Structure and magnetic properties of the ternary compound $Gd_3(Fe, Ti)_{29}$

Structure and magnetic properties of the ternary compound Gd$_3$(Fe, Ti)$_{29}$

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Abstract. The ternary compound Gd$_3$(Fe, Ti)$_{29}$, which has the monoclinic Nd$_3$(Fe, Ti)$_{29}$ structure, has ben successfully prepared from a starting composition of Gd$_{8.5}$Fe$_{86}$Ti$_{5.5}$ by annealing at 1080 °C for 3 d. The Gd:Fe:Ti ratio for 3:29, determined by energy dispersive x-ray analysis (EDAX), is 9.1:85.7:5.2. Thermo-gravimetric analysis gives a magnetic ordering temperature of 524(3) K for Gd$_3$(Fe, Ti)$_{29}$. The lattice parameters, determined by refinement of powder x-ray diffraction data, are $a = 10.6409(16)$ Å, $b = 8.5658(9)$ Å, $c = 9.7375(15)$ Å and $\beta = 97.017(14)°$. ^{57}Fe Mössbauer measurements on Gd$_3$(Fe, Ti)$_{29}$ yield an average hyperfine field of 24.4(2) T at 293 K, which corresponds to an average Fe magnetic moment of about $1.6\mu_B$.

1. Introduction

A new ternary phase R$_3$(Fe, T)$_{29}$ (R = Nd [1, 2] Pr [3], Sm [4], Tb [5] and Y [6]; T = Ti, V, Cr and Mn [7, 8], and x in the range of 4–6 at.%) has recently been identified. The crystallographic structure of Nd$_3$(Fe, Ti)$_{29}$ (3:29) has been determined by means of x-ray diffraction [9] and neutron diffraction [10]. The structure is monoclinic with the space group $P2_1/c$ (No 14). There are two Nd sites, namely 2a and 4e, and fifteen Fe(Ti) sites in the structure, one 2d and fourteen 4e sites.

This new Nd$_3$(Fe, Ti)$_{29}$ monoclinic structure is derived from the hexagonal CaCu$_5$ (1:5) structure by the process of dumb-bell substitution

$$R_{1-\delta}(2T)_\delta T_5 \rightarrow RT_Z$$
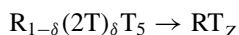
where R = rare earth (cf Ca) and T = transition metal (Cu). Within this crystallographic model, the well known rhombohedral Th$_2$Zn$_{17}$ (2:17R) structure corresponds to a $\delta = \frac{1}{3}$ replacement and the tetragonal ThMn$_{12}$ (1:12) structure corresponds to a $\delta = \frac{1}{2}$ replacement [2]. The dumb-bell substitution which produces the 3:29 structure is $\delta = \frac{2}{5}$ [2, 9]. Thus, the structure of Nd$_3$(Fe, Ti)$_{29}$ is intermediate between the well known rhombohedral Th$_2$Zn$_{17}$ and tetragonal ThMn$_{12}$ structures and, in fact, is formed by the alternate stacking of 2:17 and 1:12 segments, in the ratio 1:1. Such structural relationships were considered by Stadelmaier

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in 1984 [11] who predicted the occurrence of a number of novel structures including the 3:29 structure. The success of this dumb-bell substitution model in predicting the formation of new rare-earth intermetallic structures immediately suggests two questions: firstly, how many light R elements can form the 3:29 structure, and secondly, how will the fact that the 2:17 structure for heavy R elements is hexagonal (Th_2Ni_{17}) rather than rhombohedral affect the formation and structure of a 3:29 derivative? In this paper, we address the former question.

The $R_3(Fe, Ti)_{29}$ (R = Pr, Nd and Sm) compounds are ferromagnetic with reported Curie temperatures in the range 373–486 K. Nitrogenation enhances the Curie temperature of these intermetallics, reaching about 710 K for $Sm_3(Fe, Ti)_{29}N_y$ [1, 12], which is comparable to that of $R_2Fe_{17}N_y$, 740 K [13]. The room-temperature saturation magnetization of $Sm_3(Fe, Ti)_{29}N_y$, $\mu_0 M_s \sim 1.32$ T, is also close to that of $Sm_2Fe_{17}N_y$, $\mu_0 M_s = 1.45$ T, and the uniaxial anisotropy field of the 3:29 nitride exceeds 10 T at 293 K [4]. There are similar enhancements in Curie temperature and uniaxial anisotropy in the carbides $Sm_3(Fe, Ti)_{29}C_y$ [14]. These observations suggest that $Sm_3(Fe, Ti)_{29}N_y$ might be an alternative hard nitride magnet to $Sm_2Fe_{17}N_{3-\delta}$ and $NdFe_{11}TiN_{1-\delta}$ [13]. We refer the reader to [15] for a review of recent work on the $R_3(Fe, T)_{29}$ compounds.

In this paper, we present a study of the preparation and characterization of the new compound $Gd_3(Fe, Ti)_{29}$, and we include the well known $Gd_2(Fe, Ti)_{17}$ and $Gd(Fe, Ti)_{12}$ compounds for comparison.
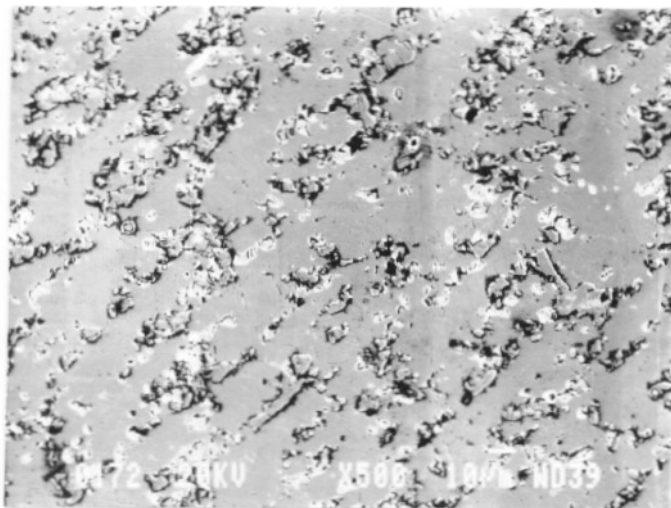

Figure 1. An SEM micrograph of the annealed $Gd_{8.5}Fe_{86}Ti_{5.5}$ sample, where the dominant phase is 3:29 (light grey).

2. Experimental details

Three samples with starting compositions $Gd_{10.5}Fe_{86}Ti_{3.5}$ (A), $Gd_{8.5}Fe_{86}Ti_{5.5}$ (B) and $Gd_{7.5}Fe_{85}Ti_{7.5}$ (C) (with a 10% excess of Gd) were prepared by arc-melting the high-purity ($\geqslant 99.9\%$) constituents in an argon atmosphere. Samples were subsequently annealed under an argon atmosphere in sealed quartz tubes for periods of 3 d at $1000\,^\circ$C (A), $1080\,^\circ$C (B)
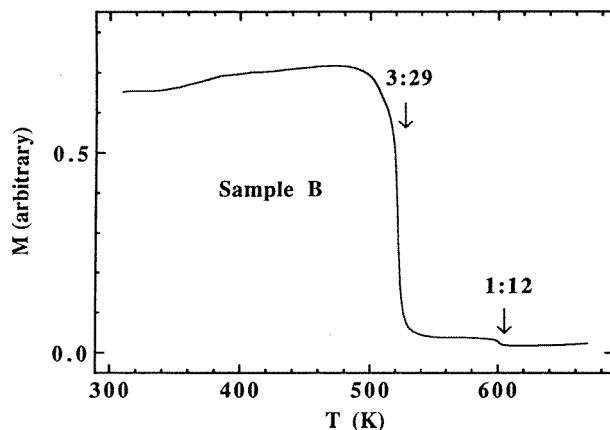
Figure 2. TGA data for the annealed sample of $Gd_{8.5}Fe_{86}Ti_{5.5}$, where the dominant phase is 3:29, $T_C = 524(3)$ K, with an impurity phase of 1:12, $T_C = 603(3)$ K.

and 1000 °C (C). The samples were characterized by (i) powder x-ray diffraction (XRD) using Cu Kα radiation on a Siemens D5000 diffractometer (the 3:29 powder x-ray data were analysed using a computer program for Rietveld analysis at fixed wavelength [16, 17]), (ii) scanning electron microscopy using Jeol JSM840 microscope (SEM) equipped with a Link System AN10 000 energy dispersive spectrometer (EDAX), (iii) thermo-gravimetric analysis (TGA) using a Perkin–Elmer TGA-7 in the presence of a small magnetic field for the determination of Curie temperatures (T_C) and (iv) [57]Fe Mössbauer spectroscopy carried out at 293 K in a standard transmission geometry using a [57]CoRh source, calibrated with an α-Fe foil.

3. Results and discussion

SEM analyses indicate that the dominant phases are (i) 2:17R in sample A, (ii) 3:29 in sample B and (iii) 1:12 in sample C, respectively. In all samples the intergranular regions contain a Gd-rich impurity phase, and for sample B an additional 1:12 impurity phase (less than 8% relative area of the SEM micrograph) is observed. The Gd:Fe:Ti ratios determined from EDAX analyses of 2:17R, 3:29 and 1;12 phases are given in table 1. These ratios are similar to those observed in the Nd–Fe–Ti [1, 2] and Pr–Fe–Ti systems [3], e.g. Gd:Fe:Ti = 9.1:85.7:5.2 for $Gd_3(Fe, Ti)_{29}$ compared to Nd:Fe:Ti = 9.4:86.5:4.1 and 9.7:85.7:4.6 for $Nd_3(Fe, Ti)_{29}$ and Pr:Fe:Ti = 9.2:85.9:4.9 for $Pr_3(Fe, Ti)_{29}$. In figure 1 we show the SEM micrograph of sample B, in which the dominant 3:29 phase (light grey) is evident.

The Curie temperatures, determined by TGA, of the 2:17R, 3:29 and 1:12 phases are given in table 1. As observed in other R–Fe–Ti [1, 7, 15] systems, the magnetic ordering temperature increases in the order 2:17R $\rightarrow$ 3:29 $\rightarrow$ 1:12. This observation reflects the fact that the novel 3:29 phase is an intermediate phase between the 2:17R and 1:12 phases [2, 9]. Figure 2 shows the TGA data for sample B, in which a tail at temperatures higher than the Curie temperature of the 3:29 phase ($T_C = 524(3)$ K) is evident, which is consistent with the SEM/EDAX observation that the impurity in sample B is the 1:12 phase (figure 1).

Powder XRD patterns for the 2:17R, 3:29 and 1:12 phases are shown in figure 3, and the corresponding lattice parameters deduced from these patterns are listed in table 1. For the 3:29 phase, the theoretical XRD pattern, which was generated by employing the atomic
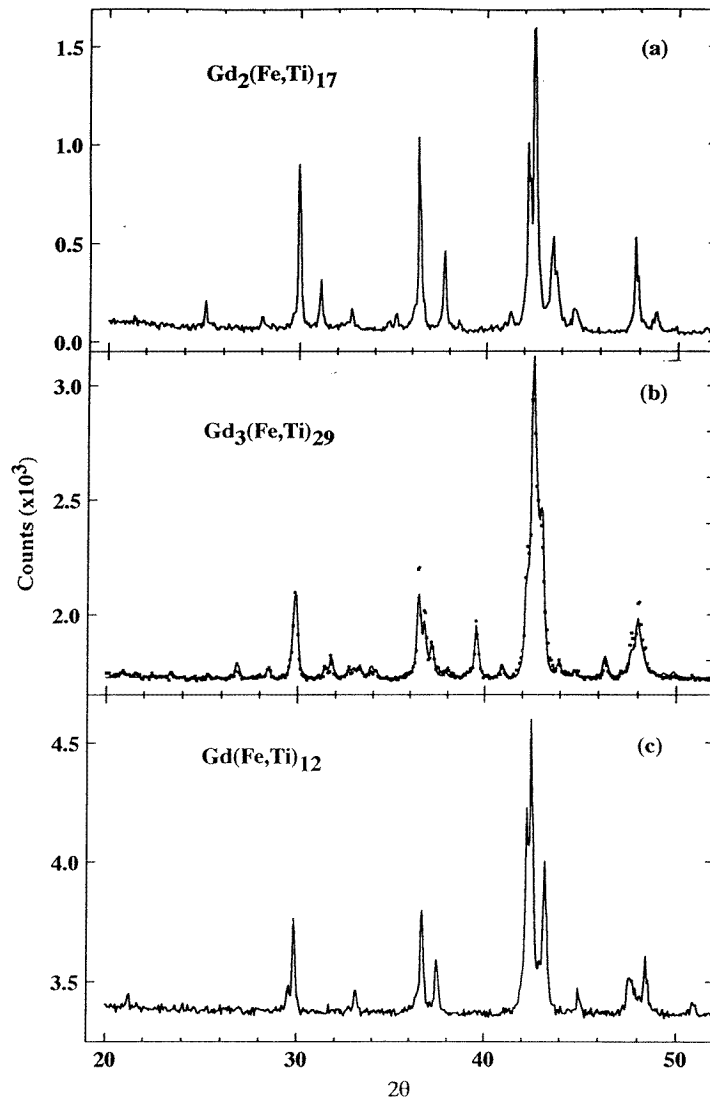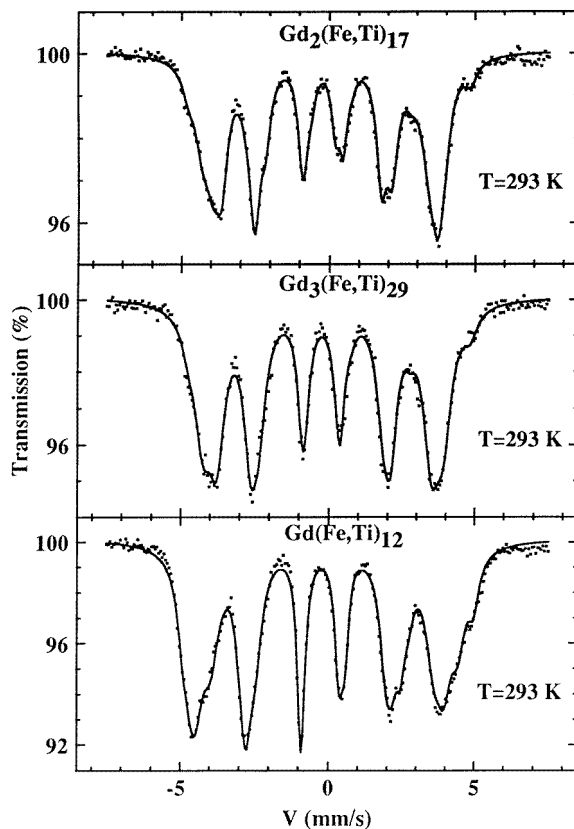
Figure 3. Powder XRD patterns (Cu Kα) for the three annealed samples: (a) $Gd_{10.5}Fe_{86}Ti_{3.5}$, (b) $Gd_{8.5}Fe_{86}Ti_{5.5}$ and (c) $Gd_{7.5}Fe_{84}Ti_{7.5}$. The solid line represents the experimental data, except in pattern (b) where it represents the theoretical fit to the experimental data shown by points (see text).

positions of the monoclinic $Nd_3(Fe, Ti)_{29}$ structure [9], is represented by the solid line. The refinement for the 3:29 phase gives excellent agreement with the experimental data and yields lattice parameters of $a = 10.6409(16)$ Å, $b = 8.5658(9)$ Å, $c = 9.7375(15)$ Å and $\beta = 97.017(14)°$. Thus, all results obtained on the 3:29 phase to date show that for R = Pr, Nd, Sm, Gd, Tb and Y, the 3:29 phase crystallizes in the monoclinic $Nd_3(Fe, Ti)_{29}$. The predicted 3:29 structure [9] for heavy rare earths beyond Tb is yet to be identified.

Figure 4 shows the ^{57}Fe Mössbauer spectra collected at 293 K for the three samples studied. The theoretical fits to these spectra are represented by the solid lines. Our analyses

Table 1. Gd:Fe:Ti compositions, lattice parameters, Curie temperatures (T_C) and ^{57}Fe average hyperfine fields (at 293 K) ($\mu_0\langle H_{hf}\rangle$) of the three phases found in the ternary Gd–Fe–Ti system.

Phase	Gd:Fe:Ti	a (Å)	b (Å)	c (Å)	β (°)	T_C (K)	$\mu_0\langle H_{hf}\rangle$ (T)
2:17R	9.9:86.7:3.4	8.561(3)	—	12.476(3)	—	504(3)	20.0(2)
3:29	9.1:85.7:5.2	10.6409(16)	8.5658(9)	9.7375(15)	97.017(14)	524	24.4
1:12	7.2:85.9:6.9	8.556(3)	—	4.800(3)	—	601	24.8

Figure 4. ^{57}Fe Mössbauer spectra (at 293 K) of the three annealed samples: (a) $Gd_{10.5}Fe_{86}Ti_{3.5}$, (b) $Gd_{8.5}Fe_{86}Ti_{5.5}$ and (c) $Gd_{7.5}Fe_{84}Ti_{7.5}$. (Solid lines represent theoretical fits to these spectra.)

of these three spectra employed three magnetically split sextets with variable linewidths. Inclusion of extra subspectra in the fitting procedure has little effect on the average hyperfine field value; the large number of Fe sites (fifteen) in 3:29 precludes a more detailed spectral analysis. The ^{57}Fe average hyperfine field of $Gd_3(Fe, Ti)_{29}$ at 293 K is 24.4(2) T, which corresponds to an average Fe magnetic moment of about $1.6\mu_B$. The higher value of the ^{57}Fe average hyperfine field in $Gd_3(Fe, Ti)_{29}$ compared to that of $Nd_3(Fe, Ti)_{29}$ (20.8 T) [18] reflects the difference in their Curie temperatures: 524 K for R = Gd and 396 K for Nd [12].

4. Conclusion

A new ternary intermetallic phase $Gd_3(Fe, Ti)_{29}$ has been successfully prepared. Detailed analysis of its powder XRD pattern shows that this new 3:29 compound crystallizes in the recently discovered monoclinic $Nd_3(Fe, Ti)_{29}$ structure. EDAX analysis gives a Gd:Fe:Ti ratio for 3:29 of 9.1:85.7:5.2. The Curie temperature of $Gd_3(Fe, Ti)_{29}$ is 524(3) K and the ^{57}Fe average hyperfine field is 24.4(2) T at 293 K, which corresponds to an average Fe magnetic moment of about $1.6\mu_B$.

Acknowledgments

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