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Influence of Mn substitution on the structure and magnetic properties of $\text{Sm}_2\text{Co}_{17}$ compounds

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Abstract

The effect of Mn substitution for Co on the structure and magnetic properties of $\text{Sm}_2\text{Co}_{17-x}\text{Mn}_x$ compounds with $x = 0-8$ were investigated by means of x-ray diffraction (XRD) and magnetization measurements. XRD patterns show that all samples are single phase with rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure. The substitution of Mn for Co leads to a monotonic increase in unit cell volume. The saturation magnetization increases slightly for $x \leq 2$, then decreases quickly with increasing Mn content. The Curie temperature T_C is found to decrease monotonically with increasing Mn concentration. XRD measurement on magnetically aligned samples exhibits an easy-axis type of magnetic anisotropy at room temperature with $x = 1-7$. The magnetocrystalline anisotropy field $\mu_0 H_A$ is found to increase with increasing Mn concentration, attaining a maximum value of 14 T at $x = 1$.

1. Introduction

Rare-earth cobalt intermetallic compounds R_2Co_{17} have attracted much attention since the discovery of $\text{Sm}_2\text{Co}_{17}$ magnets [1]. Although they have high saturation magnetization, it is hard to find practical applications for the R_2Co_{17} series compounds in the high-energy product magnets, due to the unfavourable anisotropy. These compounds have either weak uniaxial (e.g., $\text{Sm}_2\text{Co}_{17}$) or planar (e.g., Y_2Co_{17} , $\text{Pr}_2\text{Co}_{17}$) anisotropy. In previous studies, the effect of the various elemental substitutions (such as Ga, Al and Si) for Fe in the R_2Fe_{17} compounds on the formation, structure and magnetic properties, especially the magnetocrystalline anisotropy, has been investigated [2, 3]. The results indicate that these non-magnetic atoms play an important role in determining the easy magnetization direction (EMD) of these compounds. Recent studies have shown that the substitution of Ga, Al and Mn also has a significant effect on the magnetocrystalline anisotropy in R_2Co_{17} -based compounds [4–11]; for example the EMDs of $\text{Y}_2\text{Co}_{17-x}\text{Mn}_x$ ($x \geq 1$) [6], $\text{Gd}_2\text{Co}_{17-x}\text{Al}_x$ ($x \geq 5$) [9] and $\text{Gd}_2\text{Co}_{17-x}\text{Ga}_x$ ($x \geq 1$) [10] compounds are uniaxial at room temperature. As a result of increase of the *c*-axis anisotropy

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of the transition-metal sublattice, the spin-reorientation transitions in $R_2Co_{17-x}Mn_x$ ($R = Pr, Nd, Tb, Dy, Ho$) [11] compounds, in which the second-order Stevens coefficient α_2 of the rare earth is negative, were observed. In this paper, the influence of the substitution of Mn for Co in $Sm_2Co_{17-x}Mn_x$ ($x = 0-8$) compounds on the structure and magnetic properties is reported.

2. Experiment

The $Sm_2Co_{17-x}Mn_x$ ($x = 0-8$) alloys were prepared by arc melting in an argon atmosphere of high purity. The raw materials of Sm, Co and Mn were at least 99.9% pure. The as-cast ingots were annealed under vacuum at 1273 K for 100 h, and then quenched into water. X-ray diffraction (XRD) using Cu $K\alpha$ radiation was used to determine phase purity, crystal structure and lattice parameters. The saturation magnetic moment μ_s at 5 K was deduced from the data collected on free powder samples using a SQUID magnetometer in a field up to 6.5 T. The Curie temperature T_C was determined from the temperature dependence of magnetization measured with a SQUID magnetometer ($0 < T < 400$ K) and a Faraday balance ($T \geq 300$ K) in a field of 0.1 T. The aligned samples for the magnetocrystalline anisotropy studies were prepared by mixing the powder with epoxy resin and aligning in a magnetic field of 1 T. The XRD measurement was also used to determine the easy magnetization direction (EMD) at room temperature. The anisotropy field H_A was obtained from the magnetization curves measured along and perpendicular to the direction of alignment.

3. Results and discussion

XRD patterns indicate that all samples are single phase with the rhombohedral Th_2Zn_{17} -type structure. The XRD pattern of $x = 2$ is presented in figure 1 as an example. The lattice parameters a and c and the unit cell volumes v are listed in table 1. The lattice parameters a and c increase monotonically with increasing Mn content. The unit cell volume is found to increase nearly linearly at a rate of about 5.3 \AA^3 per Mn atom. Such an increase of unit cell volume is similar to the Ga substitution for Co in $Sm_2Co_{17-x}Ga_x$ compounds [4].

Table 1. The lattice parameters a and c , unit cell volume v , Curie temperature T_C , magnetic moment μ_s at 5 K and magnetocrystalline anisotropy field H_A of $Sm_2Co_{17-x}Mn_x$ compounds.

Compounds	a (\AA)	c (\AA)	v (\AA^3)	T_C (K)	μ_s ($\mu_B \text{ fu}^{-1}$)	H_A (kOe)
Sm_2Co_{17}	8.400	12.215	746.42	1203	23.7	7.1
$Sm_2Co_{16}Mn_1$	8.438	12.245	754.96	1085	27.1	14
$Sm_2Co_{15}Mn_2$	8.457	12.276	760.32	962	29.3	13.5
$Sm_2Co_{14}Mn_3$	8.475	12.317	766.22	809	25.8	12.6
$Sm_2Co_{13}Mn_4$	8.502	12.370	774.27	571	23.1	11.1
$Sm_2Co_{12}Mn_5$	8.504	12.397	776.5	475	19.5	9.5
$Sm_2Co_{11}Mn_6$	8.515	12.415	779.51	359	15.9	6.3
$Sm_2Co_{10}Mn_7$	8.537	12.440	785.22	330	—	1.8
$Sm_2Co_9Mn_8$	8.563	12.469	791.78	72.9	7.06	7.1

Figure 2 presents the magnetization curves of $Sm_2Co_{17-x}Mn_x$ ($1 \leq x \leq 8$) free powders. For $1 \leq x \leq 7$, it shows a typical ferromagnetic behaviour, while for $x = 8$, it shows a non-typical ferromagnetic behaviour, which suggests that the compounds are very likely magnetically inhomogeneous in this intermediate concentration range [12]. For $x = 8$, it is

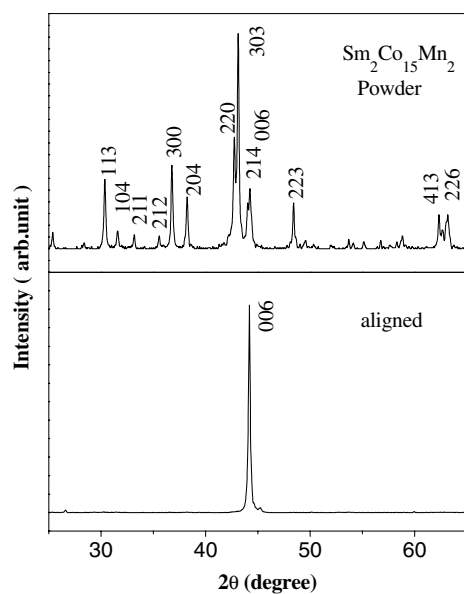


Figure 1. X-ray diffraction patterns at room temperature of powder and magnetic aligned samples of $\text{Sm}_2\text{Co}_{15}\text{Mn}_2$ compounds.

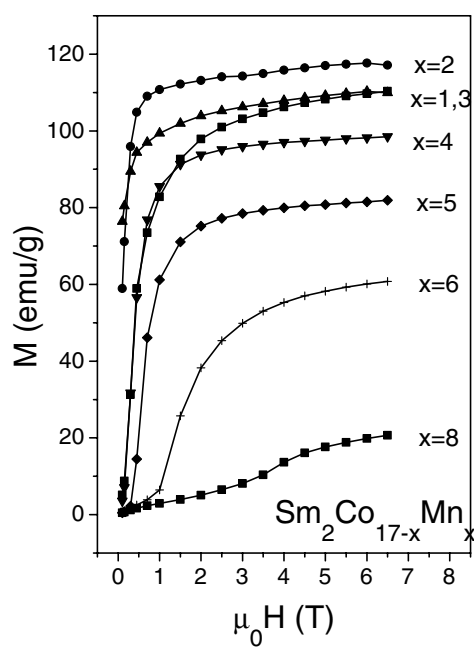


Figure 2. The magnetization curves of the $\text{Sm}_2\text{Co}_{17-x}\text{Mn}_x$ compounds.

composed of ferromagnetic clusters and also many anti-ferromagnetic clusters. Therefore a non-typical ferromagnetic behaviour is observed for the sample.

The values of saturation magnetization μ_s for $\text{Sm}_2\text{Co}_{17-x}\text{Mn}_x$ compounds at 5 K are listed

in table 1 and shown in figure 3; also the data of $\text{Sm}_2\text{Co}_{17-x}\text{Ga}_x$ are plotted for comparison [4]. The saturation magnetization increases slightly for $x \leq 2$, then decreases quickly with increasing Mn content. This behaviour is quite different from that of $\text{Sm}_2\text{Co}_{17-x}\text{Ga}_x$, which shows a nearly linear decrease of saturation magnetization. From figure 3 one can also observe that the decline in saturation magnetization of $\text{Sm}_2\text{Co}_{17-x}\text{Ga}_x$ is faster than that in the case of a simple magnetic dilution, while for $\text{Sm}_2\text{Co}_{17-x}\text{Mn}_x$ μ_s is much larger than the value of the simple dilution for $x \leq 7$. This phenomenon implies that the change in saturation magnetization is not only due to the reduced Co content, but also due to the change of the magnetic moment per Co atom. Similar results are also found in the $\text{Y}_2\text{Co}_{17-x}\text{M}_x$ ($M = \text{Si}, \text{Al}, \text{Ga}, \text{Mn}$) [6]. As found in $\text{Y}_2\text{Co}_{17-x}\text{Mn}_x$ compounds, μ_{3d} increases slightly for $x \leq 2$, then decreases slowly with increasing Mn content, which implies that Mn atoms carry magnetic moment and couple parallel to the Co moment. It is well known that the large spatial extent of the 3d wavefunctions leads to 3d-electron energy bands rather than to a 3d level [13]. So the change of the 3d-band structure by the substitution of M and a transfer of the outer electrons of M to the 3d band should be taken into consideration. Different substitution of M will result in different changes of magnetization.

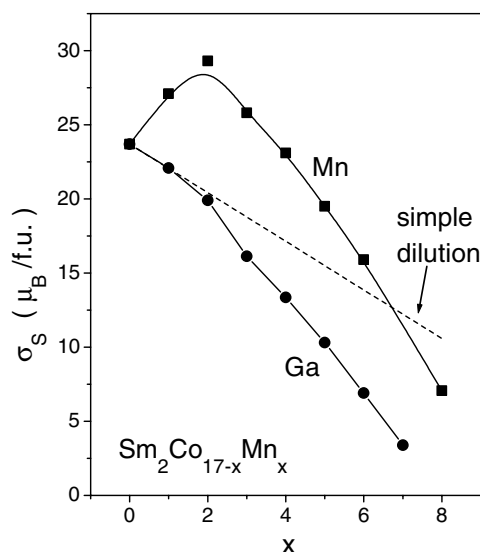


Figure 3. Concentration dependence of the saturation moments at 5K for $\text{Sm}_2\text{Co}_{17-x}\text{M}_x$ ($M=\text{Mn}, \text{Ga}$) compounds and also the data of the simple dilution model.

Figure 4 gives the temperature dependence of magnetization of $\text{Sm}_2\text{Co}_{17-x}\text{Mn}_x$ ($x = 0-8$) compounds. For high Mn concentration such as $x = 5-7$, the $M(T)$ curve of the compounds shows a complicated behaviour. The drastic drop of the magnetization at low temperature is associated with unfreezing of domain-wall movement or the first order rotation of the magnetization vector. Such drops were not observed when cooling the samples in a field. Similar phenomena were also observed in the $\text{Sm}_2(\text{Co},\text{Ga})_{17}$ [5] and $\text{R}(\text{Co},\text{M})_5$ [14] compounds and all these have been ascribed to the presence of narrow Bloch walls [15]. At the lowest temperature the thermal energy is not yet strong enough to surmount the energy barrier needed to move the narrow walls. This leads to the absence of an appreciable net magnetization in the low temperature region. At temperatures of sufficiently high thermal energy, the field applied can remove all the walls from the sample so that the net magnetization is large. If the

sample is cooled in the presence of a magnetic field prior to the measurements, the typical initial rise in the M versus T curves is generally absent. The origin of narrow walls is the large ratio of the magnetocrystalline anisotropy energy to the exchange energy. It is well known that the anisotropy energy increases strongly with decreasing temperature owing to the strongly temperature-dependent rare-earth contribution. The compounds with Sm have comparatively large rare-earth anisotropy. The Mn substitution for Co strongly decreases the Curie temperature and the exchange energy, which brings the ratio of the magnetocrystalline anisotropy energy to the exchange energy into the narrow Bloch wall regime.

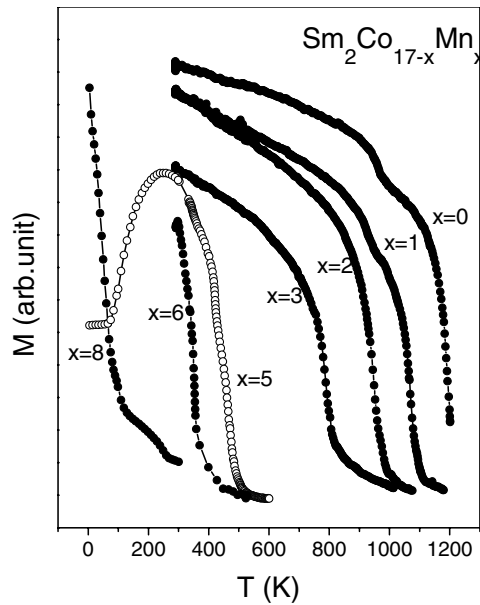


Figure 4. The temperature dependence of the magnetization of $\text{Sm}_2\text{Co}_{17-x}\text{Mn}_x$ compounds.

From figure 5 it is found that Curie temperature T_C decreases monotonically with increasing M concentration, which is nearly the same for $M = \text{Ga}$ and Mn except for high Mn concentration [4]. It is well known that the Curie temperature is mainly determined by the T-T interaction in the rare-earth-transition-metal intermetallic compounds because the Sm-Co exchange-coupling constant is found to be about one order of magnitude smaller than that of exchange coupling between Co-Co (18.64×10^{-22} J). In the molecular-field description, if we only consider the T-T interaction, the relation between T_C and exchange interaction constant should be

$$3k_B T_C = 2J_{TT} Z_{TT} S_T (S_T + 1)$$

where J_{TT} stands for the T-T exchange interaction constant. S_T is the so-called pseudospin, which is related to the magnetization of the 3d sublattice M_T by

$$M_T = -g_T S_T \mu_B.$$

So T_C is determined by both J_{TT} and M_T .

At first M_T (Mn) is slightly increased with small Mn substitution; the decrease in T_C is mainly due to the decrease of J_{TT} . Then the decreases of both Co-Co exchange interaction and magnetization result in a rapid decrease of T_C with further increasing M substitution.

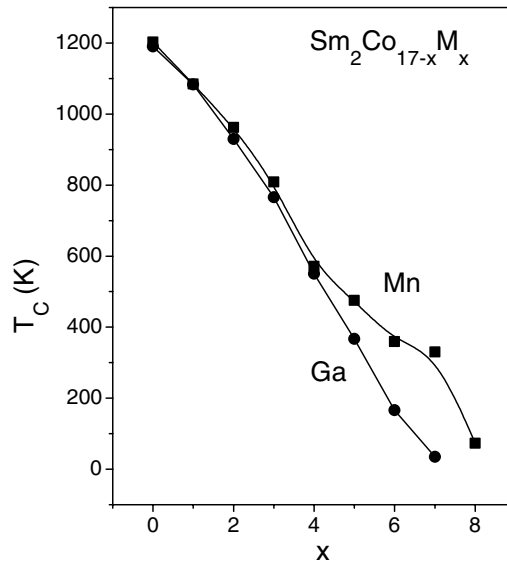


Figure 5. Concentration dependence of the Curie temperature of $\text{Sm}_2\text{Co}_{17-x}\text{M}_x$ ($M = \text{Mn}, \text{Ga}$) compounds.

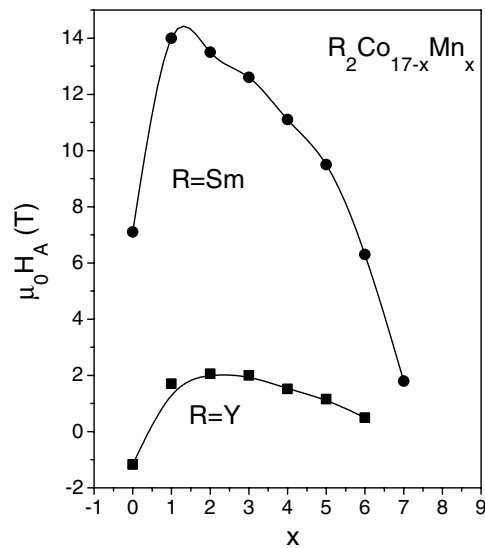


Figure 6. Concentration dependence of the anisotropy field of $\text{Sm}_2\text{Co}_{17-x}\text{Mn}_x$ and $\text{Y}_2\text{Co}_{17-x}\text{Mn}_x$ compounds.

Because $M_T(\text{Mn})$ is found to be larger than $M_T(\text{Ga})$, it can be concluded that Ga atoms have a larger effect in decreasing the exchange interaction than Mn atoms do.

XRD measurements on magnetically aligned powder samples demonstrate that the EMDs of $\text{Sm}_2\text{Co}_{17-x}\text{Mn}_x$ compounds at room temperature are all c -axis. Figure 1 gives a XRD pattern of $x = 2$. The magnetocrystalline anisotropy fields $\mu_0 H_A$ at room temperature are listed in table 1 and shown in figure 6. $\mu_0 H_A$ is found to increase sharply with Mn concentration,

attaining a maximum value of 14 T at $x = 1$, then decrease with the increased Mn concentration.

It is well known that the overall magnetocrystalline anisotropy of R–T compounds consists of two contributions originating from the R and T sublattices. For Sm₂Co_{17–x}Mn_x compounds, the net anisotropy constant of the total lattice can be expressed as follows:

$$K_1^{Tot} = K_1^T + K_1^{Sm} = K_1^T - 3/2\alpha_J \langle r^2 \rangle (3J_z^2 - J(J+1)) A_2^0.$$

The anisotropy of the rare-earth sublattice can be described by the product of the second-order crystal parameter A_2^0 and the second-order Stevens coefficient α_J on the basis of the single-ion model [16], where the second-order crystal field parameter A_2^0 depends on the crystal structure and composition of the given compound. For the Sm³⁺ ion, $\alpha_J > 0$ and a negative A_2^0 makes the Sm sublattice with $K_1^{Sm} > 0$ have axial anisotropy.

The effect of Mn substitution on the magnetocrystalline anisotropy of the T sublattice can be derived from the results of the Y₂Co_{17–x}Mn_x compounds since Y is a non-magnetic atom, which is also presented in figure 6. Substitution of Mn for Co leads to a change of the magnetocrystalline anisotropy of the Co sublattice from the basal plane to the *c*-axis and strongly increases the uniaxial anisotropy of Y₂Co_{17–x}Mn_x. The magnetocrystalline anisotropy field H_A is found first to increase and then decrease with increasing Mn concentration, attaining a maximum value of 20.6 kOe at $x = 3$. The change of the easy magnetization direction from the basal plane to the *c*-axis and the increase of H_A can be attributed to a preferential occupation on the plane seeking 6c dumbbell cobalt sites by the alloying elements (Al, Ti, Mn, Fe) [17]. In Y₂Co₁₇ compounds, the 18f site of Co makes a positive contribution to the anisotropy (*c*-axis), while the 18h, 9d and 6c sites make negative contributions (basal plane). In particular, the 6c site was the largest negative contribution [18]. The neutron diffraction study on Y₂Co_{17–x}Mn_x compounds [19] demonstrated that 90% of Mn atoms prefer to occupy the 6c sites, while 5% of Mn atoms occupy the 18h and 9d sites respectively, meanwhile the Mn atoms completely avoid the 18f sites.

However, from figure 6 the drastic change of magnetocrystalline anisotropy of Sm₂Co_{17–x}Mn_x compounds cannot solely be attributed to the contribution of the T sublattice. The Mn substitution also leads to an increase of the Sm sublattice anisotropy, which is the result of increase in the amplitude of the negative A_2^0 . So Mn substitution also had a large effect on the second-order crystal field parameter A_2^0 , which depends on the crystal structure and composition.

Acknowledgment

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