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Crystal structure and magnetic properties of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ compounds

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Abstract. A series of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ ($x = 0.011$–0.034, $y = 0$–0.393) samples have been prepared. Single-phase samples assigned as 3:29 compounds with the monoclinic lattice are obtained in the following composition regions: $x = 0.011$, $0 \leqslant y \leqslant 0.307$; $x = 0.022$, $0 \leqslant y \leqslant 0.313$; and $x = 0.034$, $0 \leqslant y \leqslant 0.393$. The solid-solution limit of cobalt in $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ increases with the Ti content. The cell parameters a, b and c show anisotropic decreases with the Co content, i.e. a and b decrease significantly and c decreases slightly in the composition range investigated. The Curie temperature is increased by the substitution of Co for Fe in $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$. The saturation magnetization first increases and then decreases with the Co content. The dependence of the intrinsic magnetic properties of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ on the Co and Ti contents is presented. The compounds exhibit an easy-magnetization direction on the a–b plane corresponding to the $CaCu_5$-type structure at room temperature. The anisotropy field H_a of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ is decreased and the magnetocrystalline anisotropy constant K_1 is increased by the substitution of Co for Fe. No spin reorientation is observed in the alternating-current susceptibility measurement between 77 K and the Curie temperature.

1. Introduction

The novel rare-earth iron intermetallic compounds $R_3(Fe, M)_{29}$ (R = Ce, Pr, Nd, Sm, Gd, Tb, Dy and Y; M = Ti, V, Cr, Mn, Nb and Mo) and their nitrides have attracted considerable attention [1–14] since the discovery of $R_2(Fe, V)_{17}$ (R = Y, Nd, Sm and Gd) with a 2:17 superstructure and $Nd_2(Fe, Ti)_{19}$ [15–17]. X-ray and neutron diffraction investigations established that the precise stoichiometry of $Nd_2(Fe, Ti)_{19}$ should be $Nd_3(Fe, Ti)_{29}$ with a monoclinic symmetry, and $Nd_3(Fe, Ti)_{29}$ is a derivative of a $CaCu_5$-type compound [17–19]. In our previous work we investigated the phase relation of the Gd–Fe–Ti ternary system at 1373 K, and the crystal structure and magnetic properties of $Gd_3(Fe_{1-x}Ti_x)_{29}$ compounds [20, 21]. $Gd_3(Fe_{1-x}Ti_x)_{29}$ compounds are stable exclusively at high temperature with $x = 0.011$–0.034 and exhibit a planar magnetocrystalline anisotropy. Extensive

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investigations on 2:17 compounds reveal that most of the Fe-based 2:17 compounds are of easy-plane magnetocrystalline anisotropy, while the magnetocrystalline anisotropies of 2:17 compounds containing a mixture of cobalt and iron can be easy-axis ones [22]. It was reported that the magnetocrystalline anisotropy of $La_2(Co, Ti)_{17}$ changes from easy axis to easy plane after a certain amount of cobalt is substituted for with iron [23]. Studying improvement of the magnetocrystalline anisotropy is of significance not only for a fundamental understanding but also for the potential applications of the materials. In this work we try to use cobalt to substitute for some of the iron in $Gd_3(Fe_{1-x}Ti_x)_{29}$ ($x = 0.011$, 0.022 and 0.034) in order to change the easy-magnetization direction of the 3:29 compounds from easy plane to easy axis.

2. Experimental procedure

A mixture with appropriate proportions of metallic gadolinium, iron, cobalt and titanium with a high purity of at least 99.9% was melted by arc melting under a high-purity argon atmosphere in a water-cooled copper hearth, and remelted several times to ensure a full homogenization. Subsequently the samples were wrapped in tantalum foil and annealed at 1373 K for four days in an evacuated quartz tube; this was followed by quenching of the samples in ice-water. The samples were first characterized by powder x-ray diffraction (XRD) using a four-layer monochromatic focusing transmission Guinier–de Wolff camera with Co Kα radiation.

The single-phase quality of the samples was examined by means of both thermomagnetic analysis (TMA) and x-ray diffraction. The XRD experiment was carried out using a Rigaku model D/max-2400 diffractometer with Cu Kα radiation and a graphite monochromator. The XRD data from $2\theta = 10^\circ$ to 100° were collected in a step-scan mode with a step of $2\theta = 0.02^\circ$ and a sampling time of 2 s per step. The TMA was carried out in a low field of about 0.04 T from room temperature to above the Curie temperature (T_C) using a vibrating-sample magnetometer (VSM). The ac susceptibility (χ_{ac}) of the samples between 77 K and the Curie temperature was measured by a permeameter at a frequency of 320 Hz in a magnetic field of about 4.0×10^{-4} T. The magnetization of the samples was determined using an extracting-sample magnetometer (ESM) in magnetic fields up to 65 kOe at 1.5 K.

3. Results and discussion

3.1. The stability and crystal structure of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$

Figure 1(a) shows a typical XRD pattern of single-phase $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$. The XRD pattern can be indexed with respect to a monoclinic lattice with lattice parameters close to those reported for the 3:29 compounds [1–14]. XRD and TMA revealed that single-phase samples of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ were obtained in the following composition ranges: $x = 0.011$, $0 \leqslant y \leqslant 0.307$; $x = 0.022$, $0 \leqslant y \leqslant 0.313$; and $x = 0.034$, $0 \leqslant y \leqslant 0.393$. A mixture of monoclinic 3:29 phase, rhombohedral 2:17 phase and α-Fe was revealed by XRD in the samples with: $x = 0.011$, $0.307 < y < 0.322$; $x = 0.022$, $0.313 < y < 0.393$; and $x = 0.034$, $0.393 < y < 0.447$. The rhombohedral 2:17 phase coexists with α-Fe in the following composition ranges: $x = 0.011$, $0.322 < y \leqslant 0.989$; $x = 0.022$, $0.393 < y \leqslant 0.978$; and $x = 0.034$, $0.447 < y \leqslant 0.966$. Therefore, the amount of Co substitution for Fe in the 3:29 phase increases with Ti content. However, we failed to prepare the $Gd_3(Co_{1-x}Ti_x)_{29}$ compound for $x = 0.011$–0.060 under the present synthesis conditions.

The composition dependence of the cell parameters of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ is shown

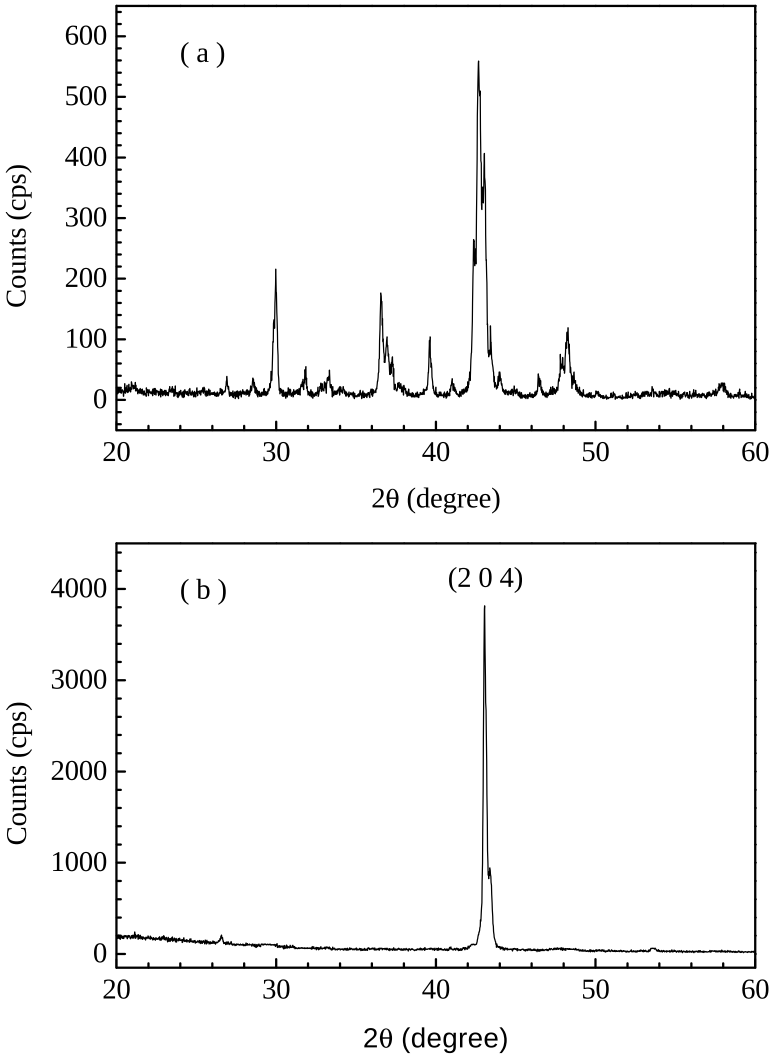

Figure 1. X-ray diffraction patterns of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ ($x = 0.034$, $y = 0.195$). (a) Annealed and (b) field-aligned samples.

in figure 2. At a fixed Ti content, the lattice parameters *a* and *b* decrease strongly with the Co content, while *c* decreases slightly. The anisotropic decreases of the cell parameters could be attributed to the metallic radius of Co being smaller than that of Fe on the one hand and a possible preferential substitution of Co for Fe on the other hand.

3.2. Magnetic properties

Finely powdered particles of a sample were mixed with epoxy resin and filled into a cylindrical tube, which was connected to a motor driving it to spin in an applied magnetic field of about 1.2 T with the cylindrical axis perpendicular to the applied field until the epoxy resin solidified. The magnetization ($M_\perp$) along the hard-magnetization direction (HMD) was measured by

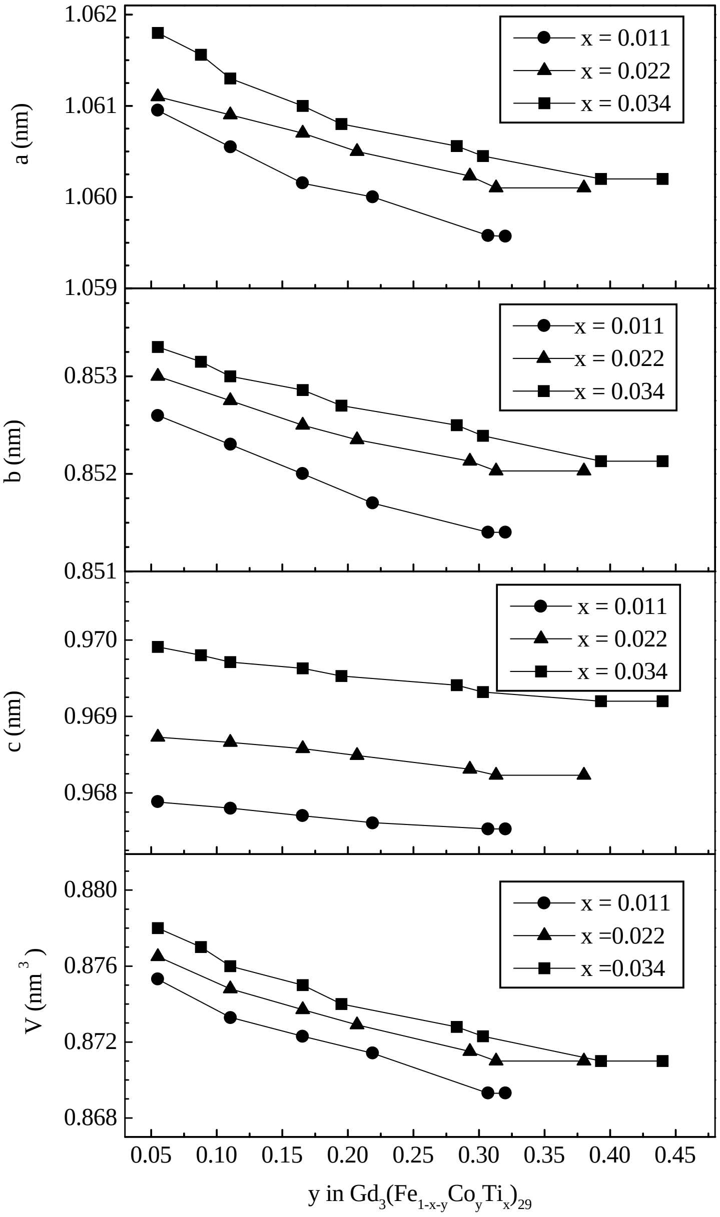

Figure 2. The dependences of the cell parameters of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ on the Co and Ti contents.

applying a magnetic field parallel to the cylindrical axis of the tube. A field-aligned specimen of a semi-disc shape with the aligning field parallel to the disc plane was prepared to examine the easy-magnetization direction (EMD) of the sample by means of XRD. The magnetization ($M_\parallel$) along the EMD was determined for free powdered particles of a sample, i.e. the fine particles are free to reorient in an applied magnetic field. The magnetization curves at 1.5 K of the field-aligned and fine free particles of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ are shown in figure 3. By plotting $\Delta M = M_\parallel - M_\perp$ versus B and linearly extrapolating ΔM to zero, the anisotropy field,

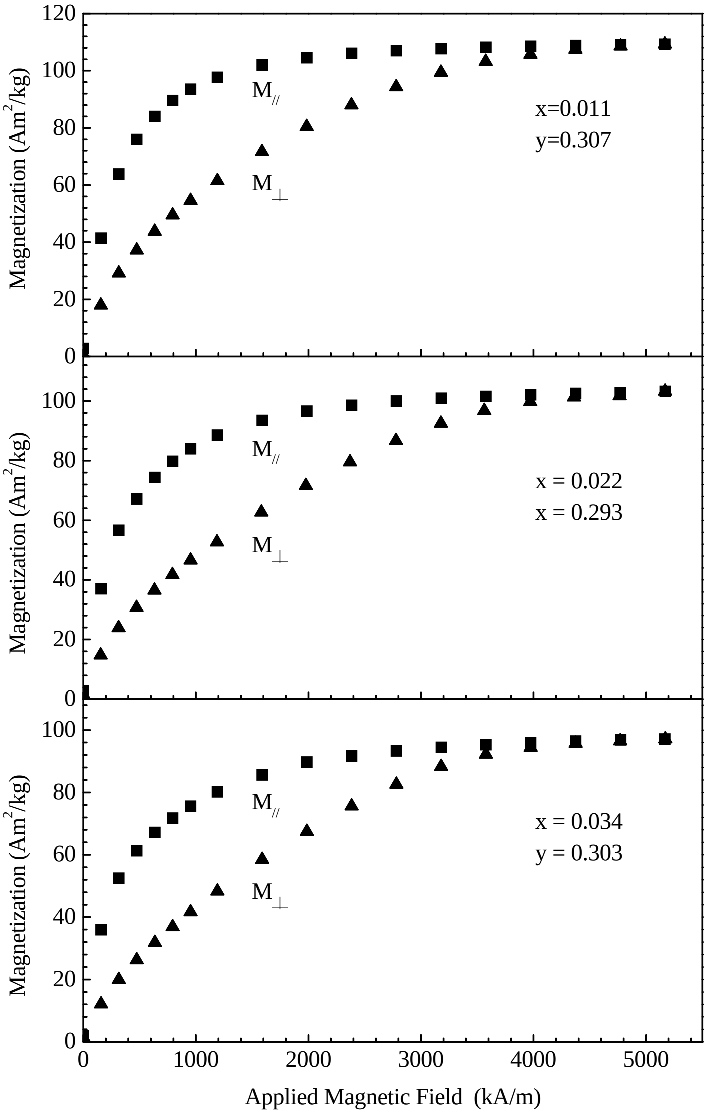

Figure 3. The field dependences of the magnetization at 1.5 K along the easy- ($M_{\parallel}$) and the hard- ($M_{\perp}$) magnetization directions of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$.

$\mu_0 H_a$, can be estimated; the values are listed in table 1. The XRD pattern of the field-aligned sample shows that the (2 0 4) peak, which is equivalent to the (0 0 10) peak in the hexagonal $CaCu_5$ structure, is enhanced for all $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ as shown in figure 1(b). Since the aligning magnetic field is parallel to the disc plane of the specimen, figure 1(b) indicates that the (2 0 4) direction is the hard-magnetization direction, i.e. the easy-magnetization direction of the compounds is on the *a–b* plane with respect to the $CaCu_5$-type structure. Figure 4 shows the dependence of the anisotropy field of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ on y (Co content) and x (Ti content). Since the orbital momentum of gadolinium is zero, the magnetocrystalline anisotropy essentially originates from the (Fe, Co) sublattice. Figure 4 reveals that the anisotropy field first decreases slightly and then rapidly when $y > 0.25$.

Table 1. The intrinsic magnetic parameters of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$.

		μ_0H_a (T)	M_s (A m^2 kg^{-1})	μ_s (μ_B/f.u.)	$\mu_{Fe,Co}$ (μ_B)	K_1 (J mol^{-1})	T_C (K)
$x = 0.011$	$y = 0.000$	6.0	103.6	38.8	2.08	−324.6	517
	$y = 0.055$	5.9	111.4	41.8	2.19	−343.6	613
	$y = 0.110$	5.7	113.1	42.5	2.21	−336.7	678
	$y = 0.166$	5.6	115.1	43.4	2.25	−336.6	739
	$y = 0.219$	5.5	112.9	42.6	2.22	−324.3	813
	$y = 0.307$	4.5	110.4	41.8	2.19	−259.4	885
$x = 0.022$	$y = 0.000$	6.2	102.0	38.1	2.08	−329.8	527
	$y = 0.055$	6.1	108.9	40.8	2.18	−345.8	620
	$y = 0.110$	5.8	110.7	41.5	2.20	−335.3	691
	$y = 0.166$	5.6	111.9	42.1	2.23	−327.3	747
	$y = 0.207$	5.5	110.0	41.5	2.20	−316.0	807
	$y = 0.293$	4.9	107.9	40.8	2.18	−276.1	850
	$y = 0.313$	4.5	105.3	39.9	2.15	−247.5	886
$x = 0.034$	$y = 0.000$	6.4	94.3	35.2	2.00	−313.1	538
	$y = 0.055$	6.1	106.1	39.7	2.17	−338.0	637
	$y = 0.110$	5.9	106.9	40.1	2.18	−329.4	701
	$y = 0.166$	5.8	108.8	40.9	2.21	−329.6	752
	$y = 0.195$	5.8	107.9	40.6	2.20	−326.8	770
	$y = 0.283$	5.3	105.2	39.7	2.17	−291.2	862
	$y = 0.303$	5.1	102.2	38.6	2.13	−270.1	876
	$y = 0.393$	3.3	102.2	38.8	2.14	−176.1	933

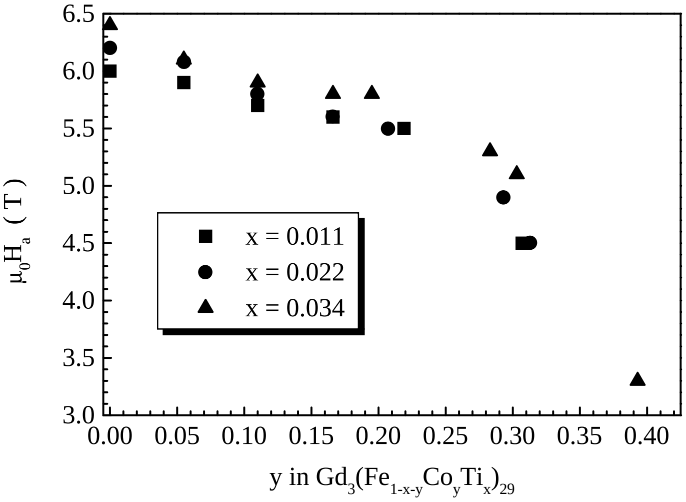

Figure 4. The dependence of the anisotropy field of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ on the Co and Ti contents.

The saturation magnetization M_s of the samples at 1.5 K was derived from the M–$1/H$ plot of the free powdered particles of a sample by extrapolating $1/H$ to zero on the basis of the data for the higher-field part. The values of the saturation magnetization of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ are listed in table 1. Figure 5 shows the dependence of the saturation magnetization on x and y. The saturation magnetization exhibits a maximum around $y = 0.17$ for $x = 0.011$–0.034, which is similar to the observation for binary Fe–Co alloys and possibly indicative of a crossover

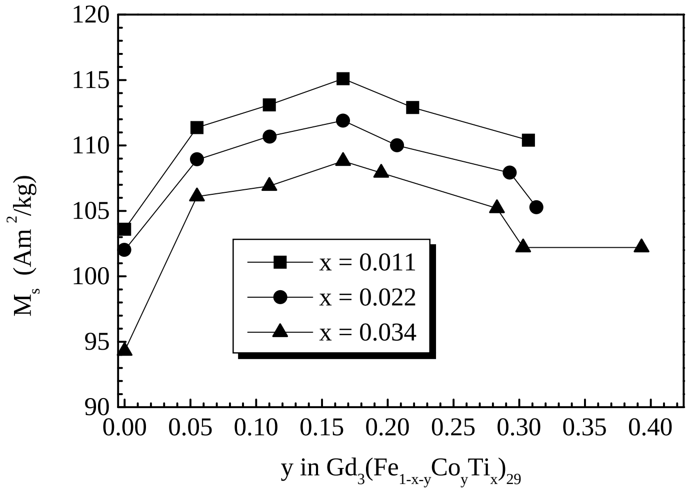

Figure 5. The dependence of the saturation magnetization of Gd$_3$(Fe$_{1-x-y}$Co$_y$Ti$_x$)$_{29}$ on the Co and Ti contents.

from weak to strong ferromagnetism. At a constant Co content, the saturation magnetization decreases with Ti content, which may be attributed to a dilution effect of nonmagnetic titanium and/or a change of environment around the magnetic atoms (Fe, Co).

For a compound with an easy-plane magnetocrystalline anisotropy, there exists a relation among the anisotropy field, H_a, the saturation magnetization, M_s, and the magnetocrystalline constant, K_1:

$$H_a = -2K_1/\mu_0 M_s.$$

From the data given in table 1, K_1 can be estimated for Gd$_3$(Fe$_{1-x-y}$Co$_y$Ti$_x$)$_{29}$. Figure 6 shows the dependence of K_1 on x and y in Gd$_3$(Fe$_{1-x-y}$Co$_y$Ti$_x$)$_{29}$. K_1 increases with

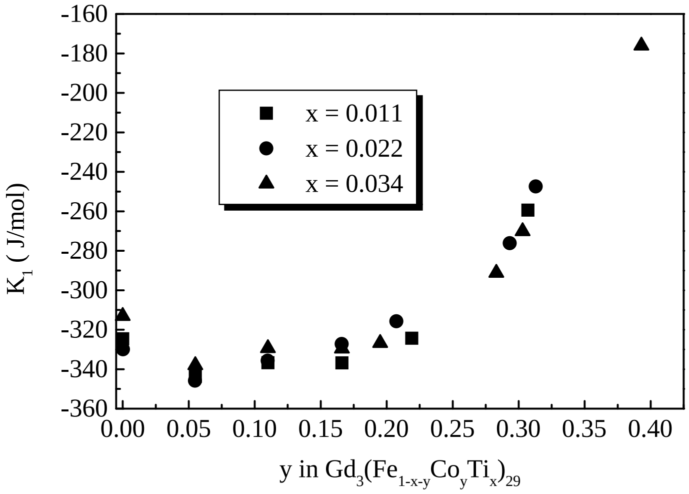

Figure 6. The composition dependence for Gd$_3$(Fe$_{1-x-y}$Co$_y$Ti$_x$)$_{29}$ of the magnetocrystalline constant K_1.

Co content towards a positive value. Rapid increase of K_1 occurs when $y > 0.25$. In other words, the substitution of Co for Fe does reduce the planar anisotropy of the parent compound $Gd_3(Fe_{1-x}Ti_x)_{29}$ and tends to drive the compound from an easy-plane to an easy-axis magnetocrystalline anisotropy.

The magnetic moments per unit formula, μ_s(1.5 K), of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ are also listed in table 1. Assuming that gadolinium possesses the magnetic moment of a free trivalent ion, i.e. $\mu_{Gd}(0\ K) = 7\ \mu_B$, and that the moment of the Gd sublattice couples antiferromagnetically with that of the (Fe, Co) sublattice, the moment per magnetic transition metal atom (Fe, Co) can be derived from μ_s(0 K) ($\approx\mu_s$(1.5 K)):

$$\mu_{Fe,Co} = [\mu_s(0\ K) + 3\mu_{Gd}(0\ K)]/29(1-x).$$

The values of $\mu_{Fe,Co}$ derived are listed in table 1. The composition dependences of μ_s and $\mu_{Fe,Co}$ are similar to that of M_s. However, it is intriguing that the substitution of Co for Fe affects the magnetic moment of the 3d atom only slightly in the composition range investigated and that $\mu_{Fe,Co}$ is very close to the value for pure iron (=2.2 μ_B), although the effects of the substitution on the cell parameters, anisotropy field, magnetocrystalline constant and Curie temperature (see below) are substantial.

A typical thermomagnetic curve for $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ is shown in figure 7. The values of the Curie temperature derived from the thermomagnetic analysis are listed in table 1. Figure 8 shows the composition dependence of the Curie temperature of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$. The Curie temperature increases almost linearly with the Co content. The ac susceptibility, χ_{ac}, between 77 K and room temperature does not reveal any magnetic transition.

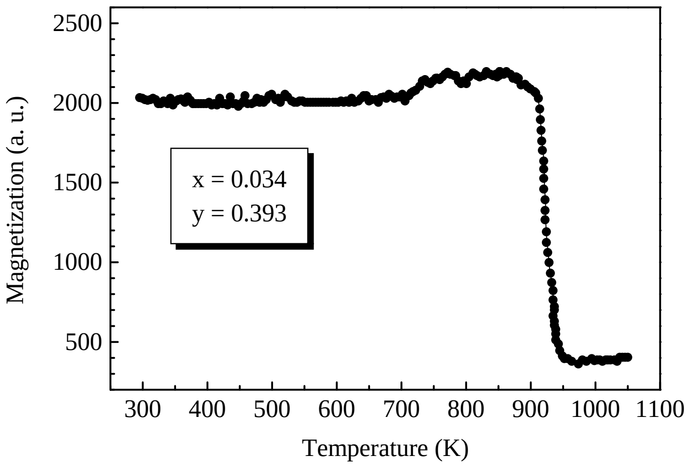

Figure 7. A typical thermomagnetic curve of $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$.

4. Summary

$Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ crystallizes in a monoclinic lattice. The degree of substitution of Co for Fe in the 3:29 phase increases with Ti content: $x = 0.011$, $0 \leqslant y \leqslant 0.307$; $x = 0.022$, $0 \leqslant y \leqslant 0.313$; and $x = 0.034$, $0 \leqslant y \leqslant 0.393$. The cell parameters a and b are substantially decreased by the substitution of Co for Fe, but c is decreased slightly. The Curie temperature is increased almost linearly by the substitution of Co for Fe. The saturation

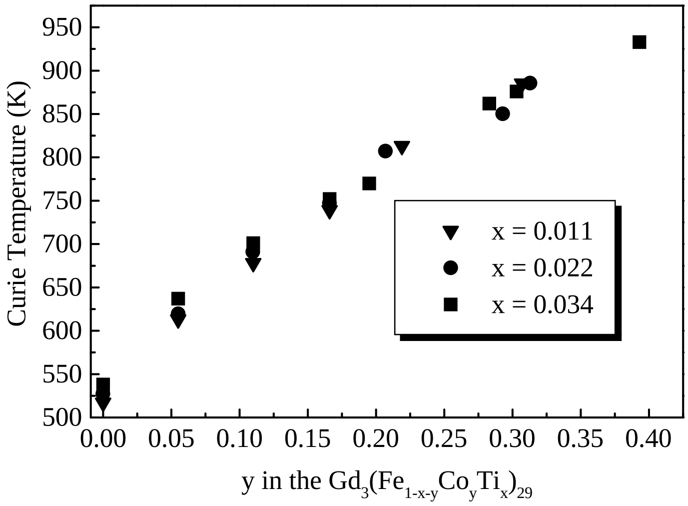

Figure 8. The composition dependence for $Gd_3(Fe_{1-x-y}Co_yTi_x)_{29}$ of the Curie temperature.

magnetization of the compound first increases and then decreases as the Co content increases. The compound exhibits a planar magnetocrystalline anisotropy on the *a*–*b* plane corresponding to the hexagonal $CaCu_5$ structure. The substitution of Co for Fe decreases the anisotropy field and increases the magnetocrystalline constant, tending to drive the Fe-based 3:29 compound from an easy-plane to an easy-axis magnetocrystalline anisotropy.

Acknowledgments

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