Structural, Magnetic, and Mössbauer Studies of Transition Metal-Doped Gd2Fe16Ga0.5TM0.5 Intermetallic Compounds (TM = Cr, Mn, Co, Ni, Cu, and Zn)

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Structural, Magnetic, and Mössbauer Studies of Transition Metal-Doped Gd$_2$Fe$_{16}$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$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, and Zn) compounds were investigated in this study. Rietveld analysis of X-ray data indicates that all the samples crystallize in the hexagonal Th$_2$Ni$_{17}$ structure. The lattice parameters a, c, and the 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 room temperature was observed for Co, Ni, and Cu of 69, 73, and 77 emu/g, respectively, while a minimum value was observed for Zn (62 emu/g) doping in Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$. The highest Curie temperature of 590 K was observed for Cu doping which is 15 and 5% higher than Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$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$_2$Fe$_{16}$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$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ compounds as compared to pure Gd$_2$Fe$_{17}$ or Gd$_2$Fe$_{16}$Ga makes Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ a potential candidate for high-temperature industrial magnet applications.

Keywords: permanent magnetic materials; 2:17 intermetallic; Mössbauer spectroscopy; Curie temperature; X-ray diffraction; Rietveld analysis

1. Introduction

The rare-earth intermetallic compounds R$_2$Fe$_{17}$ have energy product ($BH_{max}$) and $H_c$ to be about 26 MGOe and 15 kOe, respectively [1]. Beside these properties, they exhibit low Curie temperature ($T_c$). For example, 473 K for Gd$_2$Fe$_{17}$ and 300 K for Dy$_2$Fe$_{17}$ along with low magnetic anisotropies [2]. Various strategies have been employed addressing issues related to improving magnetic anisotropy, magnetization, and Curie temperature of R$_2$Fe$_{17}$ compounds. Metalloids such as C, N, and H atoms are added to improve the magnetic anisotropy and Curie temperature [3–6]. However, high-temperature processing of these interstitially modified compounds is difficult. Subsequently, the addition of non-magnetic atoms such as Al, Ga, and Si for iron in the R$_2$Fe$_{17-\delta}$M$_\delta$ compound was investigated and showed Curie temperature enhancement at high non-magnetic atom content. Among Al, Si, and Ga, Ga substituted compounds show high $T_c$, e.g., for Sm$_2$Fe$_{16}$Ga, $T_c$ was ~485 K [7]; for Dy$_2$Fe$_{16}$Ga, $T_c$
was ~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 $\text{R}_2\text{Fe}_{17}$ compounds is explained on the basis of exchange interaction strength between Fe–Fe pairs [9]. This is based on the assumption that the exchange interactions favor ferromagnetic ($r > r_c$) or antiferromagnetic ($r < r_c$) properties, where $r_c \approx 2.5\ \text{Å}$. 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 lattice unit cell expansion, except in Si-substituted $\text{RE}_2\text{Fe}_{17-x}\text{Si}_x$, 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 $\text{R}_2\text{Fe}_{17}$ intermetallic, $\text{Gd}_2\text{Fe}_{17}$ is of special interest, as it has the highest Curie temperature, $T_C$. Among the doped $\text{R}_2\text{Fe}_{17-x}\text{M}_x$ ($\text{M} = \text{Al, Si, Ga}$), Ga-doped compounds display higher $T_c$ [15]. In this regard, the present work investigates the effect of doping transition metal (TM) atoms in Ga-doped $\text{Gd}_2\text{Fe}_{17}\text{Ga}_{0.5}\text{TM}_{0.5}$ compounds and compares the results with $\text{Gd}_2\text{Fe}_{17}$. 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↑ states below the Fermi level or allow charge transfer out of the 3d band, provided that the spin-down density of states exceed the spin-up density [16].

This study discusses the change in the structural and magnetic properties in $\text{R}_2\text{Fe}_{17}$ compounds when Fe is substituted in $\text{R}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$ 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 $\text{R}_2\text{Fe}_{17}$ compounds so as to improve $T_c$ without affecting the saturation magnetization.

2. Experimental Section

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, USA. The parent alloys $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$ were prepared by arc melting the stoichiometric amount of the aforementioned elements under a high purity argon atmosphere. The ingots were melted several times to ensure the high degree of homogeneity.

X-ray diffraction (XRD) experiment was carried out with Cu Kα ($\lambda \approx 1.5406\ \text{Å}$) radiation using 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° and a collection time of 2 s/step. The XRD analysis was performed by the well-known structural refinement Rietveld method [17] 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 2b and 2d site (0, 0, 0.25) and (0.333, 0.667, 0.75), Fe is fixed at 4f, 6g, 12j, and 12k (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 were used to minimize the difference between a calculated profile and the observed data.

Magnetic properties of the powder sample were investigated at room temperature (RT) using a vibrating sample magnetometer (VSM) in the maximum field of 1.2 T. To minimize the effect of the demagnetizing field, the samples were compacted at 3000 psi, cut into rectangular parallelepiped with the length-to-width ratio greater than 3, and embedded in epoxy. A modified thermogravimetric
analyzer (DuPont 910) equipped with a permanent magnet was used to determine the Curie temperature of composite samples. In this procedure, 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 ferromagnetic to paramagnetic), and the reduced attraction for the magnet results in a sharp apparent weight loss or gain (depending on the TGA design).

The Mössbauer spectra of the samples were obtained at RT using a 25 mCi $^{57}$Co source in a Rh foil mounted on a constant acceleration drive system (SEE Co., Minneapolis, MN, USA) in transmission geometry. The velocity scale of the Mössbauer spectrometer was calibrated by measuring the hyperfine field of $\alpha$-Fe foil, at room temperature. The Mössbauer spectra were analyzed using WMoss software from SEE Co. They were fitted using a standard nonlinear least squares minimization routine with sub-spectra intensities constrained to match crystallographic probabilities.

### 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 Figure 1a. The inset in Figure 1a, the enlarged $2\theta$ view between 41.5 and 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 increases from TM = Cr to Zn (Table 1). The refined Rietveld profiles are presented in Figure 1b for $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$ systems. In Table 1, the $R_{\text{obs}}$ values are calculated from the observed and calculated structure factors. Since it is a mixed system, the $R_{\text{obs}}$ possibly adds errors (less than 5%) in the structure factor. These small errors reflect on the low angle, and the intensity counts range is between 25 and 100, which is minimal. This error may be because of multiple factors such as background errors, the preferred orientation, multiplicity factors, and instrumental errors. Moreover, these errors are minimal when compared to the high angle reflection $2\theta$ range of 35–45$^\circ$. The refined structural parameters viz. lattice parameters $a$, $c$, the $c/a$ ratio, the unit cell volume, and the reliability indices are given in Table 1. 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 the hexagonal Th$_2$Ni$_{17}$ structure with the $P6_3/mmc$ symmetry group. Figure 2 show the lattice parameters as a function of the TM atomic number in $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$. It can be observed in Figure 2 that the variation in lattice parameter, $a$, is more pronounced than that in $c$ in the doped compounds. This is also evident from the variation in the $c/a$ ratio (Table 1), which indicates the 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 about lattice expansion. The observed trend in lattice parameter closely follows TM metallic radii (Figure 2).

### Table 1. Structural parameters derived from Rietveld refinement of powder XRD data of $\text{Gd}_2\text{Fe}_{17}$ and $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{0.5}\text{TM}_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga).

| Parameter         | Cr   | Mn   | Gd$_2$Fe$_{17}$ Fe | Co   | Ni   | Cu   | Zn   | Gd$_2$Fe$_{16}$Ga$_{0.5}$ TM$_{0.5}$ |
|-------------------|------|------|-------------------|------|------|------|------|-------------------------------|
| 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$^3$) | 526.97 | 527.32 | 522.2634          | 525.15  | 523.60 | 526.06 | 528.21 | 528.5749                  |
| $R_{\text{obs}}$ (%) | 5.67  | 4.44  | 2.48              | 4.53     | 3.21   | 3.99   | 2.31   | 6.43                        |
| $\varepsilon R_{\text{obs}}$ (%) | 4.32  | 5.21  | 3.55              | 5.31     | 4.21   | 4.87   | 3.65   | 7.12                        |
| $R_{\psi}$ (%)    | 6.22  | 7.87  | 9.12              | 8.31     | 7.32   | 7.22   | 5.32   | 10.55                       |
| $\varepsilon R_{\psi}$ (%) | 7.87  | 8.96  | 10.54             | 9.32     | 8.32   | 10.11  | 7.78   | 12.54                      |
the previous Neutron diffraction [22,23] and 57Fe Mössbauer studies [24–26] on R$_2$Fe$_{17}$−$_x$Ga$_x$ where Ga atoms preferentially occupy mainly the 18$h$(12$k$) site in the Th$_2$Zn$_{17}$ structure for $x$ < 4. The number of Fe and R nearest neighbors (NNs) for Fe atoms at various crystallographic sites in R$_2$Fe$_{17}$ compounds is as follows; at the Fe 6$c$ site (dumbbell site), there are 13 Fe NNs and 1 R NNs; at the Fe 9$d$ site, there are 10 Fe NNs and 2 R NNs; at Fe 18$f$, there are 10 Fe NNs and 2 R NNs; at the Fe 18$h$ site there are 9 Fe NNs and 3 R NNs. In addition, the Wigner–Seitz cell volume follows 6$c$(4$f$) > 18$h$(12$k$) > 18$f$(12$j$) > 9$d$(6$g$). This shows that Ga and TM atoms for 12$j$ and 12$k$ sites suggest that the Ga affinity for R atoms surpasses the Wigner–Seitz site volume [15].

Figure 1. (a) XRD powder profile for Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga). (b) Rietveld refined XRD data of Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga).
The atomic site occupancy for Gd, Fe, Ga, and TM atoms derived from Rietveld refinement are listed in Table 2. 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$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ is listed in Table 2. It is evident from Table 2 that Ga prefers 12j and 12k sites, and TM avoids 4f sites and prefers to remain closer to Ga at 12j and 12k sites. The TM atoms display occupancy preference with the order 12j~12k > 6g > 4f. Thus, the 6c(4f) dumbbell site is the least affected site by the TM substitution. Results of site occupancy are in close conformity with the previous Neutron diffraction [22,23] and $^{57}$Fe Mössbauer studies [24–26] on R$_2$Fe$_{17}$−$_x$Ga$_x$ where Ga atoms preferentially occupy mainly the 18h(12k) site in the Th$_2$Zn$_{17}$ structure for x < 4. The number of Fe and R nearest neighbors (NNs) for Fe atoms at various crystallographic sites in R$_2$Fe$_{17}$ compounds is as follows; at the Fe 6c site (dumbbell site), there are 13 Fe NNs and 1 R NNs; at the Fe 9d site, there are 10 Fe NNs and 2 R NNs; at Fe 18f, there are 10 Fe NNs and 2 R NNs; at the Fe 18h site there are 9 Fe NNs and 3 R NNs. In addition, the Wigner–Seitz cell volume follows 6c(4f) > 18h(12k) > 18f(12j) > 9d(6g). 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 2. Atomic site occupancy derived from Rietveld refinement for Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga).

| TM  | Gd1(2b) | Gd2(2d) | Fe(4f) | Fe(6g) | Fe(12j) | Fe(12k) | Ga(4f) | Ga(6g) | Ga(12j) | Ga(12k) | TM(4f) | TM(6g) | TM(12j) | TM(12k) |
|-----|---------|---------|--------|--------|---------|---------|--------|--------|---------|---------|--------|--------|---------|---------|
| Cr  | 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  |
| Mn  | 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  |
| Fe  | 0.0854  | 0.0815  | 0.1706 | 0.2580 | 0.4973  | 0.5293  |         |        |         |         |        |        |         |         |
| Co  | 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  |
| Ni  | 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  |
| Cu  | 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  |
| Zn  | 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  |
| Ga  | 0.0812  | 0.0836  | 0.1455 | 0.2314 | 0.4285  | 0.4863  | 0.0094 | 0.0193 | 0.0309  | 0.0341  |         |        |         |         |
The Fe–Fe site-to-site bond distances are listed in Table 3 and are plotted in Figure 3. It can be observed in Table 3 that the 4f–4f bond distances are smallest (~2.40 Å), and 12j–12j (2.46 Å) and 12j–12k (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 increase 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$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) derived from Rietveld refinement.

Table 3. Interatomic Fe–Fe distances (in Å) for Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga) obtained from Rietveld refinement.

| Fe–Fe Sites | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga |
|-------------|----|----|----|----|----|----|----|----|
| 4f–4f       | 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–12k     | 2.4610(13) | 2.4600(13) | 2.4620(4) | 2.4570(2) | 2.4571(11) | 2.4453(11) | 2.4764(11) | 2.5800(12) |

RT magnetization vs. field plot for Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ is shown in Figure 4. The RT magnetic parameters derived from the hysteresis curves are plotted in Figure 5 and are listed in Table 4. The “law of approach” to saturation magnetization was used to determine the saturation magnetization, $M_s$. The law of approach describes the relationship between magnetization $M$ on the applied magnetic field for $H$ greater than coercive field $H_c$. The magnetization near $M_s$ can be written as $[27], M = M_s\left[1 - \frac{a}{H} - \frac{b}{H^2}\right] + \kappa H$, where $M$ is the magnetization, $H$ is the applied magnetic field, and $M_s$ is the saturation magnetization attained at a high field. The term $\kappa H$ represents the field-induced increase in the spontaneous magnetization of the domains. This term is very small at a temperature well below the Curie temperature and could be neglected. The term “$a$” is generally interpreted as due to microstress and ignored in the high field region, and “$b$” as due to crystal anisotropy. Where magneto-crystalline is a 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 $M$-s and the slope of which gives the magneto-crystalline anisotropy constant. Interesting variation in $Ms$ is noticed with the TM atom doping. The $Ms$ was observed to decrease first with Cr and Mn doping and then increase with TM atomic number up to Cu, and it decreased for Zn and Ga doping. The highest $Ms$ ~77 emu/g was observed with Cu doping in Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$, while a low $Ms$ was observed upon Cr (60 emu/g), Mn (57 emu/g), and Zn (59 emu/g) doping. As compared to Gd$_2$Fe$_{17}$ (67 emu/g), Gd$_2$Fe$_{16}$Ga$_{0.5}$Cu$_{0.5}$ (77 emu/g) showed an increase of 15% in the $Ms$ value. The observed variation in $Ms$ 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 [28,29].

Accordingly, the exchange interactions between iron atoms situated at distances smaller (greater) than 2.45 Å are negative (positive). In the R$_2$Fe$_{17}$ majority of Fe–Fe, distances favor a negative interaction [37]. 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$_2$Fe$_{17}$ 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 ~2.4 Å (Figure 3), which is less than 2.45 Å needed for ferromagnetic ordering [38].

Table 4. Room temperature saturation magnetization, $Ms$, and Curie temperature, $T_C$, of Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga).

| Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ | $Ms$ (emu/g) | $T_C$ (K) |
|------------------------------------|-------------|-----------|
| Cr                                 | 59.78       | 571       |
| Mn                                 | 56.75       | 526       |
| Gd$_2$Fe$_{17}$                    | 67.00       | 513       |
| Co                                 | 68.61       | 587       |
| Ni                                 | 72.61       | 557       |
| Cu                                 | 76.79       | 570       |
| Zn                                 | 59.04       | 537       |
| Gd$_2$Fe$_{16}$Ga$_1$              | 67.49       | 559       |

The measured Curie temperature, $T_C$, of Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ compounds is plotted in Figure 5 as a function of TM atomic number. It is evident from Figure 5 that the TM doping affects the $T_C$ of Gd$_2$Fe$_{16}$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$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ as compared to that of Gd$_2$Fe$_{17}$ (513 K) and a 4% increase as compared to Gd$_2$Fe$_{16}$Ga (559K). In the Fe-rich R$_2$Fe$_{17}$ 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 [9,34–36]. Accordingly, the exchange interactions between iron atoms situated at distances smaller (greater) than 2.45–2.50 Å are negative (positive). In the R$_2$Fe$_{17}$ majority of Fe–Fe, distances favor a negative interaction [37]. 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$_2$Fe$_{17}$ 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 ~2.4 Å (Figure 3), which is less than 2.45 Å needed for ferromagnetic ordering [38].
It is to be noted that the increase in $T_c$ has been reported earlier with higher Al, Ga, and Si content (at $x > 2$) in $R_2Fe_{17-x}M_x$ ($M = \text{Al, Ga, and Si}$) [15] but with a concomitant reduction in $Ms$ due to large Fe replacement with non-magnetic atoms. A $T_c$ value of 581 K has been reported earlier in the YGdFe$_{16}$CoGa [39] compound, but a reported $T_c \approx 586$ K of Gd$_2$Fe$_{16}$Ga$_{0.5}$Co$_{0.5}$ exceeds that of the former compounds. Thus, the observed increase in $T_c$ in TM-doped Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ compounds is highest with a minimum replacement of Fe atoms.

![Figure 4](image-url)  
**Figure 4.** Room temperature $M$ vs. $H$ plot of Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga).

![Figure 5](image-url)  
**Figure 5.** Saturation magnetization, $Ms$, Curie temperature, $T_c$, and Bohr magneton number as a function of TM atomic number in Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga).

The Friedel model [40] 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 NN 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 $R_2Fe_{17}$ 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 the $\lambda/d$ ratio. Since the substitution of Co, Ni, and Cu brings in lattice volume reduction as compared to $R_2Fe_{16}Ga$; there is an increase in the $\lambda/d > 1$ and $T_c$ [39,40]. The reported theoretical studies attribute changes in the Curie temperature in substituted $R_2Fe_{17−x}TM_x (TM = Al, Si, Ga, and Ti)$ intermetallic to be electronic in origin other than due to the simple volume expansion effect and hence bond distances [41–43].

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 [41,44]. In fact, theoretical calculations performed using the LSDA+U method showed enhancement between Fe–Fe atoms in the presence of Ga in $Gd_2Fe_{17−x}Ga_x$ compounds, which in turn shows to enhance $T_c$ for low Ga ($x < 3$) content [45]. Thus, the 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 intermetallic such as $Gd_2Fe_{16}Ga$ (~410 K) [46], $Gd_2Fe_{16}Ga_{0.5}Ti_{0.5}$ (556 K) [47], $Dy_2Fe_{16}Ga$ (~462 K) [8], $Co_2Fe_{16}Ga$ (~320 K) [48], $Sm_2Fe_{16}Ga$ (~505 K) [49], or $Sm_2Fe_{16}Ga_{0.8}Ti_{0.2}$ (~435 K) [50], 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) Mössbauer spectra for $Gd_2Fe_{16}Ga_{0.5}TM_{0.5}$ are shown in Figure 6. The intermetallic $R_2Fe_{17}$ with a $Th_2Ni_{17}$ structure have the easy direction of magnetization and hyperfine field lying in the basal plane along the $a$ or $b$ axes of the unit cell [51,52]. This easy basal plane direction of magnetization complicates the Mössbauer 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 [53]. 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 an absence or presence of impurity phase, respectively [48,54–56]. 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 fields and a single common line-width was assumed for all eight sextets. The isomer shifts (IS, $\delta$) for the magnetically inequivalent sites were constrained to be the same, whereas the hyperfine field ($HF, B_{hf}$) was expected to vary at pairs of magnetically inequivalent sites due to variations in the dipolar and orbital contributions to the magnetic hyperfine fields [57].

The $^{57}Fe$ Mössbauer 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 sub-spectra with different magnetic hyperfine fields.

The hyperfine parameters derived from the fitting are listed in Table 5, and weighted average (Wt.Avg.) hyperfine field (HF) and isomer shifts (IS, $\delta$) are plotted in Figure 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(18b) sequence, which is similar to the sequence observed in other $R_2Fe_{17}$ compounds [58,59]. It is obvious that 4f (6c) site has the maximum hyperfine field, since it has the maximum number of Fe nearest neighbors, whereas, the 18b (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, Tables 3 and 5. 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$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ compounds. The Wt. Avg. HF value reaches the maximum for Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$Co$_{0.5}$, to a value ~252 kOe followed with a gradual decline in its value, reaching a value of 246 kOe for Gd$_2$Fe$_{16}$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 kOe/µB, which has been reported for Y–Fe systems [60,61]. The average value of Fe magnetic moment for Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ is plotted in Figure 5. In general, Fe magnetic moment holds up to the value of 1.68 µB only for Fe, Co, and Ni substitution in Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$.

The isomer shift values were assigned in relation to the Wigner–Seitz cell volume, i.e., the greater the Wigner–Seitz cell volume, the greater the isomer shift (Table 5) [62]. Therefore, as V(4f) > V(12j)~V(12k) > V(6g), their corresponding IS is as follows: δ4f > δ12j~δ12k > δ6g. The room temperature values of Wt.Avg. IS for Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ are negative, and the magnitudes of IS increase with an increasing TM atomic number in Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$. The IS is proportional to the total s-electron charge density at the iron nucleus, which is the sum of the spin-up and spin-down s-electron density and lattice site volume; an increasing s-electron density at the iron nucleus is indicated by a decreasing isomer shift. The observed behavior of the IS value could be attributed to the competition between lattice site volume and the complex nature of hybridization in Fe–Ga–TM [63,64], which all affect the s-electron charge density at the iron nucleus. A volume contraction is observed until TM = Ni, followed by unit cell expansion until TM = Zn doping in Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$. However, the Wt.Avg. IS value becomes less negative with TM = Co and onward. Thus, this behavior of IS indicates electronic effects at play in dictating IS behavior of the Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ compound. The increased IS value with Co, Ni, Cu, Zn, and Ga in Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ could be associated with the increased number of the 3d electrons, which increases the shielding of the s-electrons from the nucleus. In earlier TM atoms viz. Cr and Mn, the 3d band is broader and heavily hybridized with the conduction band [40]. These make electrons freer and thus have a greater presence at the Fe nucleus, which makes IS more negative. The increased screening of s-electrons via 3d electrons beyond TM = Fe doping in Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ could be the reason for enhanced IS.
Figure 6. Fitted RT Mössbauer spectra of Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga).

Figure 7. Weighted average hyperfine parameters, hyperfine field, and isomer shift, as a function of TM atomic number for Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga).
Table 5. RT Mössbauer hyperfine parameters for Gd$_2$Fe$_{17}$ and Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ (TM = Cr, Mn, Co, Ni, Cu, Zn, and Ga).

| TM     | 4f  | 6g$_1$ | 6g$_2$ | 12j$_1$ | 12j$_2$ | 12j$_3$ | 12k$_1$ | 12k$_2$ | Doublet | Wt.Avg. |
|--------|-----|--------|--------|---------|---------|---------|---------|---------|---------|---------|
| Cr     |     |        |        |         |         |         |         |         |         |         |
|        | B (kOe) | 303.0 | 231.6 | 244.1 | 212.5 | 271.2 | 278.5 | 198.0 | 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 (%) | 10.0 | 15.2 | 17.8 | 12.5 | 4.3 | 18.5 | 9.9 | 11.7 |         |
| Mn     |     |        |        |         |         |         |         |         |         |         |
|        | B (kOe) | 302.3 | 230.0 | 254.3 | 210.1 | 265.2 | 275.1 | 202.0 | 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 | −0.079 | 0.434 | −0.17 |         |         |
|        | Area (%) | 8.2 | 16.3 | 17.6 | 8.7 | 23.1 | 10.6 | 10.7 | 6.2 |         |
| (Gd$_2$Fe$_{17}$) | | | | | | | | | | |
| Cr     |     |        |        |         |         |         |         |         |         |         |
|        | B (kOe) | 304.0 | 246.2 | 254.6 | 220.5 | 272.3 | 286.3 | 205.6 | 260.2 | 252.1 |
|        | IS (mm/s) | 0.11 | −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 | 273.2 | 283.0 | 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 | −0.099 | 0.015 | −0.039 | 0.263 | −0.245 |         |
|        | Area (%) | 11.5 | 16.0 | 16.1 | 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 | 263.9 | 252.54 |
|        | 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 (%) | 11.0 | 3.5 | 9.3 | 8.0 | 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 | 268.0 | 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 (%) | 22.0 | 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 | 265.0 | 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 | 14.0 | 15.3 | 13.5 | 11.7 | 17.3 | 6.8 | 9.9 |         |
4. Conclusions

The effect of double substitution of Ga and TM in Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ on structural and magnetic properties was compared with Gd$_2$Fe$_{17}$ compounds. These compounds were found to crystallize in a hexagonal Th$_2$Ni$_{17}$ structure. Lattice parameters and unit cell volume of TM-doped Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ compounds showed dependence on the atomic radii of the TM dopant. The variance of the $c/a$ ratio with the substitution in these compounds showed anisotropic unit cell volume expansion. The Rietveld analysis showed the preferred occupancy of TM for 12k and Ga for 12k and 12j sites. Overall, no direct correlation was observed between the trend in Curie temperature and bond distances. The observed $T_c$ reached a maximum value of 587 K for cobalt substitution, which is 15% higher than the $T_c$ value of Gd$_2$Fe$_{17}$. Furthermore, 15% and 14% enhancement in $M_s$ was observed for Cu-substituted Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$ compound as compared to Dy$_2$Fe$_{17}$ and Dy$_2$Fe$_{16}$Ga$_3$ compounds, respectively. Furthermore, unlike other doped compounds of intermetallic RE$_2$Fe$_{17}$ compounds (R = Ho, Y), 15% and 14% enhancement in $M_s$ was observed for Cu-substituted Gd$_2$Fe$_{16}$Ga$_{0.5}$TM$_{0.5}$, even small TM doping (TM = Co, Ni, and Cu) brought about a simultaneous enhancement in $M_s$ and $T_c$. The combined magnetic and Mössbauer study points to the fact that the observed improvement in $T_c$ and $M_s$ could be attributed to electronic effects resulting from Fe-3d hybridization with a substituted TM atom electronic shell. A concomitant improvement in $M_s$ and $T_c$ is desirable for the magnetic industry. The study elucidates that the judicious selection of dopants and its content can improve the $M_s$ and $T_c$ of the R$_2$Fe$_{17}$ intermetallic compounds.

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