



Article

# Structural, Magnetic and Mossbauer studies of Transition metal-doped $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$ intermetallic compounds (TM=Cr, Mn, Co, Ni, Cu, and Zn)

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**Abstract:** The effect of transition metal substitution for Fe and the structural and magnetic properties of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM=Cr, Mn, Co, Ni, Cu, and Zn) compounds were investigated. Rietveld analysis of X-ray diffraction indicates that all the samples crystallize in the hexagonal  $Th_2Ni_{17}$  structure. The lattice parameters: a, c and unit cell volume show TM ionic radii dependence. Both Ga and TM atoms show preferred site occupancy for 12j and 12k sites. The saturation magnetization at maximum room temperature was observed for Co, Ni, and Cu of 69, 73, and 77 emu/g, respectively while minimum value was observed for Zn (62emu/g) doping  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$ . Highest Curie temperature of 590K was observed for Cu doping which is 15% and 5% and higher than  $Gd_2Fe_{17}$  and  $Gd_2Fe_{16}Ga$  compounds, respectively. The hyperfine parameters viz. hyperfine field and isomer shift, show systematic dependence on the TM atomic number. The observed magnetic and Curie temperature behavior in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  is explained on the basis of Fe(3d)-TM(3d) hybridization. The superior Curie temperature and magnetization value of Co, Ni, and Cu doped  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  compounds as compared to pure  $Gd_2Fe_{17}$  or  $Gd_2Fe_{16}Ga$  makes  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  a potential candidate for high-temperature industrial magnet applications.

**Keywords:** Permanent magnetic materials; 2:17 intermetallics; Mossbauer Spectroscopy; Curie temperature; X-ray diffraction; Rietveld analysis

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## 1. Introduction

The rare-earth intermetallic compounds  $R_2Fe_{17}$  have energy product  $(BH)_{max}$  and  $H_c$  to be about 26 MGOe and 15 kOe, respectively [1]. In spite of these properties, they exhibit low Curie temperature ( $T_c$ ). For example, 473 K for  $Gd_2Fe_{17}$  and 300 K for  $Dy_2Fe_{17}$  along with low magnetic anisotropies [2]. Various strategies have been employed addressing issues related to improving magnetic anisotropy, magnetization and Curie temperature of  $R_2Fe_{17}$  compounds. Metalloids such as C, N, and H atoms are added to improve the magnetic anisotropy and Curie temperature [3,4,5,6]. However, high-temperature processing of these interstitial modified compounds is difficult. Subsequently, the addition of non-magnetic atoms such as Al, Ga, and Si for iron in the  $R_2Fe_{17-x}M_x$  compound was investigated which in fact showed Curie temperature enhancement at high non-magnetic atom content. Among Al, Si, and Ga, Ga substituted compounds show high  $T_c$ , e.g.,  $Sm_2Fe_{16}Ga$ ,  $T_c \sim 485$  K [7] and  $Dy_2Fe_{16}Ga$ ,  $T_c \sim 462$  K [8]. However, this improvement in  $T_c$  is overshadowed by a concomitant deterioration in saturation magnetization as iron atoms are being replaced by non-magnetic atoms.

The Curie temperatures  $T_c$  in the  $R_2Fe_{17}$  compounds was explained on the base of strength of exchange interaction between Fe-Fe pairs [9]. It is based on the assumption that the exchange interactions favor ferromagnetic ( $r > r_c$ ) or antiferromagnetic ( $r < r_c$ ), where  $r_c \sim 2.5$  Å. Hence,  $T_c$  is assumed dependent on the competition between ferromagnetic and antiferromagnetic exchange interactions between neighboring pairs of Fe-Fe ions located at various crystallographic positions. This means that  $T_c$  enhancement can be achieved via unit cell lattice expansion, except in Si-substituted  $RE_2Fe_{17-x}Si_x$ , favoring ferromagnetic exchange interaction between Fe-Fe pairs. Usually, such lattice expansion is possible either via substituting for Fe ions by ions with the larger ionic radii [10,11] or via insertion of interstitial atoms in the unit cell [12,13]. It was observed that there are two ingredients influencing  $T_c$  value: local magnetic moment values and exchange interaction values [14].

Among  $R_2Fe_{17}$  intermetallic,  $Gd_2Fe_{17}$  is of special interest as it has the highest Curie temperature,  $T_c$ . Among the doped  $R_2Fe_{17-x}M_x$  ( $M=Al, Si, Ga$ ), Ga doped compounds display higher  $T_c$  value [15]. Given the above, the present work investigates effect of doping transition metal (TM) atoms in Ga doped  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  compounds and compare the results with  $Gd_2Fe_{17}$ . It is expected that the doping of TM atoms with ionic radii greater than Fe will bring unit cell volume expansion and hence improve Fe-Fe exchange interaction enough to couple Fe-Fe moments ferromagnetically; thus, improving

the Curie temperature of the compound. Furthermore, there also lies the possibility of improving magnetic moment of Fe via Fe-TM 3d band hybridization which can either bring band narrowing or increase exchange splitting by moving the 3d $\uparrow$  states below the Fermi level or allow charge transfer out of the 3d band, provided the spin-down density of states exceed the spin-up density [16].

This study discusses the changes in the structural and magnetic properties in R<sub>2</sub>Fe<sub>17</sub> compounds when Fe is substituted in R<sub>2</sub>Fe<sub>16</sub>Ga<sub>0.5</sub>TM<sub>0.5</sub> compounds with transition metal TM = Cr, Mn, Co, Ni, Cu, and Zn. The main aim of the study is to bring structural and band related changes to R<sub>2</sub>Fe<sub>17</sub> compounds such as to improve T<sub>c</sub> without impacting the saturation magnetization.

## 2. Experimental

The raw materials of Gd, Fe, Ga and TM (TM=Cr, Mn, Co, Ni, Cu, and Zn) with 99.9% purity were purchased from Sigma Aldrich. The parent alloys Gd<sub>2</sub>Fe<sub>16</sub>Ga<sub>0.5</sub>TM<sub>0.5</sub> were prepared by arc melting the stoichiometric amount of aforementioned elements under a high purity argon atmosphere. The ingots were melted several times to ensure the high degree of homogeneity.

XRD was carried out with CuK $\alpha$  ( $\lambda \sim 1.5406$  Å) radiation on a Bruker (D8 Advance) diffractometer. The powder X-ray data sets were collected in the 2 $\theta$  range from 20° to 75° with a step size of 0.042°. The XRD analysis was performed by the well-known structural refinement Rietveld [17] method using the JANA2006 [18] software package to fit the experimental and calculated diffraction patterns. The initial crystal structure parameters were used as given by Liao et al. [19]. In the hexagonal setting, Gd was fixed at the 2*b* and 2*d* site (0, 0, 0.25) and (0.333, 0.667, 0.75), Fe is fixed at 4*f*, 6*g*, 12*j*, and 12*k* (0.333 0.667 0.105), (0.5 0 0), (0.333 0.969 0.25), and (0.167 0.333 0.985). The profile was constructed using a pseudo-Voigt function. Profile asymmetry was introduced by employing the multi-term Simpson rule integration devised by Howard [20]. A surface roughness correction was also applied using the Pitschke, Hermann, and Matter [21] model. In this technique, structural parameters, lattice parameters, peak shift, background profile shape and preferred orientation parameters are used to minimize the difference between a calculated profile and the observed data.

Magnetic properties of the powder sample were investigated at room temperature using vibrating sample magnetometer (VSM) in the maximum field of 1.2T. In order to minimize

the effect of demagnetizing field, the samples were compacted at 3000psi and cut into rectangular parallelepiped with the ratio of length to a width larger than three times and embedded in epoxy. Modified thermogravimetric analyzer (DuPont 910) equipped with a permanent magnet was used to determine Curie temperature of composite samples. In this procedure, a magnetic material is placed inside an empty, tared TGA pan located near a strong magnet. The material is then heated. At the Curie temperature ( $T_c$ ), the magnetic properties disappear (i.e., the material goes from diamagnetic to paramagnetic) and the reduced attraction for the magnet results in a sharp apparent weight loss or gain (depending on the TGA design).

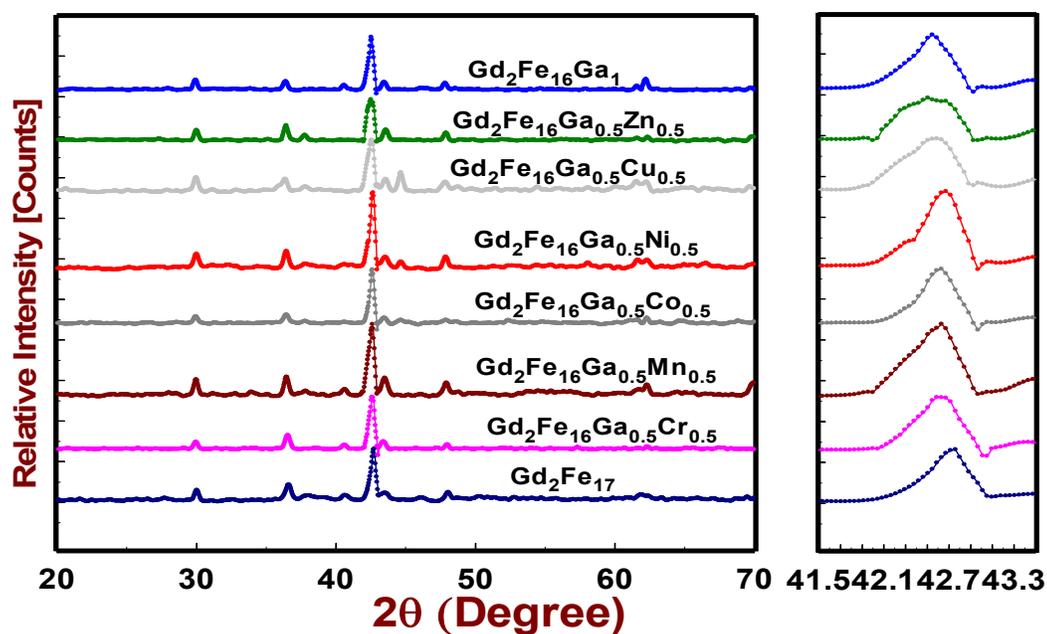
The Mossbauer spectra of the samples were obtained at room temperature (RT) using a 25 mCi  $^{57}\text{Co}$  source in an Rh foil mounted on a constant acceleration drive system (SEE Co. Minneapolis, USA) in transmission geometry. The velocity scale of the Mossbauer spectrometer was calibrated by measuring the hyperfine field of  $\alpha$ -Fe foil, at room temperature. The Mossbauer spectra were analyzed using WMoss software from SEE Co. The spectra were least-square fitted with the hyperfine field ( $f$  &  $f$ ), isomer shift (IS) and quadrupole splitting (QS) as variables.

### 3. Results and Discussion

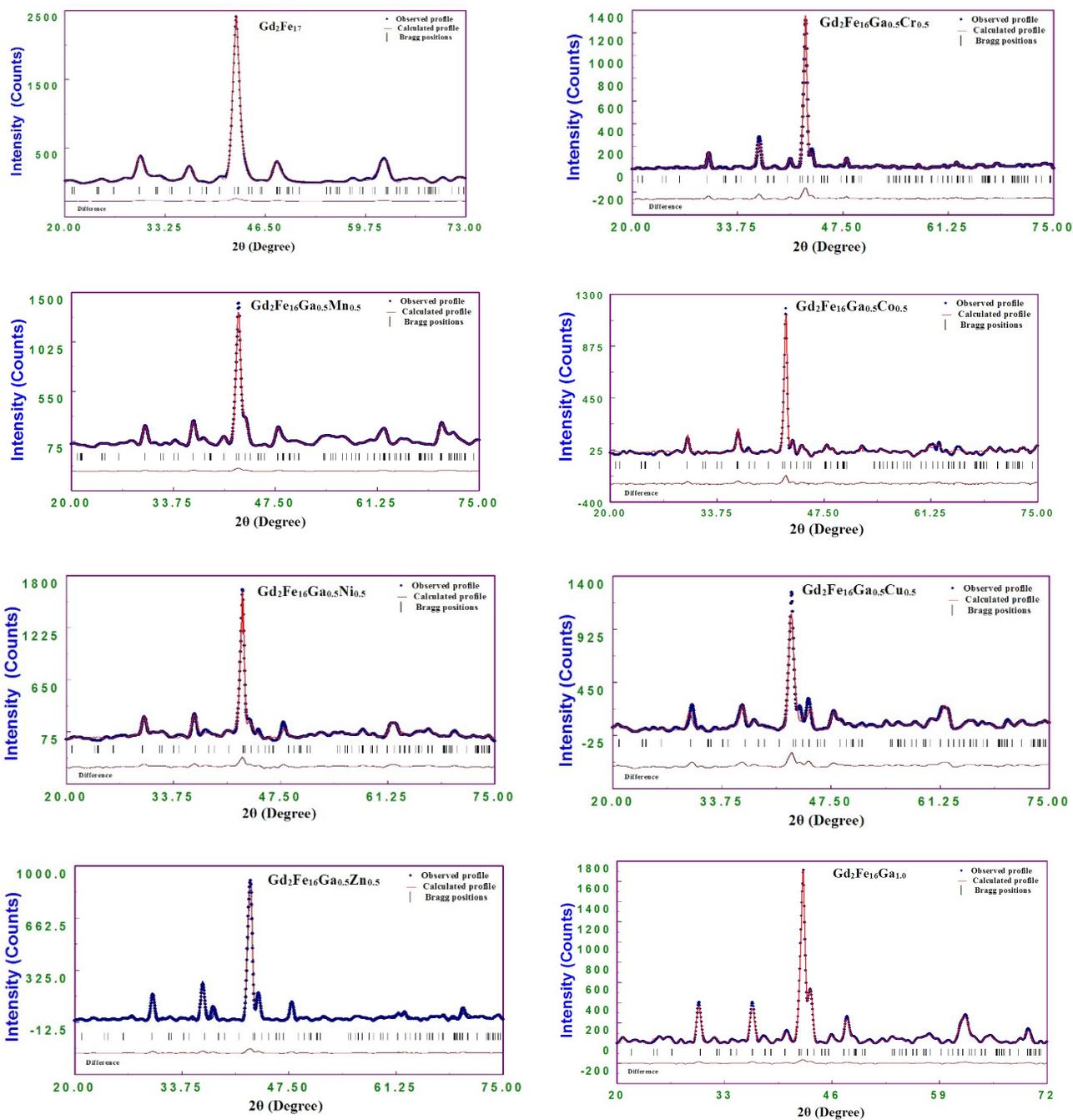
The raw powder profile for  $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$  systems is presented in **Fig. 1 (a)**. The inset **Fig. 1(a)**, the enlarged  $2\theta$  view between  $41.5^\circ - 43.3^\circ$ , shows that there is a shift in  $2\theta$  towards the lower angle which indicates the expansion of the unit cell with the substitution of increasing atomic number of TM in the compound. This observation is in accordance with the increasing size of the substitution atom whose metallic radii increase as going from TM=Cr to Zn, **Table I**. The refined Rietveld profiles are presented in **Fig. 1(b)** for  $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$  systems. The refined structural parameters, lattice parameters  $a$ ,  $c$ ,  $c/a$  ratio, unit cell volume, and the reliability indices are given in **Table I**. From the Rietveld analysis, the refined profile indicates that  $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$  compounds crystallize in hexagonal  $\text{Th}_2\text{Ni}_{17}$  structure with  $P6_3/mmc$  symmetry group. **Fig. 2** show the lattice parameters as a function of TM atomic number in  $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$ . It is observed from **Fig. 2** that the variation in lattice parameter  $a$  is more pronounced than that in  $c$  in doped compounds. This is also evident from the variation in  $c/a$  ratio (**Table I**), which indicates anisotropic expansion of unit cell volume with TM atom doping. The doping of, Cr up to Co, brings lattice contraction while Ni, Cu, and Zn brings in lattice expansion. The observed trend in lattice parameter closely follows TM metallic radii, **Fig. 2**.

**Table 1:** Structural parameters from Rietveld refinement of powder XRD data of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM= Cr, Mn, Fe, Co, Ni, Cu, Zn, and Ga) with  $Gd_2Fe_{17}$ .

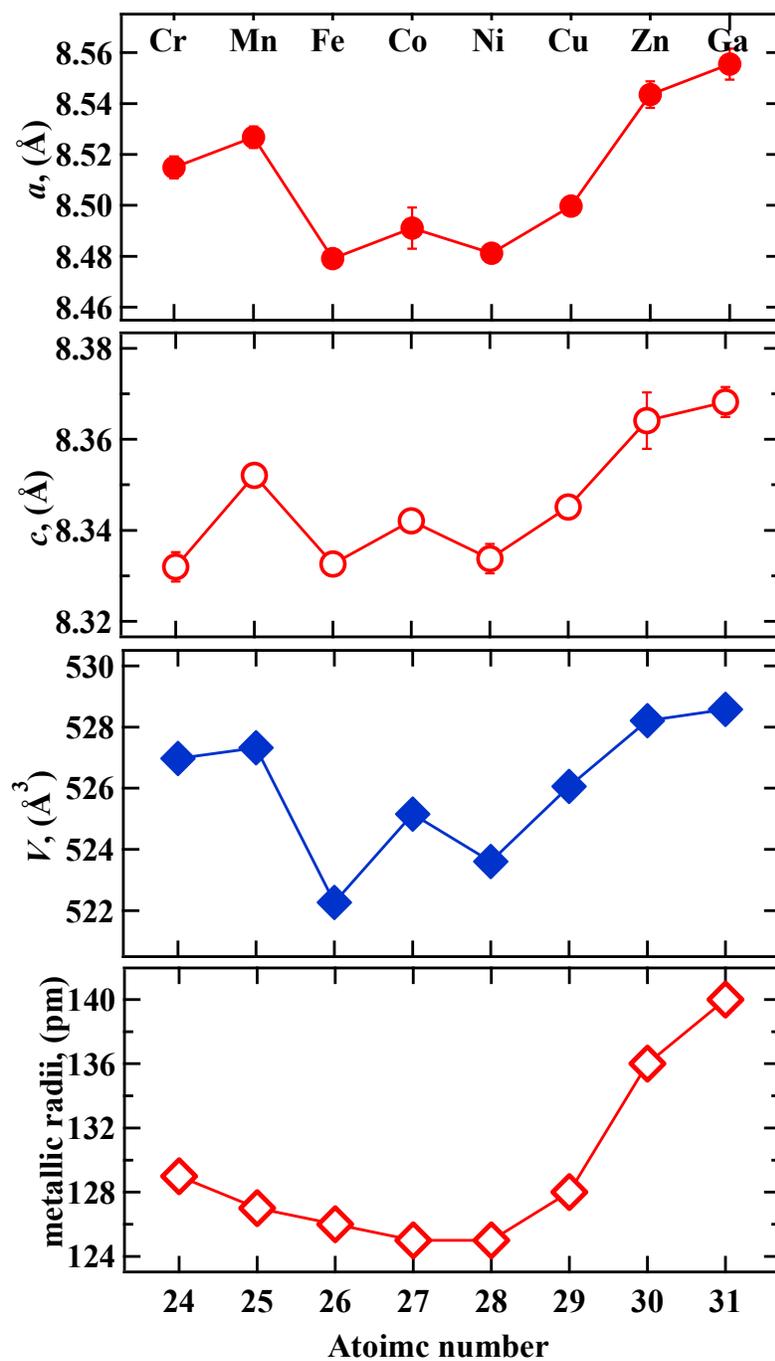
Parameter	Cr	Mn	$Gd_2Fe_{17}$ Fe	Co	Ni	Cu	Zn	$Gd_2Fe_{16}Ga$ Ga
Metallic radii (pm)	127	126	129	125	125	128	136	140
a (Å)	8.5149(43)	8.5267(42)	8.4791(21)	8.4911(81)	8.4812(24)	8.4997(32)	8.5435(52)	8.5555(61)
c (Å)	8.3320(32)	8.3521(22)	8.3326(6)	8.3421(8)	8.3338(32)	8.3451(16)	8.3641(62)	8.3682(33)
c/a	0.9785	0.9795	0.9827	0.9824	0.9826	0.9818	0.9790	0.9781
Cell Volume (Å <sup>3</sup> )	526.97	527.32	522.2634	525.15	523.60	526.06	528.21	528.5749
R <sub>obs</sub> (%)	5.67	4.44	2.48	4.53	3.21	3.99	2.31	6.43
wR <sub>obs</sub> (%)	4.32	5.21	3.55	5.31	4.21	4.87	3.65	7.12
R <sub>p</sub> (%)	6.22	7.87	9.12	8.11	7.32	7.22	5.32	10.55
wR <sub>p</sub> (%)	7.87	8.86	10.54	9.32	8.32	10.11	7.78	12.54



**Figure 1 (a):** XRD powder profile for  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with  $Gd_2Fe_{17}$ .



**Figure 1(b):** Rietveld refined XRD data of Gd<sub>2</sub>Fe<sub>16</sub>Ga<sub>0.5</sub>TM<sub>0.5</sub> (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with Gd<sub>2</sub>Fe<sub>17</sub>.



**Figure 2:** Lattice parameters via Rietveld refinement, and metallic radii of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  as a function of TM atomic number.

The atomic site occupancy for Gd, Fe, Ga and TM atoms derived from Rietveld refinement is listed in **Table II**. The site notations are given for rhombohedral structure with

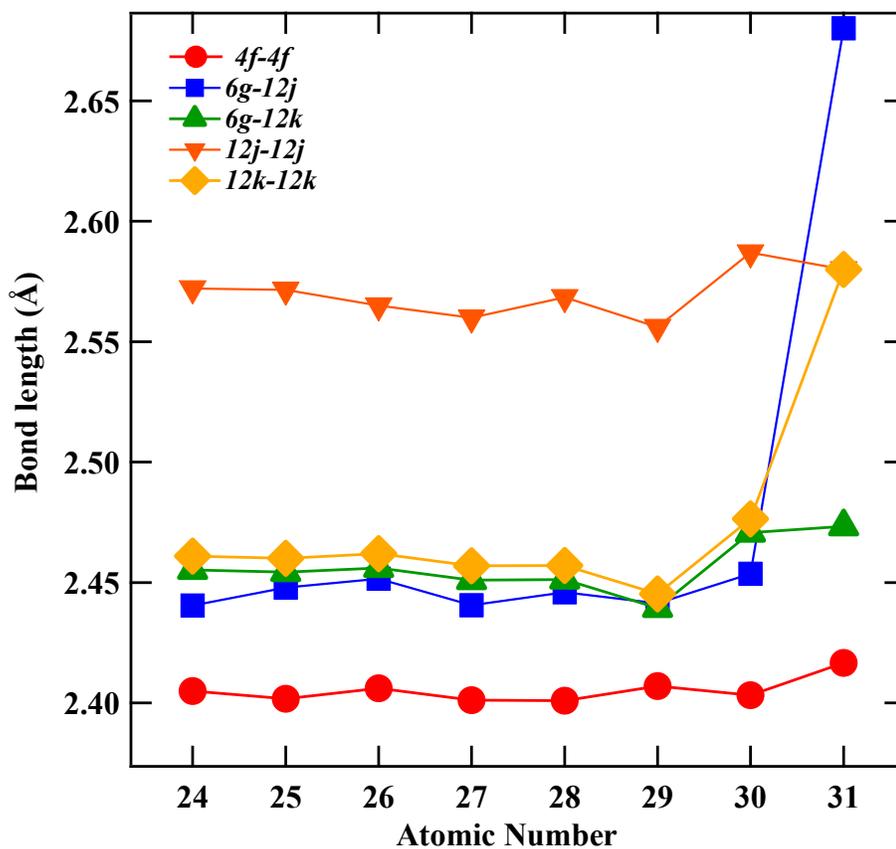
corresponding hexagonal notation viz.  $6c(4f)$ ,  $9d(6g)$ ,  $18f(12j)$  and  $18h(12k)$ . The crystallographic site preference exhibited by TM in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  is listed in **Table II**. It is evident from **Table II** that Ga prefers  $12j$  and  $12k$  sites to other sites, while TM avoids  $4f$  sites and prefers to remain closer to Ga at  $12j$  and  $12k$  sites. The TM atoms display the occupancy preference in order of  $12j \sim 12k > 6g > 4f$ . Thus, the  $6c(4f)$  dumbbell site is the least affected by the TM substitution. Results of site occupancy are in close conformity with the previous Neutron diffraction [22,23] and  $^{57}Fe$  Mossbauer studies [24,25,26] on  $R_2Fe_{17-x}Ga_x$  where Ga atoms preferentially occupy mainly the  $18h(12k)$  site in the  $Th_2Zn_{17}$  structure for  $x < 4$ . The number of Fe and R nearest neighbors (NN) for Fe atoms at various crystallographic sites in  $R_2Fe_{17}$  compounds is as follow; at Fe  $6c$  site (dumbbell site) there are 13 Fe NN and 1 R NN, at Fe  $9d$  site there are 10 Fe NN and 2 R NN, at Fe  $18f$  there are 10 Fe NN and 2 R NN, and at Fe  $18h$  site there are 9 Fe NN and 3 R NN. In addition, the Wigner-Seitz cell volume follows  $6c(4f) > 18h(12k) > 18f(12j) > 9d(6g)$  trend. This shows that Ga and TM atoms for  $12j$  and  $12k$  sites suggest that the Ga affinity for R atoms surpasses the Wigner-Seitz site volume [15].

**Table II:** Atomic site occupancy derived from Rietveld refinement for  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, Ga) with  $Gd_2Fe_{17}$ .

TM	<i>Gd1(2b)</i>	<i>Gd2(2d)</i>	<i>Fe(4f)</i>	<i>Fe(6g)</i>	<i>Fe(12j)</i>	<i>Fe(12k)</i>	<i>Ga(4f)</i>	<i>Ga(6g)</i>	<i>Ga(12j)</i>	<i>Ga(12k)</i>	<i>TM(4f)</i>	<i>TM(6g)</i>	<i>TM(12j)</i>	<i>TM(12k)</i>
<i>Cr</i>	0.0861	0.0809	0.1581	0.2360	0.4580	0.4956	0.0047	0.0068	0.0148	0.0112	0.0072	0.0032	0.0159	0.0181
<i>Mn</i>	0.0829	0.0846	0.1510	0.2327	0.4379	0.5017	0.0042	0.0061	0.0128	0.0108	0.0082	0.0041	0.0166	0.0188
<i>Fe</i>	0.0854	0.0815	0.1706	0.2580	0.4973	0.5293								
<i>Co</i>	0.0835	0.0827	0.1509	0.2410	0.4589	0.4891	0.0057	0.0118	0.0112	0.0115	0.0047	0.0093	0.0144	0.0157
<i>Ni</i>	0.0861	0.0809	0.1518	0.2527	0.4323	0.4824	0.0081	0.0117	0.0062	0.0171	0.0069	0.0103	0.0147	0.0162
<i>Cu</i>	0.0839	0.0821	0.1503	0.2435	0.4521	0.4803	0.0052	0.0121	0.0118	0.0109	0.0051	0.0083	0.0151	0.0169
<i>Zn</i>	0.0816	0.0839	0.1511	0.2321	0.4310	0.4956	0.0045	0.0058	0.0124	0.0102	0.0075	0.0042	0.0179	0.0129
<i>Ga</i>	0.0812	0.0836	0.1455	0.2314	0.4285	0.4863	0.0094	0.01938	0.0309	0.0341				

The Fe-Fe site-to-site bond distances are listed in **Table III** and are plotted in **Fig. 3**. It is observed from the **Table III**, that the  $4f-4f$  bond distances are smallest ( $\sim 2.40$  Å) and  $12k-12k$  (2.46 Å) and  $12j-12j$  (2.57 Å) distances are greatest of all. Other bond distances such as  $6g-12j$ ,  $6g-12k$  and  $12k-12k$  have values close to 2.45 Å and do not show much variation with TM doping. It is to be noted that because of the aforementioned variation in bond distances, it is highly unlikely that these bond-length changes will have a drastic effect on

the Curie temperature of the compounds. In fact, a slight reduction in bond-distances is observed up to Cu substitution, which ideally should lead to an increasing in antiferromagnetic exchange coupling between Fe-Fe moments and hence Curie temperature reduction. The observed changes in bond-distances are in-line with the metallic radii of the TM atoms, **Figure 2**.



**Figure 3:** Atomic site-site bond lengths as a function of TM atomic number in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with  $Gd_2Fe_{17}$ .

**Table III:** Interatomic Fe–Fe distances (in Å) for  $Gd_2Fe_{16y}Ga_{0.5}TM_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with  $Gd_2Fe_{17}$ .

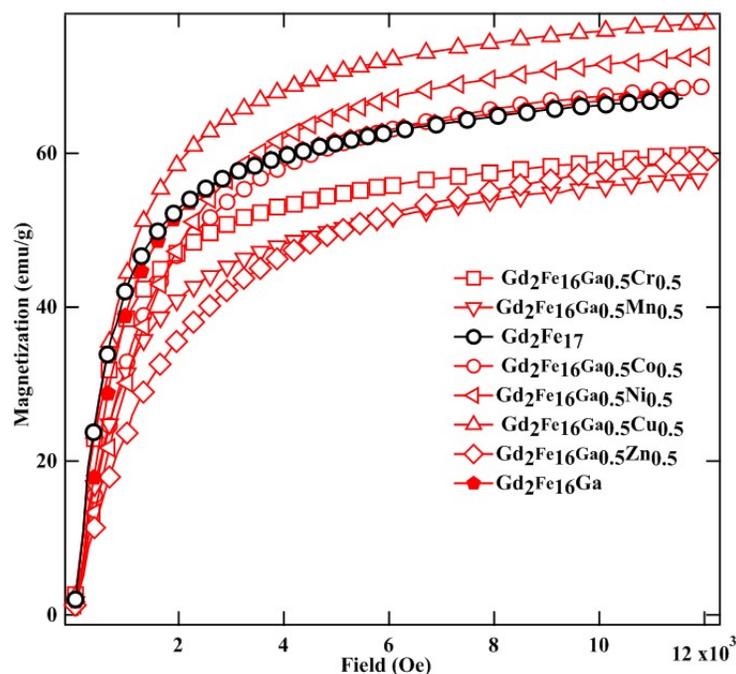
Fe-Fe sites	<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	<i>Zn</i>	<i>Ga</i>
4f-4f	2.4050(4)	2.4018(13)	2.4061(3)	2.4012(5)	2.4010(11)	2.4070(3)	2.4032(2)	2.4166(21)
6g-12j	2.4405(9)	2.4479(9)	2.4516(2)	2.4406(16)	2.4460(3)	2.4414(7)	2.4536(3)	2.6801(3)
6g-12k	2.4552(13)	2.4543(5)	2.4560(2)	2.4510(7)	2.4513(3)	2.4394(11)	2.4707(2)	2.4734(3)
12j-12j	2.5721(3)	2.5715(2)	2.5650(1)	2.5600(7)	2.5684(2)	2.5561(2)	2.587(21)	2.5800(3)
12k-2k	2.4610(13)	2.4600(13)	2.4620(4)	2.4570(2)	2.4571(11)	2.4453(11)	2.4764(11)	2.5800(12)

Room temperature magnetization vs. field plot for  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  is shown in **Fig. 4**. The room temperature magnetic parameters derived from VSM are plotted in **Fig. 5** and are listed in **Table IV**. The Law of Approach to Saturation,  $M = M_s(1 - A/H - B/H^2) + \chi \cdot H$  was used to determine the saturation magnetization. The last term is the forced magnetization term.  $A$  is a constant correlated with the contribution of micro-stress/inclusions, and  $B$  is a constant correlated with magneto-crystalline anisotropy. Where magneto-crystalline is dominant term, a plot of  $M$  vs.  $1/H^2$  in the high field region gives a straight line, the intercept of which (with the  $M$ -axis) gives the saturation magnetization and the slope of which gives the magneto-crystalline anisotropy constant. Interesting variation in saturation magnetization,  $M_s$ , is noticed with the TM atom doping. The  $M_s$  was observed to decrease first with Cr and Mn doping and then increase with TM atomic number up to Cu and then decreased for Zn and Ga doping. Highest  $M_s \sim 77$  emu/g was observed with Cu doping in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$ . While low saturation magnetization was observed upon Cr (60 emu/g), Mn (57 emu/g), and Zn (59 emu/g) doping. As compared to  $Gd_2Fe_{17}$  (67 emu/g),  $Gd_2Fe_{16}Ga_{0.5}Cu_{0.5}$  (77 emu/g) showed an increase of 15% in  $M_s$  value. The observed variation in  $M_s$  can be attributed to the Fe(3d)-TM (3d) hybridization effect of orbitals. The extent of Fe(3d)-3d hybridization raises or lowers the bandwidth, which eventually changes the magnetic moment of Fe atoms [27,28]. The electronic configuration of Cr ( $[Ar]4s^13d^5$ , Mn  $[Ar]4s^23d^5$ , Fe  $[Ar]4s^23d^6$ , Co  $[Ar]4s^23d^7$ , Ni  $[Ar]4s^23d^8$ , Cu  $[Ar]4s^13d^{10}$ , Zn  $[Ar]4s^23d^{10}$  and Ga  $[Ar] 4s^2 4p^13d^{10}$ ). In case of early transition metals, 3d states are positioned at higher energies than those of Fe. Due to exchange splitting  $3d\downarrow$  spin-down states have moved up in energy, and therefore close to the 3d states of early transition metals. Thus, the hybridization of 3d states of early transition metals is stronger with  $3d\downarrow$  spin-down states than  $3d\uparrow$  spin-up states of Fe. As a result, the fraction of spin down  $3d\downarrow$  states of early transition metals found in the energy region of Fe 3d is increased. Since the Fermi level is

situated in this region, anti-ferromagnetic coupling follows. For the late transition metals, the situation is reversed and ferromagnetic coupling follows [29,30,31]. In view of this explanation, Cr, and Mn-doped  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  show lower magnetization while Co, Ni, and Cu doped samples show increasingly higher magnetization. A rather rapid decrease in  $M_s$  has been reported in  $Er_2Fe_{17-x}Mn_x$  with increasing Mn content, which has been attributed to the antiferromagnetic coupling between Fe and Mn [32]. The lower magnetization values of Zn and Ga results from the magnetic dilution effect upon replacing magnetic Fe with non-magnetic Zn and Ga.

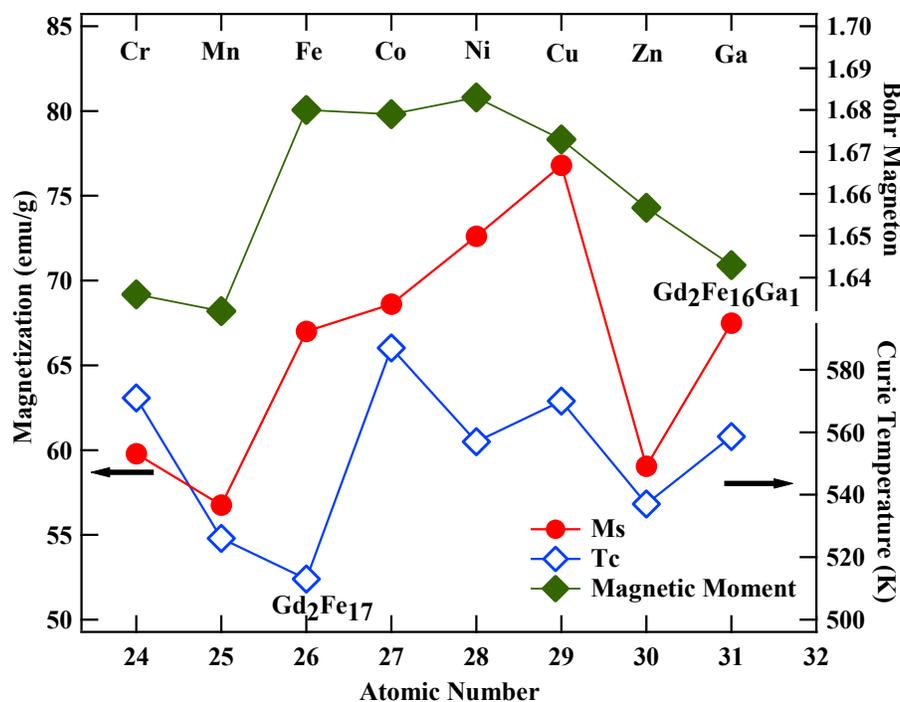
**Table IV:** Room temperature saturation magnetization and Curie temperature of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with  $Gd_2Fe_{17}$ .

$Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$	$M_s(\text{emu/gm})$	$T_c (\text{K})$
Cr	59.78	571
Mn	56.75	526
$Gd_2Fe_{17}$	67.00	513
Co	68.61	587
Ni	72.61	557
Cu	76.79	570
Zn	59.04	537
$Gd_2Fe_{16}Ga_1$	67.49	559



**Figure 4:** Room temperature  $M$  vs.  $H$  of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with  $Gd_2Fe_{17}$ .

The measured Curie temperature,  $T_c$ , of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  compounds is plotted in **Fig. 5** as a function of TM atomic number. It is evident from **Fig.5** that the TM doping affects the  $T_c$  of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  compounds. The Curie temperature reaches a maximum value of 587 K for Co doping followed by a reduction in  $T_c$  with increasing TM atomic number. A 15% increase in  $T_c$  was observed upon Co doping in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  as compared to that of  $Gd_2Fe_{17}$  (513 K) and a 4% increase as compared to  $Gd_2Fe_{16}Ga$  (559K). In the Fe-rich  $R_2Fe_{17}$  intermetallic, the  $T_c$  is mainly determined by the strength and number of Fe-Fe exchange interactions. The strength of Fe-Fe exchange interaction is strongly dependent on the interatomic Fe-Fe distances described [9,33,34,35]. Accordingly, the exchange interactions between iron atoms situated at distances smaller (greater) than 2.45–2.50 Å are negative (positive). In the  $R_2Fe_{17}$  majority of Fe-Fe distances favor the negative interaction [36]. The negative exchange interaction can be reduced either by volume expansion or by reducing the number of Fe-Fe pairs with negative exchange interactions. The low  $T_c$  observed in parent  $Gd_2Fe_{17}$  compound is believed to be due to the short Fe–Fe interatomic distances found at the  $4f(6c)$  sites in the hexagonal (rhombohedral) structure which couple antiferromagnetically since their separation is  $\sim 2.4$  Å, **Fig. 3**, which is less than 2.45 Å needed for ferromagnetic ordering [37]. It is to be noted that increase in  $T_c$  has been reported earlier with higher Al, Ga, and Si content (at  $x > 2$ ) in  $R_2Fe_{17-x}M_x$  ( $M=Al, Ga, Si$ ) [15] however with a concomitant reduction in  $M_s$  due to large Fe replacement with non-magnetic atoms. A  $T_c$  value of 581 K has been reported earlier in  $YGdFe_{16}CoGa$  [38] compound but reported  $T_c \sim 586$  K of  $Gd_2Fe_{16}Ga_{0.5}Co_{0.5}$  exceeds that of the former compounds. Thus, the observed increase in  $T_c$  in TM doped  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  compounds is highest with a minimum replacement of Fe atoms.

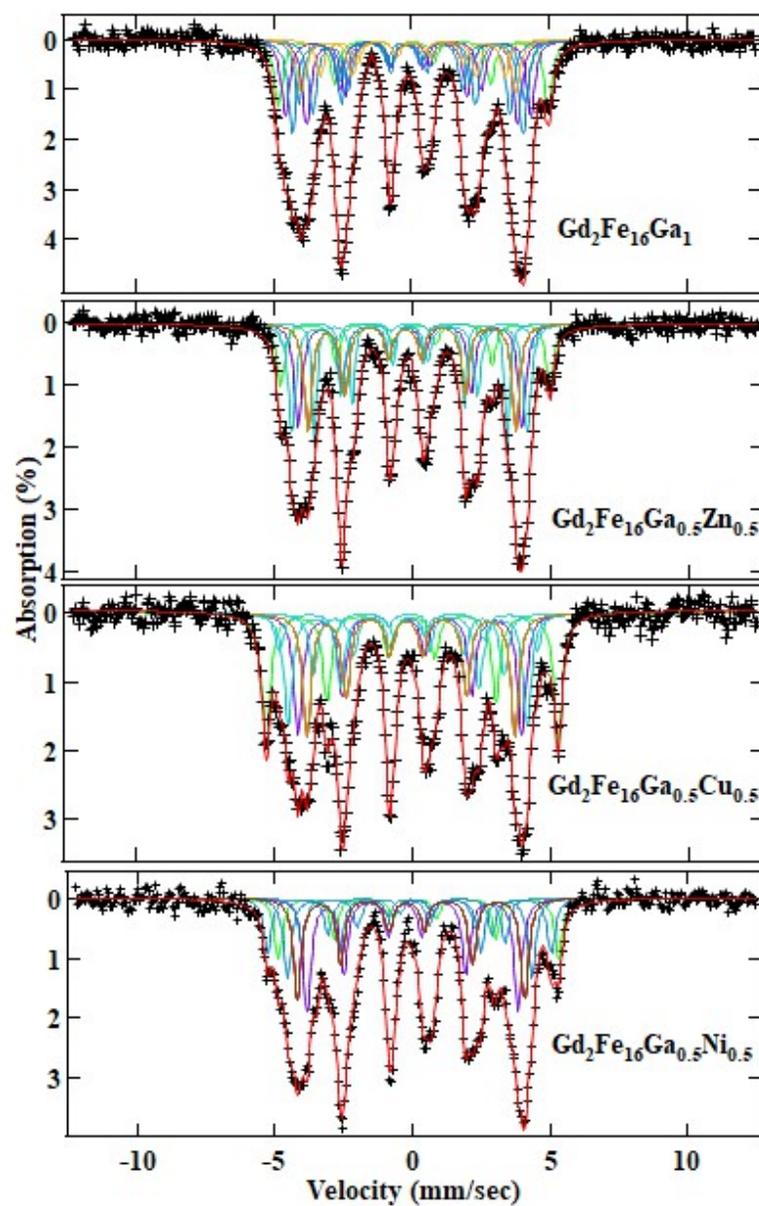


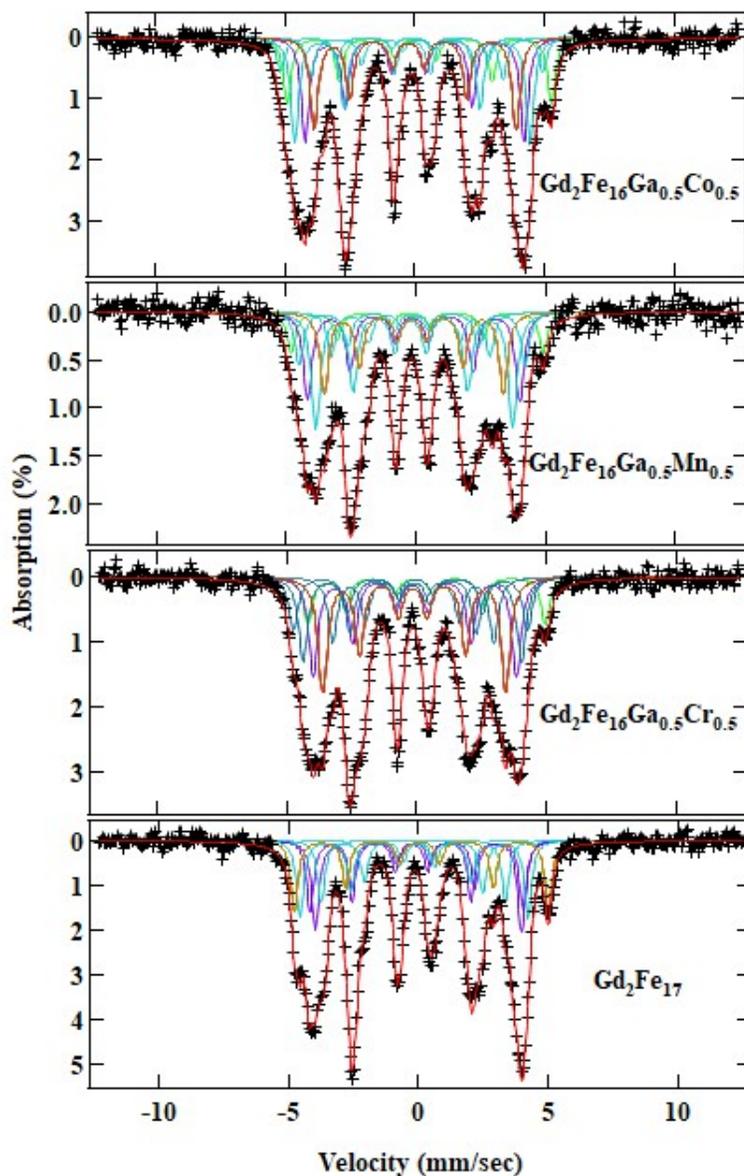
**Figure 5:** Saturation magnetization, Curie temperature, and Bohr magneton number as a function of atomic number in  $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with  $\text{Gd}_2\text{Fe}_{17}$ .

Friedel model [39] can also be used to explain the observed variation in  $T_c$ . According to this model the strength of interaction between two magnetic moments would be strong and ferromagnetic, if  $\lambda/d > 1$ , where distance “d” between these magnetic atoms is smaller than the distance “ $\lambda$ ” covered by the main peak of the Friedel oscillations. In compounds containing 3d transition metals, it has been established that the magnetic coupling is governed mainly by the nearest-neighbor interactions and is proportional to the lattice parameters. Furthermore,  $\lambda$  is found to be inversely proportional to the Fermi wave vector,  $k_f$ . For the 3d band in the  $\text{R}_2\text{Fe}_{17}$  compounds,  $k_f$  is large. Substitution of TM decreases the holes in the 3d band and hence decreases  $k_f$ . The substitution of Ga leads to lattice expansion and hence increases “d”, which will have an effect of reducing  $\lambda/d$  ratio. Since the substitution of Co, Ni and Cu brings in lattice volume reduction as compared to  $\text{R}_2\text{Fe}_{16}\text{Ga}$ ; there is hence an increase in the,  $\lambda/d > 1$  and  $T_c$  [37, 38]. The reported theoretical studies attribute changes in the Curie temperature in substituted  $\text{R}_2\text{Fe}_{17-x}\text{T}_x$  (T=Al, Si, Ga, and Ti) intermetallics to be electronic in origin other than due to the simple volume expansion effect and hence bond-distances [40,41,42]. The effect of the substitution is to

fill out the Fe-3d spin-up sub-bands which alter the magnetic moment of the compound and hence the strength of exchange interaction [39,43]. In fact, theoretical calculations performed using LSDA+U method showed that enhancement between Fe-Fe atoms in the presence of Ga in  $Gd_2Fe_{17-x}Ga_x$  compounds, which intern was shown to enhance Curie temperature for low Ga ( $x < 3$ ) content [44]. Thus, observed higher  $T_c$  values of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  as compared to that of pure  $Gd_2Fe_{17}$  could be attributed to this effect as well. In comparison to various doped intermetallics such as  $Gd_2Fe_{16}Ga$  (~410 K) [45],  $Gd_2Fe_{16}Ga_{0.5}Ti_{0.5}$  (556 K) [46],  $Dy_2Fe_{16}Ga$  (~462K) [8],  $Ce_2Fe_{16}Ga$  (~320K) [47],  $Sm_2Fe_{16}Ga$  (~505K) [48], or  $Sm_2Fe_{16.2}Ti_{0.8}$  (~435K) [49], the reported compound  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  with Co, Ni, and Cu substitution certainly exhibits higher  $T_c$  and  $M_s$ , thus ensuring their potential use as high temperature permanent magnet applications.

The room temperature (RT) Mossbauer spectra for  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  are shown in **Fig. 6**. The  $R_2Fe_{17}$  intermetallic with  $Th_2Ni_{17}$  structure, have the easy direction of magnetization and hyperfine field lying in the basal plane along  $a$  or  $b$  axes of the unit cell [50,51]. This basal plane easy direction of magnetization complicates the Mossbauer spectral analysis of  $R_2Fe_{17}$  compounds because it involves four crystallographically inequivalent iron sites. The reason for the inequivalent iron site is the vector character of the hyperfine field and tensor character of the electric field gradient [52]. Thus, this inequivalency demands further magnetic splitting of  $g$ ,  $j$ , and  $k$  iron sites. Mössbauer studies of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  have been conducted accordingly, either with 8 or 10 magnetic sextets, with absence or presence of impurity phase, respectively [46,53,54,55]. The Mössbauer spectral analysis was carried out with magnetic sextets assigned to the  $4f$ ,  $6g$ ,  $12j$ , and  $12k$  sites in  $Gd_2Fe_{17}$ . The  $6g$ ,  $12j$ , and  $12k$  sites were further split into 2, 3, and 2 corresponding to the site occupancies of Fe atoms in the crystal structure of  $R_2Fe_{17}$  with the planar anisotropy. The intensities of the six absorption lines of each sextet were assumed to follow the 3:2:1 intensity ratio expected for randomly oriented powder samples in zero magnetic field and a single common line-width was assumed for all the eight sextets. The isomer shifts (IS,  $\delta$ ) for the magnetically inequivalent sites were constrained to be the same, whereas the hyperfine field (HF,  $B_{hf}$ ) were expected to vary at pairs of magnetically inequivalent sites due to variations in the dipolar and orbital contributions to the magnetic hyperfine fields [56]. The  $^{57}Fe$  Mossbauer spectra show hyperfine split sextets in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  revealing that the samples are magnetically ordered and all of them have different subspectra with different magnetic hyperfine fields.

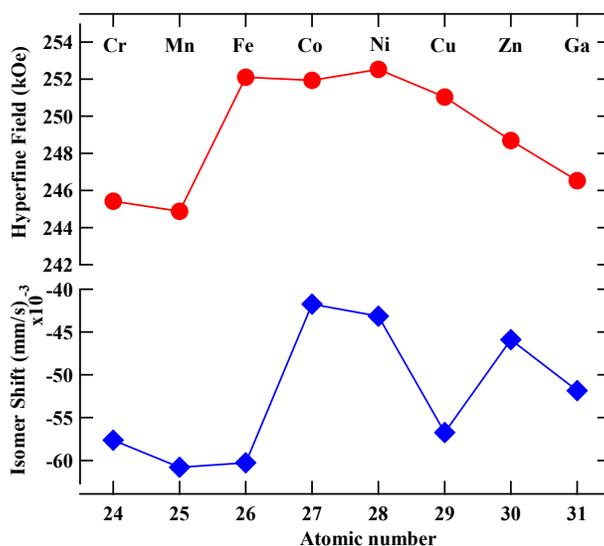




**Figure 6:** Fitted room temperature Mossbauer spectra of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with  $Gd_2Fe_{17}$ .

The hyperfine parameters derived from the fitting are listed in **Table V**, and weighted average (Wt.Avg.) hyperfine field (HF) and isomer shifts (IS,  $\delta$ ) are plotted in **Fig. 7**. There exists a direct correlation between hyperfine field values of a site to its near neighbor (NN) iron sites. In case of  $Th_2Ni_{17}$  structure,  $12k$  site has 9 NN Fe sites (1 ( $4f$ ), 2 ( $6g$ ), 4 ( $12j$ ), 2( $12k$ )),  $12j$  has 10 NN Fe sites (2 ( $4f$ ), 2 ( $6g$ ), 2 ( $12j$ ), 4 ( $12k$ )),  $6g$  has 10 NN Fe sites (2 ( $4f$ ), 0 ( $6g$ ), 4 ( $12j$ ), 4( $12k$ )), and  $4f$  site has 11 NN Fe sites (1 ( $4f$ ), 3 ( $6g$ ), 6 ( $12j$ ), 3 ( $12k$ )). Following the NN distribution, the observed HF values are in  $4f(6c) > 12j(18f) > 6g(9d) > 12k(18h)$  sequence, which is similar to the sequence observed in

other  $R_2Fe_{17}$  compounds [57,58]. It is obvious that  $4f(6c)$  site has the maximum hyperfine field, since it has the maximum number of Fe nearest neighbors, whereas, the  $18h(12k)$  site has the minimum number of Fe neighbors and consequently has the least HF value. Although  $6g(9d)$  and  $12j(18f)$  sites have the same number of Fe neighbors, the former has comparatively smaller Fe-Fe distances and hence a larger hyperfine field, **Table III** and **Table V**. The Cu and Mn-doped  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  display a low Wt. Avg. HF values as compared to other TM doped  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  compounds. The Wt. Avg. HF value reaches the maximum for  $Gd_2Fe_{17}$  and  $Gd_2Fe_{16}Ga_{0.5}Co_{0.5}$ , to a value  $\sim 252$  kOe followed with a gradual decline in its value, reaching to a value of 246 kOe for  $Gd_2Fe_{16}Ga_1$ . This decrease in HF value results from the decreased magnetic exchange interactions resulting from Fe replacement with non-magnetic Cu, Zn, and Ga atoms. Furthermore, under the first approximation, the hyperfine field is assumed proportional to the magnetic moment. We obtained the Fe moment using the hyperfine coupling constant of  $150 \text{ kOe}/\mu_B$ , which has been reported for Y-Fe systems [59,60]. The average value of Fe magnetic moment for  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  is plotted in **Fig. 5**. In general, Fe magnetic moment holds up to the value of  $1.68 \mu_B$  only for Fe, Co, and Ni substitution in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$ .



**Figure 7:** Weighted average hyperfine parameters viz. Hyperfine field and Isomer shift, as a function of atomic number for  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with  $Gd_2Fe_{17}$ .

1 **Table V:** RT Mossbauer hyperfine parameters for  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) with  $Gd_2Fe_{17}$ .

TM		$4f$	$6g_1$	$6g_2$	$12j_1$	$12j_2$	$12j_3$	$12k_1$	$12k_2$	Doublet	Wt. Avg.
Cr	B(kOe)	303	231.6	244.1	212.5	271.2	278.5	198	255.3		245.424
	IS(mm/s)	0.102	-0.121	-0.121	-0.1	-0.1	-0.1	0.011	0.011		-0.0576
	QS(mm/s)	0.351	0.116	0.162	0.073	-0.157	-0.009	0.35	-0.0446		
	Area (%)	10	15.2	17.8	12.5	4.3	18.5	9.9	11.7		
Mn	B(kOe)	302.3	230	254.3	210.1	265.2	275.1	202	255.6		244.882
	IS(mm/s)	0.078	-0.117	-0.117	-0.124	-0.124	-0.124	0.039	0.039		-0.0608
	QS(mm/s)	0.28	0.093	0.093	-0.157	0.149	-0.079	0.434	-0.17		
	Area (%)	8.2	16.3	17.6	8.7	23.1	10.6	10.7	6.2		
(Gd <sub>2</sub> Fe <sub>17</sub> )	B(kOe)	304	246.2	254.6	220.5	272.3	286.3	205.6	260.2		252.1
	IS(mm/s)	0.07	-0.13	-0.13	-0.115	-0.115	-0.115	0.035	0.035		-0.0603
	QS(mm/s)	0.067	0.296	0.21	-0.019	0.009	-0.116	0.358	-0.487		
	Area (%)	13.8	15.5	19.8	6.1	13.6	11.9	6.16	11.7		
Co	B(kOe)	315.2	242.7	262.9	215.6	271.3	283	203.2	264.6		251.932
	IS(mm/s)	0.11	-0.119	-0.119	-0.098	-0.098	-0.098	0.056	0.056		-0.0417
	QS(mm/s)	0.139	0.272	0.238	-0.399	0.015	-0.039	0.263	-0.245		
	Area (%)	11.5	16	18.1	7.1	18.4	5.9	10.1	10.8		
Ni	B(kOe)	310.1	239.1	257.4	220.6	276.7	285.2	201.9	263.3	44.4	252.524
	IS(mm/s)	0.113	-0.129	-0.129	-0.09	-0.09	-0.09	0.044	0.044	0.5	-0.0432
	QS(mm/s)	0.265	0.458	0.055	-0.036	0.042	-0.079	0.138	0.151	-0.5	
	Area (%)	11	3.5	9.3	8	18.6	8.3	14.3	16.6	8.4	
Cu	B(kOe)	312.2	234.5	252.1	214.8	269.2	290.3	200.2	268	45.9	251.032
	IS(mm/s)	0.113	-0.137	-0.137	-0.128	-0.128	-0.128	0.062	0.062	0.387	-0.0567

	QS(mm/s)	0.021	0.172	0.102	-0.005	-0.083	-0.103	-0.358	-0.17	-0.39	
	Area (%)	22	20.8	20.4	10.3	18.7	6.5	1.9	2.6	2.8	
Zn	B(kOe)	303.4	234.5	252.3	217.1	265	280.7	211.3	256.4		248.689
	IS(mm/s)	0.088	-0.141	-0.141	-0.101	-0.101	-0.101	0.062	0.062		-0.0459
	QS(mm/s)	0.041	0.252	0.125	0.098	-0.0001	-0.033	0.178	-0.145		
	Area (%)	11.3	19.4	18.8	13.2	19.5	4.3	3.4	9.1		
Ga	B(kOe)	304.8	235.6	238.3	222.8	255.1	283.8	208.2	252.9		246.529
	IS(mm/s)	0.059	-0.109	-0.109	-0.113	-0.113	-0.113	0.05	0.05		-0.0518
	QS(mm/s)	0.025	-0.086	0.211	0.216	0.275	-0.023	0.093	-0.147		
	Area (%)	12.3	14	15.3	13.5	11.7	17.3	6.8	9.9		

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7 The isomer shift values were assigned in relation to the Wigner-Seitz cell volume, i.e. the  
8 greater the Wigner-Seitz cell volume, the greater the isomer shift, **Table V** [61]. So, as  
9  $V(4f) > V(12j) \sim V(12k) > V(6g)$ , their corresponding IS follow as  $\delta 4f > \delta 12j \sim \delta 12k > \delta 6g$ . The  
10 room temperature values of Wt. Avg. IS for  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  are negative and the  
11 magnitudes of IS increase with increasing TM atomic number in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$ . The IS  
12 is proportional to the total *s*-electron charge density at the iron nucleus, which is the sum of  
13 the spin-up and spin-down *s*-electron density and lattice site volume; an increasing *s*-  
14 electron density at iron nucleus is indicated by a decreasing isomer shift. The observed  
15 behavior of IS value could be attributed to the competition between lattice site volume and  
16 complex nature of hybridization between Fe-Ga-TM [62,63], which all affect the *s*-electron  
17 charge density at the iron nucleus. A volume contraction is observed until TM=Ni followed  
18 with unit cell expansion till TM=Zn doping in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$ . However, the Wt. Avg.  
19 IS value becomes less negative with TM=Co and onward. Thus, this behavior of IS  
20 indicates electronic effects at play in dictating IS behavior of  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  compound.  
21 The increased IS value for with Co, Ni, Cu, Zn, and Ga in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  could be  
22 associated with the increased number of the 3d electrons which increases the shielding of  
23 the *s*-electrons from the nucleus. In earlier TM atoms viz. Cr and Mn, the 3d band is  
24 broader and heavily hybridized with the conduction band [38]. These make electrons freer  
25 and thus have a greater presence at the Fe nucleus, which makes IS more negative. The  
26 increased screening of *s*-electrons via 3d electrons beyond TM=Fe doping in  
27  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  could be the reason for enhanced IS.

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#### 29 **4. Conclusion**

30 The effect of double substitution Ga and TM in  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  on structural and  
31 magnetic properties is compared with  $Gd_2Fe_{17}$  compounds. These compounds were found  
32 to crystallize in hexagonal  $Th_2Ni_{17}$  type structure. Lattice parameters and unit cell volume  
33 of TM doped  $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$  compounds show dependence on atomic radii of TM  
34 dopant. The variance of *c/a* ratio with the substitution in these compounds shows anisotropic  
35 unit cell volume expansion. The Rietveld analysis show preferred occupancy of Ga for 12*k*  
36 and 12*j* while TM for 12*k* sites. Overall, no direct correlation was observed between the  
37 trend in Curie temperature and bond-distances. The observed *T<sub>c</sub>* reached a maximum value  
38 of 587 K for cobalt substitution, which is 15% higher than *T<sub>c</sub>* value of  $Gd_2Fe_{17}$ .  
39 Furthermore, 15% and 14% enhancement in *M<sub>s</sub>* was observed for Cu substituted

40 Gd<sub>2</sub>Fe<sub>16</sub>Ga<sub>0.5</sub>TM<sub>0.5</sub> compound as compared to Dy<sub>2</sub>Fe<sub>17</sub> and Dy<sub>2</sub>Fe<sub>16</sub>Ga<sub>1</sub> compounds,  
41 respectively. Furthermore, unlike other doped compounds of RE<sub>2</sub>Fe<sub>17-x</sub>M<sub>x</sub> (M=Al, Si, Ga)  
42 intermetallic, where improvements in T<sub>c</sub> is comprised with the reduction in M<sub>s</sub>, in the  
43 present studied compound Gd<sub>2</sub>Fe<sub>16</sub>Ga<sub>0.5</sub>TM<sub>0.5</sub>, even small TM doping (TM=Co, Ni, and  
44 Cu) brings in a simultaneous enhancement in M<sub>s</sub> and T<sub>c</sub>. The combined magnetic and  
45 Mossbauer study points to the fact that the observed improvement in T<sub>c</sub> and M<sub>s</sub> could be  
46 attributed to electronic effects resulting from Fe-3d hybridization with substituted TM atom  
47 electronic shell. A concomitant improvement in M<sub>s</sub> and T<sub>c</sub> is desirable for the magnetic  
48 industry. The study elucidates that the judicious selection of dopants and its content can  
49 improve M<sub>s</sub> and T<sub>c</sub> of the R<sub>2</sub>Fe<sub>17</sub> intermetallic compounds.

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