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Rare-earth and transition metal sublattice contributions to magnetization and magnetic anisotropy of $R(TM,Ti)_{12}$ single crystals

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Abstract

The substitution effect of Fe by Co on magnetic properties (magnetization, anisotropy field, Curie temperature) of $R(TM,Ti)_{12}$ (R=Y, Sm; TM=Fe, Co) single crystals have been studied. The temperature and composition dependence of magnetization and magnetic anisotropy constants K_1 and K_2 in the range 77–1000 K have been determined using torque and vibrating specimen magnetometry techniques. ^{57}Fe Mossbauer spectra of powdered samples of $SmFe_{11-x}Co_xTi$ have been studied at room temperature. The easy magnetization direction of $RFe_{11-x}Co_xTi$ single crystals was found to be coinciding with the c axis for $x \leq 5$. A characteristic maximum in concentration dependence of saturation magnetization is found for $x \approx 3$. The concentration dependence of magnetic anisotropy constant K_1 for $RFe_{11-x}Co_xTi$ single crystals exhibited a maximum at $x \approx 1$. It is found that the Sm-sublattice contribution to magnetic anisotropy decreases rapidly with increasing Co concentration. © 1998 Published by Elsevier Science S.A.

Keywords: Ternary rare earth compounds; Magnetization; Torque moments; Magnetic anisotropy constants

1. Introduction

Iron rich rare-earth intermetallic compounds with the $ThMn_{12}$ structure are an important class of magnetic materials. Some of the compounds of the type $R(TM,Ti)_{12}$ are characterized by fairly high values of the Curie temperature, saturation magnetization and magnetocrystalline anisotropy [1–3]. Attractive features of the $R(TM,Ti)_{12}$ compounds are their relatively simple tetragonal crystalline structure. So, these compounds are interesting in understanding the fundamental physics problems.

The purpose of the present paper is a detailed study of rare-earth and transition metal sublattice contributions to magnetization and magnetic anisotropy of $R(TM,Ti)_{12}$ (R=Y, Sm; TM=Fe, Co) single crystals.

2. Experimental

$RFe_{11-x}Co_xTi$ ($0 \leq x \leq 5$) alloys were prepared by induction melting under argon atmosphere of constituent elements of purity at least 99.95 wt %. The ingots were remelted for homogenization. X-ray diffraction was used to control the single phase in samples. The ingots were preheated and cooled slowly in order to increase the grain size. The single crystals $RFe_{11-x}Co_xTi$ were extracted from the solidified ingots, weighed 2–20 mg and were oriented by the conventional back Laue reflection method.

The magnetization has been measured using a vibrating sample magnetometer in the temperature range 77–1000 K in magnetic fields up to 16 kOe. Thermomagnetic analysis was used to measure the Curie temperature T_c. Torque magnetometer was used to study the magnetic anisotropy behavior. Torsion measurements were carried out in the temperature range 77–1000 K. The available maximum field was 16 kOe. All samples were disc-shaped in (110) plane and were approximately 3–5 mm in diameter. Before computing the values of the anisotropy constants from the resulting torque curves the correction [4] was applied since the external magnetic field was not sufficiently strong to produce complete alignment of magnetization along the field direction. The magnetic anisotropy constants were obtained from the corrected torque curves by determining successive harmonics by a least squares method.

3. Results and discussion

Fig. 1 shows the composition dependence of the Curie temperatures for $RFe_{11-x}Co_xTi$ (R=Y, Sm) compounds. T_c reaches 538 K and 600 K for $YFe_{11}Ti$ and $SmFe_{11}Ti$, respectively. These values are significantly lower than that

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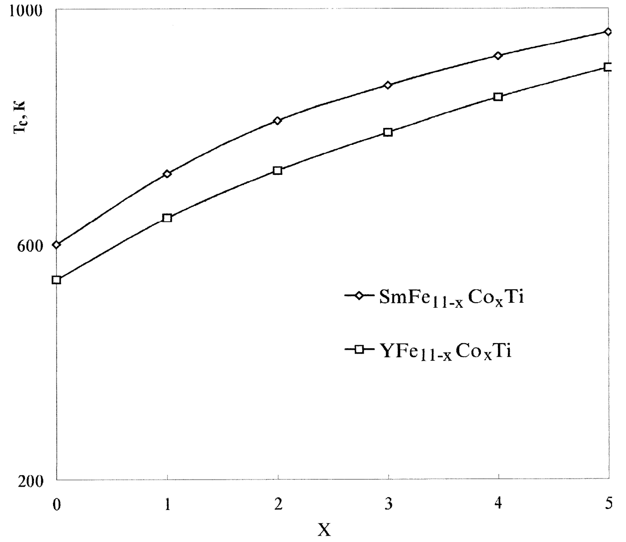

Fig. 1. Composition dependence of the Curie temperature for $SmFe_{11-x}Co_xTi$ and $YFe_{11-x}Co_xTi$.

of metallic Fe ($T_c=1050$ K). T_c was found to increase rapidly at the rate of ≈ 100 K per substituted Co atom in the range $x<2$ and then this tendency decreased at higher Co concentration. The Curie temperatures for Sm-containing compounds are higher than those of the corresponding compounds with Y owing to the effect of the R–TM intersublattice exchange interaction. These data show that the ordering temperatures of this compounds is mainly governed by the 3d–3d exchange interactions.

In the $ThMn_{12}$-type structure the transition element (Fe, Co) and Ti atoms can occupy three different sites: 8i, 8j and 8f. The Ti and Co atoms occupy preferentially the 8i and 8f sites, respectively, according to the neutron data [5]. Table 1 shows the interatomic distances in the $SmFe_{11}Ti$ (for $YFe_{11}Ti$ [6]). These distances between two Fe atoms on 8f sites and 8i is very short and smaller for $YFe_{11}Ti$, than that for $SmFe_{11}Ti$. The preferential substitution of Fe with Co on the 8f site lead to the drastic increase in Curie temperature of $RFe_{11-x}Co_xTi$ compounds for $0\leq x\leq 2$.

Fig. 2 shows, that the values of saturation magnetization for the $SmFe_{11-x}Co_xTi$ compounds at room temperature are slightly larger than that for the corresponding $YFe_{11-x}Co_xTi$ compounds suggesting a parallel alignment of the 3d and 4f moments. ^{57}Fe Mossbauer experiments give us information about the values of localized 3d moments for the three sites. Mossbauer studies of $YTi(Fe_{1-x}Co_x)_{11}$ ($x=0$, 0.2, 0.4, 0.6, 0.8 and 1.0) was reported by Li et al [7]. We obtained Mossbauer spectra of $SmFe_{11-x}Co_xTi$ with $0\leq x\leq 6$ at $T=300$ K [8]. As shown in Fig. 2, the hyperfine field of all three sites increases with Co substitution at first, reaches the maximum at $x=4$ and then decreases. The average moment of Fe atoms changes in the 1.63–1.96 μ_B range, while that of Co changes in the 1.13–1.24 μ_B range with the increasing Co concentration. The concentration dependence of saturation magnetization for the $RFe_{11-x}Co_xTi$ (R=Y, Sm) single crystals exhibited a maximum at $x\approx 3$. According to Pauling–Slater curve for a binary $Fe_{1-x}Co_x$ alloys, the maximum occurs at $x\approx 0.3$, too. This behavior can be understood in terms of band theory.

Table 1
Interatomic distances between Fe atoms in $SmFe_{11}Ti$ (in Å)

Site i	d, Å	Site j	d, Å	Site f	d, Å
i–i	2.397	j–f	2.466	f–f	2.386
i–f	2.627	j–i	2.679	f–j	2.466
i–j	2.679	j–i	2.680	f–i	2.627
i–j	2.680	j–j	2.663		

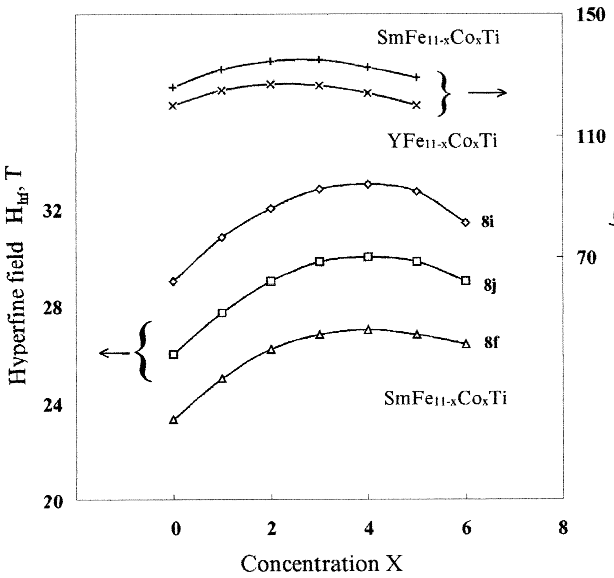

Fig. 2. Composition dependence of the saturation magnetization of $SmFe_{11-x}Co_xTi$ and $YFe_{11-x}Co_xTi$; dependence of the hyperfine fields over the three inequivalent sites on Co concentration for $SmFe_{11-x}Co_xTi$ ($T=300$ K).

Then, we have studied rare-earth and transition metal sublattice contributions to magnetic anisotropy of $RFe_{11-x}Co_xTi$ (R=Y, Sm) single crystals. If an external magnetic field H is applied to a crystal, the free energy of the tetragonal crystal can be expressed as:

$$\begin{aligned} E &= E_a - H\times M_s\times\cos(\theta-\varphi) \\ &= K_1\times\sin^2\theta + K_2\times\sin^4\theta + K_3\times\sin^4\theta\times\cos 4\psi - H \\ &\quad \times M_s\times\cos(\theta-\varphi)\,, \qquad (1) \end{aligned}$$

where M_s is the saturation magnetization, θ is the angle between the c-axis and the vector of magnetization, ψ is the angle between the projection of the magnetization vector in the basal plane of the crystal and one of the a-axes, φ is the angle between H and the c-axes, $(\theta-\varphi)$ is the angle between M_s and H, K_1, K_2 and K_3 are the anisotropy constants. In our case the anisotropy within the basal plane can be neglected, i.e. K_3 is approximately zero. Equilibrium is achieved, when E reaches a minimum:

$$\partial E/\partial\theta = \partial E_a/\partial\theta + H \times M_s \times \sin(\theta - \varphi)$$
$$= \partial E_a/\partial\theta + [M_s \times H] = 0\,, \qquad (2)$$

where $[M_s \times H]$ is the torque L exerted by the crystal anisotropy and is counterbalanced by the external field. The torque in (110) plane is expressed as:

$$L_{110} = -2K_1 \sin\theta\cos\theta - 4K_2\sin^3\theta\cos\theta\,. \qquad (3)$$

The analysis of the corrected torque curves $L(\theta)$ shows that the easy magnetization direction coincides with c axis in the whole investigated temperature and Co concentration range ($0 \leq x \leq 5$). The concentration dependence of the magnetic anisotropy constant K_1 for $RFe_{11-x}Co_xTi$ (R=Y, Sm) single crystals at $T=300$ K is shown in Fig. 3. The first anisotropy constant has a maximum value at $x=1$ ($K_1=4.5\cdot10^7$ erg cm^{-3} for $SmFe_{10}CoTi$, $K_1=0.98\cdot10^7$ erg cm^{-3} for $YFe_{10}CoTi$) and for $x>1$ decreases with the increasing x. The Fe local anisotropy is axial, while that of Co is planar [3]. A change in the sign of anisotropy is expected to take place in the composition range $5<x<6$. The largest contribution to magnetic anisotropy of Sm-sublattice was obtained for $SmFe_{11}Ti$ and $SmFe_{10}CoTi$ compounds, then this contribution decreased with the increasing Co concentration.

The magnetization curves of $RFe_{11-x}Co_xTi$ were also measured in pulse fields up to 240 kOe using induction method in the temperature range 4.2 K–300 K [9,10]. The anisotropy constants K_1 and K_2 were early estimated using the Sucksmith–Thompson method [11], too. Good agreement was obtained between this method and the present results.

Fig. 4 shows temperature dependence of anisotropy constants K_{1R} and K_{2R} of the Sm sublattice ($K_{1R}=K_1-K_{1Fe}$, $K_{2R}\approx K_2$, closed circle: Sucksmith–Thompson method, open circle: method of analysis of the corrected torque curves) for $SmFe_{11}Ti$.These experimental data are compared with model, based on the single ion theory taking into account the effect of the first excited state of $Sm^{3+6}H_{7/2}$ [12,13]. The total Hamiltonian may be written as

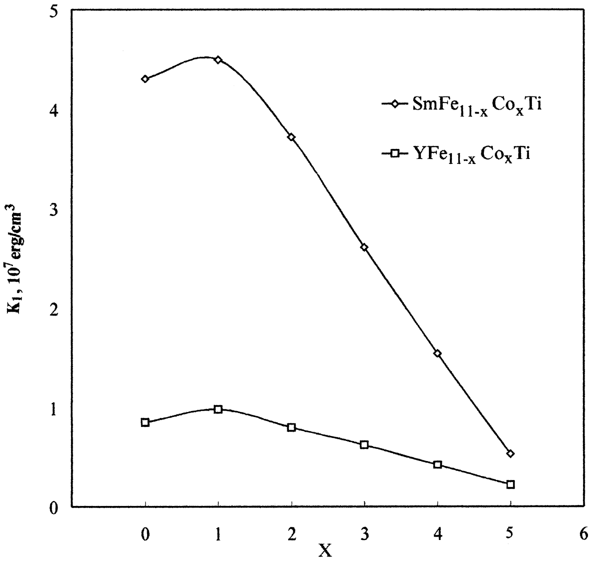

Fig. 3. Composition dependence of the anisotropy constant K_1 for $SmFe_{11-x}Co_xTi$ and $YFe_{11-x}Co_xTi$ at $T=300$ K.

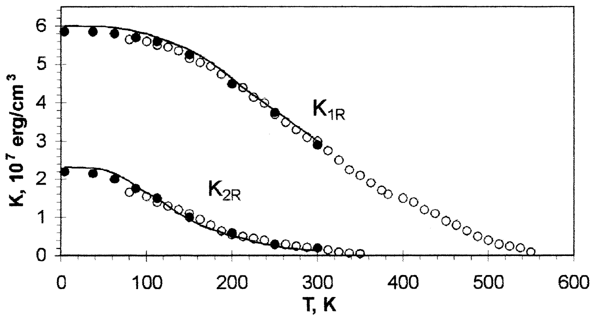

Fig. 4. Experimental temperature dependence of the Sm-sublattice contribution to the magnetic anisotropy $K_{1R}=K_1-K_{1Fe}$ and $K_{2R}\approx K_2$ for $SmFe_{11}Ti$ (open symbols: method of analysis of the corrected torque curves; filled symbols: Sucksmith–Thompson method) and their approximations by calculated curve [12] (solid line).

$$H = H_{so} + H_{cf} + H_{ex}\,, \qquad (4)$$

where H_{so} is the spin-orbit coupling Hamiltonian, H_{cf} the crystalline electric field (CEF) Hamiltonian and H_{ex} the interaction of rare-earth moment with the exchange field. A comparison of the experimental results with calculated data (solid line [12] in the Fig. 4) shows that the model is in good accordance with the experimental results.

4. Conclusions

This study shows that the magnetic Sm-sublattice gives the small and almost constant contribution to magnetization for $SmFe_{11-x}Co_xTi$ single crystals in the whole investigated composition range ($0 \leq x \leq 5$) and the great contribution to magnetic anisotropy for $x \leq 1$. The high anisotropy of the Sm-sublattice arises from a CEF and exchange-induced admixture of the higher multiplet levels into the ground-state multiplet of Sm^{3+} [13]. Co has a strong influence on the magnetic anisotropy of Sm-sublattice and the magnetic anisotropy constant K_1 drastically decreases for $x>1$. As it was mentioned above Curie temperatures increase monotonically with increasing the content of Co, this leads to increasing the f–d exchange constants and, perhaps, to increasing the energy gap between $^6H_{5/2}$ and $^6H_{7/2}$ multiplets. Simultaneously, the anisotropy constant K_1 depends on the total angular momentum J (Eq. (26) of [14]). We can expect, that the energy of magnetocrystalline anisotropy decreases, if the effect of the excited state $J=7/2$ is slight at higher Co concentration.

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