Chapter V

Results and Discussion

The experimental procedures discussed in the previous chapter allow us to determine the magnetization of nitrided Sm-Co compounds. In Chapter 3 we provide some information about the theoretical model. We first obtain the method to control the amount (in the mole fraction) of nitrogen in the nitrided compounds. We have obtained X-ray diffraction data to see if there is any change in the crystal structure. Finally we obtained the magnetization of the specimen.

Nitrogenation Process

As we point out in the previous chapter, we are mainly interested in the $SmCo_5$, Sm_2Co_7 and Sm_2Co_{17} compounds. Specimens of these compounds were annealed at various temperatures to control the amount of nitrogen absorbed. The annealing temperatures and the weight of the specimens are shown in table 5.1 a, b and c for $SmCo_5$, Sm_2Co_7 and Sm_2Co_{17} respectively. Using equation 4.1 and the weight before and after annealing we obtain mole fraction of nitrogen absorbed. Figure 5.1 shows graphical connection between the annealing temperature and nitrogen mole fraction absorbed.

The amount of nitrogen (in mole fraction) which is given in table 5 for all of the specimens is seen to increase monotonically with increasing temperature. The absorption rate for Sm_2Co_{17} are somewhat smaller than the other two intermetallic compounds. This maybe due to the crystal structure of $Sm_2Co_{17}N_x$ which allows only x=3 at maximum (Mukai and Fujimoto, 1992). The occupation site of nitrogen in rhombohedral Th_2Zn_{17} structure is the 9e site. This was confirmed by two

independent methods, neutron scattering on the $Nd_2Fe_{17}N_x$ (Yang et al.,1991) and the SmL111 edge X-ray absorption fine structure (EXAFS) on the $Sm_2Fe_{17}N_{2.5}$ (Otani et al.,1991). The occupation site of nitrogen in $SmCo_5$ and Sm_2Co_7 has not been reported. The 2:7 intermetallic presents some difficulties. The only ternary compounds of Sm_2Co_7 which has been reported is $Sm_2Co_7B_3$. Its crystal structure is somewhat different from that of Gd_2Co_7 which is believed to have the same crystal structure as Sm_2Co_7. $Sm_2Co_7B_3$ structure belongs to P6/mmm space group(Yang, Lee and Choi, 1994) while Gd_2Co_7 belongs to R3m space group (Yoshie et al.,1992). The difference in the crystal structure of ternary compounds and the host presents difficulties when considering $Sm_2Co_7N_x$ compounds. One can not be sure of the occupation site and the maximum mole fraction of nitrogen for this compound. It is possible that Sm_2Co_7 and $SmCo_5$ allowed the nitrogen to occupy more than 3 sites in one unit cell. Narumon(1995) points out that the increasing of nitrogen mole fraction are strongly due to the anneal temperature so the increase rate of this report follows the previous one. Mulder et al. (1992) obtain $Gd_2Co_{17}N_x$ ($x = 3$) by annealing at 450 °C for 65 hours in purified nitrogen gas much longer than our treatment. The nitrogen absorption rate of Sm_2Co_{17} are lower than Sm_2Fe_{17}. Zouganelis et al. (1991) obtain $Sm_2Fe_{17}N_{2.3}$ at 500°C 2 hours heat treatments. The lower diffusion of nitrogen in Sm_2Co_{17} is probably a result of the smaller unit cell i.e. a=8.407 A° and c=12.225 A° for Sm_2Co_{17}, a = 8.556 and c=12.445 A° for Sm_2Fe_{17}.

X-Ray Diffraction Results

The lattice parameter and the influence of the nitrogenation process on the crystal structure of Sm-Co compounds are obtained from the X-ray diffraction study. Figure 5.2 is the X-ray diffraction pattern of what obtained from the X-ray machine at the Metallurgy and Materials Science Research Institute. The lattice parameters were determined by the least square fitting program. Table 5.3 gives the lattice parameters of all the specimens in comparison to Sm-Fe compound and Sm-Co compounds without nitrogen. Figure 5.3 shows the crystal structure of the three

compounds. We did not see the large changes in the lattice parameters reported for Sm_2Fe_{17} nitrogenation.

The results from XRD pattern allow us to determine the lattice constant of the ternary nitride Sm-Co-N compounds. The lattice parameters of $SmCo_5N_x$ and $Sm_2Co_{17}N_x$ are not much different from those of $SmCo_5$ and Sm_2Co_{17}. The maximum values of lattice parameters of $SmCo_5N_x$ are a=4.998A° and c= 4.052A° compare to those $SmCo_5$ i.e. a= 4.997A° and c= 3.978A°. For $Sm_2Co_{17}N_x$, a=8.453A° and c=12.265A°, and for Sm_2Co_{17} a=8.402A_o and c= 12.172A°. We have seen that the lattice parameter of both of $SmCo_5N_x$ and $Sm_2Co_{17}N_x$ increases very little. Our values of lattice parameters of $Sm_2Co_{17}N_x$ agree with those of the previous study (Narumon, 1995). Katter et al.(1992) obtain 2-7% increase of a and c of $Sm_2Fe_{17}N_{2.9}$ and $Sm_2Co_{17}N_{2.7}$. In our study, the lattice parameters increase only 0.8% since the nitrogen mole fraction increase in our study are very low.

We can not report the lattice parameter of $Sm_2Co_7N_x$ since these is no reported the X-ray data of this specimen. We expect the crystal structure of Sm_2Co_7 to be similar to that $SmCo_5$. Yoshie et al.(1992) reported the crystal structure of Gd_2Co_7 which is believed to be the same as Sm_2Co_7 as "The crystal structure of Gd_2Co_7 belong to the R3m space group which stack three $RECo_5$ cells along the c-axis and to replace one of the two Co atom at the 2c sites by a rare earth atom in every third cell followed of the adjacent rare earth atoms" (Yoshie et al., 1992). This is the picture shown in figure 5.3. The XRD pattern allows us to investigate the effect of nitrogen on some of the lattice sites in the crystal structure. In $Sm_2Co_7N_x$, it is obvious that some peak around the angle between 15-20° has their intensity increase monotonically from low annealed temperature to high annealed temperature e.g. 270°C to 500°C. The increase of these peaks in $SmCo_5N_x$ and $Sm_2Co_{17}N_x$ is not evident. The higher annealed temperature leads to the increase of the disorder in the system which is detected by the broader of the peaks in the XRD patterns. The peak bordering was seen in all of the specimen.

Saturation Magnetization

The saturation magnetization are obtained from the hysteresis graph. These properties are presented in emu/g unit which allow us to interpret the microscopic behavior. Figures 5.5 and 5.6 is the relation between the mole fraction of nitrogen and saturation magnetization in emu/g and μ_B/F.U. Table 5.4 gives also the value of magnetization.

The effect of nitrogen absorption on a saturation magnetization of RE_2Fe_{17} compounds has been reported in the literature. Katter et al. reports the increase in the magnetization from 1.09T to 1.51 T for Sm_2Fe_{17} and $Sm_2Fe_{17}N_{2.94}$. The increase is monotonical with x, the nitrogen mole fraction, increase. In a second report, Katter et al.(1992) reported that the magnetization increased from 1.09T (Sm_2Fe_{17}) to 1.52T for $Sm_2Fe_{17}N_{2.9}$.

In our investigation of the $SmCo_5$ and Sm_2Co_7 compounds the saturation magnetization initially increase and then decrease as more nitrogen was absorbed by the system as shown in figures 5.4 and 5.5. The increase in the saturation magnetization of $RE_2Fe_{17}N_x$ was interpreted as being due to change in Fe-Fe interaction, arising from the expansion of unit cell volume. Qiau et al.(1992) in their study of $RE_2Fe_{17}C_x$ compounds, found that the molecular field coefficient of Fe-Fe interaction increase when C are introduced into the system. In our investigate, the lattice parameter did not increase very much when compare to RE-Fe compounds. Explanation of the behavior of the saturation magnetization of $SmCo_5N_x$ and $Sm_2Co_7N_x$ does not lie with the volume effect explanation.

The itinerant electron picture must be used to interpret our results. This model is based on the assumption that *3d* electrons in Co are the main contributor to the saturation magnetization. Gu and Lai (1992) has calculated the density of states

of Nd_2Fe_{17} and $Nd_2Fe_{17}N_x$ (x=3). Their results for Nd_2Fe_{17} confirm that Fe plays the dominate role in determining the saturation magnetization.

The difference in saturation magnetization behavior of $SmCo_5N_x$ and $Sm_2Co_7N_x$ from these of the nitrogen free host due to the increase in the number of the electrons. The additional electrons come from the nitrogen being absorbed. This doping of the electrons causes the Fermi energy to shift up. The total number present spin up and down electrons change as explain on the chapter 3 figure 3.8. There is a maximum population of total magnetic moment somewhere when the Fermi energy shift from low to high level. Unfortunately figure 3.8 was calculated on the base of a simple approximation and can not be used to determine the exact value of Fermi energy and the maximum point of the magnetization.

$SmCo_5N_x$ and $Sm_2Co_7N_x$ have a maximum magnetization value at x=1.64 and 4.16 respectively. To account for the initial increased which is then followed by decreases, we must assume that the subband in the *3d* band of both systems are unfilled. The Fermi energy shifted when the additional electrons are doped into the system. When the lower subband are filled, further increase in the Fermi energy leads to the reduction of the total number of spin up electrons and therefore a decrease of the saturation magnetization. The explanation for the behavior of $Sm_2Co_{17}N_x$ is similar except that one subband is already filled in the absorbed nitrogen. Raising the Fermi energy by doping electrons into the system will decrease the difference between the number of spin up and spin down electrons. This causes the monotonic decrease in the saturation magnetization.

These results are compared to the saturation magnetization of Sm-Co compounds without nitrogenation. The Sm-Co compounds were prepared by mechanically alloyed to form $SmCo_5$ and Sm_2Co_{17}. Wecker, Katter and Schultz (1991) obtained 0.56 T and 1.2 T ($\approx$ 70 and 140 emu/g) for $SmCo_5$ and Sm_2Co_{17} respectively, Lui et al. (1992) obtained 44 emu/g for $SmCo_5$. The saturation magnetization of two previous works are higher than ours investigation in both with

and without nitrogenation Sm-Co compounds i.e. 12.7, 13.5 and 21.1 emu/g for $SmCo_5$,Sm_2Co_7 and Sm_2Co_{17}, 26.9, 30.3 and 23.3 for $SmCo_5N_{1.64}$,$Sm_2Co_7N_{4.16}$ and Sm_2Co_{17} $N_{0.69}$. If we consider only ours results, it was seen that the nitrogenation can improves the saturation magnetization of Sm-Co compounds. However, there are many parameters to consider if one tries to make a good magnetic materials. These parameters such as Curie temperature and coercive force. The search for a good magnetic materials must considers them too.

Temperature (°C)	Weights of $SmCo_5$ (g)		N_2 Mole fraction	Density (g/cm^3)
	Before	After		
200	11.3592	11.5402	0.5063	5.5740
225	11.3572	12.1858	2.3182	5.8702
250	10.7749	11.3255	1.6236	6.3492
300	13.2108	14.7578	3.7208	5.2335
325	11.4797	12.9665	4.1152	5.9314
350	14.6659	16.6399	4.2767	5.9255

Table 5.1(a) Weights of $SmCo_5$ before and after annealed under nitrogen atmostphere at various temperatures for 4 hours.

Temperature (°C)	Weights of Sm_2Co_7 (g)		N_2 Mole fraction	Density (g/cm^3)
	Before	After		
225	21.0338	21.2320	0.4756	6.0670
260	20.2781	20.6431	0.9170	6.0095
270	21.2055	21.8300	1.5000	5.8509
280	20.0868	21.6257	3.9030	5.5885
325	20.0070	21.6388	4.1550	5.8977
350	20.0028	21.9622	4.9902	4.9300
375	19.9995	22.1350	5.4369	5.7928
400	20.0011	22.3652	6.0184	5.4856
425	20.0019	23.5829	6.2575	5.7766
450	20.2916	23.4925	8.0321	5.3171

Table 5.1(b) Weights of Sm_2Co_7 before and after annealed under nitrogen atmostphere at various temperatures for 4 hours.

Temperature (°C)	Weights of Sm_2Co_{17} (g)		N_2 Mole fraction	Density (g/cm^3)
	Before	After		
300	12.4428	12.5350	0.6898	5.2574
350	12.0798	12.1843	0.8046	5.7121
400	12.3777	12.4928	0.8654	5.2017
450	12.7449	12.8689	0.9051	5.1432
500	13.3785	13.5886	1.4609	3.6058

Table 5.1(c) Weights of Sm_2Co_{17} before and after annealed under nitrogen atmostphere at various temperatures for 4 hours.

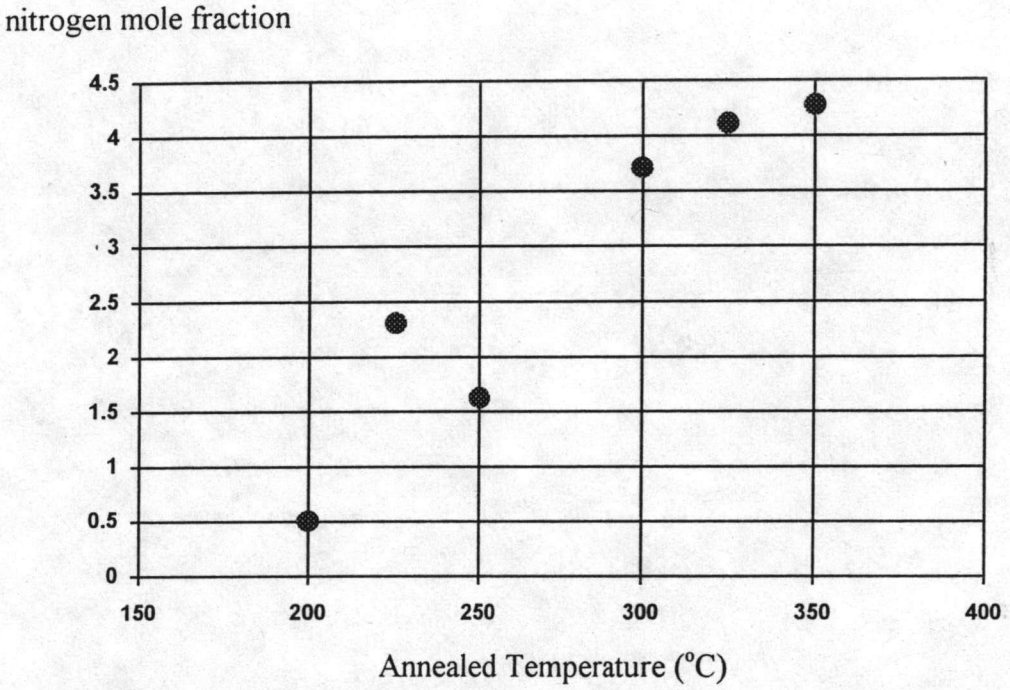

Figure 5.1(a) Relation between annealed temperature and mole fraction of nitrogen $SmCo_5$.

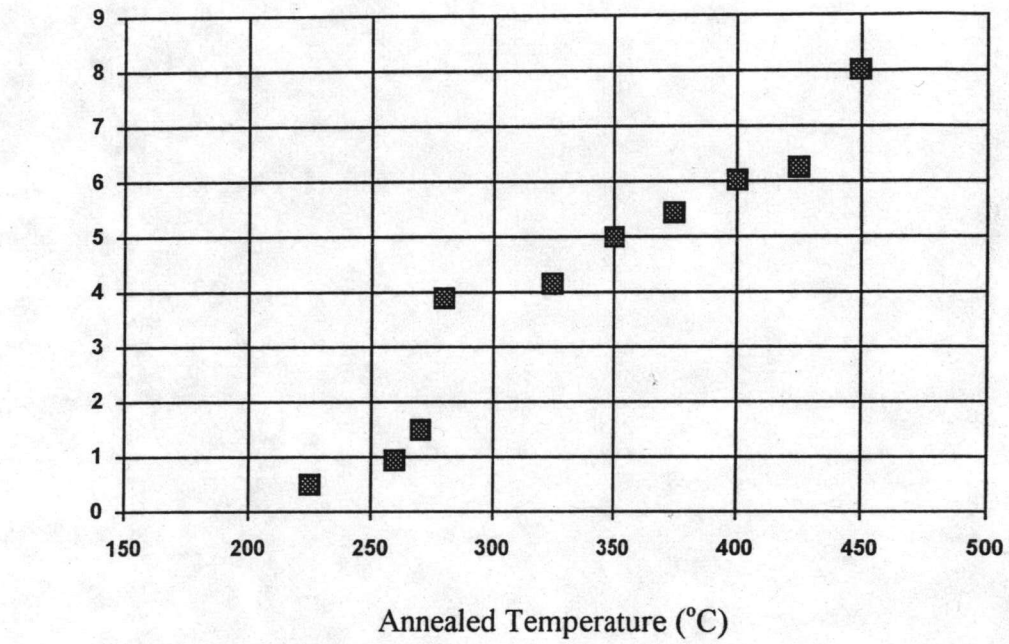

Figure 5.1(b) Relation between annealed temperature and mole fraction of nitrogen Sm_2Co_7.

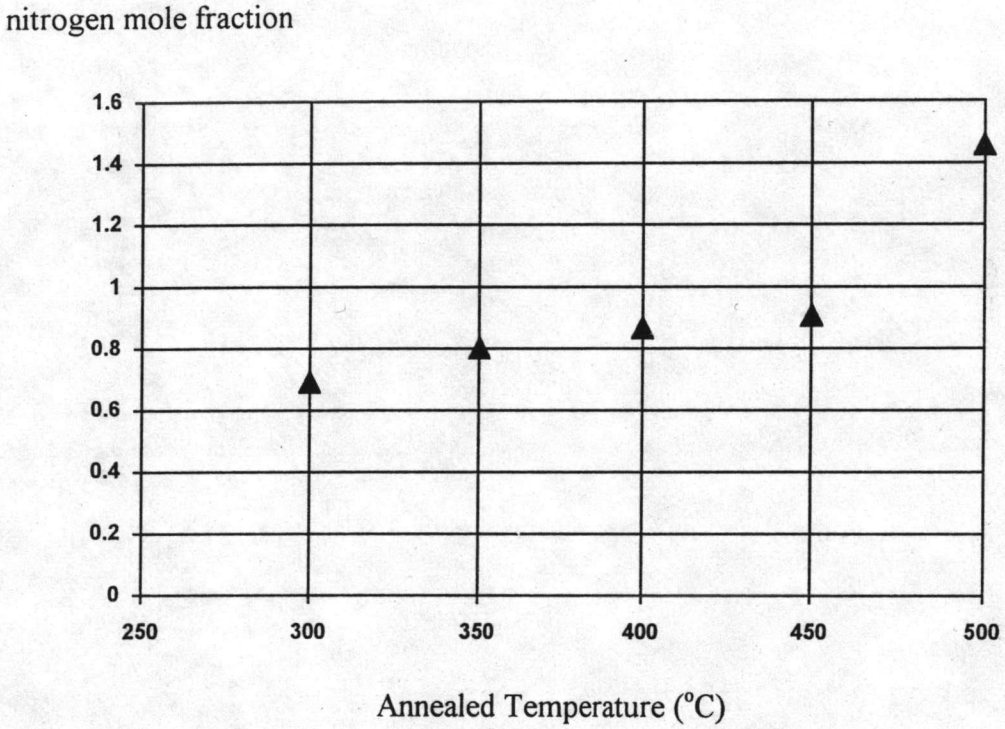

Figure 5.1(c) Relation between annealed temperature and mole fraction of nitrogen Sm_2Co_{17}.

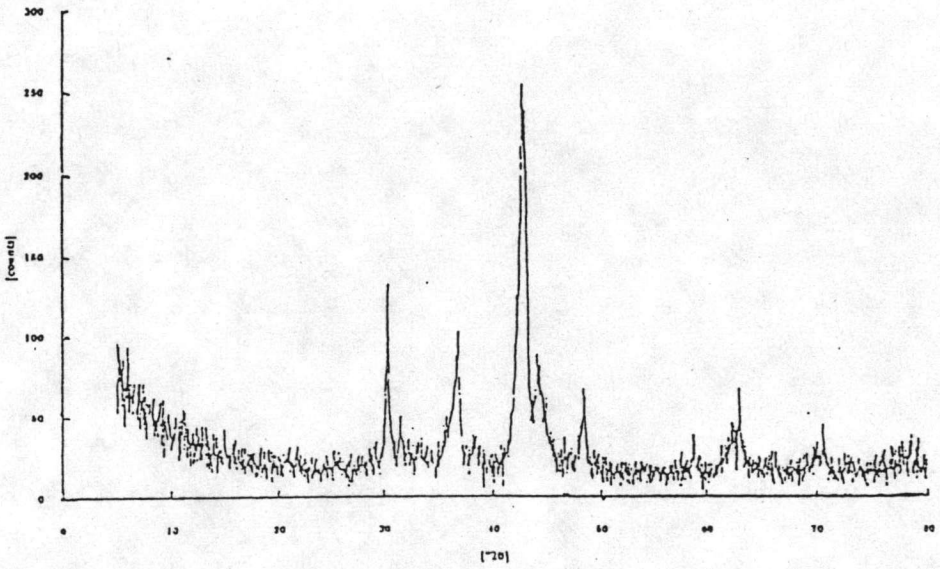

Figure 5.2 XRD pattern of $Sm_2Co_{17}N_x$ annealed at 300°C 4 hours.

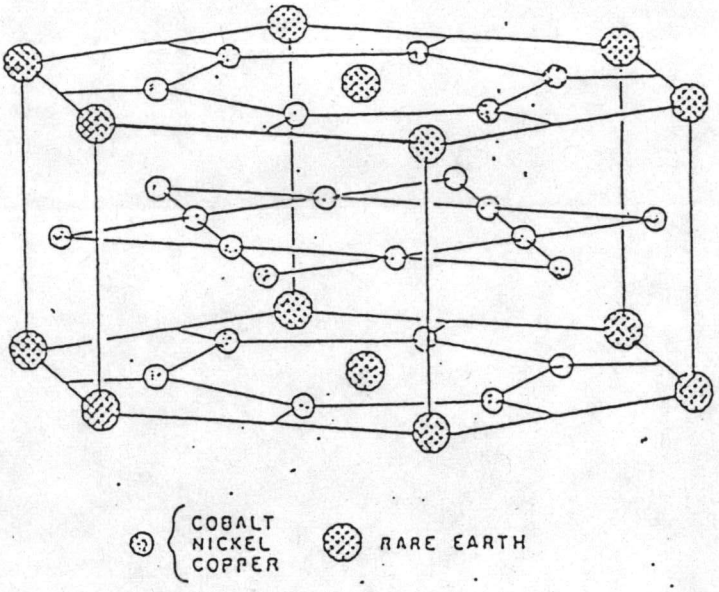

Figure 5.3 (a)

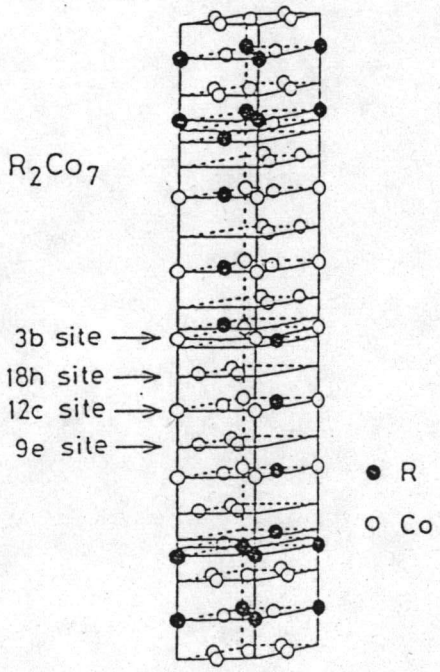

Figure 5.3 (b)

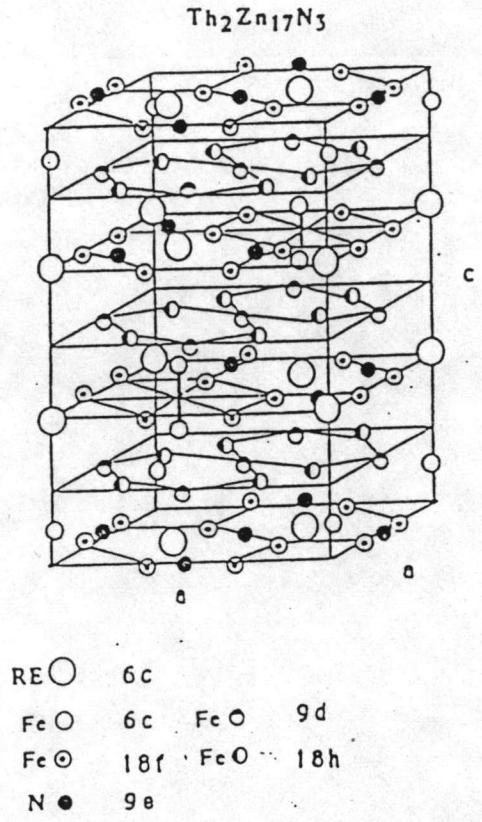

Figure 5.3 (c)

Figure 5.3 Crystal structures of $SmCo_5$ (a), Sm_2Co_7 (b) and Sm_2Co_{17} (c). Crystal structures of 1-5 compounds is closely with 2-7 compounds while Sm_2Co_{17} appears in rhombohedral phase.

(a)

d value	hkl	Angle	Intensity
2.929	101	15.25	60
2.498	110	17.96	36
2.164	200	20.85	36
2.116	111	21.35	100
1.989	002	22.79	24

(b)

d value	hkl	Angle	Intensity
2.916	113	17.86	50
2.425	300	21.64	60
2.098	220	25.24	100
2.081	303	25.46	100
2.041	214	25.99	40
1.866	223	28.64	60

Table 5.2 (a) and (b) X-ray data of $SmCo_5$ and Sm_2Co_{17} selects only a dominant peak.

(a)

Mole of nitrogen	Lattice parameters	
	a (A°)	c (A°)
0.506	4.993	3.9438
2.318	4.994	3.9779
1.623	4.998	3.9623
3.721	4.996	3.9628
4.115	4.951	4.0518
4.277	4.966	4.0028

(b)

Mole of nitrogen	Lattice parameters	
	a (A°)	c (A°)
0.689	8.435	12.256
0.804	8.445	12.246
0.865	8.436	12.253
0.905	8.452	12.265
1.460	8.453	12.244

Table 5.3 (a) and (b) are the lattice parameter of $SmCo_5 N_x$ and $Sm_2Co_{17} N_x$ respectively.

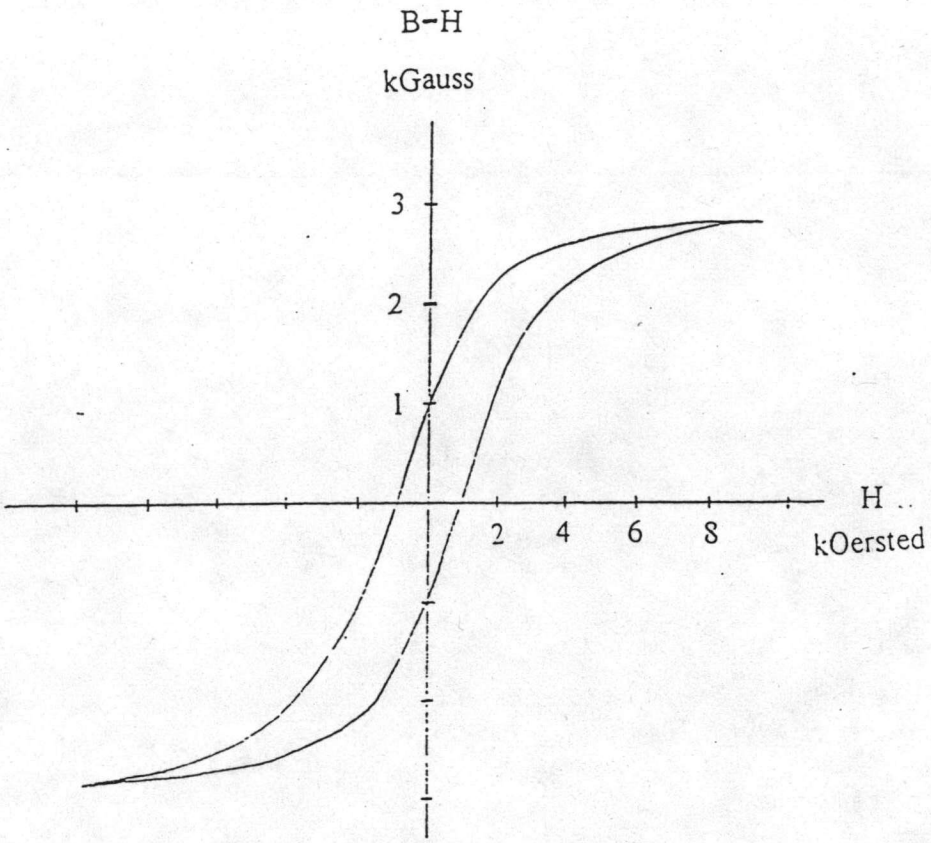

Figure 5.4 Hysteresis loop of Sm-Co compounds.

(a)

Temperature (°C)	Mole fraction	Saturation magnetization	
		emu/g	μ_B/f.u.
200	0.506	15.0	1.21
225	2.318	19.3	1.66
250	1.624	26.9	2.25
300	3.720	22.0	2.03
325	4.115	18.1	1.63
350	4.276	12.5	1.13

(b)

Temperature (°C)	Mole fraction	Saturation magnetization	
		emu/g	μ_B/f.u.
225	0.47	16.34	2.11
260	0.92	19.21	2.50
270	1.50	20.96	2.75
280	2.90	25.45	3.43
325	4.16	30.24	4.17
350	4.99	29.72	4.15
375	5.44	28.59	4.04
400	6.02	25.69	3.67
425	6.26	20.77	2.99
450	8.03	14.72	2.17

(c)

Temperature (°C)	Mole fraction	Saturation magnetization	
		emu/g	μ_B/f.u.
300	0.689	23.29	5.47
350	0.804	14.65	3.45
400	0.865	16.48	3.88
450	0.905	18.65	4.39
500	1.461	20.09	4.77

Table 5.4 (a), (b) and (c) are the saturation magnetization of $SmCo_5N_x$, $Sm_2Co_7N_x$ and $Sm_2Co_{17}N_x$ between annealed temperature and nitrogen mole fraction.

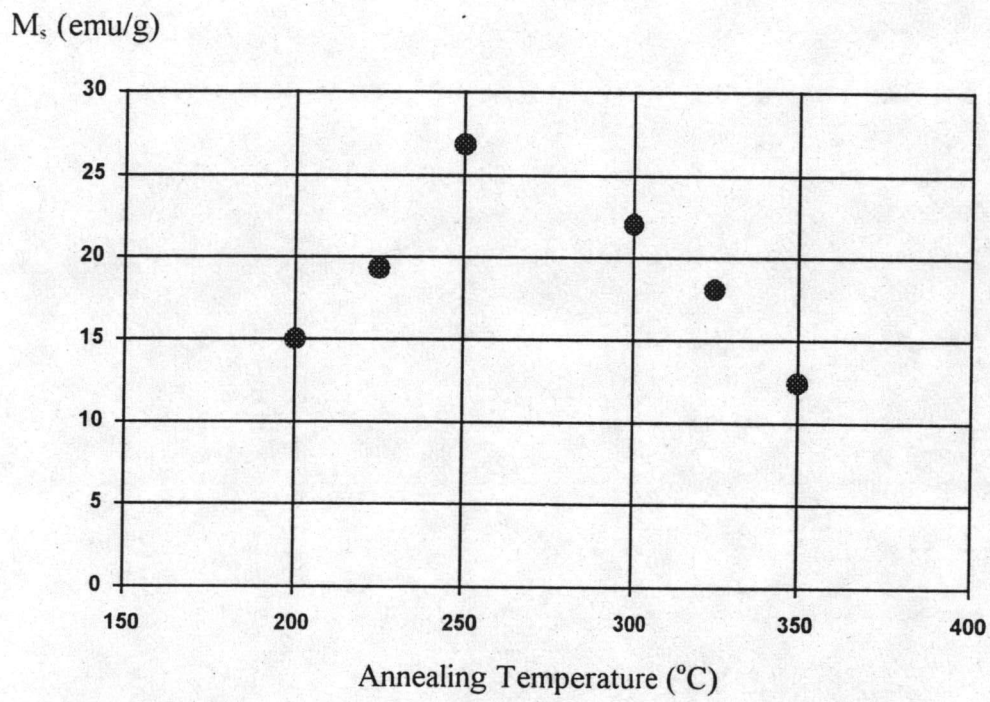

Figure 5.5(a) Relation between saturation magnetization and annealed temperature in electromagnetic unit per gram of $SmCo_5N_x$.

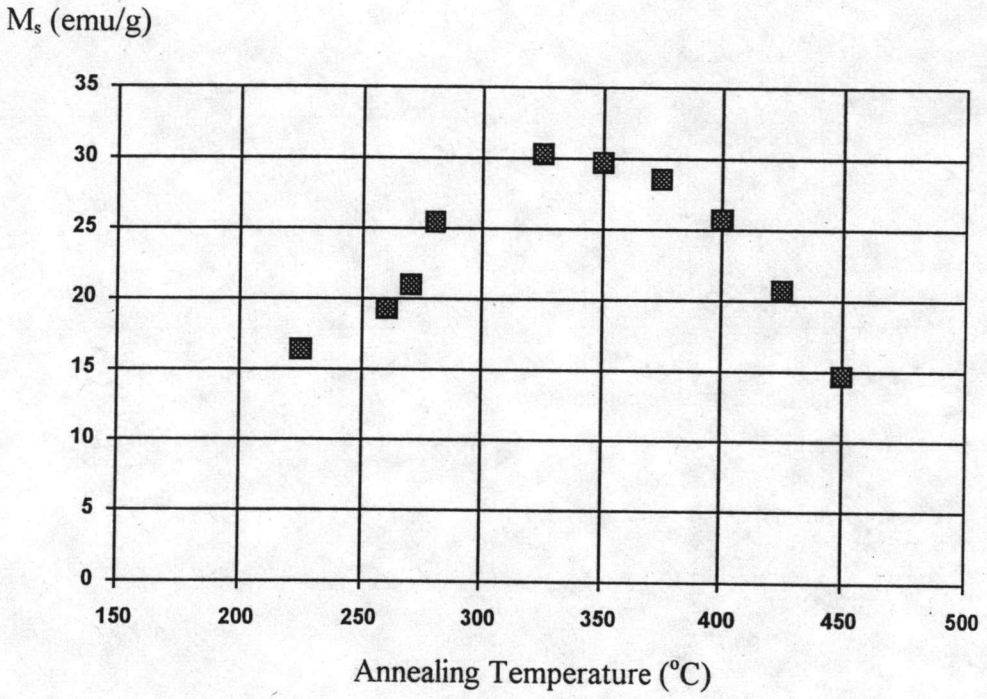

Figure 5.5(b) Relation between saturation magnetization and annealing temperatures in electromagnetic unit per gram of $Sm_2Co_7N_x$.

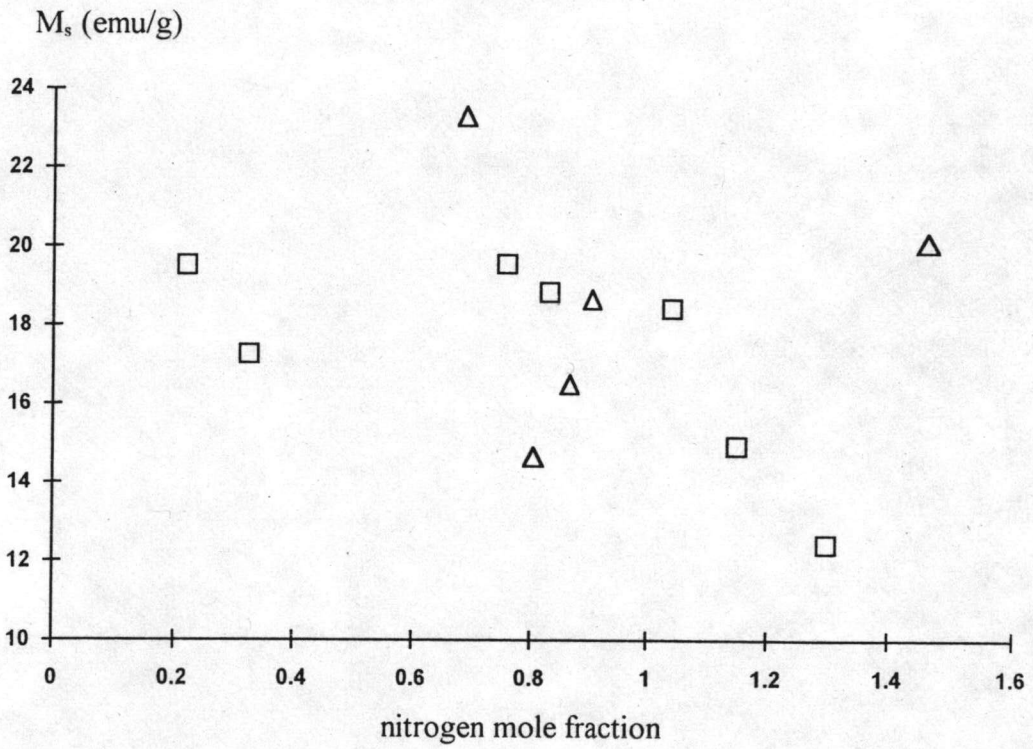

Figure 5.5 (c) Relation between saturation magnetization and nitrogen mole fraction in electromagnetic unit per gram of $Sm_2Co_{17}N_x$. Ours results denoted as Δ, previouse results (Narumon, 1995) denoted as □.

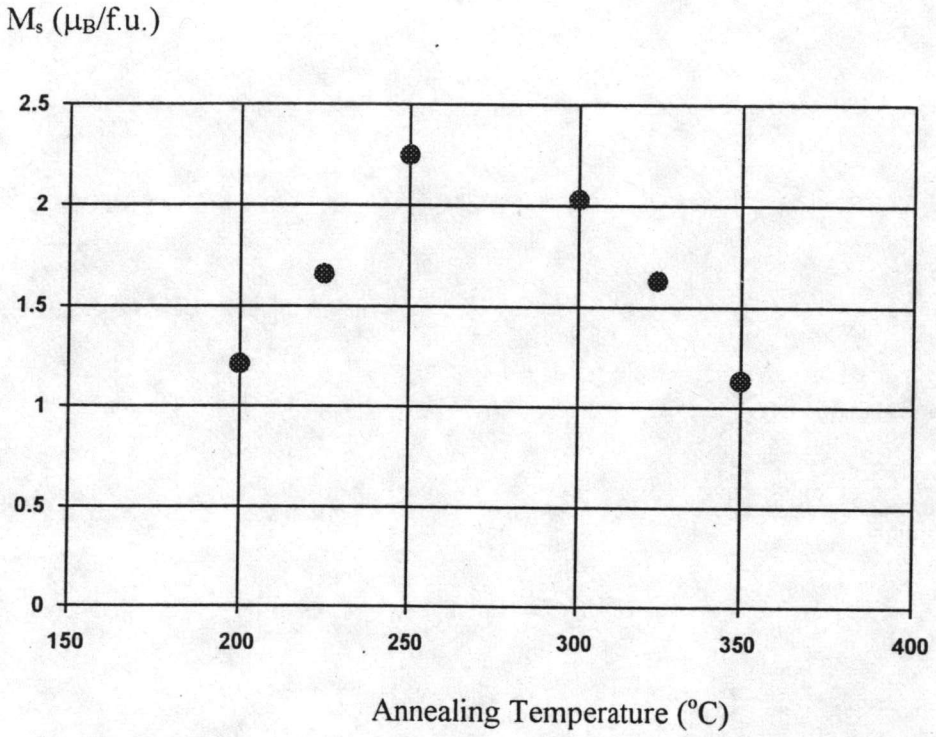

Figure 5.6(a) Relation of saturation magnetization in Bohr magneton per formula unit of $SmCo_5N_x$ and annealing temperatures.

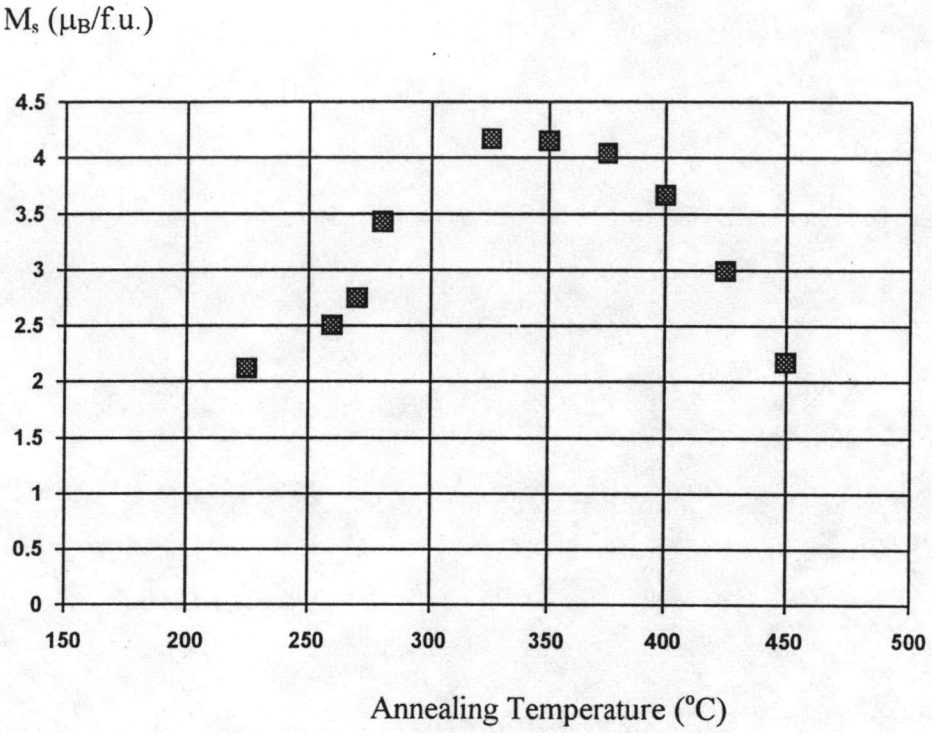

Figure 5.6(b) Relation of saturation magnetization in Bohr magneton per formula unit of $Sm_2Co_7N_x$ and annealing temperatures.

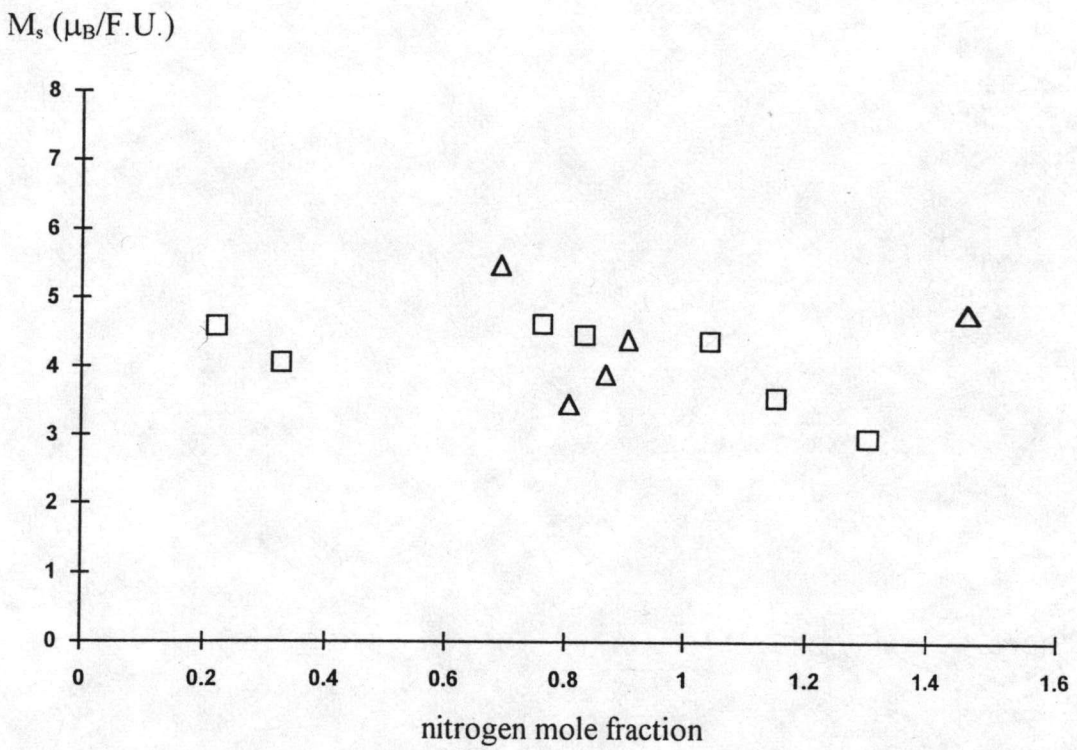

Figure 5.6 (c) Relation between saturation magnetization and nitrogen mole fraction in Bohr magneton per formula unit of $Sm_2Co_{17}N_x$. Ours results denoted as Δ, previouse results (Narumon, 1995) denoted as □.