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Effect of Ga and Zr Substitution on the Properties of $Dy_2Fe_{17-X}Zr_X$ and $Dy_2Fe_{16}Ga_{1-x}Zr_X$ ($0 \le x \le 1$) Intermetallic Compounds Prepared via Arc Melting Process

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Abstract: The effects of substitution of Zr and Ga on the structural and magnetic properties of Dy₂Fe₁₇ intermetallic compound were investigated in this study. The Rietveld analysis confirmed that the crystalline system was a Th₂Ni₁₇ structure. Lattice parameters *a* (Å) and *c* (Å), unit cell volume (Å³), and bonding distance (Å) were calculated using Rietveld analysis. The unit cell volume of Dy₂Fe_{17-x}Zr_x and Dy₂Fe₁₆Ga_{1-x}Zr_x increased linearly with Zr and Ga substitution. The Curie temperature (Tc) of Dy₂Fe_{17-x}Zr_x and Dy₂Fe₁₆Ga_{1-x}Zr_x was found to be Zr content-dependent. The maximum Curie temperatures were observed at 510 K (*x* = 0.75 Zr content) for Dy₂Fe_{17-x}Zr_x and 505.1 K (*x* = 0.5 Zr content) for Dy₂Fe₁₆Ga_{1-x}Zr_x, which are 102 K and 97 K higher than the value found for Dy₂Fe₁₇, respectively. The room-temperature Mössbauer analysis showed a decrease in the average hyperfine field and increases in the isomer shift with Zr doping. The overall improvement in Curie temperature with the substitution strategy of Zr–Ga substitution in 2:17 intermetallic compounds could find potential use of these magnetic compounds in high-temperature applications.

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

1. Introduction

Intermetallic compounds (rare-earth elements (R) and 3*d*-transition elements (T)) possess outstanding magnetic properties because of their high saturation magnetization (Ms). R_2Fe_{17} compounds were studied in late the 1970s, and the values of (BH)_{max} and coercivity (Hc) were found to be about 26 MGOe and 15 kOe, respectively; however, they have low Curie temperature (~473 K for Gd₂Fe₁₇ and ~300 K for Dy₂Fe₁₇) and low magnetic anisotropies [1]. Many studies were done to improve the Curie temperatures of Dy₂Fe₁₇ [2–4] either by replacing the Fe atoms with non-magnetic atoms (Al, Si, Ga) [5] or by doping refractory atoms (Ti, V, Mo, Nb, W, Zr) in the Fe site [6–10]. It was also found that substitution of magnetic atoms (Co, Ni, Cr, Mn, Ni) [11] and non-metals (C, N, H) in the R_2Fe_{17} lattice also increased the Curie temperature of R_2Fe_{17} compounds [12–15]. The substitution of non-magnetic atoms at Fe sites was reported to increase ferromagnetic coupling, which in turn increases the Curie temperature [16,17] and magneto-crystalline anisotropy [18]. The introduction of nitrogen on interstitial sites of $R_2Fe_{17}N_x$ also increased the Curie temperature. This happens because the unit cell volume expansion increases the distance between iron atoms with a greater degree of exchange interaction [19,20]. Betancourt et al. (2003) [21] reported that Zr and Nb substitution could also improve magnetic properties. The Curie temperatures of Ce₂Fe₁₇ [22], Gd₂Fe₁₇ [5] Dy₂Fe₁₇ [8], Pr₂Fe₁₇ [23], etc. are improved by the addition of elements like Si, Cr, Mn, and Ga. The substitution of a non-magnetic atom such as Ga into the R₂Fe₁₇ brings a concomitant decrease in magnetization, which affects the energy product of the permanent magnets [18]. Furthermore, it is possible to increase the magnetic moment via Fe–Zr 3*d* band hybridization, which can cause band narrowing or increase exchange splitting by moving the 3*d*↑ states below the Fermi level, or which can allow charge transfer out of the 3*d* band, provided the spin-down density of states exceeds the spin-up density [24].

The present work focuses on substituting the Fe atom with elements Zr and Ga in Dy_2Fe_{17} . The substitution of non-magnetic atoms was limited to up to x = 1 to prevent a significant reduction in saturation magnetization. Doping of Zr and Ga atoms can increase the lattice parameters *a* and *c*, as well as the unit cell volume, and improve the Fe–Fe exchange interaction. The dysprosium element was chosen as it has a high Bohr magneton value (10.63 µB), which brings enhancement in the magnetic properties of the intermetallic compound.

2. Experimental

The raw materials of Dy, Fe, Zr, and Ga were used with ~99.9% purity and purchased from Sigma Aldrich. The samples $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$ (x = 0.00, 0.25, 0.50, 0.75, 1.00) were prepared via arc melting in a high-purity argon atmosphere. The ingots were melted several times to ensure homogeneity. The prepared alloys were made into fine powders, and the X-ray powder datasets were collected using a Bruker (D8 Advance) diffractometer with a monochromatic incident beam of CuK_{α} ($\lambda \approx 1.5406$ Å) radiation with the 2 θ range from 20° to 70° with a step size of 0.042°. The XRD analysis was performed using the well-known refinement Rietveld method [25] with the JANA2006 [26] software package. The purpose of this refinement process is to minimize the difference between the theoretically modeled profile and the observed one as a function, $\sum_{hkl} W_{hkl} (|F_o| - |F_c|)^2$, where W_{hkl} is the weight assigned to each observation, and F_O and F_C are the observed and calculated structure factors.

A vibrating sample magnetometer (VSM) with a maximum field of 1.2 T was used to investigate the magnetic properties of powder samples at room temperature (RT). The samples were compacted at 3000 psi and cut into rectangular parallelepipeds with a ratio of length to width larger than three, and they were embedded in epoxy in order to minimize the effect of the demagnetizing field.

The Mössbauer spectra of the samples were obtained at RT using a 25-mCi ⁵⁷Co source in Rh foil mounted on a constant acceleration drive system (SEE Co. Minneapolis, USA) in transmission geometry. The velocity scale of the Mössbauer spectrometer was calibrated by measuring the hyperfine field of α -Fe foil, at room temperature. The Mössbauer spectra were analyzed using the WMoss software from SEE Co. The spectra were least-square fitted with the hyperfine field (HF), isomer shift (IS), and quadrupole shift (QS) parameters as variables.

3. Results and Discussion

Figure 1 represent the representative Rietveld refinement profiles of $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$ (x = 0.00, 0.25, 0.50, 0.75, 1.00). The Rietveld [25] fittings reveal a nice matching of the observed and calculated profiles for both systems. A small additional phase $DyFe_3$ was observed for x = 1 Zr content during refinement. During the refinement process, the scale, structural parameters, lattice parameters, peak shift, preferred orientation, background profile functions, thermal parameters, and surface roughness were refined until the observed XRD profile matched well with the calculated profile. The initial crystal structure parameters were used as given by Liao et al. [27]. In the hexagonal setting, Dy was fixed at the 2*b* (0, 0, 0.25) and 2*d* (0.333, 0.667, 0.75) sites, and Fe was fixed at the 4*f* (0.333, 0.667, 0.105), 6*g* (0.5, 0, 0), 12*j* (0.333, 0.969, 0.25), and 12*k* (0.167, 0.333, 0.985) sites. The profile was constructed using a pseudo-Voigt function. Profile asymmetry was introduced by employing the multi-term Simpson rule integration devised by Howard [28]. A surface roughness correction

was also applied using the Pitschke, Hermann, and Matter [29] model. Table 1 shows the refined structural parameters for both $Dy_2Fe_{16-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$. From Table 1, the refined results confirmed that the unit cell volume (Å³) increased with x-content. The plots for lattice parameters *a* and *c* and unit cell volume (V) are shown in Figure 2a,b. This increase in volume may have occurred because of a bigger atom Ga ($r_{ionic} = 0.62(3)$ Å) and Zr ($r_{ionic} = 0.84(3)$ Å) [30] sitting at the smaller iron ($r_{ionic} = 0.55(3)$ Å) atom site. The increasing lattice parameters confirmed that both Zr and Ga addition to the host lattice was done properly. Table 2 represents the site occupancy table for $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$, which shows that the Zr atom occupied all 4*f*, 6*g*, 12*j*, and 12*k* sites, but the 12*j* and 12*k* sites were mostly impacted by the Zr substitution (Figure 3a). The site occupancies of Zr and Ga for $Dy_2Fe_{16}Ga_{1-x}Zr_x$ are plotted in Figure 3*b*, and the values are presented in Table 2. From these results, both Zr and Ga atoms prefer to be in 12*j* and 12*k* sites with a minimum affinity for 4*f* and 6*g* sites [5,31], and the increase in Zr occupancy and the decrease in Ga occupancy at 12*j* and 12*k* site show that the Zr atom was replaced by the Ga atom in $Dy_2Fe_{16}Ga_{1-x}Zr_x$.



Figure 1. Rietveld refinement profile for (a) Dy_2Fe_{17} , (b) $Dy_2Fe_{16.5}Zr_{0.5}$, (c) $Dy_2Fe_{16.25}Zr_{0.75}$ and (d) $Dy_2Fe_{16}Ga_{0.25}$.

Table 1. Lattice parameters and unit cell volume of $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$ obtained from Rietveld refinements.

	x	a (Å)	c (Å)	V (Å ³)	R _{obs} (%)	wR _{obs} (%)	R _p (%)	wR _p (%)
	0	8.45541(11)	8.29036(4)	513.303(18)	4.17	5.95	10.65	14.49
	0.25	8.46147(19)	8.29361(13)	515.456(21)	3.13	4.16	12.32	15.43
$Dy_2Fe_{17-x}Zr_x$	0.5	8.46963(16)	8.30442(12)	516.913(16)	4.16	4.33	11.91	17.21
	0.75	8.4749(14)	8.30836(11)	517.725(21)	4.52	5.11	9.32	10.12
	1	8.53823(17)	8.33743(19)	522.429(13)	5.01	6.99	9.96	10.21
	0	8.46324(3)	8.29025(3)	514.013(26)	5.97	6.17	10.21	12.13
	0.25	8.46943(15)	8.28922(7)	514.265(28)	5.65	6.97	13.64	16.98
$Dy_2Fe_{16}Ga_{1-x}Zr_x$	0.5	8.48437(12)	8.29985(5)	517.221(23)	4.52	5.11	9.32	10.12
	0.75	8.51833(7)	8.32536(7)	519.498(13)	5.21	6.12	12.21	11.21
	1	8.53823(17)	8.33743(19)	522.429(13)	5.01	6.99	9.96	10.21



Figure 2. Lattice parameters *a* and *c* and unit cell volume of (**a**) $Dy_2Fe_{17-x}Zr_x$ and (**b**) $Dy_2Fe_{16}Ga_{1-x}Zr_x$ as a function of Zr content.

Table 2. The site occupancy table for $Dy_2Fe_{17-x}Zr_x$, and $Dy_2Fe_{16}Ga_{1-x}Zr_x$.

	x	Fe(4 <i>f</i>)	Fe(6g)	Fe(12 <i>j</i>)	Fe(12k)	Zr(4f)	Zr(6g)	Zr(12 <i>j</i>)	Zr(12k)
	0.00	16.9(59)	24.3(6)	49.5(95)	50.9(31)	0	0	0	0
Site occupancy for	0.25	16.5(2)	24.1(7)	52.0(1)	48.0(4)	0.4(3)	0.52(6)	0.74(1)	0.68(13)
Dive Four Zr (%)	0.50	15.7(1)	24.3(4)	48.5(12)	47.5(7)	0.47(14)	1.32(15)	1.41(3)	2.11(17)
$Dy_2 Pe_{1/-X} Z_{1X} (70)$	0.75	15.9(2)	23.9(5)	47.7(1)	47.1(17)	0.73(8)	1.40(3)	2.20(6)	2.20(15)
	1.00	15.6(4)	22.6(4)	31.5(1)	47.0(3)	0.98(7)	2.61(6)	3.14(3)	2.84(11)
	x	Ga(4 <i>f</i>)	Ga(6g)	Ga(12j)	Ga(12k)	Zr(4f)	Zr(6g)	Zr(12 <i>j</i>)	Zr(12k)
	0.00	0.86(21)	1.36(15)	3.57(16)	3.14(23)	0	0	0	0
Site occupancy for	0.25	0.88(43)	1.13(43)	2.13(12)	2.16(11)	0.27(12)	0.38(14)	0.71(36)	0.72(41)
Dy ₂ Fe ₁₆ Ga _{1-x} Zr _x	0.50	0.49(31)	0.73(42)	1.47(13)	1.47(32)	0.49(41)	0.73(32)	1.43(32)	1.45(11)
(%)	0.75	0.14(22)	0.37(62)	0.74(16)	0.73(31)	0.62(21)	1.51(21)	1.85(22)	1.92(13)
	1.00	0	0	0	0	0.98(7)	2.61(6)	3.14(3)	2.84(11)



Figure 3. The percentage occupancy of (**a**) Fe and Zr at iron sites in $Dy_2Fe_{17-x}Zr_x$, and (**b**) Fe and Zr at Ga sites in $Dy_2Fe_{16}Ga_{1-x}Zr_x$ as a function of Zr content.

Table 3 represents the distance between the Fe–Fe neighbor sites, Ms, and Tc for $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$, and the values are plotted in Figure 4a,b. It can be observed from Table 3 that the average bond distance between each site changes with the concentration of both Zr and Ga (4*f*–4*f*

≈ 2.42 Å; $12k-12k \approx 2.46$ Å; $12j-12j \approx 2.52$ Å). The 12j-12j sites show that both Zr and Ga prefer to stay in the same sites.

x	Bond length Dy ₂ Fe _{17-x} Zr _x (Å)						Bond length $Dy_2Fe_{16}Ga_{1-x}Zr_x$ (Å)				Dy ₂ Fe _{17-x} Zr _x		Dy ₂ Fe ₁₆ Ga _{1-x} Zr _x	
	4 <i>f</i> -4 <i>f</i>	6g–12j	6g–12k	12 <i>j</i> –12 <i>j</i>	12 <i>k</i> –12 <i>k</i>	4 <i>f</i> -4 <i>f</i>	6g–12j	6g–12k	12 <i>j</i> –12 <i>j</i>	Ms (emu/g)	Tc (K)	Ms	Tc (K)	
0.00	2.406	2.418	2.443	2.425	2.44	2.418	2.433	2.455	2.442	62.94	408	61.58	488	
0.25	2.407	2.495	2.63	2.552	2.449	2.423	2.443	2.469	2.443	60.78	456	60.48	500.1	
0.50	2.412	2.542	2.669	2.56	2.458	2.435	2.462	2.479	2.488	58.57	503.9	57.25	505.1	
0.75	2.427	2.801	2.693	2.572	2.464	2.437	2.466	2.483	2.499	55.04	510	56.39	502.5	
1.00	2.439	2.851	2.772	2.592	2.488	2.439	2.85	2.771	2.592	52.07	425	52.07	425	

Table 3. Distance between the Fe–Fe neighbor sites, Ms, and Tc for $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$.



Figure 4. Dependence of bond lengths on x of (a) $Dy_2Fe_{17-x}Zr_x$, and (b) $Dy_2Fe_{16}Ga_{1-x}Zr_x$.

The room temperature magnetic properties obtained from the M vs. H measurement for $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$ are plotted in Figure 5a,b, respectively. The M vs. H plot shows that the saturation magnetization (Ms) decreases with an increase in the Zr substitution in both $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$. To determine the saturation magnetization, the "law of approach" was used, which describes the relationship between magnetization M on the applied magnetic field for H greater than the coercive field *Hc*. The magnetization near *Ms* can be written as $M = Ms(1 - \frac{a}{H} - \frac{b}{H^2}) + \kappa H$ [11,32], where *M* is the magnetization, *H* is the applied magnetic field, and $M_{\rm S}$ is the saturation magnetization attained at high field. The field-induced increase in the spontaneous magnetization of the domains is represented by the term κ H. 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" is interpreted 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 Ms and the slope of which gives the magneto-crystalline anisotropy constant. The decrease in saturation magnetization in $Dy_2Fe_{17-x}Zr_x$ with the increase in Zr content is attributed to the substitution of non-magnetic Zr atom for the Fe atom. This decrease in the saturation magnetization is the result of the dilution effect, i.e., replacing the Fe atom (2.2 μ_B) with non-magnetic Zr atom. A similar reduction in Ms was reported earlier for Dy₂Fe_{17-x}Ga_x [18], Ce₂Fe_{17-x}Ga_x [33], Sm₂Fe_{17-x}Ga_x [34], and Dy₂Fe_{17-x}Nb_x [35] compounds. From Figure 5c, it is observed that the saturation magnetization decreases linearly from 62.94 emu/g to 52.07 emu/g per Zr atom for $Dy_2Fe_{17-x}Zr_x$; however, magnetization decreases from 61.58 emu/g to 52.07 emu/g for $Dy_2Fe_{16}Ga_{1-x}Zr_x$. The dropdown of magnetization in both cases could be due to the reduction of the magnetic moment of iron upon Zr substitution, as well as the band filling effect coming from four valence electrons from Zr while doping.



Figure 5. Room temperature (RT) M vs. H plot of (a) $Dy_2Fe_{17-x}Zr_x$ and (b) $Dy_2Fe_{16}Ga_{1-x}Zr_x$; (c) magnetization (Ms) vs. *x* for $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$.

The Curie temperature (Tc) of $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$ as a function of Zr content is shown in Figure 6, and corresponding data are listed in Table 3. It is observed that, for $Dy_2Fe_{17-x}Zr_x$, Curie temperature increases from 408 K (x = 0.00) to a maximum of 510 K (x = 0.75) and then decreases to 425 K (x = 1.00). The achieved Curie temperature of Dy₂Fe_{16.25}Zr_{0.75} is 102 K higher than that of Dy_2Fe_{17} . It is observed from Figure 4a,b that the bond length increases with the increase in the Zr content. In general, the Curie temperature in rare-earth intermetallic is due to three kinds of exchange interactions, namely, the 3*d*–3*d* exchange interactions, i.e., between the magnetic moment of the Fe sub-lattice (J_{FeFe}), 4f-4f exchange interaction, i.e., the interaction between the magnetic moment within the R sub-lattice (J_{RR}), and the inter sub-lattice 3d-4f exchange interaction (J_{RFe}). It is reported that the Curie temperature (Tc) increases with an increase in J_{FeFe} [5]. Thus, the increase or decrease in Tc in the R_2Fe_{17} intermetallic may be due to the increase or decrease in the interaction parameter J_{FeFe} . The interactions between the rare-earth spins (4f-4f) are assumed to be weak and negligible in comparison with the other two types of interactions. The low T_C observed in parent Dy_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 [36], since their separation is less than 2.45 Å (Figure 4a,b), needed for ferromagnetic ordering [37]. In the compounds with hexagonal structure the Fe(4f)-Fe(4f) interactions are strongly negative, whereas the Fe(6g)-Fe(12j), Fe(6g)-Fe(12k), and Fe(12k)-Fe(12k) interactions are weakly negative. Thus, the increase in Tc is considered due to the increase in strength of the Fe–Fe exchange coupling that occurs from the increase in Fe–Fe bond lengths for each R₂Fe₁₇ compound. The strength of Fe–Fe exchange interaction highly depends on interatomic Fe–Fe distance [38,39]. 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} , the majority of Fe–Fe distances favor the negative interaction [18]. The negative exchange interaction can be reduced either by volume expansion or by reducing the number of Fe–Fe pairs with negative exchange interactions. It is noted that the increase in Tc was reported earlier with Ga substitution (x = 1) [18]; however, the simultaneous substation of non-magnetic Ga and Zr atoms enhances the Curie temperature of the intermetallic without significantly lowering the saturation magnetization. It is found that, for Dy₂Fe₁₆Ga_{1-x}Zr_x, Curie temperature increases slowly from 488 K (x = 0.00) to a maximum of 505.1 K (x = 0.50) and then decreases to 425 K (x = 1.00). The maximum Tc observed in Dy₂Fe₁₆Ga_{0.5}Zr_{0.5} (505.1 K) is 17.1 K greater than that of Dy₂Fe₁₆Ga₁ and 97 K higher than that of Dy₂Fe₁₇. Overall co-substitution of Zr and Ga shows a greater degree of enhancement in Tc over the single substation.



Figure 6. Comparative study for the Tc vs. *x* for $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$.

The Mössbauer spectra are plotted in Figure 7a,b for $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$ (x = 0.00, 0.25, 0.50, 0.75, 1.00) respectively. The resulting spectra were fitted using the WMOSS program. The hyperfine field (B_{hf}), isomer shift (δ or IS), and quadrupole splitting (Δ or QS), as well as the percentage of area occupied by the different sites, were extracted from the fit. Since the Dy_2Fe_{17} compounds have a basal magnetization, eight magnetic sextets are required to fit their Mössbauer spectra. The fitted data shown in Figure 7a,b were determined with eight magnetic sextets assigned to 4*f*, 6*g*, 12*j*, and 12*k* sites in Dy_2Fe_{17} . Doublets were used at x = 1 Zr content for the additional phase paramagnetic phase (DyFe₃) observed during Mössbauer fitting. While fitting Mossbauer spectra, the relative areas of 4*f* and 4*e* sites were adjusted, and the relative areas of 6*g*₄, 6*g*₂, 12*j*₈, 12*j*₄, 12*k*₈, and 12*k*₄ were constrained in the ratio 4:2:8:4:8:4 [40].

The hyperfine parameters derived from the fitting are listed in Table 4, and the hyperfine field (HF) and isomer shifts (IS) are plotted in Figure 8a,b. There exists a direct correlation between hyperfine field values of a site with its near neighbor (NN) iron sites. In the case of the Th₂Ni₁₇ structure, the 12*k* site has nine NN Fe sites (one (4*f*), two (6*g*), four (12*j*), two (12*k*)), the 12*j* site has 10 NN Fe sites (two (4*f*), zero (6*g*), four (12*k*)), the 6*g* site has 10 NN Fe sites (two (4*f*), zero (6*g*), four (12*j*), four (12*k*)), and the 4*f* site has 11 NN Fe sites (one (4*f*), three (6*g*), six (12*j*), three (12*k*)). Following the NN distribution, the observed HF values are in the order 4f(6c) > 12j(18f) > 6g(9d) > 12k(18h), which is similar to the sequence observed in other R₂Fe₁₇ compounds [40,41]. It is obvious that the 4f(6c) site has the maximum hyperfine field, since it has the maximum number of Fe nearest neighbors, whereas the 18*h*(12*k*) site has the minimum number of Fe neighbors and, consequently, has the lowest 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. The hyperfine field (B_{hf}) decreases with increasing Zr content. The decrease in the hyperfine fields could be from the decrease in

magnetic moments of iron in $Dy_2Fe_{17-x}Zr_x$. It is found that 9.23% of total area is occupied by the $DyFe_3$ paramagnetic phase for x = 1 Zr content. This observation supports the formation of an additional paramagnetic phase $DyFe_3$ as confirmed from the XRD Rietveld refinement.



Figure 7. RT Mössbauer spectra for (a) $Dy_2Fe_{17-x}Zr_x$, and (b) $Dy_2Fe_{16}Ga_{1-x}Zr_x$.

 $\label{eq:table 4. The RT hyperfine parameters, HF (kOe), IS (mm/s), QS (mm/s), and area (\%) of the Dy_2Fe_{17-x}Zr_x and Dy_2Fe_{16}Ga_{1-x}Zr_x.$

Composition		x	4 <i>f</i>	4 <i>e</i>	6g ₄	6g ₂	12j ₈	12j ₄	12k ₈	$12k_4$	Doublet
		0.00	261	248	217	202.4	245.6	189	199.7	203.7	
	HF (kQe)	0.25	260.2	248.5	215.3	200.3	245	187	197.9	200.4	
		0.50	261.1	247.1	214.9	198.6	245.8	184	198.7	201.9	
	(0.75	258.4	248.7	216.6	200	245	186	198	199.9	
		1.00	262.1	249	236.5	200.5	245.3	176	218.1	181.3	34
		0.00	-0.114	-0.228	-0.333	-0.33	-0.326	-0.33	-0.39	-0.39	
	IS	0.25	-0.096	-0.234	-0.341	-0.34	-0.331	-0.33	-0.39	-0.39	
	(mm/s)	0.50	-0.088	-0.028	-0.109	-0.11	-0.111	-0.11	-0.34	-0.34	
	(mmq0)	0.75	-0.092	0.124	-0.135	-0.14	-0.091	-0.09	-0.39	-0.39	
Dy ₂ Fe _{17-x} Zr _x		1.00	-0.27	0.158	-0.12	-0.12	0.059	0.06	-0.37	-0.37	0.06
		0.00	0.152	0.191	0.152	0.303	-0.295	0.40	0.083	-0.58	
	OS	0.25	0.152	0.16	0.128	0.296	-0.291	0.40	-0.03	-0.58	
	(mm/s)	0.50	0.119	0.163	0.175	0.289	-0.276	0.40	0.121	-0.50	
	(mmyo)	0.75	0.178	0.301	0.157	0.335	-0.199	0.40	-0.03	-0.58	
		1.00	0.123	0.25	-0.048	0.155	-0.25	0.35	0.042	-0.58	-0.39
	Area (%)	0.00	4.0	1.91	15.3	17.5	4.3	19.5	10.9	13.1	
		0.25	5.5	8.20	17.7	17.4	6.3	16.0	10.4	13.3	
		0.50	6.2	6.70	21.9	17.3	6.0	117	9.60	15.1	
		0.75	5.25	4.00	21.0	19.0	7.6	14.0	14.81	13.5	
		1.00	4.2	4.90	11.2	31.9	6.2	4.21	23.1	15.2	9. 23
		0.00	278.7	249.7	230.2	214.9	260	218.2	196.5	220	
	HF	0.25	282.9	249.9	224.5	204	288.1	164.8	220.3	195.3	
	(kOe)	0.50	267.6	267.9	229	204	254.2	123.4	226.8	185.3	
	(0.75	266.7	243.7	238.1	199.4	248.6	120.7	219.2	178.3	
		1.00	262.1	248.9	236.5	200.4	245.3	122	218.1	181.3	34
	IS	0.00	-0.126	-0.301	-0.309	-0.309	-0.422	-0.422	-0.254	-0.254	
		0.25	-0.257	-0.335	-0.356	-0.356	0.215	0.215	-0.301	-0.301	
	(mm/s)	0.50	-0.227	-0.509	-0.367	-0.367	0.068	0.068	-0.327	-0.327	
Dy-FourCar 7r		0.75	-0.252	0.145	-0.37	-0.37	0.041	0.041	-0.373	-0.373	0.07
Dy2re ₁₆ Gd _{1-x} ZI _x		1.00	-0.27	0.158	-0.378	-0.378	0.058	0.058	-0.37	-0.370	0.06
	QD	0.00	0.158	0.0107	0.133	0.259	-0.418	-0.48	0.259	-0.58	
	(mm/s)	0.25	0.084	-0.102	-0.093	-0.568	0.500	-0.477	0.284	0.178	
		0.50	-0.069	-0.7	-0.196	0.201	0.500	-0.134	0.249	0.118	
		0.75	-0.029	-0.6	-0.102	0.156	0.500	-0.214	0.057	0.079	
		1.00	-0.181	-0.6	-0.049	0.155	0.390	-0.142	0.042	0.136	-0.388
		0.00	13.7	15.9	20.0	21.0	10.5	5.50	11.9	3.90	
	Area	0.25	5.20	16.7	18.8	4.62	5.50	2.60	19.0	20.2	
	(%)	0.50	7.40	7.8	18.7	17.7	6.17	5.50	22.1	14.1	
	(79)	0.75	6.75	3.80	28.2	4.30	3.00	26.8	12.0	14.4	
		1.00	4.20	4.87	11.2	31.9	6.16	4.20	23.1	15.2	9.23



Figure 8. RT Mössbauer hyperfine parameters plots for (a) $Dy_2Fe_{17-x}Zr_x$, and (b) $Dy_2Fe_{16}Ga_{1-x}Zr_x$.

On average, the isomer shifts (IS) of all sites increase with the increase in Zr content. The increase in the isomer shift (IS) could be related to the volume expansion resulting from the Zr substitution for Fe. The volume expansion lowers the *s*-electron density at the Fe nuclei, which leads to an increase in isomer shift (IS). At higher Zr content (x = 1.00), a decrease in isomer shift (IS) was observed. This decrease in the isomer shift may be due to the combined effect of volume expansion and the increase in electron density. The decrease in hyperfine fields on Dy₂Fe₁₆Ga_{1-x}Zr_x is attributed to the decrease in magnetization because of the competition between the positive effect on magnetic moments due to the bond length and the negative effect caused by magnetic dilution due to the non-magnetic atom substitution. The average isomer shift (IS) of all sites increases with increasing Zr content except for the 12*k* site.

4. Conclusions

The effects of substitution of Ga and Zr in intermetallic compounds Dy₂Fe₁₇ prepared via arc melting were carefully studied. The intermetallic compounds were α -Fe free and found to crystallize in hexagonal the Th_2Ni_{17} type structure. Paramagnetic phase DyFe₃ was observed for x = 1 and confirmed using Mössbauer spectroscopy. From the Rietveld refinement, it was observed that most Zr atoms occupied 12*j* and 12*k* sites of Fe for $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$ intermetallic compounds. Lattice parameters *a* and *c* and unit cell volume increased with the substitution of Zr and Ga. The Fe–Fe bond length increased with Zr substitution. However, the maximum change in Fe–Fe bond length was observed for 6g-12j, 6g-12k, and 12j-12j sites. This change in bond length was found to be affected by the strength of Fe–Fe exchange interaction. The maximum Tc was observed in $Dy_2Fe_{16}Ga_{0.5}Zr_{0.5}$ (505.1 K) for a double substitution of Ga and Zr; however, for a single substitution, maximum Tc was observed at 510 K in $Dy_2Fe_{16.25}Zr_{0.75}$. This increase in the Curie temperature was attributed to an enhancement in Fe-Fe positive exchange interaction. The saturation magnetization, Curie temperature, and Fe hyperfine fields were remarkably affected by Zr substitution. The hyperfine field values decreased for both $Dy_2Fe_{17-x}Zr_x$ and $Dy_2Fe_{16}Ga_{1-x}Zr_x$ with Zr doping due to the decrease in the magnetic moment of Fe atoms. The isomer shift (IS) showed an increase in nature due to the increase in volume effect. The Co-doped 2:17 intermetallics with improved Tc and Ms ensures their potential use in high-temperature permanent magnet applications.

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