

On the Structural and Magnetic Properties of $R_2Fe_{17-x}(A,T)_x$ ($R = \text{Rare Earth}$; $A = \text{Al, Si, Ga}$; $T = \text{Transition Metal}$) Compounds

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R_2Fe_{17} ($R = \text{rare earth}$) intermetallic compounds constitute one of the most important classes of materials identified as high-energy permanent magnet materials. They crystallize either in the rhombohedral Th_2Zn_{17} structure (for light R) or in the hexagonal Th_2Ni_{17} structure (for heavy R). In this article, we discuss the variations in the lattice parameters (unit cell volume), site occupancies and Curie temperature when non-transition and transition metals are substituted for Fe in R_2Fe_{17} compounds.

Introduction Iron-rich rare-earth (R) intermetallic compounds of the type R_2Fe_{17} have been drawing considerable attention owing to their applications as permanent magnet materials [1–3]. R_2Fe_{17} compounds possess maximum saturation magnetization among all the binary R – TM intermetallics ($TM = \text{transition metal}$) [4, 5]. However, they have relatively low Curie temperatures (T_C) and magnetic anisotropy. The reason for the low T_C is that some of the Fe-Fe distances are less than the critical value of 2.45 Å needed for ferromagnetic exchange. These Fe pairs couple antiferromagnetically leading to low values of T_C [6, 7]. On the other hand, the Fe sublattice anisotropy in all these compounds is planar irrespective of the R [4]. The R sublattice anisotropy originates mainly from the crystalline electric fields acting on the 4f orbital and is axial only for Sm, Er and Tm, whose Stevens factors (α_J) are positive. However, the total anisotropy is smaller since R sublattice anisotropy is smaller in magnitude when compared with Fe sublattice anisotropy thereby making the resulting anisotropy planar. In order to increase the

total anisotropy and T_C in R_2Fe_{17} compounds, various approaches have been adopted. Rare earth sublattice anisotropy can be increased by a proper choice of rare earths taking into account the crystal structure and crystal field parameters or by reducing the Fe sublattice anisotropy, which is planar by substituting non-magnetic element for Fe. This will, in addition alter the crystal field at the R site due to the hybridization between 5d and the 6p electrons of R and valence electrons of the non-magnetic atoms and therefore, alter the R sublattice anisotropy as well. It was reported that the magnetic properties of R_2Fe_{17} compounds can be drastically improved by the interstitial modification with nitrogen (N) or carbon (C) [8–10]. Some of the investigations have been reviewed by Rama Rao et al. [11].

In this review, we discuss the changes in the structural and magnetic properties reported when Fe is substituted in R_2Fe_{17} compounds with either non-transition metals such as Ga, Al or Si or transition metals.

Structural Aspects R_2Fe_{17} compounds with light rare earths crystallize in rhombohedral Th_2Zn_{17} type structure whereas with heavy rare earths in hexagonal Th_2Zn_{17} type structure. However, coexistence of hexagonal and rhombohedral forms is found for Ce_2Fe_{17} [12]. The compounds with $R = Gd, Tb, Y$ can exist in both the forms depending on the annealing conditions. Both hexagonal and rhombohedral structures are derived from the $CaCu_5$ type structure by the ordered substitution of one third of rare-earth atoms by a pair (dumbbell) of Fe atoms. The formation of the structure can thus be written as $3 RFe_5 - R + 2 Fe = R_2Fe_{17}$ [13]. Figure 1 shows the unit cell of hexagonal and rhombohedral structures. The number of formula units present in the hexagonal and rhombohedral cell is two and three, respectively. The rhombohedral structure has one R site (6c) and four Fe sites (6c, 9d, 18f, 18h), whereas the hexagonal structure has two R sites (2b, 2d) and four Fe sites (4f, 6g, 12j, 12k) [1]. The structure possesses octahedral and tetrahedral interstitial sites [14, 15].

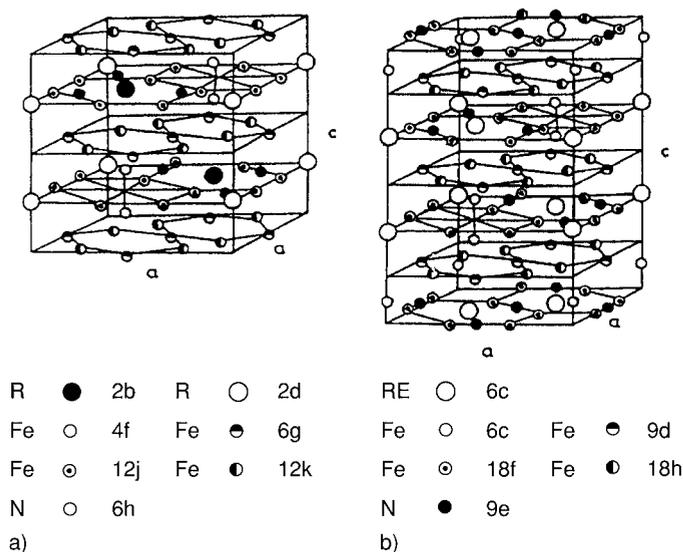


Fig. 1. Crystal structure of a) hexagonal and b) rhombohedral R_2Fe_{17} structure

Lattice parameters and unit cell volume In R_2Fe_{17} compounds, the lattice parameters a and c and the unit cell volume (V) vary differently for different substituents for Fe. Tb_2Fe_{17} [16], Dy_2Fe_{17} [17], Ho_2Fe_{17} [18], Er_2Fe_{17} [19, 20], Tm_2Fe_{17} [20, 21] and Y_2Fe_{17} [22] crystallize in hexagonal structure. When Ga is substituted for Fe in these compounds, transformation from hexagonal to rhombohedral structure and coexistence of both the structures at a certain Ga concentration or in a range of Ga concentrations have been observed. Figure 2a shows some of these observations reported in $Tm_2Fe_{17-x}Ga_x$ [20, 21] and $Y_2Fe_{17-x}Ga_x$ [22]. The lattice parameters and the unit cell volume increased with increase of Ga content in all the compounds. On the other hand, R_2Fe_{17} compounds containing lighter rare earths and their Ga substituted compounds, $Ce_2Fe_{17-x}Ga_x$ [23, 24], $Nd_2Fe_{17-x}Ga_x$ [25, 26] crystallize in rhombohedral structure. The transformation from hexagonal to rhombohedral structure has also been reported when light rare earths are substituted with heavy rare earths as reported in $(Er_{1-x}Pr_x)_2Fe_{17}$ system [19]. In this system the transformation occurs at $x = 5$.

Al when substituted for Fe in R_2Fe_{17} compounds increases the lattice parameters and in turn the unit cell volumes. $Tb_2Fe_{17-x}Al_x$ [27] and $Ho_2Fe_{17-x}Al_x$ [28] crystallize in the hexagonal structure at low Al concentrations, and at higher concentrations in rhombohedral structure. The lattice parameters and the unit cell volume increase with increasing Al concentrations. The variation of unit cell volume with Al content in $Tb_2Fe_{17-x}Al_x$ is shown in Fig. 2b for $x \geq 2$ which crystallizes in rhombohedral phase where as such transformation occurs in $Ho_2Fe_{17-x}Al_x$ at $x \geq 3$. On the other hand, the light rare earth containing compounds such as $Ce_2Fe_{17-x}Al_x$ [29] and $Nd_2Fe_{17-x}Al_x$ [30] crystallize in rhombohedral structure. So is the case with $ErPrFe_{17-x}Al_x$ [31]. The variation of the unit cell volume with Al content in these systems is also shown in Fig. 2b. Substitution of Si for Fe in $Ce_2Fe_{17-x}Si_x$ [32], $Y_2Fe_{17-x}Si_x$ and $Tm_2Fe_{17-x}Si_x$ compounds [33] leads to a contraction of a axis and expansion of c axis and consequent reduction of the unit cell volume as shown in Fig. 3a. In $Tm_2Fe_{17-x}Si_x$, the hexagonal structure is

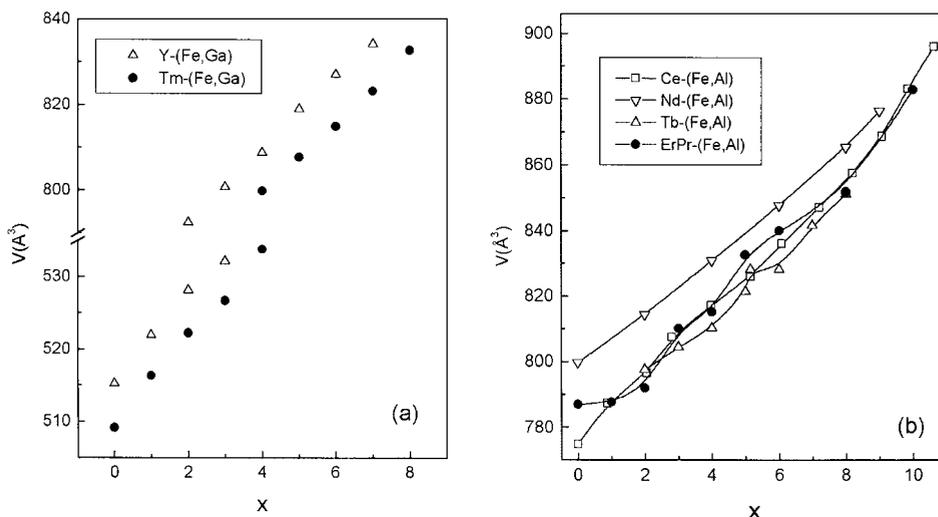


Fig. 2. Dependence of unit cell volume (V) on x for a) $Y_2Fe_{17-x}Ga_x$ [22], $Tm_2Fe_{17-x}Ga_x$ [20, 21] compounds and b) $CeFe_{17-x}Al_x$ [29], $NdFe_{17-x}Al_x$ [30], $Tb_2Fe_{17-x}Al_x$ [28], $ErPrFe_{17-x}Al_x$ [31] compounds

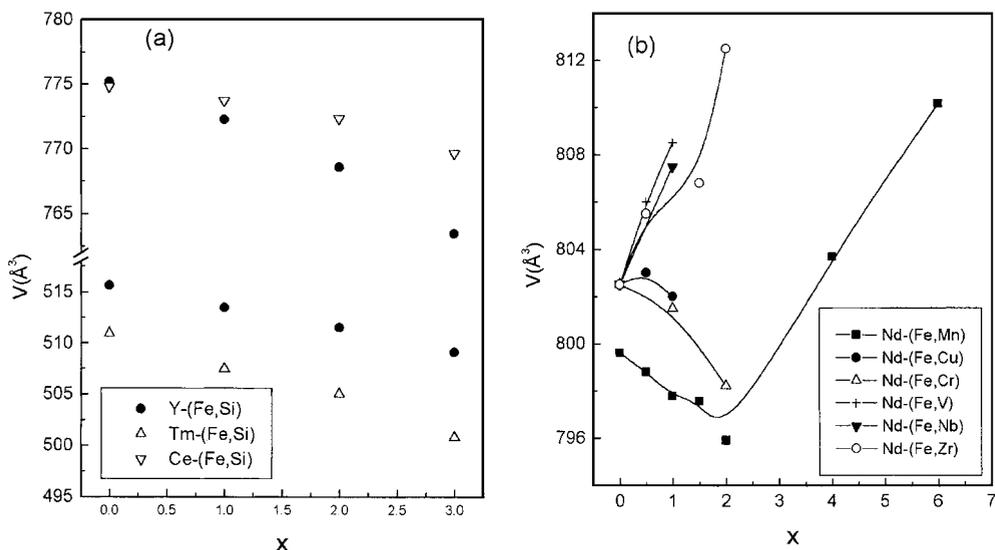


Fig. 3. Dependence of unit cell volume (V) on x for a) $\text{YFe}_{1-x}\text{Si}_x$ [33], $\text{TmFe}_{1-x}\text{Si}_x$ [33] and $\text{CeFe}_{1-x}\text{Si}_x$ [32] compounds and b) $\text{Nd}_2\text{Fe}_{17-x}\text{M}_x$ ($M = \text{Mn, Cu, Cr, V, Nb, and Zr}$) [34–38] compounds

found up to $x = 3$ whereas, in $\text{Y}_2\text{Fe}_{17-x}\text{Si}_x$ both the hexagonal and rhombohedral structures coexist in the range $x = 0-3$.

In $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ ($x = 0-6$), Ezekwenna et al. [34] have reported that the lattice constants a and c and the unit cell volume decrease initially with increasing Mn content up to $x = 2$ and then increase with further increase of Mn. These results are shown in Fig. 3b. Wang et al. [35] reported similar results on $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ ($x = 0-8$) excepting that the region of decrease of lattice constants and the unit cell volume is in the range $x = 0.5-2.5$. Other transition-metals ($T = \text{Ti, V, Cr, Cu, Zr, Nb}$) have also been substituted for Fe in $\text{Nd}_2\text{Fe}_{17-x}\text{T}_x$ [36–38]. With increasing V, Nb and Zr content, the unit cell volume has increased whereas Cr, Cu tend to decrease the unit cell volume. These results are also shown in Fig. 3b. Ti has increased the unit cell volume to a large extent. It may be pointed out that the a and c values and in turn the unit cell volume reported by Ezekwenna et al. [34] for $\text{Nd}_2\text{Fe}_{17}$ is lower than that reported by Al-Omari et al. [38].

We have seen that the variations in the lattice parameters and the unit cell volume behave differently for different substituents in R_2Fe_{17} compounds. The ‘size effect’ is responsible for the variations when non-transition metals such as Ga, Al, Si are substituted for Fe. Ga and Al have atomic radii larger than Fe and that of Si is smaller than Fe. The volume of the unit cell when substituted with Ga and Al for Fe increased whereas with Si it has decreased. The situation is different when the substituents are transition metals. In $\text{Nd}_2\text{Fe}_{17}$, various first-row transition elements (Ti, V, Cr, Mn, Cu) and second-row transition elements (Zr, Nb) have been substituted for Fe [34–38]. Since V, Nb, Zr have larger atomic radii compared to Fe, an increase in the unit cell volume was observed when these elements are substituted for Fe. Similar behaviour should also be expected for Mn. Ezekwenna et al. [34] observed an initial decrease up

to $x = 2$ and then an increase in the unit cell volume. On the other hand Cu and Cr which have smaller atomic radii tend to decrease the unit cell volume. But it should be noted that the increase in the unit cell volume is $\approx 3\text{--}5 \text{ \AA}^3$ per V, Zr or Nb atom although these transition metal substituents possess large atomic radius. In contrast, the change in the unit cell volume when Ga and Al are substituted (which have comparably smaller atomic radii than the transition metal substituents but bigger than Fe) is $\approx 9 \text{ \AA}^3$ per Al or Ga atom. This suggests that the transition metal substituents bond to Fe and Nd atoms more strongly in the $\text{Nd}_2\text{Fe}_{17}$ compounds than the non-transition metals. Probably for the same reason, the initial decrease in the unit cell volume of the Mn substituted $\text{Nd}_2\text{Fe}_{17}$ compound may also be associated with the bonding in solid solutions [34].

Site occupancies Both hexagonal and rhombohedral R_2Fe_{17} compounds possess four inequivalent Fe sites. These sites in the hexagonal and rhombohedral structure are 4f, 6g, 12j, 12k and 6c, 9d, 18f, 18h, respectively. Since most of the systems that will be discussed here possess rhombohedral structure, we will confine to the sites corresponding to that structure alone. The number of Fe and R nearest neighbours (nn) for Fe atoms at various crystallographic sites in R_2Fe_{17} compounds is shown in Table 1. 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. The Fe–Fe bond distance at the dumbbell site (6c) is $\approx 2.4 \text{ \AA}$. The Wigner-Seitz cell volume is largest for 6c, followed by 18h, 18f, and 9d with the smallest Wigner-Seitz cell volume.

From neutron diffraction experiments, the percentage of Ga, Al, Si, Mn site occupancies of the Fe site in several R_2Fe_{17} have been reported. Some of these results are shown in Figs. 4–6.

The Al site occupancies for Fe are similar in $\text{Ce}_2\text{Fe}_{17-x}\text{Al}_x$ [29], $\text{Nd}_2\text{Fe}_{17-x}\text{Al}_x$ [30], and $\text{Tb}_2\text{Fe}_{17-x}\text{Al}_x$ [27]. In these series of compounds, at low Al concentrations ($x < 6$) Al occupies 18h site and occupies the 6c and 18f sites almost randomly. On the other hand at $x > 6$, Al highly favours 6c and 18f sites. Throughout the composition range, Al completely avoids 9d sites. Al has a larger metallic radius than Fe and therefore avoids the 9d site which has the smallest Wigner-Seitz cell volume. Then why does Al prefer 18h site to 6c site at $x < 6$, even though 6c site has the largest Wigner-Seitz cell volume? In this range, 6c–6c bond distances are very short and therefore Al avoids 6c site. It is believed that the site occupancies are not just governed by the Wigner-Seitz cell volume alone but also by the nature of the nearest neighbours that a particular site

Table 1

Number of Fe and R neighbours for Fe atoms at various crystallographic sites in R_2Fe_{17} compounds

site	number of nearest neighbours (nn)					total no. of Fe nn	total no. of R nn
	Fe (6c)	Fe (9d)	Fe (18f)	Fe (18h)	R (6c)		
Fe (6c)	1	3	6	3	1	13	1
Fe (9d)	2	0	4	4	2	10	2
Fe (18f)	2	2	2	4	2	10	2
Fe (18h)	1	2	4	2	3	9	3

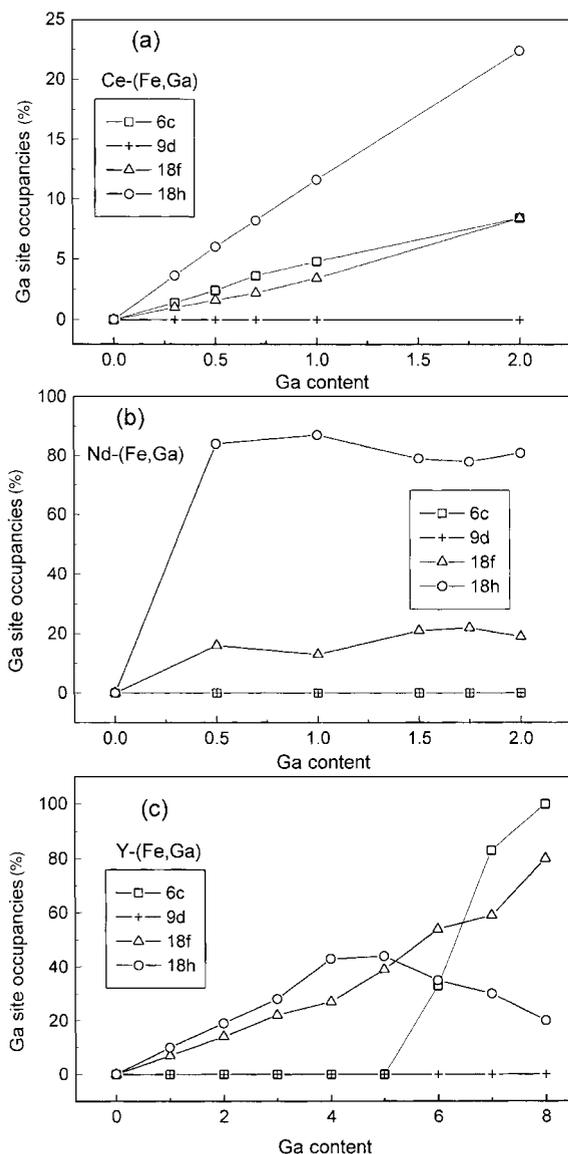


Fig. 4. The percentage of Ga occupancy of the Fe sites in a) $\text{CeFe}_{1-x}\text{Ga}_x$ [24], b) $\text{NdFe}_{1-x}\text{Ga}_x$ [25], and c) $\text{YFe}_{1-x}\text{Ga}_x$ [39] compounds

has. At low Al concentrations, Al prefers the occupancy of 18h site which has the most (three) rare-earth nearest neighbours. This is probably associated with the favourable heat of mixing between Nd and Al compared to Nd and Fe. A similar trend is favoured in the other compounds as well. At higher Al concentrations, 6c and 18f sites are randomly preferred. 6c site has been preferred at high Al concentration because this 6c site has the largest number of 9d nearest neighbours and in this way, the number of Al near neighbour pairs is minimized [30].

$\text{Ho}_2\text{Fe}_{17-x}\text{Al}_x$ crystallizes in the hexagonal structure for $x = 1, 2$, in a mixture of hexagonal and rhombohedral structure for $x = 3$ and rhombohedral structure for $x = 4$.

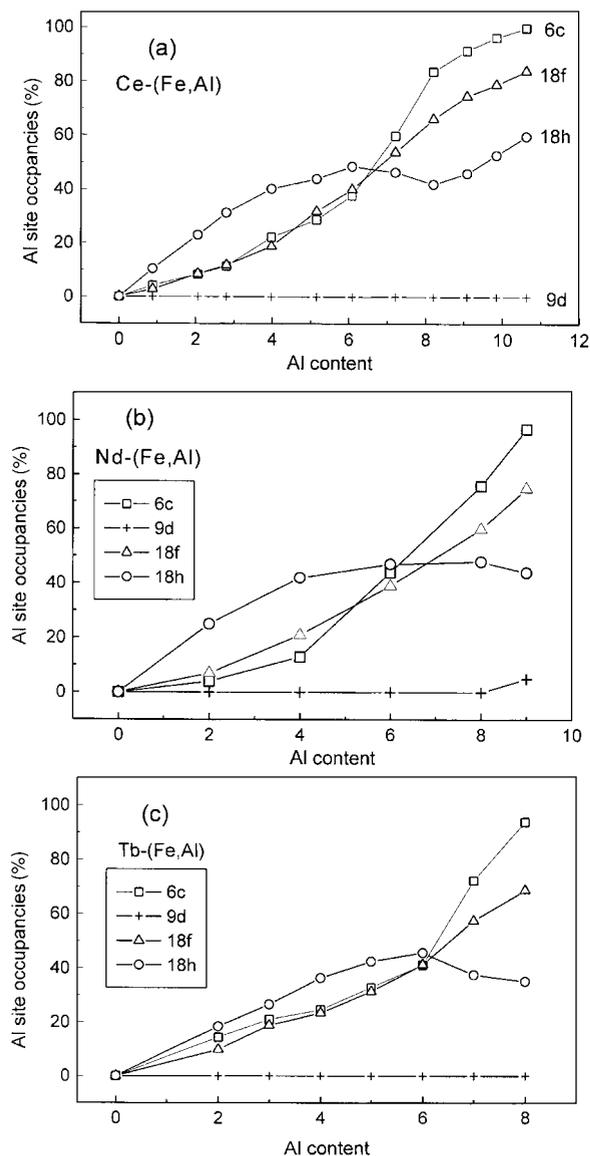


Fig. 5. The percentage of Al occupancy of the Fe sites in a) $\text{CeFe}_{1-x}\text{Al}_x$ [29], b) $\text{NdFe}_{1-x}\text{Al}_x$ [30], and c) $\text{TbFe}_{1-x}\text{Al}_x$ [27] compounds

The percentage of Al site occupancies for Fe observed by Yelon et al. [28] is shown in Fig. 6. For uniformity, at all compositions, the site occupancies are represented corresponding to rhombohedral structure only. At low concentrations ($x < 2$) the 18h and 18f and at $x > 2$ the 18h, 6c and 18f sites get progressively occupied. The surprising feature is that 9d occupancy comes down to zero at $x = 4$. In other words, the occupancies at $x = 4$ (pure rhombohedral structure) resembles the features observed in $\text{Ce}_2\text{Fe}_{17-x}\text{Al}_x$, $\text{Nd}_2\text{Fe}_{17-x}\text{Al}_x$ and $\text{Tb}_2\text{Fe}_{17-x}\text{Al}_x$ at low Ga or Al concentrations.

In $\text{Nd}_2\text{Fe}_{17-x}\text{Ga}_x$ [25] and $\text{Y}_2\text{Fe}_{17-x}\text{Ga}_x$ [39], at low concentrations, Ga prefers mostly 18h site and then 18f site, completely avoiding 6c and 9d sites. In $\text{Y}_2\text{Fe}_{17-x}\text{Ga}_x$, at high-

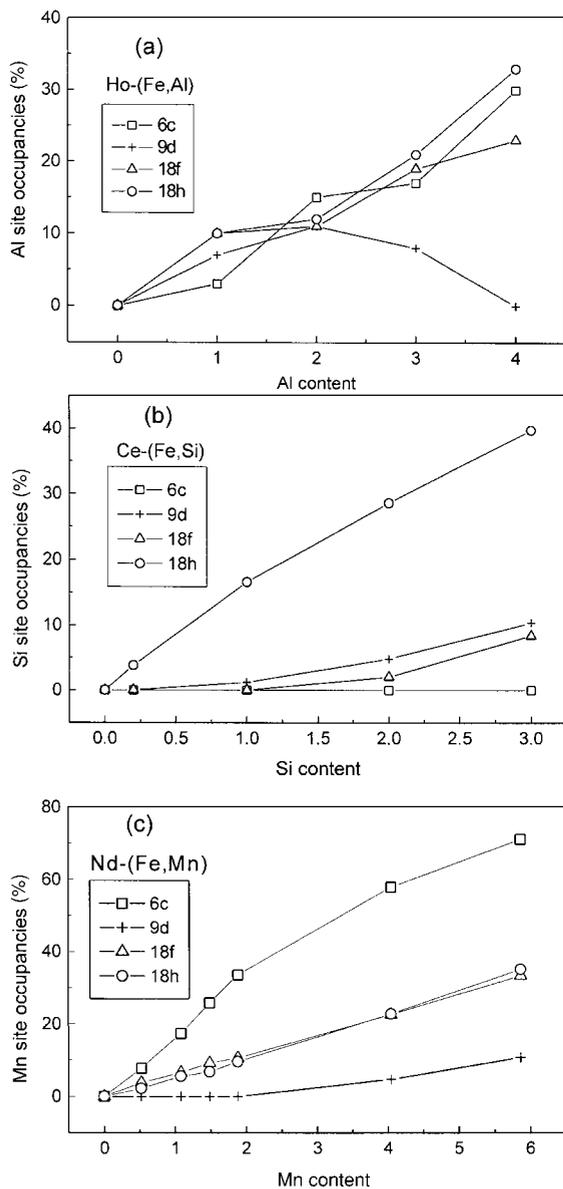


Fig. 6. The percentage of a) Al occupancy of the Fe sites in $HoFe_{17-x}Al_x$ [28], b) Si occupancy of the Fe sites in $CeFe_{17-x}Si_x$ [32], and c) Mn occupancy of the Fe sites in $NdFe_{17-x}Mn_x$ [34] compounds

er concentrations Ga occupancy at 6c site rapidly goes from 0% at $x = 5$ to 100% at $x = 8$. There is a continuous increase of occupancy at the 18f site with increasing Ga content whereas the occupancy of 18h site starts decreasing at $x > 5$. The 9d site is not at all occupied even at higher Ga content. Ga occupancy of Fe sites in $Ce_2Fe_{17-x}Ga_x$ has almost the same features with a slight difference [24]. In this system, it is found that the 6c site also gets occupied even at low Ga concentrations, and this occupancy is comparable to that of 18f site. Of course, a non-occupancy of 9d site is also seen in

$\text{Ce}_2\text{Fe}_{17-x}\text{Ga}_x$. The marked preference of Ga for 18h site suggests that the affinity of R atoms surpasses the Wigner-Seitz site volume.

In $\text{Tm}_2\text{Fe}_{10}\text{Ga}_7$ [21] the site occupancies of Ga for Fe site are 80% at 6c site, 65% at 18f site and 25% at 18h site which are similar to the values reported in $\text{Y}_2\text{Fe}_{17-x}\text{Ga}_x$ [39]. On the other hand, the site occupancies found in hexagonal $\text{Ho}_2\text{Fe}_{15}\text{Ga}_2$, $\text{Er}_2\text{Fe}_{15}\text{Ga}_2$, $\text{HoErFe}_{15}\text{Ga}_2$ are $\approx 19\%$ at 12k site and $\approx 14\%$ at 12j site [40]. These 12j and 12k sites in hexagonal structure correspond to 18f and 18h sites, respectively, in rhombohedral structure.

As in Al and Ga substituted compounds, Si in $\text{Ce}_2\text{Fe}_{17-x}\text{Si}_x$ preferentially occupies 18h site and to a small extent 9d and 18f sites, completely avoiding the 6c site as shown in Fig. 6b [32]. On the other hand, as can be seen from Fig. 6c, Mn in $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ mostly prefers 6c site which has the largest Wigner-Seitz cell volume and 18h and 18f sites randomly [34]. The 9d site, which has the smallest Wigner-Seitz cell volume, does not get filled upto $x = 2$ and above that marginally. Yelon et al. [36] have found the site affinity of various transition metal substituents (Cu, Zr, Nb, Ti, V) for Fe in $\text{Nd}_2\text{Fe}_{17}$. These transition metal substituents show a complex site affinity. For example, 6c site is preferred by Ti and V atoms whereas Cu prefers to occupy 9d and 18h sites. On the other hand, Nb atoms prefer the 6c and 18h sites and Zr atoms, 6c and 18f sites. It was suggested that a steric effect can explain the occupancies of Ti, V, Cu for Fe whereas the steric effect and the coordination effect are responsible for Zr and Nb occupying the Fe sites.

Magnetic Properties Changes in magnetization and T_C have been observed in several R_2Fe_{17} compounds. Magnetization is found to decrease with increasing non-transition metal and transition metal substituents for Fe in several R_2Fe_{17} compounds, viz. $\text{Dy}_2\text{Fe}_{17-x}\text{Ga}_x$ [17], $\text{Ho}_2\text{Fe}_{17-x}\text{Ga}_x$ [18], $\text{Sm}_2\text{Fe}_{17-x}\text{Ga}_x$, $\text{Er}_2\text{Fe}_{17-x}\text{Ga}_x$ [20], $\text{Tm}_2\text{Fe}_{17-x}\text{Ga}_x$ [20, 21], $\text{Y}_2\text{Fe}_{17-x}\text{Ga}_x$ [22], $\text{Ce}_2\text{Fe}_{17-x}\text{Ga}_x$ [24], $\text{Nd}_2\text{Fe}_{17-x}\text{Ga}_x$ [26], $\text{Ce}_2\text{Fe}_{17-x}\text{Al}_x$ [29], $\text{Nd}_2\text{Fe}_{17-x}\text{Al}_x$ [30], $\text{ErPrFe}_{17-x}\text{Al}_x$ [31], $\text{Ce}_2\text{Fe}_{17-x}\text{Si}_x$ [32], $\text{Y}_2\text{Fe}_{17-x}\text{Si}_x$, $\text{Tm}_2\text{Fe}_{17-x}\text{Si}_x$ [33], $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ [34, 35] and $\text{Nd}_2\text{Fe}_{17-x}\text{M}_x$ ($M = \text{Cu, Cr, V, Nb, Zr}$) [38]. The substituents decrease the Fe magnetic moment thereby decreasing the magnetization. This is normally referred to as “magnetic dilution effect”. For low values of Ga concentration ($x = 1, 2$), Venkatesan et al. [20] found an initial increase in magnetization of $\text{Er}_2\text{Fe}_{17-x}\text{Ga}_x$ and $\text{Tm}_2\text{Fe}_{17-x}\text{Ga}_x$ and this has been attributed to the increase in the Fe–Fe exchange interaction compared to the magnetic dilution.

The variations of T_C observed in several R_2Fe_{17} compounds when Fe is substituted with a non-transition metal [18, 20–22, 24, 26, 28–32, 41] or transition metal substituents [35, 38] are shown in Figs. 7 and 8. The low T_C observed in parent R_2Fe_{17} compounds is believed to be due to the short Fe–Fe interatomic distances found at the 6c (dumbbell) sites in the rhombohedral structure (4f sites are the corresponding ones in the hexagonal structure) which couple antiferromagnetically since their separation is $\approx 2.4 \text{ \AA}$ which is less than 2.45 \AA needed for ferromagnetic ordering [42].

With Ga, Al, Si substituents in R_2Fe_{17} compounds, it was observed that at low concentrations ($x = 3-4$), T_C increases initially and then decreases at higher concentrations. On the other hand, such initial increase in T_C with transition metal elements was limited to low concentrations ($x = 0.5-1$). An anomalous increase of T_C was observed in $\text{Tm}_2\text{Fe}_{17-x}\text{Ga}_x$ [21] and $\text{Y}_2\text{Fe}_{17-x}\text{Ga}_x$ [22], at higher Ga concentrations ($x > 7$).

As discussed earlier, with the substitution of the non-transition metal and transition metal elements for Fe in various compounds, there is no systematic behaviour of the

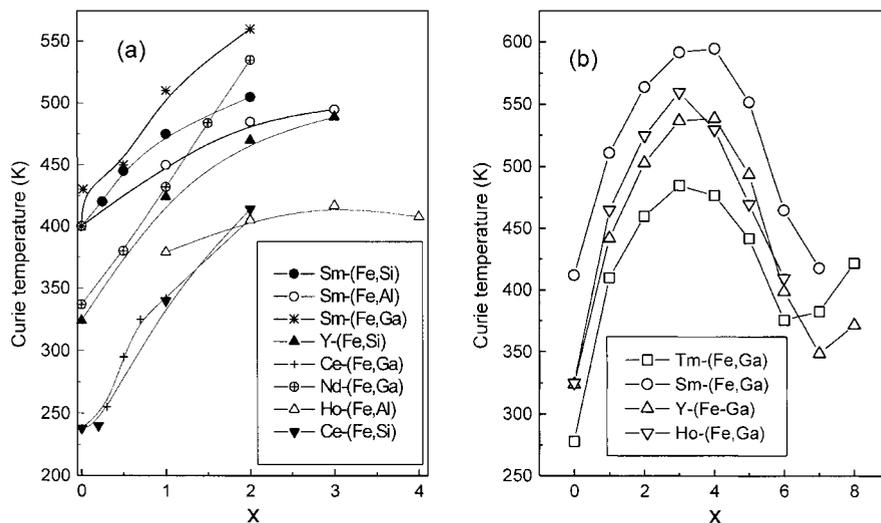


Fig. 7. Dependence of Curie temperature on x for a) $CeFe_{17-x}Ga_x$ [24], $NdFe_{17-x}Ga_x$ [26], $SmFe_{17-x}Ga_x$ [41], $HoFe_{17-x}Al_x$ [28], $SmFe_{17-x}Al_x$ [41], $CeFe_{17-x}Si_x$ [32], $YFe_{17-x}Si_x$ [33] and $SmFe_{17-x}Si_x$ [41] compounds and b) $HoFe_{17-x}Ga_x$ [18], $YFe_{17-x}Ga_x$ [22], $SmFe_{17-x}Ga_x$ [20] and $TmFe_{17-x}Ga_x$ [20, 21] compounds

changes in the lattice constants including the unit cell volume or the site occupancies. Consequently, as can be seen from Figs. 9 and 10, the variation of Fe-Fe bond lengths differs for various substituents.

In general, the T_C in rare earth intermetallic compounds is governed by three kinds of exchange interactions, viz. 3d-3d exchange (J_{FeFe}), 4f-4f exchange (J_{RR}) and 3d-4f

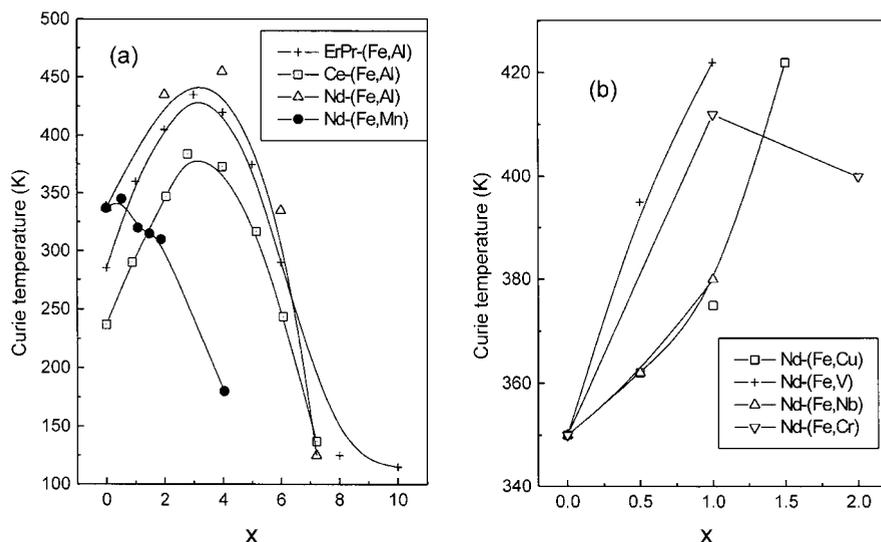


Fig. 8. Dependence of Curie temperature on x for a) $CeFe_{17-x}Al_x$ [29], $NdFe_{17-x}Al_x$ [30], $ErPrFe_{17-x}Al_x$ [31] and $NdFe_{17-x}Mn_x$ [35] compounds and b) $NdFe_{17-x}Cu_x$, $NdFe_{17-x}V_x$, $NdFe_{17-x}Nb_x$ and $NdFe_{17-x}Cr_x$ [38] compounds

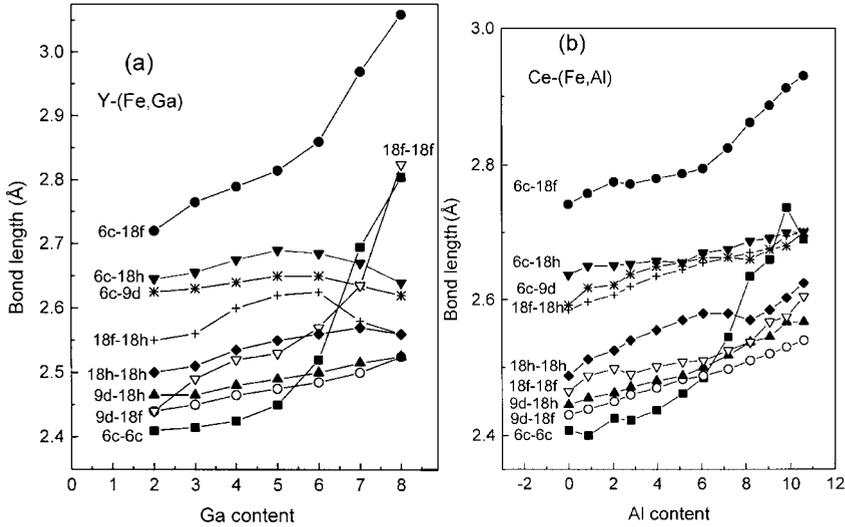


Fig. 9. Dependence of bond lengths on x for a) $\text{YFe}_{1-x}\text{Ga}_x$ [39] and b) $\text{CeFe}_{1-x}\text{Al}_x$ [29] compounds

exchange (J_{RFe}). The 4f–4f exchange interaction is the weakest of all the interactions and can be neglected. However, if we consider a R–Fe system where R is nonmagnetic, then it is possible to get the contribution to T_C from Fe–Fe interaction alone.

Several authors have evaluated the variation of 3d–3d exchange interaction parameter, J_{FeFe} as a function of Ga, Al, Si substitutions for Fe in R_2Fe_{17} compounds by means of a mean-field analysis [20, 21, 29, 39]. The results are shown in Fig. 11.

In $\text{Ce}_2\text{Fe}_{17-x}\text{Al}_x$ [29] and $\text{Ce}_2\text{Fe}_{17-x}\text{Si}_x$ [32], T_C increased with increase of Al or Si content initially and then decreased. Similar behavior was also observed in other systems as well (Figs. 7 and 8). In all the Ga and Al substituted compounds, the unit cell volume increased with increasing Ga or Al content whereas in Si substituted compounds (Fig. 3a) the unit cell volume decreased with increasing Si content. In $\text{Ce}_2\text{Fe}_{17-x}\text{Si}_x$, the 6c–6c dumbbell separation decreased (Fig. 10) with increase of Si content suggesting that the change in T_C is unlikely to originate from the changes in 6c–6c distance. The exchange cou-

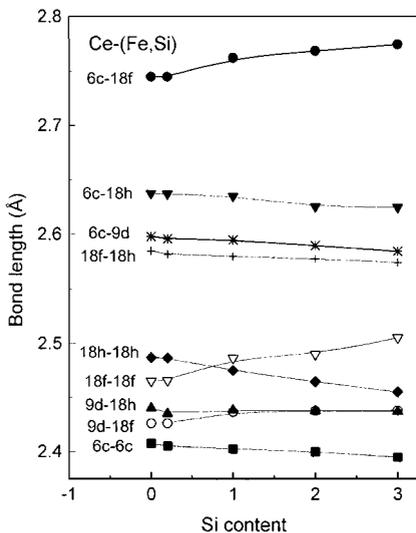


Fig. 10. Dependence of bond lengths on x for $\text{CeFe}_{1-x}\text{Si}_x$ [32] compound

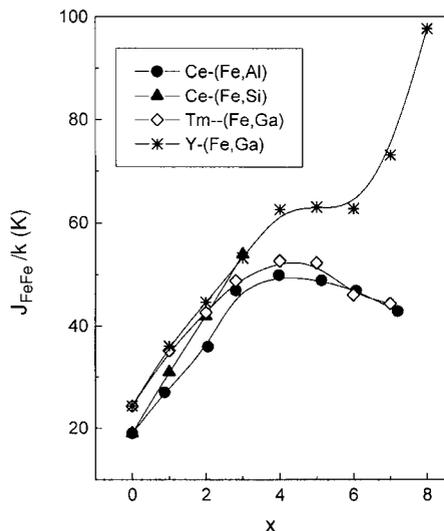


Fig. 11. Dependence of J_{FeFe} on x in $CeFe_{1-x}Al_x$ [29], $CeFe_{1-x}Si_x$ [32], $TmFe_{1-x}Ga_x$ [20] and $YFe_{1-x}Ga_x$ [39]

pling constant J_{FeFe} , evaluated using the mean-field analysis, increased with increasing Si content in $Ce_2Fe_{17-x}Si_x$ in the composition range studied ($x = 0-3$). This suggests that Si atoms occupy preferentially the Fe sites other than 6c sites enhancing the positive exchange interaction. It was also suggested that the different degrees of mixing of the iron 3d band with solute valence band could be responsible for different Curie temperatures observed in these systems [29].

In $Sm_2Fe_{17-x}Ga_x$, $Er_2Fe_{17-x}Ga_x$ and $Tm_2Fe_{17-x}Ga_x$ [20] it was found that J_{FeFe} increased up to $x = 3$ and then decreased with further increase of Ga content. The variation of T_C in these compounds has the same trend suggesting that the positive exchange dominates over the magnetic dilution during the increasing trend of T_C and at higher Ga concentrations, the magnetic dilution predominates due to the reduction of number of Fe-Fe pairs. It was also reported that the intersublattice coupling constant, J_{RFe} , is very small compared to J_{FeFe} and is almost independent of Ga concentration suggesting that T_C is mainly controlled by J_{FeFe} .

An anomalous increase of T_C was reported in $R_2Fe_{17-x}Ga_x$ at higher Ga content [39, 43, 44]. In order to find out this unexpected variation, Wang et al. [39] have discussed the relationship between the structural variations and the Fe-Fe exchange interactions in the $Y_2Fe_{17-x}Ga_x$ system. Y being non-magnetic, only Fe-Fe exchange interactions (J_{FeFe}) are present in the system. From neutron diffraction studies, the Ga concentration dependences of the Fe-Fe bond lengths in $Y_2Fe_{17-x}Ga_x$ ($x = 0-8$) system have been obtained and are shown in Fig. 9a. From the figure it can be seen that the lengths of 6c-6c, 6c-18f and 18f-18f bonds increase rapidly with increasing x content. A monotonous but slow increase is found for 9d-18f, 9d-18h and 18h-18h bonds. On the other hand, the lengths of 6c-9d, 6c-18h and 18h-18h bonds increase first and then decrease. The Fe-Fe exchange interaction (J_{FeFe}) determined using the mean-field approximation is shown in Fig. 11. It has also been observed that the average of the spin of the Fe atom (S_{Fe}) and average number of the nearest Fe neighbours of an Fe atom decrease with increasing Ga content. The T_C increases initially up to $x = 4$, then decreases and increases again for $x = 7, 8$ as can be seen from Fig. 7b. Taking all this into consideration, including the Ga site occupancies (Fig. 4c), it has been concluded that Fe-Fe bond length of 2.55 Å may be the optimal value required for ferromagnetic Fe-Fe exchange at higher Ga concentration in the $Y_2Fe_{17-x}Ga_x$ system.

Sabirianov and Jaswal [45] have evaluated the self-consistent spin-polarized electronic structure and magnetic properties of $Sm_2Fe_{17-x}A_x$ ($A = Ga, Al, Si$) systems using the linear-muffin-tin-orbitals (LMTO) method in the atomic sphere approximation. The cal-

culated magnetization data were compared with the available experimental data. They have also considered the enhancement of T_C due to the substitution of Ga, Al, Si for Fe. This was explained considering a simple model which is within the purview of the band theory, but which takes into account the effects of spin fluctuations on T_C as proposed by Mohn and Wohlfarth [46]. Earlier Jaswal et al. [47] have used this model to explain the observed increase in T_C in R_2Fe_{17} compounds on nitrogenation. In this model

$$T_C \propto M_0^2/\chi_0, \quad (1)$$

where M_0 is the Fe magnetization per unit cell at 0 K and χ_0 is the enhanced ferromagnetic susceptibility at 0 K and is given as

$$1/\chi_0 = 1/4\mu_B^2 \{1/[N_\uparrow(E_F)] + 1/[N_\downarrow(E_F)] - 2I\}, \quad (2)$$

where I is the Stoner exchange parameter; $N_\uparrow(E_F)$, $N_\downarrow(E_F)$ is the average ‘spin-up’ and ‘spin-down’ density of states (DOS), respectively, per Fe atom at the Fermi level. Their calculations also showed very little variations in magnetizations with Ga, Al and Si for Fe. Therefore, it was inferred that the major part of changes in T_C arises from the changes in $N_\uparrow(E_F)$, $N_\downarrow(E_F)$. It can be seen from Eq. (2), that a decrease in DOS at E_F enhances T_C . Spin-polarized DOS calculated at the four inequivalent Fe sites (6c, 9d, 18f, 18h) suggest that 6c, 18f and 18h sites enhance T_C , the enhancement being maximum for the 18h site and minimum for 6c site. The volume decreases slightly from Sm_2Fe_{17} to $Sm_2Fe_{16}Si$ and in spite of this, T_C increases by $\approx 21\%$. This has been attributed to Si–Fe hybridization being lower than that of Fe–Fe leading to the narrowing of d-bands of Fe atoms surrounding Si.

Ching and Huang [48] have estimated the Curie temperatures of Nd_2Fe_{17} , $Nd_2Fe_{17-x}Si_x$ ($x = 0-3$), $Nd_2Fe_{17}Ga_2$ and $Nd_2Fe_{17}Al_2$ compounds using the electron structure results calculated according to the local spin-density approximation and the spin-fluctuation model of Mohn and Wohlfarth [46]. These results gave a quantitative account of the T_C variation in these compounds.

Sabiryanov and Jaswal [49] have performed the ab-initio calculations of T_C of $Sm_2Fe_{16}Ga$ and $Sm_2Fe_{16}Si$ and found that the presence of Ga and Si increases the exchange interaction parameter and hence the T_C . This increase is the largest when Si occupies the 18h site which was also reported experimentally by Middleton et al. [32]. The changes in the exchange parameters with doping are related to lowering of the hybridization of the Fe atoms with their neighbours and magnetovolume effect. The T_C values obtained using Monte Carlo calculations (based on the Heisenberg model and using the exchange parameters) are in good agreement with the reported experimental values. It was pointed out by Al-Omari et al. [38] that there is no significant improvement in magnetization and T_C when transition metals are substituted for Fe in Nd_2Fe_{17} due to a relatively small reduction in the hybridization produced by these substituents compared to non-transition metals such as Ga, Al and Si.

Another approach to account for the variations in T_C has been given by Suresh et al. [50] based on a phenomenological model proposed by Friedel et al. [51]. In this model which explains the variations of T_C with substitutional and interstitial modifications of R_2Fe_{17} compounds, the effects of spatial fluctuations of magnetic moments on T_C were also considered. According to this model, there is an empirical relation between T_C , μ_{eff}

(effective magnetic moment per atom), λ (wavelength of the Friedel oscillations) and d (interatomic distance between magnetic ions), which is given by

$$T_C = C\mu_{\text{eff}}^2 f(\lambda/d), \quad (3)$$

where C is the constant of proportionality (in terms of μ_B^2) with dimensions of K , and $f(\lambda/d)$ is an increasing linear function of (λ/d) . A linear variation of T_C/μ_{eff}^2 with (λ/d) was found for Fe, Co and Ni. μ_{eff} decreases with increase of Al and Ga substitution for Fe in R_2Fe_{17} compounds at low concentrations. At these concentrations, (λ/d) increases and this predominates over the decrease in μ_{eff} leading to an increase in T_C . However, with further increase in substituents, the reduction in μ_{eff} dominates leading to a decrease in T_C . Therefore, using the above empirical relation it is possible to qualitatively account for the variations in T_C of R_2Fe_{17} compounds which are modified substitutionally. It was also found that such an argument could be extended to interstitially modified R_2Fe_{17} compounds as well.

Summary ‘Size effect’ is responsible for the variations in lattice constants, and in turn the unit cell volume, when non-transition metals such as Ga, Al and Si are substituted for Fe in R_2Fe_{17} compounds. On the other hand, when the transition metals (TM) are substituted for Fe, they bond to Fe and R atoms more strongly than non-transition metals leading to a reduction in the unit cell volume. This is in spite of the fact that TM elements have bigger radii than Fe and much bigger radii than Ga, Al and Si.

Occupancies of the Fe sites in R_2Fe_{17} when non-transition metals and transition metals are substituted for Fe are governed by the Wigner-Seitz volume in some cases, and preference of R atoms as nearest neighbours in other cases. A combined effect of these two is also seen in some systems. Therefore, a prediction of the site occupancies for different substituents is an interesting but difficult question.

Several authors have explained the behaviour of T_C when non-transition metals and transition metals are substituted for Fe. The variation of J_{FeFe} gave a reasonable account of the variations, so is the empirical model based on Friedel model. Using electronic structure calculations, magnetization has been evaluated with reasonable success. The spin-fluctuation model of Mohn and Wohlfarth could predict the changes in T_C . The ab-initio calculations attempted recently in $Sm_2Fe_{16}Ga$ and $Sm_2Fe_{16}Si$ suggest that Ga and Si increase the exchange parameters and are related to the magnetovolume effect and lowering of hybridization of the Fe atoms. These values when employed in Monte Carlo simulations, gave a good prediction of T_C .

Because of a large reduction in hybridization produced by non-transition metal substituents when compared to transition metal substituents, a significant improvement can be predicted in magnetization and T_C in R_2Fe_{17} compounds when non-transition metals are substituted for Fe.

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