

MAGNETIC AND STRUCTURAL PROPERTIES OF  $\text{SmTiFe}_{11-x}\text{Co}_x$  ALLOYS \*S.F. CHENG, V.K. SINHA<sup>1</sup>, Y. XU, J.M. ELBICKI, E.B. BOLTICH, W.E. WALLACE, S.G. SANKAR and D.E. LAUGHLIN*MEMS Department and Mellon Institute, Carnegie Mellon University, Pittsburgh, PA 15213, USA*

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$\text{SmTiFe}_{11-x}\text{Co}_x$  ( $0 \leq x \leq 11$ ) alloys were synthesized and studied by X-ray, SEM, EDXS and magnetometry at fields up to 90 kOe in the temperature range of 4.2–1100 K. It is established that almost single-phase materials exhibiting a  $\text{ThMn}_{12}$  type structure can be formed only for  $x < 2$ . The results of SEM and EDXS analyses indicate the presence of extraneous phases of  $\text{Th}_2\text{Zn}_{17}$  type structure and Fe–Co–Ti ternary at higher Co concentrations ( $x \geq 2$ ). The Co/Fe ratio is found to be the same in both the 1:12 and 2:17 phases and increases with increasing Co content. The  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys exhibit high saturation magnetization (120–145 emu/g) in the temperature range 4.2–295 K. A characteristic maximum in composition dependence of saturation magnetization is found for  $x \approx 2$ . The  $\text{SmTiFe}_{11}$  compound possesses high anisotropy fields ( $\approx 102$  kOe at 295 K) which is decreased in the presence of Co, and the material is magnetically soft at higher Co concentrations. The  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys exhibit a first-order magnetization process, which is quite evident in  $\text{SmTiFe}_9\text{Co}_2$  at 77 and 4.2 K. The Curie temperatures are significantly increased by Co substitution, especially at low Co concentration. The direction of easy magnetization in these alloys appears to change from axial to cone to planar with increasing Co content.

## 1. Introduction

A high energy permanent magnet has to meet severe requirements in regard to high magnetization, sufficiently high Curie temperature, high anisotropy with a uniaxial easy magnetization direction, excellent physicochemical properties, low cost, etc. By virtue of a favorable combination of properties,  $\text{SmCo}_5$  and its structural derivatives such as  $\text{Sm}_2\text{Co}_{17}$  have been known as useful permanent magnetic materials for a number of years [1–3]. Efforts to replace Co with the inexpensive Fe, which also has a higher magnetic moment, have been unsuccessful, since the R–Fe (R = rare earth) binaries do not form a compound isomorphous with  $\text{SmCo}_5$ . The other R–Fe binaries have

either inadequate magnetization and anisotropy or too low a Curie temperature [4,5]. The discovery [6–8] of the ternary compound  $\text{Nd}_2\text{Fe}_{14}\text{B}$  has opened a new era in the development of permanent magnets. These Fe-rich Fe–R–B permanent magnets have large coercivities and energy products in excess of 45 MGOe [6–9]. However, their Curie temperature is relatively low ( $\approx 300^\circ\text{C}$ ) and this leads to a large temperature coefficient of coercivity that limits the range of their application. Also, these materials have relatively low corrosion resistance. The shortcomings of the  $\text{R}_2\text{Fe}_{14}\text{B}$  magnets and their derivatives have led to the search for novel Fe-rich ternary compounds that might serve as alternatives for starting materials in permanent magnet applications. While working with the sputtered Fe-rich rare earth compounds, Cadieu et al. [10] reported several years ago that the  $\text{SmFe}_5$  crystalline phase occurred in thin films in a metastable state when a third stabilizing element was added. The most effective stabilizing element was found to be

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titanium. Motivated by this result, Ohashi et al. [11] recently reported a new compound,  $\text{SmTiFe}_{10}$ , having simple tetragonal structure with unit cell dimensions of  $a = 6.06$  and  $c = 16.77$  Å. The theoretical density of this compound was, however, in considerable disagreement with the bulk ingot density. Ohashi et al. [12] and Stadelmaier et al. [13] subsequently resolved the discrepancy by re-indexing the X-ray diffraction pattern and establishing that  $\text{SmTiFe}_{10}$  was, in fact, the body-centered tetragonal compound  $\text{SmTiFe}_{11}$  (or  $\text{SmTiFe}_{12}$ ) which is isomorphous with  $\text{ThMn}_{12}$ . Buschow and co-workers [14,15] have recently reported the magnetic properties of several  $\text{RFe}_{10}\text{M}_2$  ( $\text{R} = \text{Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, Y}$  and  $\text{M} = \text{Si, Ti, V, Cr, Mo}$  and  $\text{W}$ ) compounds which also occur in the  $\text{ThMn}_{12}$  structure. The magnetocrystalline anisotropy in this class of compounds arises as a result of the electrostatic interaction of the asymmetric 4f electron charge cloud with the electric charges of the surrounding metal atoms.

For permanent magnet applications the  $\text{R}(\text{Fe, Ti})_{12}$  systems in which  $\text{R} = \text{Sm}$  are promising, since in this system the combined R- and Fe-sublattice magnetizations and anisotropies add. The  $\text{SmTiFe}_{11-x}\text{Co}_x$  systems are of considerable scientific and technological interest for detailed investigations in regard to their structural and magnetic properties. Insertion of Co in replacement of Fe raises  $T_c$ . Except for the studies by Ohashi et al. [11,12], there are no published data on the  $\text{SmTiFe}_{11-x}\text{Co}_x$  systems.

The purposes of the present investigation were to precisely characterize the structure and phase stability of the  $\text{SmTiFe}_{11-x}\text{Co}_x$  systems using X-ray, EDXS, optical and scanning electron microscopy and to determine their magnetic properties between liquid helium temperature and  $T_c$ .

## 2. Experimental

The  $\text{SmTiFe}_{11-x}\text{Co}_x$  ( $x = 0$  to 11) systems were prepared by melting together metals of purity 99.9 wt% or better in a 450 kHz water-cooled copper boat induction furnace. Melting was done under a high purity, flowing argon atmosphere and the alloys were melted several times to insure homogeneity. The samarium loss of the alloy during

melting was compensated by adding an appropriate excess amount and weighing the alloy after each melting. As-cast ingots were wrapped in Ta-foil, sealed into quartz tubes filled with argon and annealed at  $1000^\circ\text{C}$  for one week. X-ray diffraction, thermomagnetic analysis (TMA), optical and scanning electron microscopy in conjunction with EDXS were employed to establish if the alloys were single-phase materials and to determine the nature of extraneous phases, if any. X-ray diffraction analysis was performed on randomly oriented and aligned (in magnetic fields up to 16 kOe) powdered samples with the use of a Rigaku diffractometer and  $\text{Cr-K}_\alpha$  radiation. Lattice parameter refinement was accomplished by a computer procedure using Cohen's least square method. TMA was performed by recording magnetization vs. temperature curves at low external magnetic fields ( $< 4$  kOe) in the temperature range 295–1100 K, with the use of a Faraday-type magnetic balance. The Curie temperatures ( $T_c$ ) of the various alloys were determined from the TMA data. Spin-reorientation temperatures ( $T_{sr}$ ) were determined from the low field  $M$  vs.  $T$  curve using a rough chunk, according to the method described earlier [16].

A vibrating sample magnetometer (VSM) with external field up to 16 kOe was used for determination of the saturation magnetization ( $M_s$ ) and anisotropy field ( $H_A$ ). Measurements were made at 295 and 77 K with decreasing field.  $M_s$  values were obtained on loose alloy powders ( $< 37$   $\mu\text{m}$ ) from magnetization isotherms, using Honda plots ( $M$  vs.  $1/H$ ).  $H_A$  measurements were made on samples aligned in wax by recording magnetization versus field curves in the easy and hard directions. The linear portion of the hard axis curve was first shifted to the origin to correct for particle misalignment. The  $H_A$  value was then determined by the intersection of the extrapolated easy and hard axes curves. VSM measurements were also carried out for a few  $\text{SmTiFe}_{11-x}\text{Co}_x$  samples, for both loose and magnetically aligned (in epoxy) powders, at 273, 77 and 4.2 K in external fields up to 90 kOe, using a VSM superconducting magnet. A Cam Scan Series IV with a PGT System IV was used for SEM and EDXS experiments.

### 3. Results and discussion

#### 3.1. X-ray diffraction analyses

The X-ray diffraction data of  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys with  $x$  less than 2 indicated the alloys to be single-phase materials having the body-centered tetragonal  $\text{ThMn}_{12}$ -type structure. At higher Co concentrations, i.e.,  $x > 2$ , additional phases of the rhombohedral  $\text{Th}_2\text{Zn}_{17}$  structure were observed. However, the major phase occurred in the  $\text{ThMn}_{12}$ -type structure. Fig. 1 shows a portion of the diffraction pattern of the representative  $\text{SmTiCo}_{11}$  compound. It may be observed that in addition to the diffraction lines from the 1:12 and 2:17 ( $a = 8.36$ ;  $c = 4.70$  Å) ( $a = 8.36$ ;  $c = 12.27$  Å) phases there is an additional line at  $67.7^\circ$ ,

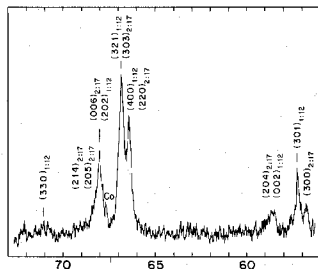


Fig. 1. X-ray diffraction pattern of the  $\text{SmTiCo}_{11}$  alloy.

which may be indexed as (002) of a hexagonal Co-based phase. Because of close crystallographic equivalence [17] many of the diffraction lines from the 1:12 and 2:17 phases are too close to one another to be distinguishable (fig. 1). By comparing the intensity ratios of the two phases to the relative intensities of these lines for  $\text{SmTiFe}_{11}$  (experimental) and  $\text{Sm}_2\text{Co}_{17}$  (from the ASTM table), the amount of 2:17 phase in the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys ( $6 \leq x \leq 11$ ) was estimated. The 2:17 impurity phase was in the range of 20 to 32% in close agreement with our metallographic results (see below). The computed lattice constants of the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys for the 1:12 phase are listed in table 1. As shown, the lattice parameters decreased with increasing Co content. This would indicate that the Co is incorporated in the primary phase. The computed theoretical density with 2 formula units in the unit cell and the experimentally measured density using the weight-loss method in toluene are listed in columns 5 and 6 (table 1). It is interesting to note that the theoretical and experimental densities match excellently (within the limit of experimental error of  $\approx 1.5\%$ ) in the homogeneity range, e.g.,  $0 \leq x \leq 2$ . Some deviations start beyond  $x > 2$ , which may be attributed to the appearance of extraneous phases(s) as observed by X-ray and metallography. The present lattice constant and density data are in good agreement with those of Ohashi et al. [11,12].

Observations were also made on the field-oriented (up to  $\approx 16$  kOe) powdered samples of  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys. Depending on the easy

Table 1  
Crystallography, density and direction of easy magnetization data for  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys

Composition $x$	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	Density (g/cm <sup>3</sup> )		Direction of easy magnetization
				theoretical	experimental	
0	8.53	4.78	347.8	7.76	7.53	axial
1	8.534	4.769	347.3	7.80	7.88	axial
2	8.532	4.767	347.0	7.83	8.06	axial
4	8.502	4.759	344.0	7.96	8.05	cone
6	8.461	4.742	339.5	8.13	8.49	cone
8	8.433	4.733	336.6	8.27	8.26	planar(?) <sup>a)</sup>
11	8.359	4.695	328.1	8.56	8.62	planar(?) <sup>a)</sup>

<sup>a)</sup> A considerable amount of 2:17 phase is present.

magnetization direction, particular ( $hkl$ ) intensities were observed to be enhanced or suppressed. By comparing the intensity ratios of (002), (202), (321) and (400) planes in the random and aligned powders, the directions of easy magnetization were determined. The results are summarized in table 1, column 7. It is interesting to note that the  $\text{SmTiFe}_{11-x}\text{Co}_x$  compounds, having lower Co-concentration, display a uniaxial magnetization parallel to the  $c$ -axis.

### 3.2. Optical and scanning electron microscopy

All the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys were examined by optical microscopy. Almost single-phase microstructure was observed for Co-concentrations of  $x \leq 2$ . At higher concentrations, the alloys exhibited an additional phase, whose relative amount appeared highest in  $\text{SmTiCo}_{11}$ . In order to characterize the matrix and the extraneous phases further, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS) studies were carried out. The back-scattered image of a few representative alloys,  $\text{SmTiFe}_{10}\text{Co}$ ,  $\text{SmTiFe}_9\text{Co}_2$  and  $\text{SmTiCo}_{11}$  are shown in fig. 2a–c. It is apparent that the  $\text{SmTiFe}_{10}\text{Co}$  is composed primarily of the matrix (“A”) phase, the  $\text{SmTiFe}_9\text{Co}_2$  has small amounts of another (“B”) phase, whereas  $\text{SmTiCo}_{11}$  has a considerable amount of “B” phase as an eutectic type mixture and a third (“C”) phase appearing as particles.

### 3.3. Energy-dispersive X-ray spectroscopy

EDXS analysis indicates the “B” phase to be of 2:17 stoichiometry (rare earth:transition metal) compound. The “C” phase was identified to be a ternary solid solution of Fe, Co and Ti containing a negligible amount of Sm. From the EDXS spectrum data, Co:Fe and Sm:Ti ratios were computed for the 1:12 stoichiometry “A” phase and the 2:17 stoichiometry “B” phase. The results are summarized in table 2.

It is of considerable interest to note that there is no compositional difference with respect to Fe and Co concentrations in the 1:12 (“A”) and 2:17 (“B”) phases in any of the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys. It thus appears that the phase transforma-

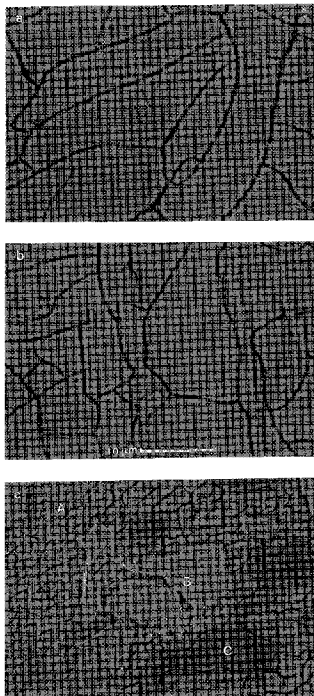


Fig. 2. Back-scattered images of  $\text{SmTiFe}_{11-x}\text{Co}_x$  (a, b, c:  $x = 1, 2, 11$ ).

tion perhaps occurs due to changes in the Sm:Ti ratio. This may occur because both the 2:17 and the 1:12 phases are structural derivatives of the 1:5 compound [17]. The energy barriers of the phase transformation from 1:12 to 2:17 are therefore not expected to be high. The formula unit of the 1:5 derivative can be written as

Table 2  
Summary of EDXS data for concentration ratios of elements in 1:12 ("A") and 2:17 ("B") phases

Alloy	Phase type	Co/Fe ratio	Sm/Ti ratio
$\text{SmTiFe}_{10}\text{Co}_1$	A	0.093	0.89
	B	0.089	-
$\text{SmTiFe}_9\text{Co}_2$	A	0.2	0.77
	B	0.2	2.08
$\text{SmTiFe}_7\text{Co}_4$	A	0.54	0.77
	B	0.53	1.71
$\text{SmTiFe}_5\text{Co}_6$	A	1.14	0.75
	B	1.13	2.1
$\text{SmTiFe}_3\text{Co}_8$	A	2.49	0.71
	B	2.45	-
$\text{SmTiCo}_{11}$	A	-	0.71
	B	-	1.92

$T_{5m+2n}R_{m-n}$ , where  $m$  is the number of 1:5 unit cells and  $n$  the number of R atoms replaced by T-pairs, e.g., for example,  $m = 4$  and  $n = 2$  for bct 1:12 compound, whereas  $m = 9$  and  $n = 3$  for the rhombohedral 2:17 compound. If Ti were to occupy the dumbbell sites in both the 1:12 i sites and 2:17 phases (c sites), the ratio of Sm to Ti in the latter should be twice that in the former phase. The present results of the Sm:Ti ratio ( $\approx 2.7$ ) is fairly close to the required value, indicating that Ti atoms perhaps preferentially occupy the dumbbell sites in both the phases. Further investigations by neutron diffraction and other techniques are, however, necessary to support our present proposal in regard to the site occupancy by Ti.

The presence of the third "C" phase (Fe-Co-Ti) is required by mass conservation. Our X-ray data also indicate the presence of this phase. During X-ray diffraction analysis it was observed that the diffraction angles for the matrix phase (1:12) and the extraneous phases, "B" and "C", changed with increasing Co-concentration of the host alloy  $\text{SmTiFe}_{11-x}\text{Co}_x$  (especially for  $x > 2$ ). Similarly, the  $T_c$  in these alloys increases both for the matrix phase and the extraneous phases, with increasing Co content of the alloy (see below). These observations appear possible only if Co partitions equally to the matrix and the extra-

neous phases. Our results of X-ray, SEM, EDXS and TMA, therefore, are in agreement. The formation of secondary phases in the Co-rich  $\text{SmTiFe}_{11-x}\text{Co}_x$  compounds indicates that Co is less stable than Fe in the  $\text{RMn}_{12}$ -type structure, which would be expected since Co is further away from Mn in the periodic table than is Fe. The present results indicate that Fe may be substituted by Co in the  $\text{SmTiFe}_{1-x}\text{Co}_x$  alloys of 1:12 structures; however, the phase appears to be unstable for  $x > 2$ . The present result is in sharp contrast with the results of Ohashi et al., who reported the phase to be stable up to  $x = 11$  [11,12]. A detailed SEM and EDXS analysis of the  $\text{RTiFe}_{11-x}\text{Co}_x$  ( $R = \text{rare earth}$ ) is currently in progress and the results will be published separately [18].

### 3.4. TMA studies

The composition dependencies of the Curie temperatures ( $T_c$ ) for the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys derived from TMA results are shown in fig. 3 and summarized in table 3.  $T_c$  values were determined using the customary  $M^2$  vs.  $T$  plots. It is observed that substitution of Fe by Co produces an average increase in  $T_c$  of approximately 70 K per substituted Co atom ( $0 \leq x \leq 4$ ). For higher Co concentrations the increase of  $T_c$  is reduced to approximately 43 and 26 K per added Co atom of the alloy for  $x = 6$  and 8, respectively, after which  $T_c$  acquires a constant value. Normally, one would expect  $T_c$  to vary with composition in the single-phase region but to become compositionally invariant when the limit of solid solubility is exceeded and a second phase appears. The unusual

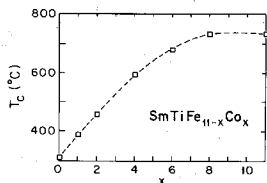


Fig. 3. Composition dependence of  $T_c$  in the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys.

Table 3

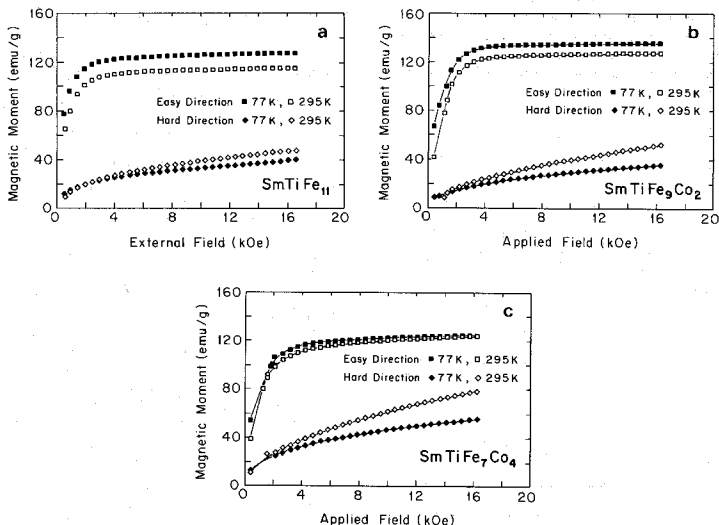
Curie temperatures and summary of magnetic data of the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys (applied field = 16 kOe maximum)

Composition $x$	Curie <sup>a)</sup> temperature (K)	Saturation magnetization <sup>b)</sup> at 295 K			Anisotropy fields at different temperatures (kOe)	
		$\alpha_s$ (emu/g)	$4\pi M_s$ (kG)	$\mu_B/\text{f.u.}$	295 K	77 K
0	581	119.1	11.6	17.3	102	218
1	661	130.6	12.8	19.1	81	173
2	729	132	13.0	19.4	68	153
4	864	130.7	13.1	19.3	—	—
6	949	127.7	13.0	19.0	—	—
8	1005	114.0	11.9	17.1	—	—
11	1004	94.0	10.1	14.3	—	—

<sup>a)</sup> Data for 1:12 phase.<sup>b)</sup> Composite data for 1:12 and 2:17 phase materials (see text).

phase relations in this system (see above) are responsible for the dependence of  $T_c$  on composition in the two-phase region. The decrease of

interatomic distances and a preferential substitution of Co for Fe in regions where there is negative exchange may account for the strengthening

Fig. 4. Field dependence of magnetization at different temperatures for  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys ( $x = 0, 2, 4$ ).

of the overall exchange [15,16] interaction and thus for an increase of  $T_c$ . The  $\text{SmTiFe}_5\text{Co}_6$  sample exhibited an irregularity (step) in the  $M$  vs.  $T$  curve. This phenomenon was attributed to a spin reorientation. The spin-reorientation temperature ( $T_{sr}$ ) for  $\text{SmTiFe}_5\text{Co}_6$  was determined to be 498 K. This appears to represent a change in magnetization direction from conical to either axial or planar with increasing temperature. The  $\text{SmTiFe}_5\text{Co}_8$  alloy shows some evidence of spin reorientation near its Curie temperature. As noted above, this alloy has approximately 25% of the  $\text{Sm}_2(\text{Ti}_{0.08}\text{Co}_{0.65}\text{Fe}_{0.27})_{17}$  phase, which has been reported [18] to remain uniaxial throughout the temperature range. Therefore, the spin-reorientation behavior is attributed to the 1:12 phase. However, due to the appearance of this behavior near the proximity of  $T_c$ , our interpretation is not conclusive. Buschow and co-workers [14,20] observed similar spin-reorientation effect in the  $\text{DyFe}_{10}\text{V}_2$  compound, which they attributed to competition between low-temperature-dominant R-sublattice anisotropy and the high-temperature-dominant Fe-

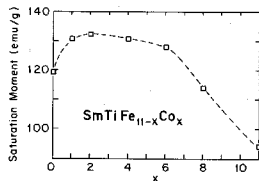


Fig. 5. Composition dependence of magnetization in  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys.

sublattice anisotropy. Similar considerations apply to the present systems. We have also observed [21] spin reorientation in other  $\text{RTiFe}_{11-x}\text{Co}_x$  ( $R = \text{Y}$  and rare earths) alloys.

### 3.5. VSM studies

The field dependence of magnetization (up to  $\approx 16$  kOe) for oriented powders of representative

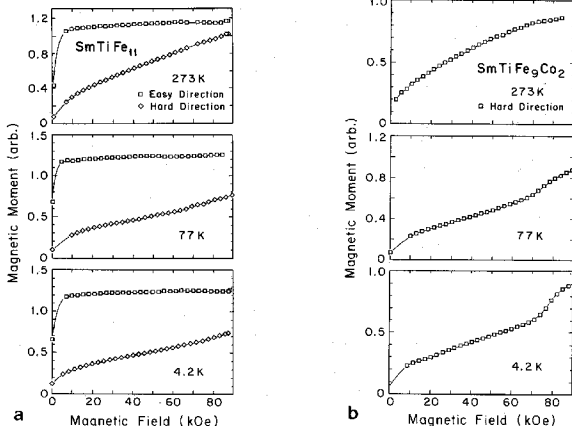


Fig. 6. Field dependence of magnetization (up to  $\approx 90$  kOe) at different temperatures for  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys ( $x = 0, 2$ ).

Table 4  
Summary of magnetic data of the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys in high field ( $\approx 90$  kOe maximum) at different temperatures

Alloy	273 K			77 K			4.2 k		
	$\sigma_s$ (emu/g)	$4\pi M_s$ (kG)	$\mu_B/\text{f.u.}$	$\sigma_s$ (emu/g)	$4\pi M_s$ (kG)	$\mu_B/\text{f.u.}$	$\sigma_s$ (emu/g)	$4\pi M_s$ (kG)	$\mu_B/\text{f.u.}$
$\text{SmTiFe}_{11}$	118.5	11.5	17.2	143.3	14.0	20.8	144.6	14.1	21.0
$\text{SmTiFe}_{10}\text{Co}_1$	139.1	13.6	20.3	145.0	14.2	21.2	145.9	14.3	21.3
$\text{SmTiFe}_9\text{Co}_2$	139.2	13.7	20.5	145.2	14.3	21.3	146.0	14.4	21.5

alloys,  $\text{SmTiFe}_{11}$  and  $\text{SmTiFe}_9\text{Co}_2$  and  $\text{SmTiFe}_7\text{Co}_4$  are shown in fig. 4a–c. The results of anisotropy fields ( $H_A$ ), saturation magnetization and other magnetic data for the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys are summarized in table 3. The composition dependence of  $M$  for the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys at 295 K is plotted in fig. 5. It is interesting to note that  $M_s$  acquires a maximum value at  $x \approx 2$ , followed by a subsequent decrease. As discussed elsewhere [22], the presence of a maximum in  $M_s$  is not only characteristic of Fe–Co binary alloys, but also of the R–Fe–Co ternaries.  $H_A$  for the  $\text{SmTiFe}_{11}$  alloy is 218 and 102 kOe at 77 and 295 K, respectively.  $H_A$  appears to decrease in magnitude by replacement of Fe with Co. The  $M_s$  and  $T_c$  data are in reasonable agreement with those of Ohashi et al. [12]. However, anisotropy field values were found to be higher than those reported earlier.

The field dependence of magnetization for the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys ( $0 \leq x \leq 2$ ) at 4.2, 77 and 273 K were determined up to fields of 90 kOe using a VSM equipped with a superconducting magnet. Experiments were performed both for the loose powders and powders aligned in epoxy under a magnetic field. The field dependence of representative alloys,  $\text{SmTiFe}_{11}$  and  $\text{SmTiFe}_9\text{Co}_2$ , at different temperatures are shown in fig. 6a, b and the magnetization data for various alloys are summarized in table 4. It was observed in the high-field magnetic measurements that  $\sigma_{\parallel}(B)$  and  $\sigma_{\perp}(B)$  did not coincide even up to 90 kOe for the  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys at the three different temperatures. The  $H_A$  of  $\text{SmTiFe}_{11}$  at 273 K was determined by the extrapolation technique to be 143 kOe.

At 77 and 4.2 K, it appears that there is an upward displacement of the magnetization curve in the hard direction, which indicates a tendency to first-order magnetization process (FOMP). This phenomenon is more pronounced in the  $\text{SmTiFe}_9\text{Co}_2$  compound, which displays FOMP behavior at 73 and 78 kOe at 77 and 4.2 K, respectively (fig. 6b). Therefore,  $H_A$  should be defined as the onset of FOMP behavior in the descending  $M$  vs.  $H$  curve [23]. This value is found to be 73 kOe for  $\text{SmTiFe}_9\text{Co}_2$  at 77 K, compared to 153 kOe as determined by extrapolation from the low field data.

#### 4. Conclusions

The  $\text{SmTiFe}_{11-x}\text{Co}_x$  alloys appear to be promising candidates as permanent magnets because of their high saturation magnetization and anisotropy. The magnetic ordering temperatures for these alloys are comparable to that of  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . Co appears to destabilize the  $\text{SmTiFe}_{11}$  ( $\text{ThMn}_{12}$ -type structure) ternary intermetallic. The present investigation shows that replacement of Fe by Co in  $\text{SmTiFe}_{11-x}\text{Co}_x$  beyond  $x \approx 2$  leads to the appearance of a considerable amount of extraneous phases (primarily of 2:17 stoichiometry). Our results are in contrast with those of Ohashi et al. [11,12], who reported the  $\text{SmTiFe}_{11-x}\text{Co}_x$  compounds to be stable up to  $x = 11$ . In view of the absence of  $\text{ThMn}_{12}$ -type of compound in the binaries, Sm–Fe, Sm–Ti, Sm–Co, Ti–Fe, Ti–Co or Co–Fe system, the presence of the pseudoternary compounds,  $\text{SmTiFe}_{11-x}\text{Co}_x$  ( $x < 2$ ) are most in-



teresting, as they open new possibilities for novel magnetic materials.

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