

# Crystal Structure and Low Temperature Magnetic Properties of Melt-Spun $\text{Sm}_2\text{Co}_7\text{B}_3$ Compound

C.J.Yang, W.Y.Lee, and S.D.Choi

*Electromagnetic Materials Laboratory, Research Institute of Industrial Science & Technology, P.O.Box 135, Pohang 790-330, Korea*

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Low temperature magnetic properties and crystal structures of melt-spun  $\text{Sm}_2\text{Co}_7\text{B}_3$  compound were characterized. The magnetic measurements in the temperature range 77 K ~ 450 K indicated that a spin-reorientation took place at about 150 ~ 160 K. A large anisotropy was observed ( $H_a = 135$  kOe at 300 K, 725 kOe at 77 K) for  $\text{Sm}_2\text{Co}_7\text{B}_3$  although the magnetic moment is rather low. The crystal structure of the  $\text{Sm}_2\text{Co}_7\text{B}_3$  compound was analyzed in detail by Rietveld analysis of powder diffraction pattern, and it was revealed that B(4h) atoms are not placed in the Sm(2e) layer but in between the Sm(2e) and Co(6i<sub>1</sub>) layers.

## I. Introduction

Recently, the  $\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$  ( $n=1, 2, \dots, \infty$ ) type compounds, which are derivatives of the  $\text{RCo}_5$  type ( $\text{R}=\text{rare earth}$ ), attracted a considerable interest [1~3]. All the previous studies suggested a huge magnetocrystalline anisotropy for the  $\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$  compounds.  $\text{SmCo}_4\text{B}$  ( $n=1$ ) was reported[2] to show an anisotropy field of 906 kOe at 4.2 K, and  $\text{Sm}_2\text{Co}_7\text{B}_3$  ( $n=3$ ) was reported[4] to exhibit an anisotropy field of 130 Tesla at 4.2 K. Such a huge anisotropies used to be explained in terms of the electrostatic interaction of the crystal field[2, 5, 6]. The nature of the electrostatic field effect is regarded to be associated with the point symmetry of the atomic sites in the underlying crystal structure. However, no study has been reported on the exact crystal structure of the  $\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$  compounds. In this work we intend to refine the crystal structure of the  $\text{Sm}_2\text{Co}_7\text{B}_3$  compound by using an advanced X-ray powder technique (Rietveld method) as a precursor to the future study of magnetocrystalline anisotropy, and we report low temperature magnetic behavior of the compound to examine its applicability as a permanent magnet.

## II. Experimental

The alloy samples of  $\text{Sm}_2\text{Co}_7\text{B}_3$  composition were

prepared by an induction melting under an Ar atmosphere using 99.95 % pure raw elements. An additional 10 % Sm was added to compensate the loss caused by Sm evaporation during melting. The cast compound was homogenized at 1000 °C for 50 hours to obtain single phase  $\text{Sm}_2\text{Co}_7\text{B}_3$ . Melt-spun ribbons of the identical stoichiometry were also made using a substrate speed of 12 m/sec at which single phase  $\text{Sm}_2\text{Co}_7\text{B}_3$  compound was obtained. The magnetic measurements were carried out using cylindrical powder compacts ( $\phi = 3$  mm,  $L = 10$  mm) which was magnetically aligned along the axial direction. The compact was prepared by bonding particles with an average size of 32  $\mu\text{m}$  under a magnetic field, 10 kOe using an epoxy resin. A vibrating sample magnetometer(Toei's) was used by applying the maximum field of 16 kOe to examine the low temperature magnetic behavior from liquid nitrogen temperature up to 400 °C, and a thermomagnetic analyzer(Perkin-Elmer's TGA-7) was used to identify the magnetic transformation up to Curie point. The crystal structural simulation was carried out by refining the observed X-ray diffraction pattern using the Rietveld program [7, 8].

## III. Results and Discussion

### A. X-ray refinement and crystal structure

The crystal structure of  $\text{Sm}_2\text{Co}_7\text{B}_3$  was identified

from both the cast and the melt-spun samples. Fig.1

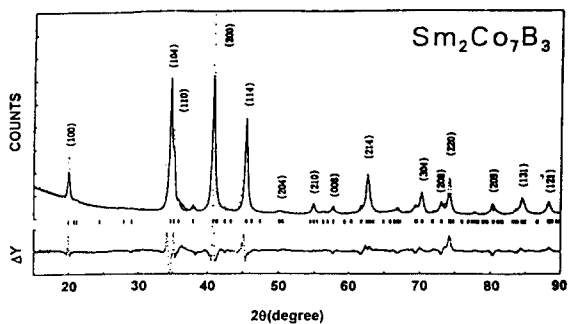


Fig. 1. Powder diffraction patterns of melt-spun  $\text{Sm}_2\text{Co}_7\text{B}_3$ . The dotted line refers to the observed pattern and the solid line to the calculated fit. The deviation of the calculated fit from the observed data is indicated at the bottom of the figure.

shows the powder diffraction patterns of the melt-spun  $\text{Sm}_2\text{Fe}_7\text{B}_3$  compound refined by using RIETAN program. The dots refer to the observed pattern and the solid line to the calculated fit. The dotted line shown at the bottom of the figure indicates the degree of deviation of the calculated fit from the observed pattern. The X-ray refinements for both the cast and the melt-spun compounds consistently demonstrated a good fit to the  $P6/mmm$  space group with the weighted factor  $R_{wp}=0.152$  and the integrated intensity factor  $R_1=0.028$ . The determined lattice parameters are  $a=5.1087 \text{ \AA}$  and  $c=12.777 \text{ \AA}$ , which are not quite the same as those reported ( $a=5.088 \text{ \AA}$   $c=12.79 \text{ \AA}$ ) by Ido et al. [4] who used a cast sample. The structural coordinates of the refined crystal are tabulated in Table I and the simulated model is

Table I. Refined structural coordinates of atomic sites of melt-spun  $\text{Sm}_2\text{Co}_7\text{B}_3$  compound

lattice parameter	sites	coordinates		
		x	y	z
$a=5.1087 \text{ \AA}$	Sm(1a)	0.0000	0.0000	0.0000
$b=12.770 \text{ \AA}$	Sm(1b)	0.0000	0.5000	0.0000
	Sm(2e)	0.0000	0.0000	0.2610
$P6/mmm$	Co(2c)	0.3333	0.6667	0.0000
	Co(6i <sub>1</sub> )	0.5000	0.0000	0.1596
$R_{wp}=0.152$	Co(6i <sub>2</sub> )	0.5000	0.0000	0.3857
$R_1=0.028$	B(2d)	0.3333	0.6667	0.5000
	B(4h)	0.3333	0.6667	0.1990

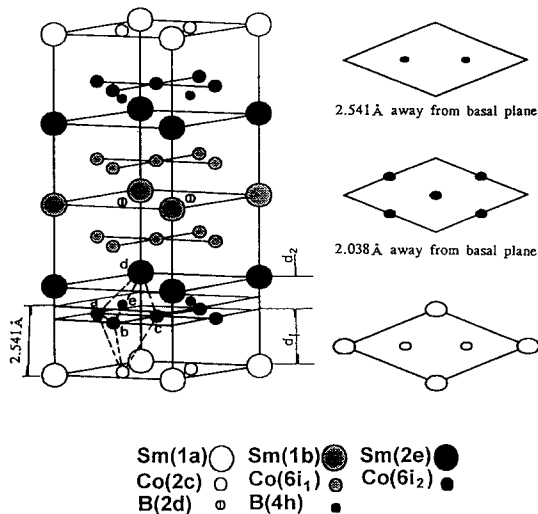


Fig. 2. The unit cell of  $\text{Sm}_2\text{Co}_7\text{B}_3$  in a hexagonal cell.

presented in Fig. 2. Two formula units of 24 atoms constitute one unit cell. As shown in Fig. 2, Co atoms occupy three different equivalent sites, Co(2c), Co(6i<sub>1</sub>) and Co(6i<sub>2</sub>). This  $\text{Sm}_2\text{Co}_7\text{B}_3$  compound results from replacing the Co atoms on the plane of Sm(2e) sites in the  $\text{SmCo}_5$  crystal structure by B(4h) atoms. It was worth noting that unlike the reports published so far, those replaced B(4h) atoms are not placed exactly on the Sm(2e) layer but in between layers of Sm(2e) and Co(6i<sub>1</sub>), i. e.,  $0.792 \text{ \AA}$  away from the Sm(2e) layer, while other B(2d) atoms substitute for the Co atoms of identical position on the Sm(1b) layer in the  $\text{SmCo}_5$  crystal.

Unlike the  $\text{SmCo}_5$ , the inter-layer distance,  $d_2$ , between Sm(2e) and Co(6i<sub>1</sub>) atoms is not the same as the distance,  $d_1$ , between the Co(6i<sub>1</sub>) and Sm(1a) layers in the  $\text{Sm}_2\text{Co}_7\text{B}_3$ . The distances  $d_1$  and  $d_2$  were found to be  $1.295 \text{ \AA}$  and  $2.038 \text{ \AA}$ , respectively. The present study suggests that the reported crystal structure of the  $\text{Sm}_2\text{Co}_7\text{B}_3$ [2, 4] may possibly be incorrect. The calculated interatomic distances of the refined  $\text{Sm}_2\text{Co}_7\text{B}_3$  crystal are tabulated in Table II which principally regards the hexagonal in Fig. 2.

### B. Low temperature magnetic properties

Fig. 3 shows the low temperature magnetic properties of the melt-spun  $\text{Sm}_2\text{Co}_7\text{B}_3$  measured from 77 K

Table II. Calculated interatomic distances of  $\text{Sm}_2\text{Co}_7\text{B}_3$  crystal(see the hexahedral cell in Fig. 2)

atoms	distance(Å),
Co(6i <sub>2</sub> ) - Co(6i <sub>1</sub> ): c axial	2.8873
Sm(2e) - Sm(1a) ; -	3.3330
Sm(2e) - Sm(1b) ; -	3.0520
Co(2c) - Co(6i <sub>1</sub> ) : a, b, c atoms	4.4021
Sm(2e) - Co(6i <sub>1</sub> ) : a, c, d -	2.8638
Sm(2e) - Co(6i <sub>1</sub> ) : b, d -	4.6099
B(4h) - Co(4i <sub>1</sub> ) : a, b, e -	1.5582
B(4h) - Co(4i <sub>1</sub> ) : b, e -	3.9342
B(4h) - Sm(2e <sub>1</sub> ) : d, e -	3.0539

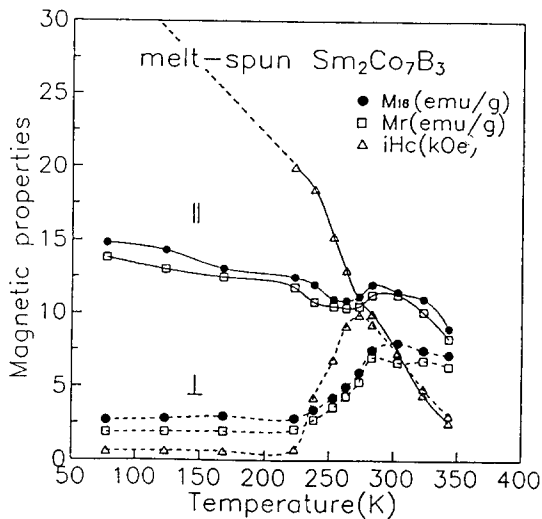


Fig. 3. Variations of the magnetic properties of melt-spun  $\text{Sm}_2\text{Co}_7\text{B}_3$  as a function of temperature.

to 350 K. The magnetic moments measured along the directions parallel( $\parallel$ ) or perpendicular( $\perp$ ) to the axial direction vary with temperature. Both the magnetic moment measured under the applied field of 16 kOe( $M_{16}$ ) and the residual moments measured along the parallel direction decrease gradually with increasing temperature and drop at about 225 K, and then begin to rise at 250 K and recover the moment observed at 225 K. Surprisingly, the magnetic moment measured along the perpendicular direction, which shows no considerable change below 225 K, rises abruptly at 225 K. The moment values observed in the both

directions tend to meet each other at about 350 K. We tried to explain this behavior in terms of the spin reorientation which will be described later. The coercivity in the parallel direction at 77 K was too high(perhaps higher than 35 kOe) to be measured with the maximum field used in this study, 16 kOe. It decreases rapidly to 8 kOe at 300 K.

To obtain the anisotropy field of  $\text{Sm}_2\text{Co}_7\text{B}_3$ , a magnetically-aligned compact sample was prepared using the single crystal powders made from a cast compound. Figs. 4(a) and (b) compare the magnetization

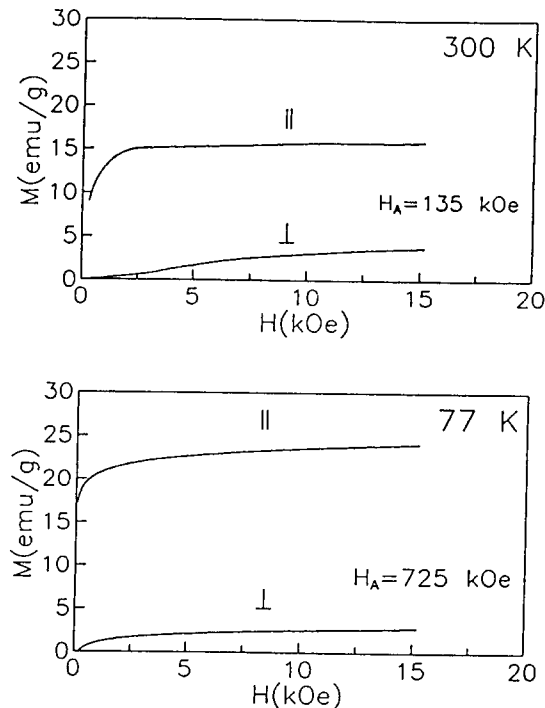


Fig. 4. Magnetization curves of a magnetically aligned  $\text{Sm}_2\text{Co}_7\text{B}_3$  compact sample measured along the direction parallel or perpendicular to the c-axis.

curves obtained at 300 K and 77 K, respectively. At 300 K an anisotropy field of 135 kOe was observed, while a huge anisotropy of 725 kOe was measured at 77 K. Those anisotropy fields were estimated by extrapolating the curve through polynomial fitting. However, the experimentally

saturated magnetic moment under applied field of 16 kOe at 300 K was only 25 emu/g although the coercivity (iH<sub>c</sub>) observed along the perpendicular direction seemed to exceed 25 kOe. One can realize that both the magnetic moment and coercivity are underestimated due to the weak field in this study comparing with that Ido et al. [4, 9] who derived the values from the measurement at 4.2 K under a high field (30 T). Table III

Table III. Comparison of magnetic properties calculated from experimental data for the Sm<sub>2</sub>Co<sub>7</sub>B<sub>3</sub>

	H <sub>a</sub> (kOe)	iH <sub>c</sub> (T)	M <sub>s</sub> (emu/g)	T <sub>c</sub> (K)	magnetic moment μ <sub>B</sub> /f.u.	moment μ <sub>B</sub> /Co
Ido et al. <sup>4,9</sup> (a=5.088Å (b=12.790Å)	130	275		402	3.68 (Ref. 9)	0.30
present work (a=5.1087Å (c=12.777Å)	725	25	25	403	3.195	

summarizes the calculated average magnetic moment per formula unit, μ<sub>B</sub>/f.u. A moment of 3.195 μ<sub>B</sub>/f.u. was obtained in the present work, which is smaller than that of Ref. (4) and (9). On calculating the moment, Ido et al. [4, 9] assumed that Sm ion moment is negligibly small, and the B(4h) atoms are placed exactly on the Sm(2e) layer. In fact, the Co atomic moment is largely decreased by neighboring B atoms. Actually this case happened between Sm(2e) and B(4h) layers shown in Fig. 2.

In order to clarify if the magnetic anomaly observed in Fig. 3 is a symptom of spin reorientation or not, low temperature torque curves were measured from 77 K to 300 K under a 16 kOe field, and shown in Fig. 5. The sample used was a cylindrical powder compact, 3 mm φ × 10 mm L. The powders of under 32 μm size were prepared from a cast ingot having the grain size larger than 30 m, and magnetically aligned perpendicularly to the axial direction of the sample bonded by an epoxy resin. The torque curves were measured by placing the sample with its axis parallel to rotational axis,

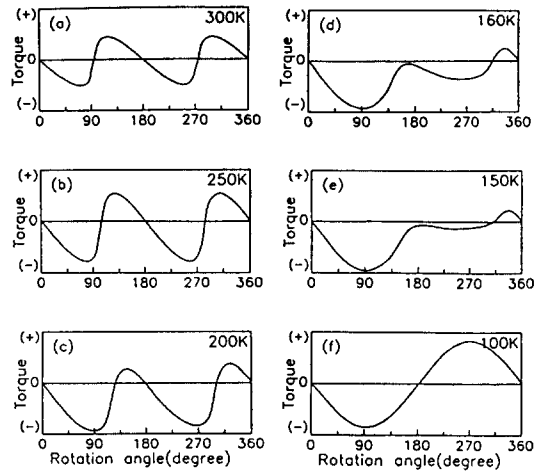


Fig. 5. Torque curves versus rotation angles of field-oriented Sm<sub>2</sub>Co<sub>7</sub>B<sub>3</sub> powder compact measured at low temperatures

which is perpendicular to the field direction. If the alignment is assumed to be perfect, the easy axis, [0001] of each Sm<sub>2</sub>Co<sub>7</sub>B<sub>3</sub> crystal makes angle θ with respect to the magnetization. The magnetocrystalline anisotropy in hexagonal symmetry is expressed as [10, 11]:

$$E = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^4 \theta \cos^4 \phi + \dots$$

where φ is the angle easy axis projected onto the crystallographic plane parallel to the field direction and perpendicular to the rotational axis. Since the sample was a multicrystalline powder compact, the last term of the right side of the above expression will be disregarded. The torque, δE/δθ, measured at 300 K ~ 200 K shown in Fig. 5 exhibits a typical variation in accordance with the above equation. At 150 to 160 K the torque curve changes its periodicity, but the curve returns to its normal shape at 100 K again. Taking the magnetization behavior in Fig. 3 and the torque curves in Fig. 5 into account, one can realize that some type of spin reorientation takes place at about 150 ~ 160 K. An ac susceptibility measurement in Fig. 6, also suggests the spin reorientation at 150 to 160 K. For

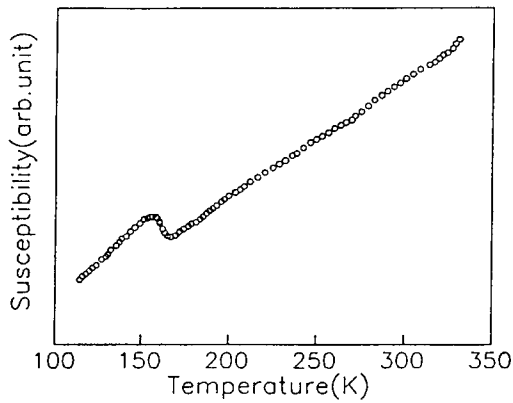


Fig. 6. Variation of the AC susceptibility of the field-oriented  $\text{Sm}_2\text{Co}_7\text{B}_3$  as a function of temperature.

Such an imperfectly field-aligned condition, the magnetocrystalline anisotropy energy seems to be equilibrated with the torque exerting by the external field at instantaneous moment[10]:

$$\begin{aligned} \delta E / \delta \theta &= 2K_1 \sin \theta \cos \theta + 4K_2 \sin^3 \theta \cos \theta \\ &= H \cdot M(\theta) \cos \theta = H \cdot M_s (1 - p \sin^2 \theta) \cos \theta \end{aligned}$$

where the  $M_s$  is the saturation magnetization, and  $p$  is a parameter indicating the degree of anisotropy,  $[(M_{\parallel c \text{ axis}}) - (M_{\perp c \text{ axis}})] / M_s$ . Therefore whether the observed spin reorientation would be

due to the anisotropy change from axial to plane or to cone is not clear, and its determination is beyond the scope of this paper.

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## 급냉응고된 $\text{Sm}_2\text{Co}_3\text{B}_7$ 화합물의 결정구조와 저온 자기특성

양충진 · 최승덕 · 이우영

산업과학기술연구소 신소재부문 자성재료분야, 790-330

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급속냉각기술로 제조된  $\text{Sm}_2\text{Co}_3\text{B}_7$  화합물의 저온자기특성(77~450 K 범위)과 결정구조를 연구하여 경자성 재료로서의 응용가능성을 조사하였다. P6/mmm 공간격자의  $\text{Sm}_2\text{Co}_3\text{B}_7$ 은 150~160 K 에서 spin-reorientation 현상을 보였으며, 결정자기이방성 자계(Ha)는 300 K 에서 135 kOe, 77 K 에서 725 kOe의 거대 이방화 에너지를 보였다. 그러나 자기능률(magnetic moment)은 25 emu/g에 그쳤다. Rietveld 분석에 의하여  $\text{Sm}_2\text{Co}_3\text{B}_7$ 의 결정구조를 밝혔으며 B(4h) 원자는 지금까지 보고된 바와는 달리 Sm(2e)면에 위치하는 것이 아니고 Sm(2e)면에서 0.792 Å 떨어져 Sm(2e)면과 Co(6i)면 사이에 위치함을 알았다.