

Structural and magnetic properties of $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds

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Abstract

Structural and magnetic properties of the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds with x ranging from 0.4 to 1.0 have been investigated by X-ray diffraction and magnetic measurements. It was found that all the compounds are of single phase and crystallize in the $\text{Nd}_3(\text{Fe,Ti})_{29}$ -type structure. The higher Co content substituted for Fe requires a higher Cr content to stabilize the 3:29 structure. The Curie temperature T_c decreases monotonically with increasing Co and Cr contents from 736 K for $x=0.4$ and $y=4.5$ to 285 K for $x=1.0$ and $y=7.5$. The saturation magnetization M_s decreases monotonically with increasing Co and Cr contents. It is noteworthy that all the compounds investigated show room temperature easy-axis type of anisotropy and the anisotropy field increases with increasing Co content, going through a maximum at around $x=0.8$ and $y=6.5$, then decreases with further increasing Co content. In order to improve the permanent magnetic properties it is necessary to reduce the content of the stabilizing element.

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1. Introduction

Since the $\text{Nd}_3(\text{Fe,Ti})_{29}$ phase [1–4] with monoclinic symmetry and space group $A_{2/m}$ was discovered, much attention has been paid to $\text{R}_3(\text{Fe,T})_{29}$ compounds, where R stands for rare earth or Y, and T for stabilizing element, like Ti. Recently, a series of the $\text{R}_3(\text{Fe,T})_{29}$ compounds have been synthesized for $\text{R}=\text{Ce, Pr, Nd, Sm, Gd, Tb, Dy, Y}$, and $\text{T}=\text{Ti, V, Cr, Mo, etc.}$ [5–11]. Yang et al. [12] and Hu et al. [13] have investigated structure and magnetic properties of the $\text{Sm}_3(\text{Fe,Ti})_{29}\text{N}_4$ compounds and found that the compounds have outstanding intrinsic permanent magnetic properties and may be a candidate for permanent magnet application. However, the stability of all interstitial compounds at high temperature is not satisfactory. Yang et al. [14] and Wang et al. [15] have synthesized the Co-based $\text{Gd}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds and have found that when the Co content x exceeds ~ 0.4 the compounds show room temperature easy-axis type of anisotropy. However, due to the antiferromagnetic coupling between

Gd moments and the transition metal moments the compounds have a very low saturation magnetization and therefore cannot be used as permanent magnetic material. It is likely that in order to increase the saturation magnetization a light rare earth element R should be chosen, because the latter has a ferromagnetic coupling with the transition metal moment in the rare earth-transition metal intermetallics. Tang et al. [16] have synthesized the $\text{Nd}_3\text{Fe}_{29-x-y}\text{Co}_x\text{Ti}_y$ compounds ($x \leq 6.44$ and $1.35 \leq y \leq 1.69$) and Shah et al. [17] have synthesized the $\text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5}$ compounds ($x \leq 6$). They found that the Curie temperature and saturation magnetization of these compounds increase with Co content, but an easy-axis type of anisotropy, which is very important for permanent magnet application, could not be obtained. In this paper a study on the synthesis, structure and magnetic properties of the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds is presented.

2. Experimental

Ingots with the composition $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ ($0.4 \leq x \leq 1.0$) were prepared by arc-melting the constituent

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elements with a purity of at least 99.9% under protection of argon atmosphere. All the ingots were melted at least four times for homogenization. In order to compensate for the loss of Sm during melting and annealing, a 5% excessive amount of Sm relative to the stoichiometric composition was added. Then the alloys were sealed in a quartz tube and annealed under protection of argon atmosphere at 1403 K for 72 h, followed by quenching in water. X-ray diffraction (XRD) patterns and thermomagnetic analysis were employed to check the phase homogeneity. The thermomagnetic curves were measured in a vibrating sample magnetometer (VSM) from 77 K to above the Curie temperature in a low field of 0.05 T. The Curie temperatures were derived from the M^2-T curves by extrapolating M^2 to zero. The magnetization curves were measured at 5 K in a SQUID magnetometer in external magnetic fields up to 5 T. The saturation magnetizations M_s were obtained by plotting $M-1/B$ curves and extrapolating $1/B$ to zero.

In order to investigate the magnetocrystalline anisotropy, fine-powdered particles were mixed with epoxy resin and packed in a plastic tube of cylindrical shape, then the epoxy was allowed to harden while the plastic tube was positioned in an applied magnetic field of ~ 1 T with the cylinder axis parallel to the field direction, so that the cylinder axis direction becomes the easy magnetization direction (EMD).

3. Results and discussion

XRD and thermomagnetic analysis show that all the investigated $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds with x ranging from $x=0.4$ and $y=4.5$ to $x=1.0$ and $y=7.5$ are of single phase and crystallize in the $\text{Nd}_3(\text{Fe,Ti})_{29}$ -type structure. As an example, Fig. 1(a) shows the XRD pattern of the $\text{Sm}_3\text{Co}_{21.5}\text{Cr}_{7.5}$ compound, which was quite well indexed on the basis of the $\text{Nd}_3(\text{Fe,Ti})_{29}$ -type of structure with monoclinic symmetry and space group $A_{2/m}$. The lattice constants a , b , c , and the unit-cell volume V were derived from the XRD patterns and are listed in Table 1. It can be seen that a higher Co content substituted for Fe requires a higher Cr content to stabilize the 3:29 structure. The lattice constants a , b , c , and the unit-cell volume V decrease monotonically with increasing Co and Cr contents due to the smaller radius of Co atom compared with that of Fe.

In order to examine room temperature magnetocrystalline anisotropy the XRD patterns of the magnetically aligned powder sample of the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds were measured and are shown in Fig. 1(b). It is seen that for all the investigated compounds, the (204) reflection becomes dominant and other reflections have disappeared, which suggests that these compounds show easy-axis type of anisotropy. Based on the transformation relationship between the RCO_5 (1:5) structure and the

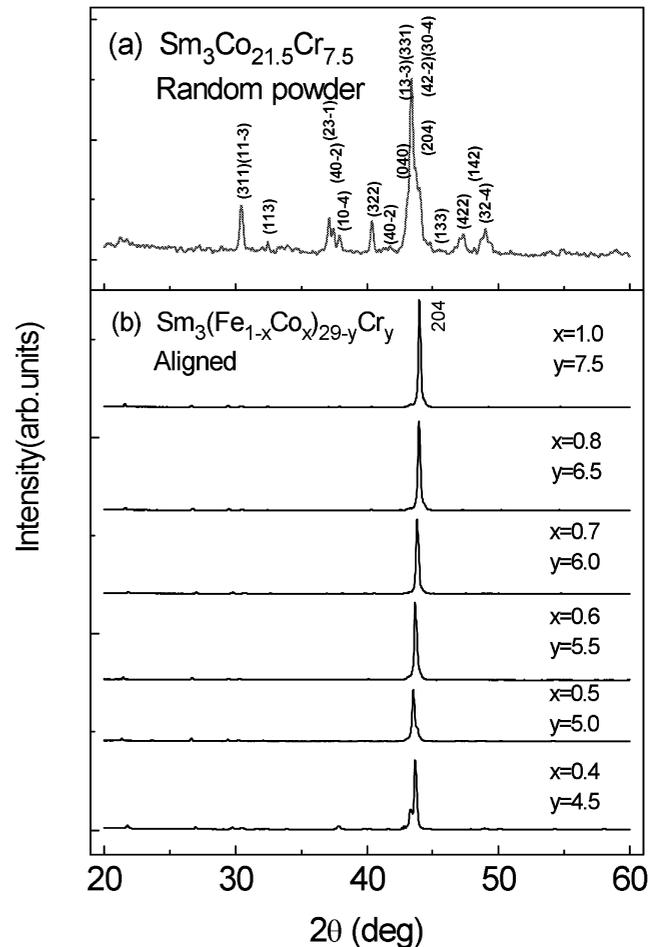


Fig. 1. XRD patterns of (a) the powdered $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ samples and (b) the magnetically aligned $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ samples.

monoclinic $\text{Nd}_3(\text{Fe,Ti})_{29}$ (3:29) structure, it is easily seen that the (204) reflection in the $\text{Nd}_3(\text{Fe,Ti})_{29}$ (3:29) structure corresponds to the (001) reflection in the RCO_5 (1:5) structure. So these compounds have an easy magnetization direction parallel to the [001] direction of 1:5 structure.

A study of the $\text{Y}_3(\text{Fe,Ti})_{29}$ compounds indicated that the magnetocrystalline anisotropy contribution resulting from the Fe-sublattice leads to an easy axis along the [110] direction of the 1:5 structure [18]. A study of the $\text{Gd}_3(\text{Co,Cr})_{29}$ compounds indicated that the magnetocrystalline anisotropy contribution resulting from the Co-sublattice leads to an easy axis along the [001] direction of the 1:5 structure [15]. As first order approximation, the magnetocrystalline anisotropy contribution resulting from the rare-earth sublattice can be described by the anisotropy constant K_1^{Sm} which is determined by the product of the second-order crystal field parameter A_{20} and the second-order Stevens coefficient α_j . It can be expressed by

$$K_1^{\text{Sm}} = -\frac{3}{2} \alpha_j \langle r^2 \rangle (3J^2 - J(J+1)) A_{20}, \quad (1)$$

where the quantities in angular brackets represent the

Table 1

Structure and magnetic parameters of $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ ($0.4 \leq x \leq 1.0$, $4.5 \leq y \leq 7.5$) compounds

Composition	a (Å)	b (Å)	c (Å)	β (deg)	V (Å ³)		
$x=0.4, y=4.5$	10.518	8.482	9.661	96.7	855.9		
$x=0.5, y=5.0$	10.510	8.466	9.625	96.9	850.3		
$x=0.6, y=5.5$	10.490	8.458	9.610	96.9	846.5		
$x=0.7, y=6.0$	10.464	8.458	9.605	96.8	844.0		
$x=0.8, y=6.5$	10.456	8.455	9.602	97.0	842.7		
$x=0.9, y=7.0$	10.436	8.418	9.578	96.9	835.2		
$x=1.0, y=7.5$	10.442	8.403	9.530	97.0	829.9		
	T_c (K)	$\mu_0 H_a$ (293 K) (T)	$\mu_0 H_a$ (5 K) (T)	M_s (5 K) ($\mu_B/\text{f.u.}$)	M_s (293 K) ($\mu_B/\text{f.u.}$)	K_1 (293 K) (MJ/m ³)	K_2 (293 K) (MJ/m ³)
$x=0.4, y=4.5$	736	2.8	6.0	40.3	36.3	0.32	0.11
$x=0.5, y=5.0$	688	3.4	8.5	30.7	28.9	0.68	0.26
$x=0.6, y=5.5$	663	4.2	11.3	25.5	24.4	1.13	0.51
$x=0.7, y=6.0$	607	5.1	14.2	21.0	20.3	1.30	0.68
$x=0.8, y=6.5$	566	6.0	18.1	18.4	17.4	1.39	0.82
$x=0.9, y=7.0$	440	4.5	15.5	14.7	12.0	0.71	0.42
$x=1.0, y=7.5$	285	–	–	8.7	–	–	–

expectation values. A_{20} is the second order crystal-field parameter that depends on the crystal structure and the composition of a given compound. It has been reported [19] that, in the Fe-rich 3:29 compounds $A_{20} < 0$ for $4e$ sites and $A_{20} > 0$ for the $2a$ sites. But the sum total of A_{20} at two Sm sites is negative. Considering that the value of α_j is positive for Sm, the value of K_1^{Sm} is positive. This suggests that the magnetocrystalline anisotropy contribution resulting from the Sm-sublattice in the Fe-rich $\text{Sm}_3\text{Fe}_{29-x}\text{Co}_x\text{Cr}_y$ compounds leads to an easy axis along the [001] direction of the 1:5 structure. In the Co-rich 3:29 compounds, although up to now no data of A_{20} have been published, by comparing the magneto-

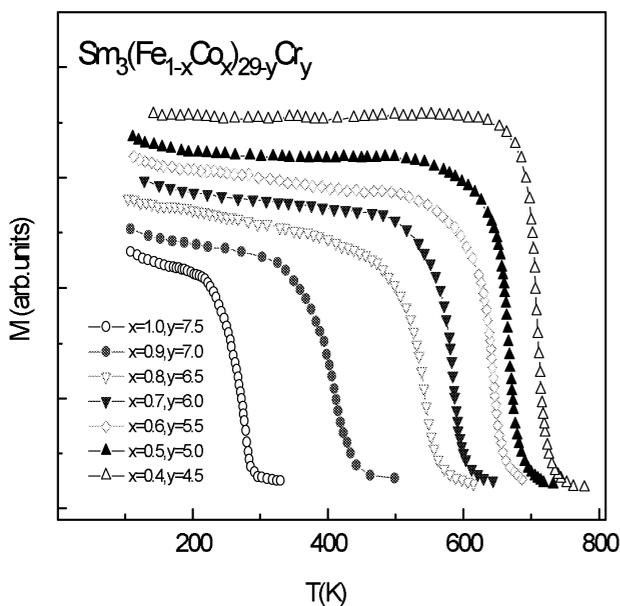


Fig. 2. Thermomagnetic curves of the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds.

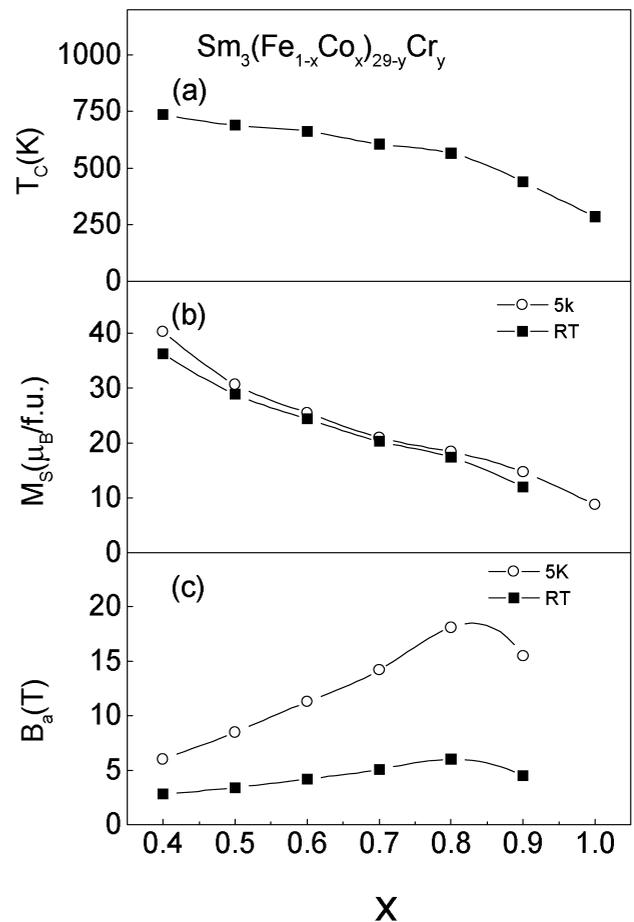


Fig. 3. (a) Curie temperature T_c , (b) saturation magnetization M_s and (c) magnetocrystalline anisotropy field B_a of the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds as functions of Co content.

crystalline anisotropy in the Co-rich $\text{Sm}_3\text{Fe}_{29-x-y}\text{Co}_x\text{Cr}_y$ compounds with that of $\text{Gd}_3\text{Fe}_{29-x-y}\text{Co}_x\text{Cr}_y$ (both have easy-axis type of anisotropy), it is found that the anisotropy of the $\text{Sm}_3\text{Fe}_{29-x-y}\text{Co}_x\text{Cr}_y$ compounds is much higher than that in the corresponding $\text{Gd}_3\text{Fe}_{29-x-y}\text{Co}_x\text{Cr}_y$ compounds. This suggests that the easy axis resulting from the Sm-sublattice in the Co-rich $\text{Sm}_3\text{Fe}_{29-x-y}\text{Co}_x\text{Cr}_y$ compounds is also along the [204] direction ([001] direction of 1:5 compound). Based on the analysis mentioned above it can be understood that in the Fe-based $\text{Sm}_3(\text{Fe}, \text{Cr})_{29}$ compounds the contribution of Fe-sublattice to the anisotropy is dominant and the compounds show a easy-plane type of anisotropy. When Co is substituted for Fe and Co content exceeds a certain value the contribution of Co- and Sm-sublattice to the anisotropy leads to the appearance of the easy-axis type of anisotropy.

Fig. 2 shows the thermomagnetic curves for the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds measured in a field of 0.05 T. The composition dependence of Curie temperatures T_c is shown in Fig. 3(a) and also listed in Table 1. It can be seen that with increasing Co and Cr contents the Curie temperature T_c decreases monotonically from 736 K for $x=0.4$ and $y=4.5$ to 285 K for $x=1.0$ and $y=7.5$. Such a composition dependence of T_c may result from the competition between the increase of T_c caused by the stronger Co–Co and Co–Fe exchange interactions compared with those of Fe–Fe interactions [20] and the decrease of T_c caused by the decrease of the transition metal atom number with increasing Cr content.

The magnetization curves were measured at 5 K and room temperature using a SQUID magnetometer in external magnetic fields up to 5 T applied in parallel or perpendicularly to the alignment direction. As an example Fig. 4 shows the magnetization curves of the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds measured at 293 K. The saturation magnetization M_s was derived on the basis of the saturation parts of the magnetization curves measured in the easy magnetization direction. The values of M_s as a function of Co content are shown in Fig. 3(b) and are also listed in Table 1. It can be seen that the values of M_s of the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds decrease monotonically with increasing Co and Cr contents. This has been explained for the Co composition dependence of the M_s in the $\text{Gd}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds [15] in terms of a rigid band model [21]. In the present case of the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds with $x \geq 0.4$, the up-spin band is entirely occupied, and the down-spin band begins to be filled up, and as a result, the average magnetic moment of the 3d-sublattice decreases gradually with increasing Co content. Moreover, the increase of the number of Cr atoms also leads to a further decrease of the average magnetic moment of the 3d-sublattice. The experimental results mentioned above indicate that in order to improve the Curie temperature and saturation magnetization a smaller amount of the stabilizing element is necessary.

The values of the anisotropy field B_a were obtained from $\Delta M-H$ plots by extrapolating the straight line parts to

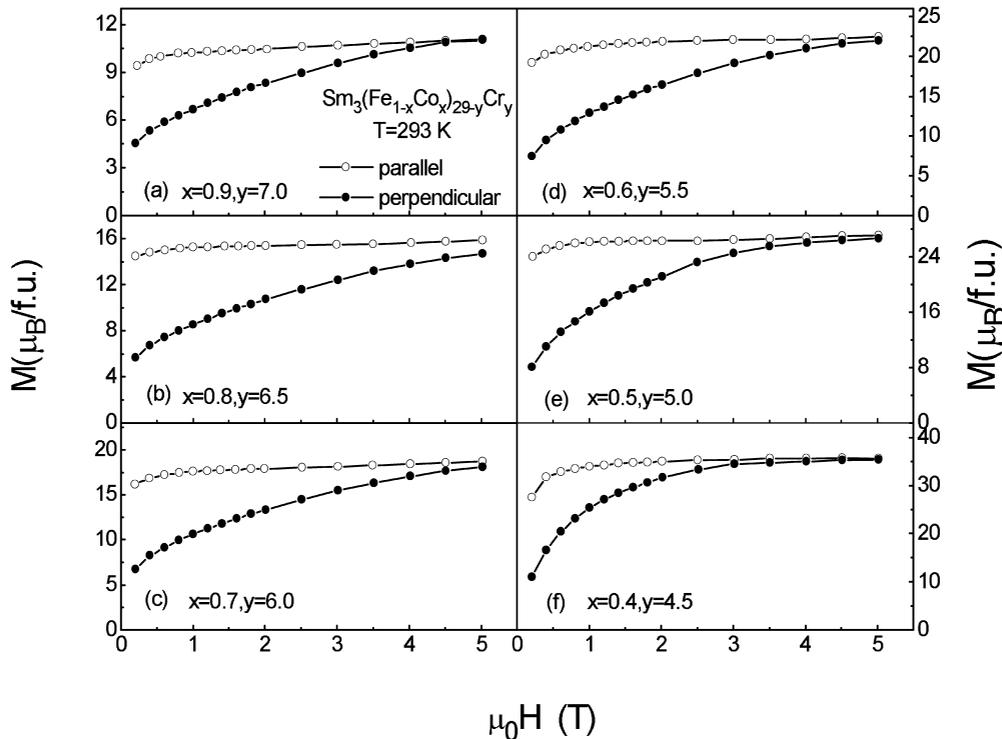


Fig. 4. Magnetization curves of the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds at 293 K.

zero, where $\Delta M = M_{\perp} - M_{\parallel}$, M_{\perp} and M_{\parallel} being the magnetization in the easy and hard magnetization direction, respectively.

The Co concentration dependence of B_a at 5 K and room temperature are shown in Fig. 3(c). It can be seen that B_a increases with increasing Co content, going through a maximum of 6.0 T at room temperature and 18.1 T at 5 K, and then decreases with further increasing Co content.

Magnetocrystalline anisotropy K_1 and K_2 of the compounds with uniaxial anisotropy are determined by the Sucksmith-Thompson equation [22]

$$\frac{B}{\mu_0 M} = \frac{2K_1}{\mu_0 M_s^2} + \frac{4K_2}{\mu_0 M_s^4} M^2 + N \quad (2)$$

where M is the magnetization measured in the external field B_a applied perpendicularly to the EMD and N the demagnetization factor. The values of K_1 and K_2 were derived by fitting Eq. (2) to the magnetization curves in hard magnetization direction as listed in Table 1. It can be seen that the values of K_1 at room temperature are positive for all the investigated compounds. This provides a further indication of the uniaxial anisotropy. The values of K_1 and K_2 increase monotonically with increasing Co content going through a maximum at $x=0.8$ and $y=6.5$ and then decrease with further increasing Co content, showing a similar Co composition dependence to the anisotropy field B_a .

In summary the $\text{Sm}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds have been synthesized for x ranging from 0.4 to 1.0. The higher Co content substituted for Fe requires a higher Cr content to stabilize the 3:29 structure. The Curie temperature T_c decreases monotonically with increasing Co and Cr content from 736 K for $x=0.4$ and $y=4.5$ to 285 K for $x=1.0$ and $y=7.5$. The saturation magnetization M_s decreases with increasing Co and Cr contents. It is worth noting that all the compounds investigated show a room temperature uniaxial anisotropy and the anisotropy field increases with increasing Co content, going through a maximum at $x=0.8$ and $y=6.5$, and then decreases with further increasing Co content. In order to improve the permanent magnetic properties of the 3:29-type compounds it is necessary to reduce the content of the stabilizing element.

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References

- [1] S.J. Collocott, R.K. Day, J.B. Dunlop, R.L. Davis, in: Proceedings of the 7th International Symposium on Magnetic Anisotropy and Coercivity in Rare Earth-Transition Metal Alloys, Canberra, 1992, p. 437.
- [2] H.S. Li, J.M. Cadogan, J.M. Xu, S.X. Dou, H.K. Lin, *Hyperfine Interact.* 94 (1993) 1929.
- [3] Z. Hu, W.B. Yelon, *J. Appl. Phys.* 76 (1994) 6147.
- [4] O. Kalogirou, V. Psycharis, L. Saettas, D. Niarchos, *J. Magn. Magn. Mater.* 5 (1995) 270.
- [5] M.R. Ibarra, L. Morellon, J. Blasco, L. Pareti, P.A. Algarabel, J. Garcia, F. Albertini, A. Paoluzzi, *J. Phys. Condens. Matter.* 6 (1994) L771.
- [6] F.M. Yang, B. Nasunjilegal, H.Y. Pan, J.L. Wang, R.W. Zhao, B.P. Hu, Y.Z. Wang, H.S. Li, J.M. Cadogan, *J. Magn. Magn. Mater.* 135 (1994) 298.
- [7] C.D. Fuerst, F.E. Pinkerton, J.F. Herbst, *J. Appl. Phys.* 76 (1994) 6144.
- [8] J.M. Cadogan, H.S. Li, A. Margarian, J.B. Dunlop, D.H. Ryan, S.J. Collocott, R.L. Davis, *J. Appl. Phys.* 76 (1994) 6138.
- [9] X.-F. Han, H.-g. Pan, H.-L. Liu, F.-M. Yang, *Phys. Rev. B* 56 (1997) 8867.
- [10] H. Pan, F. Yang, Y. Chen, X. Han, N. Tang, C. Chen, Q. Wang, *J. Phys. Condens. Matter.* 9 (1997) 2499.
- [11] F. Huang, J.K. Liang, Q.L. Liu, X.L. Chen, G.Y. Huo, *J. Phys. Condens. Matter.* 10 (1998) 9183.
- [12] F.M. Yang, B. Nasunjilegal, J.L. Wang, H.Y. Pan, W. Qin, N. Tang, R.W. Zhao, B.P. Hu, Y.Z. Wang, G.C. Liu, H.S. Li, J.M. Cadogan, *J. Appl. Phys.* 76 (1994) 1971.
- [13] B.P. Hu, G.C. Liu, Y.Z. Wang, B. Nasunjilegal, N. Tang, F.M. Yang, H.S. Li, J.M. Cadogan, *J. Phys. Condens. Matter.* 6 (1994) L595.
- [14] D. Yang, J.L. Wang, N. Tang, Y.P. Shen, F.M. Yang, *Appl. Phys. Lett.* 74 (1999) 4020.
- [15] W.Q. Wang, J.L. Wang, N. Tang, G.H. Wu, F.M. Yang, H.M. Jin, *J. Appl. Phys.* 90 (2001) 1920.
- [16] N. Tang, X.Y. Yin, D. Yang, J.L. Wang, G.H. Wu, F. Yang, Y.P. Shen, X.P. Zhong, *J. Appl. Phys.* 87 (2000) 5272.
- [17] V.R. Shah, G. Markandeyulu, K.V.S. Rama, M.Q. Huang, K. Silisha, M.E. McHenry, *J. Appl. Phys.* 85 (1999) 4678.
- [18] D. Courtois, H.S. Li, J.M. Cadogan, *Solid State Commun.* 98 (1996) 565.
- [19] H.-S. Li, D. Courtois, J.M. Cadogan, *J. Appl. Phys.* 79 (1996) 4622.
- [20] J.L. Wang, N. Tang, R.W. Zhao, F.M. Yang, R. de Boer, *J. Magn. Magn. Mater.* 166 (1997) 355.
- [21] Y. Matsuura, S. Hirosawa, H. Yamamoto, S. Fujimura, M. Sagawa, *Appl. Phys. Lett.* 46 (1985) 308.
- [22] W. Sucksmith, J.E. Thompson, *Proc. R. Soc. London, Ser. A* 225 (1954) 362.