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$Sm_3(Fe,Co,Mo)_{29}$ compounds: promising materials for permanent magnets*

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The outstanding hard-magnetic properties are reported of $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ compounds with x=12, 14, 16. In this alloy system, only a small amount of Mo is needed to stabilize the 3:29 structure so that the magnetic properties are not seriously affected by the presence of this nonmagnetic element. Substitution of Co for Fe leads to a significant increase of the magnetic anisotropy, and for $x \geq 14$ the easy magnetization direction changes from easy plane to the easy axis. In this alloy system, the compound $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$ is a very promising candidate for permanent magnet applications. Its room temperature saturation magnetization ($\mu_0 M_s$=1.5 T) and anisotropy field (B_{an}=6.5 T) are comparable to the values for $Nd_2Fe_{14}B$ ($\mu_0 M_s$=1.6 T and B_{an} =7 T). However, the Curie temperature of $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$ is 1020 K, which is appreciably higher than that for $Nd_2Fe_{14}B$ (T_C=588 K).

Keywords: permanent magnet material, anisotropy, saturation magnetization, Curie temperature
PACC: 7550B, 7550C, 7530G, 7520E

1. Introduction

The discovery of the compound $Nd_2Fe_{14}B$[1−3] with its large room temperature saturation magnetization ($\mu_0 M_s$=1.6 T), and anisotropy field (B_{an}=7.0 T) has been a milestone in the permanent magnet development and has given a new impetus to the investigation on the Fe-rich rare-earth-transition-metal intermetallic compounds. Despite of the excellent performance of Nd-Fe-B based magnets, their application is restricted to a rather small temperature range because of the relatively low Curie temperature (T_C=588 K) of $Nd_2Fe_{14}B$. Therefore, the search for permanent magnet materials with higher Curie temperature is of utmost importance.

Recently, much attention has been paid to the research on compounds of the type R_3 $(T,M)_{29}$, where R denotes a rare-earth element, T for a transition metal such as Fe or Co, and M for a stabilizing element like Ti, Mo, V, Cr or Mn. Also the nitrides of the R_3 $(T,M)_{29}$ compounds have been the subject of research,[4−8] particularly because the easy magnetization direction (EMD) can be influenced by introduction of interstitial nitrogen atoms. Yang *et al*[9] and Hu *et al*[10] have synthesized $Sm_3(Fe,Ti)_{29}N_y$ compounds with a strong easy-axis anisotropy and high-saturation magnetization by means of a gas-solid reaction. Unfortunately, at high temperatures the stability of all the interstitial compounds is not maintained. Pan *et al*[11] have synthesized the compound $Sm_3(Fe,Mo)_{29}$ with a very low content of the stabilizing element Mo, which is important because in this case the magnetic properties are only slightly affected by the non-magnetic Mo. However, since in the Fe-based 3:29 compounds the contribution of the Fe sublattice to the magnetocrystalline anisotropy is along the $[40\bar{2}]$ direction ([110] direction of the 1:5 structure),[12] the $Sm_3(Fe,Mo)_{29}$ compound exhibits easy-plane type of anisotropy, and therefore cannot be used as a starting material for the production of permanent magnets. Later, Yang *et al*[13] and Wang *et al*[14] found that $Gd_3(Fe_{1-x}Co_x)_{29-y}Cr_y$ compounds possess an easy-axis anisotropy at room temperature for $x \geq 0.4$ and also have a high Curie temperature. However, in these compounds, due to antiferromagnetic coupling between the Gd and the transition-

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metal moments, the saturation magnetization is not very high. In addition, in these compounds, the amount of Cr needed for stabilization of the crystal structure is much larger than the amount of Mo and also increases with increasing Co content,[11,14] which leads to a decrease of the Curie temperature and the saturation magnetization.

2. Experiment

$Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ compounds with x=12, 14, 16 were prepared by arc melting the constituent metals of high purity (99.9% or higher) in a water-cooled copper crucible in an argon atmosphere. The ingots were melted five times to ensure homogeneity; and 30% excess of Sm with respect to the stoichiometric composition was added to compensate the loss of it during melting and annealing. After the arc-melting process, the ingots were sealed in evacuated quartz tubes and annealed at 1473 K for 72 h followed by water quench. x-ray diffraction (XRD) with Cu-$K\alpha$ radiation was used to identify the phases and to determine the lattice parameters of the compounds. Thermomagnetic analysis (TMA) was performed in a magnetic balance in a field of 0.1 T at temperatures ranging from room temperature to above the Curie temperature. Magnetization curves were recorded in a SQUID magnetometer at 5 and 293 K in fields up to 5 T. Fine powders were mixed with epoxy resin and put in a plastic tube of cylindrical shape. The mixture was allowed to solidify in an applied magnetic field of about 1 T with the cylinder axis parallel to the field direction, so that the EMD was along the cylinder axis and the hard magnetization direction (HMD) perpendicular to this axis.

3. Results and discussion

The XRD and TMA measurements show that all the $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ (x=12, 14, 16) compounds investigated crystallize in the $Nd_3(Fe, Ti)_{29}$-type structure. A small amount of 2:17 phase was present which, for $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$, was estimated to be 4at%. This estimate is based on the chemical analysis by means of inductively coupled plasma atomic-emission spectrometry, which shows the atomic ratio of Sm, Fe, Co and Mo in this compound to be 3.0:12.0:16.0:0.85. As an example, the XRD pattern of a randomly oriented-powder sample of $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$ is shown in Fig.1(a). The XRD patterns of the compounds can be quite well indexed based on the $Nd_3(Fe,Ti)_{29}$-type structure with a monoclinic symmetry and space group $A_{2/m}$. The lattice parameters derived from the XRD patterns of randomly oriented powders are listed in Table 1, together with the data of Sm_3 (Fe, Mo)$_{29}$ (from Ref.[11]). It is seen that substitution of Co for Fe leads to a decrease of the lattice parameters a, b, and c, which is due to the smaller atomic radius of the Co atom compared with Fe.

Table 1. Structure and magnetic parameters of $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ (x=0, 12, 14, 16) compounds.

x	a/nm	b/nm	c/nm	β/(°)	V/nm^3	EMD (293 K)	T_C/K	B_{an} (293K)/T	B_{an} (5 K)/T	$\mu_0 M_s$ (293 K)/T	$\mu_0 M_s$ (5 K)/T
16	1.048	0.846	0.962	96.81	0.847	[204]	1020	6.5	9.4	1.50	1.58
14	1.051	0.848	0.965	96.67	0.854	[204]	970	5.7	10.0	1.50	1.58
12	1.052	0.848	0.965	96.65	0.855	isotropic	920	—	—	1.70	1.78
0*	1.063	0.857	0.973	96.88	0.880	plane	445	4.1	13.4	1.07	1.35

*Deduced from Tables 1 and 2 of Ref.[11].

In order to examine the magnetic anisotropy at room temperature, the XRD patterns of magnetically aligned-powder samples of $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ with x=14 and 16 were measured at room temperature. As an example, the XRD pattern of $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$ is given in Fig.1(b). It shows that, after alignment, the (204) reflection becomes dominant and that other peaks have disappeared. Based on the transformation relationship between the RCo_5 (1:5) structure and the monoclinic $Nd_3(Fe,Ti)_{29}$ (3:29) structure, one knows that the (204) reflection in the $Nd_3(Fe,Ti)_{29}$ (3:29) structure corresponds to the (001) reflection in the RCo_5 (1:5) structure. This indicates that the anisotropy is of easy-axis type in these two compounds. The XRD pattern of magnetically aligned powders of $Sm_3Fe_{16.1}Co_{12}Mo_{0.9}$ has also been measured and it is found that no reflection is particularly enhanced or reduced. This can be explained by the significant change of the magnetic anisotropy upon substituting Co for Fe, which leads to a change of the easy magnetization direction in the $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ system from easy plane

to easy axis when x varies from 0 to 16. For x=12, the anisotropy is about zero and no enhanced reflections are observed.

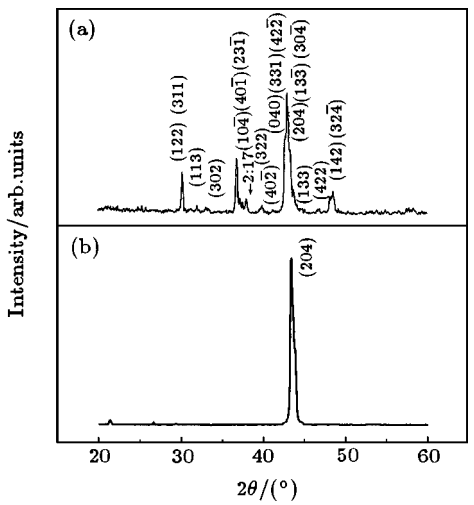


Fig.1. XRD patterns for (a) a random-powder $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$ sample and (b) a magnetically aligned $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$ sample.

As an example, the magnetization curves at 5 and 293 K of $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$ are shown in Fig.2. The values of the anisotropy field B_{an} (see Table 1) were obtained by plotting $\Delta\mu_0 M$ ($=\mu_0 M_{easy} - \mu_0 M_{hard}$) versus B and by linearly extrapolating $\Delta\mu_0 M$ to zero. Besides the change of the anisotropy from easy plane to easy axis, it can be seen that, at room temperature, B_{an} reaches a value of 6.5 T for x=16.

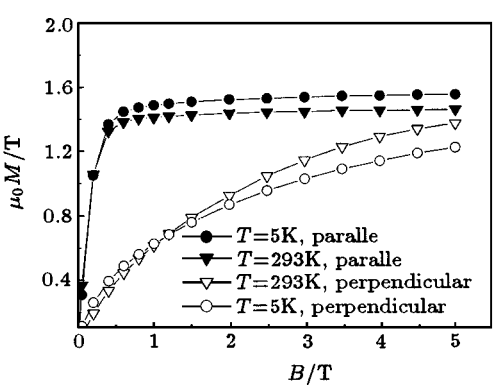


Fig.2. Magnetization curves of the $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$ compounds at 5 and 293 K.

In $Y_3(Fe,Ti)_{29}$ compounds,[12] the contribution of the Fe sublattice to the anisotropy is along the $[40\bar{2}]$ direction ([110] of the 1:5 structure) whereas, in $Gd_3(Co,Cr)_{29}$ compounds,[15] the contribution of the Co sublattice is along the [204] direction ([001] direction of the 1:5 structure). The contribution of the Sm sublattice to the anisotropy can, in first-order approximation, be described by the anisotropy constant K_1^{Sm},

$$K_1^{Sm} = -\frac{3}{2}\alpha_J < r^2 >< 3J^2 - J(J+1) > A_{20}, \quad (1)$$

where the quantities in angular brackets represent the expectation values. A_{20} is the second-order crystal-field coefficient that depends on the crystal structure and the composition of a given compound. It was reported that the sum of the A_{20} values at the two Sm sites in 3:29 compounds is negative.[16] Considering that the sign of the second-order Stevens coefficient α_J is positive for Sm, it follows that the value of K_1^{Sm} is positive. So the magnetocrystalline-anisotropy contribution resulting from the Sm sublattice is along the [204] direction ([001] direction of the 1:5 structure). The Fe-based $Sm_3(Fe,Mo)_{29}$ compounds show easy-plane type of anisotropy because the contribution of the Fe sublattice to the anisotropy is dominant. When Co is substituted for Fe and the Co content increases, the easy-plane anisotropy of the compound decreases. At a Co content corresponding to x=12, the easy-plane anisotropy vanishes and the compound becomes isotropic. Further increasing the Co content, the contribution of the Co sublattice to the anisotropy becomes dominant, which together with the contribution of the Sm sublattice, causes the compounds to exhibit an easy-axis anisotropy.

Figure 3 shows the temperature dependence of the magnetization of the $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ compounds measured in an applied field of 0.1 T. The Curie temperatures listed in Table 1 have been derived from M^2-T curves by extrapolating M^2 to zero. It can be seen that T_C increases from 445 K for x=0 to 1020 K for x=16. It is well known that, in $R_3(T, M)_{29}$ compounds, the T-T exchange interaction is the strongest interaction that determines the magnetic-ordering temperature. Similar to the case of $Y(Fe,Co)_{10}Si_2$,[17] it may be that, in the $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ system, the exchange interaction of the Co–Co pairs and the Co–Fe pairs is larger than that of the Fe–Fe pairs. Therefore, it is expected that the substitution of Co for Fe would lead to an increase of T_C. Moreover, it is noteworthy that the concentration of the stabilizing element Mo in the $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ compounds is quite low, unlike the case of $Gd_3Fe_{29-x-y}Co_xCr_y$,[14] in which for a large Co content, the Cr content increases with increasing Co content, leading to a decrease of T_C.

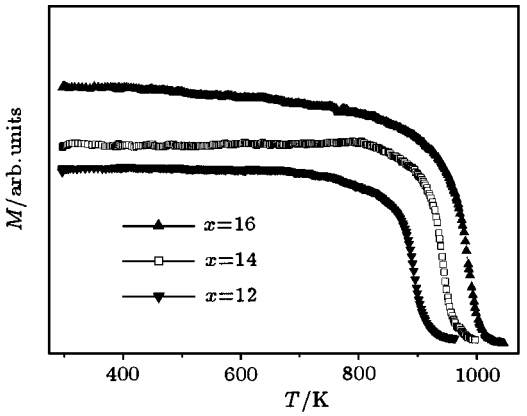


Fig.3. Thermomagnetic curves of $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ compounds in a field of 0.1 T.

The values of the saturation magnetization $\mu_0 M_s$ (see Table 1) were obtained by plotting $\mu_0 M_s$ versus $1/B$ and by extrapolating $1/B$ to zero. The values of $\mu_0 M_s$ for $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ (x=12, 14, 16) at 293 K are much larger than the value for $Sm_3(Fe,Mo)_{29}$. The $\mu_0 M_s$ (293 K) value for $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ amounts to 1.70 T around x=12, then slightly decreases with increasing Co content, and reaches 1.5 T for x=16. This has been explained in terms of a rigid-band model in which, with increasing Co content, the spin-up band of the 3d band of Fe is gradually filled up,[18] so that the average magnetic moment of the 3d sublattice gradually increases with increasing Co content. When the Co content increases further, the spin-up band becomes full, and the spin-down band begins to be filled up, so that the average magnetic moment of the 3d sublattice gradually decreases with increasing Co content.

4. Conclusion

In summary, $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ compounds (x=12, 14, 16) with a monoclinic $Nd_3(Fe,Ti)_{29}$-type structure (space group $A_{2/m}$) have been synthesized. The lattice constants a, b, c and unit-cell volume V decrease monotonically with increasing Co content. Compared with the $Sm_3(Fe,Mo)_{29}$ compound, the Curie temperature, the room temperature saturation magnetization and the anisotropy of the $Sm_3Fe_{28.1-x}Co_xMo_{0.9}$ compounds with x=14, 16 are considerably improved. The compound $Sm_3Fe_{12.1}Co_{16}Mo_{0.9}$ shows a high Curie temperature, high room temperature saturation magnetization and high anisotropy field, and is a very promising candidate for the permanent magnet application.

References

[1] Sagawa M, Fujimura S, Togawa N, Yamamoto H and Matsuura Y 1984 *J. Appl. Phys.* **55** 2083
[2] Croat J J, Herbst J F, Lee R W and Pinkerton F E 1984 *J. Appl. Phys.* **55** 2078
[3] Herbst J F 1991 *Rev. Mod. Phys.* **63** 819
[4] Wang W Q, Wang J L, Tang N, Bao F Q, Wu G H, Yang F M and Jin H M 2001 *Acta Phys. Sin.* **50** 752 (in Chinese)
[5] Cadogan J M, Li H S, Margarian A, Dunlop J B, Ryan D H, Collocott S J and Davis R L 1994 *J. Appl. Phys.* **76** 6138
[6] Wang W Q, Wang J L, Tang N, Bao F Q, Wu G H, Yang F M and Jin H M 2001 *Acta Phys. Sin.* **50** 1534 (in Chinese)
[7] Pan H G, Chen C P, Wang X H, Han X F and Yang F M 1998 *Acta Phys. Sin.* **47** 316 (in Chinese)
[8] Kalogiriou O, Psychairs V, Saettas L and Niarchos D N 1995 *J. Magn. Magn. Mater.* **146** 335
[9] Yang F M *et al* 1994 *J. Appl. Phys.* **76** 1971
[10] Hu B P, Liu G C, Wang Y Z, Nasunjilgal B, Tang N, Yang F M, Li H S and Cadogan J M 1994 *J. Phys.: Condens. Matter.* **6** L595
[11] Pan H G, Yang F M, Chen C P, Han X F, Tang N, Hu J F, Wang J L, Zhao R W, Zhou K W and Wang Q D 1996 *J. Magn. Magn. Mater.* **159** 352
[12] Courtois D, Li H S and Cadogan J M 1996 *Solid State Commun.* **98** 565
[13] Yang D, Wang J L, Tang N, Shen Y P and Yang F M 1999 *Appl. Phys. Lett.* **74** 4020
[14] Wang W Q, Wang J L, Yang D, Tang N, Yang F M, Wu G H and Jin H M 2001 *Chin. Phys. Lett.* **18** 969
[15] Wang W Q, Wang J L, Tang N, Wu G H, Yang F M and Jin H M 2001 *J. Appl. Phys.* **90** 1920
[16] Li H S, Courtois D and Cadogan J M 1996 *J. Appl. Phys.* **79** 4622
[17] Wang J L, Tang N, Zhao R W, Yang F M and de Boer F 1997 *J. Magn. Magn. Mater.* **166** 355
[18] Matsumoto Y, Hirosawa S, Yamamoto H, Fujimura S and Sagawa M 1983 *Appl. Phys. Lett.* **46** 308