

## Recent advances in 2 : 17 and 3 : 29 permanent magnet materials

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**Abstract.** The structural and magnetic properties of 2 : 17 compounds, their nitrides and carbides and the recent development of the novel 3 : 29 compounds are discussed.

**Keywords.** Permanent magnet materials; 2 : 17 compounds; 3 : 29 compounds.

### 1. Introduction

Ever since the discovery of  $\text{RCO}_5$  [R = rare earth] materials as high energy density permanent magnets (Strnat *et al* 1967), main attention has been focussed on the R–TM (transition metal) intermetallics.  $\text{SmCo}_5$  is known to exhibit excellent magnetic properties for permanent magnet applications. Therefore, it was felt that  $\text{R}_2\text{Co}_{17}$  (2 : 17 compounds), which is derived from the  $\text{RCO}_5$  structure, and having large R : TM ratio may possess high saturation magnetization and anisotropy. However, the substitutional sites play a very decisive role in the Co sublattice anisotropy. A compromise between the high saturation magnetization of  $\text{Sm}_2\text{Co}_{17}$  and high magnetic hardness of  $\text{SmCo}_5$  was attained by careful metallurgical routes and an optimum composition,  $\text{SmCo}_{7.7}$  was obtained in which some of the Co is replaced by Fe, Cu and Zr (Buschow 1988a).

Co being expensive, research has been concentrated on intermetallic compounds containing Fe.  $\text{RFe}_5$  compounds do not exist across the whole lanthanide series. The counterpart of  $\text{R}_2\text{Co}_{17}$ , viz.  $\text{R}_2\text{Fe}_{17}$  compounds were explored in detail.  $\text{R}_2\text{Fe}_{17}$  compounds possess large saturation magnetization (R = light rare earths, where R and Fe moments couple ferromagnetically) but the Curie temperatures ( $T_C$ ) are very low and anisotropy is planar.

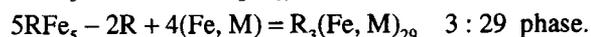
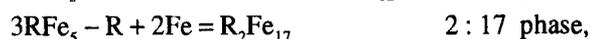
A novel type of permanent magnet material  $\text{Nd}_2\text{Fe}_{14}\text{B}$  discovered by Sagawa *et al* (1984) and Croat *et al* (1984) with the tetragonal structure has attracted lot of attention because of its high energy product.  $\text{Nd}_2\text{Fe}_{14}\text{B}$  possesses large saturation magnetization and anisotropy. In  $\text{R}_2\text{Fe}_{14}\text{B}$ , 3d anisotropy favours easy *c*-axis and the crystal fields are such that Nd and Pr rather than Sm exhibit excellent magnetic properties. Eventhough Nd–Fe–B is not superior to Sm–Co based magnets with regard to coercivity the large energy product and cost

factor make this material attractive for room temperature applications. The main drawbacks of the Nd–Fe–B magnet is the low  $T_C$  (590 K) which restricts its potential for high temperature applications and its weak corrosion resistance. The structural and magnetic properties of  $\text{R}_2\text{Fe}_{14}\text{B}$  have been extensively reviewed by Buschow (1988a) and Herbst (1991).

Coe and Sun (1990) found that in  $\text{R}_2\text{Fe}_{17}$  compounds, interstitial modification by nitrogen and carbon can increase the saturation magnetization,  $T_C$  and magneto-crystalline anisotropy. In the case of  $\text{Sm}_2\text{Fe}_{17}$ , about 150% increase in the saturation magnetization and ~ 400° increase in the  $T_C$  are reported after nitrogenation. Moreover, the anisotropy changes from easy plane to easy axis. The reasons for these drastic changes in the magnetic properties are due to the expansion of the unit cell, associated changes in the 3d band and changes in the rare earth crystal fields due to presence of nitrogen and carbon.

The search for new magnetic materials with better thermal and magnetic performance led to the discovery of new intermetallic phases,  $\text{R}(\text{Fe}, \text{M})_{12}$  (Buschow 1988b) and  $\text{R}_3(\text{Fe}, \text{M})_{29}$  (Collocott *et al* 1992) which are known as 1 : 12, and 3 : 29 compounds, respectively. In both the compounds, the presence of a third element M (= Ti, V, Cr, Mn, Mo, W) is necessary for the stabilization of the phase.

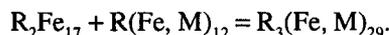
The 1 : 12, 2 : 17 and 3 : 29 phases can be derived from the basic hexagonal  $\text{CaCu}_5$  structure as shown below, where R and Fe occupy Ca and Cu sites, respectively (Li *et al* 1994a).



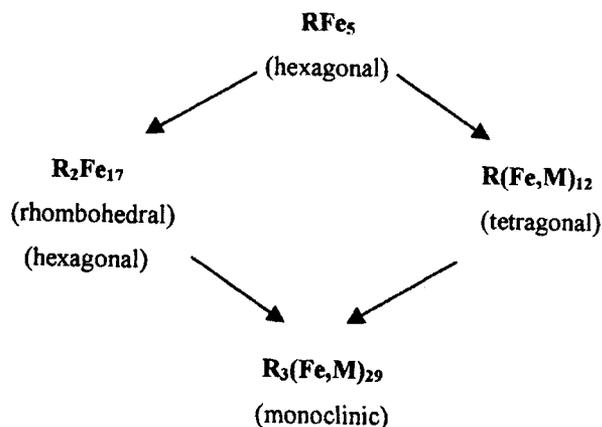
Therefore, replacement of 1/3 of the R atoms by a pair of Fe atoms (known as dumb-bell atoms) results in

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$R_2Fe_{17}$  structure, 2/5 of the R atoms by Fe atoms results in  $R_3(Fe, M)_{29}$  structure and half of the R atoms by Fe atoms results in  $R(Fe, M)_{12}$  structure. Moreover, 3 : 29 phase is shown to be derivable from the alternate stacking of 1 : 12 and 2 : 17 segments as described by



The interrelation between these structures can be schematically represented as



$R(Fe, M)_{12}$  are iron rich compounds with a tetragonal unit cell and  $I4/mmm$  space group (Buschow 1988b). They possess large saturation magnetization and high  $T_C$ . In this type of compounds, Fe sublattice anisotropy favours the tetragonal  $c$ -axis. The nature of rare earth anisotropy is decided by the second order Steven's coefficient ( $\alpha_j$ ) of the rare earth. When  $\alpha_j$  is +ve ( $R = Sm, Er$  etc) the R sublattice anisotropy favours easy  $c$ -axis and when  $\alpha_j$  is -ve ( $Pr, Nd$  etc) the R sublattice anisotropy favour easy plane (Li and Coey 1991). Interstitial modification by nitrogen or carbon leads to changes in the magnetic properties. The maximum number of nitrogen or carbon atoms that can be accommodated in these compounds is one per formula unit. In the case of nitrides, when  $\alpha_j$  is +ve the R sublattice anisotropy favours easy plane and when  $\alpha_j$  is -ve the R sublattice anisotropy favours easy  $c$ -axis. Since the amount of nitrogen that is absorbed is less compared to 2 : 17 compounds, the increase in  $T_C$  is comparatively low.

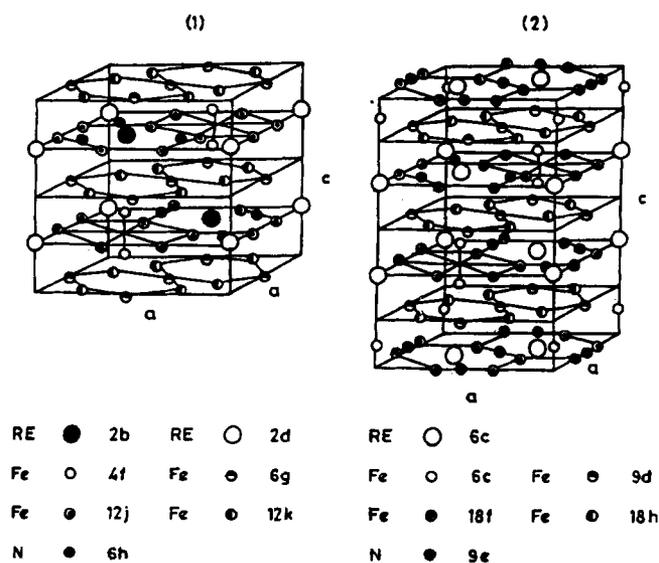
Recent investigations of structural and magnetic properties of substitutionally and interstitially modified 2 : 17 and 3 : 29 compounds are discussed below.

## 2. Structural and magnetic properties of $R_2Fe_{17}$ compounds

$R_2Fe_{17}$  compounds crystallize in rhombodhedral ( $Th_2Zn_{17}$  type) and hexagonal ( $Th_2Ni_{17}$  type) symmetry, respectively for light and heavy rare earths. The space groups are

$R\bar{3}m$  and  $P6_3/mmc$ , respectively. Figure 1 shows the unit cell of both the structures (Buschow 1977). The compounds with  $R = Gd, Tb$  and  $Y$  can exist in both forms depending on the annealing conditions. Hexagonal form of  $Ce_2Fe_{17}$  has also been reported to coexist with the rhombodhedral structure (Buschow and van Wieringen 1970).  $R_2Fe_{17}$  compounds possess large magnetization, low  $T_C$  and planar anisotropy. The reasons for low  $T_C$  is mainly attributed to the large number of short Fe-Fe bonds ( $< 2.45 \text{ \AA}$ ), where the moments are coupled anti-ferromagnetically, which weakens the strength of the exchange interactions (Valeanu *et al* 1994). In  $R_2Fe_{17}$  compounds, the Fe sublattice anisotropy is planar and R sublattice anisotropy is axial only for those rare earths with +ve  $\alpha_j$  ( $Sm, Er$  and  $Tm$ ). The total anisotropy constant  $K_1(\text{total}) = K_1(R) + K_1(Fe)$ . Since  $|K_1(R)| < |K_1(Fe)|$  the total anisotropy remains planar for all the  $R_2Fe_{17}$  compounds.  $Tm$  overcomes the Fe sublattice anisotropy at low temperatures and the total anisotropy becomes axial below 72 K (Gubbens *et al* 1976).

It has been found that elements with small atomic radius can occupy interstitial sites of the  $R_2Fe_{17}$  host lattice and cause distortions in the lattice giving rise to various kinds of changes in the magnetic properties (Coey and Sun 1990). Carbon and nitrogen are found to affect the magnetic properties drastically compared to hydrogen. Hydrides and nitrides can be prepared by the gas phase interstitial modification (GIM) methods whereas, carbides can be prepared by arc melting and melt spinning methods in addition to the GIM process (Liu *et al* 1987). Due to the high melting point of carbon, Fe and C are melted together first to form  $Fe_3C$



**Figure 1.** Unit cells of (1) hexagonal ( $Th_2Ni_{17}$ -type) and (2) rhombodhedral ( $Th_2Zn_{17}$ -type)  $R_2Fe_{17}$  compounds. The different crystallographically inequivalent rare earth and Fe atoms and the interstitial N atoms are also shown (Buschow 1977).

which has a lower melting temperature. Then  $\text{Fe}_3\text{C}$  is melted along with the corresponding constituent elements in arc furnace under argon atmosphere. In order to avoid the formation of  $\text{R}_2\text{Fe}_{14}\text{C}$  phase during cooling, the ingots after annealing are quenched into ice-water mixture (Venkatesan *et al* 1998a). Carbides of  $\text{R}_2\text{Fe}_{17}$  can also be prepared by arc melting and subsequent melt spinning using a suitable quenching rate (Shen *et al* 1992). Common features of the arc melted and melt spun interstitial carbides are their high temperature stability contrary to the metastability of the materials prepared by GIM process. Another interesting phenomenon observed in arc melted carbides is the structural transformation from the hexagonal  $\text{Th}_2\text{Ni}_{17}$  type structure to the rhombohedral  $\text{Th}_2\text{Zn}_{17}$  type structure with increasing carbon concentration (Sun *et al* 1990a). On the other hand, the modification of the  $\text{R}_2\text{Fe}_{17}$  structures by interstitial nitrogen and carbon atoms introduced by the GIM process is essentially to expand the unit cells, without changing the rhombohedral or hexagonal symmetry of the parent compounds.

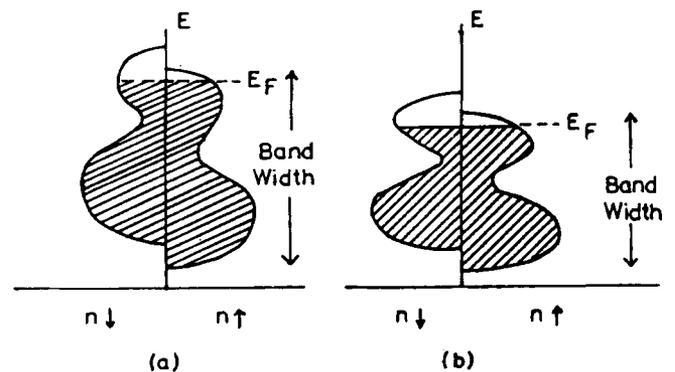
From the X-ray and neutron diffraction studies, the interstitial atoms (carbon and nitrogen) were initially reported to occupy the 3a sites, which were in between the dumb-bell iron atoms (Luo *et al* 1987). But, it was later established that the interstitial atoms occupy the 9e sites in rhombohedral  $\text{Th}_2\text{Zn}_{17}$  type structure or 6h site in hexagonal  $\text{Th}_2\text{Ni}_{17}$  type structure (Block and Jeitschko 1987; Helmholdt and Buschow 1989). These sites are formed by a rectangle of Fe atoms and two rare earth atoms at opposite corners. In general, in  $\text{R}_2\text{Fe}_{17}$  compounds,  $T_C$  is mainly dominated by the exchange interaction of the Fe sublattice, which is strongly dependent on the Fe-Fe distance. Bonds less than 2.45 Å contribute to the antiferromagnetic exchange which lowers the  $T_C$ . The Fe-Fe distance in the dumb-bell 4f or 6c sites is typically 2.4 Å which contributes to the reduction in the  $T_C$ . When the non-magnetic atoms like Al, Ga partially substitute for Fe atoms, the  $T_C$  is enhanced initially due to lattice expansion. With further increase of the non-magnetic elements, magnetic dilution takes place resulting in the reduction of  $T_C$  (Wang and Dunlap 1993; Li *et al* 1994c, 1995). However, a different behaviour is observed in Si substituted compounds, where  $T_C$  increases initially inspite of reduction in the unit cell volume. This has been attributed to the preferential occupancy of Si atoms at some of the sites which participate in the antiferromagnetic exchange thereby reducing the negative contribution to  $T_C$  (Li *et al* 1995).

The increase in saturation magnetization upon nitrogenation is due to magnetovolume effect (MVE). When nitrogen or carbon atoms reside in the interstitial sites, the lattice expands and the 3d-3d overlap decreases. The volume dependence of magnetization is given by Coehoorn (1989)

$$\frac{V}{M} \left\{ \frac{\partial M}{\partial V} \right\}_{H=0} = \left\{ \frac{5}{3} \right\} \frac{2I}{\left[ \frac{1}{N_{\uparrow}(E_f)} + \frac{1}{N_{\downarrow}(E_f)} - 2I \right]}, \quad (1)$$

where  $N_{\uparrow}$  and  $N_{\downarrow}$  are the densities of states at the Fermi level and  $I$ , the stoner parameter. Since  $\text{R}_2\text{Fe}_{17}$  system is a weak ferromagnet (both the sub bands are unfilled), for a given increase in unit cell volume, the increase in magnetization is large. As seen from figure 2 the 3d band gets narrowed after nitrogenation, which leads to the localization of the 3d bands resulting in an increase in the Fe magnetic moment. The short Fe-Fe bonds are elongated as a result of the expansion of the unit cell, thus favouring more ferromagnetic exchange and increasing the  $T_C$ . The  $T_C$  increases by about 400° after nitrogenation in  $\text{R}_2\text{Fe}_{17}$  compounds. The increase in magnetocrystalline anisotropy after nitrogenation is due to modification of the crystal fields due to the presence of nitrogen atoms situated very close to the rare earth ions.

In  $(\text{Er}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{17-x}\text{Al}_x$ , with increasing Al content the magnetization monotonically decreases whereas,  $T_C$  increases up to  $x=0.3$  and then decreases (Suresh and Rama Rao 1996a).  $(\text{Er}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{17}$  upon nitrogenation shows a large volume change with substantial increase ( $\sim 400^\circ$ ) in  $T_C$  for  $N=2.6$ , but the nitrogen intake and  $T_C$  decrease with increasing Al content (Suresh and Rama Rao 1996b). These variations have been attributed to the reduction in the magnetovolume effect (Suresh and Rama Rao 1996b) as shown in figure 3. Harris *et al* (1998) have confirmed from the extended X-ray absorption fine structure (EXAFS) measurements of the Fe, K, and Pr and Er  $L_{III}$  absorption edges that the nitrogenation dilates both the Fe-Fe and the (Pr,Er)-Fe bonds, thus raising the  $T_C$  via magnetovolume effect. Figure 4 shows the plot of the radial coordinates versus Fourier transform amplitude for Pr  $L_{III}$  EXAFS for  $(\text{Er}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{17-x}\text{Al}_x\text{N}_y$ .



**Figure 2.** Schematic representation of 3d-bands (a) before and (b) after nitrogenation (Buschow 1977).

Suresh *et al* (1998) have qualitatively explained the variation of  $T_C$  upon substitutional and interstitial modifications of  $R_2Fe_{17}$  compounds based on Friedel approach. According to this model there is an empirical relation between  $T_C$ ,  $\mu_{eff}$  (effective magnetic moment per atom),  $\lambda$  (wavelength of the Friedel oscillations) and  $d$  (interatomic distance of magnetic ions) which is given as

$$T_C = C\mu_{eff}^2 f\left(\frac{\lambda}{d}\right), \quad (2)$$

where,  $C$  is the constant of proportionality having the units of  $K/\mu_B^2$ . This model is found to hold good for Fe, Co and Ni as seen by the linear variation of  $T_C/\mu_{eff}^2$  with  $(\lambda/d)$  in figure 5. In the case of substitutionally modified (Al or Ga) compounds, even though  $\mu_{eff}$  decreases with Al or Ga contents, the increase in  $(\lambda/d)$  predominates initially giving rise to an increase in  $T_C$ . However, with further substitution, reduction in  $\mu_{eff}$  dominates leading to decrease in the  $T_C$ . In the case of nitrogenated compounds, there will be an increase in  $(\lambda/d)$  due to a small charge transfer from nitrogen to the Fe 3d band. This along with the increase in  $\mu_{eff}$  results in a large increase in  $T_C$ .

It was found that the substitution of Ga or Si in  $R_2Fe_{17}C_x$  compounds can stabilize their structure (Li *et al* 1994c, 1995). The arc melted  $Sm_2(Fe, Ga)_{17}C_x$  with  $x \geq 1.5$  and relatively lower Ga concentration have  $T_C$  higher than 600 K and a room temperature anisotropy

field higher than 130 kOe (Shen *et al* 1995). A high coercivity of 15 kOe at room temperature was obtained in the  $Sm_2(Fe, Ga)_{17}C_x$  compounds prepared by melt spinning (Shen *et al* 1993). The value of  $T_C$  is found to increase with increasing C content. The  $T_C$  increases from 480 K for  $x=0$  to 587 K for  $x=2$ , which is 260 K higher than that of  $HoErFe_{17}$ .

In hard magnetic materials, the anisotropy energy originates from both the rare earth and 3d sublattices. The rare earth contribution to the magnetocrystalline aniso-

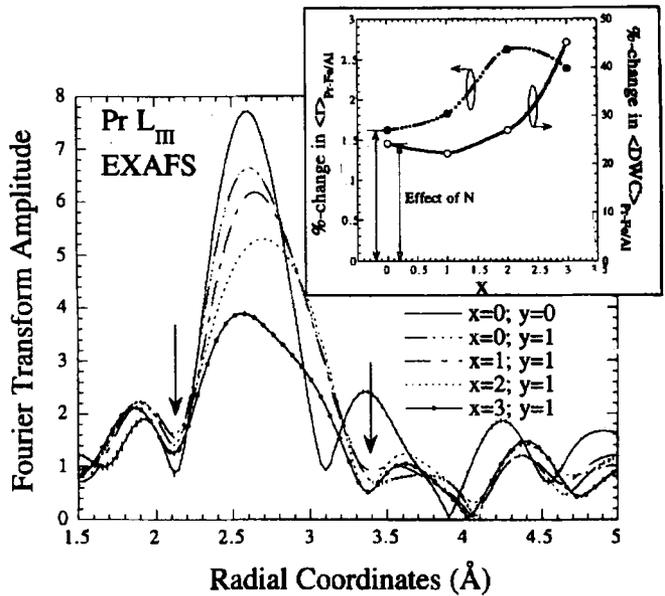


Figure 4. Fourier transformed Pr L<sub>III</sub> EXAFS for  $(Er_{0.5}Pr_{0.5})_2Fe_{17-x}Al_xN_y$  (Harris *et al* 1998).

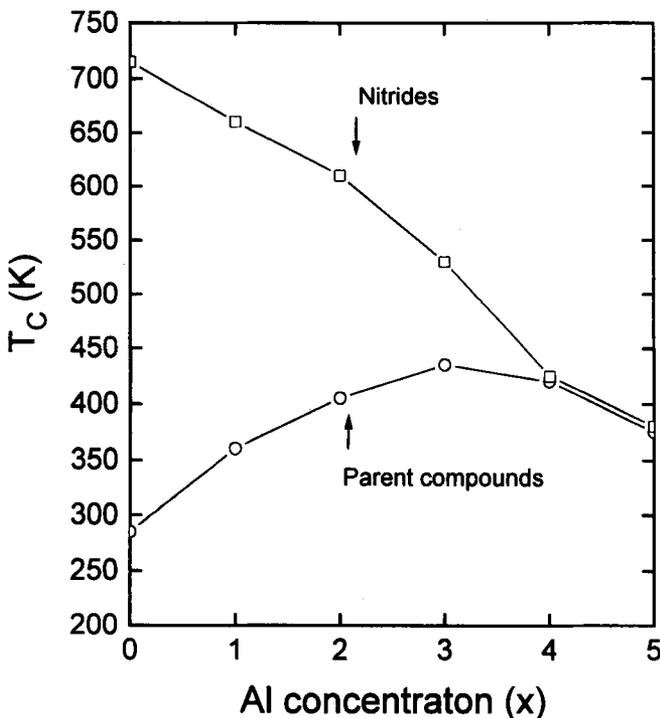


Figure 3. Reduction in MVE as a function of Al and N contents in  $(Er_{0.5}Pr_{0.5})_2Fe_{17-x}Al_x$  (Suresh and Rama Rao 1996b).

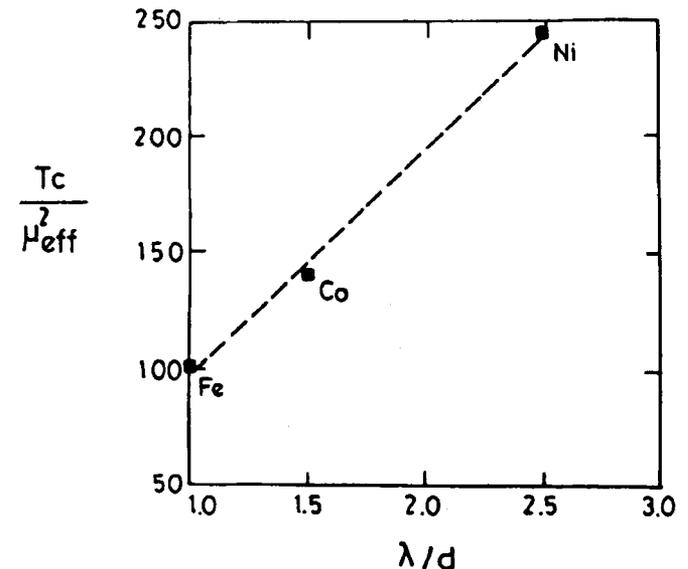


Figure 5.  $T_C/\mu_{eff}^2$  vs  $\lambda/d$  graph of Fe, Co and Ni (Friedel model) (Suresh *et al* 1998).

tropy is dominant at low temperatures whenever the  $4f$  ions have non-zero orbital moments. The easy magnetization direction [EMD] of the  $R_2Fe_{17}$  compounds lies in the basal plane in the whole magnetically ordered temperature range except for  $Tm_2Fe_{17}$  where a change of the easy magnetization direction from basal plane to  $c$ -axis occur at around 72 K (Gubbens *et al* 1976) with decreasing temperature. This is mainly attributed to the competition between the easy plane Fe and the easy axis Tm sublattice anisotropies. Interstitial modification by nitrogen or carbon has led to a change of the magnetic anisotropy. In the interstitially modified compounds, spin reorientation occurs not only for Tm but also for Sm and Er. In the case of  $Sm_2Fe_{17}N_x$  compounds, the anisotropy is found to be strongly uniaxial along with high  $T_C$  and very high magnetization which makes it promising candidate for permanent applications (Coe and Sun 1990). The  $Sm_2Fe_{17}N_x$  and  $Sm_2Fe_{17}C_x$  prepared by gas-solid reaction show the uniaxial anisotropy field of 150 kOe for carbide and 140 kOe for nitride (Katter *et al* 1990) at room temperature.

The total anisotropy can be increased either by increasing the rare earth anisotropy or decreasing the planar Fe sublattice anisotropy. The first order anisotropy constant for rare earth is related to the dominant crystal field coefficient through the relation (Hu *et al* 1994a),

$$K_1^R = -\left(\frac{3}{2}\right) \alpha_J \langle 3J_z^2 - J(J+1) \rangle \langle r_{4f}^2 \rangle A_2^0, \quad (3)$$

where,  $r_{4f}$  is the radius of the  $4f$  orbital and  $A_2^0$  is the second order crystal field parameter. The sign  $A_2^0$  is dependent on the symmetry of the R site. The sign  $A_2^0$  is negative in the case of rhombohedral structure. But in the hexagonal cell, out of the two inequivalent R sites, 2b has negative  $A_2^0$  and 2d has positive  $A_2^0$ . By virtue of this relation, the product of  $\alpha_J$  and  $A_2^0$  has to be positive in order to achieve total uniaxial anisotropy.

Greedan and Rao (1973) have shown that in  $Er_{2-x}Pr_xCo_{17}$ , both Er and Pr occupy 2b and 2d preferentially so that the contribution to R anisotropy will be always axial. Planar anisotropy of the Fe sublattice anisotropy can be reduced by substitution of non-magnetic elements like Ga, Al, Si, B, Ti etc. Following this, Suresh and Rama Rao (1996a) have studied  $ErPrFe_{17-x}Al_x$  system and Venkatesan *et al* (1998b) have studied  $HoErFe_{17-x}Ga_x$  in order to investigate the effect of substitution of Al and Ga and the magnetic properties. Table 1 gives the  $T_C$  and EMD at RT in some of the substitutionally and interstitially modified 2 : 17 compounds.

### 3. Structural and magnetic properties of $R_3(Fe, M)_{29}$ compounds

In 1992, Collocott *et al* reported a novel class of R-TM,  $R_3(Fe, M)_{29}$  (3 : 29 compounds) which possess intrinsic

properties for permanent magnet applications. Initially, this ternary phase was thought of having R : TM stoichiometry to be 2 : 19 and was assigned a rhombohedral unit cell. Cadogan *et al* (1994a) identified that this system crystallizes in monoclinic symmetry. In subsequent developments, Fuerst *et al* (1994) determined the space group to be  $P21/c$ . Later, Li *et al* (1994a) by X-ray diffraction and Hu and Yelon (1994) by neutron diffraction confirmed that the actual stoichiometry is in fact, 3 : 29. They also described that this unit cell can be derived from the alternate stacking of 1 : 12 and 2 : 17 segments in the ratio 1 : 1. In 1995, Kalogirou *et al* by a detailed structural analysis showed that the correct choice of space group can be  $A2/m$  which involves a lesser number of Fe inequivalent sites (eleven) compared to thirteen in  $P21/c$ . This reduces the number of constraints in the refinements. This choice of space group was later confirmed by Yelon and Hu (1996) from neutron diffraction studies.

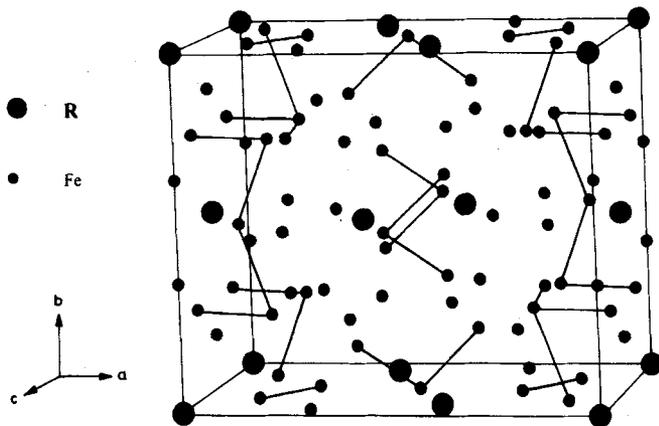
The unit cell of  $R_3(Fe, M)_{29}$  is shown in figure 6. There are two formula units per unit cell with two inequivalent sites for R and eleven inequivalent sites for Fe. This structure can be derived from the hexagonal  $RFe_5$ -type basis unit by replacement of R by a pair of Fe atoms (dumb-bells) as mentioned earlier. A third element is essential for the stabilization of the 3 : 29 phase. 3 : 29 materials are reported to form with R = Ce, Pr, Nd, Sm, Gd, Tb, Dy and Y and M = Ti, V, Cr, Mn, Mo (Cadogan *et al* 1994b; Ibarra *et al* 1994; Li *et al* 1994b; Margarian *et al* 1996). From the calculation of the hole size, it was reported that 4 nitrogen atoms and

**Table 1.** The Curie temperature ( $T_C$ ) and the easy magnetization direction (EMD) of some substitutionally and interstitially modified 2 : 17 compounds.

Compound	$T_C$ (K)	EMD (RT)	Reference
$Sm_2Fe_{17}$	389	Planar	(Coe and Sun 1990)
$Sm_2Fe_{17}N_{2.7}$	750	Axial	(Coe and Sun 1990)
$Sm_2Fe_{17}C_2$	670	Axial	(Hu and Liu 1991)
$Pr_2Fe_{17}C_2$	654	Planar	(Altounian <i>et al</i> 1993)
$Ho_2Fe_{17}$	327	Planar	(Sun <i>et al</i> 1990b)
$Ho_2Fe_{17}N_{2.7}$	710	Planar	(Buschow 1991)
$Pr_2Fe_{17}$	290	Planar	(Suresh 1996c)
$Pr_2Fe_{17}N_{2.7}$	720	Planar	(Suresh 1996c)
$Er_2Fe_{17}$	296	Planar	(Sun <i>et al</i> 1990b)
$Er_2Fe_{17}N_{2.7}$	690	Planar	(Suresh 1996c)
$Er_2Fe_{15}Ga_2C_2$	607	Planar	(Venkatesan <i>et al</i> 1998a)
$ErPrFe_{17}$	285	Planar	(Suresh 1996c)
$HoErFe_{17}$	328	Planar	(Venkatesan <i>et al</i> 1998b)
$ErPrFe_{15}Al_2$	405	Cone	(Suresh 1996c)
$ErPrFe_{15}Al_2N_{1.9}$	610	Cone	(Suresh 1996c)
$HoErFe_{15}Ga_2$	486	Planar	(Venkatesan <i>et al</i> 1998b)
$HoErFe_{15}Ga_2C_2$	612	Planar	(Venkatesan <i>et al</i> 1998a)

6 hydrogen atoms, per formula unit, can occupy interstitial sites in 3 : 29 compounds (Ryan *et al* 1994). Hu *et al* (1996) from neutron diffraction studies reported that Ti occupies 4g and 4i sites and N occupies 4f and 4i sites.

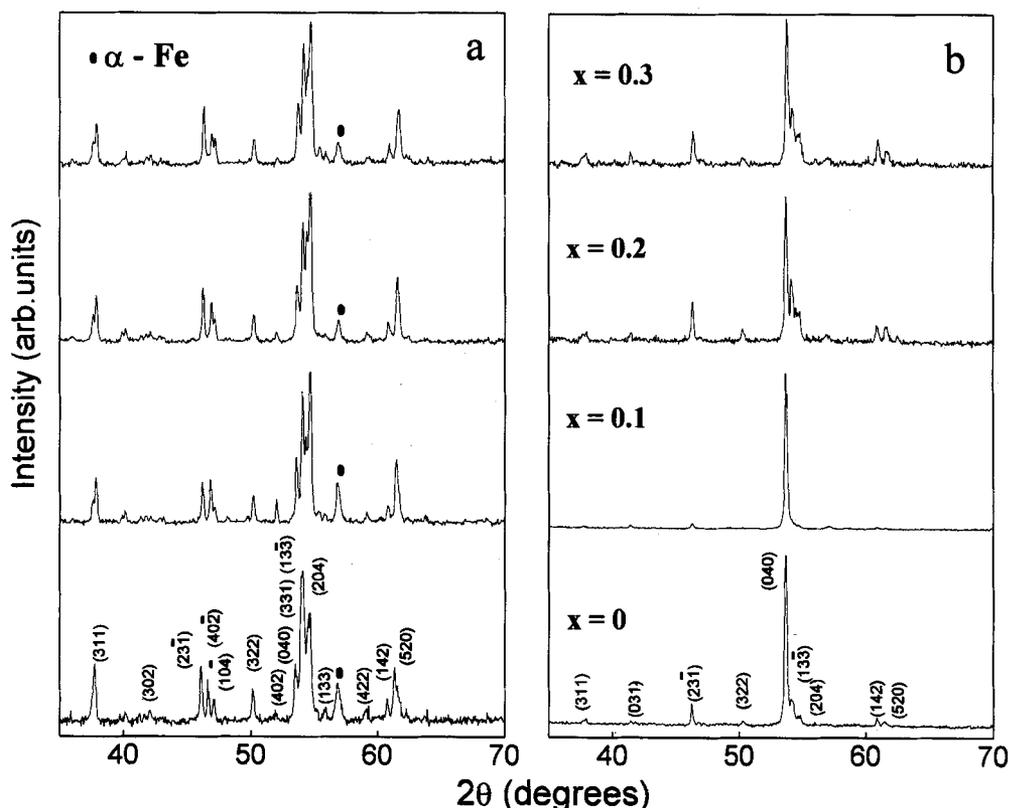
The saturation magnetization and  $T_C$  of these compounds are intermediate to their 2 : 17 and 1 : 12 counter-



**Figure 6.** Unit cell of  $R_3(Fe, M)_{29}$  compounds with  $b$ -axis up. Big spheres represent the R atoms and small spheres represent the Fe/Ti atoms. Bonds less than 2.45 Å (antiferromagnetic bonds) are also shown (Shah *et al* 1998a).

parts which is in accordance with the R-TM ratio of the respective compounds. The unit cell of 3 : 29 compound contains several Fe-Fe bonds (see figure 6) having bond lengths  $< 2.45$  Å which weakens the strength of exchange interactions resulting in a low  $T_C$ . As discussed earlier, substitution elements like Al, Ga found to increase the  $T_C$  in 2 : 17 compounds. So far, there are very few reports regarding the substitution of Ga and Al for Fe in any 3 : 29 compounds. Even though there was a mention of  $Nd_3(Fe, Al)_{29}$  by Cadogan *et al* (1994b), structural and magnetic details are not available. Substitution of Ga for Fe in  $Sm_3(Fe, Mo)_{29}$  has been reported by Pan *et al* (1997). The amount of Ga that can replace Fe is limited to  $\sim 10$  at%. Further substitution of Ga leads to the formation of 1 : 12 phase. Ga substitution increases the  $T_C$  from 445 K for  $x=0$  to 483 K for  $x=3$  in  $Sm_3Fe_{28-x}Ga_xMo_{10}$ . This may be due to the increase in Fe-Fe distance due to the lattice expansion. The saturation magnetization decreases with Ga concentration which can be due to the magnetic dilution.  $Sm_3(Fe, Mo)_{29}$  has planar anisotropy, but with the introduction of Ga, the anisotropy changes from easy plane to easy cone.

Co substitution in  $Pr_3Fe_{27.5}Ti_{1.5}$  ( $x=0-0.3$ ) showed very interesting properties (Shah *et al* 1998a). 30 at% of Fe was replaced by Co and was reported to form in nearly single phase with traces of  $\alpha$ -Fe. At higher Co concen-



**Figure 7.** XRD of (a) randomly and (b) magnetically oriented  $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$  compounds. The samples were oriented at 12 kOe (Shah *et al* 1998b).

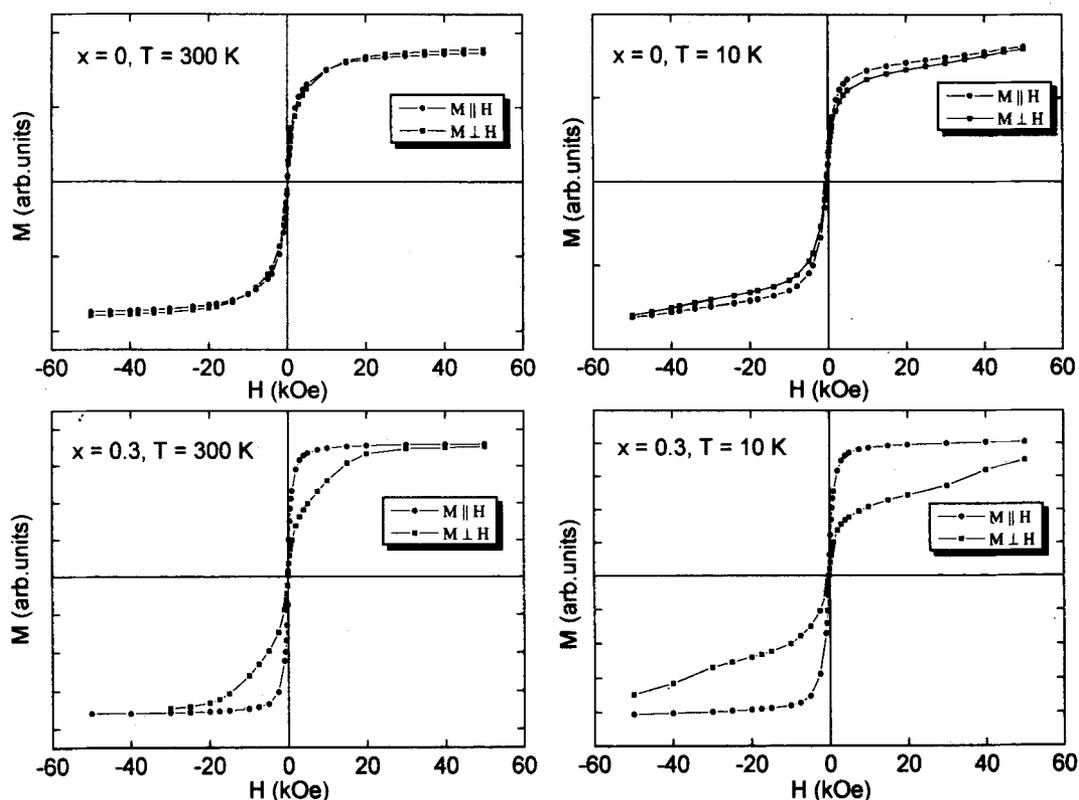
trations, an additional phase of  $\text{Pr}(\text{Fe}/\text{Co}, \text{Ti})_{12}$  was also observed. The saturation magnetization increases up to  $x=0.3$ . In many of the Fe rich R-Fe intermetallics, when Fe is replaced by Co, there exists a concentration at which the saturation magnetization becomes maximum. This is explained on the basis of rigid band model (Slater-Pauling curve) (Matsura *et al* 1985). Initially the spin-up sub-band is filled resulting in an increase in the difference between spin-up and spin-down states hence a net increase in the magnetization. Once the spin-up bands are completely filled, then spin-down states starts getting filled and consequently the net magnetization starts decreasing. The value of this critical concentration is found to vary for different R-(Fe, Co) intermetallics. In the case of  $\text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5}$ , the Co concentration ( $x$ ) at which the saturation magnetization becomes maximum is found to be  $>0.3$ .

In  $\text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5}$  compounds,  $T_C$  increases with increasing Co concentration. An increase of 67 K/Co atom for  $x \leq 0.1$  and 40 K/Co atom in the range  $0.1 \leq x \leq 0.3$  in  $T_C$  were observed. This may be a consequence of the preferential occupation of Co atoms at some of the Fe sites where there is an antiferromagnetic exchange between the magnetic moments. Co atoms residing at these sites can in fact reduce the negative contribution to the exchange and increase the  $T_C$  (Shah *et al* 1998a).

Neutron diffraction studies on these compounds also suggest such preferential occupancy (Harris 1998).

Most of the 3:29 compounds exhibit planar anisotropy. Courtois *et al* (1996) predicted that the EMD of the Fe sublattice anisotropy favours  $b$ -plane and R sublattice anisotropy favours  $b$ -axis for rare earths having  $\alpha_j -ve$  (Pr, Nd, Tb and Dy) and  $b$ -plane for rare earths having  $\alpha_j +ve$  (Sm). In  $\text{Pr}_3(\text{Fe}, \text{Ti})_{29}$ , at room temperature, the R sublattice anisotropy overcomes the Fe sublattice anisotropy and EMD is along the  $b$ -axis. In  $\text{Sm}_3(\text{Fe}, \text{Ti})_{29}$  the EMD is in the  $b$ -plane, but after nitrogenation the EMD changes over to the  $c$ -axis of the  $\text{CaCu}_5$  basis unit and the anisotropy becomes uniaxial (Yang *et al* 1994). In  $\text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5}$  compounds, from the XRD of random and oriented (at a field of 12 kOe) samples (figure 7), it was observed that the EMD is almost along the  $b$ -axis for  $x=0.1$  and near the  $b$ -axis for  $x=0, 0.2$  and  $0.3$ . The magnetization data on these samples, which is shown in figure 8, indicates the increase of anisotropy field with increasing Co concentration (Shah *et al* 1998b).

From crystal field calculations in 3:29 compounds, Li *et al* (1996) have shown that the dominant crystal field coefficient  $A_2^0$  which determines the rare earth anisotropy (3) has opposite signs at the two rare earth inequivalent sites viz.  $2a$  and  $4i$ . This opens up the possibility of mixing of rare earths with different signs



**Figure 8.** Magnetization curves for  $\text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5}$  ( $x=0$  and  $0.3$ ) along and perpendicular to the direction of orientation at 10 K and 300 K. The samples were oriented at 12 kOe (Shah *et al* 1998b).

**Table 2.** The Curie temperature ( $T_C$ ) and the easy magnetization direction (EMD) of some substitutionally and interstitially modified 3:29 compounds.

Compound	$T_C$ (K)	EMD (RT)	Reference
$\text{Pr}_3\text{Fe}_{27.6}\text{Ti}_{1.4}$	393	Axial	(Cadogan <i>et al</i> 1994a)
$\text{Nd}_3\text{Fe}_{27.55}\text{Ti}_{1.45}$	419	Planar	(Cadogan <i>et al</i> 1994a)
$\text{Sm}_3\text{Fe}_{27.9}\text{Ti}_{1.1}$	469	Planar	(Cadogan <i>et al</i> 1994a)
$\text{Nd}_3\text{Fe}_{26.65}\text{V}_{2.35}$	480	Axial	(Cadogan <i>et al</i> 1994a)
$\text{Gd}_3\text{Fe}_{26.65}\text{V}_{2.35}$	524	Planar	(Cadogan <i>et al</i> 1994a)
$\text{Nd}_3\text{Fe}_{19.34}\text{Mn}_{9.66}$	< 295	-	(Cadogan <i>et al</i> 1994a)
$\text{Sm}_3\text{Fe}_{28}\text{Mo}_{1.0}$	445	Planar	(Pan <i>et al</i> 1997)
$\text{Sm}_3\text{Fe}_{26.5}\text{Ga}_{1.5}\text{Mo}_{1.0}$	470	Cone	(Pan <i>et al</i> 1997)
$\text{Sm}_3\text{Fe}_{25}\text{Ga}_3\text{Mo}_{1.0}$	483	Cone	(Pan <i>et al</i> 1997)
$\text{Y}_3\text{Fe}_{27.5}\text{Ti}_{1.6}$	386	Planar	(Télliez-Blanco <i>et al</i> 1996)
$\text{Pr}_3\text{Fe}_{27.5}\text{Ti}_{1.5}$	392	Axial	(Shah <i>et al</i> 1998b)
$\text{Pr}_3\text{Fe}_{27.5}\text{Ti}_{1.5}\text{N}_x$	721	Cone	(Psycharis <i>et al</i> 1996)
$\text{Pr}_3\text{Fe}_{19.25}\text{Co}_{8.25}\text{Ti}_{1.5}$	793	Axial	(Shah <i>et al</i> 1998b)
$\text{Sm}_3(\text{Fe}, \text{M})_{29}$	486	Planar	(Yang <i>et al</i> 1994)
$\text{Sm}_3(\text{Fe}, \text{Ti})_{29}\text{N}_5$	750	Axial	(Yang <i>et al</i> 1994)
$\text{Nd}_3(\text{Fe}, \text{Ti})_{29}$	437	Cone	(Kalogirou <i>et al</i> 1995)
$\text{Nd}_3(\text{Fe}, \text{Ti})_{29}\text{C}_{7.1}$	575	Axial	(Gjoka <i>et al</i> 1996)

of  $\alpha_j$  in order to improve the anisotropy, if they preferentially occupy these inequivalent sites. Preliminary investigations with rare earths (R = Nd with  $\alpha_j$  - ve and Sm with  $\alpha_j$  + ve) carried out by Sanchez *et al* (1996) did not reveal any improvement in the anisotropy.

Interstitial modifications by hydrogen, carbon and nitrogen (Cadogan *et al* 1994b) have also been attempted in 3:29 compounds to improve the magnetic properties. For example, in  $\text{Sm}_3(\text{Fe}, \text{Ti})_{29}$  upon nitrogenation, the EMD becomes uniaxial and the room temperature anisotropy field ( $H_A$ ) increases from 34 kOe to 128 kOe. Increase in magnetization and  $T_C$  have also been observed. In  $\text{Sm}_3(\text{Fe}, \text{Ti})_{29}\text{N}_5$ , a remanence field ( $B_r$ ) of 1.04 T, an intrinsic coercivity  $\mu_0 H_C$  of 0.83 T and an energy product  $(BH)_{\text{max}}$  of  $105 \text{ kJm}^{-3}$  at room temperature have been reported (Hu *et al* 1994b). Carbonation by arc-melting leads to decomposition of the 3:29 phase (Ryan *et al* 1994), but by GIM, using methane it was possible to introduce nearly seven carbon atoms in  $\text{Nd}_3(\text{Fe}, \text{Ti})_{29}$  (Gjoka *et al* 1996). Table 2 gives  $T_C$  and EMD in some of the 3:29 compounds investigated recently.

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