Spin reorientation and magnetoelastic coupling in $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ ($x = 0, 0.125, 0.25$, and 0.375) alloy system.

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Tb_6FeBi_2 adopts a noncentrosymmetric crystal structure and orders ferromagnetically at $T_{C1} = 250$ K with an additional magnetic transition at $T_{C2} = 60$ K. The low temperature magnetoelastic response in this material is strong, and is enhanced by cobalt substitution. Here, the temperature dependence of the atomic and magnetic structure of $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ ($x = 0, 0.125, 0.25$, and 0.375) is reported from powder X-ray diffraction (XRD) and powder neutron diffraction (PND) measurements. Below the Néel temperature a ferrimagnetic ordering between the terbium and iron moments exists in all compounds studied. Related to the enhanced magnetostructural response, the Co-doped compounds undergo a crystallographic phase transition below about 60 K. This transition also involves a canting of the magnetic moments away from the c-axis. The structural transition is sluggish and not fully completed in the parent Tb_6FeBi_2 compound, where a mixture of monoclinic and hexagonal phases is identified below 60 K. The spin reorientation transition is discussed in terms of competing exchange interactions and magnetocrystalline anisotropies of the two Tb sites and Fe/Co sublattices.

1. INTRODUCTION

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 and belong to the non-centrosymmetric space group $P-62m$.^{1, 2} Whereas many of these compounds show ferromagnetic order, Tb_6FeBi_2 and Tb_6FeSb_2 are most noteworthy, as their Curie temperatures are only slightly below room temperature.³⁻⁵ The multi-sublattice nature of this rare-earth-transition-metal alloy is likely to result in competing anisotropies and exchange interactions that can yield complex temperature and field dependent phase diagrams.⁶⁻⁹ In addition, the non-centrosymmetric character of space group $P-62m$ is expected to lead to exotic magnetic properties: the lack of inversion symmetry allows Dzyaloshinskii-Moriya (DM) spin-orbit interactions, which are known to lead to chiral magnetic order and the formation of skyrmions.¹⁰⁻¹²

In addition to interest in the complex, non-collinear magnetism that can arise in non-centrosymmetric crystal structures, R_6TX_2 materials have potential technological applications for magnetic refrigeration.⁴ A neutron diffraction study by Morozkin et al. revealed that Tb_6FeBi_2 remains hexagonal at all temperatures while undergoing two magnetic transitions: at $T_{C1} = 250$ K, the Tb moments were found to align ferromagnetically along the c -axis and at $T_{C2} = 60$ K, the Tb moments form an incommensurate magnetic structure with a propagation vector of $[0, 0, 0.35]$ that coincides with the c -axis.⁵ In this low-temperature magnetic ordering, the Tb moments cant by approximately 6° from the c -axis.⁵

Recently, we initiated a comprehensive study of the elastic, magnetic, and structural properties of $Tb_6Fe_{1-x}Co_xBi_2$ with $x = 0, 0.125, 0.25$, and 0.375 .^{13, 14} While our

results confirm the existence of two magnetic transitions, the large elastic softening observed at T_{C2} hints that a structural transition may accompany the second magnetic transition. Preliminary XRD did indeed show a splitting of the (3 0 0) peak in the cobalt-doped compounds below T_{C2} . In the present paper, we report a thorough structural study of the $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ series, using both XRD and neutron diffraction as a function of temperature. These measurements allow for a complete refinement of the atomic and magnetic structure and reveal that a ferrimagnetic ordering between the terbium and iron moments exists in all compounds studied. The second magnetic transition corresponds to a spin reorientation in a spin-canted magnetic structure. This is accompanied by a structural transition from hexagonal to monoclinic, which is sluggish and not fully completed in the parent Tb_6FeBi_2 compound, where a mixture of monoclinic and hexagonal phases is identified below 60 K.

2. EXPERIMENTAL DETAILS

Polycrystalline ingots of each compound used in this study were synthesized by melting appropriate amounts of Tb, Co, Fe, and Bi using a plasma arc melter under Ar atmosphere. Excess Bi was added to compensate for the amount lost during melting. Each compound was arc-melted on a water-cooled copper hearth and flipped two additional times in order to ensure chemical homogeneity. The ingots were then wrapped in Ta foil, sealed in evacuated quartz tubes and annealed. The samples were annealed at 827°C for seven days, followed by an additional five days of annealing at 500°C. Upon completion of the heat treatment, the samples were quenched in an ice water bath. Room temperature X-ray diffraction analysis confirmed that the samples were nearly single

phase. Comparison of X-ray diffraction intensities limits the impurity concentration to approximately 2%. The impurity phases could not be positively identified. The diffraction peaks are sharp and can be indexed with the hexagonal Zr_6CoAs_2 structure.¹³

For phase identification, a Philips Materials Research Diffractometer with a curved graphite crystal monochromator was utilized. $\text{Cu K}_{\alpha 1}$ radiation, 45 kV, 40 mA, and a 0.4° divergent slit were used to collect diffraction data with 2θ between 10 - 70° with a 0.02° step size for 50 minutes. X'Pert High Score Plus and PowderX¹⁵ 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 - 2θ 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. $\text{Cu K}_{\alpha 1}$ radiation, 40 kV, 30 mA, and a 0.5° divergent slit were used to collect diffraction data with 2θ between 20 - 100° with a step size of 0.017° . Fullprof was used for data analysis.¹⁶

Powder neutron 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 monochromator. For data collection, a detector array consisting of 44 ^3He tubes was scanned in two segments to cover the total 2θ 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. 17. 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). Crystal and magnetic structure refinements were performed using FullProf.¹⁶

3. RESULTS AND DISCUSSION

3.1. Crystallographic Structure

In order to confirm the low-temperature structure of the parent compound, careful XRD and neutron diffraction data were collected on a high purity sample using the set-up described above. While X-ray diffraction is a powerful technique to study structural changes, neutron diffraction has the advantage that it can also probe a material's magnetic structure (or changes thereof). Figure 1 shows three PND spectra obtained for the parent compound: the first spectrum was obtained at 280 K, i.e. above the Curie temperature T_{C1} ; the second pattern was obtained at 75 K, between the Curie temperature and the low-temperature magnetic transition T_{C2} ; and the third spectrum was recorded at 4 K, below T_{C2} . Tables I and II summarize the data collection parameters as well as some of the crystal data. For $x = 0, 0.125$, and 0.375 , refinements were performed on a combination of $1.54 \text{ \AA}$ and $2.41 \text{ \AA}$ data. At 280 K and 75 K, our neutron patterns match closely with those reported by Morozkin et al.⁵ As expected from the previous work, the data can be fit with a hexagonal crystal structure (described by the noncentrosymmetric space group $P-62m$) at both 280 K and 75 K. The unit cell information at temperatures above the Curie temperature is given in Table III. The largest deviation from Ref. 5, 0.5%, occurs for the volume; all other parameters differ by less than 0.3%.⁵ One particularly interesting aspect of the crystal structure is the distribution of the Tb atoms

over two inequivalent Wyckoff positions, 3g and 3f, with a different coordination environment. While the Tb1 is tetrahedrally coordinated by two Fe and two Bi atoms, the Tb2 has square pyramidal coordination (with a coordination number of five: four Bi and one Fe). The different coordination geometries are likely to lead to rather different crystal field anisotropies for the magnetic ions occupying the two positions. A view of the Tb₆FeBi₂ crystal structure, with different coordination geometries for the two non-equivalent Tb sites, is shown later in the paper as part of Figure 5.

The data reported by Morozkin⁵ for the $x = 0$ compound showed that the observed transitions at T_{C1} and T_{C2} are magnetic in character. However, our data clearly show that the lower transition is accompanied by a structural distortion, as illustrated in Figure 2. Powder X-ray diffraction was used to examine the low temperature crystal structure of the material without the complications which arise from the magnetic scattering. However, refinements of the 11 K X-ray data on Tb₆FeBi₂ are not trivial, as neither a single hexagonal nor a single monoclinic structure can model the data. An acceptable model is obtained with a mixed-phase analysis, comprised of approximately 37% of the hexagonal phase $P-62m$ and 63% of the monoclinic phase $P1m1$ (which is a subgroup of $P-62m$). It may be noted that this mixed phase was not detected in our previous study of Tb₆FeBi₂.¹³ Tb₆FeBi₂ is likely near the structural instability, and this instability is enhanced by cobalt doping. The observation of different behaviors in nominally undoped Tb₆FeBi₂ samples suggests some variation in composition exists between them, possibly caused by the vaporization of bismuth during arc melting. Supporting this, we note that there is a small difference in lattice parameters determined at 100 K between the sample

studied here ($a = b = 8.2688(8) \text{ \AA}$, $c = 4.2015(4) \text{ \AA}$) and the sample studied in Ref. 13 ($a = b = 8.2741(1) \text{ \AA}$, $c = 4.2004(1) \text{ \AA}$).

Refinement of the low temperature data for the Co-doped compounds is more straightforward, as these compounds undergo a full structural transition to the monoclinic $P1m1$ structure. It is worth noting that structural refinements in other subgroups of the parent $P-62m$ space group (e.g. Cm and $C2$) were also attempted but the results were not satisfactory.

This structural transition was revealed earlier using XRD¹³ and is now confirmed by PND data. As is shown in Table IV, the deviation from hexagonal to monoclinic is subtle for the doped compounds. The two lattice parameters that can change for a transition from hexagonal to monoclinic to occur are the deviation of β from 120° and the deviation of a from b . The variation between a and b for the cobalt-doped compounds does not exceed 0.02%. Among the cobalt-doped compounds, β increases with increasing cobalt content, reaching a maximum of 120.33° in the $x = 0.375$ compound. Interestingly, the value of β for the monoclinic phase of the parent compound, however, does not follow the trend and falls within the range of values determined for the doped compounds.

This tendency of the parent compound to not match the trend set forth by the doped compounds continues throughout the various refinement parameters. One tentative explanation as to the cause of this discrepancy is the existence of internal stresses due to the presence of competing crystallographic phases in the undoped sample. Another possibility is that there is a better model for the parent compound that cannot be determined with the current data. Because of this constant discrepancy, only the trends of the cobalt-doped samples will be discussed.

The lattice parameters a and b are found to increase with increasing cobalt doping but contract with decreasing temperature from 300 K to 60 K, as shown for $x = 0.375$ in Figure 3. Upon transitioning to the monoclinic phase, however, both lattice parameters of the doped compounds begin to expand rather than contract with decreasing temperature. On the other hand, the monoclinic β angle increases with decreasing temperature for each of the compounds.

In contrast to the expansion found in the basal-plane, c contracts with increasing cobalt content. Each of the cobalt-doped compounds has similar temperature dependence, a slight contraction along the c -axis with decreasing temperature from 300 K to 60 K, followed by a slight expansion coinciding with the structural transition.

The atomic positions for each compound are given in Table V. Because the cobalt atoms randomly replace the iron atoms, the iron and cobalt sites are treated as the same. We found it informative to follow the temperature dependence of the Tb-Fe bond lengths, which are the most relevant to the magnetic exchange interactions in $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$. Figure 4 displays the variation with temperature of these bonds for the compounds with $x=0.125$ and 0.375 . The separation of the two bonds (Tb1-Fe and Tb2-Fe) into three different subsets corresponds to the split of Tb positions into six inequivalent sites in the $P1m1$ symmetry. The Fe/Co atoms continue to be distributed randomly on a single crystallographic site. As readily visible in Figure 4, the Tb displacement (bond length distribution around the average value) becomes larger upon increasing the Co doping. The same effect is apparent when comparing the monoclinic angle (β), presented in Table IV. One should also note that the average Tb-Fe distance does not change appreciably across the structural transition.

3.2. Magnetic structure

In much the same way that the high-temperature data corroborate the hexagonal unit cell, so too is the paramagnetic model proposed by Morozkin⁵ confirmed above ~250 K. However, below the Curie temperature, the refinement of our neutron diffraction data deviates from the study reported by Morozkin.⁵ While the ferromagnetic alignment of the terbium atoms between T_{C1} and T_{C2} agrees with Ref. 5, 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 5 (b). This ferromagnetism between terbium atoms and ferrimagnetism between iron and terbium is not uncommon.¹⁸⁻²¹ In addition, the incommensurate magnetic structure with a constant propagation vector of $[0,0,0.350(1)]$ below T_{C2} proposed in Ref. 5 was not confirmed by our study. As displayed in the inset of Figure 1, the low-angle region of 4 K data does not show any magnetic peak. The absence of this magnetic order may be related to the structural distortion observed in our sample.

The detection of the aforementioned structural change is very important with regard to determining the low-temperature magnetic structure. The results of the symmetry analysis completed using the SARAh representational analysis program²² indicate that the magnetic configurations described by a single irreducible representation (IR) exhibit magnetic moments that are confined to the basal plane for $P1m1$ or the c -axis for $P-62m$. While above the structural distortion ($T > 50K$) the neutron data can be well described using a collinear magnetic structure with the Tb moments aligned parallel to

the c -axis, below the transition a non-collinear spin arrangement that combines the basis vectors (parallel and perpendicular to the c -axis) of two different IRs had to be considered. The Tb moments continue to be ferromagnetically coupled among themselves but their direction is canted away from the c -axis. This new non-collinear magnetic structure is shown in Figure 5 (c). To minimize the number of variables, the magnetic moments of Tb atoms derived from equivalent sites were constrained to be the same ($m_{Tb11} = m_{Tb12} = m_{Tb13}$, $m_{Tb21} = m_{Tb22} = m_{Tb23}$). The separation of the a and c parameters is so small in our samples that resolving the contributions from each of the different planes is not possible with our data. Therefore, the a - and c - moment projections have been constrained to identical values in this analysis.

Under the assumption that the moments are equal along the a and c 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 VI and at all temperatures measured in Figure 6. The angles in both Table VI and Figure 6 represent the rotation of the moments relative to their orientation in the ferrimagnetic collinear arrangement. 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 all three magnetic sites approach saturation with decreasing temperature. Because the moments are constrained to the c -axis until the structural transition occurs, the angle θ increases rapidly between 60 K and 50 K. The angle then continues to increase below 50 K but at a slower rate.

The low-temperature magnetic structure is reminiscent of the non-collinear structure reported for the ErM_3 ($\text{M} = \text{Ni}, \text{Fe}$) intermetallic compounds,⁶⁻⁹ where the magnetic structure is determined by the competition between (i) the Er-Fe exchange interactions which favor a ferrimagnetic collinear structure and (ii) the anisotropies of the Er1, Er2 and Fe sites. In ErNi_3 , in which Ni magnetism is negligible, the spin reorientation occurring below 10 K is primarily due to competition between the local anisotropies of two crystallographically inequivalent Er sites whose thermal variations are different. In the case of ErFe_3 , the magnetism of the $3d$ metal is well established leading to high Curie temperatures, and the $4f$ - $3d$ magnetic interactions and the local anisotropy of the $3d$ moments are coming into play. Moreover, it has been determined that the low-temperature magnetic transition is accompanied by an atomic displacement giving rise to changes in the electric field gradients at the Er sites.

A similar mechanism can be proposed for our system, where the two Tb sites may exhibit different magnetocrystalline anisotropies. In addition, iron typically interacts antiferromagnetically with terbium while terbium atoms interact ferromagnetically with each other.¹⁸⁻²¹ It is likely that the spin reorientation below 50 K finds its origin in a competition between the Tb-Fe exchange energy, the two Tb magnetocrystalline anisotropies and the in-plane Fe sublattice anisotropy, which in turn could cooperatively induce the lattice distortion. Once the orientation of the magnetic moments is unrestrained to a single direction upon transformation to monoclinic symmetry, the Fe and Tb2 moments move to align along the basal plane. As such, the Fe and Tb2 moments remain largely antiparallel. The ferromagnetic interaction between Tb1 and Tb2 moments keeps Tb2 from aligning completely parallel to Fe. The canted nature of

the Tb2 moments also works to cant the Tb1 moments away from the *c*-axis.

Interestingly, the substitution of Fe with Co leads to a slight decrease of the canting angle and, at the same time, to an increase of the atomic displacement. The decrease of the canting could be explained by the softening of the Fe anisotropy by the Co atoms, whose anisotropy tends to be uniaxial. Under this scenario the increase of the atomic displacement may seem counterintuitive, but it could indicate that the balance between the magnetic and elastic energies is still evolving. Extending this study to other doped systems with non-magnetic transition metal elements may be particularly insightful to further understand this magneto-elastic behavior.

4. Conclusion

Our investigation into $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ ($x = 0, 0.125, 0.25, \text{ and } 0.375$) using XRD and PND has confirmed that all compounds are hexagonal (*P*-62*m*) above 60 K. Below 60 K, however, the cobalt-doped samples are characterized by the monoclinic *P*1*m*1 structure while the parent compound is characterized by a mixture of the monoclinic *P*1*m*1 and hexagonal *P*-62*m* structures. Powder neutron diffraction also revealed that the iron moments need to be included in the magnetic structure below T_{C1} , resulting in a ferrimagnetic arrangement above T_{C2} . Upon the structural transformation below T_{C2} , the magnetic structure transforms to a complex canted arrangement.

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Captions

Figures:

FIG. 1. (Color online) Neutron patterns of Tb_6FeBi_2 at 280 K (above the Curie temperature), 75 K (between the two magnetic transition temperatures), and at 4 K (below the low-temperature magnetic transition temperature). Inset: Low-angle data at 4 K. The arrow indicates the 2θ position where Morozkin et al. observed an incommensurate peak in Ref. [5]. A neutron wavelength of 2.41 Å was utilized for each pattern.

FIG. 2. (Color online) X-ray diffraction pattern of Tb_6FeBi_2 at 11 K with phase refinement based upon the monoclinic model. Cu $K_{\alpha 1}$ radiation with a wavelength of 1.54 Å was utilized. Inset: A representative portion of the spectrum comparing the refinements using the single monoclinic model (top) and the mixed monoclinic and hexagonal model (bottom).

FIG 3: Lattice parameters and angle (β for high-temperature phase, gamma for low-temperature phase) as a function of temperature for $\text{Tb}_6\text{Fe}_{0.625}\text{Co}_{0.375}\text{Bi}_2$.

FIG. 4 Variation with temperature of the Tb – Fe distances in $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$, corresponding to the two inequivalent Tb sites (Tb1, Tb2) for two different dopings $x=0.125$ (open symbols) and $x=0.375$ (filled symbols) . Below the structural transition, each of the Tb sites splits into three different subsets.

FIG. 5. (Color online) (a) A view of the Tb_6FeBi_2 crystal structure, with different coordination geometries for the two inequivalent Tb sites. (b) The ferrimagnetic collinear magnetic structure at 75 K. (c) The ferrimagnetic non-collinear magnetic structure at 4 K.

FIG. 6. (Color online) The moment on the (a) Tb1, (b) Tb2, and (c) Fe sites. The angle θ made with respect to the ferrimagnetic collinear orientation of the (d) Tb1, (e) Tb2, and (f) Fe sites. The dashed lines indicate the magnetic transition.

Tables:

Table 1. Powder neutron diffraction data collection parameters and refinement results for $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ above T_{C1} .

Table 2. Powder neutron diffraction data collection parameters and refinement results for $\text{Tb}_6\text{Fe}_{1-x}\text{Co}_x\text{Bi}_2$ below T_{C2} .

Table 3. Lattice parameters a , c , and c/a as determined by neutron diffraction above the Curie temperature.

Table 4. Lattice parameter data of the low-temperature structure as determined by neutron powder diffraction.

Table 5. Atomic positions for each compound at 4 K as determined by neutron diffraction.

Table 6. 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.

Table 1

	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
Temperature, K	280 K	300 K	280 K	280 K
Variables	16	18	22	17
Crystal System	Hexagonal	Hexagonal	Hexagonal	Hexagonal
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>
<i>R</i> -Bragg				
1.538 Å Pattern	10.2	-	-	4.18
2.41 Å Pattern	10.9	14.4	14	8.08
Goodness of fit, χ^2	2	1.31	3.52	1.56
Volume (Å ³)	250.27(1)	250.27(1)	249.17(1)	248.95(1)
Calculated density (g/cm ³)	9.47	9.473	9.518	9.529

Table 2

	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
Temperature, K	4 K		4 K	4 K	4 K
Variables	53		52	35	52
Crystal System	Monoclinic	Hexagonal	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>P1m1</i>	<i>P-62m</i>	<i>P1m1</i>	<i>P1m1</i>	<i>P1m1</i>
Phase	63 wt.%	37 wt.%	100 wt.%	100 wt.%	100 wt.%
<i>R-Bragg</i>					
1.538 Å Pattern	8.31	7.69	3.94	-	7.15
2.41 Å Pattern	6.66	5.25	3.25	4.68	4.23
Goodness of fit, χ^2	4.12	4.12	1.11	3.44	4.39
Volume (Å ³)	248.17(2)	248.02(2)	248.63(2)	247.69(1)	247.44(2)
Calculated density (g/cm ³)	9.551	9.557	9.536	9.575	9.587

Table 3

Composition	T (K)	a (Å)	c (Å)	c/a
x = 0	280	8.2892(1)	4.2058(1)	0.5074
x = 0.125	300	8.2991(2)	4.1957(1)	0.5056
x = 0.25	280	8.2956(2)	4.1809(1)	0.5040
x = 0.375	280	8.3003(2)	4.1726(1)	0.5027

Table 4

Composition	Crystal System	T (K)	a (Å)	b (Å)	c (Å)	β
x = 0	Monoclinic	4	8.2316(6)	8.2853(4)	4.2110(2)	120.219(7)
	Hexagonal	4	8.2629(3)	8.2629(3)	4.1947(3)	γ=120.000
x = 0.125	Monoclinic	4	8.2829(4)	8.2844(4)	4.1917(1)	120.186(1)
x = 0.25	Monoclinic	4	8.2875(2)	8.2857(2)	4.1769(1)	120.278(2)
x = 0.375	Monoclinic	4	8.2937(4)	8.2930(4)	4.1681(1)	120.331(1)

Table 5

x = 0	x	Y	z	x = 0.125	x	y	z
Tb11	0.242(8)	0.018(6)	0	Tb11	0.246(6)	-0.001(5)	0
Tb12	0.027(9)	0.245(6)	0	Tb12	0.013(7)	0.243(5)	0
Tb13	0.781(7)	0.758(6)	0	Tb13	0.779(7)	0.770(5)	0
Tb21	0.02(1)	0.603(7)	0.5	Tb21	0.019(8)	0.621(5)	0.5
Tb22	0.637(8)	0.010(7)	0.5	Tb22	0.597(7)	-0.002(5)	0.5
Tb23	0.438(8)	0.426(6)	0.5	Tb23	0.419(6)	0.398(5)	0.5
Fe1	0.016(9)	0.030(7)	0.5	Fe1	0.018(6)	0.027(5)	0.5
Bi1	0.663(7)	0.335(7)	0	Bi1	0.681(9)	0.342(8)	0
Bi2	0.34203	0.6654	0	Bi2	0.34203	0.6654	0
x = 0.25	x	Y	z	x = 0.375	x	y	z
Tb11	0.232(7)	0.000(8)	0	Tb11	0.247(5)	0.006(5)	0
Tb12	0.021(7)	0.27(1)	0	Tb12	0.005(5)	0.243(5)	0
Tb13	0.772(7)	0.779(9)	0	Tb13	0.783(5)	0.769(5)	0
Tb21	0.009(8)	0.63(1)	0.5	Tb21	0.008(5)	0.589(5)	0.5
Tb22	0.592(8)	0.01(1)	0.5	Tb22	0.625(5)	0.009(5)	0.5
Tb23	0.414(6)	0.40(1)	0.5	Tb23	0.405(5)	0.407(5)	0.5
Fe1	0.040(5)	0.018(8)	0.5	Fe1	0.045(4)	0.008(5)	0.5
Bi1	0.67316	0.34113	0	Bi1	0.682(7)	0.344(7)	0
Bi2	0.34203	0.6654	0	Bi2	0.34203	0.6654	0

Table 6

Composition	Tb1		Tb2		Fe		R-Magnetic	
	Magnitude (μ_B)	θ ($^\circ$)	Magnitude (μ_B)	θ ($^\circ$)	Magnitude (μ_B)	θ ($^\circ$)	1.54 Å	2.41 Å
x = 0*	9.2(3)	18.3(7)	9.1(3)	60.0(5)	2.0(3)	76(3)	6.03	5.92
x = 0.125	8.9(1)	17.8(5)	9.0(2)	50.2(1)	1.6(2)	66.8(9)	3.39	2.9
x = 0.25	9.3(3)	15.7(7)	9.1(3)	46.3(1)	1.6(3)	42(3)	-	4.58
x = 0.375	9.1(1)	14.4(5)	9.2(2)	43.7(1)	1.6(3)	65.8(2)	3.96	3.48

* Monoclinic Phase

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5
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Figure 6