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Structure and magnetic properties of the intermetallic compounds $Gd_3Fe_{29-x}Ta_x$

Q L Liu[†], G H Rao[†] and J K Liang[†][‡]

† Institute of Physics and Centre for Condensed Matter Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, People's Republic of China
‡ International Centre for Materials Physics, Academia Sinica, Shengyang 110015, People's Republic of China

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Abstract. Novel ternary intermetallic compounds $Gd_3Fe_{29-x}Ta_x$ (x = 0.5 and 0.6) with the $Nd_3Fe_{29-x}Ti_x$ -type structure were synthesized with Ta as a new stabilizing element, and their crystal structures and magnetic properties were investigated by x-ray powder diffraction and magnetic measurement. The lattice parameters are a = 10.5895, b = 8.5348, c = 9.6988 Å, and $\beta = 96.940^{\circ}$ for x = 0.5, and a = 10.5938, b = 8.5379, c = 9.7018 Å, and $\beta = 96.943^{\circ}$ for x = 0.6. Rietveld refinement of the crystal structure reveals that Ta atoms occupy exclusively three crystallographic positions (4g, 4i_3, 4i_4), each with only one neighbouring Gd atom. According to the refinement results, the chemical compositions of the compounds are $Gd_3Fe_{28.55}Ta_{0.45}$ for x = 0.5, and $Gd_3Fe_{28.46}Ta_{0.54}$ for x = 0.6. The compounds exhibit a planar magnetocrystalline anisotropy perpendicular to the [102] direction. The Curie temperature T_c , saturation moment M_s , and an isotropy field H_A are 502 K, 39.1 $\mu_B/f.u.$, and 7.3 T for x = 0.5 and 508 K, 38.9 $\mu_B/f.u.$, and 7.2 T for x = 0.6, respectively.

1. Introduction

Since the discovery of the excellent permanent magnetic material $Nd_2Fe_{14}B$, much effort has been devoted to the search for novel rare-earth-transition metal intermetallics in the Ferich region whose magnetic properties might surpass those of $Nd_2Fe_{14}B$, which is limited in application by its comparatively low Curie temperature. Two families of intermetallics, the rhombohedral R_2Fe_{17} compounds (R = rare earth) with Th₂Zn₁₇-type or Th₂Ni₁₇-type structure [1, 2] and the tetragonal $RFe_{12-x}M_x$ (M = Ti, V, Cr, Mn, Nb, Mo, W, or Si) compounds with $ThMn_{12}$ -type structure [3–5], have received special attention since they are both able to absorb N and C as interstitial atoms, with remarkable improvements in their magnetic properties. Recently, a family of ternary intermetallic compounds, R₃(Fe, M)₂₉ (M = Ti, V, Cr, Mn, Mo, Nb), in which the stabilizing element M is indispensable for stabilizing the structure of '3:29' compounds, was discovered [6-9]. Like R₂Fe₁₇ and $RFe_{12-x}M_x$ compounds, $R_3(Fe, M)_{29}$ compounds are also able to absorb N and C as interstitial atoms, leading to a remarkable improvement in their magnetic properties, which makes them favourable potential candidates for permanent magnetic applications [10]. First, a monoclinic crystal structure of space group $P2_1/c$ and Nd₃(Fe, Ti)₂₉ as the precise stoichiometric composition of the $R_3(Fe, M)_{29}$ compounds were identified on the basis of x-ray powder diffraction (XRD) by Li et al [11] and neutron powder diffraction by Hu and Yelon [12]. Subsequent investigations suggested that the structure of the Nd₃(Fe, Ti)₂₉ compounds can

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be described more accurately by the space group A2/m than by $P2_1/c$ [13, 14]. Extensive investigations on R₃(Fe, M)₂₉ compounds with M = Ti, V, Cr, Mn, Mo, and Nb seem to show that the Curie temperature and saturation magnetization of the compounds increase with the decrease of the minimum amount of the stabilizing element M. Therefore, it is desirable to synthesize new compounds with the smallest possible amount of stabilizing element. It has already been proved that elements in the fourth period (Ti, V, Cr, Mn) and fifth period (Nb, Mo) of the periodic table can stabilize R₃(Fe, M)₂₉ compounds, but it remains to be verified whether elements in the sixth period would also stabilize the '3:29' compounds.

We have successfully synthesized new compounds $Gd_3Fe_{29-x}Ta_x$, in which a minimal amount of stabilizing element, $x \approx 0.5$, is needed. Here we report the structural and magnetic properties of these compounds. Due to a large difference between the atomic scattering factors of Ta and Fe, the preferential occupancies of Ta of different crystallographic positions in the structure of $Gd_3Fe_{29-x}Ta_x$ are successfully determined by Rietveld refinement of x-ray powder diffraction data.

2. Experimental procedure

 $Gd_3Fe_{29-x}Ta_x$ (x = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0) samples were prepared by the arc melting of an appropriate amount of metallic Gd, Fe, and Ta with purity >99.9% in an argon atmosphere under ambient pressure. The weight loss of the samples during melting was less than 1.0%. After arc melting, the samples were annealed in vacuum at 1373 K for one week, and this was followed by water quenching. Phase identification of the samples was carried out by both thermomagnetic analysis and x-ray powder diffraction (XRD)

XRD data were collected by a Rigaku Rint-2400 diffractometer with Cu K α radiation (the wavelength of K α_1 is 1.5405 Å and the wavelength of K α_2 is 1.5444 Å) and a graphite monochromator, operating in a step-scan mode with a scanning step of $2\theta = 0.02^{\circ}$ and a sampling time of 2 s. Temperature dependences of the magnetization (M-T curves) were measured by using a Faraday balance and a vibrating-sample magnetometer at a low field of about 0.05 T and the results were taken with temperature decreasing. The Curie temperatures were determined by linearly extrapolating M^2 to zero in the M^2-T curves. Magnetization (M-H) curves were measured at 1.5 K by use of an extracting sample magnetometer in a magnetic field ranging from 0 to 65 kOe. The saturation magnetization was derived according to the law of approach to saturation. The easy-magnetization direction (EMD) was identified on the basis of the x-ray diffraction pattern of the magnetically aligned samples. The aligning was done by mixing fine particles of a sample with epoxy resin and allowing them to harden in a magnetic field of 1 T.

3. Results and discussion

Figure 1 shows the XRD patterns of the annealed samples of $Gd_3Fe_{29-x}Ta_x$ (x = 0.4, 0.5, 0.6, 0.8). These patterns reveal that the compounds $Gd_3Fe_{29-x}Ta_x$ (x = 0.5 and 0.6) are almost single phase with very small amounts of Fe_2Ta as impurities, and crystallize in the $Nd_3Fe_{29-x}Ti_x$ -type structure. Figure 1 also shows that with the increase of Ta content x, the amount of Fe_2Ta increases, and there is a small amount of α -Fe in samples with x = 0.4. This implies that the homogeneous range in the $Gd_3Fe_{29-x}Ta_x$ system is probably 0.4 < x < 0.7. Comparing with the results reported for other $Gd_3Fe_{29-x}M_x$ compounds (M = Ti, V, Cr, Mn, Mo, Nb), it is seen that $Gd_3Fe_{29-x}Ta_x$ compounds can be formed with the least amount of the stabilizing element Ta, i.e. $x \approx 0.5$.



Figure 1. XRD patterns of $Gd_3Fe_{29-x}Ta_x$ samples (x = 0.4, 0.5, 0.6, and 0.8).

The Rietveld powder diffraction profile-fitting technique [15] was adopted to refine the crystal structure of $Gd_3Fe_{29-x}Ta_x$ by using the program DBW-9411 [16]. The initial structure model was built on the basis of the $Nd_3Fe_{29-x}Ti_x$ -type structure with the space group A2/m [14]. Fe₂Ta was included as the second phase in the XRD profile fitting. Due to the large difference between the atomic scattering factors of Ta and Fe, the preferential occupancies of Ta of different crystallographic positions in the structure of $Gd_3Fe_{29-x}Ta_x$ can be determined successfully by Rietveld refinement of x-ray powder diffraction data. During the refinement, we put Ta atoms at all possible sites, and then refine the occupancies at these sites as free parameters. The results show that Ta atoms occupy exclusively three sites, each with only one neighbouring Gd atom, namely 4g, 4i₃, and 4i₄ (see table 1). According to the refinement results, the chemical compositions of the compounds are $Gd_3Fe_{28.5}Ta_{0.45}$ for the sample $Gd_3Fe_{28.5}Ta_{0.5}$ and $Gd_3Fe_{28.46}Ta_{0.54}$ for the sample $Gd_3Fe_{28.4}Ta_{0.6}$. The Ta content in $Gd_3Fe_{29-x}Ta_x$ is less than in the nominal composition. This may be due to the existence of a very small amount of Fe₂Ta in samples and the loss of Gd during melting.

	Gd ₃ Fe _{28.5} Ta _{0.5}				Gd ₃ Fe _{28.4} Ta _{0.6}				
Atom site	x	у	z	% Ta	x	у	z	% Ta	Neighbours
Gd 2a	0.0	0.0	0.0		0.0	0.0	0.0		20Fe
Gd 4i	0.4036	0.0	0.8137		0.4037	0.0	0.8129		19Fe
Fe 2c	0.5	0.0	0.5		0.5	0.0	0.5		10Fe + 2Gd
Fe 4e	0.0	0.25	0.25		0.0	0.25	0.25		10Fe + 2Gd
Fe 4g	0.0	0.3592	0.0	6.4	0.0	0.3601	0.0	9.4	13Fe + 1Gd
Fe 4i ₁	0.1129	0.0	0.7200		0.1112	0.0	0.7185		10Fe + 2Gd
Fe 4i ₂	0.2946	0.0	0.0948		0.2915	0.0	0.0892		9Fe + 3Gd
Fe 4i ₃	0.2555	0.0	0.5166	10.6	0.2571	0.0	0.5236	11.6	13Fe + 1Gd
Fe 4i ₄	0.1429	0.0	0.2955	5.4	0.1419	0.0	0.2951	5.8	13Fe + 1Gd
Fe 8j ₁	0.6287	0.1471	0.6801		0.6267	0.1438	0.6848		10Fe + 2Gd
Fe 8j ₂	0.8101	0.2147	0.0877		0.8078	0.2148	0.0907		10Fe + 2Gd
Fe 8j3	0.4054	0.2508	0.0641		0.4043	0.2500	0.0618		9Fe + 3Gd
Fe 8j ₄	0.1992	0.2532	0.1557		0.1959	0.2529	0.1534		10Fe + 2Gd
a = 10.5895(1), b				5348(1)	<i>a</i> =				
	c = 9.6988(1) (Å) $\beta = 96.940(1)^{\circ}$ $R_p = 7.85\%, R_{wp} = 9.93\%$ $R_{exp} = 5.80\%$				c = 9.7018(1) (Å)				
					$\beta = 96.943(1)^{\circ}$				
					$R_p = 7.37\%, R_{wp} = 9.32\%$				
					$R_{exp} = 6.79\%$				

Table 1. Rietveld refinement results for $Gd_3Fe_{28.5}Ta_{0.5}$ and $Gd_3Fe_{28.4}Ta_{0.6}$ compounds; space group A2/m; the *B*-factors of all atoms are set to zero.

of the final composition $Gd_3Fe_{28.55}Ta_{0.45}$ and the starting composition $Gd_3Fe_{28.5}Ta_{0.5}$, 5% of Fe_2Ta is calculated, assuming that about 1.5% of the Gd vaporized during melting, which is in agreement with the Fe_2Ta content (about 4%) calculated from the ratio of the main XRD lines for this impurity and for the matrix. In the same way, for the sample $Gd_3Fe_{28.4}Ta_{0.6}$, about 6% of Fe_2Ta is derived from the Rietveld analysis, assuming the loss of 2% of the Gd during melting, and about 7% of Fe_2Ta is calculated from the ratio of the main XRD lines. So, the sites and concentration in the structure of Ta derived from Rietveld analysis are reasonable. The final refinement results are shown in table 1. Figure 2 shows the Rietveld refinement results for XRD patterns of the sample $Gd_3Fe_{28.5}Ta_{0.5}$, including the experimental and calculated patterns, as well as the intensities of the difference between the experimental and calculated data. The pattern factor R_p , the weighted pattern factor R_{wp} , and the expected pattern factor R_{exp} are 7.85%, 9.93%, and 5.80, respectively.

Since neither Gd₃Fe₂₉ nor Gd₃Ta₂₉ is stable, the occurrence of a Gd₃Fe_{29-x}Ta_x phase with the Nd₃Fe_{29-x}Ti_x-type structure implies that it has to be regarded as a ternary intermetallic compound. The ternary character of the compound is further evidenced by the fact that the Ta atoms preferentially occupy only three crystallographic positions in the structure (4g, 4i₃, 4i₄). The fact that the M atoms occupy the dumb-bell sites may be explained in terms of enthalpy effects. In fact, there is no intermetallic compound in the Gd–Ta binary system [17]. This implies that the enthalpies of formation of alloys between Gd and Ta is positive. It can be seen from table 1 that each of the sites occupied by Ta has only one neighbouring Gd atom, while other sites have two or more neighbouring Gd atoms. In other words, these sites have by far the smallest area of contact with Gd atoms. In view of the positive enthalpy contribution associated with Gd and Ta contact, one may therefore expect these sites to be preferred by Ta atoms. Similar effects are observed in RFe_{12-x}M_x (M = Ti, V, Cr, Mo, W) compounds [3].

The *M*-*T* curves of samples $Gd_3Fe_{29-x}Ta_x$ (x = 0.5 and 0.6) are shown in figure 3. The



Figure 2. The Rietveld refinement results for the XRD patterns of the $Gd_3Fe_{28.5}Ta_{0.5}$ samples, including the experimental and calculated intensities as well as intensities of the difference between the experimental and calculated data.



Figure 3. The temperature dependence of the magnetization for $Gd_3Fe_{29-x}Ta_x$ samples measured by a vibrating-sample magnetometer in a low field.

Curie temperature T_c of the compound $Gd_3Fe_{29-x}Ta_x$ was determined by linearly extrapolating M^2 to zero in the M^2-T curves and the results are listed in table 2. In order to measure the magnetocrystalline anisotropy field H_A , finely powdered particles were mixed with epoxy resin and used to fill two cylindrical containers and one disk-shaped container. One cylinder and the disk were mounted on a motor which rotates them around their axes in a perpendicular magnetic field of about 1.0 T, and the other cylinder was placed statically in the external magnetic field with its axis parallel to the field direction until the epoxy resin solidified. The former cylinder was used to prepare samples for measurements of the magnetization in the hard-magnetization direction (HMD), the latter for measurements of the magnetization in the EMD. The disk samples are adapted for x-ray diffraction to investigate the HMD of the samples. The XRD pattern of the sample Gd₃Fe_{28.5}Ta_{0.5} in the HMD is plotted in figure 4. It can been seen that the compound Gd₃Fe_{28.5}Ta_{0.5} exhibits planar anisotropy, and the HMD is in the direction [102]. Figure 5 shows the *M*-*H* curves for the samples $Gd_3Fe_{29-x}Ta_x$ (x = 0.5 and 0.6) measured with the applied field parallel to the EMD or the HMD, respectively. The anisotropy field H_A of the compound Gd₃Fe_{29-x}Ta_x was derived by linearly extrapolating ΔM to zero in the ΔM -H curve ($\Delta M = M_{\parallel} - M_{\perp}$). The saturation magnetization M_s for these compounds was deduced from the M-H curve in the EMD.

Table 2. The magnetic data for the Gd₃Fe_{28.5}Ta_{0.5} and Gd₃Fe_{28.4}Ta_{0.6} compounds: the Curie temperature T_c (in K), the saturation moments M_s (in A m² kg⁻¹ and $\mu_B/f.u.$), and the anisotropy field H_A at 1.5 K.

Compounds	<i>Т</i> _с (К)	$\begin{array}{c} M_s \\ (\mathrm{A} \ \mathrm{m}^2 \ \mathrm{kg}^{-1}) \end{array}$	M_s (μ_B /f.u.)	<i>Н</i> _А (Т)
Gd ₃ Fe _{28.5} Ta _{0.5}	502	101.5	39.1	7.3
Gd ₃ Fe _{28.4} Ta _{0.6}	508	100.3	38.9	7.2



Figure 4. The XRD patterns of magnetically aligned powder samples Gd₃Fe_{28.5}Ta_{0.5}.



Figure 5. The magnetization curves of magnetically aligned powder samples $Gd_3Fe_{29-x}Ta_x$ at 1.5 K with the field applied parallel to the EMD or HMD.

Table 2 gives the intrinsic magnetic parameters of the Gd₃Fe_{29-x}Ta_x (x = 0.5 and 0.6) compounds, including the Curie temperature T_c , the saturation magnetization M_s , and the anisotropy field H_A at 1.5 K. Comparing with the saturation magnetization M_s of other Gd-based '3:29' compounds, 38.1 $\mu_B/f.u.$ for Gd₃Fe_{29-x}Ti_x (x = 0.6) [18], 33.6 $\mu_B/f.u.$ for Gd₃Fe_{29-x}V_x (x = 0.6) [19], 35.9 $\mu_B/f.u.$ for Gd₃Fe_{29-x}Cr_x (x = 1.0) [19], 36.39-35.30 $\mu_B/f.u.$ for Gd₃Fe_{29-x}Nb_x (x = 0.9-1.3) [9], and 36.5 $\mu_B/f.u.$ for Gd₃Fe_{29-x}Mo_x (x = 0.75) [8], it is seen that the saturation magnetizations M_s of the Gd₃Fe_{29-x}Ta_x compounds are higher than those of the other Gd₃Fe_{29-x}M_x (M = Ti, V, Cr, Mo, Nb) compounds. This can be attributed to the fact that the minimum amount of Ta required to stabilize the '3:29' compounds is smaller than that of other metals M.

4. Conclusions

New ternary intermetallic compounds $Gd_3Fe_{29-x}Ta_x$ (x = 0.5 and 0.6), with $Nd_3Fe_{29-x}Ti_x$ type structure were synthesized with Ta, in the sixth period of the periodic table, as a new stabilizing element. Rietveld refinement results show that Ta atoms occupy exclusively three crystallographic positions (4g, 4i₃, 4i₄), each with only one neighbouring Gd atom. According to the refinement results, the chemical compositions of the compounds are $Gd_3Fe_{28.55}Ta_{0.45}$

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for x = 0.5 and Gd₃Fe_{28.46}Ta_{0.54} for x = 0.6. The compounds exhibit planar anisotropy perpendicular to the [102] direction. The Curie temperature T_c , the saturation moment M_s , and the anisotropy field H_A are 502 K, 39.1 $\mu_B/f.u.$, and 7.3 T for the Gd₃Fe_{28.5}Ta_{0.5} compound and 508 K, 38.9 $\mu_B/f.u.$, and 7.2 T for the Gd₃Fe_{28.4}Ta_{0.6} compound, respectively. The saturation magnetizations M_s of these compounds are higher than those of other Gd₃Fe_{29-x} M_x (M = Ti, V, Cr, Nb, Mo) compounds, essentially due to the fact that the required minimum content of stabilizing element in these compounds is the least among all reported 3:29 compounds.

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