Chapter I

General Properties of Rare Earth-Transition Magnets

Introduction

In this chapter we will discuss the type of magnetic materials which are now being widely used i.e., the rare earth-transition compounds. These permanent magnetic materials were developed over the past 25 years. Rare earth-transition compounds have high coercivity, stability at suitable temperature and high energy product. In the first and the second section, we will present a general description of both transition metal and rare earth elements, in the third section we will deal with the rare earth transition compounds and with the general properties of a specific type of these compounds, the Sm-Co compounds.

Magnetism of Rare Earth(RE) Elements

The rare earth metals are the elements in the periodic table that can be separated from the other elements in the periodic table by their anomalous properties. The outer electron configuration of these elements are the same (except in the $4f$ shell) and so their chemical properties are similar. Due to this similarity in their chemical properties, it is difficult to separate these elements from each other and to obtain them in pure form. This series varies from the light rare earth, ^{58}Ce, to heavy rare earth, ^{71}Lu. Two other elements are normally considered as rare earth because of their similar chemical properties; La just before Ce in the periodic table, and Y, which comes in the same position as La in the preceding row. The Rare earth elements differ in the number of electrons in the $4f$ shell, $4f^1$ for ^{58}Ce to $4f^{14}$ for ^{71}Lu. The electrons in $4f$ shell, which are called unfilled inner shell, contribute to the

magnetic properties of rare earth elements. The electron configuration of rare earth element are shown in figure 1.1. The $5d^1$ and $6s^2$ electrons of rare earth are easily removed and results in tripositive ions in ionic compounds. Anomalous ionic compounds of rare earth occurs with Eu and Yb since they have a divalent ion core with the excess electrons going into the $4f$ shell. This gives them the same electronic configuration as Gd and Lu respectively.

The electrons in the $4f$ shell are closely bound inside the outer closed shells and they play a small role in chemical bounding. As a result, the $4f$ electrons are screened by the other closed shell ($5s^2$, $5p^6$, $5d^1$ and $6s^2$) from the crystal field. In the simplest approximation, the $4f$ electrons are treated just like isolated ions. The $4f$ shell has 7 fold degeneracy corresponding to orbital quantum number $l = 3$. The magnetic quantum number of the orbital are -3, -2, -1, 0, 1, 2 and 3 for each orbital state. Two electrons with different spin quantum number, 1/2 and -1/2, can occupy each orbital quantum state. The arrangements of an electrons in $4f$ shell follows Hund's rule, (i) the spin arrangement should have a maximum total spin angular momentum, (ii) the orbital angular momentum should be a maximum value and (iii) the total angular momentum be calculated by $|L-S|$ for less than half full and $S+L$ for more than half full. The third rule is a consequence of the sigh of the intrinsic spin and orbital spin. In less than half full, the lowest energy corresponds to antiparallel alignment of both spin moments while in more than half full, the holes are presented and the lowest energy of the hole corresponds to parallel alignment of both spin moments. The electron arrangements of rare earth element follow from both Pauli principle and Hund's rule are shown in figure 1.2.

As we mention above, the $4f$ electrons contribute strongly to the magnetic moments of the system. Two phenomena occur when one combines the rare earth elements and the transition metal together, the crystal field interaction and the spin orbit coupling. The former dominates in the situation where the electrons are so rarely screened by the outer electron shell. This occurs with $3d$ electrons in the transition metal and it will be discussed in length in the next section. In the case of

4f electrons, they are screened from the crystal field by *5s* and *5p* shell. The effect of crystal field is small compare to the spin orbit coupling term. The magnetic moment of *4f* electrons comes from both the intrinsic spin and orbital spin, i.e. from total angular momentum, J. Thus $\mu = g\mu_B J$.

Magnetism of Transition Metal(TM)

Magnetism of a pure transition elements or metallic compounds is due almost entirely to a nearly free electrons in *3d* shell electrons which is an unfilled shell in these elements. The iron group ions, Fe, Co and Ni are the well known magnetic materials. They have 6, 7 and 8 electrons in this shell respectively. The *3d* shell contain 10 electrons at maximum. The L and S value of electrons in *d* shell follow figure 1.3 and the electron configuration of the iron group or *3d* group is that of figure 1.4.

For TM ions embedded in a solid, there are two large perturbations acting on the magnetic moment of 3d electrons. The first is the crystal field and the second is the spin orbit coupling term which was discussed in the case of rare earth ion earlier. The influence of both terms on the transition elements are not the same for all TM. For some iron group elements, the crystal field interaction dominates the spin orbit coupling but not the Coulomb interaction between an electron and ion. In other member of iron group and in other transition metals series, the crystal field and the spin orbit term are both comparable to the Coulomb coupling. The energy splitting caused by the crystal field, is due to the situation where the full rotation symmetry acting on an isolated ions is perturbed by the lowest symmetry of the field created by surrounding ions. Consider the case where the octahedral symmetry field perturbs the full rotation field to split the energy of the higher symmetry eigen value. An example of this energy splitting is illustrated by the case of 5 fold degeneracy. The wave function of *d* band which $l = 2$ are given by

$$\varphi_{zy} = R(r)\sin^2\theta\sin 2\phi = \frac{R(r)}{r^2}xy$$

$$\varphi_{x^2-y^2} = R(r)\sin^2\theta\cos 2\phi = \frac{R(r)}{r^2}(x^2-y^2)$$

$$\varphi_{yz} = R(r)\sin\theta\cos\theta\sin\phi = \frac{R(r)}{r^2}yz \qquad\qquad 1.1$$

$$\varphi_{zx} = R(r)\sin\theta\cos\theta\cos\phi = \frac{R(r)}{r^2}zx$$

$$\varphi_{z^2} = R(r)(3\cos^2\theta-1) = \frac{R(r)}{r^2}(2z^2-x^2-y^2)$$

The Hamiltonian of octahedral field is given by

$$H_p = A + D(x^4+y^4-z^4-3y^2z^2-3z^2x^2-3x^2y^2) \qquad\qquad 1.2$$

The first order shift in the energy of the ion due to the perturbation is given by the diagonal matrix elements of H_p, i.e.

$$\Delta E_n = \int \varphi_n^* H_p \varphi_n d\tau \qquad\qquad 1.3$$

Since φ_{xy}, φ_{zx} and φ_{yz} have the same symmetry, the degeneracy of these three states is not removed by the octahedral field. ΔE for these three electrons will be the same. The other two states, $\varphi_{x^2-y^2}$ and φ_{z^2} will be equally perturbed. Thus, the original five fold degenerate orbital level is splitted into two levels, one triply and the other doubly degenerate.

In order to determine the magnetic moment of an electron in *3d* shell we first compare of calculated value and experimental value of an effective magneton number, the number which tells us how many electrons in the *3d* shell contribute to a magnetic moments, see table 1.1. It was seen that the experimental value agree very well with the calculated value when the magnetic moment depends only on electron spin. We therefore neglect the spin orbital moment.

The quenching of the orbital angular momentum is due to the zero average value of L_z obtained if one use the wave function in equation 1.1. One obtain $<L_z> = 0$ for all degeneracy wave function. Thus the magnetic moment of transition ion or $3d$ electrons depend only on the intrinsic spin, i.e., $\mu = g\mu_B S$.

RE-TM Compounds

Recently, RE-TM compounds have play an important part in the fields of magnetic materials. The RE-TM compounds that are mostly widely used as permanent magnetic materials can be separated into two groups, one is the cobalt-base magnets and the other is the iron-base magnets. RE-TM magnets have an energy product and coercivity 10-30 times higher than those of the permanent magnets that was used before e.g. steels ferrite, ESD and alnicos. The Nd-Fe-B compounds, another new generation of permanent magnets which has seen rapid development since 1983, use more cheaper raw materials than Sm-Co compound. They, however, have stability problems at working temperature. For a magnetic substance to qualify for application, three basic properties are required; high saturation magnetization, the high Curie temperature and a single direction in the crystal lattice, along with the preferred spontaneous magnetization vector points. RE-TM compounds consist of various ratio of rare earth and transition elements e.g. RE-TM, 1-5 compounds for short, 1-7, 2-7, 2-17 etc. The crystal structure e.g. 1-5 is hexagonal, 2-7 is rhombohedral or hexagonal, 2-17 is rhombohedral (Th_2Ni_{17}) in Sm_2Co_{17} and hexagonal in Er_2Fe_{17} (Qiao et al., 1992) is responsible for a high coercivity of there magnets. This phenomena, the high coercivity, involve both magnetocrystalline anisotropy and mechanism of coercive force. Figures 1.5 and 1.6 show the formation of rare earth-cobalt base magnet and rare earth-iron base magnet.

We will first deal with the RE-Fe compounds, the iron-base compounds. These have been have most recently investigated compounds. Most of them are RE_2Fe_{17} compounds. Figure 1.7 shows the Curie temperature of RE_2Fe_{17} compare to rare earth-cobalt base magnet. It is seen that RE-Fe compounds have lower Curie

temperature when compared to RE-Co compounds. Ray and Strnat (1972) attempted to increase this properties by inserting some Co into RE-Fe compounds to form the $RE_2(Co_{1-x}Fe_x)_{17}$ phase. Not only did the Curie temperature rise but the insertion of such element lead to change in the magnetocrystalline anisotropy from easy basal plane to easy axis anisotropy in some of the rare compounds. Figures 1.8 and 1.9 show the magnetic symmetry and Curie temperature of $RE_2(Co_{1-x}Fe_x)_{17}$ phase.

Other ways to improve the magnetic properties is to insert some light elements such as nitrogen to form $RE_2Fe_{17}N_x$, carbon to form $RE_2Fe_{17}C_x$ and hydrogen to form $RE_2Fe_{17}H_x$. The insertion of the third elements is one way to improve the magnetic properties of this compounds, e.g., increase the Curie temperature. The substitution of light elements such as H, C and N has improved the Curie temperature by about 200-400 $^{\circ}C$ (Isnard et al., 1994). Much attentions have been paid to the Sm compounds. Sm in these compounds is responsible for the high coercivity (Strnat and Strnat, 1991). Neutron scattering method has been used to determine the occupation sites of the interstitial elements. The insertion of such elements produces no change in crystal structure. In the rhombohedral Th_2Zn_{17} structure, Sm_2Fe_{17} compounds, C and N occupy in 9e site, the octahedral site (Qiao et al., 1992). The maximum allowed insertion is X=3 (Mukai and Fujimoto, 1992). The nitrogenation of Sm_2Fe_{17} change its magnetic nature from planar, which leads to the poor magnetic properties, to uniaxial anisotropy, which leads to improved magnetic properties (Mukai and Fujimoto, 1992). Table 1.2 shows the magnetic properties of RE_2Fe_{17} interstitial compounds.

Sm-Co Compounds

The Sm-Co compounds are the most recently used magnetic materials, especially $SmCo_5$. Figure 1.6 which shows the Curie temperature for Co rich to Co poor compounds $RECo_{13}$ has the best value. Unfortunately $RECo_{13}$ exist only as $LaCo_{13}$. Its crystal structure is cubic which lead to the poor magnetocrystalline anisotropy. An other Co rich compounds are RE_2Co_{17} which form both hexagonal

and rhombohedral phase depending on whether light or heavy rare earth is used. While the RE_2Co_{17} have higher Curie temperature than other Co rich compounds such as $RECo_5$, their crystalline anisotropy field are considerable lower than that of the $RECo_5$. Figure 1.10 shows the relationship of intrinsic magnetization and external field in both easy direction and hard direction.

In general, cobalt and rare earth spin moments are antiparallel. For the $RECo_5$ compounds, containing light rare earth compounds, (Ce to Eu), they are ferromagnetic while for those containing the heavy rare earth compounds (Tb to Yb), they are ferrimagnetic. A coercivity of Sm-Co compounds exceed 65.5 KOe for as-milled $SmCo_5$ powders heat treated at 973 K. The high anisotropy fields 250-440 KOe (Lui et al., 1992), is due to the high magnetocrystalline anisotropy. Crystal structure of such material, $CaCu_5$ hexagonal for $SmCo_5$, is responsible for high magnetocrystalline anisotropy.

In the other compounds such as Sm_2Co_{17} and Sm_2Co_7, the anisotropy field is low. The anisotropy fields of Sm_2Co_{17} is 65KOe, 5-7 times less than that of $SmCo_5$ (Strnat and Strnat, 1991). RE_2Co_{17} and RE_2Co_7 come in both hexagonal and rhombohedral phase. In two previous studies on Sm_2Co_{17} and Sm_2Co_7, nitrogenation process form $Sm_2Co_{17}N_x$ and $Sm_2Co_7N_x$, led to coercivity less than that of $SmCo_5$. The best value for the two compounds are 396 Oe for $Sm_2Co_7N_x$ and 1.4 KOe for $Sm_2Co_{17}N_x$. The nitrogenation of the RE-Co compounds has not been investigated extensively. The reason for this is RE-Co compounds (without the nitrogenation) have the desired magnetic properties. The Co in them contribute to high saturation magnetization, whereas the Fe in RE-Fe compounds does not. As we mentioned the magnetic properties of RE-Fe compounds can be improved by insert the third element, mostly the light elements, to form a new compounds. The third elements mostly are N, C, H or B. The latter results in the new compound, Nd-Fe-B compound, which has undergone rapid development since 1983. The improvements can be seen in the coercivity, saturated magnetization, curie temperature e.g.

RE_2Fe_{17}, the effect of carbon in $Sm_2Fe_{17}C_x$ is to increase the Curie temperature from 415 $^\circ$C to 493 $^\circ$C for x=0.5 and 552 $^\circ$C for x=1 (Qiao et al., 1992).

There are many other ways to improve the magnetic properties. Specimen preparation is one of them. Lui and co-worker showed that the coercive force of $SmCo_5$ compound can be increased by mechanical alloying. The coercivity of their specimen increased to 65KOe, much larger than the 20 KOe of isotropic magnets prepared by the standard powder metallurgy route. Ding, Street and McCromick (1992) have reported similar increase in Sm_2Fe_{17} compound after nitrogenation of as-milled powder. They found that the coercivity of the specimen at maximum applied fields, 50 KOe, is 31.3 KOe. They also noticed that the fields were not sufficient high to achieve the saturation of magnetization. In their process, they used a two step heat treatment, the first is to form the Sm_2Fe_{17} phase, with Th_2Zn_{17} structure, from the amorphous as-milled powder and a second, to form $Sm_2Fe_{17}N_x$ by nitriding. In both steps, vaporization of Sm occurred. They also detected an increase in the alpha-Fe phase and a small amount of $SmFe_3$. Extra amount of Sm is needed to avoid the formation of the soft and non magnetic phase. It should be noted that the vaporization of Sm was not mentioned in the investigation of $SmCo_5$ (Lui et al., 1992).

Aim of Study

The effect of nitrogenation on the magnetic properties of rare earth-transition compounds have been widely reported. Most of them are concerned with the Fe-based magnet, especially in Sm_2Fe_{17}. In this study, we are concern with the insertion of nitrogen into Sm_nCo_m to form the $Sm_nCo_mN_x$ phase and see how the nitrogenation effect to the magnetization of these materials. The experimental results of the saturation magnetization are qualitatively interpreted by mean of the Stoner collective electron model. The aim of this experiment is to obtain the dependence of magnetization on the mole fraction of nitrogen absorbed, which is

controlled by the annealed temperature. This investigation covers various composition of rare earth-transition compounds, i.e., $SmCo_5$, Sm_2Co_7 and Sm_2Co_{17}.

Ce	Pr	Nd	Pm	Sm	Eu	Gd
$4f^2 6s^2$	$4f^3 6s^2$	$4f^4 6s^2$	$4f^5 6s^2$	$4f^6 6s^2$	$4f^7 6s^2$	$4f^7 5d^1 6s^2$

Tb	Dy	Ho	Er	Tm	Yb
$4f^8 5d^1 6s^2$	$4f^{10} 6s^2$	$4f^{11} 6s^2$	$4f^{12} 6s^2$	$4f^{13} 6s^2$	$4f^{14} 6s^2$

Figure 1.1 The electron configuration of rare earth elements.

Spin	Orbital						
	3	2	1	0	-1	-2	-3
1/2	i	ii	iii	iv	v	vi	vii
-1/2	viii	ix					

Figure 1.2 Spin and orbital state of electrons in 4f shell follow Pauli's principle and Hund's rule.
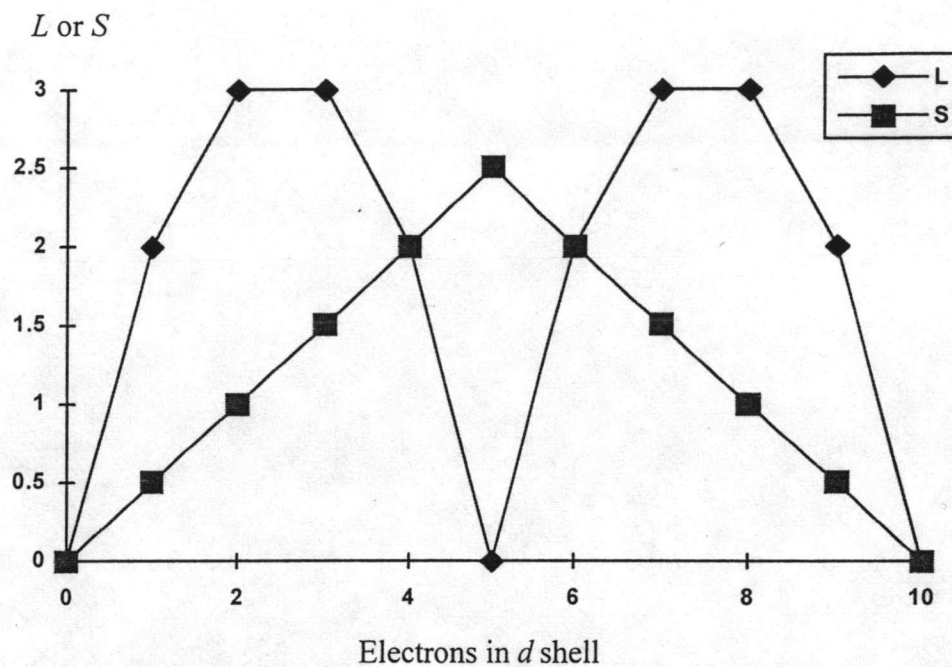
Figure 1.3 The variations of L and S for the ground states of iron-group ions as the d band is filled. (Martin, 1967)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$

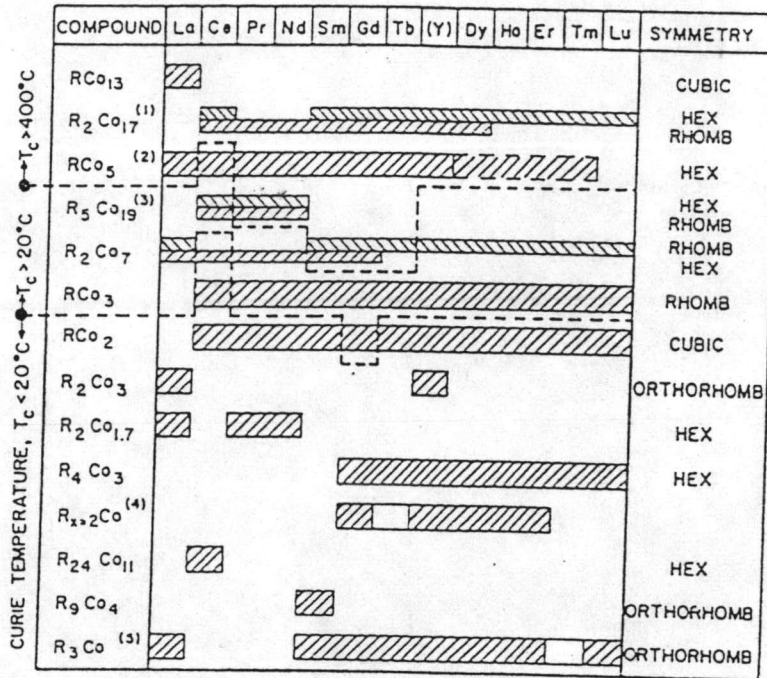Figure 1.4 Electron configuration of iron-group ions.

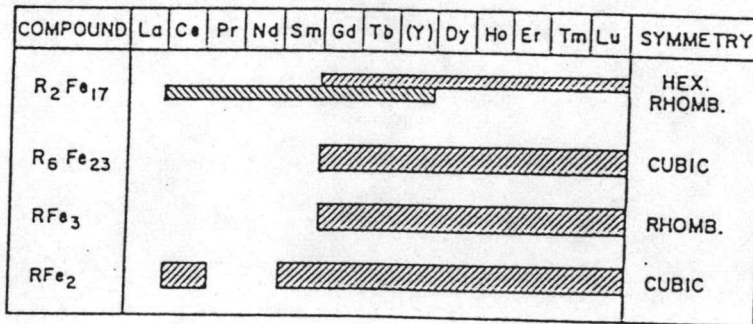Figure 1.5 Various form of rare earth-cobalt compounds include the Curie temperature and crystal symmetry. (Strnat, 1972)

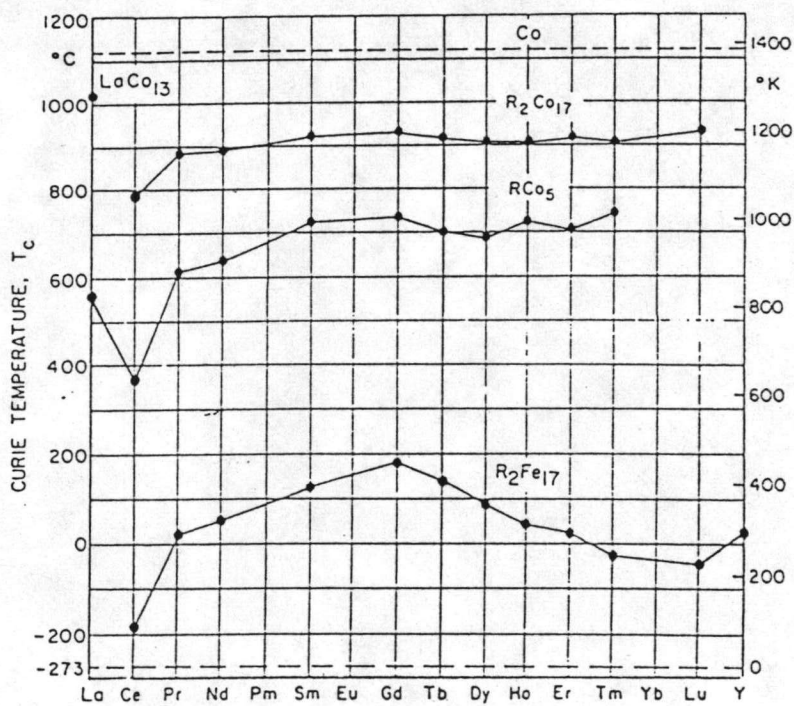Figure 1.6 Summary of rare earth-iron intermetallic phase. (Strnat, 1972)

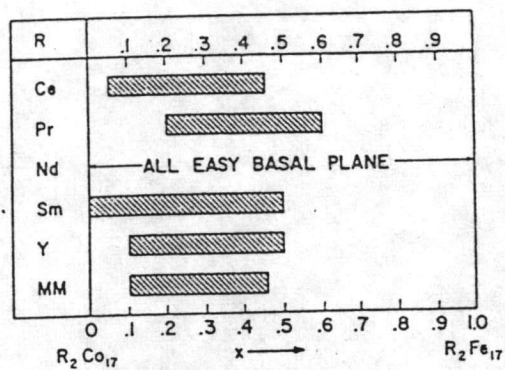Figure 1.7 Curie temperature of RECo5, RE2Co17 and RE2Fe17 compounds compare to the Co-rich compound, LaCo13, and Co.

Figure 1.8 Magnetic symmetry of $RE_2(Co_{1-x}Fe_x)_{17}$ compounds. Share areas indicate the rang of x in which the crystallographic c axis is the direction of easy magnetization. (Ray and Strnat, 1972)
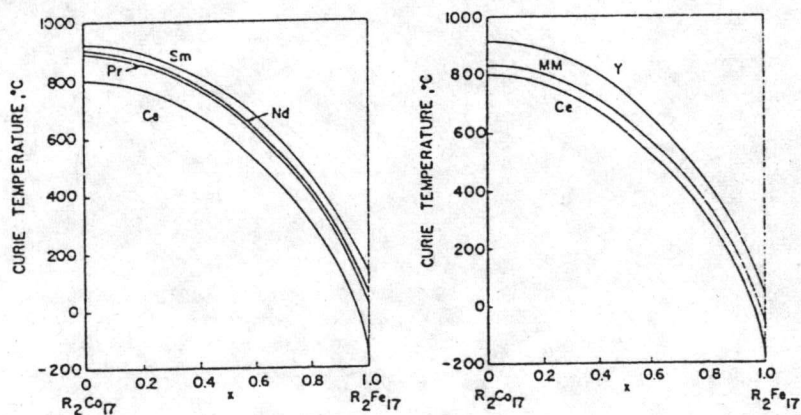

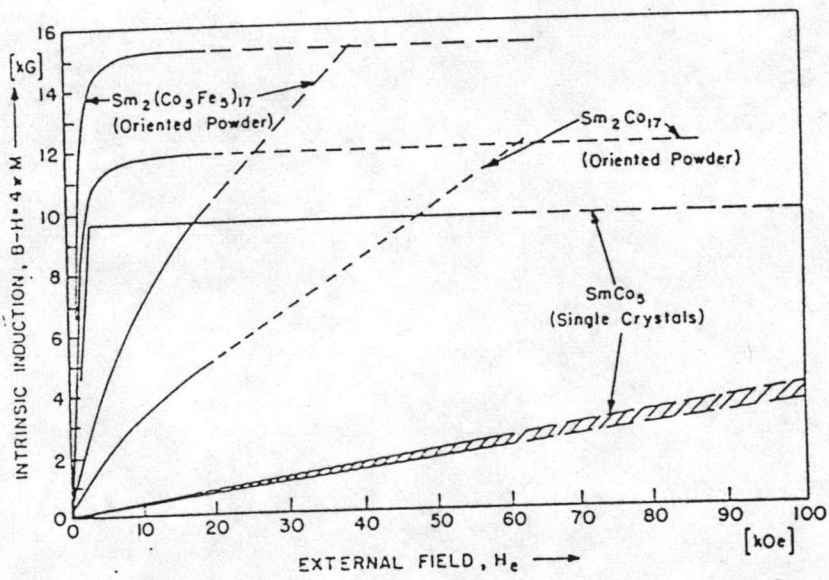Figure 1.9 Curie temperatures of $RE_2(Co_{1-x}Fe_x)_{17}$.

Figure 1.10 Relation between external magnetic field and intrinsic magnetic moments of both hard and easy direction.

Ion	p(calc) $g(J(J+1))^{1/2}$	p(calc) $2(s(s+1))^{1/2}$	p(exp)
Ti^{3+}, V^{4+}	1.55	1.73	1.8
V^{3+}	1.63	2.83	2.8
Cr^{3+}, V^{2+}	0.77	3.87	3.8
Mn^{3+}, Cr^{2+}	0	4.90	4.9
Fe^{3+}, Mn^{2+}	5.92	5.92	5.9
Fe^{2+}	6.70	4.90	5.4
Co^{2+}	6.63	3.87	4.8
Ni^{2+}	5.59	2.83	3.2
Cu^{2+}	3.55	1.73	1.9

Table 1.1 Effective magneton numbers for iron group ions.

Compounds	M_s(T)	B_a(T)	$(BH)_{max}$ (KJm^{-3})	T_c(K)
$Sm_2Fe_{17}C_{3-\delta}$[*]	1.45	16	418	668
$Sm_2Fe_{17}N_{3-\delta}$[*]	1.54	22	472	749
Sm_2Fe_{17}[**]	1.03	< 1.0	--	116
$Sm_2Fe_{17}N_{2.1}$[**]	1.54	> 6.0	--	470
$Sm_2Fe_{17}C_{1.1}$[**]	1.24	4.0	--	207
$Sm_2Fe_{17}C_{1.1}N_1$[**]	1.53	> 8.0	--	471

[*] Sun, Otani and Coey (1992)
[**] Coey and Sun (1990)

Table 1.2 Magnetic properties of Sm_2Fe_{17} intermetallic compounds.