

## Magnetic properties of $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$ ( $x=0, 0.05, 0.1, 0.15, 0.2$ )

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The pseudobinary Laves phase  $R^1R^2\text{Fe}_2$  magnetostrictive compounds have one degree of freedom by which the largest anisotropy constant  $K_1$  is minimized to obtain the best performing material. However, by including a third rare earth element, additional degree of freedom is obtained, which allows a better way to choose a material for application. In the present study, Ho has been chosen as it exhibits positive magnetostriction, similar to Tb and Dy. Substitution of Mn for Fe leads to the realization of improved magnetostriction values and reduction in the anisotropy. In the present paper magnetic properties of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$  ( $x=0, 0.05, 0.1, 0.15, 0.2$ ) are presented. The compounds have formed in single phase with cubic Laves phase structure. The lattice parameter is found to increase from 7.327 to 7.347 Å with increasing the Mn concentration to 0.2. The Fe/Mn–Fe/Mn distance is less than 2.66 Å, the critical distance below which the Fe and Mn moments could be antiferromagnetically ordered, leading to a decrease in the Curie temperature from 592 to 537 K. At 80 K, saturation magnetization is found to increase from 120 emu/g ( $x=0$ ) to 125 emu/g ( $x=0.1$ ) and then to decrease to 105 emu/g ( $x=0.2$ ). The magnetostriction increases from  $1000 \times 10^{-6}$  ( $x=0$ ) to  $1050 \times 10^{-6}$  ( $x=0.1$ ) with Mn and decreases to  $775 \times 10^{-6}$  with further increment of Mn ( $x=0.2$ ). Spontaneous magnetostriction is found by the splitting of the (440) peak. © 2007 American Institute of Physics. [DOI: 10.1063/1.2709727]

The pseudobinary Laves phase ( $R_x^1R_y^2\cdots$ )  $\text{Fe}_2$  compounds ( $R$ =rare earth,  $x+y+\cdots=1$ ) are known to possess large magnetostriction at room temperature because of the large spin-orbit interaction.<sup>1</sup> However, they also have large magnetocrystalline anisotropy, which necessitates high magnetic field strengths to saturate the magnetization and magnetostriction.<sup>2,3</sup>

It has been shown that the anisotropy in  $\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$  and  $\text{Tb}_{1-x}\text{Ho}_x\text{Fe}_2$  compounds could be minimized by a suitable combination of rare earths.<sup>4</sup> There is one degree of freedom in these compounds, namely, the first order anisotropy constant that could be minimized by controlling  $x$ . By adding a third rare earth element, an additional degree of freedom has been obtained and both the first order anisotropy constant ( $K_1$ ) as well as second order anisotropy constant ( $K_2$ ) could be minimized.<sup>5,6</sup> Ho has been chosen as the third rare earth element since, such as Tb and Dy, Ho also possesses a large and positive magnetostriction.

The replacement of Fe by Mn in polycrystalline  $\text{Dy}_{1-x}\text{Tb}_x\text{Fe}_2$  has been reported to cause the magnetocrystalline anisotropy compensation temperature to decrease and effectively required larger Tb content for the same.<sup>7</sup> In addition, the saturation magnetostriction has been reported to increase. Mössbauer measurements have shown that the easy magnetization direction for Mn containing compound is in the  $\langle 111 \rangle$  direction at 300 K.<sup>8</sup> The effect of Mn substitution

on the magnetic properties of anisotropy compensated  $\text{Ho}_{0.85}\text{Tb}_{0.15}\text{Fe}_2$  and  $\text{Dy}_{0.73}\text{Tb}_{0.27}\text{Fe}_2$  has been investigated and spin fluctuations reported near the Curie temperature.<sup>9</sup> It has been shown that the Mn magnetism in these compounds is not stable and that this instability could give rise to large magnetovolume anomalies. The occurrence of these anomalies depends on the Mn–Mn interatomic distance. There is a critical distance ( $d_c=2.66$  Å) below which Mn moment is unstable. When the Mn–Mn distance is significantly lower than  $d_c$ , Mn is nonmagnetic and the compound exhibits ferromagnetic ordering, characteristic of the rare earth moments only. When the Mn–Mn interatomic distance is just below  $d_c$  Mn magnetism is induced by cooperative exchange interactions, but no magnetovolume effects are observed. When the Mn–Mn spacing is greater than  $d_c$ , the Mn magnetism is well stabilized and Mn ordering is accompanied by large magnetovolume effect.<sup>10</sup> These results indicate that a small amount of Mn substitution could play an important role in improving the magnetostrictive properties of the Laves phase intermetallics.

The compound  $\text{Ho}_{0.85}\text{Tb}_{0.15}\text{Mn}_2$  is found to exhibit a large magnetoresistance (27%) at 9 T, around the ordering temperature.<sup>11</sup> Williams and Koon have reported the largest saturation magnetostriction for the compound  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{1.95}$  among the  $\text{Tb}_x\text{Dy}_y\text{Ho}_z\text{Fe}_{1.95}$  compounds.<sup>5</sup> In continuation of such studies, we report the effect of Mn on the structural and magnetic properties of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_2$ .

Polycrystalline samples of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$

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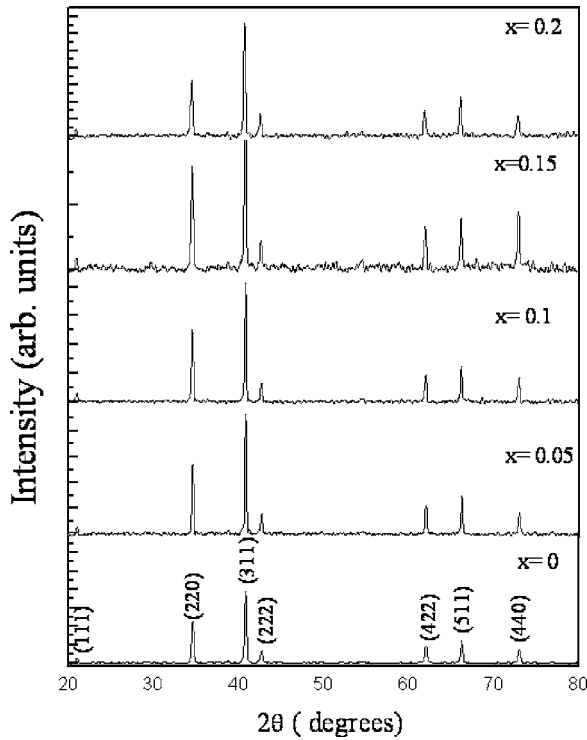


FIG. 1. Powder x-ray diffraction patterns of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$ .

( $x=0, 0.05, 0.1, 0.15, 0.2$ ) were prepared by arc melting the constituent elements Dy, Tb, Ho of 99.9% purity, Fe of 99.95% purity, and Mn of 99.99% purity in an arc furnace under argon atmosphere. The weight loss due to Mn because of its high vapor pressure was compensated for by adding 5% of the weight of Mn in excess. The melting was carried out several times for homogeneity. The weight loss after the final melting was less than 0.5%. The arc melted ingots were homogenized in vacuum (pressure  $<10^{-5}$  Torr) at 900 °C for a week and furnace cooled. Structural characterization was carried out by powder x-ray diffraction with Cu  $K\alpha$  (1.5405 Å) radiation at room temperature. Magnetization measurements were carried out using a PAR 155 vibrating sample magnetometer in the temperature range of 80–700 K up to an applied field of 1.2 T. The magnetostriction measurements were carried out at room temperature using strain gauge technique.

X-ray diffraction patterns (Fig. 1) show that all  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$  ( $x=0-0.2$ ) compounds are essentially single Laves phase with  $\text{MgCu}_2$ -type structure. The

TABLE I. Concentration of Mn ( $x$ ), lattice parameter ( $a$ ), (Mn/Fe)–(Mn/Fe) distance [ $d_{\text{Mn/Fe}}-(\text{Mn/Fe})$ ], Curie temperature ( $T_c$ ), saturation magnetization ( $M_s$ ) and magnetostriction ( $\lambda$ ), and spontaneous magnetostriction ( $\lambda_{111}$ ) for  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$ .

$x$	$a$ (Å) ( $\pm 0.002$ )	$d_{(\text{Mn/Fe})-(\text{Mn/Fe})}$ (Å)	$M_s$ (emu/g)		$\lambda$ ( $\times 10^{-6}$ )	$\lambda_{111}$ ( $\times 10^{-6}$ )
			80 K	$T_c$ (K)		
0	7.327	2.591	120	592	1018	1050
0.05	7.330	2.591	123	580	1031	1081
0.1	7.336	2.594	125	563	1050	1157
0.15	7.344	2.596	118	548	928	1020
0.2	7.347	2.598	105	537	775	—

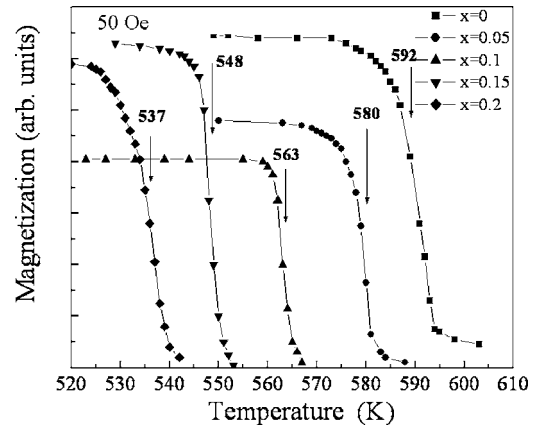


FIG. 2. Temperature variation of magnetization for  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$ .

lattice parameter increases steadily from 7.327 Å for  $x=0$  to 7.347 Å for  $x=0.2$  due to the larger metallic radius of the Mn compared with the Fe. The (Mn/Fe)–(Mn/Fe) interatomic distance was calculated as  $(\sqrt{2})a/4$  where  $a$  is lattice parameter. The values of lattice parameters and  $d_{(\text{Mn/Fe})-(\text{Mn/Fe})}$  values are given in Table I.

Figure 2 shows the temperature variation of magnetization curves of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$  ( $x=0, 0.05, 0.1, 0.15, 0.2$ ) compounds at the field of 50 Oe. It is seen from the figure that the Curie temperature decreases with increasing Mn content. For all the compounds except for the  $x=0.2$  compound, sharp transitions at the respective Curie temperatures are observed. For the  $x=0.2$  compound, a broad transition ( $\Delta T=20$  K) could correspond to the spin fluctuations near the Curie temperature. As the values of  $d_{(\text{Mn/Fe})-(\text{Mn/Fe})}$  in  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$  do not exceed 2.61 Å, the Mn moments could have antiferromagnetic exchange with the Fe or the other Mn atoms.<sup>12</sup> The reduction in the Curie temperature ( $T_c$ ) of this system presumably results from antiferromagnetic Fe–Mn interactions, which is similar for  $\text{Dy}_{0.6}\text{Tb}_{0.3}\text{Pr}_{0.1}\text{Fe}_{1-x}\text{Mn}_x$ .<sup>13</sup> In addition, the reduction in Fe/Mn–Fe/Mn and Tb/Dy/Ho–Fe/Mn exchange interactions could also contribute to the decrease in the Curie temperature upon addition of Mn. Figure 3 shows the mag-

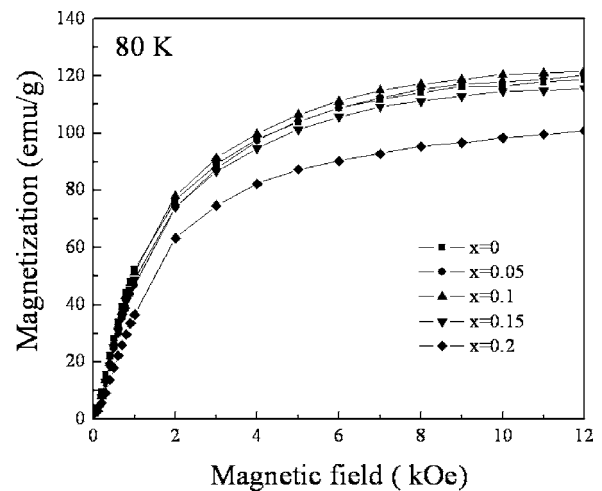


FIG. 3. Magnetization curves of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$  at 80 K.

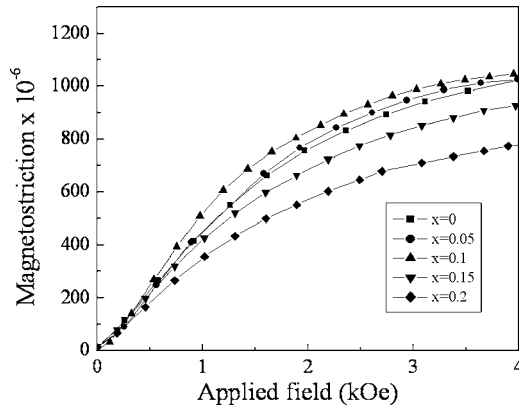


FIG. 4. Magnetostriction curves of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$ .

netization curves at 80 K. From the figure it is seen that the magnetization values have not saturated up to 12 kOe. The saturation magnetization was determined from the Honda plots ( $M$  vs  $1/H$ ). For the initial concentration (up to  $x=0.1$ ) of Mn, the saturation magnetization (Table I) is found to increase and further increment of Mn concentration leads to decrease of the saturation magnetization. The initial increase in the saturation magnetization can be explained on the basis of the fact that as the nearest  $d_{(\text{Mn/Fe})-(\text{Mn/Fe})}$  distances are less than the critical distance, Mn atoms do not carry any magnetic moment. Hence, the increase in the Mn concentration dilutes the magnetic moment of the transition metal sublattice. In the present, case since Tb, Dy, and Ho are heavy rare earths, the dominating rare earth moments and Fe moments are antiparallel.<sup>14,15</sup> Such a behavior has been reported in earlier studies as well.<sup>9,16</sup> The decrease in the saturation magnetization after  $x=0.1$  is due to the heavy rare earth moments being antiparallel to those of the transition metal moments. The substitution of Mn for Fe results in a decrease of the Fe magnetic moment leading to a reduction of the exchange field at the rare earth sites. Consequently, the rare earth moments are reduced, resulting in a decrease of the total magnetic moment.

The magnetostriction for polycrystalline  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$  alloys was carried out up to 4000 Oe. Figure 4 shows the magnetostriction curves of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$ . It is seen that the magnetostriction (at 4000 Oe) slightly increases for  $x=0.1$  compound and further substitution of Mn causes a decrease in the magnetostriction.

It is well known that the spontaneous magnetostriction leads to distortion of the crystal structure when a magnetic material is cooled down below its Curie temperature.<sup>17,18</sup> On the other hand, a rhombohedral or tetrahedral distortion led by magnetostriction coefficient can be identified. X-ray slow scan (step size of  $0.002^\circ$  with a dwell time of 6 min) was performed for the (440) XRD peak after eliminating the effect of  $K\alpha_2$  radiation and are shown in Fig. 5. The peak is seen to split into two in all the compounds. The spontaneous magnetostriction is found using the equation<sup>18</sup>

$$\lambda_{111} = 2 \frac{d_{440} - d_{4\bar{4}0}}{d_{440} + d_{4\bar{4}0}},$$

where  $d_{440}$  and  $d_{4\bar{4}0}$  are the  $d$  values in pseudocubic indices. The largest spontaneous magnetostriction was observed to be

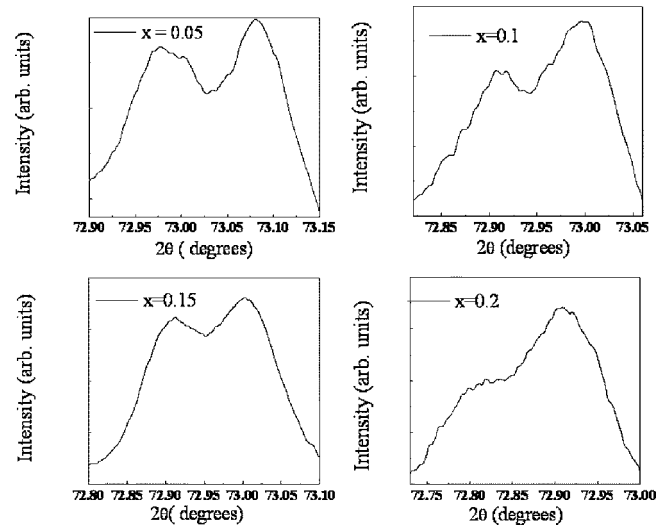


FIG. 5. Profiles of the (440) line of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$  cubic Laves phase.

$1157 \times 10^{-6}$  for the  $x=0.1$  compound. For the  $x=0.2$  compound, the split is not clear. From these results the increment in the magnetostriction at  $x=0.1$  can be explained on the basis of the increment in the spontaneous magnetostriction in  $\langle 111 \rangle$  direction.

The magnetic properties of  $\text{Tb}_{0.28}\text{Dy}_{0.57}\text{Ho}_{0.15}\text{Fe}_{2-x}\text{Mn}_x$  were investigated. The lattice parameter is found to increase with Mn concentration, whereas the Curie temperature is found to decrease. At  $x=0.2$  spin fluctuations are observed near the Curie temperature. The saturation magnetization is found to increase up to  $x=0.1$  and to decrease for the higher Mn concentrations. The room temperature magnetostriction is found to increase up to  $x=0.1$  and to decrease for further increment in the Mn concentration. The spontaneous magnetostriction is found to reach maximum at  $x=0.1$  ( $1157 \times 10^{-6}$ ).

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