antiparallel with the terbium moments, as shown in Figure 38 (b). This ferromagnetism between terbium atoms and ferrimagnetism between iron and terbium is not uncommon^[39-41].

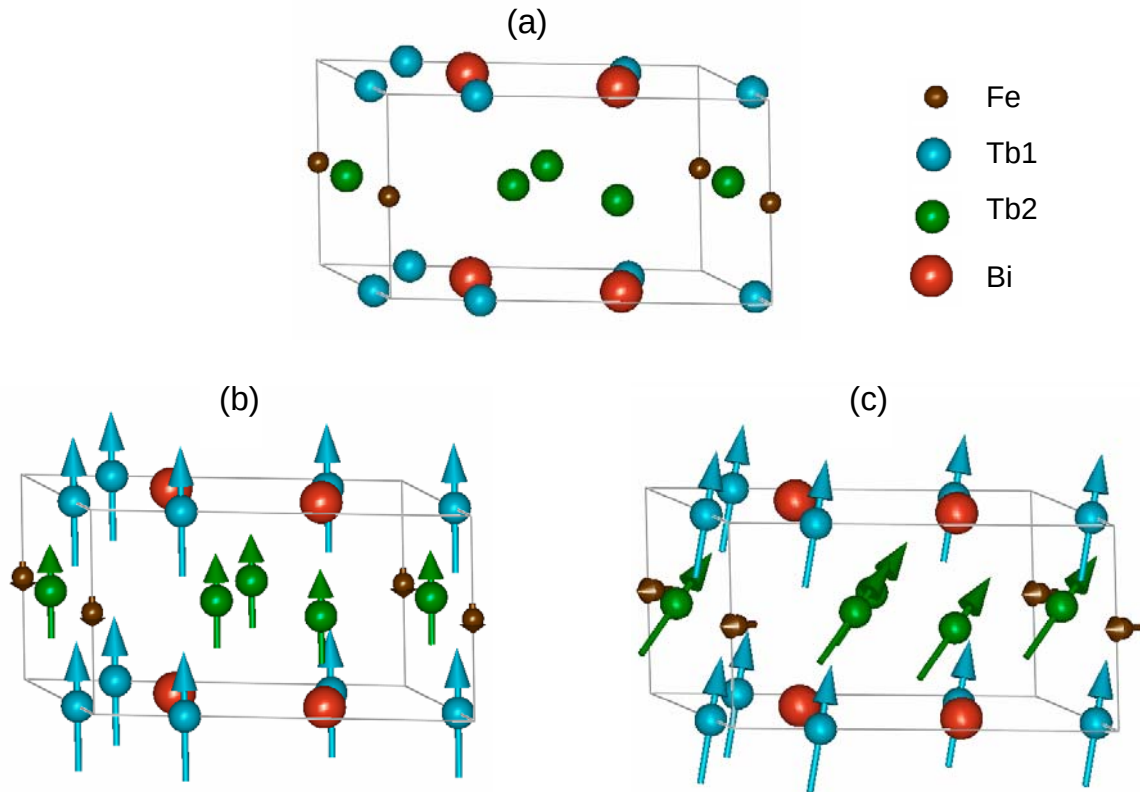


Figure 38: (a) The unit cell of Tb_6FeBi_2 . (b) The ferrimagnetic collinear magnetic structure at 75 K. (c) The ferrimagnetic non-collinear magnetic structure at 4 K.

The detection of the aforementioned structural change is very important with regard to determining the low-temperature magnetic structure. The magnetic moments are confined to either the basal plane or the c -axis for the space group $P-62m$ (in this case, the c -axis). Upon transformation to the monoclinic $P1m1$, the moments are free to have components in both the c -axis and basal plane. Analyzing the data with this new degree of freedom changes the results drastically and provides insight into the magnetic interactions present. This new non-collinear magnetic structure is shown in Figure 38 (c).

It should be noted that the moments along the a and b directions in the basal plane cannot be resolved and have been set as equal in this analysis. This is due to overlapping contributions from equivalent planes, or powder averaging. Ideally, this should not be the case with a monoclinic system because planes such as the $(1\ 0\ 0)$ and $(0\ 1\ 0)$ are no longer equivalent. The separation of the a and b parameters is so small in our samples, however, that resolving the contributions from each of the different planes is not possible.

Under the assumption that the moments are equal along the a and b directions, both the magnitude of the moment and the angle with respect to the c -axis were determined for each of the magnetic atom sites (two terbium, one iron). These results are shown for all four compounds at 4 K in Table 10 and at all temperatures measured in Figure 39. The magnetic moment is not determined separately for the cobalt atoms because the iron site is a disordered mix of iron and cobalt atoms. As such, the moment on the iron site is an average of the moments of the two types of atoms. The moments on both the Tb1 and Tb2 sites increase with decreasing temperature until saturation is achieved near 10 K. Because the moments are constrained to the c -axis until the

structural transition occurs, the angle θ increases rapidly from 60 K to 50 K. The angle then continues to increase below 50 K but at a slower rate.

Table 10: The magnitude and angle θ made with respect to the c-axis for each of the three atomic sites at 4K as determined by powder neutron diffraction

Composition	Tb1		Tb2		Fe		R-Magnetic
	Magnitude (μ_B)	θ ($^\circ$)	Magnitude (μ_B)	θ ($^\circ$)	Magnitude (μ_B)	θ ($^\circ$)	
x = 0	8.8(3)	15(1)	9.3(6)	46(2)	-2(4)	90(5)	4.84
x = 0.125	8.9(2)	18(1)	8.9(5)	51(1)	-1.6(6)	66(7)	3.03
x = 0.25	9.1(3)	16(1)	9.1(6)	46(2)	-1.6(5)	49(11)	4.58
x = 0.375	9.1(2)	14(1)	9.2(4)	44(1)	-1.6(6)	66(8)	3.48

Figure 40 is provided in order to clarify the notation used to report the Fe magnetic moment and angle. As is shown, the moment is reported as negative in Table 10 and Figure 39 because it falls below the horizontal axis. The angle is then reported as the distance from the negative c-axis, with a positive value indicating a clockwise measurement. One more note of interest is the x-axis label “60° from *a* and *b*”. Because the magnetic component had to be set as equal for the *a* and *b* axes, the vector describing the magnetic moment lies directly between the two.

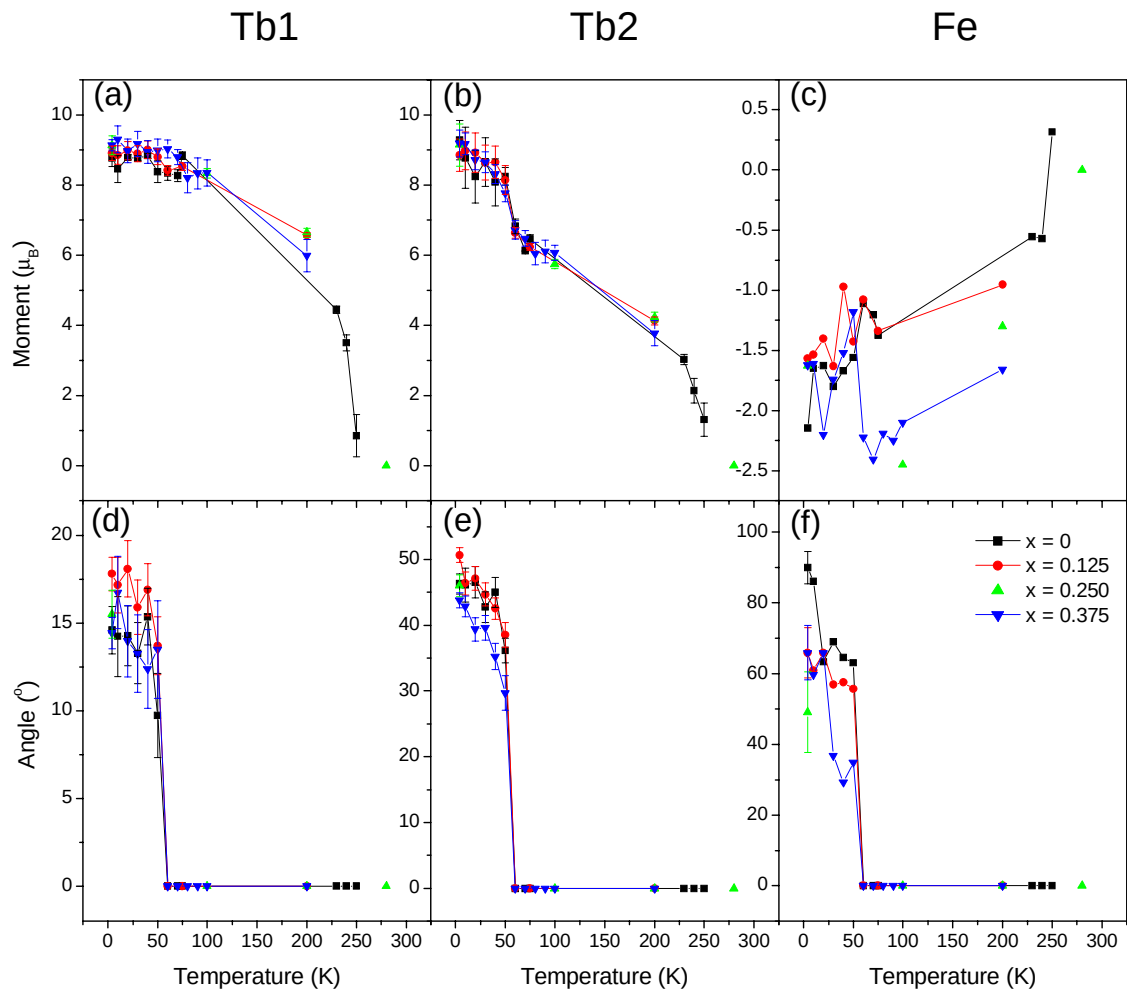


Figure 39: The moment on the (a) Tb1, (b) Tb2, and (c) Tb3 sites. The angle θ made with respect to the c-axis for the (d) Tb1, (e) Tb2, and (f) Fe sites

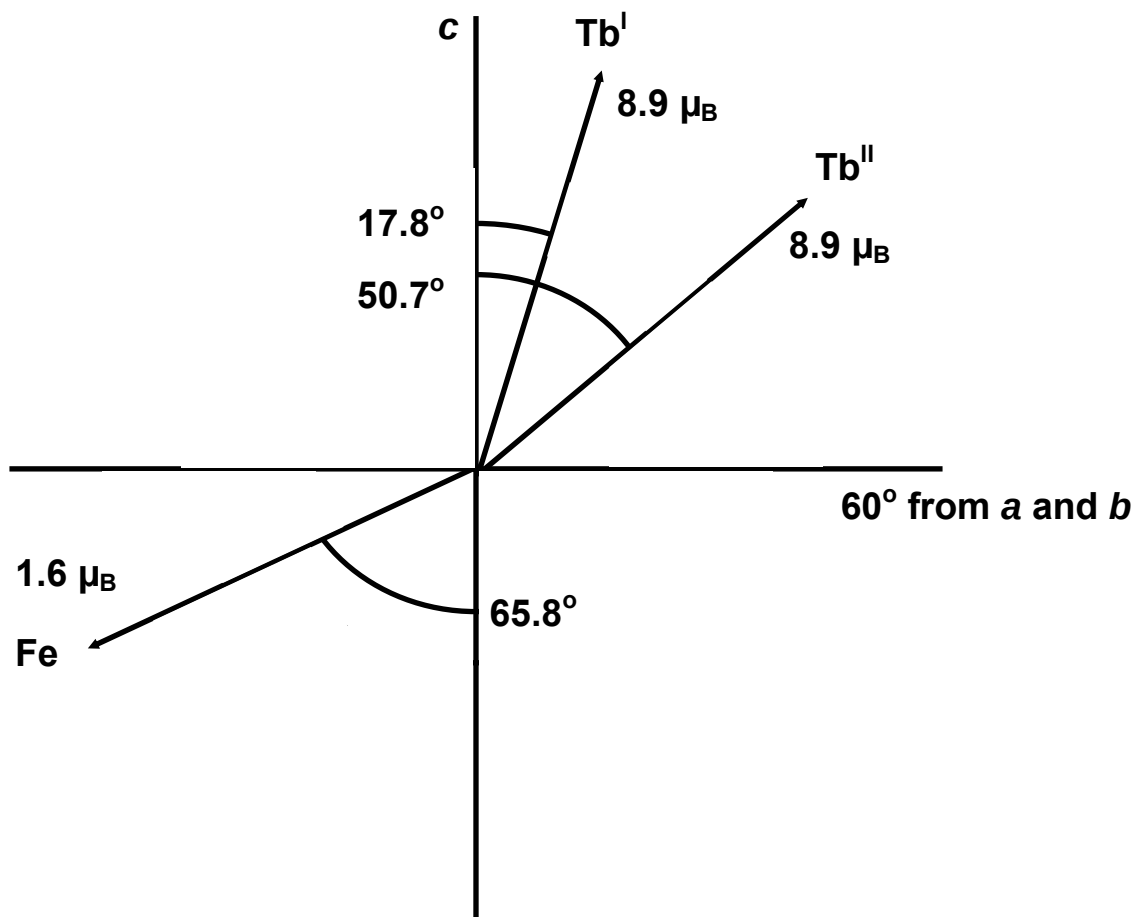


Figure 40: Orientation of $\text{Tb}_6\text{Fe}_{0.875}\text{Co}_{0.125}\text{Bi}_2$ magnetic moments at 4K

The iron site behaves similarly to the two terbium sites. The magnitude of the moment increases as the temperature decreases. Unfortunately, the moment on the iron site is not as well determined as the moments on the terbium sites. Because of this, little else can be said of the magnitude of the iron moments.

Much like the moment on the iron site, the angle θ is not as well determined for the iron site as for the terbium sites. Fortunately, the results are well-enough determined at 4 K to make an observation. There is a large difference between the θ angles that the iron moments make with respect to the *c*-axis when comparing the undoped and

cobalt-doped compounds. The cobalt-doped compounds have θ values that fall into the same range when including error bars. The parent compound, however, lies much higher than the others at approximately 90° .

A plausible explanation for the orientation of the magnetic moments utilizes two previously mentioned findings. First, iron has been known to interact antiferromagnetically with terbium while terbium atoms interact ferromagnetically with each other. Second, once the orientation of the magnetic moments is unrestrained to a single direction upon transformation to monoclinic symmetry, the iron and Tb1 moments move to align along the basal plane. As such, the iron and Tb1 moments remain largely antiparallel. The ferromagnetic interaction between Tb1 and Tb2 moments keeps Tb1 from aligning completely parallel to Fe. The canted nature of the Tb1 moments also works to cant the Tb2 moments away from the c-axis.

This sort of magnetic arrangement is not unprecedented. The rhombohedral system ErFe_3 has been found to have two inequivalent Er sites and one Fe site ^[42]. The two Er sites have different easy axes, one along the c-axis and the other in the basal plane. The Fe site also has an easy axis along the basal plane. It was determined that “at any temperature the magnetic structure is determined by competition between (i) the Er-Fe exchange interactions which probably favor a ferrimagnetic collinear structure and (ii) the anisotropies of the Er^{I} , Er^{II} , and Fe sites” ^[42]. This competition results in the magnetic alignment shown in Figure 41, which closely resembles our findings in Figure 40.

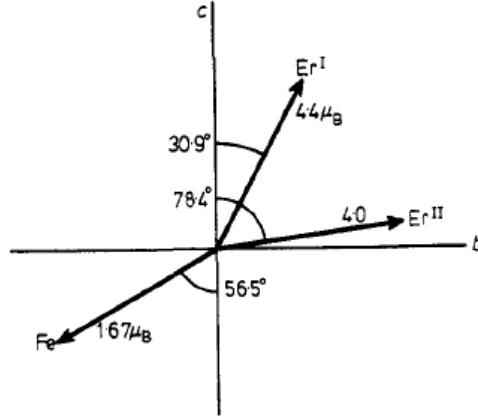


Figure 41: The orientation of the magnetic moments of ErFe_3 ^[42]

4. Conclusions

Capacitance dilatometry has been used to determine the magnetostrictive qualities of the $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ family of compounds. A variety of measurement techniques were employed to further explain the magnetostriction findings, resulting in the following conclusions:

- (1) VSM experiments revealed the presence of two magnetic transitions, one at $T_{C1} \sim 250$ K and another at $T_{C2} \sim 60$ K. Neutron diffraction experiments revealed that the magnetic structure changes from paramagnetic to a collinear ferrimagnetic ordering of the terbium and iron moments at T_{C1} . The transition at T_{C2} causes the moments on each site to cant away from the c-axis by differing amounts.
- (2) Low-temperature XRD and neutron diffraction experiments also revealed the presence of a previously unreported structural transition at approximately the same temperature as T_{C2} . Refinements on the data showed that the low temperature structure changes with Co-doping. The parent compound most likely transforms from a hexagonal to triclinic structure while the cobalt-doped compounds transform from a hexagonal to

monoclinic structure ($P1m1$).

(3) Capacitance dilatometry experiments showed that there is negligible magnetostriction above ~ 100 K. Below 100 K, however, the magnitude of the magnetostriction increases with decreasing temperature and increased cobalt content. The maximum magnetostriction achieved was approximately -980 ppm, at a magnetic field of 6 T and a temperature of 5 K.

(4) RUS measurements showed a gradual softening as the compounds were cooled below T_{C1} until approaching a temperature near T_{C2} , at which point the softening became much more pronounced. The softening also increased with the continued addition of cobalt. This large degree of softening is linked to the structural change.

(5) The elastic softening, resulting in large amounts of magnetoelastic coupling, allows the magnetostriction to reach such large values at low temperatures. This elastic softening (and by extension, the magnetostriction) is enhanced by the addition of cobalt due to the increased disorder in the system.

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Vita

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After receiving his M.S., Michael continued in Dr. Keppens lab as a Ph.D. student in Materials Science and Engineering. His research involved the search for and characterization of giant magnetostrictive materials using techniques such as (but not limited to) RUS, capacitance dilatometry, and neutron diffraction. During his time working toward his Ph.D., he was not only a research assistant but also a teaching assistant for multiple undergraduate laboratories. Michael completed his Ph.D. in Materials Science and Engineering in July 2012.