JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 11, November 2009, p. 1576 - 1580

Structural and magnetic properties of Gd-Fe-Nb-Zr intermetallic compounds

C. SARAFIDIS, N. SHELOUDKO[a], A. KOTOULAS, C. SERLETIS, K. G. EFTHIMIADIS,
M. GJOKA[b], O. KALOGIROU*
Faculty of Physics, "St. Kl. Ohridski" University of Sofia, 1164-Sofia, Bulgaria
[a]*Dept. of Physics, Aristotle University of Thessaloniki, 54 124 Thessaloniki, Greece*
[b]*NCSR Demokritos, Institute for Materials Science, 153 10 Ag. Paraskevi, Athens, Greece*

Phase formation as well as the influence of Nb and Zr in the structural and magnetic properties in a series of intermetallic compounds with nominal composition $Gd_8Fe_{86}Nb_{6-x}Zr_x$ (x= 1.5, 3.0, 4.5) were studied. No serious crystallographic effects for the change in stoichiometry were identified. The major phase formed was found to be the hexagonal 2:17 compound. Curie temperature is enhanced compared to that of the parent Gd_2Fe_{17} compound and increases with increasing Nb. Magnetization measurements were analyzed by Sucksmith-Thompson method and the anisotropy field and constants at room temperature and 110 K were calculated.

(Received August 10, 2009; accepted November 12, 2009)

Keywords: Rare earth iron alloys, R_2Fe_{17}, Magnetocrystalline anisotropy

1. Introduction

Iron-based rare-earth compounds have attracted attention as promising candidates for permanent magnet developments. The R_2Fe_{17} intermetallic compounds (2:17) with R = Pr, Nd, Sm crystallize in the rhombohedral Th_2Zn_{17}-type structure and the heavy rare earths prefer the hexagonal Th_2Ni_{17}-type structure, whereas Gd_2Fe_{17} can be formed in both structures [1]. The tetragonal $R(Fe,M)_{12}$ compounds (1:12), can be obtained only in the presence of a stabilizing element such as Si, Ti, V, Cr, Mo and W substituting Fe [2]. Similarly, the monoclinic $Nd_3(Fe,Ti)_{29}$-type compounds (3:29) are formed only by the partial substitution of Fe atoms by Ti, V, Cr, Mn, Mo, W [3]. In a search for new compounds with improved magnetic properties, a lot of elements have been tested as to whether or not they can substitute for R, Fe, or M in this structure. Concerning zirconium it has been shown that in rare earth transition metal intermetallic compounds Zr can substitute either rare earth atoms or transition metal atoms [4], while it prevents the participation of unreacted iron during the preparation of the materials, a common problem in rare earth – transition metal intermetallics. Up to now, little attention has been paid, however, to investigate Zr-substituted rare earth transition metal phases. Sakurada et al. [5] have reported that in the $(Nd,Zr)Fe_{10}Si_2$ system, zirconium occupies the neodymium site and facilitates the formation of a $ThMn_{12}$-type phase. In $Nd_2Fe_{17-x}Zr_x$ zirconium has been found to substitute for iron and a single Th_2Zn_{17}-type phase could be obtained for $x<1.5$ [6]. In Ref. 4 the effect of Zr additions on the existence range, crystal structure and magnetic properties of $Gd(Fe,Mo)_{12}$ has been studied. Furthermore, it has been reported [7,8] that Zr is soluble in analogous rare-earth and cobalt compounds of type R_2Co_{17} and RCo_5, where it substitutes for rare-earth atoms as well as for Co atoms. Regarding Gd_2Fe_{17} several substitutions have been used such as Al, Mn [9], V [10], Ga [11] and Cr [12] and their influence on the structural and magnetic properties on the parent compound has been reported. In this work we used Nb and Zr in order to study the phase formation of Gd-Fe intermetallic compounds with the nominal stoichiometry $Gd_8Fe_{86}(Nb,Zr)_6$. Such a stoichiometry is close to the 1:12 compounds if we consider Nb and Zr both substituting Fe atoms. On the other hand, if Zr substitutes rare earth atoms, the chosen Gd-Zr to Fe-Nb ratio is close either to the 2:17 compounds or the 3:29.

2. Experimental

$Gd_8Fe_{86}Nb_{6-x}Zr_x$ (x= 1.5, 3.0, 4.5) alloys were prepared by arc-melting appropriate amounts of high purity metals, under Ar atmosphere. The samples were melted twice in order to achieve better homogenization. Each sample was wrapped in tantalum foil, encapsulated in evacuated quartz tubes, annealed for 72 hours at 1373 K followed by water quenching. X-ray powder diffraction (XRD) with CuKα radiation was used for the characterization of the samples. The Curie temperature (T_C) was determined from magnetization measurements carried out at a field of 100 mT using a vibrating sample magnetometer, while the saturation magnetization (M_S)

was also measured at powder samples. In order to study the magnetic anisotropy of the compounds, XRD patterns of magnetically aligned powder samples with the alignment direction normal to the sample holder were taken. Magnetic anisotropy field at RT and 110 K was derived from the ΔM–H ($\Delta M = M_{\parallel} - M_{\perp}$) curves by extrapolating ΔM to zero, where $M_{\parallel}$ and $M_{\perp}$ are magnetization of the magnetically oriented at RT in a rotating field of 1T and epoxy resin samples with the applied field parallel and perpendicular to the easy magnetization direction, respectively. The Sucksmith-Thompson method was applied on the hard demagnetization curves.

3. Results and discussion

XRD diffraction patterns and thermomagnetic measurements showed practically no difference between the samples before and after annealing. For this study samples prior to annealing process were selected. The XRD diffraction patterns of the three compounds before annealing are almost identical. Rietveld analysis showed that the compounds were crystallized in the hexagonal 2:17 phase with some traces of the monoclinic 3:29 and the rhombohedral 2:17 phases (see Table 1). A small amount of unreacted α-Fe was also present in the samples.

Table 1 Composition and unit cell parameters for the $Gd_8Fe_{86}Nb_{6-x}Zr_x$ alloys.

x	phase (wt.%)	a (Å)	c (Å)	V (Å^3)	c/a
1.5	2:17H (90.6) 3:29 (6.4) α-Fe (1.6) 2:17R (1.4)	8.486 (1)	8.344 (1)	520.29	0.9833
3.0	2:17H (83.2) 3:29 (7.1) α-Fe (3.1) 2:17R (6.6)	8.482 (2)	8.363 (2)	521.04	0.9860
4.5	2:17H (87.8) 3:29 (3.0) α-Fe (2.2) 2:17R (7.0)	8.475 (3)	8.375 (2)	520.97	0.9882

In Fig. 1 the XRD diffraction pattern of the sample with x= 4.5 and the corresponding Rietveld analysis is presented. It is known that Gd can form both the rhombohedral and the hexagonal 2:17 phases [1]. When there is an excess of the rare earth the formation of the hexagonal 2:17 phase is preferred [13]. The fact that our samples crystallized in the hexagonal symmetry indicates that Zr occupied Gd sites forming an excess of (Gd,Zr) atoms compared to the 2:17 stoichiometry. Changing the Zr to Nb ratio doesn't largely affect the crystallographic parameters of the materials' main phase. From the values of Table 1 we observe a small reduction in the a-axis parameter while the c-axis is slightly increasing with the increase of Nb content. Also, compared to the parent Gd_2Fe_{17} compound with a = 8.55 and c = 8.24 [14] a decrease in the a-axis parameter and an increase of c-axis is observed, reflecting a larger c/a ratio for the substituted compounds.

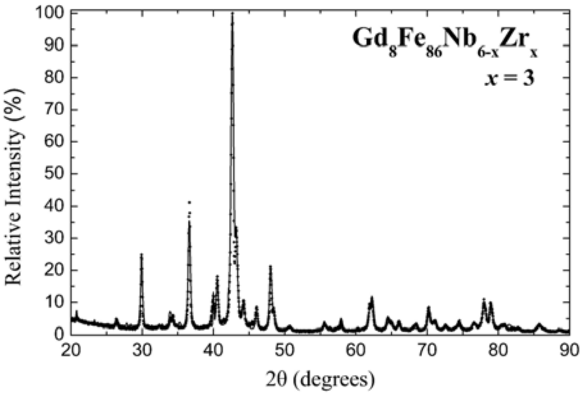

Fig. 1. Observed (crosses) and calculated (solid line) X-ray powder diffraction patterns (CuKα) of the $Gd_8Fe_{86}Nb_{6-x}Zr_x$ (x= 3.0) alloy.

Table 2. Curie temperatures (T_C) and saturation magnetization (M_S) of $Gd_8Fe_{86}Nb_{6-x}Zr_x$ (x= 1.5, 3.0, 4.5) alloys.

Compound	T_C (K)	M_S ($A\cdot m^2/kg$)	
$Gd_8Fe_{86}Nb_{6-x}Zr_x$		297 K	110 K
x = 1.5	516	79.7	83.8
x = 3.0	507	82.0	86.6
x = 4.5	499	84.0	86.2

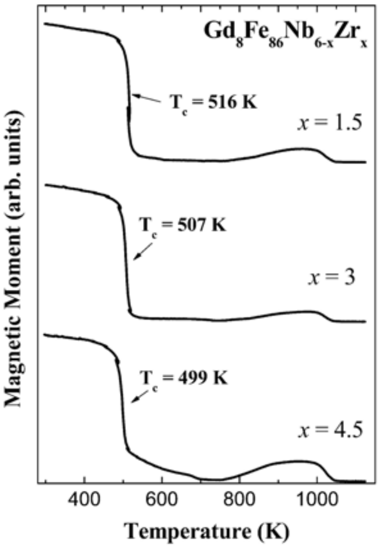

Fig. 2. Magnetization versus temperature curves for the $Gd_8Fe_{86}Nb_{6-x}Zr_x$ alloys.

In Fig. 2 the magnetization versus temperature curves for the alloys under study are shown. The calculation of the Curie temperatures from the plots shows that by increasing Nb and correspondingly decreasing Zr, Curie temperature slightly increases. In all cases the Curie temperature is enhanced compared to the T_C value of the parent Gd_2Fe_{17} compound, 479 K [14]. The samples show a small degree of oxidation above 700 K. In Table 2 the T_C values together with the corresponding M_S ones are presented. The saturation magnetization values were determined from measurements in powder samples. M_s increase with the concentration of Zr. The magnetic moment of Gd_2Fe_{17} compound is formed by Gd and Fe sublattice's moments: $M_s = M_{Fe} - M_{Gd}$. If Zr replaces for Gd, then the Gd sublattice moment should decrease, and the total magnetic moment of the compound should increase, which is our case. The magnetic ordering temperature in R – T compounds is primarily dependent on the magnitude of the exchange interactions between transition metal atoms [15]. A decrease of the T_C with the Zr content may result from an increase of the Fe – Fe distances, for which the magnetic exchange integral is positive. The enhancement of the ordering temperature has been observed in Al, Ga, Si and Cr substituted R_2Fe_{17} compounds [11,12].

In order to determine the nature of the magnetocrystalline anisotropy, XRD patterns were taken on magnetically oriented powder samples with the orientation level parallel to the sample holder in a rotating magnetic field. Thus, the observed reflections correspond to the hard magnetization direction. In Fig. 3 the diffraction pattern of the x = 3.0 sample is shown, as an example. Similar patterns were recorded for the other two compounds. The strong peak observed corresponds to the (0 0 l) reflection of the 2:17 phase, thus revealing the presence of easy plane anisotropy, as in the case of the parent Gd_2Fe_{17} compound [14].

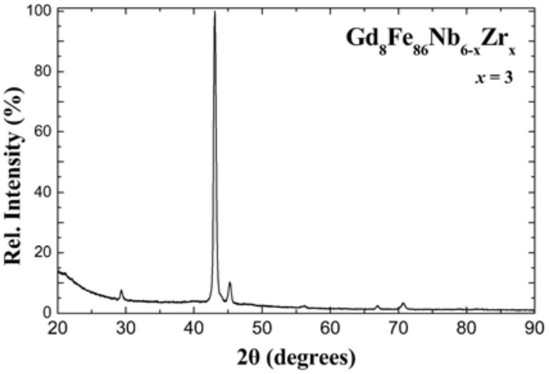

Fig. 3. XRD diffraction pattern of the magnetically oriented (CuKα) $Gd_8Fe_{86}Nb_{6-x}Zr_x$ (x= 3.0) alloy.

The magnetization curves, measured on oriented in rotating field samples along the hard magnetization direction ($[001]_{2:17}$) and in the plane normal to it, at 297 K and at 110 K, are shown in Fig. 4. A rapid rise in $M_\perp$ vs. H in small applied fields is observed, followed by a linear increase in higher (above about 1T) fields, without any visible remanence in demagnetization curves. For a perfectly aligned sample it would be expected to show no remanence in the hard direction. The rapid rise of magnetization in hard direction should be due to domain wall processes in a few non-single domain particles in the sample. For a first estimate of the contribution from the perpendicular fraction the linear part of the demagnetization $M_\perp$(H) curves was extrapolated to $H = 0$, to $M_{\perp lin}(0)$ values, and these values were substracted from the measured curves, since at $H = 0$ the truly aligned single domain particles have zero magnetization in hard direction. The ($M_\perp$- $M_{\perp lin}(0)$) vs. H curves were corrected by a factor $\alpha = \dfrac{M_s - M_{\perp lin}(0)}{M_s}$ to simulate the magnetization of 1 g of aligned material. The obtained values for the anisotropy field from ΔM–H curves, where the curved portion of the $M_\perp$(H) plot was substracted, are listed in Table 3.

In higher fields, when domain processes are no longer active, the increasing of magnetization can be assumed to be due to rotation of the magnetic moment, and can be treated by single domain theory. For uniaxial single crystal with the easy magnetization direction normal to the field, the energy per unit volume can be defined as $E = K_1 \sin^2\theta + K_2 \sin^4\theta - \mu_0 H M_s \cos\theta$, where θ is the angle between the magnetization vector and the z-axis and K_1 and K_2 are the anisotropy constants, when the higher order anisotropy constants are neglected. The z-axis here is assumed to correspond to the hard magnetization direction ($[001]_{2:17}$). The calculation of the anisotropy constants was based on Sucksmith – Thompson method [16]. The K_1 and K_2 values were derived from the linear part of modified Sucksmith-Th. $\mu_o H/(M_\perp - M_{\perp lin}(0))$ against $(M_\perp - M_{\perp lin}(0))^2$ plots, corrected by α. From K_1 values the anisotropy field was calculated as $\mu_o H_A = -2K_1/M_S$.

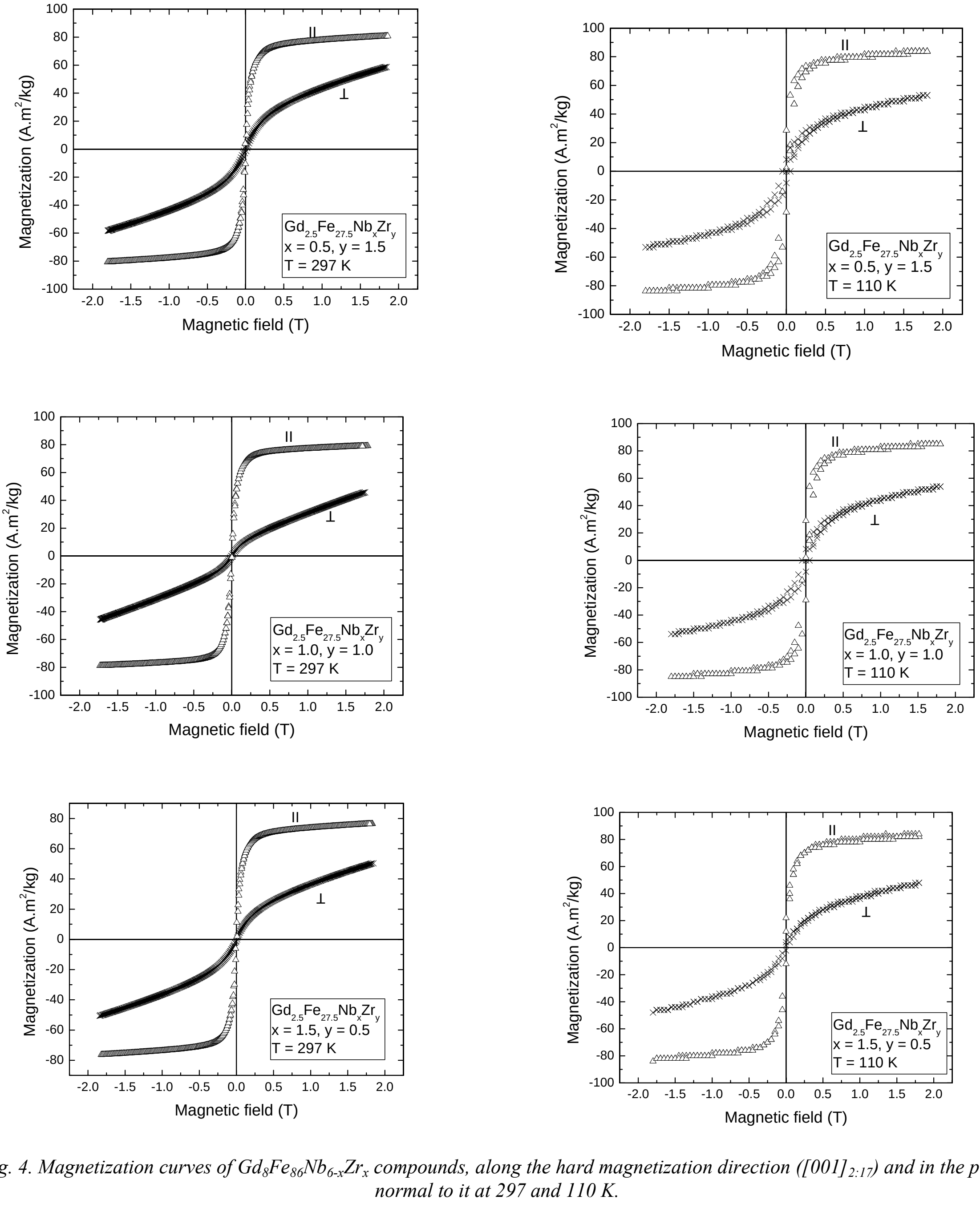

Fig. 4. Magnetization curves of $Gd_8Fe_{86}Nb_{6-x}Zr_x$ compounds, along the hard magnetization direction ($[001]_{2:17}$) and in the plane normal to it at 297 and 110 K.

The obtained values for the anisotropy constants and the anisotropy field at RT are listed in Table 3a,b. K_1 and K_2 satisfy the relations for easy plane type of anisotropy, which are $K_1 < 0$, $K_2 > 0$ and $(K_1+2K_2) < 0$.

The anisotropy field and the anisotropy constants do not change over 3% upon the content of Nd/Zr. The RT anisotropy field (3.8 T ÷ 3.4 T) is slightly smaller compared to that of the parent Gd_2Fe_{17} compound, 4.02 T [14]. The obtained values for the anisotropy constants are of the same order of magnitude as those obtained for Y_2Fe_{17} single crystal [17].

Table 3. Anisotropy field ($\mu_0 H_A$) and anisotropy constants K_1 and K_2 of $Gd_{2.5}Fe_{27.5}Nb_xZr_y$ compounds at RT and at 110 K.

$Gd_{2.5}Fe_{27.5}Nb_xZr_y$ x,y	T (K)	K_1 (J/kg)	K_1 (J/kg)	$\mu_0 H_A = -\frac{2K_1}{M_s}$ (T)	$\mu_0 H_A$ from ΔM (T)
$x = 1.5, y = 0.5$	297	-153	7	3.8	3.8
	110	-250	40	6.0	5.3
$x = 1.0, y = 1.0$	297	-147	2	3.6	3.6
	110	-250	35	5.8	5.5
$x = 0.5, y = 1.5$	297	-144	6	3.4	3.4
	110	-237	26	5.5	5.4

The total anisotropy in the R – T compounds is a result of the R sublattice and 3*d* sublattice contributions. The Gd atoms have no orbital magnetic moment and make no contribution to the anisotropy. The obtained results for the anisotropy parameters of the compounds under investigation and their independence on the Zr content strengthen the assumption that the 2:17 phase is formed, where Zr atoms occupy rare earth sites.

4. Conclusions

In the present work the preparation and the basic study of the structural and magnetic properties of $Gd_8Fe_{86}Nb_{6-x}Zr_x$ (x= 4.5, 3.0, 1.5) alloys is presented. The analysis of the XRD diagrams showed that all samples consist of a basic intermetallic phase which crystallizes in the hexagonal 2:17 phase (Th_2Ni_{17}-type) indicating that Zr atoms occupy rare earth sites. The Curie temperature slightly increases with Nb content. The magnetocrystalline anisotropy of the compounds has a planar character with parameters independant to the content of Zr.

Acknowledgements

This work was supported by the 089-c bilateral Greek-Bulgarian project of the General Secretary for Research and Technology Greece and by grant BG – 15/2005.

References

[1] W. E. Wallace, Prog. Solid State Chem. **16**, 127 (1985).
[2] D. B. de Mooij and K.H.J. Buschow, J. Less-Common Met. **136**, 207 (1988).
[3] V. Psycharis, M. Gjoka, O. Kalogirou, E. Devlin and D. Niarchos, J. Alloys Compd. **270**, 21 (1998).
[4] M. Zinkevich, N. Matterna, I. Bachera, S. Puerta, J. Alloys Compd. **336**, 320 (2002).
[5] S. Sakurada, A. Tsutai, M. Sahashi J. Alloys Compd. **187**, 67 (1992).
[6] I. A. Al-Omari, Y. Yeshurun, S.S. Jaswal, J. Zhou, D.J. Sellmeyer, J. Magn. Magn. Mater. **217**, 83 (2000).
[7] S. Derkaoui, N. Valignat and C.H. Allibert, J. Alloys Compd. **232**, 296 (1996).
[8] A. Lefevre, M.Th. Cohen-Adad and B.F. Mentzen, J. Alloys Compd. **256**, 207 (1997).
[9] T.H. Jacobs, K.H.J. Buschow, G.F. Zhou, J.P. Liu, X. Li, F.R. de Boer, J. Magn. Magn. Mater. **104-107** (Part 2), 1275 (1992).
[10] M. Sorescu and M. Valeanu, Intern. J. Inorg. Mater. **1**, 303 (1999).
[11] F. Maruyama and H. Nagai, Solid State Commun. **135**, 424 (2005).
[12] J. Pospısil, J. Poltierova Vejpravova, D. Niznansky, V. Sechovsky, J. Magn. Magn. Mater. **310**, e629 (2007).
[13] J. Liang, Q. Liu, F. Huang, G. Rao, X. Chen, Prog. Nat. Sci. **12**, 81 (2002).
[14] X.C. Kou, F.R. de Boer, R. Grössinger, G. Wiesinger, H. Suzuki, H. Kitazawa, T. Takamasu and G. Kido, J. Magn. Magn. Mater. **177-181** (Part 2), 1002 (1998).
[15] J.M.D. Coey, Rare Earth Iron Permanent Magnets, Oxford University Press, New York (1996).
[16] W. Sucksmith and J.E. Thompson, Proc. Roy. Soc. (London) **225**, 362 (1954).
[17] S. Sinnema, Ph.D. Thesis, University of Amsterdam (1988).

---

*Corresponding author: orestis@lab3.physics.auth.gr