Journal of Alloys and Compounds 264 (1998) 76–81

Magnetic properties of $Tb_2Co_{17-x}Ga_x$ compounds studied by magnetic measurements and neutron diffraction

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Received 26 May 1997

Abstract

The magnetic properties of $Tb_2Co_{17-x}Ga_x$ compounds (x=1,3,5 and 7) were studied by means of neutron diffraction and magnetic measurements. The refinement results of the neutron powder diffraction patterns show that initially the Ga atoms occupy almost exclusively the 18h site in the rhombohedral Th_2Zn_{17} structure and presumably are responsible for the sign reversal of the Co sublattice anisotropy. For $x \geq 3$ the Ga atoms increasingly occupy the 6c and 18f sites at the cost of the 18h site that shows a decreasing Ga occupancy in this concentration range. The 9d site is completely avoided by the Ga atoms over the whole concentration range. The sign reversal of the Co sublattice anisotropy is attributed to filling of the 18h site with Ga. From magnetic measurements and neutron diffraction it is derived that the Co moment strongly decreases in size with Ga concentration. There is also a strong decrease of the Curie temperature with Ga concentration. © 1998 Elsevier Science S.A.

Keywords: Co rich rare earth compounds; Magnetic measurements; Neutron diffraction; Crystal structure; Magnetic structure

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1. Introduction

In a previous investigation, the magnetic properties of $R_2Co_{17-x}Ga_x$ compounds with R=Gd and R=Sm were studied by means of magnetic measurements and X-ray diffraction on magnetically aligned powders [1]. These measurements have shown that increasing Ga concentration leads to a sign reversal of the magnetocrystalline Co-sublattice anisotropy from easy-plane anisotropy for low Ga concentration to easy-axis anisotropy for higher Ga concentration. In the $Sm_2Co_{17-x}Ga_x$ compounds, the Sm-sublattice anisotropy and the Co-sublattice anisotropy add constructively. This leads to materials of considerable magnetic hardness and the occurrence of narrow domain walls, in particular at relatively high Ga concentrations. By contrast, the $Dy_2Co_{17-x}Ga_x$ compounds were reported to have an easy-plane type anisotropy over almost the whole concentration range investigated [2]. In the present study, we have extended the investigation to $Tb_2Co_{17-x}Ga_x$ compounds which we studied by magnetic measurements but also by neutron diffraction with the aim to find a correlation between the preferential site occupation of the Ga atoms and the sign reversal of the Co sublattice anisotropy with Ga concentration.

2. Experimental

Samples of $Tb_2Co_{17-x}Ga_x$ were prepared by arc melting starting materials of at least 99.9% purity. After arc melting the samples were wrapped into Ta foil, sealed into an evacuated quartz tube and annealed for three weeks at 900 °C. The X-ray diffraction diagrams showed that the annealed samples were approximately single phase, their crystal structure corresponding to the rhombohedral Th_2Zn_{17} structure type. X-ray diffraction data on magnetically aligned samples were obtained for the $Tb_2Co_{17-x}Ga_x$ compounds with x=1,3 and 5 because they have sufficiently high Curie temperatures so that the powder particles could be magnetically aligned at room temperature.

The neutron powder diffraction experiments were made on the ROTAX high-intensity powder diffractometer, a

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PII S0925-8388(97)00261-2

facility present at the ISIS spallation neutron source [3]. Data were collected in the backscattering mode ($2\Theta=124.5°$) and forward scattering mode ($2\Theta=37.5°$) over the entire 20 ms time frame between ISIS pulses, providing a range of accessed d-spacings from 0.4 to 15 Å. Data were taken at room temperature for all compounds investigated and at 5 K for the two $Tb_2Co_{17-x}Ga_x$ compounds with the highest Ga concentrations ($x=5$ and 7).

The magnetic measurements were made on powdered material on a SQUID magnetometer in the temperature range 5–300 K in magnetic fields up to 6 T. The measurements above 300 K were made on a home-built magnetometer based on the Faraday principle, using polycrystalline lumps in order to avoid oxidation at elevated temperatures as far as possible.

3. Results

The $Tb_2Co_{17-x}Ga_x$ compounds with $x=1$, 3 and 5 have Curie temperatures above room temperature so that it was possible to take X-ray diffraction data on magnetically aligned samples. From these data it was derived that all three compounds have an easy magnetisation direction at room temperature perpendicular to the c axis. An example of such an X-ray diagram is shown in Fig. 1 for the compound with $x=5$, where it can be compared with an X-ray diagram of a non-aligned sample.

Examples of neutron diffraction diagrams are shown in Fig. 2. The powder neutron diffraction data were analyzed by the Rietveld method [3]. The nuclear scattering lengths employed in the refinement were $b_{Tb}=0.738\times10^{-12}$ cm, $b_{Co}=0.249\times10^{-12}$ cm and $b_{Ga}=0.7288\times10^{-12}$ cm. The results of the Rietveld refinements are presented in Tables 1 and 2.

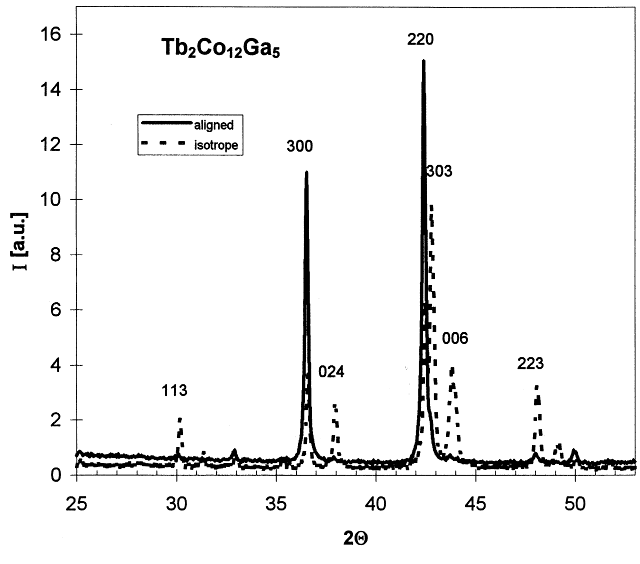

Fig. 1. Comparision of X-ray diagrams taken before and after magnetic alignment of the powder particles of $Tb_2Co_{12}Ga_5$.

Results of magnetic measurements showing the temperature dependence of the magnetisation are displayed in Fig. 3. It is seen that the magnetic ordering temperatures of the four $Tb_2Co_{17-x}Ga_x$ compounds investigated decrease strongly with Ga concentration. For the compound with $x=1$, the Curie temperature is higher than the measuring range available to us. The Curie temperatures of the remaining compounds has been listed in Table 3. For the compound with $x=7$ the Curie temperature has decreased to 95 K. The compound with $x=5$ gives rise to a well developed compensation temperature at about 130 K.

The field dependence of the magnetisation at 4.2 K of the four $Tb_2Co_{17-x}Ga_x$ compounds investigated is shown in Fig. 4. The spontaneous moments, obtained by extrapolation of the magnetic isotherms to zero field strength, have been listed in Table 3. The Ga substitution is seen to give rise to a fairly strong decrease of the magnetisation. This is seen more clearly in Fig. 5 where we have plotted the spontaneous magnetic moment per formula unit $Tb_2Co_{17-x}Ga_x$ versus Ga concentration. For Tb_2Co_{17} we used the data compiled in Ref. [4]

4. Discussion

In several previous investigations [5–8], neutron powder diffraction was used to study the site occupation of the non-magnetic elements M in rare earth compounds of the type $R_2Fe_{17-x}M_x$ (M=Al, Ga and Si). In all examples studied, quite substantial deviations from a statistical site distribution of the non-magnetic atoms over the four available Fe sites (6c, 9d, 18f and 18h) were observed. A similar strong deviation from a statistical distribution is observed also in the compounds studied in the course of the present investigation. This can be seen more clearly in Fig. 6 where we have plotted the site occupations derived from the refinement of the neutron data listed in Table 1. One of the most prominent features of the results shown in Fig. 6 is that the Ga atoms completely avoid occupying the 9d site. The 6c and 18f sites are avoided by the Ga atoms only initially, whereas for concentrations higher than $x=3$ the Ga atoms are seen in the figure to develop a very strong preference for these sites. Quite remarkable is the occupation of the 18h site which is seen to be the only one occupied by Ga in the low Ga concentration range. However, for Ga concentrations larger than $x=3$ the occupation of this site by Ga atoms decreases with increasing Ga concentration.

It is interesting to compare the preferred site occupation by the Ga atoms displayed in Fig. 6 with that found in $Tb_2Fe_{17-x}Ga_x$ [8]. The Ga atoms avoid the 9d site completely also in this compound, and the 6c and 18f sites become close to fully occupied by Ga atoms for Ga concentrations exceeding $x=8$. The remarkable feature that increasing Ga concentration leads to decreasing Ga occupation of the 18h site was observed also here. This has

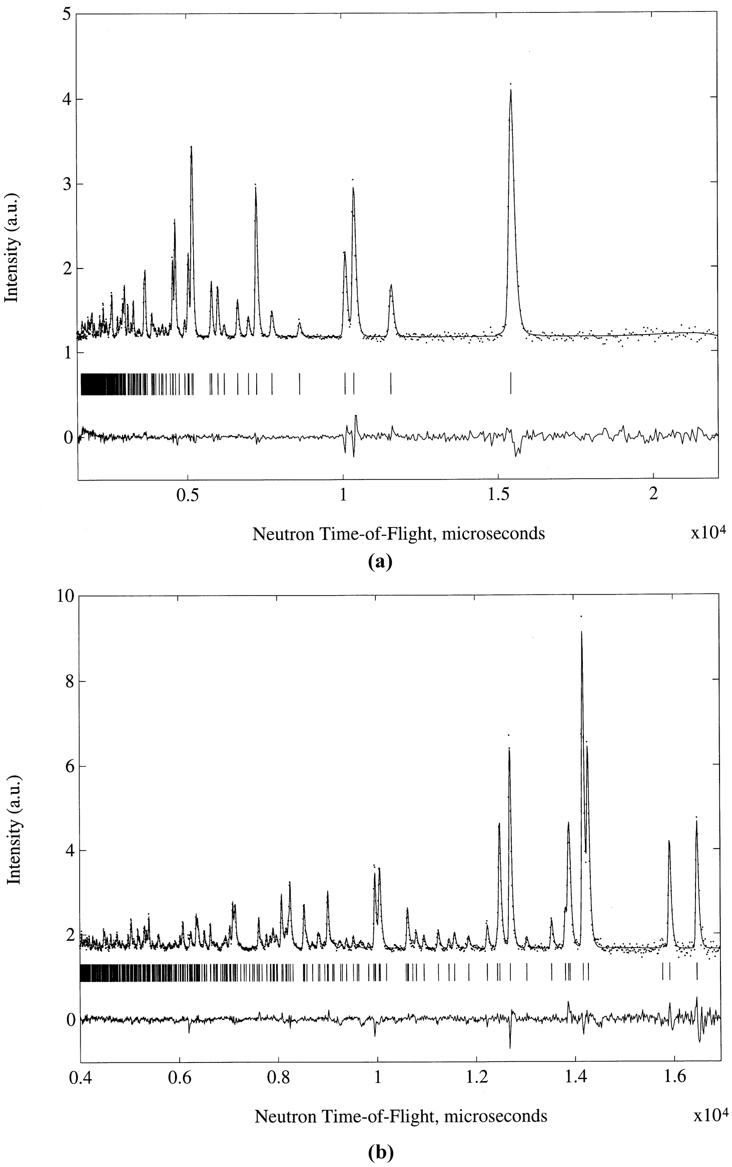

Fig. 2. Observed and calculated neutron diffraction pattern at 293 K for $Tb_2Co_{14}Ga_3$ for forward scattering (a) and backscattering (b) detector banks.

been attributed to the development of an almost ternary compound of the composition $Tb_2Fe_9Ga_8$ with the Ga atoms restricted to the 6c and 18f sites.

The preferred site occupation of substituted non-magnetic elements, when studied as a function of concentration, has been most helpful in finding the origin of the initial Curie temperature enhancement observed in many Fe based 2:17 compounds, since it showed that neither the presence of the so-called Fe-dumb bell pairs, nor the increase of the unit cell volume play an important role [5–7]. In the present study, the observed concentration dependent preferred site occupation proves equally helpful because it sheds some light on the concentration dependent changes of the Co sublattice anisotropy. The preferred moment direction in Gd_2Co_{17} is perpendicular to the c axis [2], but recent results of X-ray diffraction made on magnetically aligned $Gd_2Co_{17-x}Ga_x$ samples with $x \geq 2$ showed that the easy magnetization direction at room temperature corresponds to the c axis in these compounds, meaning that the Co sublattice anisotropy changes sign from negative to positive with increasing Ga concentration. This suggests that there is a preferential substitution of the Ga atoms into those Co sites that contribute negatively to the Co-sublattice anisotropy. Bearing in mind that this change in sign of the Co sublattice anisotropy occurs already for rather low Ga concentrations, the results displayed in Fig. 6 show that it must be caused by the Ga occupation of the 18h site, because this site is the only one occupied by Ga for $x \geq 3$. Our conclusion therefore is that the 18h Co atoms contribute negatively to the Co sublattice anisotropy in R_2Co_{17} compounds.

The total anisotropy in the $Tb_2Co_{17-x}Ga_x$ compounds

Table 1
Refined room temperature lattice constants, positional parameters, site occupancies and magnetic moments for $Tb_2Co_{17-x}Ga_x$ intermetallics

Compound	$Tb_2Co_{16}Ga$	$Tb_2Co_{14}Ga_3$	$Tb_2Co_{12}Ga_5$	$Tb_2Co_{10}Ga_7$
a (Å)	8.39761(29)	8.45915(23)	8.52517(5)	8.65196(5)
c (Å)	12.23844(16)	12.33580(16)	12.4088(17)	12.34647(14)
V_{cell} (Å^3)	747.40	764.4	781.0	800.4
Tb, 6c, z	0.34106(54)	0.34109(47)	0.34268(49)	0.34909(25)
Co/Ga, 6c, z	0.08915(99)	0.09554(91)	0.09622(68)	0.11008(30)
Co/Ga, 18f, x	0.29269(83)	0.29268(64)	0.29551(51)	0.30879(25)
Co/Ga, 18h, x	0.49982(70)	0.50114(47)	0.50081(40)	0.50107(31)
Co/Ga, 18h, z	0.15946(80)	0.15413(49)	0.15371(42)	0.14979(31)
% Ga, 6c	0.0	0.0	31.6(3)	80.3(5)
% Ga, 9d	0.0	0.0	0.0	0.0
% Ga, 18f	0.0	0.0	34.3(2)	62.4(2)
% Ga, 18h	17.7(5)	52.5(4)	38.5(3)	27.5(2)
R_{wp} %	3.66	3.51	4.11	2.74
R_{exp} %	1.46	1.43	1.66	1.27
ξ^2	6.25	6.02	6.11	4.67
μ, Tb, 6c, μB	$-5.3(2)^a$	$-3.8(3)^a$	$-1.5(3)^a$	
μ, Co, 6c, μB	$1.3(2)^a$	$1.5(3)^a$	$0.8(2)^a$	
μ, Co, 9d, μB	$1.9(2)^a$	$1.4(3)^a$	$0.8(2)^a$	
μ, Co, 18f, μB	$1.6(2)^a$	$1.2(3)^a$	$0.9(2)^a$	
μ, Co, 18h, μB	$1.6(2)^a$	$1.2(3)^a$	$0.4(2)^a$	
μ, cell, μB	50.7	38.2	16.8	
μ, f.u., μ_B	16.9	12.7	5.6	

[a] Moments aligned along the [100] direction.

can be described as the sum of the contributions of the Co sublattice and rare-earth sublattice:

$$K_1^{tot} = K_1^{Co} + K_1^{R} = K_1^{Co} - 3/2\alpha_J < r^2 > A_2^0 < O_2^0 > \qquad (1)$$

In this expression the fact is used that the anisotropy of the rare-earth sublattice is crystal-field induced, and in lowest-order approximation can be given by the last term of Eq. (1), where the second-order crystal-field parameter A_2^0 depends on the crystal structure and composition of a given compound and where the temperature dependence of the rare-earth sublattice anisotropy is mainly determined by the thermal average of the Stevens operator $<O_2^0>$. For the underlying crystal structure the second-order crystal-field parameter A_2^0 is negative [4], and together with a negative sign of the second-order Stevens constant α_J for R=Tb, one finds that K_1^R is negative. The data obtained for the $Gd_2Co_{17-x}Ga_x$ compounds have shown that for the concentrations considered here a positive value of K_1^{Co} has to be associated with the Co sublattice anisotropy, meaning that the Tb and Co sublattice anisotropy contributions are of opposite sign.

Table 2
Refined lattice constants, positional parameters and magnetic moments at 5 K for $Tb_2Co_{12}Ga_5$ and $Tb_2Co_{10}Ga_7$

Compound	$Tb_2Co_{12}Ga_5$	$Tb_2Co_{10}Ga_7$
a (Å)	8.51079(9)	8.63758(7)
c (Å)	12.38626(30)	12.32720(30)
V_{cell} (Å^3)	777.5	797.1
Tb, 6c, z	0.34142(87)	0.35041(61)
Co/Ga, 6c, z	0.09300(11)	0.11102(75)
Co/Ga, 18f, x	0.29652(77)	0.30758(57)
Co/Ga, 18h, x	0.50063(58)	0.50071(69)
Co/Ga, 18h, z	0.15147(63)	0.15004(68)
R_{wp} %	2.69	2.50
R_{exp} %	1.78	1.50
ξ^2	2.28	2.77
μ, Tb, 6c, μB	$-6.0(5)^a$	$-6.3(5)^b$
μ, Co, 6c, μB	$1.1(2)^a$	$0.3(2)^b$
μ, Co, 9d, μB	$0.9(2)^a$	$0.5(2)^b$
μ, Co, 18f, μB	$1.5(2)^a$	$0.3(2)^b$
μ, Co, 18h, μB	1.6(2)a	$0.3(2)^b$
μ, cell, μB	14(2)	29(3)
μ, f.u., μB	4.7(1)	9.7(1)

[a] Moments aligned along the [100] direction.
[b] Moments aligned along the [001] direction.
Site occupancies are the same as at room temperature.

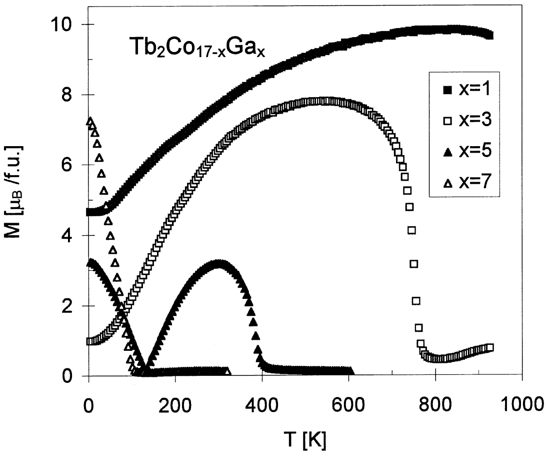

Fig. 3. Temperature dependence of the magnetisation of $Tb_2Co_{17-x}Ga_x$ compounds measured in a field of 0.1 T.

Table 3
Curie temperatures, T_c (K), and spontaneous moments, M_0 (μB/f.u.), at 4.2 K for several $Tb_2Co_{17-x}Ga_x$ compounds

Compound	$Tb_2Co_{16}Ga$	$Tb_2Co_{14}Ga_3$	$Tb_2Co_{12}Ga_5$	$Tb_2Co_{10}Gad$
T_c	>900	755	388	95
M_0	7.2	1.6	4.1	9.8

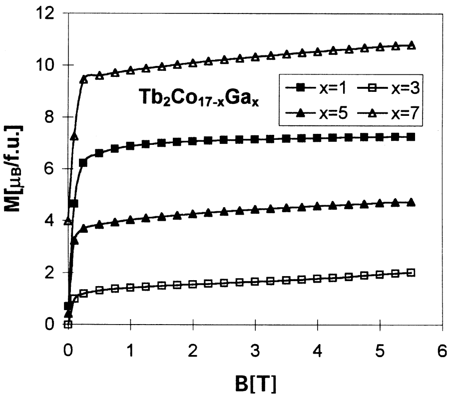

Fig. 4. Field dependence of the magnetic moment of $Tb_2Co_{17-x}Ga_x$ compounds measured at 4.2 K with decreasing field.

It can be derived from the data shown in Fig. 3 that the $Tb_2Co_{17-x}Ga_x$ compounds with $x=1$, 3 and 5 have Curie temperatures above room temperature and the results listed in Table 1 show that the easy magnetisation direction at room temperature is perpendicular to the c axis. This means that the easy-plane Tb sublattice anisotropy dominates the easy axis Co sublattice anisotropy even at room temperature. Similar results were also found in the series of $Dy_2Co_{17-x}Ga_x$ compounds [2]. These results are furthermore consistent with an easy c axis anisotropy observed in the series $Sm_2Co_{17-x}Ga_x$ compounds [1] if one takes account of the fact that the second order Stevens factor αJ for Sm has a sign different from that of Tb and Dy.

Generally, one may expect that the value of K_1^R strongly increases with decreasing temperature due to the strong temperature dependence of $<O_2^0>$. Because the Tb sublattice anisotropy is dominant already at room temperature for the compounds with $x=1$, 3 and 5, no change in easy magnetisation direction is expected upon cooling, explaining the absence of any spin reorientation phenomena in these materials. Surprisingly, from the data shown in Table 2 it follows that the easy magnetisation direction in the compound with $x=7$ is different from those of the other compounds in that it is parallel to the c direction even at low temperatures ($K_1^{tot}>0$). This means that the Tb sublattice anisotropy has become reduced in absolute value and no longer dominates the Co sublattice anisotropy ($K_1^{Co}>0$), or that the Tb sublattice anisotopy has changed its sign. In terms of Eq. (1) this would mean that A_2^0 has changed its sign or, at least, has become strongly reduced in value. An increasing contribution of higher-order crystal field terms to the anisotropy may also be responsible for this effect.

5. Concluding remarks

As in a preceding investigation on $RCo_{5-x}Ga_x$ compounds [9], we have exploited the large difference in scattering length between Co and Ga to obtain reliable experimental information of the sites preferentially occupied by the Ga atoms in $Tb_2Co_{17-x}Ga_x$ compounds ($x\geq7$). Results obtained for compounds of the series

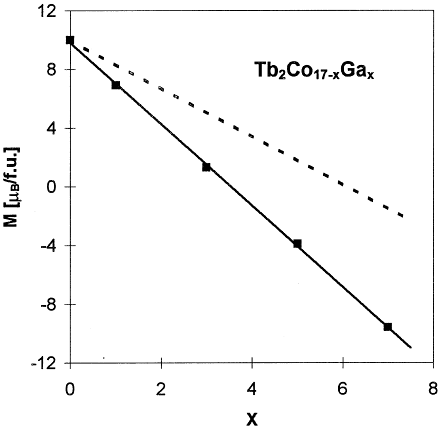

Fig. 5. Concentration dependence of the spontaneous moment at 4.2 K of $Tb_2Co_{17-x}Ga_x$ compounds. The broken line corresponds to magnetic dilution when assuming that the Co moments do not change with Ga concentration.

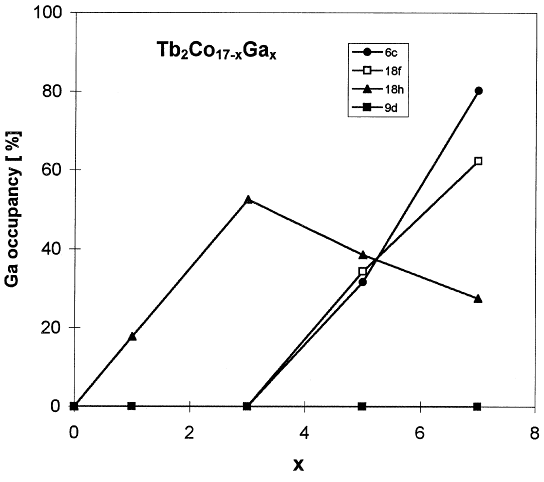

Fig. 6. Concentration dependence of Ga atom occupation of the four available sites in the Th_2Zn_{17} type structure of the $Tb_2Co_{17-x}Ga_x$ compounds.

$Gd_2Co_{17-x}Ga_x$ had shown [1], that the Co sublattice anisotropy changes from planar to axial with increasing Ga concentration. Since it is realistic to assume that the preferred site occupation is similar in both series of compounds our neutron diffraction results show that this sign reversal occurs in a concentration range where the Ga atoms substitute exclusively into the 18h site. This suggests that the negative Co sublattice anisotropy in R_2Co_{17} compounds is dominated by a strongly negative contribution of the 18h type Co atoms that becomes reduced by Ga substitution. Our results are also indicative of a strong change in the crystal-field induced Tb sublattice anisotropy with Ga concentration, but further experiments are planned to verify this point.

References

[1] D. Zhang, D.P. Middleton, E. Brück, F.R. de Boer, Z.D. Zhang and K.H.J. Buschow, J. Alloys Comp. (1997) in press.

[2] S.Y. Zhang, B.G. Shen, B. Liang, Z.H. Cheng, J.X. Zhang, H.W. Zhang, J.G. Zhao and W.S. Zhan, J. Alloys Comp. (1997) in press.

[3] W. Schäfer, E. Jansen, R. Skowronek, G. Will, W. Kockelmann, W. Schmidt, H. Tietze-Jaensch, Nucl. Instrum. Methods A 364 (1995) 179.

[4] J.J.M. Franse, R.J. Radwanski, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, Vol. 7, North Holland, Amsterdam 1993, pp. 307.

[5] G.J. Long, G.K. Marasinghe, O.A. Pringle, Z. Hu, W.B. Yelon, D.P. Middleton, K.H.J. Buschow, F. Grandjean, J. Appl. Phys. 76 (1994) 6731.

[6] Z. Hu, W.B. Yelon, S. Mishra, G.J. Long, O.A. Pringle, D.P. Middleton, K.H.J. Buschow, F. Grandjean, J. Appl. Phys. 76 (1994) 443.

[7] D.P. Middleton, S.R. Mishra, G.J. Long, O.A. Pringle, Z. Hu, W.B. Yelon, F. Grandjean, K.H.J. Buschow, J. Appl. Phys. 78 (1995) 5568.

[8] O.A. Pringle, Gary J. Long, S.R. Mishra, Dimitri Hautot, F. Grandjean, D.P. Middleton, K.H.J. Buschow, Z. Hu, H. Luo, W.B. Yelon, J. Appl. Phys. (1997) in press.

[9] O. Moze, L. Pareti, A. Paoluzi, K.H.J. Buschow, Phys. Rev. B 53 (1996) 11550.