NMR study of 2–17 cobalt-based intermetallic compounds with samarium

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Abstract

The influence of the Sm and B atoms on the magnetic properties of $(Y_{1-x}Sm_x)_2Co_{17}$ and $Sm_2Co_{17-x}B_x$ has been studied by means of NMR and magnetic measurements. The change of magnetic anisotropy of $(Y_{1-x}Sm_x)_2Co_{17}$ is explained by the contribution of magnetic anisotropy at each Co site obtained from NMR. The Co atom at the 12j site contributes to the c-axis anisotropy the most. © 1998 Elsevier Science B.V. All rights reserved.

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The compound R_2Co_{17} (R = rare earth) has been studied extensively and the Sm–Co 2–17-type magnets are commercially available. RCo_4B and RFe_4B have been investigated because of their high magnetic anisotropy and large intrinsic coercivity [1, 2]. In order to explain the change of magnetic anisotropy by the contribution of magnetic anisotropy at each Co site and examine the influence of the B atoms on the magnetic properties in 2–17 Sm cobalt compound, the ^{59}Co NMR and magnetic measurements of $(Y_{1-x}Sm_x)_2Co_{17}$ and $Sm_2Co_{17-x}B_x$ have been carried out. Depending on the rare-earth element, R_2Co_{17} crystallizes with a hexagonal Th_2Ni_{17}-type structure or a rhombohedral Th_2Zn_{17}-type one. The Co sites in the hexagonal structure are 4f, 6g, 12j and 12k, whose equivalent Co sites in the rhombohedral one are 6c, 9d, 18f and 18h, respectively.

The samples were prepared in an induction furnace in a purified argon atmosphere and were annealed for one week at 900°C. Structural analysis was carried out using X-ray diffraction with Cu K_α radiation at room temperature. To determine the easy direction of magnetization, X-ray diffraction analyses of aligned powders were performed. Magnetic measurements were carried out in fields of up to 15 kOe at 77 K using a vibrating sample

magnetometer. Magnetization versus temperature curves were measured under an external field of 0.2 kOe and the spin reorientation temperatures (T_{SR}) were determined. Spin-echo NMR measurements were performed using a conventional incoherent spectrometer at 4.2 K.

$(Y_{1-x}Sm_x)_2Co_{17}$ formed in the hexagonal structure for $0 \leqslant x \leqslant 0.2$ and in the rhombohedral one for $0.3 \leqslant x \leqslant 1$. The lattice constants a and c and the unit-cell volume V increase with the Sm content. The ratio c/a increase for $0 \leqslant x \leqslant 0.2$ and decrease for $0.3 \leqslant x \leqslant 1$. The change from the hexagonal to rhombohedral structure is accompanied by an expansion along the a-direction and a contraction in the c-direction. $Sm_2Co_{17-x}B_x$ have a rhombohedral structure and are obtained for $0 \leqslant x \leqslant 1$. The lattice constants a and c increase with the B content, resulting in an increase of V. The value of $\Delta V/V$ is 0.4% with x from 0 to 1. The phase diagram of the magnetic anisotropy of $(Y_{1-x}Sm_x)_2Co_{17}$ was obtained. This result consists with X-ray diffraction result. At 4.2 K the easy direction of magnetization changes from the c plane to the c-axis for $0.1 < x < 0.15$. For $Sm_2Co_{17-x}B_x$, the easy direction of magnetization is parallel to the c-axis. The intensity ratio, $(0\ 0\ 6)/(2\ 2\ 0)$, increases with the B content; thus the particle orientation to the external field increases. RCo_4B is obtained through an ordered substitution of Co at the 2c site in RCo_5 by the B atom [3]. The 2c site in RCo_5 is the same as the 18f site in R_2Co_{17} crystallographically, and B atom is substituted for the Co atom at the 18f site for

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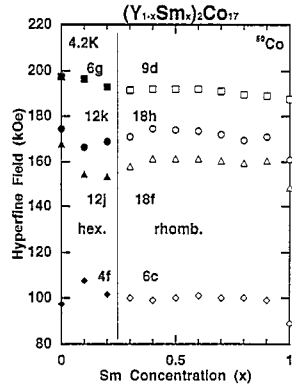* Corresponding author. Fax: + 81 263 37 2438; e-mail: vfg04652@niftyserve.or.jp.

Fig. 1. Concentration dependence of the ⁵⁹Co hyperfine fields in $(Y_{1-x}Sm_x)_2Co_{17}$ at 4.2 K.

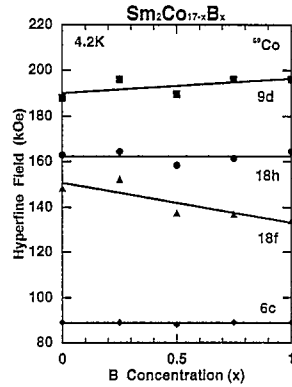Fig. 2. Concentration dependence of the ⁵⁹Co hyperfine fields in $Sm_2Co_{17-x}B_x$ at 4.2 K.

Table 1
The values of $\Delta H_{hf}(i)$, $\Delta\mu_{orb}(i)$ for each Co site in $(Y_{1-x}Sm_x)_2Co_{17}$ for $0 \leqslant x \leqslant 0.1$, E_s in Y_2Co_{17} [7] and $H_R(i)$ in Sm_2Co_{17} obtained at 4.2 K

Site	4f	12j	12k	6g
$\Delta H_{hf}(i)$ (kOe)	− 8.0	13.8	8.8	1.3
$\Delta\mu_{orb}(i)$ (μ_B)	0.00	0.03	0.02	0.01
E_s in Y_2Co_{17} (cm⁻¹)	− 18.0	12.0	− 5.2	− 3.5
Site	6c	18f	18h	9d
$H_R(i)$ (kOe)	11.6	13.2	13.0	9.0

coupling constants; $\alpha = - 130$ kOe/μ_B [6] and $\beta = 650$ kOe/μ_B [7]. H_R is the transferred hyperfine field caused by polarized 4f spins of neighboring R atoms. H_d is the sum of the dipole fields due to the Co and R moments. Taking into account the Co moment at the *i*th site, $\mu_{co}(i)$, we obtain

$$\mu_{co}(i) = \mu_{spin}(i) + \mu_{orb}(i). \qquad (2)$$

Then the change in $H_{hf}(i)$, $\Delta H_{hf}(i)$, is given by

$$\Delta H_{hf}(i) = - 130\Delta\mu_{co}(i) + 780\Delta\mu_{orb}(i) + \Delta H_R(i) + \Delta H_d(i).$$

$$(3)$$

Here we estimate $\Delta\mu_{orb}(i)$ for $(Y_{1-x}Sm_x)_2Co_{17}$ with $0 \leqslant x \leqslant 0.1$ as explained below. In Eq. (1), the sign of $H_{hf}(i)$ is negative. $\Delta H_{hf}(i)$ is the observed value as shown in Table 1. $\Delta\mu_{Co}(i)$ is obtained from ΔM_s. We assume that ΔH_R is negligibly small. $H_d(i)$ is calculated for all spins within 50 Å from each Co site. $\Delta\mu_{orb}(i)$ in Eq. (3) is calculated using $\Delta H_{hf}(i)$, $\Delta\mu_{Co}(i)$ and $\Delta H_d(i)$. The obtained values of $\Delta\mu_{orb}$ are shown in Table 1. The values of $H_{hf}(i)$ at the 12j, 12k and 6g sites decrease and $\mu_{orb}(i)$ increase, when the easy direction of magnetization changes from the *c* plane to the *c*-axis. Especially, the value of $H_{hf}(i)$ at the 12j site decreases greatly and μ_{orb} increases greatly. This suggests that the Co at the 12j site contributes to the axial anisotropy the most. On the other hand, the Co at the 4f site does not contribute the axial anisotropy. This result consists with the values of local anisotropy energy per atom, E_s [7] as shown in Table 1, where positive E_s favors a moment alignment along the *c*-axis. We estimate $H_R(i)$ in Sm_2Co_{17} as shown in Table 1. Next, we estimate $\Delta\mu_{orb}(i)$ for $Sm_2Co_{17-x}B_x$ with $0 \leqslant x \leqslant 1$. We assume that $\Delta H_R(i)$ is negligibly small. The obtained values of $\Delta\mu_{orb}(i)$ are shown in Table 2. The value of $\mu_{orb}(i)$ increases at the 18f site and decreases the most at the 9d site for $0 \leqslant x \leqslant 1$. Therefore, the decrease in the Co moment is minimum at the 18f site, where the distance between Co and *n.n.* B is the longest. The decrease in the Co moment is maximum at the 9d site, where that

$Sm_2Co_{17-x}B_x$ from NMR measurement [4]. The nearest neighbors of the Co atom at the 18f site in R_2Co_{17} and those of the B atom in $R_2Co_{14}B$ are similar. In $(Y_{1-x}Sm_x)_2Co_{17}$, the saturation magnetization, M_s, increase for $0 \leqslant x \leqslant 0.2$ and decrease for $0.2 \leqslant x \leqslant 1$. This is due to the change of the crystal structure for $0.2 < x < 0.3$. The value of M_s of Sm_2Co_{17} is smaller than that of Y_2Co_{17}. For $Sm_2Co_{17-x}B_x$ the values of M_s decrease with the B content. The value of $\Delta M_s/x$ with *x* from 0 to 1 is − 3.3 μ_B/f.u. The ⁵⁹Co NMR spectra for $(Y_{1-x}Sm_x)_2Co_{17}$ and $Sm_2Co_{17-x}B_x$ are observed at 4.2 K in zero external field and the peaks are assigned to four Co sites. The concentration dependence of the ⁵⁹Co hyperfine field, $H_{hf}(Co)$, for $(Y_{1-x}Sm_x)_2Co_{17}$ and $Sm_2Co_{17-x}B_x$ are shown in Figs. 1 and 2, respectively.

In order to analyze $H_{hf}(Co)$ at the *i*th site, $H_{hf}(i)$, we use the same expression as in the previous paper [5]:

$$H_{hf}(i) = \alpha\mu_{spin}(i) + \beta\mu_{orb}(i) + H_R(i) + H_d(i). \qquad (1)$$

Here, $\mu_{spin}(i)$ is the spin moment and $\mu_{orb}(i)$ is the orbital moment of the Co atom. α and β are the hyperfine

Table 2
The values of $\Delta H_{hf}(i)$, $\Delta H_d(i)$ and $\Delta\mu_{orb}(i)$ for each Co site in $Sm_2Co_{17-x}B_x$ obtained at 4.2 K for $0 \leqslant x \leqslant 1$

Site	$\Delta H_{hf}(i)$ (kOe)	$\Delta H_d(i)$ (kOe)	$\Delta\mu_{orb}(i)$ (μ_B)
9d	− 6.4	− 0.02	− 0.03
18h	0.0	0.11	− 0.02
18f	17.2	− 0.37	0.01
6c	0.0	0.22	− 0.02

is the shortest. We conclude that the shorter the distance between Co and *n.n.* B, the larger the decrease in the Co moment in $R_2Co_{17-x}B_x$ [4]. For $Sm_2Co_{17-x}B_x$, $H_{hf}(i)$ at the 18f site decreases remarkably for $0 \leqslant x \leqslant 1$ and μ_{orb} increases. For $(Y_{1-x}Sm_x)_2Co_{17}$, $H_{hf}(i)$ at the 12j site decreases greatly and μ_{orb} increases greatly when the easy direction of magnetization changes from the *c* plane to the *c*-axis. Consequently, there is a possibility that the axial anisotropy strengthens in $Sm_2Co_{17-x}B_x$. Then we discuss the reason. B atom substitutes for the Co atom at the 18f site. Therefore, the Sm atoms are surrounded by B atoms in the *c* plane. The sign of the second order of the Stevens factor, α_J, of Sm is positive. Assuming that

B atom has a negative charge, the 4f electrons in Sm atom are distributed avoiding B atoms to get Coulomb energy. So the axial anisotropy strengthens.

In conclusion, for $(Y_{1-x}Sm_x)_2Co_{17}$, the Co atom at the 12j site, whose equivalent Co site in the rhombohedral structure is 18f, contributes to the *c*-axis anisotropy the most. For $Sm_2Co_{17-x}B_x$ there is a possibility that the axial anisotropy is strengthened by substituting Co with B.

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