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IRON-RICH PSEUDOBINARY ALLOYS WITH THE ThMn_{12} STRUCTURE OBTAINED BY MELT SPINNING: $\text{Gd}(\text{Fe}_n\text{Al}_{12-n})$, $n = 6, 8, 10$

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1. Introduction

The search for iron-rich rare earth alloys for magnetic applications recently received added impetus with the discovery of the tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [1]. Since then, several other new ternary neodymium iron borides have been discovered [2 - 6], and there has been renewed interest in the BaCd_{11} , ThMn_{12} and CdZn_{13} structure types. For example, a compound $\text{Nd}(\text{Fe}_{10}\text{Si})\text{C}_{0.5}$ with the BaCd_{11} structure has recently been stabilized with interstitial carbon [3], and $\text{Pr}(\text{Fe}_{11-x}\text{B}_x)$ has been prepared for $0.5 < x < 1.5$ [4]. A tetragonally distorted CdZn_{13} structure is reported for $\text{Pr}(\text{Fe}_{9.8}\text{Si}_{3.2})$ and $\text{Nd}(\text{Fe}_9\text{Si}_4)$ [5].

Pettifor has recently developed two-dimensional structure maps based on the "Mendeleev number" as a means for aiding the search for new pseudobinary compounds [7]. In these maps, the ThMn_{12} structure is stabilized over quite a wide area in two separate regions [8]. It is therefore of interest to try to make iron-rich $\text{R}(\text{Fe}_n\text{M}_{12-n})$ alloys with R a rare earth and M an element with a Mendeleev number slightly smaller (*e.g.* titanium, vanadium) or much larger (*e.g.* aluminium) than that of iron. Previously it has been reported by Felner and coworkers that $\text{R}(\text{Fe}_n\text{Al}_{12-n})$ alloys can be prepared by arc melting for $n = 4$ [9], $n = 5$ [10] or $n = 6$ [11] where R is

one of many of the rare earth series. In this work we show that the stability range of the ThMn_{12} structure in these compounds can be extended to $n = 8$ and 10 for $\text{R} \equiv \text{Gd}$ and Dy using a rapid-quench technique.

2. Experimental methods

The elements were first melted in an arc furnace in an atmosphere of titanium-gettered argon to give alloys of composition $\text{R}(\text{Fe}_n\text{Al}_{12-n})$ with $n = 6, 8$ or 10 and $\text{R} \equiv \text{Gd}$ or Dy .

Pieces of ingot of the order of 1 g with $n = 8$ and 10 were then melt spun in helium through a quartz orifice $300 \mu\text{m}$ in diameter onto a copper wheel moving with a surface speed of 50 m s^{-1} . Fragments of ribbon $5 - 10 \text{ mm}$ in length were thus obtained. These were subsequently annealed at 450°C for 100 h , since differential thermal analysis showed that the first thermal event occurs at about 400°C . Samples were studied before and after annealing by X-ray diffraction, magnetization measurements and Mössbauer spectroscopy.

3. Results

Before spinning, a mixture of a ThMn_{12} -structure phase, a 2-17-structure phase and $\alpha\text{-Fe}$ were present when $n = 8$ or 10 , although a pure ThMn_{12} -structure phase was found for $n = 6$. After spinning there was no longer any free iron; only the reflections of the tetragonal structure were present and the a and c parameters had decreased. In spun $\text{GdFe}_{10}\text{Al}_2$, the X-ray reflections were broadened and only the most intense ThMn_{12} structure reflections were visible. Lattice parameters of the $\text{GdFe}_n\text{Al}_{12-n}$ series are listed in Table 1. On annealing at 450°C , the X-ray patterns become sharper, but some free $\alpha\text{-Fe}$ appears for $\text{GdFe}_{10}\text{Al}_2$. Similar results are obtained for $\text{R} \equiv \text{Dy}$.

The Curie temperatures of the alloys were determined from thermal scans of the magnetization. They are plotted in Fig. 1 (for $\text{R} \equiv \text{Gd}$) as a function of n , where it can be seen that the Curie temperature of the ideal " GdFe_{12} " compound would be 600 K . The saturation magnetization at 300

TABLE 1

Lattice parameters of $\text{GdFe}_n\text{Al}_{12-n}$ ($n = 4, 5, 6, 8$ and 10)

Lattice parameter (Å)	GdFe_4Al_8 (ref. 12)	GdFe_5Al_7 (ref. 10)	GdFe_6Al_6	GdFe_8Al_4	$\text{GdFe}_{10}\text{Al}_2$
a	8.74	8.71	8.64	8.57	8.49
c	5.05	5.03	5.00	4.95	4.89

K is $2.11 \mu_B$ formula unit⁻¹, $6.07 \mu_B$ formula unit⁻¹ and $10.6 \mu_B$ formula unit⁻¹ for $n = 6, 8$ and 10 respectively.

Room temperature Mössbauer spectra of the $\text{GdFe}_{10}\text{Al}_2$ alloy before and after annealing are shown in Fig. 2. The average hyperfine field of the spun alloy is 20.9 T, and this changes on annealing at 450 °C to 23.0 T. A fit

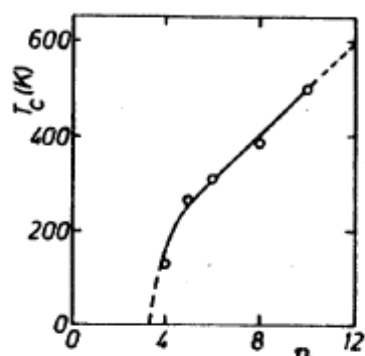


Fig. 1. Curie temperature of the $\text{GdFe}_n\text{Al}_{12-n}$ compounds as a function of n .

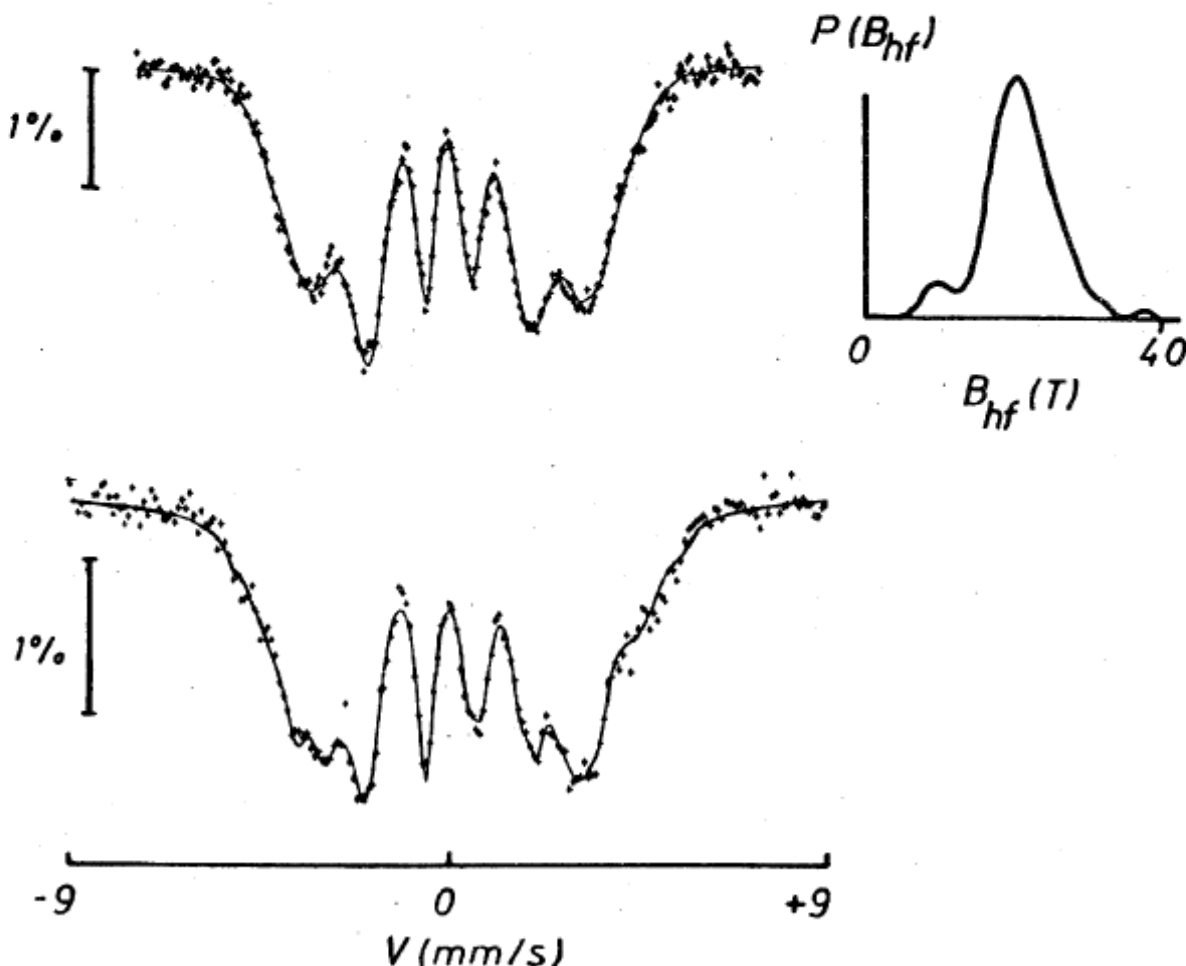


Fig. 2. Room temperature ^{57}Fe Mössbauer spectra of melt-spun $\text{GdFe}_{10}\text{Al}_2$: before annealing (above) and after annealing at 450 °C (below). The hyperfine field distribution for the pre-annealed sample is also shown.

to the Mössbauer spectrum of annealed $\text{GdFe}_{10}\text{Al}_2$ with three hyperfine components is summarized in Table 2. The average iron moment at room temperature deduced from the average hyperfine field is $1.5 \mu_B$.

The observed room temperature magnetization of $\text{GdFe}_{10}\text{Al}_2$ implies a gadolinium moment of $4.5 \mu_B$, assuming a ferrimagnetic structure in which the gadolinium sublattice is antiparallel to the iron sublattices. The gadolinium moment at room temperature is substantially reduced from its zero temperature value (about $7 \mu_B$) because of relatively weak Gd-Fe exchange ($T/T_c \approx 0.6$). Following the molecular field study of a number of R-Fe series by Belorizky *et al.* [13], this value of the gadolinium moment leads to a molecular field coupling constant $n_{\text{Gd-Fe}} = 125$ (SI units), compared with values deduced for other Gd-Fe compounds of $150 < n_{\text{Gd-Fe}} < 230$ [14].

Our fit to the Mössbauer spectrum of annealed $\text{GdFe}_{10}\text{Al}_2$ (Table 2) indicates that two of the three non-rare earth sites in this compound (subspectra I and II) are fully occupied by iron, whilst the third site (subspectrum III) is equally occupied by iron and aluminium. From an inspection of the nearest-neighbour environments of the 8i, 8j and 8f sites in the ThMn_{12} structure, shown in Table 3, we assign subspectrum I, having the largest hyperfine field, to iron in the 8i site. It is more difficult to make an unambiguous assignment for the other two sites, but coordination numbers of magnetic and non-magnetic neighbours are more clearly differentiated if aluminium substitutes preferentially in the 8j site (*i.e.* subspectrum II is 8f and subspectrum III is 8j). None of the sites has a near-zero iron moment, as was found for $\text{RFe}_n\text{M}_{12-n}$ alloys containing less iron [10, 16]. Site prefe-

TABLE 2

Hyperfine parameters deduced from a fit to the room temperature Mössbauer spectrum of the annealed $\text{GdFe}_{10}\text{Al}_2$ sample

Subspectrum	B_{hf} (T)	Δ (mm s ⁻¹)	δ (mm s ⁻¹)	%
I	26.8(4)	0.03(4)	0.05(2)	44(5)
II	18.8(4)	0.07(4)	-0.07(2)	36(5)
III	22.2(4)	-0.06(4)	-0.09(2)	20(5)

B_{hf} , hyperfine field; Δ , quadrupole splitting; δ , isomer shift (relative to $\alpha\text{-Fe}$).

TABLE 3

Nearest-neighbour environments of the sites in the ThMn_{12} structure (ref. 15)

Site	2a	8i	8j	8f
2a	—	4	8	8
8i	1	5	4	4
8j	2	4	3	4
8f	2	4	4	2

rences of iron and aluminium atoms in RFe_nAl_{12-n} were recently discussed by Melamud *et al.* [17]. These workers have carried out Wigner-Seitz constructions for this system and argue that a "substantial" moment is associated with iron atoms occupying the 8i sites, in accord with our assignment. These workers also conclude that the 8i site is the preferred site for iron and iron in the 8j or 8f sites does not carry a large moment. However, this latter conclusion is in conflict with the results of a neutron diffraction study of YFe_nMn_{12-n} by Yang *et al.* [16] who found significant moments on iron atoms occupying the 8i and the 8j sites with a near-zero moment on the 8f site iron atoms. Controversy over the iron and aluminium positions in RFe_nAl_{12-n} is still not fully resolved.

4. Conclusion

We have demonstrated that it is possible to extend the range of stability of the $ThMn_{12}$ structure in $R(Fe_nAl_{12-n})$ compounds by melt spinning. The gadolinium compounds order ferrimagnetically. The Curie temperature of the $n = 12$ end member would be approximately 600 K, which is sufficient to make it worthwhile to evaluate similar materials with a non-S-state rare earth for potential permanent magnet applications.

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