### A New Series of Rare-earth Iron Carbides $R_2Fe_{15}Si_2C_y$

by

Zheng-Wen Li

A Thesis Submitted to the Faculty of Graduate Studies in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

Department of Physics University of Manitoba Winnipeg, Manitoba

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#### A NEW SERIES OF BARE-EARTH IRON CARBIDES R2Fe15Si2Cy

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ZHENG-WEN LI

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of

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DOCTOR OF PHILOSOPHY

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### Abstract

 $R_2Fe_{17}N_y$  and  $R_2Fe_{17}C_y$  have attracted much attention because of their excellent intrinsic magnetic properties. However, these nitrides and carbides prepared by a gas-phase reaction have a major drawback, namely their chemical or structural instability at high temperature.

We have discovered that Si substitution is able to stabilize the 2:17 structure of the carbides. A new series,  $R_2Fe_{15}Si_2C_y$  (R=Nd, Sm, Gd and Er), has been prepared by heating powders of their parents in CH<sub>4</sub> gas at 700°C instead of usual 500°C. For these carbides, the carbon concentrations are close to the theoretical value of y=3 and the 2:17 structure is still retained up to 700°C. Therefore, it is possible to make these carbides into the anisotropic permanent magnets by aligning and then sintering.

The crystal structures, the Curie temperatures, the saturation magnetizations, the temperature dependences of the magnetization, the magnetic anisotropies and the spin reorientation transitions of  $R_2Fe_{15}Si_2C_y$  have been studied by x-ray diffraction and magnetic measurements. These carbides have elevated Curie temperatures as well as other magnetic properties that are modified as compared to their parents. For  $Sm_2Fe_{16}SiC_{2.7}$ , the Curie temperature is 660 K; the anisotropy field and saturation magnetization at room temperature are 95 kOe and 92 emu/g, respectively. The origin of the unexpected decrease in the magnetization is discussed.

The hyperfine fields, the distribution of Fe and Si atoms on each Fe site and the temperature dependence of the hyperfine parameters have been studied by Mössbauer spectra in an attempt to unravel the magnetic properties of these carbides on an atomic scale. The exchange integrals as a function of the distance between the Fe-Fe pairs have been obtained; the relationships between the Curie temperature and the site occupancy of Si atoms have been found. A negative exchange interaction model is proposed to interpret the origin in the greatly elevated Curie temperature for the nitrides and carbides and to predict the Curie temperatures of  $R_2(FeSi)_{17}$  compounds; this model is consistent with the experimental results.

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## List of Symbols

A	Area of Mössbauer spectra
$A_{nm}$	Crystal field coefficient
a	Lattice parameter
$B_{nm}$	Crystal field parameter
Br	Remanence
$(BH)_{max}$	<sub>az</sub> Maximum magnetic energy product
Ь	Angle factor, the area ratio of the 2nd plus 5th lines
	to the 3rd plus 4th lines
$\mathcal{B}_S$	Billouin function
с	Lattice parameter
$E_a$	Anisotropy energy
EFG	Electric field gradient
$F_i(\mathbf{A})$	The occupancy fraction of the A atoms on the <i>i</i> th site
F <sub>hkl</sub>	Structure factor
fs	Recoilless fraction for sources
fa	Recoilless fraction for absorber
G	De Gennes factor
g	Gyromagnetic ratio
$H_a$	Anisotropy field
H <sub>c</sub>	Coercive force
$H_{hf}$	Hyperfine field
$H_{Fe}$	Molecular field of Fe sublattice
$H_R$	Molecular field of R sublattice
$J_{AB}$	Exchange integrals of the A-B pairs
$J_+$	Positive exchange integral
<b>J</b> _	Negative exchange integral
$J_R$	Angular momentum of R atoms
$K_n$	The nth-order anisotropy constant
M <sub>s</sub>	Saturation magnetization
$M_{Fe}$	Fe sublattice magnetization
$M_R$	R sublattice magnetization
$N_i(\mathbf{A})$	The occupation number of the A atoms on the <i>i</i> th site

$N_d$	Demagnetization factor
$n_{AB}$	Molecular field coefficient
$O_{nm}$	Stevens operator
$\boldsymbol{Q}$	Nuclear quadrupole moment
q	The $z$ component for the principal axes of EFG tensor
$T_f$	Curie temperature
$V_{cf}$	Crystal field potential
$Z_+$	The numbers of the neighboing Fe atoms that are linked
	by positive interactions with a given atom.
Z.,	The numbers of the neighboing Fe atoms that are linked
	by negative interactions with a given atom.
$Z_R$	Partition function
$\alpha_J$	The first-order Stevens factor
$oldsymbol{eta}_J$	The second-order Stevens factor
β	Angle between the $\gamma$ -ray propogation and and hyperfine field directions
$eta_F$	Conversion coefficient between the hyperfine field and
	Fe moment
Γ	Line-width
δ	Isomer shift
ε	Quadrupole splitting
$\theta_n$	The nth-order Stevens factor
σ	Specific magnetization
$\sigma(\mathbf{E})$	The reduced resonance absorption cross-section
$\sigma_0$	The maximum resonance absorption cross-section
μι	Nuclear magnetic-dipole moment
$\mu_N$	Nuclear magneton
$\mu_B$	Borh magneton
μ <sub>Fe</sub>	Fe magnetic moment
$\mu_R$	Rare-earth moment

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### Introduction

Permanent magnets play an important role in industry and technology. Since the first permanent magnet, carbon steel, was made, permanent magnets have undergone great developments. The figure gives the best values of the magnetic energy products,  $(BH)_{max}$ , and the intrinsic coercive forces,  $H_c$ , attained as a function of time (Strnat, 1986). The best permanent magnets are rare-earth transition metal compounds. Co-based Sm-Co alloy was made during the 1970s and a maximum energy product of 33 MGOe has been achieved (Mishra et al, 1981). Febased Nd-Fe-B alloy was discovered in 1984 (Sagawa et al) and an unprecedented energy product as high as 50.6 MGOe has been obtained (Sagawa et al, 1987).



A chronology of permanent magnet development since 1900.

The discovery of Nd-Fe-B permanent magnets has initiated a worldwide search for new high-performance Fe-based permanent magnetic materials. The search produced a number of interesting new rare-earth iron compounds including  $R(Fe, M)_{12}$ with the ThMn<sub>12</sub> structure (DeBore et al, 1987), R<sub>3</sub>(Fe, M)<sub>29</sub> with the monoclinic structure (Collocott et al, 1992; Li H S et al, 1994), and the composite magnet Nd<sub>4</sub>Fe<sub>80</sub>B<sub>20</sub> (Coehoorn et al, 1988). However, the intrinsic magnetic properties of these materials do not surpass those of Nd-Fe-B. A real breakthrough was the discovery of rare-earth iron nitrides and carbides prepared by a gas-phase reaction (Coey and Sun, 1990; Coey et al, 1991).

Interstitial R-Fe carbides,  $R_2Fe_{17}C$ , were first prepared by melting the primary materials R, Fe and C followed by annealing at 1000°C (DeMooij and Buschow, 1988). The introduction of C atoms not only increases the Curie temperature, but also modifies the magnetic anisotropy for  $Sm_2Fe_{17}C$ . However, for those carbides made by alloying, the Curie temperature is only elevated 100-150° as compared to their parent, because the C concentration is rather low (y<1.6 for the heavy rareearth carbides and y≤1.0 for the light rare-earth carbides). In order to increase the C concentration two ways were proposed. One, a melt-spinning method was used to make the heavy rare-earth carbides (Shen et al, 1992). Two, a third element, Ga, was added in  $R_2Fe_{17}$  (Shen et al, 1993, 1994). By these two ways the C concentration can be raised to y≥2.

In 1990 Coey and Sun (1990) first prepared a new series of interstitial rare-earth iron nitrides  $R_2Fe_{17}N_y$  by heating powders of the  $R_2Fe_{17}$  parents in  $N_2$  or  $NH_3$  gas at 500°C. For these nitrides made by a gas-phase reaction, the N concentration can reach y=2.4 to 2.7 (very close to the theoretical value of y=3) and the intrinsic magnetic properties are superior to  $Nd_2Fe_{14}B$ . The most striking ones are an increase of the Curie temperatures by about 400° and, for  $Sm_2Fe_{17}N_y$ , a high uniaxial anisotropy with an anisotropy field of 140 kOe at room temperature.

After  $R_2Fe_{17}N_y$ , many new rare-earth iron nitrides and carbides, such as  $R_2Fe_{17}C_y$ (Coey et al, 1991a), RTiFe<sub>11</sub>N<sub>y</sub> (Yang Y C et al, 1991), RTiFe<sub>11</sub>C<sub>y</sub> (Hurley and Coey, 1992) and  $R_3(Fe, M)_{29}N_y$  (Collocott et al, 1992; Yang F M et al, 1995) were prepared by using the gas-phase reaction. Not only has much work been expended in the search for novel and improved materials, but also in the investigation of the fundamental physics involved. These investigations have included magnetic properties, crystal structure, thermodynamics, phase relations, electronic properties and bond structure. The experimental methods applied involve many techniques nowadays available to solid state scientists, including various types of magnetic measurements, x-ray diffraction, standard metallography (Huang et al, 1991; Endoh et al, 1991), Kerr microscopy (Mukai and Fujimoto, 1992), transmission electron microscopy, Mössbauer spectroscopy, neutron diffraction and nuclear magnetic resonance (Kapusta et al 1991, 1991a; Zhang Y D et al, 1995).

However, these nitrides and carbides have a major drawback, namely their structural or chemical instability at high temperatures. They will completely decompose into  $\alpha$ -Fe and RN or RC at 600°C. Because of this drawback, it is difficult for the nitrides and carbides to be made into anisotropic permanent magnets by aligning and sintering. We first discovered (Li Z W et al, 1994; 1995) that Si substitution can elevate the gas-phase reaction temperature to 700°C. For these carbides, the C concentration is close to the theoretical value of y=3 and the 2:17 structure is still retained up to  $900^{\circ}$ C. A new series,  $R_2(Fe, Si)_{17}C_y$ , has been prepared by the gas-phase reaction and their crystal structures and magnetic properties are reported in this thesis. In chapters 1-3, the basic theory of R-Fe compounds, the previous work on  $R_2Fe_{17}C_y$  and  $R_2Fe_{17}N_y$  and the theory of Mössbauer spectroscopy are reviewed. The sample preparation and the experimental procedure are decribed in chapter 4. The crystal structure and the magnetic properties of  $R_2(Fe, Si)_{17}C_y$  are reported in chapters 5 and 6. In chapters 7-9, Mössbauer spectra are used to study the magnetic properties of these carbides at an atomic level. The spin-reorientation transitions for  $Er_2Fe_{15}Si_2C_y$  are studied in chapter 8; the negative exchange interaction model is proposed in chapter 9 to interpret the origin of the greatly elevated Curie temperature for the nitrides and carbides. The main accomplishments are summarised in chapter 10.

### Chapter 1

## **Review: Magnetic Properties of R-Fe Compounds**

The figures of merit usually used to describe the attributes of a permanent magnet are the remanence,  $B_r$ , the coercive force,  $H_c$ , and the maximum energy product,  $(BH)_{max}$ . These parameters are determined from the hystersis loop lying in the second quadrant, as shown in Fig.1.1. In addition, the Curie temperature,  $T_f$ , is also an important parameter which determines the useful temperature range of the permanent magnets.

An excellent permanent magnet at room temperature must have a high saturation magnetization and a high magnetocrystalline anisotropy in order to have both a high remanence and coercive force. In addition, the theoretical maximum energy product depends on the saturation magnetization via  $(BH)_{max}=0.25M_s^2$ . The magnetic properties of the 3d transition metals and the rare-earth metals are listed in Tables 1.1 and 1.2. The 3d metals (Fe, Co and Ni) have high Curie temperatures and high saturation magnetizations at room temperature; however, their magnetocrytalline anisotropies are only  $4.6 \times 10^4$  and  $41.0 \times 10^4$  J/m<sup>3</sup> for Fe and Co, respectively. On the other hand, the rare-earth metals (4f metals) have a huge magnetocrystalline anisotropy, which is about 100-1000 times larger than that for the 3d elements; however, their Curie temperatures are below room temperature. The combination of 3d and 4f elements may produce excellent permanent magnets. In fact, the best permanent magnets were indeed discovered among the rare-earth transition (R-T) metallic compounds. Co-based Sm(Co, Fe, Cu, Zr)<sub>7.4</sub> alloy has a magnetic energy product of 33 MGOe (Mishra et al, 1981). Fe-based



Figure 1.1: The demagnetizing quadrant of a typical permanent magnet and the variation of the energy product as a function of the applied field.

	$T_C$ (K)	M <sub>s</sub> (kGs)	$K_1 (10^4 \text{ J/m}^3)$
Fe	1043	22.0	4.6
Co	1403	18.2	41.0
Ni	631	6.4	-0.5

Table 1.1: Magnetic properties of 3d transition metals.

Nd-Fe-B alloy achieves the unprecedented energy product of 50.6 MGOe (Sagawa et al, 1987). Their covercivities or magnetic energy products are 5-10 times larger than the highest value for other types of magnets, such as Alnico alloys and Ba ferrites.

In order to understand the high Curie temperature and the huge magnetocrystalline anisotropy, the exchange interaction and the crystal field interaction in the rare-earth transition compounds require further discussion.

#### **1.1 Exchange interactions**

There are three exchange interactions for the R-Fe compounds, the R-R interaction, the R-Fe interaction and the Fe-Fe interaction. The R-R interaction is the weakest and Fe-Fe interaction is the strongest. These exchange interactions

	S	L	J=L±S	ground	g	$\mu (\mu_B)$		$T_{c}$ (K)	$K_{20}$
				state		Cal.	Obs.		$(10^4 \text{ J/m}^3)$
La	0	0	0	$^{-1}S_{0}$	0	0			
Ce	1/2	3	5/2	${}^{2}F_{5/2}$	6/7	2.54	2.51		
Pr	1	5	4	$^{3}H_{4}$	4/5	3.58	2.56		
Nd	3/2	6	9/2	${}^{4}I_{9/2}$	8/11	3.62	3.40		
$\mathbf{Sm}$	5/2	5	5/2	${}^{6}H_{5/2}$	2/7	0.85	1.74		
Gd	7/2	0	7/2	<sup>8</sup> S <sub>7/2</sub>	2	7.94	7.98	293	-21
ТЬ	3	3	6	${}^{7}F_{6}$	3/2	9.72	9.77	230	9000
Dy	5/2	5	15/2	${}^{6}H_{15/2}$	4/3	10.64	10.83	179	8700
Ho	2	6	8	<sup>5</sup> I8	5/4	10.60	11.20	1 <b>32</b>	6600
Er	3/2	6	15/2	${}^{4}I_{15/2}$	6/5	9.58	9.85	85	-970
$\mathbf{Tm}$	1	5	6	${}^{3}H_{6}$	7/6	7.56	7.61	58	
Yb	3/2	6	9/2	<sup>4</sup> <i>I</i> <sub>9/2</sub>	8/11	3.62	3.40		

Table 1.2: Magnetic properties of rare-earth ions and metals.

determine the Curie temperatures of the R-Fe compounds.

#### 1.1.1 Fe-Fe interaction

There are two models for the Fe-Fe exchange interaction. One is the Heisenberg model that describes a direct interaction between two localized 3d spins. The Heisenberg Hamiltonian is given by

$$\mathcal{H}_{H} = -2\sum_{i>j} J_{ij} \mathbf{S}_{i} \cdot \mathbf{S}_{j}$$
(1.1)

where  $J_{ij}$  is the exchange integral between the *i*th and *j*th spins. The other is the itinerant electron model proposed by Stoner. Generally, the Heisenberg model is used in the case of insulators and the itinerant electron model is suitable for metals and alloys.

The Fe moments at T=0 K for R-Fe compounds are usually calculated by the itinerant electron model. Band-structure calculations have been performed for Y-Fe, Y-Co and Y-Ni compounds by Cyrot and Lavagna (1979), Shimzu and Inoue (1986,1987), Yamada and Shimizu (1986) and Coehoorn (1989). Based on the state-density curves for 3d electrons with spin-up and spin-down, the rareearth transition intermetallic compounds are divided into two catgories, weak and strong ferromagnets. If two sub-bands with opposite spin are both partly filled, the compounds are weak ferromagnets. If the sub-band with spin-up is filled up but that with spin-down is not filled, the compounds are strong ferromagnets. Usually, Y-Fe compounds are weak ferromagnets and Co-rich Y-Co compounds plus  $Y_2Ni_{17}$  are strong ferromagnets.

The Heisenberg model as adapted to the mean-field model (the spin operator  $S_j$  in (1.1) is replaced by its average value  $\langle S_j \rangle$ ) is often used to calculate the Curie temperature. Based on the mean-field theory, the molecular-field coefficient  $n_{FeFe}$  and the exchange constant  $J_{FeFe}$  that describe the magnitude of the Fe-Fe interaction, can be obtained from the Curie temperature of Y-Fe compounds

$$n_{FeFe} = T_f / C_{Fe} \tag{1.2}$$

and

$$J_{FeFe} = \frac{3k_B T_f}{2Z\hbar^2 S_{Fe}(S_{Fe}+1)}$$
(1.3)

where  $C_{Fe}$  is the Curie constant, Z is the neighboring coordination number for a given Fe atom and  $S_{Fe}$  is the spin quantum number of Fe.

#### 1.1.2 R-R interaction

The spatial extent of 4f electrons of R atoms is very small as compared to the interatomic distances. There almost is no substantial overlap of the wave functions between 4f electrons centered on different R atoms. Consequently, a direct interaction between the localized 4f electrons, like 3d electrons, is impossible. The RKKY theory (Ruderman and Kittel, 1954; Kasuya, 1956; Yosida, 1957), based on an indirect interaction betweeen the localized electrons by means of the conduction electrons, has been proposed to explain magnetic ordering in rare-earth metals. In this theory, the second-order perturbation interaction between the s conduction electrons and the localized 4f electrons is calculated by using the first-order perturbed wave function of the conduction electrons. As a result, the spin operators of the conduction electrons are eliminated and the exchange interaction for the R ions is given by

$$\mathcal{H}_{RKKY} = -\sum_{i,j} J(R_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j$$
(1.4)

where  $S_i$  and  $S_j$  are the spins of the *i*th and *j*th R atoms, respectively. The exchange interaction constant,  $J(R_{ij})$ , between the *i*th and *j*th R ions has been derived by van Vleck (1962),

$$J(R_{ij}) = -\frac{9\pi N^2}{2E_F} \Gamma_0^2 (g_J - 1)^2 F(2k_F |\mathbf{R_{ij}}|)$$
(1.5)

where  $\Gamma_0$  is the exchange interaction constant between the R spins and the conduction electron spins,  $g_J$  is the gyromagnetic ratio,  $E_F$  is the Fermi energy,  $k_F$  is the wave number at the Fermi surface and F(x) is the RKKY function, given by

$$F(x) = \frac{x \cos x - \sin x}{x^4} \tag{1.6}$$

An important conclusion of the RKKY theory is that the exchange interaction,  $J(R_{ij})$ , is an oscillatory function of the distance  $|\mathbf{R_{ij}}|^3$ . Consequently,  $J(R_{ij})$  may be positive or negative, which corresponds to ferromagnetic or antiferromagnetic ordering. In addition, this interaction is rather weak and leads to a low ordering temperature for the rare-earth metals.

#### **1.1.3 R-Fe interaction**

Because of the spatial localization of the 4f shell, the direct overlap between the 3d and 4f spins is rather small. Some models have been proposed in which the R-Fe interactions proceed through polarization of the 6s or 5d electrons (Wallace, 1968; Buschow, 1971; Campbell, 1972; Szpunar and Kozarzewski, 1977). The model suggested by Campbell involves a direct on-site 4f-5d exchange coupling. According to this scheme (as shown in Fig.1.2), the localized 4f spins create a positive localized 5d moment through the intra-ionic 4f-5d exchange and, subsequently, the direct 5d-3d exchange occurs as in normal transition metals. This interaction is negative. In combination with positive 4f-5d interactions, it leads to a parallel alignment between R and Fe moments for the light rare-earths ( $\mathbf{J} = \mathbf{L} - \mathbf{S}$ ) and to an antiparallel alignment for the heavy rare-earths ( $\mathbf{J} = \mathbf{L} + \mathbf{S}$ ).

Experimentally, the molecular-field coefficient,  $n_{FeR}$ , for R-Fe compounds can be found from an analysis of the high field magnetization curves or of the Curie temperatures. It is known that for a finely powdered sample which is free to rotate



Figure 1.2: Schematic diagram illustrating the coupling between the R and Fe moments by means of 4f-5d exchange interaction.

in the sample holder under an applied magnetic field, the free-energy expression can be written as

$$F = n_{RFe} M_{Fe} \cdot M_{R} - H_{0} \cdot (M_{Fe} + M_{R})$$
  
=  $n_{RFe} M_{Fe} M_{R} \cos \alpha - H_{0} (M_{Fe}^{2} + M_{R}^{2} + 2M_{Fe} M_{R} \cos \alpha)^{1/2}$  (1.7)

where  $M_{Fe}$  and  $M_R$  are the magnetization vectors for the Fe and R sublattices, respectively,  $H_0$  is the applied field and  $\alpha$  is the angle between the R and Fe sublattice magnetization vectors.

By minimizing this expression with respect to the angle  $\alpha$ , the following solutions are obtained

$$\begin{cases} \sin \alpha = 0 \\ \cos \alpha = [(H_0/n_{RFe})^2 - M_R^2 - M_{Fe}^2]/2M_R M_{Fe} \end{cases}$$
(1.8)

The first solution leads to  $\alpha=0$  or 180°; With the constraint  $-1 \le \cos \alpha \le 1$ , the second expression leads to

$$n_{RFe} \mid M_{Fe} - M_R \mid \leq H_0 \leq n_{RFe} (M_{Fe} + M_R)$$
(1.9)

Apprarently, there are two critical magnetic fields, viz

$$H_{1,crit} = n_{RFe} | M_{Fe} - M_R |$$
(1.10)

$$H_{2,crit} = n_{RFe}(M_{Fe} + M_R) \tag{1.11}$$

Below  $H_{1,crit}$  the R (heavy rare-earth) and Fe sublattice moments are antiparallel. Above  $H_{2,crit}$ , they are parallel. In the intermediate field range,  $H_{1,crit} < H_0 < H_{2,crit}$ , the canting angle  $\alpha$  is non-zero. The resultant magnetization,  $M = |\mathbf{M_{Fe}} + \mathbf{M_R}|$ , is given by

$$M = H_0/n_{RFe} \tag{1.12}$$

Based on (1.10), (1.11) or (1.12), the value of  $n_{RFe}$  can directly be found from the kinks or the slope of the magnetization curve in the high-field region (Verhoef et al, 1989). This technique has been used for a large number of ferrimagnetic compounds, namely R-Fe (Verhoef et al, 1992a), R-Co (Verhoef et al, 1990, 1992b; Zhou et al, 1992; Franse et al, 1992) and R-Ni (Marquina et al, 1992; DeBoer and Buschow, 1992).

In another method, based on the high-temperature approximation of the meanfield model, the Curie temperature,  $T_f$ , can be written as

$$T_f = \frac{1}{2} [T_{FeFe} + T_{RR} + \sqrt{(T_{FeFe} - T_{RR})^2 + 4T_{FeR}^2}]$$
(1.13)

where

$$T_{FeFe} = n_{FeFe}C_{Fe} \tag{1.14}$$

$$T_{RR} = n_{RR}C_R \tag{1.15}$$

$$T_{FeR} = n_{FeR} \sqrt{C_{Fe}C_R} \tag{1.16}$$

In eqs. (1.13) to (1.16),  $T_{FeFe}$ ,  $T_{FeR}$  and  $T_{RR}$  represent the contributions to the Curie temperature for the Fe-Fe, Fe-R and R-R interactions, respectively, and  $C_{Fe}$  and  $C_R$  are the Curie constants of the Fe and R sublattices, respectively. Combination of (1.13)—(1.16) leads to

$$n_{FeR} = \sqrt{\frac{(T_f - T_{FeFe})(T_f - T_{RR})}{C_{Fe}C_R}}$$
(1.17)

By applying (1.17), the values of  $n_{FeR}$  have been derived for  $R_2Fe_{14}B$ ,  $RCo_2$  (Belorizky et al, 1987) and  $RFe_2$  (Brooks et al, 1989).

#### **Crystal-field** interaction 1.2

Both the crystal-field (or crystal-electric-field) and spin-orbit interactions can produce a large magnetocrystalline anisotropy. For most of the R-Fe compounds the crystal field interaction is much weaker than the spin-orbit interaction because the 4f shell is screened by the outer 5d and 6s electrons. Consequently, the huge magnetocrystalline anisotropy energy has its origin in the crystal field interaction between the non-spherical orbitals of the 4f shell and the non-spherical electrostatic field of the environment acting on the 4f electrons.

#### 1.2.1 **Crystal-field** potential

The crystal field potential,  $V_{cf}(\mathbf{r}_i)$ , produced by a charge,  $q_j$ , at a distance  $\mathbf{R}_j$ from the origin and acting on the ith 4f electron of a given R ion can always be expressed by spherical harmonics,  $Y_{nm}(\hat{\mathbf{r}}_i)$ 

$$V_{cf}(\mathbf{r_i}) = \sum_{j} \frac{q_j}{|\mathbf{R}_j - \mathbf{r_i}|} = \sum_{n=0} r_i^n \sum_{m=-n}^n A_{nm} Y_{nm}(\hat{\mathbf{r_i}})$$
(1.18)

where  $A_{nm}$  is a crystal field coefficient and is defined as

$$A_{n,m} = \sum_{j} \frac{4\pi q_j}{(2n+1)R_j^{n+1}} (-1)^m Y_{n,-m}(\hat{\mathbf{R}}_j)$$
(1.19)

From group theory, n in (1.18) and (1.19) must be even with  $n \leq 2l$  where l is the orbital quantum number. Thus, the crystal field potential,  $V_{cf}$ , over all 4felectrons is expressed as

$$V_{cf} = \sum_{n=0}^{n} \sum_{m=-n}^{n} A_{nm} \sum_{i} r_{i}^{n} Y_{nm}(\hat{\mathbf{r}}_{i})$$
(1.20)

After considering the symmetry of the crystal structure, the above formula can further be simplified. For example, the crystal field potential for a cubic and a hexagonal structure can be written as

$$V^{cub}(\mathbf{r}) = A_{40}r^4[Y_{40} + \sqrt{\frac{5}{14}}(Y_{44} + Y_{4-4})] + A_{60}r^6[Y_{60} - \sqrt{\frac{7}{2}}(Y_{64} + Y_{6-4})] \quad (1.21)$$
$$V^{hex}(\mathbf{r}) = A_{20}r^2Y_{20} + A_{40}r^4Y_{40} + A_{60}r^6 + A_{66}r^6(Y_{66} + Y_{6-6}) \quad (1.22)$$

$$Y^{hex}(\mathbf{r}) = A_{20}r^2Y_{20} + A_{40}r^4Y_{40} + A_{60}r^6 + A_{66}r^6(Y_{66} + Y_{6-6}) \quad (1.22)$$

#### 1.2.2 Crystal-field energy

From (1.20), the crystal-field Hamiltonian is given by

$$\mathcal{H}_{cf} = e \sum_{n=0}^{n} \sum_{m=-n}^{n} A_{nm} \sum_{i} r_{i}^{n} Y_{nm}(\hat{\mathbf{r}}_{i})$$
(1.23)

There are two methods to calculate the crystal field energy. One is by a direct integration and the other is by use of the Stevens operator equivalents.

#### (a) Direct integral

The crystal field interaction can be treated as a perturbation term on the spin-orbit interaction. The zero-order wave function,  $|J, M_J \rangle$ , is expressed as a determinental product of a single-electron space wave function,  $\phi_i$ , and a spin wave function,  $\chi_i$ .

$$|J, M_J \rangle = \phi_i = \psi_i(\mathbf{r}_i) \otimes \chi_i(\mathbf{s}_i)$$
(1.24)

Thus the matrix elements of  $\mathcal{H}_{cf}$  are given by

$$< J, M_J |\mathcal{H}_{cf}| J, M'_J >_{n,m} = eA_{nm} \int \phi_i^*(\mathbf{r}_i) r_i^n Y_{nm}(\hat{\mathbf{r}}_i) \phi_i(\mathbf{r}_i) d^3 \mathbf{r}_i$$
(1.25)

Because  $\phi_i(\mathbf{r}_i) = R_{nl}(\mathbf{r}_i)Y_{lm'}(\hat{\mathbf{r}}_i)$  this integral is the product of two parts, a radial part

$$< r^{n} > = \int [R_{kl}(r_{i})]^{2} r_{i}^{n} r_{i}^{2} dr_{i}$$
 (1.26)

and an orbital part

$$\int Y_{lm'}(\hat{\mathbf{r}}_i) Y_{nm}(\hat{\mathbf{r}}_i) Y_{lm'}(\hat{\mathbf{r}}_i) d\hat{\mathbf{r}}_i$$
(1.27)

where m=m'-m'' based on a selection rule.

#### (b) The Stevens "Operator Equivalents"

This is by far the most convenient method for calculating the matrix elements of the crystal field potential between the coupled wave functions specified by J. Because the angular momentum J and the position vector  $\mathbf{r}$  are vectors, based on the Wigner-Eckart theorem, the summation in (1.23) over the 4f electrons leads to the formula

$$\sum_{\mathbf{i}} r_{\mathbf{i}}^{n} Y_{nm}(\hat{\mathbf{r}}_{\mathbf{i}}) = \theta_{n} < r^{n} > O_{nm}(J)$$
(1.28)

where  $O_{nm}(J)$  are the Stevens equivalent operators and  $\theta_n$  are the nth-order Stevens s coefficients. The 2nd, 4th and 6th Stevens coefficients are usually written as  $\alpha_J$ ,  $\beta_J$  and  $\gamma_J$ , respectively. All these quantities are tabulated (Hutchings, 1964). Thus, the crystal-field Hamiltonian of (1.23) is written as

$$\mathcal{H}_{cf} = \sum_{n} \sum_{m=-n}^{n} B_{nm} O_{nm}(J) \tag{1.29}$$

where  $B_{nm}$  is called the crystal-field parameter and is expressed as

$$B_{nm} = \theta_n < r^n > A_{nm} \tag{1.30}$$

Because of particular crystal symmetries, some terms in (1.29) disappear and  $\mathcal{H}_{cf}$  becomes reduced. For cubic symmetry with z chosen in the (001) direction,  $\mathcal{H}_{cf}$  is described by two parameters,  $B_{40}$  and  $B_{60}$ ,

$$\mathcal{H}_{cf} = B_{40}(O_{40} + 5O_{44}) + B_{60}(O_{60} - 21O_{64}), \tag{1.31}$$

whereas for hexagonal symmetry with 3h symmetry, four parameters,  $B_{20}$ ,  $B_{40}$ ,  $B_{60}$  and  $B_{66}$ , are needed,

$$\mathcal{H}_{cf} = B_{20}O_{20} + B_{40}O_{40} + B_{60}O_{60} + B_{66}(O_{66} + O_{6-6}) \tag{1.32}$$

and for tetragonal symmetry with 4/mmm symmetry, five parameters are necessary,

$$\mathcal{H}_{cf} = B_{20}O_{20} + B_{40}O_{40} + B_{44}O_{44} + B_{60}O_{60} + B_{64}O_{64}. \tag{1.33}$$

#### **1.3 Magnetocrystalline anisotropy**

The nature of the crystal field surrounding an R ion depends on the crystal field parameters,  $B_{nm} = \theta_n < r^n > A_{nm}$ . The Stevens coefficients,  $\theta_n$ , represent a shape distribution of 4f electrons. Positive or negative  $\alpha_J$  ( $\theta_2$ ) corresponds to a charge distribution shaped like a cigar or like a pancake, respectively. Sm, Er, Tm and Yb have a positive  $\alpha_J$  and the other rare-earths have a negative  $\alpha_J$ . In the case of Gd, the 4f electron has spherical symmetry because L=0 and thus  $\alpha_J=0$ . As a result, anisotropy is absent in the Gd compounds. In general, R atoms, which have a different sign of  $\alpha_J$ , will display different types of magnetic anisotropy for isostructural compounds. For example, at room temperature, Nd<sub>2</sub>Fe<sub>14</sub>B has an easy c-axis anisotropy; however, Sm<sub>2</sub>Fe<sub>14</sub>B has an easy c-plane anisotropy.

On the other hand,  $A_{nm}$  represents a property of the crystallographic arrangement surrounding a R ion. A Sm ion has a positive  $\alpha_J$ ; however, for SmTiFe<sub>11</sub> and Sm<sub>2</sub>Fe<sub>14</sub>B, the easy magnetization direction is parallel to and perpendicular to the c-axis, respectively, because of their opposite signs in  $A_{nm}$ . In many hexagonal and tetragonal structures, the most important term is the second-order field coefficient  $A_{20}$ . The  $A_{20}$  as well as  $\alpha_J$  largely determine the sign and magnitude of the uniaxial anisotropy constant  $K_{1,R}$  and hence also determine the preferred magnetization direction.

The magnetic anisotropy energy,  $E_{a,R}$  of the R sublattice can be phenomenologically described as

$$E_{a,R} = \sum_{n=0}^{n} \sum_{m=-n}^{n} K_{nm,R} \sin^n \theta \cos m\phi$$
(1.34)

where  $\theta$  and  $\phi$  are the polar and azimuthal angles of the magnetization with respect to the main symmetry axes and  $K_{nm,R}$  is the anisotropy constant. Based on the transformation properties of the Stevens operator equivalents, the relationship between the crystal-field parameters,  $B_{nm}$ , and the anisotropy constants,  $K_{nm,R}$ can be found. As an example, for tetragonal symmetry, the anisotropy energy is given by

$$E_{a,R} = K_{1,R}\sin^2\theta + (K_{2,R} + K'_{2,R}\cos 4\phi)\sin^4\theta + (K_{3,R} + K'_{3,R}\cos 4\phi)\sin^6\theta \quad (1.35)$$

and the relationships between  $K_{i,R}$ ,  $K'_{i,R}$  and  $B_{nm}$  as found by (Rudowicz, 1985; Lindgard and Danielsen, 1975) are

$$K_{1,R} = -\frac{2}{3}B_{20} < O_{20} > +5B_{40} < O_{40} > +\frac{21}{2}B_{60} < O_{60} >$$
(1.36)

$$K_{2,R} = \frac{7}{8} (5B_{40} < O_{40} > +27B_{60} < O_{60} >)$$
(1.37)

$$K_{2,R}' = \frac{1}{8} (5B_{44} < O_{40} > +5B_{64} < O_{60} >)$$
(1.38)

$$K_{3,R} = -\frac{251}{16}B_{60} < O_{60} >$$
(1.39)

$$K'_{3,R} = -\frac{11}{16}B_{64} < O_{60} > \tag{1.40}$$

The values of  $K_{nm,R}$  can be obtained experimentally from the magnetization curves of a single crystal sample measured in different directions. Thus, the crystal field parameters,  $B_{nm}$ , can be calculated in terms of (1.36)-(1.40).

#### **1.4** Two-sublattice mean field model

The magnetocrystalline anisotropy of the R-Fe compounds consists of two separate contributions associated with the R and Fe sublattices. The competition of the two anisotropies at various temperatures and applied fields leads to a complex magnetic structure. To describe the dependence of the magnetization on temperature or applied field, a two-sublattice mean field model is usually used (Yamada et al, 1988; Radwanski and Franse, 1988; Cadogan et al, 1988).

In this model, the magnetizations are defined as  $M_{Fe}=N_{Fe}<\mu_{Fe}>$  and  $M_R=-N_Rg_J\mu_BJ$ for the Fe and R sublattices, respectively, where  $N_{Fe}$  and  $N_R$  are the numbers of Fe and R atoms for a unit crystal cell, respectively. The energy expression for the Fe sublattice is given by

$$E_{Fe} = E_{a,Fe} - (\mathbf{H}_{Fe}^{ex} + \mathbf{H}_0) \cdot \mathbf{M}_{Fe}$$
(1.41)

where  $E_{a,Fe} = K_{1,Fe} \sin^2 \theta$  and  $\mathbf{H}_{Fe}^{ee} = -n_{FeR} \mathbf{M}_R$  are the Fe-sublattice anisotropy energy and the exchange field acting on the Fe sublattice, respectively,  $\theta$  is the angle between  $\mathbf{M}_{Fe}$  and the *c*-axis and  $\mathbf{H}_0$  is the applied magnetic field.

The Hamiltonian for the R ions is written as

$$\mathcal{H}_R = \sum_{nm} B_{nm} O_{nm} - (\mathbf{H}_R^{ex} + \mathbf{H}_0) \cdot \mathbf{M}_R \tag{1.42}$$

where  $\mathbf{H}_{R}^{c} = -n_{FeR} \mathbf{M}_{Fe}$  is the exchange field acting on the R ions. The free energy,  $F_{R}$ , of the R ions at a given temperature is obtained by using a partition function,  $Z_{R}$ ,

$$F_R = -k_B T \ln(Z_R) \tag{1.43}$$

where  $Z_R$  is given by

$$Z_R = \frac{\sum_i E_i \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)}$$
(1.44)

 $E_i$  are the eigenenergies of  $\mathcal{H}_R$  and can be obtained by direct diagonalization of (1.42).

Hence, the total energy of the two-sublattice system becomes

$$E_{tot} = E_{Fe} + \sum_{R} F_{R} + n_{FeR} \mathbf{M}_{R} \cdot \mathbf{M}_{Fe}$$
(1.45)

where the last term is included to avoid double counting of the intrasublattice interaction term.

It is now possible to determine the magnetic structure at any given temperature and applied field by solving the coupled equations (1.41) and (1.42) while minimizing the total energy of (1.45). A common procedure is to minimize the energy for a given set of parameters  $B_{nm}$ ,  $n_{RFe}$ ,  $K_{1,Fe}$  as a function of the direction of the sublattice magnetizations. The calculated values of the magnetization components in the direction of  $H_0$  can subsequently be compared with experimental values available for different fields  $H_0$  and at various temperatures. Based on this method Yamada et al (1988) have calculated the magnetization curves in the high field for  $R_2Fe_{14}B$ ; Hu et al (1990) found a set of the crystal field parameters from the magnetization curves in different directions for a single crystal of  $DyFe_{11}Ti$  and then computed the dependence of the magnetization direction on temperature for  $DyFe_{11}Ti$ .

### Chapter 2

## **Review: R-Fe Permanent** Magnets

Since Nd-Fe-B was discovered in 1984, there have been three major achievements in R-Fe permanent magnetic materials. (1) new rare-earth iron compounds including  $R(Fe, M)_{12}$ , with the ThMn<sub>12</sub> structure and  $R_3(Fe, M)_{29}$  with a monoclinic structure, (2) nanocomposite permanent magnets with enhanced remanence, and (3) interstitial rare-earth iron nitrides and carbides.

#### 2.1 New R-Fe compounds

#### 2.1.1 $R_2Fe_{14}B$

The super permanent magnet Nd-Fe-B was discovered by two methods. In one, Hadjipanayis et al (1983, 1984), Croat et al (1984), and Koon and Das (1984) prepared Nd-Fe-B permanent materials with  $(BH)_{max}$ =14 MGOe by rapid quenching method. In the other one, Sagawa et al (1984) made a permanent magnetic alloy, Nd<sub>15</sub>Fe<sub>77</sub>B<sub>8</sub>, with  $(BH)_{max}$ =36 MGOe by using the conventional sintering method.

All of these permanent magnetic alloys contained a novel ternary crystalline compound,  $R_2Fe_{14}B$ . Its crystal structure was soon determined by Herbst et al (1984, 1985), Givord et al (1984), and Shoemaker et al (1984).  $R_2Fe_{14}B$  has a tetragonal structure with space group  $P4_2/mnm$ . Each unit cell contains four formula units, or 68 atoms. There are six Fe sites  $16k_2$ ,  $16k_1$ ,  $8j_2$ ,  $8j_1$ , 4c and 4e sites), two R sites (4g and 4f sites) and one B site (4g site).
The magnetic properties of  $R_2Fe_{14}B$  (Herbst, 1991) are listed in Table 2.1 of Appendix 2.4. The compounds  $La_2Fe_{14}B$ ,  $Lu_2Fe_{14}B$  and  $Y_2Fe_{14}B$  are normal ferromagnets in which the magnetic properties are determined by the Fe sublattce. The average Fe moment is 2.2  $\mu_B$  at 4 K and the anisotropy field is of about 26 kOe at room temperature.

The Curie temperature of  $Nd_2Fe_{14}B$  is only 585 K. Various attempts have been made to raise the Curie temperature. Nonmagnetic atoms, such as Al, Mn, Cr, Ti and Zr reduce the Curie temperature when they replace Fe (Abache and Oesterreicher, 1986; Jurczyk and Wallace, 1987). Substitution of Co and Ni for Fe increases the Curie temperature (Matsuura et al, 1985; Burzo et al, 1985). It is surprising that the diamagnetic atoms Si and Ga substituted for Fe can also cause a considerable increase in the Curie temperature, for example, from 585 to 615 K in  $Nd_2Fe_{14-x}Si_xB$  for x=0 and x=1.5 (Pedziwiatr et al, 1987; Jurczyk et al, 1987). This unusual increase in the Curie temperature is attributed to the occupation of the 16k<sub>2</sub> site by the Si atoms (Li Z W et al, 1990).

Spin reorientation occurs in the Nd, Ho, Er, Tm and Tb compounds. They are divided into two distinct types. One originates from the competition between the Fe and R sublattices. The Fe sublattice has an easy c-axis anisotropy and prevails at high temperature. The R sublattice (R=Sm, Er, Tm and Yb) has an easy c-plane anisotropy, which dominates at low temperature. Consequently, a change of the easy magnetization direction from the c-axis to the c-plane is observed at the temperatures 320, 311 and 115 K for the compounds  $Er_2Fe_{14}B$ ,  $Tm_2Fe_{14}B$  and  $Yb_2Fe_{14}B$ , respectively. The other originates from a difference of the temperature dependence between the various terms for the R sublattice anisotropy. Callen and Callen (1966) have shown that the expectation values of  $< O_{n0} >$  depend on the reduced R sublattice magnetization  $M_R(T)/M_R(0)$  by

$$< O_{n0} > = < O_{n0} >_0 \left(\frac{M_R(T)}{M_R(0)}\right)^{n(n+1)/2}$$
 (2.1)

As a consequence of these temperature dependences the higher order contributions can be negligible at high temperatures and, therefore, lead to deviations of the easy magnetization direction from the c-axis. Spin reorientations of this type occur at 135 and 58 K with tilting angles of 32° and 22° for  $Nd_2Fe_{14}B$  and  $Ho_2Fe_{14}B$ (Wolfers et al, 1990), respectively.

## 2.1.2 $R(Fe, M)_{12}$

RFe<sub>12</sub> does not exist for any rare-earth element. A third element, such as Ti, V, Cr, Nb, Mo, W and Si, must be added to form the ternary compounds  $RFe_{12-x}M_x$  with the ThMn<sub>12</sub> structure. The values of x depend on the specific M element, such as  $0.7 \le x \le 1.25$  for Ti (Hu et al, 1990a),  $1.25 \le x \le 4.0$  for V (Buschow and de Mooij, 1989),  $1.35 \le x \le 3.5$  for Cr (Buschow and de Mooij, 1989) and  $0.5 \le x \le 4.0$  for Mo (Sun et al, 1992a).

 $RFe_{12-x}M_x$  has the tetragonal structure with the space group I4/mmm. Each unit cell contains two formula units. The R atoms are located on the 2a site and the Fe and M atoms on the 8i, 8j and 8f sites.

The average Fe magnetic moments and the Curie temperatures are observed to be 1.35-1.93  $\mu_B$  and in the range of 400 and 650 K, respectively, depending on the specific M element and the value of x. The Fe magnetic moment and the Curie temperature for the fictional compound YFe<sub>12</sub> were predicted to be 2.07  $\mu_B$  at 4.2 K and about 710 K, respectively, by extrapolation of the high-field magnetization data and the Curie temperatures of YFe<sub>12-x</sub>M<sub>x</sub> (Verhoef et al, 1988; Buschow, 1991). Up to now the maximum magnetizations are found to be 24.6  $\mu_B$ /fu at 4.2 K for YFe<sub>11.5</sub>Mo<sub>0.5</sub> (Sun et al, 1992a).

The saturation magnetizations and the Curie temperatures for  $RFe_{11}Ti$  are listed in Table 2.2 of the Appendix and the spin structures for  $RFe_{11}Ti$  and  $RFe_{10}V_2$ are shown in Fig.2.1

The Fe sublattice anisotropy favours an easy magnetization direction parallel to the c-axis. The sign of  $A_{20}$  for the R sublattice is negative. This implies that the R ions with a positive  $\alpha_J$ , such as Sm, Er, Tm and Yb, contribute to the uniaxial anisotropy; the R ions with a negative  $\alpha_J$ , such as Nd, Tb, Dy and Ho, contribute to the planar anisotropy. However, complex spin reorientation occurs. For DyFe<sub>11</sub>Ti the magnetic moments are parallel to the [100] direction below 58 K and parallel to the c-axis above 200 K; at temperatures between the two spin reorientation transitions the moment is canted (Hu et al, 1990; Andreev ea al 1990). For ErFe<sub>11</sub>Ti the canting angle is  $16\pm 2^{\circ}$  at 4.2 K and decreases progressively with increasing temperature (Andreev et al, 1988). These results show that the higher-



Figure 2.1: The dependence of the spin structure on temperatures for  $RFe_{11}Ti$  (Hu et al, 1989) and  $RFe_{10}V_2$  (Haije et al, 1990)

order (fourth- and sixth-order) terms must be taken into account.

## 2.1.3 R<sub>3</sub>(Fe, M)<sub>29</sub>

 $R_3(Fe, M)_{29}$  compounds were first discovered by Collocott et al (1992). They reported the formation of a new high-temperature phase in the Fe-rich corner of the Nd-Fe-Ti ternary phase diagram. At the beginning the new phase was denoted by  $R_2(Fe, M)_{19}$  and later the correct stoichiometry was shown to be  $R_3(Fe, M)_{29}$  (Li H S et al, 1994). Fuerst et al (1994) were the first to suggest that the new phase belongs to a monoclinic structure with the  $P2_1/c$  space group. Now the  $R_3(Fe, M)_{29}$  phase is known to form with R=Ce, Pr, Nd, Sm and Gd, and M=Ti, V, Cr and Mn (Cadogan et al, 1994; Li H S et al, 1994; Fuerst et al, 1994; Yang F M et al, 1995). No reports on the heavy rare-earth  $R_3(Fe, M)_{29}$  have appeared, except the Gd compound.

The  $R_3(Fe, M)_{29}$  structure contains two R sites (2a and 4e) and fifteen Fe(M) sites (2d and fourteen 4e sites). Like the  $R_2Fe_{17}$  and  $Th_2Mn_{12}$  structures, the  $R_3(Fe, M)_{29}$  structure can also derived from replacing R atoms by Fe-Fe dumbbells

in the hexagonal CaCu<sub>5</sub> structure,

$$\mathbf{R}_{1-\mathbf{x}}\mathbf{F}\mathbf{e}_5 + (\mathbf{2F}\mathbf{e})_{\mathbf{x}} \to \mathbf{RF}\mathbf{e}_{\mathbf{y}} \tag{2.2}$$

The  $R_2Fe_{17}$  and  $Th_2Mn_{12}$  structures represent x=1/3 and x=1/2, respectively; the  $R_3(Fe, M)_{29}$  structure represents x=2/5.

The magnetic properties of  $R_3(Fe, M)_{29}$  are listed in Table 2.3 of the Appendix. The  $R_3(Fe, M)_{29}$  compounds are ferromagnetic and the Curie temperatures in a range of 296 K (R=Ce and M=Cr) to 524 K (R=Gd and M=V). X-ray diffraction on magnetically aligned powder samples of Nd<sub>3</sub>(Fe, Ti)<sub>29</sub> and Sm<sub>3</sub>(Fe, Ti)<sub>29</sub> indicates that the easy direction of magnetization is in the *a-b* basal plane, along the [201] direction (Margarian et al, 1994; Yang F M et al, 1994). Neutron diffraction shows that the easy direction is the *a*-axis at room temperature (Hu Z and Yelon, 1994). The saturation magnetizations of Nd<sub>3</sub>(Fe, Ti)<sub>29</sub> are 58  $\mu_B$ /fu at 4.2 K and 47  $\mu_B$ /fu at room temperature, and the anisotropy fields are 98 kOe at T=12 K and 77 kOe at room temperature (Cadogan et al, 1994a). For Sm<sub>3</sub>(Fe, Ti)<sub>29</sub>, the magnetization and anisotropy field are 119 Am<sup>2</sup>/kg and 34 kOe, respectively, at room temperature (Yang F M et al, 1994)

## 2.2 Nanocomposite permanent magnets

Nanocomposite permanent magnets are usually composed of two (or more) phases. One is a hard magnetic phase and the other is a soft magnetic phase, such as  $\alpha$ -Fe or Fe<sub>3</sub>B. The outstanding property of the nanocomposite magnets is an enhanced remanence. The remanence ratio,  $B_r/B_s$ , is as high as 0.7~0.8 without any need for alignment, as compared to 0.5 for usual isotropic magnet.

The nanocomposite permanent magnet with enhanced remanence was first made by Coehoorn et al in 1988. The starting material had a composition  $Nd_4Fe_{80}B_{20}$ . After a rapid quench the material was annealed at 670°C. The remanence ratio is 0.75 and the energy product is 10.8 MGOe. This composite magnet consists of  $Nd_2Fe_{14}B$ ,  $Fe_3B$  and  $\alpha$ -Fe phases; their relative volume ratios are about 36 %, 60 % and 4 %, respectively, by Mössbauer spectra (Li Z W et al 1992). The coercive force is induced by the  $Nd_2Fe_{14}B$  phase based on the observation that the coercive force vanishes at the Curie temperature of this phase (Zhang et al, 1990; Eckert et al, 1990). Since then, a remanence ratio of 0.75, a coercive force of 3.4 kOe and an energy product of 15.1 MGOe have been achieved for  $Nd_5Fe_{70.5}Co_5Ga_1B_{18.5}$  (Hirosawa et al, 1990).

An isotropic permanent magnet was obtained by Manaf et al (1993, 1993a) starting with the composition  $Nd_8Fe_{86}B_6$  and then rapidly quenching. The remanence is 10 kG, the coercive force is 6.0 kOe and the energy product is 20 MGOe. This permanent magnet consists of two phases, a matrix of magnetically hard  $Nd_2Fe_{14}B$  with numerous particles of  $\alpha$ -Fe on grain boundaries. The average grain sizes are <30 nm and <10 nm for  $Nd_2Fe_{14}B$  and  $\alpha$ -Fe, respectively.

The other way to produce a composite magnet is by mechanical alloying followed by annealing. The composite magnets  $Sm_xFe_{100-x}N_y$  (x=5-9) made by mechanical alloying consist of  $Sm_2Fe_{17}N_y$  and  $\alpha$ -Fe phases. With increasing Sm concentration from x=5 to x=9 the remanence decreases from 13.2 kG to 10.0 kG and the coercive force increases from 1.2 kOe to 4.8 kOe. (Coey, 1995). Optimum properties are achieved for  $Sm_7Fe_{91}N_y$ . The remanence is 11.3 kG, about 80 % of the saturation magnetization, the coercive force is 3.9 kOe and the energy product is as high as 25.8 MGOe. The amount of  $Sm_2Fe_{17}N_y$  and  $\alpha$ -Fe by weight are 70 % and 30 %, respectively (Ding et al, 1992, 1993). The grain sizes of the two phases are shown to be both 15 nm diameter by transmission electron microscopy (Ding et al, 1994).

## 2.3 Interstitial R-Fe carbides and nitrides

Although  $R_2Fe_{17}$  compounds have high saturation magnetization, their low Curie temperatures and easy c-plane anisotropies at room temperature make them unattractive for application as permanent magnet materials. However, the introduction of interstitial N and C atoms can increase the Curie temperature and modify the magnetic anisotropy of  $R_2Fe_{17}$ . The crystal structural parameters and magnetic properties of  $R_2Fe_{17}C$  and  $R_2Fe_{17}N_y$  are listed in Table 2.4 and 2.5 of the Appendix.

#### 2.3.1 Crystal structures

 $R_2Fe_{17}$  compounds have two crystal structures, the rhombohedral  $Th_2Zn_{17}$  or the hexagonal  $Th_2Ni_{17}$  structure. The rhombohedral structure is found for the light rare-earth compounds (R=La to Sm) and the hexagonal structure for the heavy rare-earth compounds (R=Gd to Lu and Y). For the rhombohedral structure, Fe atoms occupy the 6c, 9d, 18f and 18h sites and R atoms the 6c site; for the hexagonal structure, Fe atoms are located on the 4f, 6g, 12j and 12k sites and R atoms the 2b and 2d sites. However, each corresponding site for the two kinds of structure has a similar local environment. Neutron and x-ray diffractions have shown that the interstitial C or N atoms occupy the 9e site in the rhombohedral structure and the 6h site in the hexagonal structure (Helmholdt and Buschow, 1989; Haije et al, 1990a; Yang Y C et al, 1991a; Ibberson et al, 1991; Jaswal et al, 1991; Miraglia et al, 1991; Yelon and Hadjipanayis 1992; Isnard et al, 1992, 1992a, 1993; Kajitani et al, 1993; Yan et al, 1993). In addition, some authors also suggested a partial occupation of the second interstitial site, the 18g site (Yelon and Hadjipanayis 1992; Kajitani et al, 1993; Yan et al, 1993).

Interstitial C or N atoms leads to an increase in the cell volume by 6-7 %, as compared to  $R_2Fe_{17}$ . A linear relationship between the cell volume and the C concentration was found for  $R_2Fe_{17}C_y$  until  $y \leq 1$ . With increasing C concentration, there is a structural transition, from the hexagonal to the rhombohedral structure for  $R_2Fe_{17}C_y$  with R=Y, Ho and Er (Sun et al, 1990a; Coene et al, 1990; Kou et al, 1991). On the other hand, the introduction of interstitial C atoms can extend the stability range of the rhombohedral structure towards the Lu end. The rhombohedral structures can be retained for  $R_2Fe_{17}C_y$  with Gd, Tb, Dy, Ho and Er made by alloying (Zhong et al, 1990) and for  $Gd_2Fe_{17}C_y$  and  $Tb_2Fe_{17}C_y$  made by the gas-phase reaction (Sun et al, 1992).

#### 2.3.2 Curie temperatures

One of the most interesting magnetic properties is the very high Curie temperatures of the rare-earth nitrides and carbides. As compared to  $R_2Fe_{17}$ , the Curie temperatures are elevated by 100-200°C for  $R_2Fe_{17}C$  made by alloying and even by 300-400°C for  $R_2Fe_{17}N_y$  and  $R_2Fe_{17}C_y$  made by a gas-phase reaction. A linear relationship between the Curie temperature and the corresponding cell volume has been shown for a series of  $Y_2Fe_{17}C_y$  and  $Gd_2Fe_{17}C_y$  carbides with various C concentrations (Liu J P et al, 1991). These results suggest that the increase in the Curie temperature is a volume effect. Analysis of the R-Fe exchange interactions in  $R_2Fe_{17}N_y$  was made using Curie temperature data (Sun et al, 1991) and also using high-field magnetization data (Liu J P et al, 1991). They found that the strength of the R-Fe interactions is weaker than that for  $R_2Fe_{17}$ ; the large increase in Curie temperature is therefore attributed to an enhancement of the Fe-Fe interaction.

#### 2.3.3 Magnetizations

The saturation magnetization at T=4.2 K for  $Y_2Fe_{17}N_y$  is 38.5  $\mu_B/fu$  which corresponds to 2.27  $\mu_B$  per Fe atom, larger than 2.09  $\mu_B$  for  $Y_2Fe_{17}$  and 2.20  $\mu_B$  for  $\alpha$ -Fe. The band structure of  $Y_2Fe_{17}N_y$  was calculated by Beuerle et al (1991) as a function of the unit cell volume, which simulated the volume expansion observed in a nitrogen absorption. The results show that on average the increase in the Fe moment is of the order of 10 %, which is in good agreement with the values found from magnetic measurements and Mössbauer spectroscopy. Similar calculations have been made by Li Y P et al (1991), Woods et al (1993), Zeng et al (1993), Gu et al (1993) and Ching et al (1994).

### 2.3.4 Magnetic anisotropy

Another interesting property of rare-earth iron nitrides and carbides is a huge magnetocrystalline anisotropy. The easy magnetization direction at room temperature lies in the c-plane for all  $R_2Fe_{17}$  compounds. For the nitrides and carbides, N and C atoms occupy the interstitial sites around the R atoms within the basal plane, which leads to an increase in the charge density of the rare-earth valence electrons in the plane and to a decrease in  $A_{20}$  to more negative values. Consequently, for the Sm, Er, Tm and Yb atoms with a positive second-order Stevens coefficient  $(\alpha_I > 0)$ , the easy c-axis anisotropy of the R sublattice is greatly enhanced.

For the Sm nitrides and carbides, interstitial C or N atoms can enhance the Sm sublattice anisotropy that compensates for the Fe sublattice anisotropy (which favors an easy magnetization direction perpendicular to the c axis) even at fairly low interstitial concentrations. It has been shown that the easy magnetization direction is parallel to the c-axis at all temperatures below the Curie temperature for Sm<sub>2</sub>Fe<sub>17</sub>C<sub>0.5</sub> (Grössinger et al, 1991; Ding and Rosenberg, 1991). For Sm<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub>, the anisotropy field,  $H_a$ , at room temperature was estimated to be 140 kOe by a magnetic measurement (Coey and Sun, 1990) and even 230 kOe by a singularpoint detection method (Katter et al, 1990; 1991). These values are much larger than those found in Nd<sub>2</sub>Fe<sub>14</sub>B and SmTiFe<sub>11</sub>, where  $H_a \sim 73$  kOe and 100 kOe, respectively. The temperature dependences of the anisotropy field for Sm nitrides and carbides have been studied by Kou et al (1990), Katter et al (1991), Chen et al (1993) and Miragile et al (1991). From high field magnetization data, the anisotropy fields at 4.2 K are found to be larger than 350 kOe for Sm<sub>2</sub>Fe<sub>17</sub>N<sub>2.7</sub> (Liu J P et al, 1991) and even to be larger than 700 kOe for Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3.0</sub> (Kato et al, 1993).

The giant magnetocrystalline anisotropy is attributed to the crystalline electric fields (CEF) acting on the Sm<sup>3+</sup> 4f shell. The crystal field coefficients ,  $A_{nm}$ , have been calculated by using the temperature dependence of the anisotropy field,  $H_a(T)$ , (Zhao et al, 1991; Li H S and Cadogan, 1991, 1992; Li H S and Coey, 1992; Kato et al, 1993; Zhao et al, 1995) or by using the temperature dependence of the magnetocrystalline anisotropy constants,  $K_1(T)$  and  $K_2(T)$  (Wolf et al, 1995). The calculated second crystal-field coefficients,  $A_{20}$ , have a range of -160— -600  $\mathrm{Ka_0^{-2}}$ .

Other  $R_2Fe_{17}N_y$  and  $R_2Fe_{17}C_y$  compounds (R=Er and Tm) with a positive  $\alpha_J$  have been found to have a spin reorientation transition from the c-plane to the c-axis below room temperature (Gubbens et al, 1989, 1991 and 1992; Hu et al, 1990a; Liu et al, 1991; Kou et al, 1991a; Grössinger et al, 1991; Hu B P and Liu, 1991; Ohno et al, 1993). This transition reflects the competition between the R sublattice and the Fe sublattice anisotropy. The spin-reorientation temperature rises with the C concentration for  $Tm_2Fe_{17}C_y$ , from 72 K for y=0 to 200 K for y=1.4; in contrast to their parent, carbides  $Er_2Fe_{17}C_y$  have a transition at  $y \ge 0.8$ .

#### 2.3.5 Mössbauer spectroscopy

<sup>57</sup>Fe Mössbauer spectra of  $R_2Fe_{17}N_y$  and  $R_2Fe_{17}C_y$  have been studied extensively by Hu et al (1991), Zouganelic et al (1991), Qi et al (1991,1992), Long et al

(1992), Pringle et al (1992), Rosenberg et al (1993), Chen X et al (1993), Kong et al (1993), Gong et al (1994) and Marasinghe et al (1994). Usually, the assignments of four subspectra are made by considering their relative areas together with the numbers of the neighboring Fe atoms of the sites. The magnitude of the hyperfine fields is in the sequence  $H_{hf}(6c) > H_{hf}(9d) > H_{hf}(18f) > H_{hf}(18h)$ . In addition, Long et al (1992) fitted their Mössbauer spectra in a different order of  $H_{hf}(9d) > H_{hf}(6c) > H_{hf}(18h) > H_{hf}(18f)$  based on the Wigner-Seitz volume of each Fe site. The average hyperfine fields are larger for  $R_2Fe_{17}N_y$  than for  $R_2Fe_{17}C_y$ ; the difference is attributed to the transferred hyperfine field from interactions with neighboring atoms (Qi et al, 1992). Based on a jump in the hyperfine field and a sign change in the quadrupole splitting, the spin-reorientation transitions have been studied for  $R_2Fe_{17}N_y$  and  $R_2Fe_{17}C_y R=Tm$  or Er (Gubbens et al, 1989, 1991; Hu et al, 1990). The spin-reorientation temperatures obtained are in good agreement with those measured by a.c. susceptibility and thermomagnetic scans.

The Mössbauer spectra of rare-earth nuclei have been used to study the rareearth sublattice anisotropy (Gubbens et al, 1989, 1991, 1992, 1994; Dirken et al, 1989, 1991; Mulder et al, 1992; Isnard et al 1994). The second-order crystal field parameter,  $A_{20}$ , can be found from the quadrupole splitting observed at the rare-earth nucleus, based on a relationship between  $A_{20}$  and  $V_{zz}$ 

$$A_{20} = -\frac{1-\sigma}{4(1-\gamma_{\infty})} V_{zz}$$
 (2.3)

where  $\sigma$  is the screening constant,  $\gamma_{\infty}$  is the Sterheimer antishielding factor, and  $V_{zz}$  is the principle axis component of the electric field gradient (EFG). From the rare-earth Mössbauer spectra, the values of  $A_{20}$  are  $-50(\pm 100)$ ,  $-200(\pm 50)$  and  $-400(\pm 50)$  Ka<sub>0</sub><sup>-2</sup> for Er<sub>2</sub>Fe<sub>17</sub>, Er<sub>2</sub>Fe<sub>17</sub>C<sub>1</sub> and Er<sub>2</sub>Fe<sub>17</sub>N<sub>2.4</sub> (Gubbens et al, 1991, 1992), respectively, are -200, -430 and -580 Ka<sub>0</sub><sup>-2</sup> for Gd<sub>2</sub>Fe<sub>17</sub>, Gd<sub>2</sub>Fe<sub>17</sub>C<sub>1.2</sub> and Gd<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> (Dirken et al, 1989, 1991), respectively, and is  $-300(\pm 50)$  Ka<sub>0</sub><sup>-2</sup> for Tm<sub>2</sub>Fe<sub>17</sub>C and Tm<sub>2</sub>Fe<sub>17</sub>N<sub>2.7</sub> (Gubbens et al, 1989, 1992, 1994).

#### 2.3.6 Substitution effect

The effects of substitution of Co for Fe in  $R_2Fe_{17}N_y$  have been studied by (Hurley and Coey, 1991; Katter et al, 1992; Xu and Shaheen, 1993). For  $Sm_2(Fe_{1-x}Co_x)_{17}N_y$ ,

with increasing Co concentration, the Curie temperatures, the saturation magnetizations and the anisotropy fields increase at first and then decrease; their maxima occur at about x=0.5, 0.2 and 0.3, respectively, (Katter et al, 1992). The magnetic properties of  $R_2(Fe_{1-x}M_x)_{17}N_y$  (M=Si, Ga, Al, Ti, V and Nb) have been reported by Hu B P et al, 1992; Tang et al, 1992; Li X W et al, 1993; Valeanu et al, 1994; Middleton and Buschow, 1994; Yang F M et al, 1994a; Liu et al, 1994; Koyama et al, 1995). The largest stability range of the 2:17 nitrides is for Al with  $0 \le x \le 0.4$ for the Sm nitrides. The N concentrations, the Curie temperatures, the saturation magnetizations and the anisotropy fields are generally reduced with increasing M concentration x.

One of the merits of  $R_2Fe_{17}C_y$  prepared by alloying is its chemical or structural stability at high temperature; however, the C concentration is rather low (y~1.0 for the light rare-earth carbides and y~1.6 for the heavy rare-earth carbides). In order to increase the C concentration two ways were proposed. One, the melt-spinning method was used to make the heavy rare-earth carbides (Shen et al, 1992; Cao et al, 1992, 1993 and Kong et al, 1992). The maximum C concentration can reach y=2.8. However, up to now, no reports on the light rare-earth carbides made by this method have appeared. Two, a third element, Ga, is added in  $R_2Fe_{17}$ . The C concentration can be raised to  $y\geq 2$ . The magnetic properties of  $R_2Fe_{15}Ga_2C_y$  have been studied (Shen et al, 1993, 1994). On the other hand, the nitrides or carbides made by the gas-phase reaction have a high N or C concentration; however, they are not stable at high temperature. This drawback can be overcome by Si substitution in  $R_2Fe_{17}C_y$  (Li Z W et al, 1994, 1995).

## Appendix

The magnetic properties as well as the crystal structural parameters of  $Nd_2Fe_{14}B$  (Herbst, 1991), RTiFe<sub>11</sub> (Hu et al, 1989; Yang Y C et al 1991),  $R_3(Fe, M)_{29}$  (Cadogan et al, 1994),  $R_2Fe_{17}C$  (Zhong et al, 1990) and  $R_2Fe_{17}N_y$  (Otani et al, 1991) are listed in Table 2.1-2.5, where  $M_s$  is the saturation magnetization,  $H_a$  is the anisotropy field,  $T_f$  is the Curie temperature, and a and c are the lattice constants.

<del></del>		4 K					
R	M <sub>s</sub>	$4\pi M_s$	Ha	$M_s$	$4\pi M_s$	Ha	$T_{c}$
	$(\mu_B/{ m f.u.})$	(kGs)	(kOe)	$(\mu_B/\text{f.u.})$	(kGs)	(kOe)	(K)
La	30.6	14.8	12	28.4	13.8	20	530
Се	<b>29.4</b>	14.7	26	<b>23.9</b>	11.7	26	424
Pr	37.6	18.4	~200	31.9	15.6	75	565
Nd	37.7	18.5	~170	32.5	16.0	73	585
Sm	33.3	16.7	>200	30.2	1 <b>5</b> .2	>150	616
Gd	17.9	9.2	19	17.5	8.9	24	661
ТЬ	13.2	6.6	~300	14.0	7.0	~220	620
Dy	11.3	5.7	~170	14.0	7.1	~150	5 <b>98</b>
Ho	11.2	5.7	>100	15.9	8.1	75	573
Er	12.9	6.6	~260	17.7	9.0	8	554
Tm	18.1	9.2	~170	22.6	11.5	8	541
Yb	23.0	12.0		23.0	12.0	524	
Lu	28.2	14.7	20	22.5	11.7	26	535
Y	31.4	31.4	18	27.8	14.1	26	565
Th	28.4	12.2	~20	24.7	14.1	26	481

Table 2.1: Magnetic properties of  $R_2Fe_{14}B$  by Herbst (1991).

Table 2.2: Magnetic properties of  $RTiFe_{11}$  by Hu et al (1989) and Yang Y C et al (1991).

R	$(\mu_B/\text{f.u.})$		$H_a($	$T_f(K)$	
	4.2K	293K	4.2K	293K	•
Pr					
Nd	21.3	16.8			547
Sm	20.1	17.0	>150	10.5	584
Gd	12.5	12.5	7.8	3.3	607
Tb	9.7	10.6			554
Dy	9.7	11.3		2.3	534
Ho	9.6				530
Er	9.2	<b>12.4</b>	8.3	2.4	505
Tm					496
Lu		15.7		2.2	488
Y	19.0	16.6	4.0	2.1	524

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			4 K		295	K	
R	Μ	at%M	M <sub>s</sub>	$H_a$	M <sub>s</sub>	Ha	T <sub>c</sub>
			$(\mu_B/f.u.)$	(kOe)	$(\mu_B/f.u.)$	(kOe)	(K)
-Y	V	8.1	41.0	3.8			439
Nd	V	8.1	50.0				480
Sm	V	8.1	41.0	23.9		17.3	<b>490</b>
Gd	V	8.1	24.0				524
Ce	Ti	5.0	47.0		31.4		322
Pr	Ti	4.5	56.4	6.3	<b>46.2</b>	4.0	373
Nd	Ti	3.6	<b>58.2</b>	9.8	47.6	7.7	396
Sm	Ti	6.3	50.8	7.8	43.6	5.8	<b>452</b>
Се	Cr	12.8	35.4				296
Nd	Cr	13.8	45.3		34.5		410
Sm	Cr	14.1	38.6		31.1		423
Nd	Mn	33.3	17.1				<295

Table 2.3: Magnetic properties of  $R_3(Fe, M)_{29}$  by Cadogan et al (1994).

Table 2.4: Crystal structual parameters and magnetic properties of  $R_2Fe_{17}C$  by Zhong et al (1990).

R	a	с	Structure	T <sub>c</sub>	$T_{SR}$	M <sub>s</sub>
	(nm)	(nm)		(K)	(K)	$(\mu_B/{ m fu})$
Y	0.859	1.245	rho	502		35.5
Се	0.854	1.242	rho	297		32.8
Pr	0.860	1.247	rho	370		
Nd	0.863	1.247	rho	449		40.6
Sm	0.864	1.248	rho	552		34.0
Gd	0.863	1.247	tho	582		23.6
Тb	0.860	1.246	rho	537		19.0
Dy	0.859	1.245	rho	515		17.0
Ho	0.857	1.245	rho	504		17.4
Er	0.854	0.833	hex	488	111	18.8
Tm	0.852	0.832	hex	498	180	24.4
Yb	0.852	0.832	hex	477		
Lu	0.849	0.832	hex	<b>490</b>		35.2

Table 2.5: Crystal structual parameters and magnetic properties of  $R_2Fe_{17}N_y$  by Otani et al (1991).

R		с	Structure	T <sub>c</sub>	$\overline{T_{SR}}$	M <sub>s</sub>
	(nm)	(nm)		(K)	(K)	$(\mu_B/{ m fu})$
Ce	0.847	1.267	rho	700		36.3
Pr	0.879	1.242	rho	720		<b>41.3</b>
Nd	0.878	1.266	rho	740		43.9
Sm	0.874	1.267	rho	750		38.2
Gd	0.871	1.265	rho	740		27.3
ТЬ	0.868	1.267	rho	730		25.0
Dy	0.867	1.267	rho	720		23.0
Ho	0.863	0.847	hex	710		24.5
Er	0.862	0.848	hex	<b>690</b>	150	20.5
Tm	0.858	0.848	hex	<b>690</b>	225	30.5
Yb	0.857	0.850	hex	675		
Lu	0.858	0.848	hex	675		
Y	0.863	0.846	hex	690		38.5

# Chapter 3

# **Review: Theory and Application** of Mössbauer Spectroscopy

When the nucleus is bonded in a solid, there is a process with a certain probability of recoilless  $\gamma$ -ray emission and absorption. Consequently, a recoilless nuclear resonance absorption can be observed. This effect, namely the Mössbauer effect, was first discovered by R. Mössbauer in 1958 (Mössbauer 1958). A few years later (1961) he was awarded the Nobel prize for his discovery.

The recoilless fraction, f, based on the Debye model, is calculated to be

$$f = \exp(-\frac{3E_R}{2k\theta_D} [1 + 4(\frac{T}{\theta})^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1}])$$
(3.1)

where  $\theta_D$  is the Debye temperature and  $E_R$  is the recoil energy for the nuclear emission or absorption. The recoilless fraction is about 0.78 for <sup>57</sup>Fe nuclei in a Rh matrix.

The natural line-width (in Joules) of the emission or absorption line,  $\Gamma$ , based on the Heisenberg uncertainty principle, is given by

$$\Gamma = \frac{0.693h}{2\pi t_{1/2}}$$
(3.2)

where h is Planck's constant and  $t_{1/2}$  is the half lifetime at the excited states. The first excited state of <sup>57</sup>Fe ( $E_0=14.4$  keV) has a value of  $t_{1/2}=97.8$  ns. Thus, the natural line-width is as sharp as  $\Gamma=4.7\times10^{-9}$  eV and the energy resolution is as high as  $\Gamma/E_0 \sim 10^{-13}$ .

The sharpness of the Mössbauer line, which can determine the energy positions of the emitted  $\gamma$ -ray from a source relative to an absorber with a high accuracy,

is the most important feature of the Mössbauer effect. Therefore, the Mössbauer effect makes it possible to resolve the hyperfine interactions between the Mössbauer nucleus and the electric and magnetic fields in the region of the nucleus in a direct way and provides a wealth of new information on electron and spin distributions around the Mössbauer nucleus.

In fact, the Mössbauer nuclear transitions are not absolutely the same in the source and absorber because the nuclei in the source and absorber have different environments. However, the energy of the  $\gamma$ -ray can be modulated by a first-order Doppler effect. By an appropriate relative motion the nuclear transitions can be accurately matched and thus resonance occurs. The counts of the  $\gamma$  radiation, N(v), which come from the source, pass through the absorber and are recorded by a detector, as a function of the Doppler velocity, v, are a Mössbauer spectrum.

Before Mössbauer spectroscopy is applied to get the information on the hyperfine interaction, two problems must be resolved: (1) The line-shape of Mössbauer spectrum and (2) the relationship between the positions of Mössbauer spectral lines and the hyperfine interaction parameters. In section 3.1 problem (1) will be discussed and in sections 3.2 and 3.3 problem (2) will be discussed.

## **3.1** Mössbauer spectral lines

The theory of the resonance absorption lines for a Mössbauer spectrum has been described by Arthur (1968), Greenwood and Gibb (1971), Asch and Kalvius (1981), and Trooster and Viegers (1981). The counts, N(v), for a Mössbauer spectrum consists of three parts:

$$N(v) = N_R + (1 - f_s)N_\gamma(\infty) + f_s N_\gamma(\infty)T(v)$$
(3.3)

where  $N_{\gamma}(\infty)$  are the counts which come from Mössbauer radiation far from the resonance,  $N_R$  are the counts of other radiation,  $f_s$  is the recoilless fraction for the source and T(v) is the transmission intensity for recoilless Mössbauer radiation. If the Mössbauer radiations are distinguished from the other radiations, (3.3) can be expressed as

$$N(v) = C_0[1 - f_0(1 - T(v))]$$
(3.4)

where

$$C_0 = N_R + N_\gamma(\infty) \tag{3.5}$$

$$f_0 = \frac{f_s N_{\gamma}(\infty)}{N_R + N_{\gamma}(\infty)}$$
(3.6)

Although the emitted  $\gamma$ -ray energy is very sharp, there still exists an energy distribution. The distribution, S(v, E), at energy E and Doppler velocity v has a Lorentzian shape and is given by

$$S(v, E) = \frac{\Gamma_s}{2\pi} \frac{(\Gamma_s/2)^2}{(E - E_0^s - E_0 v/c)^2 + (\Gamma_s/2)^2}$$
(3.7)

where  $\Gamma_s$  and  $E_0^s$  are the natural line-width and the transition energy, respectively, for the source and  $E_0$  is the transition energy for free nuclei.

On the other hand, the reduced resonance absorption cross-section,  $\sigma(E)$ , can be expressed as

$$\sigma(E) = \frac{(\Gamma_a/2)^2}{(E - E_0^a)^2 + (\Gamma_a/2)^2}$$
(3.8)

where  $\Gamma_a$  and  $E_0^a$  are the natural line-width and the transition energy, respectively, for the absorber.

The energy distribution of transmission intensity, T(v, E) is given by

$$T(v, E) = S(v, E)e^{-t_{\mathbf{a}}\sigma(E)}$$
(3.9)

and the total transmission intensity over whole energy range can be written as

$$T(v) = \int_{-\infty}^{+\infty} S(v, E) e^{-t_a \sigma(E)} dE \qquad (3.10)$$

where  $t_a$  is the effective thickness of the absorber, which is defined as

$$t_a = \sigma_0 f_a n_M \tag{3.11}$$

where  $\sigma_0$  is the maximum resonance cross-section,  $f_a$  is the recoilless fraction for the absorber and  $n_M$  is the number of Mössbauer nuclei.

By substituting (3.7) and (3.10) into (3.4), one obtains

$$N(v) = C_0 (1 - f_0 [1 - \frac{\Gamma_s}{2\pi} \int_{-\infty}^{+\infty} \frac{(\Gamma_s/2)^2}{(E - E_0^s - E_0 v/c)^2 + (\Gamma_s/2)^2} e^{-t_0 \sigma(E)} dE]) \quad (3.12)$$

When  $t_a \ll 1$ , the exponent term approximates to

$$e^{-t_a\sigma(E)} \sim 1 - t_a\sigma(E) \tag{3.13}$$

Hence,

$$N(v) = C_0 \left(1 - \frac{1}{2} f_0 t_a \frac{(\Gamma/2)^2}{[E_0 v/c - (E_0^a - E_0^s)]^2 + (\Gamma/2)^2}\right)$$
(3.14)

where  $\Gamma = \Gamma_s + \Gamma_a$  and  $E_0^a - E_0^s$  is the energy shift between the source and the absorber. The first term in the bracket is a background count. The second term represents a resonance absorption distribution. This distribution has a Lorentzian line-shape.

In fact, numerical results of (3.12) calculated by Frauenfelder (1962) have shown that, even if absorbers are not very thin, the resonance absorption is still a Lorentzian distribution with a broadened line-width,  $\Gamma_{eff} = \Gamma \cdot h(t_a)$ , where

$$h(t_a) = 1 + 0.135t_a,$$
 for  $0 < t_a < 5$  (3.15)

$$h(t_a) = 1 + 0.145t_a - 0.0025t_a^2 \quad \text{for} \quad 5 < t_a < 10 \tag{3.16}$$

Based on (3.14), the maximum absorption height,  $A_0$ , and the absorption area, A, are found to be

$$A_0 = \frac{1}{2}C_0 f_0 t_a = \frac{1}{2}C_0 \sigma_0 f_0 f_a n_M$$
(3.17)

$$A = \int_{\infty}^{\infty} N(v) dv = \frac{1}{4} \pi C_0 f_0 t_a \Gamma = \frac{1}{4} \pi C_0 \Gamma \sigma_0 f_0 f_a n_M$$
(3.18)

Eq.(3.18) indicates that the absorption area is proportional to the number,  $n_M$ , of Mössbauer nuclei.

In conclusion, based on (3.14) and (3.18), for a thin absorber, (1) Mössbauer spectral lines have a Lorentzian line-shape and (2) the areas of Mössbauer spectra are proportional to the numbers of Mössbauer nuclei in the absorber.

# **3.2** Theory of hyperfine interactions

The Hamiltonian operator for the hyperfine interaction can be expressed as

$$\mathcal{H} = \mathcal{H}(e0) + \mathcal{H}(m1) + \mathcal{H}(e2) + \dots \tag{3.19}$$

The first term in the right side of this equation,  $\mathcal{H}(e0)$ , stands for the electric monopole interaction, which leads to a shift of energy levels. The second and the third terms,  $\mathcal{H}(m1)$  and  $\mathcal{H}(e2)$  refer to the magnetic dipole and the electric quadrupole interactions. They split the nuclear energy levels into sublevels without shifting the center of gravity of the multiplet. For Mössbauer spectroscopy, only these kinds of interactions have to be considered. The higher-order interactions can be neglected because their energies are several orders of magnitude smaller than the e0, e2 and m1 interactions. In addition, the electric dipole interaction,  $\mathcal{H}(e1)$ , is parity-forbidden. These hyperfine interactions have been discussed by Matthias and Schneider (1962,1963), Kündig (1967) and Collins and Travis (1967).

#### **3.2.1** Electric monopole interaction

The electric monopole interaction is a Coulomb interaction between the nuclear charge and the electron charge density at the nucleus. It produces a energy shift, often called the isomer shift and given by (Shirley, 1964)

$$E_{\delta} = \frac{4\pi}{5} S(Z) e^2 R^2 \frac{\Delta R}{R} [|\psi(0)|_a^2 - |\psi(0)|_s^2]$$
(3.20)

where S(Z) is the relativistic factor, Z is the atomic number, R is the average nuclear radius,  $\Delta R$  is the difference between the nuclear radius for the excited and for the ground state, and  $\psi_a(0)$  and  $\psi_s(0)$  are wavefunctions at the nucleus in the source and in the absorber, respectively. Because in a Mössbauer experiment usually the source is fixed,  $|\psi(0)|_s^2 = C_1$  is a constant for various absorbers. The isomer shift, therefore, can be simplified as

$$E_{\delta} = C_0 \frac{\Delta R}{R} [|\psi(0)|_a^2 - C_1]$$
(3.21)

Since the nuclear radius is related to the spin quantum number, I, and not to the magnetic quantum number,  $m_I$ , this interaction only leads to a energy shift.

## 3.2.2 Electric quadrupole interaction

The interaction between a nucleus with a quadrupole moment and the electric-field-gradient (EFG) at this nucleus is written as

$$\mathcal{H}(e2) = -\frac{1}{6}e\mathbf{Q} \bigtriangledown \mathbf{E}$$
(3.22)

where the quadrupole moment,  $e\mathbf{Q}$ , is a tensor and its components are given by

$$(e\mathbf{Q})_{ij} = \frac{eQ}{I(2I-1)} \left(\frac{3(\hat{I}_i \hat{I}_j + \hat{I}_j \hat{I}_i)}{2} - \hat{I}^2 \delta_{ij}\right) \qquad (i, j = x, y, z)$$
(3.23)

The electric field gradient,  $\nabla E$ , is a 3×3 second-rank tensor and its components are given by

$$(\nabla \mathbf{E})_{ij} = -(\nabla^2 V)_{ij} = -\frac{\partial^2 V}{\partial i \partial j} = -V_{ij} \qquad (i, \ j = x, \ y, \ z) \qquad (3.24)$$

where V is an electric potential. Only five of the nine EFG components are independent parameters. Three of the off-diagonal elements are dependent because of the symmetric form of the EFG tensor. One diagonal element is dependent, because it can be expressed by the other two elements as follows from Laplace's equation,  $\sum V_{ii}=0$ .

Further, the "principal axes of the EFG tensor" can be defined such that the off-diagonal elements vanish and the diagonal elements are ordered as

$$|V_{zz}| \ge |V_{yy}| \ge |V_{zz}| \tag{3.25}$$

With respect to the principal axes, the EFG tensor is described by two independent parameters, usually chosen as  $V_{zz}=eq$  and the asymmetry parameter,  $\eta$ ,

$$\nabla \mathbf{E} = \begin{pmatrix} -\frac{1}{2}eq(1-\eta) & 0 & 0\\ 0 & -\frac{1}{2}eq(1+\eta) & 0\\ 0 & 0 & eq \end{pmatrix}$$
(3.26)

where  $\eta$  is defined as  $\eta = (V_{yy} - V_{zz})/V_{zz}$  and is restricted to  $0 \le \eta \le 1$ .

On substituting (3.23) and (3.26) into (3.22), the interaction  $\mathcal{H}(e^2)$  can be expressed as

$$\mathcal{H}(e2) = \frac{e^2 q Q}{4I(2I-1)} [3\hat{I}_z^2 - \hat{I}^2 + \eta(\hat{I}_x^2 - \hat{I}_y^2)]$$
(3.27)

Obviously,  $\mathcal{H}(e_2)=0$  for  $I \leq 1/2$ .

### 3.2.3 Magnetic-dipole interaction

The interaction between the nuclear magnetic-dipole moment,  $\mu_I$ , and a hyperfine magnetic field,  $H_{hf}$ , at the nucleus can be written as

$$\mathcal{H}(m1) = -\mu_{\mathbf{I}} \cdot \mathbf{H}_{\mathbf{hf}} = -g_{I}\mu_{N}\tilde{\mathbf{I}} \cdot \mathbf{H}_{\mathbf{hf}}$$
(3.28)

where  $\mu_N$  is the nuclear magneton and  $g_I$  is the gyromagnetic ratio of state I.

In fact, pure magnetic dipole interactions are rarely encountered for magnetic applications of the Mössbauer effect. Quite frequently one finds that a nuclear state is simultaneously perturbed by both magnetic dipole  $\mathcal{H}(m1)$  and electric quadrupole  $\mathcal{H}(e2)$  interactions. The total interaction Hamiltonian,  $\mathcal{H}(m1 + e2) = \mathcal{H}(m1) + \mathcal{H}(e2)$ , is a  $(2I+1) \times (2I+1)$  Hermitian matrix. The matrix elements have been derived by Matthias et al (1962) and the nonzero elements are given by

$$\mathcal{H}_{m,m} = -g_I \mu_N H_{hf} m_I + \frac{e^2 q Q}{8I(2I-1)} (3\cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi) [3m^2 - I(I+1)]$$
(3.29)

$$\mathcal{H}_{m,m\pm 1} = \frac{3e^2 q Q}{8I(2I-1)} \sin \theta (\cos \theta \mp \frac{1}{6} \eta [(1 \pm \cos \theta) e^{2i\phi} - (1 \mp \cos \theta) e^{-2i\phi}]) \cdot (2m \pm 1) [(I \mp m) (I \pm m + 1]^{1/2}$$
(3.30)

$$\mathcal{H}_{m,m\pm 2} = \frac{3e^2 q Q}{8I(I-1)} (\sin^2 \theta + \frac{1}{6} \eta [(1\pm \cos \theta)^2 e^{2i\phi} + (1\mp \cos \theta)^2 e^{-2i\phi}]) \cdot [(I\pm m+2)(I\mp m+1)(I\mp m)(i\mp m-1)]^{1/2}$$
(3.31)

where m = -I, -(I - 1), ...I - 1, I.

Mössbauer transitions between the states of  $|I_e m_e > \text{and} |I_g m_g > \text{involve only}$ the magnetic dipole (angular momentum L=1) and electric quadrupole radiations (L=2). The *M*-selection rule for the transitions is given by

$$M = 0, \pm 1$$
for the dipole radiation,  $L=1$  $M = 0, \pm 1, \pm 2$ for the quadrupole radiation,  $L=2$ 

where  $M = m_e - m_g$  and the subscripts e and g denote the excited and ground states.

For a mixture m1 + e2 transition, the transition intensities are related to the Clebsch-Gordan coefficients,  $\langle I_g m_g LM \mid I_e m_e \rangle$ , and the angle,  $\beta$ , between the

 $\gamma$ -ray propogation direction and the quantum axis by the following formula (Asch and Kalvius, 1981; Fischer and Gonser, 1981)

$$A(\beta)_{M=0} = \frac{3}{2} \sin^2 \beta |\langle I_g m_g 10 | I_e m_e \rangle|^2 + \frac{15}{8} \sin^2 2\beta |\langle I_g m_g 20 | I_e m_e \rangle|^2 \cdot \kappa^2$$
(3.32)

$$A(\beta)_{M=\pm 1} = \frac{5}{4} (1 + \cos^2 \beta) | \langle I_g m_g 1 \pm 1 | I_e m_e \rangle |^2 \mp \frac{1}{2} \sqrt{15} (\cos^2 \beta + \cos 2\beta) \cdot \langle I_g m_g 1 \pm 1 | I_e m_e \rangle \langle I_g m_g 2 \pm 1 | I_e m_e \rangle \cdot \kappa + \frac{5}{4} (\cos^2 \beta + \cos^2 2\beta) \cdot | \langle I_g m_g 2 \pm 1 | I_e m_e \rangle |^2 \cdot \kappa^2$$
(3.33)

$$A(\beta)_{M=\pm 2} = \frac{5}{4} (\sin^2 \beta + \frac{1}{4} \sin^2 2\beta) | < I_g m_g 2 \pm 2 | I_e m_e > |^2 \cdot \kappa^2$$
(3.34)

where  $\kappa$  is the mixture parameter; the  $\kappa^2$  is defined as the intensity ratio between the e2 and m1 radiations,

$$\kappa^2 = \frac{A(e2)}{A(m1)}$$
(3.35)

# 3.3 <sup>57</sup>Fe Mössbauer spectroscopy

<sup>57</sup>Fe Mössbauer spectroscopy involves a  $\gamma$ -ray transition between the excited state I=3/2 and the ground state I=1/2. With a combination of magnetic dipole and electric quadrupole interactions, the energy levels for the excited and ground states will split into some sublevels and thus there are six or eight Mössbauer spectral lines. In order to obtain the positions of these spectral lines it is necessary to find the eigenvalues of the matrix (the matrix elements are given by (3.29)—(3.31)) for the states of I=3/2 and I=1/2 and then to get the transition energies. This is a very complicated problem involving diagonalizing a  $4 \times 4$  Hermitian matrix for I=3/2. On the other hand, there exist eight transition spectral lines that have complicated intensity-expressions, based on the formulae (3.32)—(3.34).

Fortunately, for most of rare-earth iron compounds the electric quadrupole interaction is much smaller than the magnetic dipole one, i.e.  $eqQ \ll g_I \mu_N H_{hf}$ . Under this condition, the formulae for the transition energies and intensities are considerably simpler. The eigen energy for the I=1/2 state, based on (3.29), is given by

$$E_{I=1/2} = -g_g \mu_N H_{hf} m_g \qquad m_g = \pm \frac{1}{2} \qquad (3.36)$$

There is no electric quadrupole interaction because  $e^2 q Q / [4I(2I-1)] = 0$ .

For the I=3/2 state, only the diagonal elements  $\mathcal{H}_{m,m}$  remain; the non-diagonal elements may be considered approximately to be zero because  $eqQ \ll g_I \mu_N H_{hf}$ . Further, if the EFG tensor is assumed to be axially symmetric, i.e.  $\eta=0$ , the eigen energies E(I=3/2) are given by

$$E_{I=3/2} = -g_e \mu_N H_{hf} m_e + (-1)^{|m_e| + \frac{1}{2}} \frac{1}{8} e^2 q Q (3\cos^2\theta - 1) \qquad m_e = \pm \frac{3}{2}, \pm \frac{1}{2} \quad (3.37)$$

From (3.36) and (3.37) the transition energies,  $\Delta E_{3/2 \leftrightarrow 1/2}$ , involving the states I=3/2 and I=1/2 are found to be

$$\Delta E_{3/2 \mapsto 1/2} = -(g_e m_e - g_g m_g) \mu_N H_{hf} + (-1)^{|m_e| + 1/2} E_Q \qquad (3.38)$$

where  $E_Q = \frac{1}{8}e^2 q Q (3\cos^2 \theta - 1)$ .

The positions,  $P_i$  in mm/s, of the six transition lines for a Mössbauer spectrum are determined by (3.38). Fig.3.1 shows the energy levels for the magnetic dipole splitting with the electric quadrupole perturbation and the corresponding line positions in the Mössbauer spectrum. For I=1/2, the energy level of the m=+1/2state is lower than that of the m=-1/2 state, whereas for I=3/2 the levels of the m=3/2 and m=1/2 states are higher than those of the m=-3/2 and m=-1/2 states, because  $g_g$  and  $g_e$  have a positive and negative value, respectively. Based on (3.38), the hyperfine field,  $H_{hf}$ , the quadrupole splitting,  $\epsilon = 2E_Q$  and the isomer shift,  $\delta$ , are calculated to be

$$H_{hf} = c_{\alpha}(P_6 - P_1) \tag{3.39}$$

$$\epsilon = \frac{1}{2}(P_1 - P_2 - P_5 + P_6) \qquad (3.40)$$

$$\delta = \frac{1}{4}(P_1 + P_2 + P_5 + P_6) \qquad (3.41)$$

where  $c_{\alpha} = 31.1 \text{ kOe/mms}^{-1}$  is the conversion coefficient from doppler velocity to hyperfine field.

Under the condition of  $eqQ \ll g_I \mu_N H_{hf}$ , the  $\gamma$ -ray transitions can approximately be considered to be magnetic-dipole radiation. Consequently, there are



Figure 3.1: The energy level and the corresponding Mössbauer spectrum for  $eqQ \ll g_I \mu_N H$ .

Table 3.1: Angular dependence of the allowed transitions for the <sup>57</sup>Fe Mössbauer spectrum

Line No.	Transition	М	$< I_g m_g LM \mid I_e m_e >^2$	Relative intensity
1,6	$\pm 3/2 \rightarrow \pm 1/2$	±1	1	$\frac{3}{4}(1+\cos^2\beta)$
2,5	$\pm 1/2 \rightarrow \pm 1/2$	0	2/3	$\sin^2\beta$
3,4	$\mp 1/2 \rightarrow \pm 1/2$	<del>7</del> 1	1/3	$\frac{1}{4} (1 + \cos^2 \beta)$

only six transitions because the transitions for  $M=\pm 2$  are forbidden. Further, the relative transition intensities given by (3.32) and (3.33) can be simplified because  $\kappa^2 = A(e2)/A(m1) \sim 0$ , as shown in Table 3.1.

For the randomly-oriented samples, the relative intensity must be averaged over all values of  $\beta$ . Hence, the relative intensities are 3:2:1 for the 1st plus 6th lines, the 2nd plus 5th lines and 3rd plus 4th lines. For the oriented samples, when the direction of the  $\gamma$ -ray is along the direction of the hyperfine field, i.e.  $\beta = 0^{\circ}$ , the relative intensities are 3:0:1; When the direction of the  $\gamma$ -ray is perpendicular to the direction of the hyperfine field, i.e.  $\beta = 90^{\circ}$  the relative intensities are 3:4:1.

An angle factor, b, is defined as the intensity ratio of the 2nd and 5th lines to the 3rd and 4th lines. The angle  $\beta$  is related to the angle factor b by

$$\cos\beta = \sqrt{\frac{4-b}{4+b}} \tag{3.42}$$

# **3.4 Applications of Mössbauer spectroscopy**

Mössbauer spectroscopy is utilized in a wide diversity of fields, such as physics, chemistry, biology, metallurgy, geology and mineralogy. However, I focus my attention on the applications of <sup>57</sup>Fe Mössbauer spectroscopy to R-Fe compounds.

## **3.4.1 Magnetic ordering temperature**

Mössbauer spectroscopy can be used to determine the magnetic ordering temperature of materials. The intensities of a absorption line for the paramagnetic state as a function of temperature are measured. At the magnetic ordering temperature a sharp decrease in absorption intensity will occur because of the appearance of a hyperfine field. Since no external magnetic field is required for this measurement, the Mössbauer method may on occasion have some advantages over other general techniques.

## **3.4.2** Fe magnetic moments

The value of the total Fe magnetic moment can be obtained directly from a saturation magnetization measurement of R-Fe compounds with a non-magnetic R (R=Y, La or Lu). However, Mössbauer spectroscopy can be used to determine the Fe moment also. The problem faced by Mössbauer spectroscopy is knowing the conversion coefficient from hyperfine field to Fe moment. For Y-Fe compounds the conversion coefficient has been found to be about 150 kOe/ $\mu_B$  by Gubben et al (1974).

Mössbauer spectroscopy also provides a useful way to estimating the anisotropic orbital contribution to the Fe moment by comparing spectra taken above and below a spin-reorientation temperature. In some instances, quite dramatic changes in the hyperfine field occur. Based on the expression for the hyperfine field (Streever, 1979),

$$H_{hf} = \alpha \mu_S + \beta \mu_L \tag{3.43}$$

where  $\mu_S$  and  $\mu_L$  are the Fe spin moment and orbital moment, respectively, one concludes that the constants  $\alpha$  and  $\beta$  have opposite signs.

#### 3.4.3 Phase analysis

The characteristic hyperfine parameters observed in a Mössbauer spectrum can be used to identify phases in much the same way as X-ray diffraction patterns are used. Further, the relative quantity of an Fe-containing phase can also be calculated based on the corresponding area of Mössbauer subspectra. Although, for these purposes, the applicability of the Mössbauer effect is not nearly as general as x-ray diffraction, the Mössbauer effect, in some particular cases, may play a decisive role in the identification of phases. For an Nd<sub>4</sub>Fe<sub>77</sub>B<sub>19</sub> nanocomposite magnet, it is difficult to detect the Nd<sub>2</sub>Fe<sub>14</sub>B phase by x-ray diffraction because its particles are too fine. However, Nd<sub>2</sub>Fe<sub>14</sub>B can easily be distinguished from Fe<sub>3</sub>B in an Mössbauer spectrum at 600 K. At this temperature, Fe<sub>3</sub>B still has a ferromagnetic sextet spectrum; however, Nd<sub>2</sub>Fe<sub>14</sub>B has a paramagnetic doublet spectrum. The volume percentages are found to be 60%, 36% and 4% for Fe<sub>3</sub>B, Nd<sub>2</sub>Fe<sub>14</sub>B and  $\alpha$ -Fe phases, respectively (Li Z W et al, 1992). A simple linear combination of a virgin YFe<sub>11</sub>Ti spectrum and a saturated YFe<sub>11</sub>TiC<sub>y</sub> spectrum is used to fit the spectra obtained at intermediate heating temperatures and the coexistence of C-poor (or virgin) and C-rich phase is clearly demonstrated (Li et al, 1993).

#### **3.4.4** Site occupancies

Some magnetic properties, such as the Curie temperature, magnetization or magnetic anisotropy, often depend on the site distribution of Fe and other atoms for most ferrites, and in particular for the substituted R-Fe compounds. The site distributions of the Fe atoms can be calculated from the corresponding areas of the Mössbauer subspectra. Although neutron diffraction, x-ray diffraction and NMR (nuclear magnetic resonance) can also provide useful data about the site occupancies of atoms, the Mössbauer effect is usually more effective and more convenient.

Mössbauer studies of  $Y(Fe, M)_{12}$  clearly demonstrated that Ti and V have a preference for the 8*i* site (Cadogan et al, 1989; Li Z W et al, 1990a). The preferential occupancies of the Co atoms in Nd<sub>2</sub>(FeCo)<sub>14</sub>B have been studied using Mössbauer spectroscopy. The Mössbauer spectroscopy of Nd<sub>2</sub>Co<sub>14</sub>B doped with <sup>57</sup>Fe showed that Fe atoms have a strong preference for the 8*j*<sub>2</sub> site (Van Noort et al 1985). Ryan et al (1989) introduced a <sup>57</sup>Co source into a Nd<sub>2</sub>Fe<sub>14</sub>B matrix prepared with <sup>56</sup>Fe. The decreased subspectral area for the 8*j*<sub>2</sub> means that Co atoms avoid this site.

Some nonmagnetic atoms, such as Si and Ga, can raise the Curie temperture when they are used to replace Fe in  $R_2Fe_{14}B$  and  $R_2Fe_{17}$  compounds. Based on the areas of Mössbauer spectra it has been shown that Si or Ga atoms preferentially occupy the 18*f* and 6*c* sites, which leads to a decrease in the negative exchange interaction and an increase in the Curie temperature (Li Z W et al, 1990, 1995, 1995a).

### **3.4.5** Nature of the magnetic coupling

The Mössbauer effect can be used to investigate the general properties of magnetic coupling, i.e., whether the material is ferromagnetic, ferrimagnetic, antiferromagnetic or sperimagnetic. For this purpose one can apply an external magnetic field to the material and observe the intensity variation of the 2nd and 5th spectral lines. For the amorphous film  $Y_{18}Fe_{82}$ , the intensities of the 2nd and 5th lines gradually decrease with increasing applied magnetic field,  $H_0$ , and do not disappear even at  $H_0=50$  kOe (Chappert et al 1981). This shows that amorphous  $Y_{18}Fe_{82}$  is sperimagnetic.

#### **3.4.6** Spin reorientation

The competition between the anisotropies of the Fe and R sublattices may lead to a spin reorientation. The Mössbauer effect can be used to study spin reorientation by three methods.

(1) Angle dependences of the quadrupole splitting on the hyperfine field direction (or magnetization vector) can lead to several types of spectra even for an identical crystallographic site. RFe<sub>2</sub> compounds have a cubic Laves phase structure. Fe atoms are located on the 8*a* site with  $P_3m$  symmetry. The axes of the EFG are parallel to the local threefold axes of symmetry. When the magnetizations are parallel to the [100] direction, all the Fe atoms are equivalent and yield a simple six-line spectrum; when the magnetization is along the [111] and [110] directions, the Mössbauer spectrum is split into two components with the relative intensity ratio of 3:1 or 2:2, respectively, because the magnetization vectors form the various angles with the axis of the EFG. In this way the easy magnetization directions of RFe<sub>2</sub> compounds have been shown to be the [100] direction for R=Ho and Dy, the [111] direction for R=Y, Tb, Er and Tm and the [110] direction for orientation on the R composition and the temperature) have been determined for  $R_{1-x}R'_xFe_2$  (Atzmony and Dariel, 1973).

(2) The spin-reorientation temperature,  $T_{SR}$ , can also be obtained from the dependences of the hyperfine fields on the temperature. When the spin-reorientation occurs the hyperfine field will have an abrupt jump (from a planar to an axis anisotropy). This jump has its origin in the anisotropic residual orbital moment. In this way Gubbens et al (1976) found  $T_{SR}=72$  K for  $Tm_2Fe_{17}$ ; Hu et al (1989) also studied the spin reorientation for RFe<sub>11</sub>Ti compounds with R=Nd, Tb and Dy.

(3) For an aligned or single crystal sample the direction of the Fe moments can be derived from the intensity ratio between the 2nd plus 5th and the 3rd plus 4th Mössbauer spectral lines by (3.42). Nd<sub>2</sub>Fe<sub>14</sub>B has an uniaxial anisotropy at room temperature. Based on the intensity ratio, Onodera et al (1984) showed that the direction of the Fe moments below  $T_{SR}$ =135 K deviates about 23° from the c-axis. Similar intensity variations have been observed for aligned samples of Er<sub>2</sub>Fe<sub>14</sub>B (Vasquez et al, 1985; Friedt et al, 1986), Ho<sub>2</sub>Fe<sub>14</sub>B (Fruchart et al, 1987) and RFe<sub>11</sub>Ti (Hu et al, 1989a).

# Chapter 4

# **Experimental Details**

# 4.1 Sample preparation

The compounds  $R_2Fe_{15}Si_2$  (R=Y, Nd, Gd and Er) and  $Sm_2Fe_{17-x}Si_x$  (x=0, 0.5, 1, 2 and 3) were synthesized. The purities of the primary materials were >99.8 % for the rare-earth elements and >99.9 % for the other elements. An excess of the rare-earth constituent (5-8 % for Sm and 2 % for the other rare-earth elements) in the composition was added to compensate for the rare-earth loss in melting. These primary materials were melted in an arc furnace in an Ar atmosphere. To ensure homogeneity, all ingots were remelted at least three times and then were annealed at 900°C. The Sm samples were annealed for 4 h and the other samples for 72 h. X-ray diffraction showed that all samples after annealing were single phase with a 2:17-type structure; a small amount of  $\alpha$ -Fe was present in Nd<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub> and Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub> with x=0 and 0.5.

The samples of  $R_2Fe_{15}Si_2$  and  $Sm_2Fe_{17-x}Si_x$  were ground into the fine powders. These powders were heated in CH<sub>4</sub> at a pressure of about 2 bar at 700°C for 2 h to form carbides  $R_2Fe_{15}Si_2C_y$  with R=Nd, Sm, Gd and Er and  $Sm_2Fe_{17-x}Si_xC_y$ with x=1, 2 and 3. Then, the sample chamber was pumped for a few minutes to eliminate any H<sub>2</sub>. All samples were single phase with the 2:17-type structure; a small amount of  $\alpha$ -Fe was present. In addition,  $Sm_2Fe_{17}C_y$  are prepared by heating the powders of  $Sm_2Fe_{17}$  in CH<sub>4</sub> at 450°C instead of 700°C. The C concentrations by weighing were found to be about 2.5-2.7, as shown in Table 4.1

_		$R_2Fe_{15}S$	i <sub>2</sub> C <sub>y</sub>	
R	Nd	Sm	Gd	Er
У	2.6(2)	2.5(2)	2.6(2)	2.5(2)
<u></u>	S	m <sub>2</sub> Fe <sub>17-</sub> ,	"Si <sub>x</sub> C <sub>y</sub>	
х	0	1	2	3

Table 4.1: The carbon concentration by weighing for carbides.

# 4.2 Experimental equipment

#### 4.2.1 C absorption apparatus

The equipment for C absorption is shown in Fig.4.1. The sample chamber was made from quartz with a length of 250 mm and a diameter of 8 mm fitted into the furnace. The furnace was a quartz tube with a diameter of 10 mm wound with a heating coil. The quartz tube was installed into a steel tube with a length of 80 mm. A fiber with a high melting point was packed between the quartz tube and the steel tube as thermal insulation. A Ni-Cr and Ni-Al thermocouple, in contact with the bottom of the chamber, was used to measure the temperature. A power supply, with a maximum power output of 2 A at 52 V, was used to control the heating temperature. In the furnace the dependence of the temperature on the distance from the center to the end of the furnace was measured; it is also shown in Fig.4.1. The range of a constant temperature was about 30 mm with an error of about  $\pm 5^{\circ}$ C.

## 4.2.2 X-ray diffractometer

The x-ray diffraction experiments were performed using a Philips x-ray diffractometer with Cu-, Co- or Fe- $K_{\alpha}$  radiation. A schematic representation of the x-ray diffractometer is shown in Fig.4.2(A). A powder sample, C, can be rotated



Figure 4.1: Schematic representation of C absorption apparatus.

about an axis O. X-rays produced by a x-ray tube are diffracted by the sample to form a convergent beam. The beam comes to a focus at the slit F and then enters the counter G. A and B are special slits which define and collimate the incident and diffracted beams. The slits and counter are supported on the carriage E, which can be rotated about the axis O. The supports E and H are mechanically coupled so that a rotation of the counter through an angle of  $2\theta$  is accurately accompanied by a rotation of the sample through an angle of  $\theta$ .

## 4.2.3 Vibrating-sample magnetometer (VSM)

A vibrating-sample magnetometer is used to measure the magnetization of a sample. Its schematic representation is shown in Fig.4.2 (B). This method is based on the flux change in a coil when the sample is vibrated near it. The sample, is usually cemented to the end of a rod, the other end is fixed to a mechanical vibrator. The rod and sample are vibrated at about 80 Hz and with an amplitude of about 0.1 mm in a direction perpendicular to the magnetic field. The oscillating magnetic field of the sample induces an alternating emf in the detection coils. On the other hand, the vibrating rod also carries a pair of the plates of a capacitor. A dc amplifier establishes a potential on the vibrating plates and the amplitude of vibration produces a varying ac signal on the fixed capacitor plate. The signal derived from the vibrating capacitor is proportional to the amplitude and frequency of the vibration. The voltages from the two sets of coils are compared and the difference is proportional to the magnetic moment of the sample. This method is very versatile and sensitive. It can be applied to both weakly and strongly magnetic materials. The apparatus must be calibrated with a specimen of known magnetization, such as Fe or Ni.

### 4.2.4 Mössbauer spectrometer

A Mössbauer spectrometer, shown in Fig.4.3(A), consists of four parts : a source, driver, detector and multichannel analyzer.

Source The source used for the  ${}^{57}$ Fe Mössbauer spectra is the isotope  ${}^{57}$ Co in a metallic matrix. The decay scheme for  ${}^{57}$ Fe is shown in Fig.4.3(B). The radiation



Figure 4.2: Schematic representation of (A) x-ray diffractometer and (B) vibrating-sample magnetometer.

emitted from <sup>57</sup>Co consists of (1) Resonant  $\gamma$ -rays from an excited to a ground state (recoilless), (2) Non-resonant  $\gamma$ -rays from the same transitions (involving recoil), (3) Radiation from all other transitions and (4) secondary radiation produced in the matrix (mainly x-rays). The radiation from (1) (transition from I=3/2 to 1/2) produces a Mössbauer spectrum, the radiation from (2)-(4) contributes to the background.

Detector The detector is applied to record the  $\gamma$ -ray counts. The pulses from the detector are amplified, pass through a discriminator, which rejects most of the non-resonant background radiation, and finally are fed to the open channel address.

Multichannel analyzer A multichannel analyser can store an accumulated total of  $\gamma$ -counts in one of 512 individual registers known as channels. Each channel is held open in turn for a short time interval of fixed length, which is derived from a very stable constant-frequency clock device. Any  $\gamma$ -ray counts registered by the detector during that time interval are added to the accumulated total already stored in the channel.

Driver system The timing pulses from the clock are also used to synchronize a voltage waveform, which is employed as a command signal to a servo-amplifier controlling an electromechanical driver. The driver moves the source relative to the absorber in a constant acceleration with increasing channel number. In this way the energy of the  $\gamma$ -rays is modulated so that the nuclear transitions in the source and absorber can be accurately matched and thus resonance occurs.

Other equipment A cryostat and a high temperature oven with a variable temperature controller are used to collect Mössbauer spectra below and above room temperature, respectively. The precision of temperature is within  $0.5^{\circ}$ C. In addition, a superconducing magnet is also installed, which can apply a magnetic field of up to 60 kOe to the absorber.





Figure 4.3: (A) Schematic representation of Mössbauer spectrometer and (B) decay scheme of  $^{57}$ Co.

# 4.3 **Procedures and data analyses**

## 4.3.1 X-ray diffraction

X-ray diffraction experiments were performed using a Philips diffractometer with  $\operatorname{Cu} K_{\alpha}$ ,  $\operatorname{Co} K_{\alpha}$  or Fe  $K_{\alpha}$  radiation. The x-ray diffraction patterns give the position and the intensity of the diffraction lines. From the position, the lattice parameters can be obtained for a known crystal structure. On the other hand, from the intensity, the relative volume of each phase can be found for a multiphase system.

#### (1) Lattice parameters

The spacing  $d_{hkl}$  of the planes (hkl) can be obtained from the diffraction angle  $2\theta$ , based on the Bragg law,

$$2d_{hkl}\sin\theta = \lambda \tag{4.1}$$

where  $\lambda$  is the x-ray wavelength. For a hexagonal structure, the relationship between  $d_{hkl}$  and the lattice parameters, a and c, is given by

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$
(4.2)

Therefore, m lines in a x-ray diffraction pattern lead to m sets of equations with two variables, a and c. The values of a and c are usually obtained by applying a least-squares method to (4.2).

#### (2) Quantitative phase analysis

Quantitative phase analysis by x-ray diffraction is based on the intensity of the diffraction lines. For a single-phase powder sample, the integrated intensity,  $I_{hkl}$ , for the (hkl) crystal surface is given by

$$I_{hkl} = C \cdot \left(\frac{1}{V}\right)^2 \cdot \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}\right) \cdot m_{hkl} \cdot |F_{hkl}|^2 \left(\frac{\exp(-2M(\theta))}{2\mu_l}\right)$$
(4.3)

where C is a constant, V is the cell volume,  $\theta$  is the Bragg angle,  $m_{hkl}$  is the multiplicity factor,  $\exp(-2M(\theta))$  is the temperature factor,  $\mu_l$  is the line absorption coefficient, and  $F_{hkl}$  is the structure fractor. The structure factor is defined as

$$F_{hkl} = \sum_{j=1}^{j} f_j \exp[i2\pi(hx_j + ky_j + lz_j)]$$
(4.4)
where  $f_j$  is the atomic scattering factor of the *j*th atom, and  $x_j$ ,  $y_j$  and  $z_j$  are the positions of the *j*th atom.

In (4.3), the constant C is independent of the kind and amount of the diffracting sample and  $\mu_l$  is for the whole sample; the other parameters depend on  $\theta$ , hkl, and the structure of sample. One defines R as

$$R = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot m_{hkl} \cdot |F_{hkl}|^2 \exp(-2M(\theta))$$
(4.5)

Therefore, for a two-phase system, the ratio of the integrated intensities between the two phases can be written as

$$\frac{I_1}{I_2} = \frac{CR_1\upsilon_1}{2\mu_l V_1^2} / \frac{CR_2\upsilon_2}{2\mu_l V_2^2} = \frac{R_1\upsilon_1 V_2^2}{R_2\upsilon_2 V_1^2}$$
(4.6)

where  $v_i$  is the volume fraction for the *i*th phase. Once  $v_1/v_2$  is found, the values of  $v_1$  and  $v_2$  can be obtained from the additional relationship,

$$v_1 + v_2 = 1.0 \tag{4.7}$$

### 4.3.2 Magnetic measurements

### (1) Curie temperature

There exists a spontaneous magnetization for ferromagnets or ferrimagnets because of the exchange interaction. With increasing temperature, the magnetization decreases and vanishes at a certain temperature. This temperature is called the Curie temperature,  $T_f$ , which separates the paramagnetic state at  $T>T_f$  from the ferromagnetic one at  $T<T_f$ . Therefore, the Curie temperature can be obtained from a thermomagnetic scan in an applied field. The curve of magnetization versus temperature bends over to form a small "tail" near the Curie temperature, as shown in Fig.4.4(A). The Curie temperature is determined by the extrapolation of the main part of the curve. In the case of a small applied field, a linear extrapolation is usually used to obtain the Curie temperature. The magnetization behavior near the Curie temperature can be described more accurately by a parabolic curve.

Based on the mean-field theory, a reduced spontaneous magnetization,  $\sigma = M(T)/M_0$ (in this section,  $\sigma$  is the reduced spontaneous magnetization, but not the specific



Figure 4.4: For Ni metal, (A) the curve of M-T and (B) the Curie temperature,  $T_f$ . The open circles are for a linear extrapolation and the solid symbols are for a parabolic extrapolation.

magnetization), can be expressed as

$$\sigma = \mathcal{B}_{S}(x) = \frac{2S+1}{2S} \coth(\frac{2S+1}{2S}x) - \frac{1}{2S} \coth(\frac{1}{2S}x)$$
(4.8)

where

$$x = 2ZJS^2\sigma/k_BT \tag{4.9}$$

 $B_S$  is the Brillouin function, Z is the neighboring coordination number, J is the exchange integral,  $k_B$  is Boltzmann's constant, and S is the spin quantum number.

Because, for a small x,

$$coth(x) = \frac{1}{x}\left(1 + \frac{1}{3}x^2 - \frac{1}{45}x^4 + ...\right)$$
 (4.10)

 $\sigma = \mathcal{B}_s(x)$  in the first-order approximation can be expressed as

$$\sigma = \frac{S+1}{3S}x\tag{4.11}$$

At  $T=T_f$  (4.11) and (4.9) give a expression for the Curie temperature,

$$T_f = \frac{2S(S+1)}{3k_B} ZJ$$
(4.12)

On substituting (4.12) into (4.8) leads to

$$\sigma = \mathcal{B}_s[\frac{3S}{S+1}\frac{T_f}{T}\sigma]$$
(4.13)

When  $\mathcal{B}_S$  is expanded at  $T_f$  and the first three terms are taken in  $\coth(x)$ , one can show

$$\sigma^{2} = \frac{10(S+1)^{2}}{3[(S+1)^{2}+S^{2}]} \cdot \frac{T^{2}(T_{f}-T)}{T_{f}^{3}}$$

$$\sim \frac{10(S+1)^{2}}{3[(S+1)^{2}+S^{2}]} \cdot \frac{T_{f}-T}{T_{f}}$$

$$= C_{1} - C_{2}T \qquad (4.14)$$

The Curie temperature is given by

$$T_f = \frac{C_1}{C_2}$$
(4.15)

Eq.(4.14) indicates that at  $T \to T_f$ ,  $\sigma^2(T)$  is linearly related to T.

In this way, the Curie temperature of Ni is found to be 629 K and 635 K in applied fields of 0.5 kOe and 5 kOe, respectively. On the other hand, the linear extrapolation leads to a Curie temperature of 630 K for the field of 0.5 kOe. These results are shown in Fig.4.4(B). Therefore, the Curie temperatures obtained from the parabolic and the linear extrapolation are almost the same in a small field.

### (2) Saturation magnetization

In the high-field region, the relation between the magnetization, M, and the applied magnetic field, H, is called the law of approach to saturation and is usually written as

$$M = M_s \left(1 - \frac{a_1}{H} - \frac{a_2}{H^2}\right) \tag{4.16}$$

where the second term is generally interpreted as due to inclusions and/or microstructure, and the third term as due to magnetocrystalline anisotropy. In fields over ten thousand oersteds, the  $a_1/H$  is usually dominant so that the above expression reduces to

$$M = M_{\rm s}(1 - \frac{a_1}{H}) \tag{4.17}$$

High-field measurements of M can therefore be plotted against 1/H and extrapolated to 1/H=0 in order to find the values of saturation magnetization,  $M_s$ .



Figure 4.5: (A) Magnetization curves and (B) saturation magnetization obtained from the extrapolation. The solid circles and squares are the magnetization curves with and without the correction of demagnetizing field, respectively.

For magnetic measurements on ellipsoidal samples, the applied field,  $H_{app}$ , must now be corrected because of the demagnetizing effect to obtain the true field Hacting on the sample,

$$H = H_{app} - H_d = H_{app} - N_d M \tag{4.18}$$

where  $N_d$  is the demagnetizing factor and  $H_d$  is the demagnetizing field.

For example, a cylinder of an  $\alpha$ -Fe sample, 1.1 mm long and 3.2 mm in diameter, has a demagnetizing factor of 0.2. The magnetization curves as functions of the applied field,  $H_{app}$  and the true field, H are shown in Fig.4.5(A). The saturation magnetization is found to be 212.4 emu/g based on the law of approach to saturation (4.17), as shown in Fig.4.5(B).

The magnetization obtained from a vibrating-sample magnetometer is the specific magnetization,  $\sigma$ , in emu/g. The magnetization can be expressed in Gs and  $\mu_B/f.u.$ , respectively, by

$$M = \begin{cases} 4\pi\rho\sigma & \text{in Gs} \\ \rho V \sigma / n\mu_B & \text{in } \mu_B / \text{f.u.} \end{cases}$$
(4.19)

where  $\rho$  is the density, V is the cell volume, n is the number of the chemical formula units in a cell and  $\mu_B$  is the Bohr magneton.

### (3) Magnetocrystalline anisotropy

For a uniaxial crystal, the magnetization curves are significantly different when a magnetic field is applied parallel to or perpendicular to the c-axis.

When the field is applied perpendicular to the easy c-axis and  $M_s$  is rotated away from the c-axis by an angle  $\theta$ , the anisotropy energy is given by

$$E_a = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta \tag{4.20}$$

The magnetic field energy is

$$E_H = -M_s H \cos(\frac{\pi}{2} - \theta). \qquad (4.21)$$

The condition for minimum total energy is

$$2K_1 \sin \theta \cos \theta + 4K_2 \sin^3 \theta \cos \theta - M_s H \cos \theta = 0. \qquad (4.22)$$

Also, the magnetization is

$$M_{\perp} = M_s \cos(\frac{\pi}{2} - \theta). \tag{4.23}$$

Elimination of  $\theta$  from (4.22) and (4.23) gives

$$H = \frac{2K_1}{M_{\bullet}^2} M_{\perp} + \frac{4K_2}{M_{\bullet}^4} M_{\perp}^3.$$
(4.24)

If  $K_2$  is zero, the magnetization curve becomes a straight line,

$$M_{\perp} = \frac{M_s^2}{2K_1} H \tag{4.25}$$

On the other hand, when the field is applied parallel to the easy c-axis, based on (4.20), the magnetic field energy  $E_H = -M_s H \cos \theta$  and magnetization  $M_{\parallel} = M_s \cos \theta$ ,



Figure 4.6: Calculated magnetization curves and anisotropy fields.

the condition for minimum energy is given by  $\sin \theta = 0$ . The magnetization curve is a straight line parallel to the magnetic field H axis,

$$M_{\parallel} = M_s \tag{4.26}$$

The two magnetization curves intersect at

$$H_a = \frac{2K_1}{M_s}.$$
 (4.27)

 $H_a$  is called the anisotropy field, which represents the magnitude of magnetocrystalline anisotropy for a uniaxial crystal.

Fig.4.6 shows the magnetization curve for Co, calculated for  $M_s=160$  emu/g,  $K_1=4.5\times10^6$  ergs/cm<sup>3</sup>, and  $K_2=1.5\times10^6$  ergs/cm<sup>3</sup>. The dashed line is the magnetization behavior if  $K_2=0$ . The anisotropy field is 10.3 kOe for Co metal.

#### (4) Measurements

Magnetic measurements were performed using a vibrating-sample magnetometer for the  $R_2(Fe, Si)_{17}$  carbides and their parents.

(a) To determine the Curie temperatures, the dependence of the magnetization, M(T), on temperatures was measured in an applied field of 0.5 kOe and followed by a linear extrapolation of  $M^2$  versus T near the Curie temperature. Because a small amount of  $\alpha$ -Fe is present in all carbides, the background signal (due to  $\alpha$ -Fe) was subtracted when the Curie temperature was measured by fitting  $M^2$  versus T.

(b) Magnetization curves, M(H), were measured in applied fields up to 18 kOe for all  $R_2(Fe, Si)_{17}$  carbides and their parents. For the law of approach to saturation, when the fields are over twelve thousand oersteds, the dependences of both  $a_1/H$  and  $a_2/H^2$  on magnetization are linear to a good approximation; however, the  $a_1/H$  is much larger than the  $a_2/H^2$ . Therefore, the first term,  $a_1/H$ , in eq.(4.16) cannot be neglected. In addition, the saturation magnetizations,  $M_s$ , obtained from (4.16) and (4.17) are almost the same. For simplicity, the values of  $M_s$  were found by extrapolating M(H) against 1/H plots to 1/H=0 using the law of approach to saturation. For the magnetization curve, M(H), a correction for the demagnetizing field has been made.

(c) Aligned samples were prepared by mixing the fine powders with epoxy resin and then by placing the mixture in a magnetic field of 10 kOe. In order to determine the anisotropy field, magnetization curves with the field applied parallel and perpendicular to the alignment direction were obtained. Then, the two magnetization curves were extrapolated from the maximum applied field of 18 kOe and intersected at a point; the corresponding field at this point is the anisotropy field.

### 4.3.3 Mössbauer spectra

### (1) Mössbauer experiments

 $^{57}$ Fe Mössbauer spectra were collected using a conventional constant acceleration spectrometer. The  $\gamma$ -ray source was  $^{57}$ Co in a Rh matrix. The absorbers were made by immobilizing the powdered samples in benzophenone for the measurements below room temperature and in boron nitride powders in high temperatures. In addition, the aligned samples were prepared by mixing the fine powders with epoxy resin and then by placing the mixture in a magnetic field of 10 kOe. All the absorbers contained 5-8 mg/cm<sup>2</sup> of natural iron. The calibration was made by using the spectrum of  $\alpha$ -Fe at room temperature.

### (2) Mössbauer spectrum fitting

In the approximation of a thin absorber, the theoretical expression for a Mössbauer lineshape is Lorentzian (see Chapter 3.2). A Mössbauer spectrum obtained in an experiment is usually an overlap of many Lorentzian lines,

$$y_i = B + \sum_{j=1}^{N} \sum_{k=1}^{K} A_{0,jk} / \left[ 1 + \left( \frac{v_i - P_{jk}}{\Gamma_{jk}/2} \right)^2 \right]$$
(4.28)

where  $y_i$  and  $v_i$  are the counts and Doppler velocity for the *i*th channel, respectively, B is a average background count,  $A_0$ ,  $\Gamma$  and P are the height, width and position of the Mössbauer spectral line, respectively, N is the number of subspectra, and K is taken as 6, 2 and 1 for the magnetic, electrical quadrupole and monopole interactions, respectively.

In (4.28) the position, P in mm/s, is determined by three Mössbauer parameters, the hyperfine field,  $H_{hf}$ , the quadrupole splitting,  $\epsilon$ , and the isomer shift,  $\delta$ ,

$$P_k = \alpha_k H_{hf} + \beta_k \epsilon + \delta \tag{4.29}$$

For K = 1, since there are no quadrupole splittings and hyperfine fields, both  $\alpha$  and  $\beta$  are zero. For K = 2, since there is no hyperfine field,  $\alpha$  is zero and  $\beta$  is equal to -0.5 and +0.5. For K = 6, the  $\alpha$  and  $\beta$  are determined by the following formulae,

$$\begin{cases} \alpha_6 = -\alpha_1 = -(\frac{3}{2}g_e - \frac{1}{2}g_g)\mu_N \frac{c}{E_{\gamma}} \\ \alpha_5 = -\alpha_2 = -(\frac{1}{2}g_e - \frac{1}{2}g_g)\mu_N \frac{c}{E_{\gamma}} \\ \alpha_4 = -\alpha_3 = -(\frac{1}{2}g_e + \frac{1}{2}g_g)\mu_N \frac{c}{E_{\gamma}} \end{cases}$$

and

$$\beta_k = +0.5 - 0.5 - 0.5 - 0.5 - 0.5 + 0.5$$

where  $g_g$  and  $g_e$  are the gyromagnetic ratio for the ground state (I = 1/2) and the excited state (I = 3/2), respectively,  $\mu_N$  is the nuclear magneton and  $E_{\gamma}$  is the energy of the  $\gamma$ -ray.

The theoretical expressions in (4.28) can be written as

$$y_i = y(v_i, q_1, q_2, ..., q_n) = y(v_i, q_j)$$
  $j = 1 - n$  (4.30)

where  $q_j$  denotes the variable parameter in formulae (4.28) and n is the number of the variable parameters. In the fitting of a Mössbauer spectrum, one finds a set of the variable parameters,  $q_j$ , which makes the mean square difference between the theoretical value,  $y(v_i, q_j)$ , and the experimental spectrum,  $Y_i$ ,

$$\Phi = \sum_{i=1}^{m} w_i [Y_i - y(v_i, q_j)]^2$$
(4.31)

a minimum, where  $w_i$  is a weight factor taken as  $1/Y_i$ , and m is the number of experimental points.

First, a set of the initial parameters,  $q^0 = q_j^0$ , are given. Then, the  $y(v_i, q_j)$  are expanded into a Taylor series with the initial values of  $q_j^0$  and the second and more order terms are neglected, viz,

$$y(v_i, q_j) = y(v_i, q_j^0) + \sum_{k=1}^n \frac{\partial y(v_i, q_j^0)}{\partial q_k} \delta q_k$$
(4.32)

Hence  $y(v_i, q_j)$  becomes a linear function. Finally, the  $y(v_i, q_j)$  are substituted into (4.31) and the condition

$$\frac{\partial \Phi}{\partial q_j} = 0 \tag{4.33}$$

is applied to make  $\Phi$  a minimum. From (4.31)-(4.33), one obtains

$$\sum_{i=1}^{m} \frac{1}{Y_i} [Y_i - y(v_i, q_j^0) - \sum_{k=1}^{n} \frac{\partial y(v_i, q_j^0)}{\partial q_k} \delta q_k] \frac{\partial y(v_i, q_j^0)}{\partial q_j} = 0 \qquad (j, k = 1 - n) \quad (4.34)$$

A matrix A with elements

$$(\mathbf{A})_{jk} = \sum_{i=1}^{m} \frac{1}{Y_i} \frac{\partial y(v_i, q_j^0)}{\partial q_j} \frac{\partial y(v_i, q_j^0)}{\partial q_k} \qquad \qquad j, k = 1 - n \tag{4.35}$$

and a vector **D** with components

$$(\mathbf{D})_{j} = \sum_{i=1}^{m} \frac{1}{Y_{i}} [Y_{i} - y(v_{i}, q_{j}^{0})] \frac{\partial y(v_{i}, q_{j}^{0})}{\partial q_{j}} \qquad (j = 1 - n)$$
(4.36)

are defined. Hence, (4.34) can be rewritten as

$$\mathbf{D} - \mathbf{A} \cdot \delta \mathbf{q} = 0 \tag{4.37}$$

where  $\delta \mathbf{q} = \delta q_j$ . The solution of (4.37) is

$$\delta \mathbf{q} = \mathbf{A}^{-1} \cdot \mathbf{D}; \tag{4.38}$$

thus a set of new parameters

$$\mathbf{q^{(1)}} = \mathbf{q^0} + \delta \mathbf{q} \tag{4.39}$$

is obtained. Eqs.(4.31)-(4.39) construct a itinerative calculation. Finally, a set of best parameters that makes  $\Phi$  a minimum is found. This is the usual Gauss-Newton method.

However, for the Gauss-Newton method, it is necessary to solve the converse matrix in equation (4.38), which needs a large memory and requires much computer time. The method is therefore not suitable for a PC computer. Slavic (1974) suggested a new method to fit x-ray spectrum with Gaussian line shapes and obtained a satisfactory result. This method is now used to fit Mössbauer spectra. The principle is as the following. Since the values of the non-diagonal elements are supposed to be much less than the value of the diagonal elements in the matrix A of (4.35), the value of the non-diagonal elements can be considered to be approximatively zero so that the matrix A is a diagonal matrix. The formula (4.38) therefore becomes simply

$$\delta q_j = (\mathbf{A}^{-1})_{jj} \mathbf{D}_j$$
  
=  $\sum_i^m \frac{1}{Y_i} [(Y_i - y(v_i, q_j)] \frac{\partial y(v_i, q_j)}{\partial q_j}] / \sum_{i=1}^m \frac{1}{Y_i} (\frac{\partial y(v_i, q_j)}{\partial q_j})^2$  (4.40)

The (4.40) and (4.39) provide a iterative method for a set of parameters,  $q_j$ , which makes  $\Phi$  in (4.31) a minimum. The method suggested by Slavic is very suitable for a PC computer, because it is not necessary to solve the inverse matrix in (4.38). The computer program has been compiled to be used to fit Mössbauer spectrum and satisfactory results have been obtained.

## Chapter 5

# R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> Carbides — crystal structures and magnetic properties

The rare-earth iron nitrides  $R_2Fe_{17}N_y$  and carbides  $R_2Fe_{17}C_y$  made by a gasphase reaction have attracted much attention because of their excellent intrinsic magnetic properties. The most striking ones are an increase of the Curie temperature by about 400°C and, for  $Sm_2Fe_{17}N_y$  or  $Sm_2Fe_{17}C_y$ , a high uniaxial anisotropy that yields an anisotropy field larger than 140 kOe at room temperature (Coey and Sun, 1990; Coey et al, 1991). However, these nitrides or carbides have a major drawback, namely their chemical instability at high temperatures. They will completely decompose into  $\alpha$ -Fe and RC at about 600°C. Because of this drawback, it is difficult for the nitrides or carbides to be made into useful permanent magnets with high remanences, at least by normal techniques.

Recently, we have discovered that Si is able to stabilize the 2:17 structure of the carbides. A new series,  $R_2Fe_{15}Si_2C_y$  (R=Nd, Sm, Gd and Er), has been prepared by heating powders of their corresponding parents in CH<sub>4</sub> gas at 700°C instead of about 500°C. For these carbides, the carbon concentrations are close to the theoretical value of y=3 and the 2:17 structure can still be retained up to 900°C.

## 5.1 Structural stability and Si concentration

Si plays an important role in the structural or chemical stability of  $Sm_2Fe_{15}Si_2C_y$ . Mössbauer spectra and x-ray diffraction patterns with Fe  $K_{\alpha}$  radiation for powders

Method		x=0	<b>x=0.5</b>	x=1	x=2	x=3
Mössbauer	Relative area (%)	100	32(5)	9(4)	6(3)	7(3)
	Relative volume (%)	100	25(3)	6(2)	4(2)	5(2)
X-ray	Relative area (%)	100	34(7)	9(4)	7(4)	6(3)
	Relative volume (%)	100	32(4)	8(2)	6(2)	6(2)

Table 5.1: Relative volume of the  $\alpha$ -Fe(Si) phase for Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub> after heating in CH<sub>4</sub> at 700°C calculated from Mössbauer spectroscopy and x-ray diffraction.

of  $Sm_2Fe_{17-x}Si_x$  (x=0, 0.5, 1, 2 and 3) after heating in CH<sub>4</sub> at 700°C for 2 h are shown in Fig.5.1. The diffraction line of the  $\alpha$ -Fe(Si) phase is indicated by the arrows.

To obtain an accurate value for the amount of the  $\alpha$ -Fe(Si) phase, Mössbauer spectra were collected at 700, 680, 670 and 630 K (all higher than the Curie temperatures of the carbides and lower than the Curie temperature of  $\alpha$ -Fe) for the samples with x=0.5, 1, 2 and 3. The paramagnetic doublet corresponds to the carbides Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>C<sub>y</sub> and the six-line spectrum corresponds to the  $\alpha$ -Fe(Si) phase.

The relative volumes,  $v_{2:17}$  and  $v_{\alpha-Fe}$ , of the 2:17-type carbides and  $\alpha$ -Fe(Si) can be found from Mössbauer spectra and x-ray diffraction patterns. Based on the Mössbauer subspectral areas,  $A_{2:17}$  and  $A_{\alpha-Fe}$ , as well as the crystalline structure and lattice parameters of  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  and  $\alpha$ -Fe phases, the ratio of relative volumes between the two phases is given by

$$\frac{\upsilon_{\alpha-Fe}}{\upsilon_{2:17}} = \frac{A_{\alpha-Fe} \cdot V_{\alpha-Fe} \cdot N_{2:17}^{Fe}}{A_{2:17} \cdot V_{2:17} \cdot N_{\alpha-Fe}^{Fe}}$$
(5.1)

where  $V_i$  and  $N_i^{Fe}$  are the cell volume and the number of Fe atoms in a unit cell, respectively, for the *i*th phase (*i* represent the  $\alpha$ -Fe(Si) and 2:17 carbide.) Once  $v_{\alpha-Fe}/v_{2:17}$  is found, the values of  $v_{\alpha-Fe}$  and  $v_{2:17}$  can be obtained from the additional relationship

$$v_{\alpha-Fe} + v_{2:17} = 100\% \tag{5.2}$$

On the other hand, the ratio of the relative volume between the  $\alpha$ -Fe phase



Figure 5.1: Mössbauer spectra (A) and X-ray diffraction patterns (B) for  $Sm_2Fe_{17-x}Si_x$  after heating in CH<sub>4</sub> at 700°C.

and carbide can also be found from the relative integral intensity,  $I_{\alpha-Fe}$  and  $I_{2:17}$ , of the x-ray diffraction lines (see section 4.3.1) by

$$\frac{\upsilon_{\alpha-Fe}}{\upsilon_{2:17}} = \frac{I_{\alpha-Fe} \cdot V_{\alpha-Fe}^2 \cdot R_{2:17}}{I_{2:17} \cdot V_{2:17}^2 \cdot R_{\alpha-Fe}}$$
(5.3)

and

$$R_i = \frac{1 + \cos^2 2\theta_i}{\sin^2 \theta_i \cos \theta_i} \cdot m^i_{hkl} |F^i_{hkl}|^2 \exp(-2M_i(\theta_i))$$
(5.4)

where  $\theta$  is the Bragg angle,  $m_{hkl}$  is the multiplicity factor and  $F_{hkl}$  is the structure factor.

The relative volumes of  $\alpha$ -Fe(Si) and the 2:17 type carbide have been calculated by Mössbauer spectroscopy (5.1) and x-ray diffraction (5.3); the final results are listed in Table 5.1. The detailed process can be seen in the Appendix of this chapter.

Sm<sub>2</sub>Fe<sub>17</sub> powders heated in 700°C completely decompose into  $\alpha$ -Fe and SmC and there is no 2:17-type carbide. For the sample of x=0.5, a large amount of  $\alpha$ -Fe(Si) coexists with the 2:17-type carbide. The relative volume of  $\alpha$ -Fe(Si) is about 25 % by Mössbauer spectroscopy and 32 % by x-ray diffraction; probably the value obtained from the Mössbauer spectroscopy is more accurate. For samples with x≥1, the amount of  $\alpha$ -Fe(Si) drops to about 4-8 %. In an analysis similar to that of Ibberson et al (1991), the C absorption process can be written as

$$2R_2(Fe, Si)_{17} + 6C = 2R_2(Fe, Si)_{17}C_3$$
(5.5)

$$R_2(Fe, Si)_{17} + 2C = 2RC + 17(Fe, Si)$$
 (5.6)

The process (5.5) is called the C absorption process and will be discussed in section 5.2. The process (5.6) implies a chemical or structural instability in the carbides. Hence, the amount of  $\alpha$ -Fe(Si) can be considered to be an important parameter that indicates the degree of chemical or structural stability of the carbides. Sm<sub>2</sub>Fe<sub>17</sub> completely decomposes into  $\alpha$ -Fe at 700°C. However, for Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>C<sub>y</sub> with  $x\geq 1$ , even at the high temperature of 700°C, only 4-8% of  $\alpha$ -Fe(Si) is formed. In addition, x-ray diffraction and Mössbauer spectra show that Sm<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> retains the 2:17-type structure after annealing in Ar gas for 2 h, although the amount of  $\alpha$ -Fe(Si) increases. Obviously, Si is effective in stabilizing the 2:17-type structure of carbides and in preventing the decomposition of the carbides into  $\alpha$ -Fe(Si) and RC. The phase decomposition (5.6) requires an activation energy and a long-range diffusion of Fe(Si) atoms. The Si substitution may elevate the activation energy and/or decrease the diffusion constant of Fe(Si) atoms, thus stabilizing the crystal structure of the carbides.

## 5.2 C absorption model

There are two models that may describe the C absorption process (5.5). One is the phase segregation model (Colucci et al, 1992; Isnard et al, 1992; Coey and Hurley, 1992a). This model pointed out that during the N absorption process there exist two phases,  $R_2Fe_{17}$  and  $R_2Fe_{17}N_3$ . Only the percentage of the two phases varies upon the time and temperature of reaction. The nitrogenation process does not lead to an intermediate nitride. The other is the single phase model proposed by Skomski et al (1993). They thought that  $R_2Fe_{17}N_y$  produced at the nitrogenation temperature is a quasi-equilibrium gas-solid solution with a continuous range of interstitial nitrogen concentrations. This model leads to the existence of a single phase with continuously variable intermediate nitrogen concentration.

The carbides  $Sm_2Fe_{15}Si_2C_y$  with various C concentrations were prepared by heating  $Sm_2Fe_{15}Si_2$  powders at various temperatures in  $CH_4$  for 2 h followed by annealing at the same temperatures in Ar gas for 2 h.

Mössbauer spectra and x-ray diffraction patterns with Cu  $K_{\alpha}$  radiation for  $Sm_2Fe_{15}Si_2$  powder after heating in CH<sub>4</sub> at various temperatures as well as for the virgin  $Sm_2Fe_{15}Si_2$  are shown in Fig.5.2 and Fig.5.3, respectively.

The arrows  $\uparrow$  and  $\Uparrow$  in Fig.5.2 point to the position of characteristic lines for  $\operatorname{Sm}_2\operatorname{Fe}_{15}\operatorname{Si}_2\operatorname{C}_y$  and  $\operatorname{Sm}_2\operatorname{Fe}_{15}\operatorname{Si}_2$ , respectively. For the samples heated in 400-600°C, the Mössbauer spectra have the characteristics of both  $\operatorname{Sm}_2\operatorname{Fe}_{15}\operatorname{Si}_2$  (Fig.5.2 (a)) and  $\operatorname{Sm}_2\operatorname{Fe}_{15}\operatorname{Si}_2\operatorname{C}_y$  (Fig.5.2 (e)). These spectra can be considered to be a sum of two spectra. One is for  $\operatorname{Sm}_2\operatorname{Fe}_{15}\operatorname{Si}_2$ , the other is for  $\operatorname{Sm}_2\operatorname{Fe}_{15}\operatorname{Si}_2\operatorname{C}_y$ . The fitting method used is the following. A standard pattern for  $\operatorname{Sm}_2\operatorname{Fe}_{15}\operatorname{Si}_2\operatorname{C}_y$  is expressed as  $\{y_i\}(i=1,256)$ . The other pattern corresponding to  $\operatorname{Sm}_2\operatorname{Fe}_{15}\operatorname{Si}_2$  is given by four



Figure 5.2: Mössbauer spectra for  $Sm_2Fe_{15}Si_2$  before (a) and after heating in  $CH_4$  at temperatures of (b) 400°C, (c) 500°C, (d) 600°C and (e) 700°C.



Figure 5.3: X-ray diffraction patterns (top) and their fitted curves (bottom) for powders of  $Sm_2Fe_{15}Si_2$  before (a) and after heating in  $CH_4$  at temperatures of (b) 400°C, (c) 500°C, (d) 600°C and (e) 700°C. The dotted lines are for the C-rich phase and the solid lines are for the C-poor phase.

Table 5.2: The volume percentage of the C-poor and C-rich phase, v, for  $Sm_2Fe_{15}Si_2$  after heating at various temperatures,  $T_a$ , in CH<sub>4</sub> for 2 h. A is the areas obtained from Mössbauer spectra or x-ray diffraction lines.

<i>T_a</i>	virgin	400°C		500°C		600°C		700°C
		Μ	X	Μ	Х	Μ	Χ	
A (C-poor phase) (%)	100	78(7)	74(6)	55(5)	49(6)	15(8)	0	0
A (C-rich phase) (%)	0	22(7)	26(5)	45(6)	51(6)	85(8)	100	100
v (C-poor phase) (%)	100	78(7)	76(6)	54(6)	49(6)	14(8)	0	0
v (C-rich phase) (%)	0	22(7)	24(5)	46(6)	51(6)	86(8)	100	100
<y><sup>cal.</sup></y>	0	0.55	0.60	1.2	1.3	2.2	2.5	2.5
	0	0.8(2)		1.2(2)		2.5(2)		2.5

M and X represent Mössbauer spectra and x-ray diffractions, respectively.

sets of sextets with Lorentzian line-shapes,

$$\sum_{j=1}^{N} L_{ij}((A_0)_j, \Gamma_j, (H_{hf})_j, \epsilon_j, \delta_j; \boldsymbol{x}_i)$$
(5.7)

where  $L_{ij}$  is a Lorentz function with the following fitting parameters: intensity  $A_0$ , linewidth  $\Gamma$ , hyperfine field  $H_{hf}$ , quadrupole splitting  $\epsilon$  and isomer shift  $\delta$ ; x is the channel number. Each sextet corresponds to one Fe site. Thus, the experimental spectrum,  $\{Y_i\}$  (*i*=1,256) of the samples can be written as

$$Y_{i} = C_{0} - [\alpha \cdot \{y_{i}\} + \sum_{j=1}^{j} L_{ij}((A_{0})_{j}, \Gamma_{j}, (H_{hf})_{j}, \epsilon_{j}, \delta_{j}; x_{i})]$$
(5.8)

where  $C_0$  is the average background count and  $\alpha$  is a proportionality coefficient for the area ratio of spectrum  $\{y_i\}$  compared to the total spectrum. A least-squares method was used to fit Eq.(5.8). The fitted hyperfine parameters for the samples annealed at various temperatures are plotted in Fig.5.4(A). The square symbols represent the hyperfine parameters of Sm<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub> with poor C absorptions. The circle symbols represent the hyperfine parameters of Sm<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> with a rich C absorption. The relative areas for the C-rich and C-poor phases are calculated based on the fitted parameters  $\alpha$ ,  $A_0$  and  $\Gamma$ . The volume percentages for the two phases are found from (5.1). The results are listed in Table 5.2.



Figure 5.4: Hyperfine parameters (A) and lattice parameters (B) for  $Sm_2Fe_{15}Si_2$ after heating at various temperatures,  $T_a$ , in CH<sub>4</sub> for 2 h. The circles are for the C-rich phase and the squares are for the C-poor phase.

X-ray diffraction patterns (a) and (e) (Fig.5.3) are for  $\text{Sm}_2\text{Fe}_{15}\text{Si}_2$  and  $\text{Sm}_2\text{Fe}_{15}\text{Si}_2\text{C}_y$ , respectively. The patterns (b) and (c) can be considered to be an overlap of the two patterns. One corresponds to  $\text{Sm}_2\text{Fe}_{15}\text{Si}_2$ , the other to  $\text{Sm}_2\text{Fe}_{15}\text{Si}_2\text{C}_y$ . The intensity ratio of the two patterns is listed in Table 5.2. Because, for  $\text{Sm}_2\text{Fe}_{15}\text{Si}_2$ and  $\text{Sm}_2\text{Fe}_{15}\text{Si}_2\text{C}_y$ , the differences of the Bragg angle,  $\theta$ , and the structure factor,  $F_{hkl}$ , are small enough to be neglected and the multiplicity factor,  $m_{hkl}$ , is the same, the values of R in (5.4) can be considered to be the same. Consequently, the relative volumes of  $\text{Sm}_2\text{Fe}_{15}\text{Si}_2$  and  $\text{Sm}_2\text{Fe}_{15}\text{Si}_2\text{C}_y$  can be simplified as

$$\frac{\upsilon_1}{\upsilon_2} = \frac{V_1^2 \cdot I_1}{V_2^2 \cdot I_2} \tag{5.9}$$

where the subscripts 1 and 2 represent  $Sm_2Fe_{15}Si_2$  and  $Sm_2Fe_{15}Si_2C_y$ , respectively. The calculated percentages for each phase are also listed in Table 5.2. In addition, the lattice parameters were found from the positions of the diffraction lines; the results are shown in Fig.5.4(B).

The average C concentrations,  $\langle y \rangle^{\alpha l}$ , were also found from the relative volumes of Sm<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>2.5</sub> and Sm<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>; they agree with the values obtained by weighing.

In the C absorption process, the continuous variations of the lattice parameters and Mössbauer parameters are not observed. By contrast, for reaction temperatures,  $T_a$ , of 400-600°C, both the Mössbauer spectra and x-ray diffraction show that two phases exist; one is the C-poor phase,  $Sm_2Fe_{15}Si_2$ , and the other is the C-rich phase,  $Sm_2Fe_{15}Si_2C_y$ . In the C absorption process, the lattice parameters, aand c, as well as Mössbauer parameters,  $\delta$ ,  $\epsilon$  and  $H_{hf}$ , are almost the same for the C-rich phase; at the same time, the parameters are very close for the C-poor phase. With increasing reaction temperatures, only the relative amount of the C-poor and C-rich phases changes; the amount of the C-poor decreases and that of the C-rich phase increases, as shown in Fig.5.5. At  $T_a=700$ °C the  $Sm_2Fe_{15}Si_2$  powders have sufficient C absorption to become a homogeneous single phase  $Sm_2Fe_{15}Si_2C_y$ .

Obviously, the present experimental results support the the phase segregation model.



Figure 5.5: The relative volume for the C-poor and C-rich phases with increasing reaction temperature,  $T_a$ . The open symbols are for the C-poor phase and the solid symbols for the C-rich phase; the circles are the values obtained from Mössbauer spectra and the squares from x-ray diffraction.



Figure 5.6: Schematic representations of (A) the  $Th_2Ni_{17}$  structure and (B) the  $Th_2Zn_{17}$  structure.

## 5.3 Crystal structures

 $R_2Fe_{17}$  compounds crystallize in two structures, the rhombohedral  $Th_2Zn_{17}$  structure for the light rare-earth compounds and the hexagonal  $Th_2Ni_{17}$  structure for the heavy rare-earth compounds, as shown in Fig.5.6. Fe atoms occupy the 6c/4f, 9d/6g, 18f/12j and 18h/12k sites and the R atoms the 6c/2d+2b sites for the rhombohedral and hexagonal structures, respectively. Neutron diffraction experiments show that the interstitial atoms occupy the 9e/6h sites for  $R_2Fe_{17}C_y$  and  $R_2Fe_{17}N_y$  (Helmholt and Buschow, 1989; Haiji et al, 1990; Ibberson et al, 1991; )

X-ray diffraction patterns for the carbides  $R_2Fe_{15}Si_2C_y$  and their parents are shown in Fig.5.7. All diffraction lines are indexed. The two crystal structures can be distinguished based on the following criteria. (1) For the hexagonal structure there is a characteristic (203) reflection. (2) For the rhombohedral structure the



Figure 5.7: X-ray diffraction patterns for carbides  $R_2Fe_{15}Si_2C_y$  and their parents with (A) Nd, (B) Sm, (C) Gd and (D) Er. The patterns of (A), (C) and (D) are obtained using Cu  $K_{\alpha}$  radiation and the pattern (B) is obtained using Co  $K_{\alpha}$ radiation. The top and bottom in each figure are for  $R_2Fe_{15}Si_2$  and  $R_2Fe_{15}Si_2C_y$ , respectively.

	Structure	a(Å)	<i>c</i> (Å)	c/a	V (Å <sup>3</sup> )	δV/V (%)
Y <sub>2</sub> Fe <sub>15</sub> Si <sub>2</sub>	hex.	8.417(2)	8.299(3)	1.479(1)	509(1)	
Nd <sub>2</sub> Fe <sub>15</sub> Si <sub>2</sub>	rho.	8.553(4)	12.500(7)	1.461(1)	792(2)	
Nd <sub>2</sub> Fe <sub>15</sub> Si <sub>2</sub> C <sub>y</sub>	rho.	8.782(1)	12.518(2)	1.425(1)	836(1)	5.7
$Sm_2Fe_{15}Si_2$	rho.	8.521(2)	12.478(4)	1.464(1)	785(1)	
$Sm_2Fe_{15}Si_2C_y$	rho.	8.720(4)	12.500(8)	1.433(2)	823(2)	4.8
$\mathrm{Gd}_{2}\mathrm{Fe}_{15}\mathrm{Si}_{2}$	hex.	8.494(3)	8.304(3)	1.466(1)*	778(1)*	
$Gd_2Fe_{15}Si_2C_y$	rho.	8.717(5)	12.489(9)	1.433(2)	822(2)	5.7
$Er_2Fe_{15}Si_2$	hex.	8.436(5)	8.300(6)	1.476(1)*	512(2)	
$\mathrm{Er}_{2}\mathrm{Fe}_{15}\mathrm{Si}_{2}\mathrm{C}_{\mathbf{y}}$	hex.	8.625(6)	8.324(8)	1.448(2)*	536(2)	4.6

Table 5.3: Crystal structure parameters for  $R_2Fe_{15}Si_2$  and  $R_2Fe_{15}Si_2C_y$ . *a* and *c* are the lattice parameters and *V* is the cell volume.

The values with superscript \* are for the rombohedral structure.

crystal-surface indices must meet a condition of -h+k+l=3m where m is an integer. Hence, the compounds  $R_2Fe_{15}Si_2$  have the rhombohedral structure for the light rare-earth compounds and the hexagonal structure for the heavy rare-earth compounds. The carbides  $R_2Fe_{15}Si_2C_y$  retain the same structure as their corresponding parents, except for Gd carbide. Because the (203) diffraction line disappears for Gd<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub>, it follows that it turns into the rhombohedral structure from the hexagonal structure of its parent. Crystal structure transitions have been observed in  $R_2Fe_{17}C_y$  with Tb, Dy, Ho and Y made by alloying (Liu et al, 1991). According to the analysis by Buschow et al (1990), in  $R_2Fe_{17}$  there is a tendency to adopt the rhombohedral or hexagonal structure for compounds with relatively large or small cell volumes, respectively. The introduction of C or N atoms expands the cell volume and leads to a structural transition for some carbides and nitrides.

The crystal structure parameters for  $R_2Fe_{15}Si_2C_y$  and  $R_2Fe_{15}Si_2$  are listed in Table 5.3. The positions of all the diffraction lines for  $R_2Fe_{15}Si_2C_y$  move toward the left as compared to their parents. This implies that the introduction of interstitial C atoms leads to an increase in the lattice parameters, as shown in Fig.5.8. As compared to their parents, for  $R_2Fe_{15}Si_2C_y$  the parameter *a* increases by 2.3-2.7



Figure 5.8: The lattice parameters, a and c, and the cell volumes, V. The circles and the squares are for  $R_2Fe_{15}Si_2C_y$  and  $R_2Fe_{15}Si_2$ , respectively.

%; however, the parameter c only increases by about 0.2-0.8 %. The ratio of c/a, therefore, is less for the carbides  $R_2Fe_{15}Si_2C_y$  than their parents. From Fig.5.6, it is known that the interstitial C atoms are located on the rare-earth plane and have two R atoms and two Fe atoms as their nearest-neighbours. Consequently, the C atoms lead to a significant expansion of the c-plane and has relatively little influence on the c-axis. In addition, the cell volumes expand about 4-6 % after the C atoms are introduced into the lattice.

On the other hand, the lattice parameters, a and c, as well as the cell volumes, V, decrease with increasing atomic numbers of the rare-earth ions for either  $R_2Fe_{15}Si_2C_y$  or  $R_2Fe_{15}Si_2$  because of a decrease in the ion radius.

### 5.4 Curie temperatures

The thermomagnetic scans for  $R_2Fe_{15}Si_2C_y$  and  $R_2Fe_{15}Si_2$  are shown in Fig.5.9(A) and (B), respectively. The Curie temperatures are found to be 623, 630, 650 and 620 K for the carbides with R=Nd, Sm, Gd and Er, respectively, and 496, 530, 571 and 490 K for their corresponding parents (ref. to chapter 4.3.2).

The Curie temperatures for  $R_2Fe_{17}$  are rather low, only 324 K for  $Y_2Fe_{17}$  and 476 K for  $Gd_2Fe_{17}$  (Buschow 1977). When Si replaces Fe in  $R_2Fe_{17}$  compounds, the Curie temperatures are elevated about 100-180°C, as shown in Fig.5.10. Usually, the substitution of nonmagnetic atoms, M, in binary Fe-M alloys (M is a metallic element but excludes the rare-earths, R) will lead to a decrease in the Curie temperatures. This anomaly in the Curie temperatures for R-Fe compounds will be thoroughly discussed in chapter 9.

As compared to  $R_2Fe_{15}Si_2$ , the Curie temperatures for their carbides  $R_2Fe_{15}Si_2C_y$ increase by 80-130°C, as shown in Fig.5.10. The origin of this significant increase in the Curie temperature will be also discussed in chapter 9. In this section, the average exchange integrals between the Fe-Fe and Fe-R pairs are calculated.

At high temperatures it is reasonable to neglect the R-R interaction. Based on the high-temperature approximation of the mean field theory, the Curie temperature can be written as (Buschow, 1991)

$$3k_B T_f = a_{FeFe} + (a_{FeFe}^2 + 4a_{FeR} a_{RFe})^{1/2}$$
(5.10)



Figure 5.9: Thermomagnetic scans at an applied field of 0.5 kOe for (A)  $R_2Fe_{15}Si_2C_y$  and (B)  $R_2Fe_{15}Si_2$ . ( $\bigcirc$  Nd,  $\blacksquare$  Sm,  $\blacktriangle$  Gd and  $\blacktriangledown$  Er)



Figure 5.10: The Curie temperatures,  $T_f$ . The circles, squares and triangles are for  $R_2Fe_{15}Si_2C_y$ ,  $R_2Fe_{15}Si_2$  and  $R_2Fe_{17}$ , respectively, and the solid curves are the calculated values. The values for  $R_2Fe_{17}$  are taken from Buschow et al (1977).

Table 5.4: The average exchange integrals,  $J_{FeFe}$  and  $J_{FeR}$ , of the Fe-Fe and Fe-R pairs

	$R_2Fe_{17}$	$R_2Fe_{15}Si_2$	$R_2Fe_{15}Si_2C_y$
$J_{FeFe}$ (meV)	-1.7(2)	3.1(2)	4.0(3)
$J_{FeR}$ (meV)	1.3(2)	1.0(3)	0.6(2)

where

$$a_{FeFe} = Z_{FeFe} J_{FeFe} S_{Fe} (S_{Fe} + 1)$$

$$(5.11)$$

$$a_{FeR}a_{RFe} = Z_{FeR}Z_{RFe}S_{Fe}(S_{Fe}+1)J_{FeR}G \qquad (5.12)$$

The quantities  $Z_{AB}$  represent the numbers of neighboring B atoms for a given A atom,  $S_{Fe}$  is the spin quantum number of the Fe atoms,  $J_R$  is the angular momentum of the rare-earth ions,  $G=(g_R-1)^2J_R(J_R+1)$  is the de Gennes factor, and  $J_{FeFe}$  and  $J_{FeR}$  are the average exchange integrals for the Fe-Fe and the Fe-R pairs, respectively. For the 2:17-type structure,  $Z_{FeFe}$ ,  $Z_{RFe}$  and  $Z_{FeR}$  are 10.0, 19.0 and 5.4, respectively.

From (5.10)-(5.12) one can easily derive

$$9T_{f}^{2} - 6T_{f}Z_{FeFe}S_{Fe}(S_{Fe}+1)(J_{FeFe}/k_{B}) - 4Z_{RFe}Z_{FeR}S_{Fe}(S_{Fe}+1)G(J_{FeR}/k_{B})^{2} = 0$$
(5.13)

By applying the least-squares method to the above equation the average exchange integrals,  $J_{FeFe}$  and  $J_{FeR}$ , can be obtained from the Curie temperatures. The results for R<sub>2</sub>Fe<sub>17</sub>, R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub> and R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> are listed in Table 5.4.

By substituting these values of  $J_{FeFe}$  and  $J_{FeR}$  into (5.13) the Curie temperatures, as a function of the G factor, can be calculated; they are shown in Fig.5.10 as the solid curves. The calculated values agree very well with the experimental data.

As compared to their parents, the average exchange integral between the Fe-Fe pairs increases by about 30 % but the integral between the Fe-R pairs decreases by about 40 % for  $R_2Fe_{15}Si_2C_y$ . Therefore, for these carbides, the increase in Curie

temperature is attributed to an enhanced exchange interaction between the Fe-Fe pairs.

## 5.5 Magnetic anisotropies

All  $R_2Fe_{15}Si_2$  compounds have an easy c-plane anisotropy and thus they can not be made into permanent magnetic materials. One of the outstanding properties of  $R_2Fe_{15}Si_2C_y$  is an elevated Curie temperature, as described in chapter 5.4. Another is a modified magnetocrystalline-anisotropy.

X-ray diffraction patterns of aligned carbides  $R_2Fe_{15}Si_2C_y$  (R=Nd, Sm, Gd and Er) at room temperature are shown in Fig.5.11. For  $Sm_2Fe_{15}Si_2C_y$ , the intensity of the (006) reflection dramatically increases, whereas the intensities of the other reflections almost disappear. This means the emergence of an easy c-axis anisotropy. By contrast, the increased intensities of the (220) and the (300) reflections and the almost complete absence of other reflections show that an easy c-plane anisotropy is present in  $R_2Fe_{15}Si_2C_y$  with R=Nd, Gd and Er.

Mössbauer spectroscopy is also an important technique to determine the anisotropy type of samples. The Mössbauer spectra and their fitted curves for aligned  $R_2Fe_{15}Si_2C_y$ (R=Nd, Sm Gd and Er) are shown in Fig.5.12. In fitting these Mössbauer spectra, all isomer shifts, quadrupole splittings, hyperfine fields, linewidths and the area ratios of the subspectra were constrained to be the same as those for the non-aligned samples. However, the ratio of the six absorption lines in each sextet was assumed to be 3:b:1:1:b:3, where b is a fitted parameter instead of b=2 for the non-aligned samples. For a fully aligned sample the intensity ratio, b, between the 2nd plus 5th lines and the 3rd plus 4th lines should be equal to 4/3 if the sample has an easy c-plane anisotropy and b=0 if the sample has an easy c-axis anisotropy (see chapter 8.1).

The fitted values of b are 1.42, 1.35 and 1.40 for  $R_2Fe_{15}Si_2C_y$  with R=Nd, Gd and Er, respectively. This shows that the three carbides have an easy cplane anisotropy at room temperature. On the other hand, b=0.3 shows that  $Sm_2Fe_{15}Si_2C_y$  has an easy c-axis anisotropy. These conclusions are consistent with results obtained from x-ray diffraction.



Figure 5.11: X-ray diffraction patterns of aligned  $R_2Fe_{15}Si_2C_y$ . The pattern for  $Sm_2Fe_{15}Si_2C_y$  is obtained using Co  $K_{\alpha}$  radiation; the patterns for Nd, Gd and Er carbides are obtained using Cu  $K_{\alpha}$  radiation.



Figure 5.12: Mössbauer spectra of aligned  $R_2Fe_{15}Si_2C_y$ . The arrows point the 2nd and 5th spectral lines.

Table 5.5: Saturation magnetizations for  $R_2Fe_{15}Si_2$  and  $R_2Fe_{15}Si_2C_y$ .  $\sigma$  is the specific magnetization,  $M_s$  is the magnetization,  $H_{hf}$  is the hyperfine field, and  $\mu_{Fe}$  and  $\mu_R$  are the magnetic moments of Fe and R, respectively.

			R <sub>2</sub>	Fe <sub>15</sub> Si2				
	Nd		S	m	Gd		Er	
	77K	300K	77K	300K	77K	300K	77K	300K
$\sigma(\text{emu/g})$	146(2)	120(2)	132(2)	112(2)	71(1)	65(1)	78(2)	80(2)
$M_s(\mu_B/{ m f.u.})$	30.9(3)	25.4(4)	28.3(4)	24.0(4)	15.3(3)	14.0(2)	17.2(4)	17.6(4)
$H_{hf}(\mathrm{kOe})$		216(3)		223(3)		238(3)		210(3)
$\mu_{Fe}(\mu_B)$		1.44		1.49		1.59		1.40
$\mu_R(\mu_B)$		1.9		0.8		-4.9		-1.7

 $R_2Fe_{15}Si2C_y$ 

	Nd		S	m	(	ld	Er	
	77K	300K	77K	300K	77K	300K	77K	300K
$\sigma(\text{emu/g})$	119(2)	104(2)	90(3)	87(2)	59(2)	62(2)	55.5(1)	71(1)
$M_s(\mu_B/{ m f.u.})$	25.5(3)	22.2(3)	19.6(6)	18.8(4)	12.9(4)	13.5(4)	12.3(2)	15.8(2)
$H_{hf}(\mathrm{kOe})$	227(3)	201(3)	232(3)	212(3)	223(3)	198(3)	229(3)	197(3)
$\mu_{Fe}(\mu_B)$	1.51	1.34	1.55	1.41	1.49	1.32	1.53	1.31
$\mu_R(\mu_B)$	1.4	1.1	-1.9	-1.2	-4.8	-3.2	-5.3	-2.0

The values of the anisotropy field for Sm carbide will be given in section 6.4.

## 5.6 Magnetizations and hyperfine fields

The saturation magnetizations at 300 K and 77 K for  $R_2Fe_{15}Si_2C_y$  (R=Nd, Sm, Gd and Er) and their parents have been measured (ref. to Chapter 4.3.2); the results are listed in Table 5.5. Some features of  $R_2Fe_{15}Si_2C_y$  are significantly different from the nitrides.

First, the saturation magnetizations,  $M_s$ , at room temperature are 22.2, 18.8, 13.5 and 15.8  $\mu_B/f.u.$  for  $R_2Fe_{15}Si_2C_y$  where R represents Nd, Sm, Gd and Er, respectively. These values are smaller than the 25.4, 24.0, 14.0 and 17.6  $\mu_B/f.u.$ for their corresponding parents. Further, based on a proportionality coefficient, 150 kOe/ $\mu_B$ , between the hyperfine field and the Fe moment, the Fe magnetic moments,  $\mu_{Fe}$ , at room temperature are found to be 1.3-1.4  $\mu_B$  for R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> and 1.4-1.6  $\mu_B$  for R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>. This feature is significantly different from that for R<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub> (Coey and Sun, 1990) and R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>N<sub>y</sub> (Yang F M et al, 1992; Valeanu et al, 1994), for which the saturation magnetization is larger by about 4-12 % than that for their parents. This problem will be further discussed in section 7.3.3.

Second, the saturation magnetizations are almost the same for  $Sm_2Fe_{15}Si_2$  and  $Nd_2Fe_{15}Si_2$ . However, the magnetization is much smaller for  $Sm_2Fe_{15}Si_2C_y$  than for  $Nd_2Fe_{15}Si_2C_y$  at either T=300 K or T=77 K. Further, for a collinear coupling between the Fe and R moments, the R moments,  $\mu_R$  can be derived from  $M_s$  and  $\mu_{Fe}$  by

$$M_s = 15\mu_{Fe} + 2\mu_R \tag{5.14}$$

and the results are listed in Table 5.5. The magnetic moments of the R ions are positive for  $Nd_2Fe_{15}Si_2C_y$  and its parent, and negative for  $Gd_2Fe_{15}Si_2C_y$  and  $Er_2Fe_{15}Si_2C_y$  as well as for their parents. This implies a ferromagnetic coupling between the Fe and Nd moments and a ferrimagnetic coupling between the Fe and Gd or Er moments. However, it is surprising that the Sm moment is negative for  $Sm_2Fe_{15}Si_2C_y$ . The antiparallel coupling between the Fe and Sm moments leads to a low saturation magnetization for  $Sm_2Fe_{15}Si_2C_y$ . This problem will be further discussed in chapter 6.4.

## 5.7 Temperature dependence of magnetizations

The temperature dependence of the magnetization can provide some important information on spin-reorientation, magnetic coupling and exchange interactions. The magnetizations at various temperatures for  $R_2Fe_{15}Si_2C_y$  (R=Nd, Sm, Gd and Er) are shown in Fig.5.13.

The curve of  $M_s - T$  for Nd<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> has a typical ferromagnetic coupling character; the temperature derivative of the magnetizations,  $dM_s/dT$ , is negative in whole temperature range. The curves of  $M_s - T$  for Er<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> and Gd<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> have a P-type ferrimagnetic coupling character because  $dM_s/dT>0$ at low temperatures and  $dM_s/dT<0$  at high temperatures.



Figure 5.13: The temperature dependence of the magnetization of  $R_2Fe_{15}Si_2C_y$  (R=Nd, Sm, Gd and Er).

According to the two sublattice model, the molecular fields,  $H_{Fe}$  and  $H_R$ , acting on the Fe and R sublattices respectively is expressed as

$$H_{Fe}(T) = H_0 + d[15n_{FeFe}\mu_{Fe}(T) + 2n_{FeR}\mu_R(T)]$$
(5.15)

$$H_R(T) = H_0 + d[2n_{RR}\mu_R(T) + 15n_{FeR}\mu_{Fe}(T)]$$
(5.16)

where  $H_0$  is the applied field,  $\mu_{Fe}(T)$  and  $\mu_R(T)$  represent the magnetic moment of Fe and R atoms, respectively, at the temperature T.  $d=N_A\mu_B\rho/m$  converts the moment per R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> in  $\mu_B$  to Gauss, where  $N_A$  is the Avogadro's number,  $\rho$  is the density and m is the formula mass.  $n_{FeFe}$ ,  $n_{FeR}$  and  $n_{RR}$  represent the molecular field coefficients that describe the Fe-Fe, Fe-R and R-R magnetic interactions, respectively.

The temperature dependences of the sublattice magnetizations are governed by Brillouin functions

$$\mu_{Fe}(T) = \mu_{Fe}(0) \mathcal{B}_{S}(\frac{\mu_{Fe}(0) \mu_{B} H_{Fe}(T)}{k_{B}T})$$
(5.17)

$$\mu_R(T) = \mu_R(0) \mathcal{B}_{J_R}(\frac{\mu_{Fe}(0) \mu_B H_{Fe}(T)}{k_B T})$$
 (5.18)

where  $\mu_{Fe}(0)$  and  $\mu_R(0)$  are the magnetic moments of Fe and R atoms at T=0K. In the case of a collinear coupling between the Fe and R moments, the total magnetization is given by

$$M_s(T) = 15\mu_{Fe}(T) \pm 2\mu_R(T)$$
(5.19)

where the sign  $\pm$  is for ferro- and ferri-magnetic coupling, respectively.

Usually, the coefficients  $n_{AB}$  are determined by numerically solving Eqs.(5.15)-(5.18), under the condition that the magnetizations,  $M_s$ , calculated by (5.19) best correspond with the experimental magnetizations (Fuerst et al, 1986; Li H S et al, 1988; Xu and Shaheen, 1994).

In my present work, some improvements are made. First, the temperature dependence of the Fe moments are found based on the hyperfine fields at various temperatures obtained from Mössbauer spectra and a conversion coefficient, 150 kOe/ $\mu_{Fe}$ , between the hyperfine field and Fe moment. Then, the temperature dependence of the R moments is calculated from (5.19). Finally, the coefficients  $n_{AB}$  are determined by a least-square fitting to experimental data of the Fe and R
Table 5.6: The exchange interaction constants of Fe-Fe, Fe-R and R-R for  $R_2Fe_{15}Si_2C_y$ .

R	$\rho$ (g/cm <sup>3</sup> )	gj	J <sub>R</sub>	$\frac{n_{FeFe}}{(10^3)}$	$\frac{n_{FeR}}{(10^3)}$	$\frac{n_{RR}}{(10^3)}$	J <sub>FeEe</sub> (meV)	J <sub>FeR</sub> (meV)	J <sub>RR</sub> (meV)
Nd	7.12	8/11	9/2	11.8(7)	4.1(25)	2.8(33)	6.9(4)	-2.3(14)	1.0(11)
Gd	7.40	2	7/2	13.3(11)	-3.8(32)	4.7(17)	7.8(6)	-1.6(14)	0.9(3)
Er	7.65	6	15/2	12.6(6)	-0.99(75)	0.42(52)	7.6(4)	-1.3(10)	0.8(9)

moments based on (5.17) and (5.18). In this method, instead of one experimental curve of  $M_s$ -T, two curves,  $\mu_{Fe}$ -T and  $\mu_R$ -T, are fitted to find the molecular-field coefficients. Consequently, the values obtained should be more accurate and reliable.

The fitted sublattice magnetizations,  $M_{Fe}=15\mu_{Fe}$  and  $M_R=2\mu_R$ , as well as the total magnetization,  $M_s$ , are shown as solid curves in Fig.5.14 (A)-(C) for Nd<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub>, Gd<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> and Er<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub>. The fitted molecular-field coefficients,  $n_{FeFe}$ ,  $n_{FeR}$  and  $n_{RR}$ , are listed in Table 5.6. For a comparison with the results obtained from the Curie temperature, the coefficients are converted into exchange integrals by

$$J_{FeFe} = \frac{15d\mu_B}{2Z_{FeFe}}g_{Fe}^2 n_{FeFe}$$
(5.20)

$$J_{FeR} = J_{RFe} = \sqrt{\frac{2 \cdot 15}{Z_{RFe} Z_{FeR}}} d\mu_B g_{Fe} (\frac{g_R}{g_R - 1}) n_{FeR}$$
(5.21)

$$J_{RR} = \frac{d\mu_B}{Z_{RR}} (\frac{g_R}{g_R - 1})^2 n_{RR}$$
 (5.22)

where  $Z_{AB}$  represents the number of neighboring B atoms for a given A atom;  $Z_{FeFe}=10$ ,  $Z_{FeR}=5.4$ ,  $Z_{RFe}=19$  and  $Z_{RR}=4$ . With (5.20)-(5.22) the  $n_{FeFe}$  and  $n_{FeR}$ calculated by the two lattice model lead to  $J_{FeFe} \sim 6.9$ —7.8 meV,  $J_{FeR}=-1.6$ —-2.3 meV and  $J_{RR}=0.8$ —1.0 meV. The negativity of  $J_{FeR}$  is expected because of the antiparallel coupling of the Fe and R spins in either light rare-earth compounds or heavy rare-earth compounds.





## 5.8 Conclusions

(1) Si is able to elevate the gas-phase reaction temperature to 700°C and to stabilize the 2:17-type structure of the carbides  $R_2Fe_{17-x}Si_xC_y$  provided the Si concentration is  $x \ge 1$ . At the same time, these carbides  $R_2Fe_{15}Si_2C_y$  have a high C concentration ( $y \ge 2.5$ ).

(2) In the C absorption process at 400-600°C, there exist two phases; one is a C-poor phase and the other a C-rich phase. With increasing reaction temperature, the amount of the C-poor phase decreases and the amount of the C-rich phase increases. The single phase  $R_2Fe_{15}Si_2C_y$  with a saturation C concentration can be formed at the reaction temperature of 600-700°C.

(3) The carbides  $R_2Fe_{15}Si_2C_y$  with R=Nd, Sm and Er retain the same crystal structures as their corresponding parents. However,  $Gd_2Fe_{15}Si_2C_y$  turns into the rhombohedral structure from the hexagonal structure of its parent. As compared to their parents, for  $R_2Fe_{15}Si_2C_y$ , the parameter *a* increases by 2.3-2.7 %, the parameter *c* increases by only 0.2-0.8 % and the cell volume expands about 4-6 %.

(4) The Curie temperatures of  $R_2Fe_{15}Si_2C_y$  are 620-650 K. They increase by 80-130°C as compared to their parents. Based on the Curie temperature and the curves of  $M_s$ -T, the average exchange integrals in magnitude are calculated to be about 4-8 meV and 0.6-2.3 meV for the Fe-Fe and Fe-R pairs, respectively.

(5) The carbides  $R_2Fe_{15}Si_2C_y$  with R=Nd, Gd and Er have an easy c-plane anisotropy at room temperature, the same as their parents. However, the introduction of C atoms leads to a uniaxial anisotropy for  $Sm_2Fe_{15}Si_2C_y$ .

(6) The saturation magnetization for the light rare-earth carbides  $R_2Fe_{15}Si_2C_y$ is less than that for their parents. This feature is significantly different from nitrides, for which the magnetization is larger than for their parent. This is a major drawback for  $R_2Fe_{15}Si_2C_y$ 

## **Chapter 5 Appendix**

The ratio of the relative volume,  $v_{\alpha-Fe}/v_{2:17}$ , between the  $\alpha$ -Fe phase and carbide can also be found from the relative integral intensity,  $I_{\alpha-Fe}$  and  $I_{2:17}$ , of the

			A				
			Sm <sub>2</sub> F	e <sub>17</sub> Cy			α-Fe
hkl	113	300	024	220	303	006	110
2 <i>0</i>	37.6	45.3	47.5	52.9	53.5	55.4	57.0
$\sin  heta / \lambda$	0.166	0.197	0.208	0.230	0.232	0.240	0.246
<i>f</i> <sub>Fe</sub>	<b>19.8</b>	19.0	18.6	17.8	17.8	17.5	17.3
fsi	10.7	10.0	9.8	9.5	9.5	9.3	
f <sub>R</sub>	45.4	44.3	43.3	42.1	<b>41.9</b>	41.4	
fc	4.1	3.5	3.4	3.2	3.1	3.1	
F <sub>hkl</sub> (Fe,Si)	-8.1	205.	<b>-24</b> 1.	<b>453</b> .	788.	652.	34.6
$F_{hkl}(\mathbf{R})$	273.	266.	-185.	253.	246.	265.	
$F_{hkl}(C)$	-12.3	-10.8	30.6	28.8	-9.3	27.9	
F(total)	252.	460.	-396.	734.	1251.	<b>946</b> .	34.6
m <sub>hkl</sub>	12	6	6	6	6	2	12
LP	4.14	2.74	2.45	1.92	1.87	1.73	1.62
R (10 <sup>4</sup> )	<b>319</b>	348	230	622	880	309	2.327
			(B)				
			Sm <sub>2</sub> F	e17Cv		<u>α</u> -	Fe
	x=	=0 x=	0.5 x=	=1 x:	=2 x=	=3	
R(10 <sup>4</sup> )	27	07 26	83 26	79 25	62 24	87 2.3	327
V (Å <sup>3</sup>	)	83	3 83	29 8	<b>23 8</b> 3	11 23	8.6
Ia-Fe/I2	::17	0.5	06 0.1	00 0.0	07 <b>2</b> 0.0	)68	
$v_{\alpha-Fe}/v_{2}$	2:17	0.4	68 0.0	94 0.0	) <b>66</b> 0.0	061	

Table 5.7: (A) The values of R for  $\operatorname{Sm}_2\operatorname{Fe}_{17}\operatorname{C}_y$  and (B) the ratio of the relative volume,  $\upsilon_{\alpha-Fe}/\upsilon_{2:17}$ , between the  $\alpha$ -Fe phase and carbide for  $\operatorname{Sm}_2\operatorname{Fe}_{17-x}\operatorname{Si}_x\operatorname{C}_y$ .

x-ray diffraction lines by

$$\frac{\upsilon_{\alpha-Fe}}{\upsilon_{2:17}} = \frac{I_{\alpha-Fe} \cdot V_{\alpha-Fe}^2 \cdot R_{2:17}}{I_{2:17} \cdot V_{2:17}^2 \cdot R_{\alpha-Fe}}$$
(5.23)

and

$$R_i = \frac{1 + \cos^2 2\theta_i}{\sin^2 \theta_i \cos \theta_i} \cdot m_{hkl}^i |F_{hkl}^i|^2 \exp(-2M_i(\theta_i))$$
(5.24)

where  $\theta$  is the Bragg angle,  $m_{hkl}$  is the multiplicity factor and  $F_{hkl}$  is the structure factor. The detailed process is given by Table 5.7 (A) and (B).  $f_i$  is the atomic scattering factor of the atom *i*. The temperature factor  $\exp(-M(\theta))$  is neglected.

## Chapter 6

# Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>C<sub>y</sub> Carbides — structures and magnetic properties

The carbides  $R_2Fe_{15}Si_2C_y$  have greatly elevated Curie temperatures as compared to their parents. However, only Sm carbides may be made into a useful permanent magnet because they have a uniaxial anisotropy. In this section, the intrinsic magnetic properties of  $Sm_2Fe_{17-x}Si_xC_y$  are reported.

## 6.1 Crystal structures

X-ray diffraction (Fig.5.1)(B) shows that all of the carbides  $Sm_2Fe_{17-x}Si_xC_y$  (x=1, 2 and 3) retain the  $Th_2Zn_{17}$  structure, the same as their parents  $Sm_2Fe_{17-x}Si_x$ . The crystal structure parameters are listed in Table 6.1.

The lattice parameters, a and c, of the carbides  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  as well as their cell volumes decrease with increasing Si concentration, as shown in Fig.6.1, because (1) the radius of Si atoms is smaller than that of Fe atoms and (2) the C concentration decreases with Si substitution. On the other hand, the lattice parameters increase and the cell volumes expand about 5 %, as compared to their corresponding parents.

For  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x$ , the decrease in the lattice parameter *a* with Si substitution is attributed to the smaller radius of Si atoms. However, the parameter *c* is almost the same in experimental error for the compounds with  $x \leq 2$  and decreases for x=3. It is known that the 18f site is located on the c-plane and the 6c site

	a (Å)	c (Å)	c/a	V (Å <sup>3</sup> )	$\Delta V/V$ (%)
$Sm_2Fe_{17}$	8.566(4)	12.456(8)	1.454	792	
Sm <sub>2</sub> Fe <sub>16</sub> Si	8.536(4)	12.476(7)	1.462	787	
$Sm_2Fe_{16}SiC_{2.7}$	8.736(4)	12.543(8)	1.436	829	5.3
Sm <sub>2</sub> Fe <sub>15</sub> Si <sub>2</sub>	8.521(5)	12.478(10)	1.464	785	
$\mathrm{Sm}_{2}\mathrm{Fe}_{15}\mathrm{Si}_{2}\mathrm{C}_{2.5}$	8.720(4)	12.500(8)	1.433	823	4.6
Sm <sub>2</sub> Fe <sub>14</sub> Si <sub>3</sub>	8.500(8)	12.421(15)	1.461	777	
Sm <sub>2</sub> Fe <sub>14</sub> Si <sub>3</sub> C <sub>2.3</sub>	8.685(3)	12.421(6)	1.430	811	4.4

Table 6.1: Crystal structure parameters for  $Sm_2Fe_{17-x}Si_xC_y$  and their parents. *a* and *c* are the lattice parameters and *V* is the cell volume.

is along the c-axis (see Figure 5.6). The preferential occupation of Si atoms on the 18f site and a small occupancy on the 6c site for  $x \le 2$  (chapter 7.2.4) lead to a contraction in the c-plane and have little influence on the c-axis. On the other hand, for x=3, the rapid increase in the occupancies of Si atoms on the 6c site leads to an decrease in the lattice c.

### 6.2 Curie temperatures

The intrinsic magnetic properties for  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_2\text{C}_y$  and their parents are listed in Table 6.2. The Curie temperatures,  $T_f$ , the specific magnetizations,  $\sigma_s$ , and the anisotropy fields,  $H_a$ , with various Si concentrations are shown in Fig.6.2 (A), (B) and (C), respectively.

The Curie temperature for  $Sm_2Fe_{17}$  is rather low (only 410 K). With Si substitution, the Curie temperatures are elevated to a maximum of 530 K at x=2; there is a slight decrease at x=3, as shown in Fig.6.2(A).

On the other hand, the Curie temperatures for  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  with x=1, 2 and 3 are 660, 630 and 595 K, respectively. As compared to the parents, they are raised by 170, 100 and 70°C, respectively, as shown in Fig.6.2(A). The Curie temperatures,  $T_f$ , as function of the cell volume V, are plotted in Fig.6.3 and lie on a straight line. The linear relationship between  $T_f$  and V has also been discovered



Figure 6.1: Lattice parameters and cell volumes for  $Sm_2Fe_{17-x}Si_xC_y$  (circles) and their parents (squares).



Figure 6.2: (A) Curie temperatures,  $T_f$ , (B) specific magnetizations,  $\sigma_s$  and (C) anisotropy fields,  $H_a$ , for carbides  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  (circles) and their parents (squares). The solid and open symbols are for T=300 K and 77 K, respectively.

Table 6.2: Magnetic properties of  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  and their parents.  $T_f$  is the Curie temperature,  $\sigma_s$  the specific magnetization,  $M_s$  the saturation magnetization in  $\mu_B/\text{fu}$ ,  $H_{hf}$  the hyperfine field and  $H_a$  the anisotropy field.

	$\overline{T_f(\mathbf{K})}$	$\sigma_s$ (er	nu/g)	M, (µ	4 <sub>B</sub> /fu)	Hhf	(kOe)	Ha	(kOe)
	-	77K	300K	77K	300K	77K	300K	77K	300K
$Sm_2Fe_{16}Si_1C_{2.7}$	660(5)	101(2)	92(2)	22.1(4)	20.7(5)		234(3)	140	95
$Sm_2Fe_{16}Si_1$	690(5)		116(2)		25.3(4)		224(3)		
$\mathrm{Sm}_{2}\mathrm{Fe}_{15}\mathrm{Si}_{2}\mathrm{C}_{2.5}$	630(5)	90(3)	87(2)	19.5(7)	18.8(4)	232(3)	212(3)	110	85
$Sm_2Fe_{15}Si_2$	530(5)		112(2)		24.0(4)		222(3)		
$Sm_2Fe_{14}Si_3C_{2.3}$	595(5)	86(2)	83(2)	18.1(4)	17.7(4)		196(3)	90	75
$Sm_2Fe_{14}Si_3$	525(5)		109(2)		22.8(4)		213(3)		

in the series  $Y_2Fe_{17}C_y$  and  $Gd_2Fe_{17}C_y$  with various C concentrations (Liu J P et al, 1991).

## 6.3 Magnetic anisotropy

Both x-ray diffractograms and Mössbauer spectra of the aligned samples show that all the carbides  $Sm_2Fe_{17-x}Si_xC_y$  (x=1, 2 and 3) have an easy c-axis anisotropy. As an example, the x-ray diffraction pattern and Mössbauer spectrum for aligned  $Sm_2Fe_{16}SiC_y$  are shown in Fig.6.4(A) and (B), respectively.

The diffraction intensity of the  $(0\ 0\ 6)$  reflection dramatically increases, whereas the intensities of other reflections almost disappear, as shown in Fig.6.4(A). This establishes the emergence of an easy c-axis anisotropy. The area ratio, b, between the 2nd plus 5th lines and the 3rd plus 4th lines of the Mössbauer spectrum is close to zero, which implies an easy c-axis anisotropy.

In order to determine the magnitude of the anisotropy field, magnetization curves with the field applied parallel and perpendicular to the alignment direction were obtained, as shown in Fig.6.5 for  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$ . The anisotropy fields,  $H_a$ , are estimated by extrapolating from the maximum applied field of 18 kOe. The



Figure 6.3: The dependence of the Curie temperatures on the cell volumes for  $Sm_2Fe_{17-x}Si_xC_y$ .

anisotropy fields decrease with Si substitutions either at room temperature or at T=77 K, as shown in Fig.6.2 (C). For  $\text{Sm}_2\text{Fe}_{16}\text{Si}_1\text{C}_{2.7}$  the values of  $H_a$  are 95 kOe at T=300 K and 140 kOe at T=77 K. Of course, these values estimated from the extrapolation may not be very accurate, since the applied fields are so small as compared to the anisotropy fields. However, we believe that the value of  $H_a$  at room temperature for  $\text{Sm}_2\text{Fe}_{16}\text{SiC}_y$  is larger than the 73 kOe for  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and 80 kOe for  $\text{Nd}_2\text{Fe}_{11}\text{N}_y$ , but less than the 140-230 kOe values for  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ .

## 6.4 Magnetizations

The saturation magnetizations,  $M_s$ , of Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>C<sub>y</sub> decrease with Si substitution as shown in Fig.6.6(A). At T=77 K, the magnetizations are 22.1, 19.5 and 18.1  $\mu_B/f.u.$  for x=1, 2 and 3 respectively; at T=300 K, the magnetizations are 20.7, 18.8 and 17.7  $\mu_B/f.u.$ . As compared to their parents, the saturation magnetizations at room temperature decrease by 20 %.







Figure 6.5: Magnetization curves of aligned  $Sm_2Fe_{17-x}Si_xC_y$  parallel and perpendicular to the aligned direction. The solid and open circles are for the temperatures of 77 K and 300 K, respectively.



Figure 6.6: (A) saturation magnetizations,  $M_s$ , (B) hyperfine fields,  $H_{hf}$ , as well as Fe moments,  $\mu_{Fe}$ , and (C) Sm moments,  $\mu_R$ , for Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>C<sub>y</sub> (circles) and Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub> (squares).

The hyperfine fields at room temperature decrease with Si substitutions for  $Sm_2Fe_{17-x}Si_xC_y$ ; however, they can be considered to be almost constant for  $Sm_2Fe_{17-x}Si_x$ , as shown in Fig.6.6(B). The conversion coefficient,  $\beta_F=150\pm 6 \text{ kOe}/\mu_B$ , between the Fe moment and hyperfine field has been obtained from the magnetization measurement and Mössbauer spectra for  $Y_2Fe_{17}$ ,  $Y_2Fe_{17}H_y$ ,  $Y_2Fe_{17}N_y$  and  $Y_2Fe_{17}C_y$  (Qi et al, 1992). Based on the conversion coefficient of 150 kOe/ $\mu_B$  the Fe moments are found to be a constant equal to 1.50(4)  $\mu_B$  for  $Sm_2Fe_{17-x}Si_x$ . However, for  $Sm_2Fe_{17-x}Si_xC_y$ , the Fe moments decrease with Si substitution, from 1.57  $\mu_B$  for x=1 to 1.31  $\mu_B$  for x=3, as shown in Fig.6.6(B).

Further, in the case of a collinear coupling between the Fe and Sm moments, the R moments,  $\mu_{Sm}$  can be derived from  $M_s$  and  $\mu_{Fe}$  by

$$M_s = 15\mu_{Fe} + 2\mu_{Sm} \tag{6.1}$$

The results are listed in Fig.6.6(C). It is very surprising that the Sm moments are negative for all the  $Sm_2Fe_{17-x}Si_xC_y$  carbides.

The temperature dependences of the total magnetizations,  $M_s(T)$ , the magnetization of the Fe sublattice,  $M_{Fe}(T)=15\mu_{Fe}(T)$ , and the magnetization of the Sm sublattice,  $M_{Sm}(T)=2\mu_{Sm}(T)$ , for Sm<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> are shown in Fig.6.7(A). The values of  $\mu_{Fe}(T)$  are found from the hyperfine fields at various temperature,  $H_{hf}(T)$ , and the conversion coefficient,  $\beta_F=150$  kOe/ $\mu_B$ . The values of  $\mu_{Sm}(T)$  are obtained from (6.1). Fig.6.7(A) suggests an antiparallel coupling between the Fe and Sm moments.

In addition, many researchers have observed that the saturation magnetization of the Nd carbides is larger than that of the Y carbides; however, the saturation magnetization of the Sm carbides is smaller than that of the Y carbides for the 2:17type and 1:12-type carbides, as shown in Table 6.3. These imply an antiparallel coupling between the Fe and Sm moments.

Theoretically, the antiparallel structure between the Fe and Sm moments has been predicted. Usually, there is a rule for R-M (M represents a transition element) compounds, viz the magnetic moments of R and M are parallel for the light rareearth compounds and antiparallel for the heavy rare-earth compounds. This rule is based on two facts: (1) an antiferromagnetic coupling between the spins of R and M, and (2) an antiparallel and parallel arrangement between the spin and



Figure 6.7: The temperature dependence of the magnetizations for Sm<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub>. () represent the total magnetizations,  $\Box$  the Fe sublattice magnetizations, and  $\Delta$  the R sublattice magnetizations. (A)  $\beta_F$ =150 kOe/ $\mu_B$  and (B)  $\beta_F$ =180 kOe/ $\mu_B$ 

Table 6.3: Saturation magnetizations in  $\mu_B/\text{fu}$  at T=4.2 K for the carbides. The values in brackets are at room temperature and the values with the superscript \* are at T=77 K.

	Y	Nd	Sm	Ref.
R <sub>2</sub> Fe <sub>17</sub> C <sub>y</sub>	35.8	35.1	34.5	Sun et al, 1992
$R_2Fe_{17}C_y$	34.1(28.9)		30.1(26.6)	Hu and Liu, 1991
$R_2Fe_{17}C_y$	32.5(27.9)	31.8(29.0)	29.2(26.2)	Tang et al, 1992
$R_2Fe_{17}C_1$	35.5	40.6	34.0	Zhong et al, 1990
RTiFe <sub>11</sub> C <sub>y</sub>	20.5(15.5)	20.7(20.2)	18.0(13.0)	Hurley and Coey, 1992
$R_2Fe_{15}Si_2C_y$		24.8*(22.2)	19.6*(18.8)	in present work
$R_2Fe_{15}Ga_2C_y$	27.8	-	26.5	Shen et al, 1993
$R_2Fe_{14}Ga_3C_y$	24.6	27.5	23.4	Shen et al, 1993

orbital angular momenta for the light and heavy R compounds, respectively. One exception for light R is the Sm-M compounds, where the magnetic moment of the Sm<sup>3+</sup> ion,  $\mu_{Sm} = -\mu_B < L_Z + 2S_Z >$ , may be lower than the free-ion value of 0.85  $\mu_B$  (see Table 1.2) and sometimes appears to be negative. The origin of such a behavior for cubic Laves-phase compounds has been discussed by Buschow et al (1973) and attributed to the mixture of the excited J multiplets to the ground state and the crystalline electric field (CEF) potential at the  $Sm^{3+}$  sites. Malik et al (1976) have shown that, in the case of a hexagonal CEF,  $\mu_{Sm}$  takes either a positive or an negative value depending on the combination of the crystal-field coefficients  $A_{n0}$  and temperature. A calculation for Sm<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub> has shown that there exists a crossover temperature, above which the Sm moment becomes negative (Zhao et al, 1991). Yamada et al (1995) have also shown that when the second order crystal-field coefficient  $A_{20}$  is negative, with increasing  $A_{40}$ , the magnetic moment of Sm initially increases and then suddenly becomes negative, i.e. antiparallel to the Fe moments. The results calculated by Malik et al and Yamada et al are shown in Fig.6.8 (A) and (B).

By fitting the experimental anisotropy fields on the basis of the two-lattice model, the values of the crystal field parameters,  $A_{n0}$  can be deduced. The calculations not only include the exchange and crystal field interaction, but also involve the ground, the first and the second states. For Sm<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub>, the value of  $A_{20}$  has been found to be in a range between -300 and -600 Ka<sub>0</sub><sup>6</sup> (Li H S and Cadogan, 1991; Zhao et al, 1991; Kato et al, 1993) and the value of  $A_{40}$  to be +200 Ka<sub>0</sub><sup>4</sup> (Zhao et al, 1991). As predicted by Milik et al and Yamada et al, for Sm<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub>, the crystal-field coefficient  $A_{20}$  is negative and  $A_{40}$  is positive; the magnitudes of  $A_{20}$  and  $A_{40}$  are 10<sup>2</sup>-10<sup>3</sup> Ka<sub>0</sub><sup>2</sup>. If the crystal-field coefficients for Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>C<sub>y</sub> are similar to those for Sm<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub>, the antiparallel coupling between the Fe and Sm moments is a strong possibility for Sm<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub>.

Some other possibilities were also considered as follows,

(a) The magnetization of the Fe sublattice can not be expressed as  $15\mu_{Fe}$  because there is an antiparallel arrangement for some Fe sites. However, this hypothesis is not supported by experiments. Both Mössbauer spectra with an appled field for Y<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub> (Anagnostou et al, 1994) and neutron diffraction for Nd<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub> show the parallel arrangement for all Fe sites.

(b) An incorrect conversion coefficient leads to a large Fe moment for the Sm carbides. In order to obtain a positive value for the Sm moment, it has to be assumed that the coefficient is larger than 180 kOe/ $\mu_B$ . However, if  $\beta_F$ =180 kOe/ $\mu_B$  is used, many incorrect results are obtained. (1) The value of  $\beta_F$  significantly deviates from the experimental result, 150 kOe/ $\mu_B$  (Qi et al, 1992). (2) The value of the Sm moment will increase at first and then decrease with increasing temperature, as shown in Fig.6.7(B). As an example, the Sm moment is ~0 at T=77K and 0.56  $\mu_B$  at T=300 K for Sm<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub>. (3) A parallel arrangement between the Fe and Er moment swill occur for T>370°C ; the total magnetization is 15.8  $\mu_B/$ fu, the Fe moment is 181/ $\beta_F$ =1  $\mu_B$  and thus the Er moment is +0.4  $\mu_B$  for T=370°C.

### 6.5 Conclusions

(1) All carbides  $Sm_2Fe_{17-x}Si_xC_y$  with x=0, 1, 2 and 3 retain the rhombohedral structure.

(2) With increasing Si concentrations, the Curie temperatures of  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  decrease from 660 K for x=1 to 595 K for x=3; the saturation magnetizations at room temperature decrease from 92 emu/g for x=1 to 83 emu/g for x=3.

(3) All the carbides  $Sm_2Fe_{17-x}Si_xC_y$  have a uniaxial anisotropy. The anisotropy fields decrease with Si substitutions, from 95 kOe for x=1 to 75 kOe for x=3 at



Magnetic moment of Sm as a function of  $A_4^0$ , with other parameters,  $A_2^0$ =-1000Ka<sub>0</sub><sup>-2</sup>,  $A_6^0$ =0 and  $\mu_B H_m$ =20 T, by Yamada et al (1995).



Magnetic moment of Sm as a function of  $A_4^0$  by Malik et al (1996). The numbers in parantheses are the values of  $A_2 < r^2 > /k$ ,  $A_4 < r^4 > /k$  and  $A_6 < r^6 > /k$  in Kelvin, respectively.

Figure 6.8: Magnetic moment of Sm as a function of  $A_{40}$ .

room temperature and from 140 kOe for x=1 to 90 kOe for x=3 at T=77 K.

(4) For  $Sm_2Fe_{17-x}Si_xC_y$ , the Sm and Fe magnetic moments may be antiparallel; this leads to low saturation magnetizations.

(5) For  $Sm_2Fe_{16}SiC_{2.7}$ , the Curie temperature is 660 K, and at room temperature the anisotropy field and the saturation magnetization are 95 kOe and 92 emu/g, respectively.

## Chapter 7

## Mössbauer Spectroscopy

Mössbauer spectra of  $R_2Fe_{17}N_y$  and  $R_2Fe_{17}C_y$ , have been studied extensively. However, only a few papers have been appeared on  $R_2Fe_{15}Si_2C_y$ . In fact, the Mössbauer spectra for  $R_2Fe_{15}Si_2C_y$  are significantly different from those for  $R_2Fe_{17}N_y$  and  $R_2Fe_{17}C_y$ . More importantly, Mössbauer spectroscopy is one of few techniques useful for the determination of the magnetic properties of rare-earth iron compounds on an atomic scale. Hence, it is important to study the Mössbauer spectra of  $R_2Fe_{15}Si_2C_y$  in an attempt to unravel the magnetic properties of these carbides at an atomic level.

### 7.1 Analysis of Mössbauer spectra

Since the quadrupole splitting is much smaller than the magnetic hyperfine splitting for all samples, a perturbation Hamiltonian was used to analyse the Mössbauer spectral data. The parameters obtained for each six-line subspectrum by a leastsquares fitting procedure were the hyperfine field,  $H_{hf}$ , the quadrupole splitting,  $\epsilon$ , the isomer shift,  $\delta$ , the line widths and the intensities. The area ratios of the six absorption lines in each sextet were constrained to be 3:b:1:1:b:3; b is equal to 2 for the non-aligned samples and is fitted for the aligned samples. For each Fe site, the subspectral areas for  $R_2Fe_{15}Si_2C_y$  were kept the same as those for their corresponding parents  $R_2Fe_{15}Si_2$  because it is assumed that the distributions of Si and Fe atoms are not changed during the process of C absorption.

In principle, there are two ways to fit Mössbauer spectra of  $R_2Fe_{17}N_y$  and

 $R_2Fe_{17}C_y$ . In the first method, Mössbauer spectra are fitted with four subspectra, corresponding to the four crystallographically inequivalent Fe sites, 6c/4f, 9d/6g, 18f/12j and 18h/12k sites (Zouganelis et al, 1991; Zhou et al, 1993). In the other method, based on the analysis of Steiner and Haferl (1977), for compounds with an easy c-plane anisotropy, Mössbauer spectra are fitted with seven subspectra. The subspectra corresponding to the 9d/6g, 18f/12j and 18h/12k sites are divided into two components with an area ratio 2:1 because of different angles between the electric-field-gradient principle axis and the direction of the hyperfine field and also different hyperfine fields produced by the magnetic dipoles. Then seven subspectra are used to fit the Mössbauer spectra (Hu et al, 1991; Qi et al, 1991;). Both methods can provide a good fit and almost the same hyperfine parameters for each Fe site.

The site assignments of the subspectra are based on the relative areas together with the neighboring environments of the sites. The 6c/4f and 18h/12ksites have the most and the least numbers of nearest-neighbor Fe atoms (13 and 9), respectively. Thus the largest and least hyperfine fields are to be associated with the 6c/4f and 18h/12k sites, respectively. Both the 9d/6g and 18f and 12j sites have ten Fe atoms as their neighbors; however, the relative numbers of site occupancy on the two sites are 3 and 6, respectively. The subspectra for 9d/6g and 18f and 12j, therefore, can be distinguished by their subspectral areas. To summarize, the magnitudes of the hyperfine fields are in the sequence  $H_{hf}(6c/4f) > H_{hf}(9d/6g) > H_{hf}(18f/12j) > H_{hf}(18h/12k)$ .

Mössbauer spectra for  $R_2Fe_{15}Si_2$  (R=Y, Nd, Sm, Gd and Er) were fitted by four subspectra, which correspond to the four Fe sites, 6c/4f, 9d/6g, 18f/12j and 18h/12k. However, because of the influence of the C (or Si) atoms, at least five spectra are necessary to obtain a good fit to the experimental data for the carbides  $R_2Fe_{15}Si_2C_y$ .

The relative area of the subspectra is about 3/17 for the 9d/6g site in  $R_2Fe_{15}Si_2$ . In order to maintain the value for the 9d/6g site, the subspectra of  $R_2Fe_{15}Si_2C_y$  have to be split into two components. Their area ratios are listed in Table 7.1.

It is known that the 9d/6g sites have four C atoms as their first nearestneighbours (1st nn). Based on the binomial distribution model, the probabilities

	Nd	Sm	Gd	Er
C concentration, y	2.6	2.5	2.6	2.6
P(4)/P(3)	0.61:0.39	0.56:0.44	0.61:0.39	0.61:0.39
$A(9d_1)/A(9d_2)$	0.58:0.42	0.55:0.45	0.60:0.40	0.61:0.39

Table 7.1: The area ratios,  $A(9d_1)/A(9d_2)$ , between two components for the 9d/6g site and P(4)/P(3) calculated by the bionomial distribution model

of finding m adjacent C atoms for the 9d/6g sites are found by

$$P(m) = \frac{n!}{m!(n-m)!} c^m (1-c)^{n-m}$$
(7.1)

where n=4 is the number of adjacent 9e/6h sites around the 9d/6g site and c=y/3 is the relative carbon concentration. The calculated values of P(4)/P(3) are also listed in Table 7.1. The consistency between  $A(9d_1)/A(9d_2)$  and P(4)/P(3) implies that the two components for the 9d sites can be attributed to the various configurations of adjacent C atoms.

For the 6c sites, there is no 1st nn C atom. The shortest distance between the Fe (the 6c site) and C atoms is 4.53 Å. Moreover, the 18f sites are located between the 6c sites and 9e sites. As a result, the C atoms are screened by Fe atoms on the 18f sites and have little influence on the hyperfine parameters of the 6c sites. For the 18f and 18h sites, there is only one 1st nn C atom and the distances between Fe and the 1st nn C atom are 1.86 and 1.95 Å, respectively. The probabilities for finding one C atom are over 0.8 and, therefore, the probabilities for other C atom configurations are so small that they can be neglected. Hence, for most of  $R_2Fe_{15}Si_2C_y$ , there is only one component for each of the 6c, 18f and 18h sites.

However, based on my experience, the Mössbauer spectrum of samples with an easy c-axis ansitropy, such as the Mössbauer spectra of  $\text{Sm}_2\text{Fe}_{15}\text{Si}_2\text{C}_y$  at room temperature and  $\text{Er}_2\text{Fe}_{15}\text{Si}_2\text{C}_y$  at 77 K, may be more complicated. In particular, some fine structure exists in the 1st spectral lines (v~ -2.5 — -4 mm/s) for the 18f and 18h sites. In order to obtain a good fit and to maintain the relative area of about 6/17 for the 18f and 18h sites, each subspectrum for the two sites has to be split into two components, i.e.  $18f_1$ ,  $18f_2$ ,  $18h_1$  and  $18h_2$ . The area ratios of the two components are close to the ratios between the probabilities, obtained from

R		$\mathbf{R_2}$	$Fe_{15}Si_2C_y$			$R_2Fe_{15}Si_2$					
	site	$H_{hf}$	E	δ	site	$H_{hf}$	ε	δ	A		
		(kOe)	(mm/s)	(mm/s)		(kOe)	(mm/s)	(mm/s)	(%)		
					4f	262(3)	0.04(1)	0.02(1)	10.1(9)		
Y					6g	233	-0.20	-0.08	21.1(11)		
					12j	217	0.06	-0.12	30.9(14)		
					1 <b>2k</b>	197	0.15	-0.10	38.0(17)		
	6c	313(3)	0.05(1)	0.08(1)	<u>6c</u>	256(3)	0.02(1)	-0.03(1)	12.5(10)		
Nd	9d	255	0.18	0.10	9d	233	-0.03	-0.13	18.4(10)		
	18f	169	0.11	-0.16	18f	205	0.08	-0.21	33.0(13)		
	18h	164	0.27	0.22	18h	202	0.15	0.09	36.0(14)		
	6c	277(3)	0.42(1)	0.07(1)	4f	284(3)	0.05(1)	0.09(1)	10.6(9)		
Gd	9d	237	0.19	0.08	6g	253	-0.09	-0.10	20.1(17)		
	18f	178	0.06	-0.13	1 <b>2</b> j	229	0.10	-0.27	31.7(27)		
	18h	169	0.28	0.14	12 <b>k</b>	224	0.18	0.08	37.6(31)		
	4f	269(3)	0.02(1)	-0.02(1)	4f	254(3)	0.07(1)	0.03(1)	11.0(8)		
Er	<b>6g</b>	230	0.16	0.10	6g	224	-0.19	-0.14	19.6(14)		
	1 <b>2</b> j	179	0.02	-0.19	1 <b>2</b> j	201	0.07	-0.26	32.0(23)		
	12k	174	0.28	0.10	12 <b>k</b>	198	0.11	0.02	37.4(27)		

Table 7.2: Mössbauer parameters at room temperature for  $R_2Fe_{15}Si_2C_y$  and  $R_2Fe_{15}Si_2$ . Here  $H_{hf}$  is the hyperfine field,  $\epsilon$  is the quadrupole splitting,  $\delta$  the isomer shift, A is the relative area of each subspectrum associated with each crystallographic site.

formula (7.1), for zero adjacent Si atoms and for one or two adjacent Si atoms. Hence, the two components correspond to two different neighbour configurations. One is the configuration with zero Si atoms; other is the configuration with one or two Si atoms.

Based on the above analyses, Mössbauer spectra of  $R_2Fe_{15}Si_2$ ,  $R_2Fe_{15}Si_2C_y$ ,  $Sm_2Fe_{17-x}Si_x$  and  $Sm_2Fe_{17-x}Si_xC_y$  at room temperature were fitted; the Mössbauer spectra and the fitted curves are shown in Fig.7.1, 7.2, 7.3 and 7.4. The fitted hyperfine parameters are listed in Tables 7.2 and 7.3.



Figure 7.1: Mössbauer spectra at room temperature for  $R_2Fe_{15}Si_2$  together with curves for subspectra obtained by a computer fit.



Figure 7.2: Mössbauer spectra at room temperature for  $R_2Fe_{15}Si_2C_y$  together with curves for subspectra obtained by a computer fit.



Figure 7.3: Mössbauer spectra of  $Sm_2Fe_{17-x}Si_x$  at room temperature, as well as their fitted curves.



Figure 7.4: Mössbauer spectra of  $Sm_2Fe_{17-x}Si_xC_y$  at room temperature, as well as their fitted curves.

Table 7.3: Mössbauer parameters at room temperature for  $Sm_2Fe_{17-x}Si_x$  and  $Sm_2Fe_{17-x}Si_xC_y$ . Here  $\delta$  is the isomer shift,  $\bullet$  is the quadrupole splitting,  $H_{hf}$  is the hyperfine field and A is the subspectral area.

x	site	Sm	2Fe <sub>17-x</sub> Si <sub>2</sub>	Cy		Sm <sub>2</sub> Fe	$_{17-x}Si_2$	
		δ	ε	Hhf	δ	ε	H <sub>hf</sub>	A
		(mm/s)	(mm/s)	(kOe)	(mm/s)	(mm/s)	(kOe)	(%)
0	6c	0.08(1)	-0.09(1)	343(3)	0.02(1)	0.02(1)	264(3)	11.9(10)
	<b>9d</b>	-0.05	-0.10	309	-0.25	-0.10	229	17.8(16)
	18f	-0.06	-0.50	250	-0.31	0.10	209	35.8(31)
	1 <b>8h</b>	0.07	-0.16	247	0.01	0.14	206	34.5(31)
0.5	6c				0.03(1)	0.02(1)	269(3)	12.1(9)
	9d				-0.18	-0.09	236	18.6(14)
	18f				-0.32	0.08	212	33.4(25)
	18h				0.02	0.14	210	35.9(27)
1	6c	0.16(1)	-0.18(1)	322(3)	0.04(1)	0.03(1)	270(3)	11.8(8)
	9d	-0.00	-0.28	286	-0.16	-0.09	239	19.8(13)
	18f	-0.09	-0.45	212	-0.29	0.09	213	32.8(22)
	18h	0.10	-0.15	194	0.02	0.14	212	35.6(25)
2	6с	0.13	-0.14	310	0.05	0.04	268	12.0(6)
	9d	0.00	-0.26	255	-0.11	-0.07	238	20.4(13)
	18f	-0.01	-0.40	1 <b>90</b>	-0.27	0.06	211	31.3(15)
	18h	0.12	-0.14	174	0.05	0.14	208	36.3(15)
3	6c	0.17(1)	-0.11(1)	295	0.06(1)	0.04(1)	264(3)	11.4(9)
	9d	0.06	-0.13	241	-0.08	-0.04	226	23.2(8)
	18f	0.09	-0.41	177	-0.21	0.03	208	33.2(17)
	18h	0.04	-0.10	151	0.09	0.11	197	32.2(17)



Figure 7.5: The isomer shift,  $\delta$ , as a logarithm function of cell volumes,  $\ln V$ .

## 7.2 Mössbauer spectra for $R_2(Fe, Si)_{17}$

Mössbauer spectra at room temperature for  $R_2Fe_{15}Si_2$  (R=Y, Nd, Sm, Gd and Er) and  $Sm_2Fe_{17-x}Si_x$  (x=0, 0.5, 1, 2 and 3) together with the fitted subspectra are shown in Fig.7.1 and Fig.7.3. The fitted Mössbauer parameters are listed in Tables 7.2 and 7.3.

## 7.2.1 Isomer shifts

The average isomer shifts,  $\delta$ , as a logarithmic function of the cell volumes,  $\ln V$ , are plotted in Fig.7.5 and lie on a straight line.

Based on the Mössbauer spectra of  $\alpha$ -Fe under various pressures, Williamson et al (1972) gave a relationship between the isomer shift and volume,

$$\frac{d\delta}{dV/V} = \kappa \tag{7.2}$$

where  $\kappa$  is a constant. After solving the differential equation, a linear relationship between the isomer shifts and cell volumes is obtained,

$$\delta = \kappa \ln V + C \tag{7.3}$$

From the slope of the straight line in Fig.7.5, the value of  $\kappa$  is 1.80 mm/s for  $R_2Fe_{15}Si_2$ , which is larger than the 1.33 mm/s for  $\alpha$ -Fe (Williamson et al, 1972).

In terms of (3.21) in section 3.2.1, the isomer shift,  $\delta$ , can be expressed as

$$\delta = C_0 \cdot \frac{\delta R}{R} [|\psi(0)|_a^2 - C_1]$$
(7.4)

where  $C_0$  and  $C_1$  are constants,  $|\psi(0)|_a^2$  is the charge density at the Fe nucleus for the absorber, R is the radius of the Fe nucleus and  $\delta R$  is the difference of the nuclear radius between the first excited state and the ground state. Because  $\delta R/R$  is negative for the Fe nucleus,  $\delta$  will decrease/increase when  $|\psi(0)|_a^2$  increases/decreases.

The magnitude of  $|\psi(0)|_a^2$  and  $\delta$  are dependent on three factors: (1) the distribution of the *s* electrons, (2) the shielding effect of *p* and *d* electrons on *s* electrons and (3) the volume effect. For a series of  $R_2Fe_{15}Si_2$  compounds, the *s*, *p* and *d* electrons of the Fe atoms can approximately be considered to be constant because all R ions are trivalent and their *f* electrons are localized; however, the cell volumes are reduced with increasing atomic number of the rare-earth elements. The decrease in the volumes leads to a decrease in isomer shift.

### 7.2.2 Quadrupole splittings

See section 7.3.2.

#### 7.2.3 Hyperfine fields

The average hyperfine fields, calculated by weighting their subspectral areas, as plotted against  $(g_R-1)J_R$  for  $R_2Fe_{15}Si_2$  (R=Y, Nd, Sm, Gd and Er) are shown in

Fig.7.6. Except for the Y compound, the dependence is linear to a good approximation.

It has been known that the hyperfine fields at an Fe nucleus consist of two parts, viz,  $H_{hf} = H_{Fe} + H_R$ . The first term is the contribution of the Fe atoms to the hyperfine field; it includes the Fermi contact field, the orbital field, the dipole field and the transfer field produced by the adjacent Fe atoms. The second term is the transfer field produced by the adjacent R atoms. It is most conveniently expressed in terms of RKKY theory where  $H_R$  is proportional to  $(g_R-1)J_R\sum_i F(2k_Fr_i)$ . The  $\sum_i$  extends over all distances  $\mathbf{r}_i$  between the central nucleus considered and the R atoms of the lattice. The function  $F(2k_Fr)$  is the RKKY function and  $k_F$  is wave number at the Fermi surface. For a given series of isostructural compounds  $\sum_i F(2k_Fr)$  can be considered to be a constant so that  $H_R$  is proportional to  $(g_R-1)J_R$ . Thus, the average hyperfine field,  $H_{hf}$ , can be expressed as a linear function of  $(g_R-1)J_R$ .

$$H_{hf} = H_{Fe} + \alpha (g_R - 1) J_R \tag{7.5}$$

By applying the least-squares method to (7.5),  $\alpha = 10.2$  kOe for  $R_2Fe_{15}Si_2$ . The value of  $\alpha$  is 7.0 kOe for RFe<sub>11</sub>Ti (Li Z W, 1992).

#### 7.2.4 Site occupancies of Fe atoms

The relative occupancy numbers,  $N_i$ , on the 6c/4f, 9d/6g, 18f/12j and 18h/12k sites are 2:3:6:6 for 2:17-type compounds. If it is assumed that the recoilless fractions on the four sites are the same, the occupation numbers  $N_i$ (Fe) and  $N_i$ (Si) of Fe and Si atoms on the *i*th site can be estimated by

$$N_i({\rm Fe}) = C_{Fe} \frac{A_i}{\sum_{j=1}^4 A_j}$$
 (7.6)

$$N_i(\mathrm{Si}) = 1 - N_i(\mathrm{Fe}) \tag{7.7}$$

where  $C_{Fe}$  denotes the Fe composition and  $A_i$  is the area of the *i*th Mössbauer subspectrum. Based on the subspectral areas,  $A_i$ , listed in Table 7.2 and 7.3,  $N_i$ (Fe) can be calculated using (7.6); the results are listed in Table 7.4.

The occupancy fractions,  $F_i(Fe)$  and  $F_i(Si)$  of Fe and Si atoms on the four sites



Figure 7.6: Average hyperfine fields,  $H_{hf}$ , versus  $(g_R-1)J_R$  for  $R_2Fe_{15}Si_2$ .

are given by

$$F_i(\text{Fe}) = N_i(\text{Fe})/N_i \tag{7.8}$$

$$F_i(\mathrm{Si}) = 1 - F_i(\mathrm{Fe}) \tag{7.9}$$

The results are shown in Fig.7.7(A) and (B) for  $R_2Fe_{15}Si_2$  (R=Y, Nd, Sm, Gd and Er) and  $Sm_2Fe_{17-x}Si_x$ , respectively. The dotted line in the figures is for random occupancy of the four sites by the Fe and Si atoms.

It is obvious that, for either  $R_2Fe_{15}Si_2$  or  $Sm_2Fe_{17-x}Si_x$ , the Si atoms are excluded from the 9d/6g site and prefer the 18f/12j site. On the other hand, with Si substitutions, the occupancy of the Si atoms on the 18f site seems to reach saturation at a Si concentration of x=2. In contrast, the occupancy fractions of Si atoms are small for the 18h and 6c sites at low Si concentration, but increase rapidly at x=3.

These occupancies are supported by x-ray diffraction experiments (see Table 6.1). With Si substitutions, the ratio of the lattice parameters, c/a, increases at first, reaches a maximum at x=2 and then decreases. It is known that the 18*f* sites lie on the basal plane and the 6*c* sites are along the *c* axis. The Si occupancy on the 18*f* sites will lead to a contraction in the basal plane, whereas the occupancy along the 6*c* sites will shorten the lattice parameter *c*. For  $x \le 2$ , the preferential occupation on the 18*f* sites and a small occupancy on the 6*c* sites causes an increase in the ratio c/a. For x=3, the rapid increase in the occupancy of Si atoms on the 6*c* sites leads to a decrease in the ratio of c/a.

Neutron diffraction for  $Y_2Fe_{14}Si_3$  (Lin et al, 1992) has shown that Si atoms avoid the 6g site and occupy the other three sites almost equally. This implies that a half of the 4f sites are occupied by Si atoms; in other words, Si atoms prefer the 4f sites. However, Long et al (1993), based on neutron diffraction for Nd<sub>2</sub>Fe<sub>13</sub>Si<sub>4</sub>, indicated that Si atoms are excluded from the 6c sites and preferentially occupy the 18h sites.

The occupancies of the Si atoms on the four Fe sites are related to the Curie temperature. The relationship between both will be discussed in Chapt 9.

Table 7.4: Relative areas A(%) of Mössbauer subspectra and the occupation numbers  $N_i(Fe)$  of Fe atoms in each site. The numbers in the parentheses are the fitting errors in the last significant digit.

			]	R <sub>2</sub> Fe <sub>15</sub> S	i <sub>x</sub>			
		R	Y	No	1	Gd	Er	
	<u>6c</u>	A(%)	10.1(9)	12.5(	10) 10	.6(9)	11.0(8)	<u>,</u>
		N(Fe)	1.5(1)	1.9(	2) 1.	6(1)	1.7(1)	
	9 <b>d</b>	A(%)	21.1(11)	18.4(	10) 20.	1(17)	19.6(14	)
		N(Fe)	3.0(2)	2.8(	2) 3.	0(3)	2.9(2)	
	18f	A(%)	30.9(14)	33.0(	1 <b>3</b> ) 31.	7(27)	32.0(23	)
		N(Fe)	4.6(2)	5.0(	2) 4.	8(4)	4.8(3)	
	18h	A(%)	38.0(17)	36.0(	14) 37.	6(31)	37.4(27	)
		<u>N(Fe)</u>	5.7(3)	5.4(	2) 5.	6(5)	5.6(4)	
•				· · · · ·				
			Sn	12Fe <sub>17-2</sub>	,Si <sub>x</sub>		_	
	x	(	) (	).5	1	2		3
<u>6c</u>	A(%	6) 11.9	(10) 12	1(9)	11.8(8)	12.0	(6) 1	1.4(9)
	N(F	Če) 2.0	(2) 2.	D(2)	1.9(1)	1.8(	2) 1	.6(1)
<b>9d</b>	A(%	6) 17.8	(16) 18.	5(14)	19.8(13)	20.4(	13) 23	3.2(8)
	N(F	<sup>r</sup> e) 3.0	(3) 3.	l <b>(2)</b>	3.2(2)	3.1(	2) 3	.2(2)
18 <b>f</b>	A(%	6) 35.8	(31) 33.4	4(25)	32.8(22)	31.3(	15) 33	.2(17)
	N(F	'e) 6.0	(5) 5.5	5(4)	5.3(4)	4.7(	2) 4	.6(2)
1 <b>8h</b>	A(%	6) 34.5	(31) 35.9	9(27)	35.6(25)	36.3(	15) 32	.2(17)
	<i>N</i> (F	'e) 5.8	(5) 5.9	9(4)	5.7(4)	5.5(	2) 4	.5(2)



Figure 7.7: Occupation fractions of Si atoms on each site for (A)  $R_2Fe_{15}Si_2$  and (B)  $Sm_2Fe_{17-x}Si_x$ . The dotted line is for random occupancy by the Si atoms.

## 7.3 Mössbauer spectra of $R_2(Fe, Si)_{17}C_y$

Mössbauer spectra at room temperature for  $R_2Fe_{15}Si_2C_y$  (R=Nd, Sm, Gd and Er) and  $Sm_2Fe_{17-x}Si_xC_y$  together with fitted subspectra are shown in Fig.7.2 and Fig.7.4. The fitted Mössbauer parameters are listed in Tables 7.2 and 7.3. The average isomer shifts, the average quadrupole splittings and the average hyperfine fields calculated by weighting their subspectral areas are shown in Fig.7.8 (A), (B) and (C), respectively.

#### 7.3.1 Isomer shifts

The average isomer shifts are 0.06, 0.06, 0.03 and 0.00 mm/s for  $R_2Fe_{15}Si_2C_y$  with R=Nd, Sm, Gd and Er, respectively. As compared to  $R_2Fe_{15}Si_2$ , they are increased by about 0.10 mm/s. Two factors are largely responsible for the increase. One is the expansion of the cell volume because of the C atoms introduced. The other factor is the transfer of electrons from Fe to C atoms. Since the electronegativity is much larger for C than for Fe and Si, the C atoms have a tendency to attract the conduction electrons from Fe and Si. A decrease in the Fe conduction electrons will lead to an increase in the isomer shifts.

Based on the the volume expansion and the transfer of conduction electrons from Fe to C atoms, the isomer shifts calculated for  $Sm_2Fe_{17-x}Si_xC_y$  are as follows.

First, the relationship between the isomer shift and volume for  $R_2Fe_{15}Si_2$  is given by section 7.2.1, as

$$\Delta \delta_V = 1.80 \frac{\Delta V}{V} (\text{mm/s}) \tag{7.10}$$

The cell volumes expand by 5.6, 4.7, 3.7 and 2.4 % for  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  with x=0, 1, 2 and 3, respectively, as compared to the volume of 792 Å<sup>3</sup> for  $\text{Sm}_2\text{Fe}_{17}$ . Hence, the increments in the isomer shift,  $\Delta\delta_V$ , produced by the volume expansion are 0.100, 0.085, 0.067 and 0.043 mm/s for the carbides with x=0, 1, 2 and 3, respectively, based on (7.10).

Then, the average isomer shifts are -0.149 and 0.006 mm/s for  $\text{Sm}_2\text{Fe}_{17}$  and  $\text{Sm}_2\text{Fe}_{17}\text{C}_{2.4}$ , respectively. After deducting the increment of 0.074 mm/s produced by the volume expansion, the increment of the isomer shift associated with the C atoms is 0.081 mm/s, which is equal to the increment of 0.034 mm/s per C atom.


Figure 7.8: The average isomer shifts (A), average quadrupole splittings (B) and (C) average hyperfine field. The circles are for  $R_2Fe_{15}Si_2C_y$  and the squares are for  $R_2Fe_{15}Si_2$ .

x	$\delta_V ~({ m mm/s})$	$\delta_C \ (mm/s)$	$\Delta \delta^{cal.}$ (mm/s)	$\Delta \delta^{exp.}$ (mm/s)
0	0.100	0.081	0.181	0.16(2)
1	0.085	0.092	0.177	0.15(2)
2	0.067	0.085	0.152	0.14(2)
3	0.043	0.078	0.121	0.13(2)

Table 7.5: The calculated and experimental isomer shifts for  $Sm_2Fe_{17-x}Si_xC_y$ .

Because the C concentrations are 2.7, 2.5 and 2.3, the corresponding increments of the isomer shift,  $\Delta \delta_C$ , are 0.092, 0.085 and 0.078 mm/s for Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>C<sub>y</sub> with x=1, 2 and 3, respectively, as compared to their parents.

Finally, the increments of the isomer shifts for  $Sm_2Fe_{17-x}Si_xC_y$ , as compared to their corresponding parents, are given by

$$\Delta \delta = \delta - \delta_0 = \Delta \delta_V + \Delta \delta_C \tag{7.11}$$

where  $\delta$  and  $\delta_0$  are the isomer shift for  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  and  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x$ , respectively. The results are listed in Table 7.5. The values calculated,  $\Delta\delta^{cal}$ , by (7.11) are consistent with the experimental values,  $\Delta\delta^{exp}$ . Therefore, as compared to their corresponding parents, the increase in the isomer shift for the carbides  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  is attributed to the volume expansion and the transfer of conduction electrons from Fe to C.

#### 7.3.2 Quadrupole splittings

The average quadrupole splittings have a different sign for  $R_2Fe_{15}Si_2$  and  $R_2Fe_{15}Si_2C_y$ , as shown in Fig.7.8(B). The quadrupole splittings can give some information on the magnetic anisotropy. It is well known that the quadrupole splitting,  $\epsilon$ , is related to the angle,  $\theta$ , between the direction of the hyperfine field and the principal axis of the electric-field gradient (EFG) by the equation

$$\epsilon = \frac{1}{4} eqQ(3\cos^2\theta - 1) \tag{7.12}$$



Figure 7.9: The dependence of the quadrupole splittings on the C concentration, y, for  $Sm_2Fe_{17-x}Si_xC_y$ .

where Q is the nuclear quadrupole moment and q is the component of the EFG along the principal axis. When the magnetic moments are either along the c-axis or in the c-plane, the quadrupole splitting will be significantly different in sign and/or in magnitude because of the different  $\theta$  angles. Quadrupole splittings with the opposite sign imply a different type of magnetic anisotropy for R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub> and R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub>. This conclusion is also supported by the x-ray diffraction experiments (see chapter 5.5)

In addition, the average quadrupole splittings are about 0.14-0.25 mm/s for  $R_2Fe_{15}Si_2C_y$ , which are 2-3 times larger than those for  $R_2Fe_{15}Si_2$ . This shows that the interstitial C atoms produce a large asymmetry in the EFG. This effect of interstitial C atoms is obviously observed in the  $Sm_2Fe_{17-x}Si_xC_y$  series. For  $Sm_2Fe_{17-x}Si_xC_y$  with x=0, 1, 2 and 3 the average quadrupole splittings are

-0.24, -0.28, -0.25 and -0.21 mm/s, respectively, which are about four to five times larger in magnitude compared to 0.04-0.06 mm/s for their corresponding parents. The quadrupole splittings,  $\epsilon$ , as function of the C concentration, are plotted in Fig.7.9. The quadrupole splittings lie on a straight line; extrapolation to y=0 yields  $\epsilon$ =0.056 mm/s. This value is the same order of magnitude as the 0.04-0.06 mm/s observed for Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>. It follows that the large quadrupole splittings for the carbides can be attributed to the C atoms creating a large EFG.

#### 7.3.3 Hyperfine fields

The Mössbauer spectral shapes of  $R_2Fe_{15}Si_2C_y$  are greatly different from those of their parents. One of the significant differences is that for  $R_2Fe_{15}Si_2C_y$  the 1st and 6th spectral lines for the 6c/4f and 9d/6g sites are separated from those for the 18f/12j and 18h/12k sites, whereas the lines for the four Fe sites overlap for  $R_2Fe_{15}Si_2$ . This implies that the hyperfine fields on the 6c/4f and 9d/6gsites increase, whereas the fields on the 18f/12j and 18h/12k sites decrease, as compared to  $R_2Fe_{15}Si_2$ . As an example, the hyperfine fields are 310, 255, 190 and 174 kOe for the 6c, 9d, 18f and 18h sites of  $Sm_2Fe_{15}Si_2C_y$ , respectively. They, as compared to  $Sm_2Fe_{15}Si_2$ , increase by 41 and 18 kOe for the 6c and 9d sites, respectively, but decrease by 20 and 34 kOe for the 18f and 18h sites, respectively. As a result, the average hyperfine field decreases by  $\sim 5\%$  for  $Sm_2Fe_{15}Si_2C_y$ .

The relative changes of the hyperfine fields on each Fe site for  $R_2Fe_{15}Si_2C_y$ are shown in Fig.7.10, where  $\Delta H_{hf}/H_{hf}^0 = (H_{hf}-H_{hf}^0)/H_{hf}^0$ , and  $H_{hf}$  and  $H_{hf}^0$  are the hyperfine fields for  $R_2Fe_{15}Si_2C_y$  and  $R_2Fe_{15}Si_2$ , respectively. Obviously, as compared to their parents, the hyperfine fields of  $R_2Fe_{15}Si_2C_y$  (R=Nd, Sm and Er) increase for the 6c/4f and 9d/6g sites and decrease for the 18f/12j and 18h/12ksites. For  $Gd_2Fe_{15}Si_2C_y$ , the hyperfine fields decrease only by 2.5 and 6.3 % for 6cand 9d sites, respectively; however, the fields decrease by about 23 % for 18f and 18h sites. The average hyperfine fields decrease by 5-17 % for carbides  $R_2Fe_{15}Si_2C_y$ , as compared to their parents.

This difference may be related to the distances between the Fe and C atoms. The magnetic moments on each Fe site of  $Y_2Fe_{17}$ ,  $Y_2Fe_{17}C_y$  and  $Y_2Fe_{17}N_y$  have been calculated by Beuerle and Fähnle (1992) as well as Jaswal et al (1991).



Figure 7.10: The relative change of the hyperfine fields,  $\Delta H_{hf}/H_{hf}$ , for each site of  $R_2Fe_{15}Si_2C_y$ .

They have found that the interstitial atoms lead to two opposite effects. One is a geometrical effect (volume expansion) that increases the Fe moments; other is the hybridization effect of the interstitial atoms with the neighboring Fe atoms that decreases the Fe moments. It is known that the shortest distances between the C atoms and the 6c/4f and 9d/6g sites are 4.53 and 3.29 Å, respectively; however, the shortest distances of the C atoms to the 18f/12j and 18h/12k sites are only 1.86 and 1.95 Å. These short distances lead to a hybridization of the 3d electrons of an Fe atom and the 2s and 2p electrons of a neighbouring C atom. As a result, the magnetic moments or the hyperfine fields decrease for the 18f/12j and 18h/12k sites.

In addition, there exists a similar result for Fe-C martensite; the 1st nn Fe atoms around a C atom have a hyperfine field of 265 kOe and the 2nd Fe atoms have a hyperfine field of 334 kOe, which is smaller and larger than 331 kOe for  $\alpha$ -Fe, respectively (Moriya et al, 1968).

It is known that the hyperfine field on each Fe site is larger for  $R_2Fe_{17}N_y$ than for  $R_2Fe_{17}$  (Hu et al, 1991; Qi et al 1991). This shows that for the nitrides the geometrical effect is larger than the hybridization effect. By contrast, for the carbides, the hybridization effect surpasses the the geometrical effect. Qi et al (1992) also attribute the smaller Fe moments for the carbides to a greater hybridization with Fe 3d orbitals based on Miedema's model of the electron density at the Wigner-Seitz cell boundary. The charge density parameter  $n_{WS}$  is 6.86, 5.36 and 4.10 d.u. for C, Fe and N, respectively. Thus, the electrons in the C-Fe bonds tend to occupy a spin-down state and the electrons in N-Fe bonds a spin-up state. Thus, the average Fe moment is smaller for  $Y_2Fe_{17}C_y$  than that for  $Y_2Fe_{17}N_y$ .

The decrease in the hyperfine field for the 18f/12j and 18h/12k sites leads to a smaller average hyperfine field (Fe moment) as compared to  $R_2Fe_{15}Si_2$ . This is one of the causes of a rather low saturation magnetization in  $Sm_2Fe_{15}Si_2C_y$ .

### 7.4 Conclusions

(1) Because of the effect of C and Si atoms, at least five (or seven) subspectra are needed to obtain a good fit for  $R_2Fe_{15}Si_2C_y$  Mössbauer spectra.

(2) The C atoms lead to an increase in the isomer shifts as compared to the parents. This increase can be attributed to the volume expansion and the transfer of conduction electrons from Fe to C.

(3) The quadrupole splittings for  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  show a significant increase and a different sign as compared to their parents. This indicates that the C atoms lead to a larger EFG around the Fe nuclei and modify the magnetic anisotropy of their parents.

(4) For the carbides, the hyperfine fields on the 6c/4f and 9d/6g sites increase, whereas the fields on the 18f/12j and 18h/12k sites decrease, as compared to the corresponding parents. As a result, the average hyperfine field decreases. This is one of the sources of the low saturation magnetizations for the light rare-earth carbides as compared to their parents. The other sources have been discussed in chapter 6.

(5) Mössbauer spectra show that the Fe and Si atoms are not randomly distributed on the four Fe sites in the compounds  $R_2Fe_{15}Si_2$ ,  $Sm_2Fe_{17-x}Si_x$  as well as their carbides. The Fe atoms tends to occupy the 9d/6g and 18h/12k sites and the Si atoms prefer to occupy the 18f/12j site.

# Chapter 8

# Spin-Reorientation Transition for $Er_2Fe_{15}Si_2C_y$

For  $R_2Fe_{15}Si_2C_y$  the Fe sublattice favours an easy c-plane anisotropy and the R (Sm, Er and Tm) sublattice prefers an easy c-axis anisotropy. The magnetic structure and the easy-magnetization direction are governed by the competition between the Fe and R sublattice anisotropies. The carbide  $Sm_2Fe_{15}Si_2C_y$  has an easy c-axis anisotropy and the carbides  $R_2Fe_{15}Si_2C_y$  (R=Nd and Gd) have an easy c-plane anisotropy at both 77 and 300 K. However,  $Er_2Fe_{15}Si_2C_y$  has a spin reorientation transition from an easy c-plane anisotropy at high temperatures to an easy c-axis anisotropy at low temperatures.

In this chapter the spin reorientation transition will be studied. First of all, a new method is proposed. Then, spin-reorientation transitions are studied by Mössbauer spectra of the aligned sample. Finally, the transition is calculated using the two lattice model.

## 8.1 Method

The spin reorientation transition is usually determined by measuring the dependence of the ac susceptibility or the magnetization on temperature. However, Mössbauer spectroscopy is also an important technique. For a non-aligned powder sample there exists a jump in the hyperfine field during the spin reorientation transition (Gubbens et al, 1976, 1989, 1991; Hu B P et al, 1989). For an aligned sample the direction of the Fe magnetic moments can be determined by

$$\cos\theta = \sqrt{\frac{4-b}{4+b}} \tag{8.1}$$

where  $\theta$  is the angle between the directions of the hyperfine field and the  $\gamma$ -ray propagation and the angle factor, b, is the area ratio between the 2nd plus the 5th and the 3rd plus 4th lines. This method has been used to study the spin reorientation transition for Nd<sub>2</sub>Fe<sub>14</sub>B (Onodera,1984) and RFe<sub>11</sub>Ti (Hu B P et al, 1989a). However, the formula is valid only under the following conditions. (1) The sample must be fully aligned; this is very difficult to do experimentally. (2) The sample must have an easy c-axis anisotropy when aligned at room temperature. Unfortunately, the carbide Er<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> has an easy c-plane anisotropy at room temperature. Formula (8.1), therefore, cannot be used.

A sample, such as  $R_2Fe_{17}$ , was ground into very fine particles that are considered to be single crystals. An aligned sample was prepared by mixing the fine particles with epoxy resin and then placing the mixture in an applied magnetic field. When the sample has an easy-plane anisotropy, these particles are aligned along one of their *a* crystal axes in the applied magnetic field and the magnetic moments lie along either a [100], [110] or [010] direction in a zero field.

In order to get a general formula between the direction of the hyperfine field (magnetization) and the angle factor, b, for an aligned sample, a coordinate system is selected, as shown in Fig.8.1. Let the directions of both the applied field and the  $\gamma$ -ray propagation be along the Z-axis. For a fully aligned sample, the normal to the c-plane,  $\mathbf{n}$ , is perpendicular to the z-axis. For a non-fully aligned sample, the normal deviates by a small angle,  $\xi$ , i.e. the angle between the  $\mathbf{n}$  and the Z axis is  $\frac{\tau}{2}$ - $\xi$ . The probability distribution of  $\xi$  is assumed to be Gaussian, viz

$$P(\xi) = \frac{1}{\sqrt{2\pi\kappa}} \exp(\frac{-\xi^2}{2\kappa^2})$$
(8.2)

where  $\kappa$  is the standard deviation.

The area of the six absorption lines for a Mössbauer spectrum are expressed as

$$\begin{cases} A_{1,6} = \int P(\xi) \frac{3}{4} (1 + \cos^2 \beta) d\xi \\ A_{2,5} = \int P(\xi) (1 - \cos^2 \beta) d\xi \\ A_{3,4} = \int P(\xi) \frac{1}{4} (1 + \cos^2 \beta) d\xi \end{cases}$$
(8.3)



Figure 8.1: Schematic diagram for the directions of  $\gamma$ -ray propagation, magnetization and crystal axes.

where  $A_{i,j}$  represents the relative absorption area of the *i* and the *j* line and  $\beta$  is an angle between the direction of the hyperfine field (or magnetic moment) and the  $\gamma$ -ray propagation.

When spin reorientation occurs the magnetic moments on the [100], [110] and [010] directions will be rotated an angle,  $\theta$ , toward the direction [001] (c-axis) in the (100), (110) and (010) planes, respectively. The angles,  $\beta_i$ , i=1, 2 and 3, between the  $\gamma$ -ray propagation (Z axis) and the magnetic moments on the (100), (110) and (010) planes are related to the angles of  $\theta$  and  $\xi$  by

$$\begin{cases} \cos \beta_1 = \sin(\theta + \xi) \\ \cos \beta_2 = -\cos \theta \sin \xi + \frac{1}{2} \sin \theta \cos \xi \\ \cos \beta_3 = \cos \theta \sin \xi + \frac{1}{2} \sin \theta \cos \xi \end{cases}$$
(8.4)

On substituting the expressions for  $\cos \beta_i$  in (8.4) into (8.3) and using the approximations,  $\sin^2 \xi \simeq \xi^2$  and  $\cos^2 \xi \simeq 1 - \xi^2$  for small  $\xi$ , the angle factor, b, can be written as

$$b = \frac{\sum_{i}^{3} \int P(\xi) 4(1 - \cos^{2} \beta_{i}) d\xi}{\sum_{i}^{3} \int P(\xi) (1 + \cos^{2} \beta_{i}) d\xi}$$

$$= \frac{4(2-[\sin^2\theta+\kappa\sqrt{\frac{2}{9\pi}}\sin 2\theta+\kappa^2(2-3\sin^2\theta)])}{2+[\sin^2\theta+\kappa\sqrt{\frac{2}{9\pi}}\sin 2\theta+\kappa^2(2-3\sin^2\theta)]}$$
(8.5)

Hence, the angle  $\theta$  can be found by solving Eq.(8.5) if the values of  $\kappa$  and b are known.

When the moments are in the c-plane, the angle  $\theta = \pi/2$ . From (8.5), b is given by

$$b = \frac{4(1+\kappa^2)}{3-\kappa^2}$$
(8.6)

and the value of  $\kappa$  is

$$\kappa = \sqrt{\frac{3b-4}{b+4}} \tag{8.7}$$

For a fully aligned sample,  $\kappa=0$ ; Eq.(8.5) then is a very simple expression, viz

$$b = \frac{4(2 - \sin^2 \theta)}{2 + \sin^2 \theta} \tag{8.8}$$

Hence, the value of b is equal to 4/3 when the moments are in the c-plane ( $\theta = \pi/2$ ) and is equal to 4 when the moments are along the c-axis ( $\theta = 0$ )

### 8.2 Mössbauer spectra for aligned $Er_2Fe_{15}Si_2C_y$

Mössbauer spectra of  $Er_2Fe_{15}Si_2C_y$  were fitted using five or seven subspectra. Below 90 K, each subspectrum for the 6g, 12j and 12k sites was split into two components. Thus, seven subspectra are used to fit a Mössbauer spectrum. However, above 90 K, a good fit can be obtained with five subspectra; only for the 6g site are two subspectra required. The area ratios of the six absorption lines in each sextet were assumed to be 3:b:1:1:b:3, where b was a fitted parameter. The subspectral areas and the line-widths for each site at various temperatures were kept the same as those at room temperature.

Mössbauer spectra of  $Er_2Fe_{15}Si_2C_y$  from 77 to 300 K and their fitted curves are shown in Fig.8.2. The average quadrupole splittings and spectrum shifts are calculated by weighting the subspectral areas. The Mössbauer parameters at 77 K and 300 K are listed in Table 8.1.



Figure 8.2: Mössbauer spectra in 77-300 K for aligned  $Er_2Fe_{15}Si_2C_y$  together with curves for subspectra obtained by a computer fit.

	Sites	H <sub>hf</sub> (kOe)	$\epsilon  (\rm mm/s)$	$\delta (mm/s)$	в
	-4f	268(3)	0.02(2)	-0.02(2)	1.40(8)
<i>T</i> (300 K)	6g	230	0.16	0.10	1.40
	1 <b>2</b> j	179	-0.02	-0.18	1.40
	12k	194	0.28	-0.10	1.40
	4f	324(3)	-0.04(2)	0.14(2)	3.52(30)
T (77 K)	6g	279	-0.05	0.08	3.52
	1 <b>2</b> j	203	-0.46	-0.04	3.52
	18k	197	-0.07	0.14	3.52

Table 8.1: Mössbauer parameters for  $\text{Er}_2\text{Fe}_{15}\text{Si}_2$ . Here  $H_{hf}$  is the hyperfine field,  $\epsilon$  is the quadrupole splitting,  $\delta$  the isomer shift.

The Mössbauer spectrum at 77 K has two significant differences as compared to that at 300 K. One, the positions of the 2nd and 5th lines obviously move towards the right. Two, the intensities of the 2nd and 5th lines significantly increase. The average quadrupole splittings are -0.19 and 0.13 mm/s at 77 and 300 K, respectively. They are opposite in sign. On the other hand, the intensity ratios of the 2nd plus the 5th and the 3rd plus 4th,  $I_{2,5}/I_{3,4}$ , are 3.52 and 1.40 at 77 and 300 K, respectively. These results imply that a spin-reorientation transition has occured in  $\text{Er}_2\text{Fe}_{15}\text{Si}_2\text{C}_{y}$ .

#### 8.2.1 Hyperfine fields

The temperature dependences of the hyperfine fields for the four Fe sites are shown in Fig.8.3. With decreasing temperatures an increase in the hyperfine fields occurs in 90-100 K; The increase is abnormal for the 4f and 6g sites. The hyperfine fields at T=77 K are 324 and 279 kOe for the 4f and 6g sites, respectively. They increase by 20 and 21 kOe as compared to 304 and 258 kOe, the corresponding hyperfine fields at T=100 K. In the viewpoint of Streever (1979), this increase can be attributed to the orbital field and dipole field because the magnitude of the two fields is related to the direction of the Fe magnetic moments.



Figure 8.3: Dependences of hyperfine fields,  $H_{hf}$ , on temperatures.

#### 8.2.2 Quadrupole splittings and spectrum shifts

The temperature dependences of the average quadrupole splittings,  $\langle \epsilon \rangle$ , and the average spectrum shifts,  $\langle \delta \rangle$ , are shown in Fig.8.4(A) and (B), respectively.

The average quadrupole splittings are almost constant within the experimental errors,  $0.10(\pm 1)$  mm/s, from 300 K to 120 K. However, they rapidly decrease and even change their sign, from 0.13 mm/s at 120 K to -0.19 mm/s at 77 K. Because the quadrupole splitting is related to the angle between the direction of the hyperfine field and the principal axis of the electric-field gradient, the significant difference in magnitude and the change of sign clearly shows that a spin reorientation has occurred. The transition temperature corresponding to  $\langle \epsilon \rangle = 0$  is 90 K.

The spectrum shifts relative to  $\alpha$ -Fe at room temperature increase with decreasing temperature. This is consistent with the second-order Doppler shift. However, the shifts have an anomalous decrease in the 100-77 K temperature range.

#### 8.2.3 Angle factor, $b = A_{2,5}/A_{3,4}$

The angle factors of the Mössbauer spectra,  $b = A_{2,5}/A_{3,4}$ , in the temperature range of 300 to 77 K are shown in Fig.8.4(C). They are almost constant from 300 K to 100 K and rapidly increase below T=100 K. For a fully aligned sample with an easy c-plane anisotropy, the value of b should be 1.33 based on (8.8). However, the average value of b for 120-300 K is 1.39. The difference between the experimental and the theoretical value is attributed to some misaligment of the particles. Based on (8.7) the standard deviation of the Gaussian distribution (8.2) is calculated to be  $\kappa=1.78$ . On substituting the values of  $\kappa$  and b into (8.5) and solving this equation one finds the angles,  $\theta$ , of the Fe magnetic moments relative to the c-axis. The results are shown in Fig.8.5. Because  $\theta \sim 10^{\circ}$  at 77 and 80 K, within experimental error, the Fe magnetic moments can be considered to be rotated into the c-axis from the c-plane.



Figure 8.4: (A) the average quadrupole splittings,  $\epsilon$ , (B) the average spectrum shifts,  $\delta$ , and (C) the angle factors,  $b=A_{2,5}/A_{3,4}$  for T=77-300 K.



Figure 8.5: Dependence of angles,  $\theta$ , between the Fe magnetic moments and the c-axis on the temperatures. The solid line is calculated from the theoretical model.

### 8.3 Theoretical calculation

The anisotropy energy,  $E_a$ , can be expressed as

$$E_a = (K_{1,Fe} + K_{1,R})\sin^2\theta + K_{2,R}\sin^4\theta + (K_{3,R} + K'_{3,R}\cos 6\phi)\sin^6\theta \qquad (8.9)$$

where  $\theta$  and  $\phi$  are the polar angles for the magnetization vector relative to the c-axis, and the  $K_{i,Fe}$  and  $K_{i,R}$  are the anisotropy constants for the Fe and R sublattices, respectively. For the Fe sublattice, the first term,  $K_{1,Fe}$ , usually dominates. For the R lattice, the relationships between  $K_{i,R}$  and  $B_{nm}$  are obtained from (Lindgard and Danielsen, 1975)

$$K_{1,R} = -\frac{3}{2}B_{20} < O_{20} > -5B_{40} < O_{40} > -\frac{21}{2}B_{60} < O_{60} >$$
(8.10)

$$K_{2,R} = \frac{7}{8} (5B_{40} < O_{40} > +9B_{60} < O_{60} >)$$
(8.11)

$$K_{3,R} = -\frac{231}{16}B_{60} < O_{60} > \tag{8.12}$$

$$K'_{3,R} = \frac{1}{16}B^c_{66} < O_{60} >$$
 (8.13)

where  $\langle O_{nm} \rangle$  are thermal averages of the Stevens operators. The crystal field parameters can be expressed as

$$B_{nm} = \theta_n < r^n > A_{nm} \tag{8.14}$$

where  $\theta_n$  is the *n*th-order Stevens factor,  $\langle r^n \rangle$  the expectation value of the 4f radius and  $A_{nm}$  the crystal field coefficients.

For the calculation of the crystal field parameters two assumptions are made. (1) The magnetic moments of Fe and Er are collinear. (2)  $B_{nm}$  is the average of  $B_{nm}(2b)$  and  $B_{nm}(2d)$  for the 2b and 2d sites. Now the Hamiltonian for Er ions at T=0K can be written as

$$\mathcal{H}_R = \mu_R \cdot \mathbf{H}_R + \sum_{nm} B_{nm} O_{nm} \tag{8.15}$$

where  $\mathbf{H}_R = -dn_{RFe} \mathbf{M}_{Fe}$  is the molecular field acting on the Er ions,  $\mu_R = -g_J \mu_B \mathbf{J}_R$ is the magnetic moment of Er ions and d is a conversion coefficient (as defined in section 5.7). The magnetic moments of the Fe sublattice,  $M_{Fe} = 15\mu_{Fe}$ , are derived from the average hyperfine field of  $\mathbf{Er}_2 \mathbf{Fe}_{15} \mathbf{Si}_2 \mathbf{C}_y$  and the proportionality coefficient

Table 8.2: Crystal parameters,  $A_{nm}$ , for  $\text{Er}_2\text{Fe}_{15}\text{Si}_2\text{C}_{2.5}$  (in unit of  $\text{Ka}_0^{-n}$ ).

A <sub>20</sub>	A40	A <sub>60</sub>	A <sub>66</sub>
-180.6(6)	0.6(10)	-0.04(8)	-6.8(16)

of 150 kOe/ $\mu_B$  between  $\mu_{Fe}$  and  $H_{hf}$ . In addition, the values of  $K_{1,Fe}$  are taken from Li H-S and Cadogan (1992).

The second term is the crystal field interaction. For hexagonal symmetry, the  $B_{20}O_{20}$ ,  $B_{40}O_{40}$ ,  $B_{60}O_{60}$  and  $B_{66}O_{66}$  terms must be taken into account. The eigenvalues  $E_i$  and the corresponding eigenvectors,  $|i\rangle$ , are calculated by diagonalising the 15×15 matrix of (8.15). The thermal average values,  $\langle O_{nm} \rangle$ , can be obtained from

$$< O_{nm} > = \sum_{i} < i |O_{nm}|i > \frac{\exp(-E_i/k_B T)}{Z_R}$$
 (8.16)

where  $Z_R$  is the partition function.

By using iteration a set of  $B_{nm}$  and  $n_{RFe}$  were varied to fit the experimental values  $\theta(T)$  by minimizing the anisotropy energy  $E_a$  (8.9). The best fitted results are  $n_{RFe}=930$  and

$$\begin{cases} B_{20} = -0.163K \\ B_{40} = 0.016 \times 10^{-3}K \\ B_{60} = -0.148 \times 10^{-6}K \\ B_{66} = -33.9 \times 10^{-6}K \end{cases}$$

$$(8.17)$$

The crystal field coefficients  $A_{nm}$  as obtained from fitted  $B_{nm}$  values are listed in Table 8.2. Obviously, the second-order crystal field parameter,  $A_{20}$ , determines the sign and magnitude of the Er sublattice anisotropy. The value of  $A_{20}$ , -180.6 Ka<sub>0</sub><sup>-2</sup> is smaller than the -290 and -400 Ka<sub>0</sub><sup>-2</sup> obtained from the <sup>166</sup>Er Mössbauer spectra for Er<sub>2</sub>Fe<sub>17</sub>C and Er<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub>, respectively (Gubbens et al, 1991). However, it is known that the value of  $A_{20}$  obtained from rare-earth Mössbauer spectra depends on the Sterheimer antishielding factor and the screening constant used; these are difficult to determine experimentally. The fitted molecular field coefficient,  $n_{RFe}$ , is 930, which is consistent with 990 obtained from the temperature dependence of the magnetization for  $\text{Er}_2\text{Fe}_{15}\text{Si}_2$  (see section 5.7).

At a certain temperature, the anisotropy energies,  $E_a$ , as a function of the  $\theta$  angles, can be calculated by substituting (8.17) and (8.10-8.13) into (8.9). The results at T=4.2, 90 and 200 K are shown in Fig.8.6. Obviously, the minimum in the anisotropy energies at T=4.2, 90 and 200 K is located at  $\theta=0^{\circ}$ , 51° and 90°, respectively. On the other hand, for a given temperature, the  $\theta$  angle is found by solving the equation

$$\frac{\partial E_a}{\partial \theta} \to (K_{1,Fe} + K_{1,R}) + 2K_{2,R}\sin^2\theta + 3(K_{3,R} + K'_{3,R}\cos 6\phi)\sin^4\theta = 0 \quad (8.18)$$

The calculated  $\theta$ 's, as a function of temperatures, are shown as the solid line of Fig.8.5; they are in good agreement with the experimental data.

## 8.4 Conclusion

Based on the angle factors of the Mössbauer spectrum, a new method to find the angles between the direction of the Fe moments and the c-axis for a non-fully aligned sample with an easy c-axis anisotropy at room temperature is proposed and is used to determine the spin reorientation temperature.

Mössbauer spectroscopy shows that the spin reorientation transition for  $\text{Er}_2\text{Fe}_{15}\text{Si}_2\text{C}_y$ occurs at 90-100 K. At the transition temperature, the angle factors, the hyperfine fields and the quadrupole splittings of the Mössbauer spectra change suddenly.

The crystal field coefficients,  $A_{nm}$ , have been obtained by fitting the experimental data for the  $\theta$  angles. The value of  $A_{20}$  is -181 K $a_0^{-n}$ .



Figure 8.6: The anisotropy energies,  $E_a$ , as a function of the angles,  $\theta$ , at T=4.2, 90 and 200 K.

# Chapter 9

# Negative Exchange Interaction Theory and Curie Temperatures

When nonmagnetic atoms replace Fe in binary Fe-M alloys (M is a metallic element but excludes the rare-earths, R) the Curie temperatures always decrease. However, some nonmagnetic atoms, such as Al, Ga and Si, substituted for Fe in the  $R_2Fe_{17}$  compounds can elevate the Curie temperature (Plusa et al, 1986; Van Mens, 1986; Alp et al, 1987; Lin et al, 1992; Wang and Dunlap, 1993; Shen et al, 1993a). For Al- or Ga-substituted 2:17-type compounds, the source is usually attributed to a lattice expansion. However, for Si-substituted 2:17 compounds, although the Curie temperatures increase, the cell volumes decrease. This surprising property has attracted much attention. In addition, when N or C is introduced interstitially into the lattice of  $R_2Fe_{17}$  compounds, the Curie temperatures are significantly elevated. The origin of this significant increase in the Curie temperature will be discussed in this chapter.

# 9.1 Mössbauer spectra for $Sm_2Fe_{17}$ and $Sm_2Fe_{17}N_y$

Mössbauer spectra and computer fitted subspectra for  $\text{Sm}_2\text{Fe}_{17}$  and  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  are shown in Fig.9.1 and Fig.9.2. The assignment of the subspectra is determined by their relative areas and the magnitude of their hyperfine fields. The fitted area ratios of the subspectra on the 6c, 9d, 18f and 18h sites are 11.9 : 17.9 : 35.7 : 34.5 = 2.0 : 3.0 : 6.1 : 5.9 for  $\text{Sm}_2\text{Fe}_{17}$  and 10.7 : 17.8 : 35.7 : 35.8 = 1.8 : 3.0 : 6.1: 6.1 for  $\text{Sm}_2\text{Fe}_{17}N_y$ . These values are very close to the ratios of numbers of the site occupanies: 2:3:6:6. The magnitude of the hyperfine fields is in the sequence  $H_{hf}(6c) > H_{hf}(9d) > H_{hf}(18f) > H_{hf}(18h)$ .

The average spectrum shifts and quadrupole splittings between 77 K and the Curie temperature are shown in Fig.9.3(A) and (B), respectively. The average spectrum shifts decrease with increasing temperature for both  $Sm_2Fe_{17}$  and  $Sm_2Fe_{17}N_y$ , which is consistent with the second-order Doppler shift. The average quadrupole splittings can be considered almost constant or linear with a small slope in the range from 77 K to the Curie temperatures; however, they have different signs because of the different types of magnetic anisotropy for  $Sm_2Fe_{17}$  and  $Sm_2Fe_{17}N_y$ .

The dependences of the hyperfine fields on temperature are shown in Fig.9.5 (A) and (B) for  $\text{Sm}_2\text{Fe}_{17}$  and  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ , respectively. With increasing temperature, the hyperfine fields decrease at different rates for four Fe sites. For  $\text{Sm}_2\text{Fe}_{17}$  the hyperfine fields decrease most rapidly for the 9d site and most slowly for the 18h site. At T=77 K the first lines of the subspectra for the 6c and 9d sites are separated from those for the 18f and 18h sites; however, at T=300K these lines overlap. For  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  the hyperfine field decreases most rapidly for the 6c site. These features are related to the negative exchange interactions between some sites, as will be described in Section 9.3.

The doublet in the Mössbauer spectra of  $Sm_2Fe_{17}N_y$  is attributed to the superparamagnetism of fine particles, because (1) the area of the doublet increases with increasing temperature, (2) the doublet disappears when a magnetic field of about 2 kOe is applied, as shown in Fig.9.4(A), and (3) the isomer shifts for the doublet are almost the same as those for the sextets of  $Sm_2Fe_{17}N_y$ , as shown in Fig.9.4(B).

For non-interacting particles with uniaxial anisotropy, the superparamagnetic relaxation time,  $\tau$ , is given by

$$\tau = \tau_0 exp(\frac{KV}{k_B T}) \tag{9.1}$$

where  $\tau_0$  is of the order of  $10^{-10}$ - $10^{-12}$  s, V is the volume of the particles and K is the magnetic anisotropy constant. When  $\tau$  is close to the nuclear Lauor precession time,  $\tau_L$  (~  $10^{-8}$  s), Mössbauer spectrum for a magnetic sample is the overlap of



Figure 9.1: Mössbauer spectra of  $Sm_2Fe_{17}$  in a temperature range of 77 K to 430 K, as well as the curves for the subspectra obtained by a computer fitting.



Figure 9.2: Mössbauer spectra of  $Sm_2Fe_{17}N_y$  in a temperature range of 77 K to 700 K, as well as fitted subspectrum curves.



Figure 9.3: The dependences of (A) the average spectrum shift,  $\delta$ , and (B) the average quadrupole splitting,  $\epsilon$ , on the temperature. The open circles are for  $Sm_2Fe_{17}$  and the solid circles are for  $Sm_2Fe_{17}N_r$ .



Figure 9.4: (A) Mössbauer spectra at room temperature with zero and 2 kOe field. (B) Isomer shift for the doublet and sextet spectra.

a sextet and a singlet or doublet. Based on (9.1) with  $\tau = 10^{-9}$  s,  $K = 10^7$  J/m<sup>3</sup> and T = 700 K, the volume is estimated to be  $4.5 \times 10^{-27}$  m<sup>3</sup> and the corresponding estimated size of the particles is  $1.7 \times 10^{-9}$  m or 17 Å.

## 9.2 Mean-field theory

For an R-Fe compound the R-R exchange interactions can usually be neglected. Based on the mean-field theory, the Heisenberg Hamiltonian can be written as

$$\mathcal{H} = -2\sum_{i < j} J_{FeFe}^{ij} \mathbf{S}_{Fe}^{i} \cdot \mathbf{S}_{Fe}^{j} - 2\sum_{i < j} J_{FeR}^{ij} \mathbf{S}_{Fe}^{i} \cdot \mathbf{S}_{R}^{j}$$
  
$$= -\sum_{i < j} \mathbf{S}_{Fe}^{i} (2J_{FeFe}^{ij} < \mathbf{S}_{Fe}^{j} > + J_{FeR}^{ij} < \mathbf{S}_{R}^{j} >) - \sum_{i < j} J_{FeR}^{ij} \mathbf{S}_{R}^{i} < \mathbf{S}_{Fe}^{j} > (9.2)$$

where  $J_{AB}^{ij}$  is the exchange integral between the *i*th A atom and the *j*th B atom,  $\mathbf{S}_{A}^{i}$  is the spin operator of the *i*th A atom, and  $\langle \mathbf{S}_{Fe} \rangle$  and  $\langle \mathbf{S}_{R} \rangle$  are given by

$$\langle \mathbf{S}_{Fe} \rangle = -\mu_{Fe}(T)/g_{Fe}\mu_B$$
 (9.3)

$$\langle \mathbf{S}_R \rangle = \langle (g_R - 1) \mathbf{J}_R \rangle = -\gamma \mu_R(T) / \mu_B$$
 (9.4)

where  $\gamma = -(g_R - 1)/g_R$ ,  $g_{Fe} = 2$  and  $g_R = 2/7$  for the Sm ion.

In  $\text{Sm}_2\text{Fe}_{17}$  and its nitride there are four Fe sites and one R site. In order to calculate the values of the exchange integrals between Fe atom pairs some assumptions are made: (1) only the interactions between the neighboring atoms are considered, (2) all exchange integrals between the Fe and R atoms are assumed to be the same,  $J_{FeR}^{ij}=J_{FeR}$ , and (3) the magnitude of the exchange integrals,  $J_{FeFe}^{ij}$ , are related to the distances of the Fe-Fe pairs, i.e. the integral for the Fe-Fe pairs is the same if their distances are equal or very close.

After substituting (9.3) and (9.4) into (9.2), the Heisenberg Hamiltonians are given by

$$\mathcal{H}_{Fe}^{i} = -\mathbf{S}_{Fe}^{i} (\sum_{j} 2J_{FeFe}^{ij} Z_{FeFe}^{ij} \mu_{Fe}^{j}(T) / g_{Fe} \mu_{B} + J_{FeR} Z_{RFe}^{i} \gamma \mu_{R}(T) / \mu_{B}) \quad (9.5)$$

$$\mathcal{H}_{R} = -\mathbf{S}_{R} J_{RFe} \sum_{j} Z_{FeR}^{j} \mu_{Fe}^{j}(T) / g_{Fe} \mu_{B}$$
(9.6)

for the *i*th Fe site and R site, respectively, where  $Z_{AB}$  is the number of neighboring B atoms for a given A atom.

The mean-field,  $H_m$ , acting the *i*th Fe site is defined as

$$H_{m} = \frac{1}{\mu_{B}g_{Fe}} \left(\sum_{j} 2J_{FeFe}^{ij} Z_{FeFe}^{ij} \mu_{Fe}^{j}(T) / g_{Fe} \mu_{B} + J_{FeR} Z_{RFe}^{i} \gamma \mu_{R}(T) / \mu_{B}\right)$$
(9.7)

 $H_m$  is selected to be along the z-axis and thus the Fe moment is aligned along the direction of  $H_m$ . Eq.(9.5) can be rewritten as

$$\mathcal{H}_{Fe} = -g_{Fe}\mu_B S_{Fe} H_m \tag{9.8}$$

The eigenvalue of  $\mathcal{H}_{Fe}$ ,  $E_m$  is given by

$$E_m = -g_{Fe}\mu_B m H_m \tag{9.9}$$

where  $m = -S, -(S-1), \dots S-1, S$ .

The thermodynamic properties of a system can be obtained from the partition function,

$$Z_R = \sum_{m=-S}^{S} \exp(-E_m/k_B T) = \sum_{m=-S}^{S} \exp(g_{Fe}\mu_B H_m m/k_B T)$$
(9.10)

$$= \sinh[g_{Fe}\mu_B H_m (2S+1)/k_B T] / \sinh[g_{Fe}\mu_B H_m / 2k_B T]$$
(9.11)

The Fe moment is given by (9.3) and the thermal average for the operator  $S_{Fe}$  can be calculated based on

$$\langle S_{Fe} \rangle = tr[S_{Fe} \exp(-\mathcal{H}_{Fe}/k_B T)]/tr[\exp(-\mathcal{H}_{Fe}/k_B T)]$$
(9.12)

Hence,

$$\mu_{Fe}(T) = \frac{g_{Fe}\mu_B}{Z_R} \sum_{m=S}^{S} m \exp(mg_{Fe}\mu_B H_m/k_B T)$$
(9.13)

This summation is easily obtained from  $\partial Z/\partial H_m$  (9.11). The result is

$$\mu_{Fe}(T) = g_{Fe}\mu_B \mathcal{B}_S(x) = \mu_{Fe}(0)\mathcal{B}_S(x) \tag{9.14}$$

where  $x = g_{Fe} \mu_B S H_m / k_B T$  and  $\mathcal{B}_s$  is the Brillouin function,

$$\mathcal{B}_{S} = \frac{2S+1}{2S} \coth(\frac{2S+1}{2S}x) - \frac{1}{2S} \coth(\frac{1}{2S}x)$$
(9.15)

In a similar way, from the Hamiltonians  $\mathcal{H}_{Fe}^{i}$  and  $\mathcal{H}_{R}$  expressed in (9.5) and (9.6), respectively, the magnetic moments of Fe on the *i*th site and R can be written as a Brillouin function,  $B_{S}$ , with S = 1 for Fe and S = 5/2 for Sm, respectively,

$$\mu_{Fe}^{i}(T) = \mu_{Fe}^{i}(0)\mathcal{B}_{S}\left[\frac{S_{Fe}}{k_{B}T}\left(\sum_{j} 2J_{FeFe}^{ij}Z_{FeFe}^{ij}\mu_{Fe}^{j}(T)/g_{Fe}\right) - J_{FeR}Z_{RFe}^{i}\gamma\mu_{R}(T)\right]$$

$$(9.16)$$

$$\mu_{R}(T) = \mu_{R}(0) \mathcal{B}_{S}[\frac{S_{R}}{k_{B}T} J_{RFe} \sum_{j} Z_{FeR}^{j} \mu_{Fe}^{j}(T) / g_{Fe}] \qquad (9.17)$$

When a conversion cofficient,  $\beta_F$ , between the Fe moment and the hyperfine field is used, (9.16) gives

$$H_{hf}^{i}(T) = H_{hf}^{i}(0)\mathcal{B}_{S}\left[\frac{S_{Fe}}{k_{B}T}\left(\sum_{j} 2J_{FeFe}^{ij}Z_{FeFe}^{ij}H_{hf}^{j}(T)/(g_{Fe}\beta_{F})\right) - J_{FeR}Z_{RFe}^{i}\gamma\mu_{R}(T)\right]$$

$$(9.18)$$

#### 9.3 Exchange Integrals

Based on (9.18) and (9.17), the exchange integrals,  $J_{FeFe}^{ij}$ , of the Fe-Fe pairs can be found. First of all, the numbers of adjacent atoms,  $Z_{FeFe}^{ij}$  and  $Z_{FeR}^{i}$ , and their interatomic distances are listed Table 9.1. Because no exact determination of the parameters of the atomic positions could be found for Sm<sub>2</sub>Fe<sub>17</sub> and Sm<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub> in the literature, the atomic positions (Jaswal et al, 1991) for Nd<sub>2</sub>Fe<sub>17</sub> and Nd<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub> were used instead to calculate the interatomic distances. However, the lattice parameters for Sm<sub>2</sub>Fe<sub>17</sub> and Sm<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub> were used.

Secondly, the conversion coefficient  $\beta_F$  is 150 kOe/ $\mu_B$ ,  $H_{hf}^i(0)$  are taken as  $H_{hf}^i(77\text{K})$  and  $\mu_R(0)$  as  $1.6\mu_B$ . The values of  $J_{RFe}(=J_{FeR})=1.0$  and 0.6 meV are taken from Table 5.4 for Sm<sub>2</sub>Fe<sub>17</sub> and Sm<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub>, respectively. The values of  $\mu_R(T)$  are found from (9.17).

Finally, a non-linear least-squares method is applied to (9.18), where the exchange interals,  $J_{FeFe}^{ij}$ , are the fitted parameters. By iteration a set of optimum exchange integrals is found that make the mean square deviation between the calculated and experimental values of  $H_{hf}(T)$  a minimum. The fitted results are listed in Table 9.2. By substituting the fitted  $J_{FeFe}^{ij}$  into (9.18), the hyperfine fields for each Fe site as a function of temperature are calculated; the results are shown

Table 9.1: The interatomic distances (in Å) and the numbers of adjacent atoms for each site.

Sm <sub>2</sub> Fe <sub>17</sub>									
Site	<u>6c</u>	9d	18 <i>f</i>	18h		R			
<u>6c</u>	2.392×1	2.625×3	2.742×6	2.656×3	3.077×1	5.061×3	5.118×3		
9d	2.625×2		2.438×4	2.467×4	3.307×2	4.813×4			
18 <i>f</i>	2.742×2	2.438×2	2.467×2	2.553×2	3.070×2	4.934×2	5.260×1		
	[			2.657×2					
18h	2.656×1	$2.467 \times 2$	$2.553 \times 2$	$2.508 \times 2$	3.085×1	$3.203 \times 1$	$3.255 \times 1$		
			2.657×2		4.877×2				

Sm <sub>2</sub> Fe <sub>17</sub> N <sub>w</sub>	

Site	6c	9 <b>d</b>	18 <b>f</b>	18h		R			
6c	2.427×1	2.674×3	2.760×6	2.620×3	3.065×1	5.170×3	5.200×3		
9 <b>d</b>	2.674×2		2.473×4	2.469×4	3.327×2	4.875×4			
18 <b>f</b>	2.760×2	2.473×2	2.479×2	2.583×2 2.724×2	3.148×2	4.945×2	5.312×1		
18h	2.620×1	2.469×2	2.583×2 2.724×2	2.650×2	3.147×1 4.939×2	3.246×1	3.423×1		

			Sm <sub>2</sub> re	17				
Fe-Fe pair	6c-6c	9d-18f	18 <i>f</i> -18 <i>f</i>	18h-18h	18f-18h	6c-18h	18f-18h	6c-18f
			9d-18h			18 <i>f-</i> 18h	-	-
<u> </u>	2.392	2.438	2.467	2.508	2.553	2.625	2.657	2.742
$J_{FeFe}$ (meV)	-17.3(1.6)	) -1.7(4)	2.7(4)	2.5(15)	5.0(4)	6.7(8)	4.6(6)	1.4(3)
			Sm <sub>2</sub> Fe <sub>17</sub>	Ny				
Fe-Fe pair	6c-6c	9d-18f,9d-1 18f-18f	8h 18f-	18h 6c-18	3h 18h-18	h 6c-9d	18f-18h	6c-18f
d (A)	2.427	2.469-2.4	79 2.58	33 2.62	0 2.650	2.674	2.724	2.760
$J_{FeFe}$ (meV)	-4.2(6)	3.4(3)	3.8(	5) 5.6(7	') <u>4.6(8)</u>	3.9(11)	2.2(4)	1.9(3)

Table 9.2: The fitted exchange integrals,  $J_{FeFe}$ , and the interatomic distances, d.

by the solid curves of Fig.9.5(A) and (B). The calculated curves agree well with the experimental data for both  $Sm_2Fe_{17}$  and  $Sm_2Fe_{17}N_y$ .

The exchange integrals,  $J_{FeFe}^{ij}$ , as a function of the distances of the Fe-Fe pairs, are plotted in Fig.9.6. The two sets of data (for  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  and  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ ) lie very well on the same curve; it is very similar to the famous Bethe-Slater curve. This implies that the signs and magnitudes of the exchange integrals are mainly determined by the distances of the Fe-Fe pairs for both  $\text{Sm}_2\text{Fe}_{17}$  and  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ . With an increase in the distance of the Fe-Fe pairs, the exchange integrals undergo a transition from negative to positive. When the distance is smaller than 2.45 Å, the exchange interactions between the Fe atoms are negative; when the Fe atoms are located at a larger distance the interactions are positive. Further, the positive interactions increase at first and then decrease.

For  $Sm_2Fe_{17}$ , three sites (the 6c, 9d and 18f sites) involve negative exchange interactions; four of ten pairs of the 9d atom associated with its neighboring Fe atoms, two of ten pairs of the 18f atoms and one of thirteen pairs of the 6c atoms are negative interactions. Meanwhile, only the interactions between the 18h atom and its neighboring Fe atoms are positive. Hence, with increasing temperature, the hyperfine fields decrease most rapidly for the 9d site and most slowly for the 18h site.



Figure 9.5: The dependences of the hyperfine fields,  $H_{hf}$ , on the temperature for each Fe site in (A) Sm<sub>2</sub>Fe<sub>17</sub> and (B) Sm<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub>. The solid lines are the calculated curves.

•



Figure 9.6: The exchange integrals,  $J_{FeFe}$ , as a function of the distances between the Fe-Fe pairs. The open circles are for  $Sm_2Fe_{17}$  and the solid circles are for  $Sm_2Fe_{17}N_y$ .

The exchange integrals for  $\text{Sm}_2\text{Fe}_{17}N_y$  are different in two significant ways as compared to  $\text{Sm}_2\text{Fe}_{17}$ . First, the exchange integrals are elevated to J=-4.2 meV from J=-17.3 meV for the 6c-6c sites and second, the negative exchange interaction is turned into a positive one for the 9d-18f site. Consequently, with increasing temperature the hyperfine fields decrease most rapidly for the 6c site; more importantly, the Curie temperatures are greatly elevated for  $\text{Sm}_2\text{Fe}_{17}N_y$ .

#### 9.4 $T_f$ for nitrides and carbides

Based on the competition between the positive and negative exchange interactions, a model is now proposed to predict the Curie temperatures of the Y-Fe compounds as well as their nitrides and carbides. First of all, the dependence of the exchange integrals on the distance between the Fe-Fe pairs is simplified into a step function. When the distance of Fe-Fe pairs is smaller than 2.45 Å, the exchange interactions are negative; at larger Fe-Fe distances, the interactions are positive. Then, based on Fig.9.6 the positive exchange integral is taken as  $J_+=4.74$  meV on the average and the negative exchange integral is taken as  $J_-=-9.92$  meV. Finally, for Y-Fe compounds, mean field theory gives the Curie temperatures as

$$T_{f} = \frac{2S_{Fe}(S_{Fe}+1)}{3k_{B}}(Z_{+}J_{+}+Z_{-}J_{-})$$
  
=  $\frac{2S_{Fe}(S_{Fe}+1)}{3k_{B}}[ZJ_{+}+Z_{-}(J_{-}-J_{+})]$   
=  $T_{+}+T_{-}$  (9.19)

where  $Z_+$  and  $Z_-$  are the average numbers of the neighboring Fe atoms that are linked by positive and negative interactions, respectively, with a given atom and  $Z=Z_++Z_-$  is the average coordination number of an Fe atom.

The first term in (9.19),

$$T_{+} = \frac{2S_{Fe}(S_{Fe}+1)}{3k_{B}}ZJ_{+},$$
(9.20)

is the Curie temperature of the Y-Fe compounds when no negative exchange interactions are present. Because the average Fe coordination numbers are not much different,  $T_+$  is almost the same for all the compounds involved.

	Z	$Z_{-}$	$d_{Fe-Fe}$ (Å)	<i>T</i> <sub>+</sub> (K)	$T_{-}$ (K)	$T_{f}^{cal}$ (K)	$T_{f}^{exp}$ (K)
Y <sub>2</sub> Fe <sub>17</sub>	10	1.53	2.56	733	-346	387	324
$Y_2Fe_{17}N_y$	10	0.12	2.60	733	-27	706	694
$Y_2Fe_{17}C_y$	10	0.12	2.60	733	-27	706	660
YFe <sub>11</sub> Ti	9.96	0.92	2.61	730	-208	522	524
YFe11TiNy	9.96	0.25	2.63	730	-57	673	713
YFe <sub>11</sub> TiC <sub>y</sub>	9.96	0.25	2.63	730	-57	673	708
Y <sub>2</sub> Fe <sub>14</sub> B	9.64	0.71	2.58	707	-162	545	571

Table 9.3: The Curie temperatures calculated for some Y-Fe compounds and their nitrides and carbides.  $(J_{+}=4.74 \text{ meV} \text{ and } J_{-}=-9.92 \text{ meV}.)$ 

The second term,

$$T_{-} = \frac{2S_{Fe}(S_{Fe}+1)}{3k_{B}}Z_{-}(J_{-}-J_{+}), \qquad (9.21)$$

is the contribution of the negative interactions to the Curie temperature. This term is significantly different in magnitude for the various Y-Fe compounds. From the average numbers,  $Z_{-}$ , of Fe-Fe pairs associated with the negative interaction and  $J_{-}-J_{+}=-14.7$  meV, the values of  $T_{-}$  found from (9.21) are also listed in Table 9.3.

Gavigan et al (1988) emphasize the importance of the mean local Fe coordination numbers in determining the Curie temperatures for  $R_xFe_y$  compounds. However, for  $Y_2Fe_{17}$ ,  $YFe_{11}Ti$ ,  $Y_2Fe_{14}B$  as well as the nitrides and carbides, although the average coordination numbers and the average distances of Fe-Fe pairs are approximately equal, as shown in Table 9.3, their Curie temperatures are significantly different, from 324 K for  $Y_2Fe_{17}$  to about 700 K for  $Y_2Fe_{17}N_y$  and  $Y_2Fe_{17}C_y$ . The source is a large difference in the magnitude of the negative interactions for these compounds.

For Y<sub>2</sub>Fe<sub>17</sub>,  $Z_{-}=1.53$  and  $T_{-}=-346$  K, however, for Y<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub> and Y<sub>2</sub>Fe<sub>17</sub>C<sub>y</sub>,  $Z_{-}=0.12$  and  $T_{-}=-27$  K. Thus the contribution that the negative interaction makes

is decreased by 320 °C in magnitude for  $Y_2Fe_{17}N_y$  and  $Y_2Fe_{17}C_y$  as compared to  $Y_2Fe_{17}$ . Consquently, the Curie temperatures of  $Y_2Fe_{17}N_y$  and  $Y_2Fe_{17}C_y$  are enormously elevated. Similar conclusions also apply for  $YFe_{11}Ti$  and its nitride and carbide.

In addition, the Curie temperatures for  $Y_2Fe_{17}$ ,  $YFe_{11}Ti$ ,  $Y_2Fe_{14}B$  as well as their corresponding nitrides and carbides have been calculated based on (9.19)-(9.21) with  $J_+=4.74$  meV,  $J_-=-9.92$  meV and the parameters, Z and  $Z_-$ , listed in Table 9.3. The calculated Curie temperatures,  $T_f^{cal}$  agree well with the experimental data, as shown in Table 9.3.

Marasinghe et al (1996) state the dependence of the Curie temperature on the average distance of Fe-Fe pairs for R<sub>2</sub>Fe<sub>14</sub>B, R<sub>2</sub>Fe<sub>17</sub>, R<sub>2</sub>Fe<sub>17</sub>C<sub>y</sub> and R<sub>2</sub>Fe<sub>17</sub>N<sub>y</sub>, as shown in the inset of Fig.9.7. Obviously, this dependence is very weak. However, the Curie temperatures, as a function of  $Z_{-}/Z$ , are plotted in Fig.9.7 and lie on a straight line. This shows that the Curie temperature is strongly related to the relative number of the Fe-Fe pairs with negative interactions.  $T_0$  can be defined as the Curie temperature if no negative interaction were present. From the intercept of the line,  $T_0=745(3)$  K and the corresponding exchange integral  $J_+=4.82(2)$  meV are obtained if Z is approximately taken as 10. From the slope,  $J_- - J_+$  are derived to be -16.8(34) meV; thus,  $J_-$  is equal to -12.0(25) meV. The values of  $J_+$  and  $J_-$  are very consistent with those obtained from the mean-field theory.

#### 9.5 $T_f$ for Si substituted 2:17-type compounds

#### $9.5.1 R_2 Fe_{15} Si_2$

The Curie temperatures of  $R_2Fe_{15}Si_2$  (R=Y, Nd, Sm, Gd and Er) can also be calculated using the above model. For Fe-based alloys with a low solvent concentration, the dependence of the Curie temperatures on the concentrations can be considered, to a good approximation, to be linear. The first term in (9.20), therefore, can be expressed as

$$T_{+} = T_{0}(1 - \alpha \mathbf{x}) \tag{9.22}$$


Figure 9.7: The dependence of Curie temperature on  $\mathbb{Z}_{-}/\mathbb{Z}$ .

$\underline{\mathbf{R}_{2}}\mathbf{F}\mathbf{e}_{15}\mathbf{S}\mathbf{i}_{2}$								
R	Z_	$T_+$ (K)	$T_{-}$ (K)	$T_{Fe-R}$ (K)	$T_{f}^{cal}$ (K)	$T_{f}^{exp}$ (K)		
Y	1.13	710	-255	0	455	490		
Nd	1.18	710	-268	3	445	500		
Sm	1.21	710	-274	86	522	<b>530</b>		
Gd	<b>1.12</b>	710	-255	149	604	570		
Er	1.19	710	-269	-19, 37*	422, 478*	480		

Table 9.4: The Curie temperatures calculated with  $\alpha = 0.016$  and  $T_0 = 733$  K for  $R_2Fe_{15}Si_2$  (R=Y, Nd, Sm, Gd, Er).

• This value of  $T_{R-Fe}$  (with the superscript) is deduced from the Curie temperatures of  $\text{Er}_2\text{Fe}_{17}$ and  $\text{Lu}_2\text{Fe}_{17}$ ; the corresponding  $T_I^{cal}$  is also marked with the superscript.

where  $T_0=733$  K is the Curie temperature of  $Y_2Fe_{17}$  if no negative exchange interactions are present, x is the Si concentration and  $\alpha$  is a coefficient. In addition, the contribution of the R-Fe interaction on the Curie temperatures,  $T_{R-Fe}$ , should be considered. Hence, for  $R_2Fe_{15}Si_2$ , the Curie temperatures,  $T_f^{cal}$ , are given by

$$T_f^{cal} = T_0(1 - \alpha \mathbf{x}) + \frac{2S_{Fe}(S_{Fe} + 1)}{3k_B} Z_-(J_- - J_+) + T_{R-Fe}$$
(9.23)

where the value of  $\alpha$  is taken as 0.016 for Si (Li Z W et al, 1995) and the values of  $T_{R-Fe}$  are obtained from the Curie temperature of  $R_2Fe_{17}$  minus that of  $Y_2Fe_{17}$ . The values of  $Z_{-}$  are derived from the areas of the Mössbauer subspectra, viz

$$Z_{-} = \frac{1}{17} \sum_{i=1}^{4} N_{i} F_{i}(\text{Fe}) \sum_{j=1}^{4} F_{i}(\text{Fe}) Z_{j-}$$
(9.24)

where  $N_i$  and  $F_i$ (Fe) are the occupation number and the fraction of Fe atoms for the *i*th site, respectively, which have been defined in section 7.2.4;  $Z_{j-}$  is the number of Fe-Fe pairs with a negative interaction for a given by j site.

The calculated Curie temperatures are listed in Table 9.4; they are close to the experimental data.

For  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$ , a negative value of  $T_{Fe-R}$  is unreasonable. However, if the value of  $T_{Fe-R}$  is derived from the Curie temperatures of  $\text{Er}_2\text{Fe}_{17}$  and  $\text{Lu}_2\text{Fe}_{17}$  (268)

$\underline{\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x}$								
x	$\overline{Z_{-}}$	$\overline{T_+(\mathrm{K})}$	<i>T</i> <sub>-</sub> (K)	$T_{Fe-Sm}$ (K)	$T_{f}^{cal}$ (K)	$T_{f}^{exp}(\mathbf{K})$		
0	1.53	733	-346	86	473	410		
0.5	1.42	727	-322	86	491	450		
1	1.35	721	-306	86	501	490		
2	1.21	710	-274	86	522	530		
3	1.18	698	-267	86	517	525		

Table 9.5: The Curie temperatures calculated with  $\alpha = 0.016$  and  $T_0 = 733$  K for  $R_2 Fe_{17-x} Si_x$ .

K), one obtains  $T_{Fe-R}=37$  K and  $T_f^{cal}=478$  K, which agree very well with the experimental value of 490 K. It has been shown that the dependences of the Curie temperatures on  $\sqrt{G}$   $(G=(g-1)^2 J(J+1))$  can be divided into two branches for  $R_2Fe_{14}B$ ; one branch takes the Y compound as the starting point for the light rare-earth compounds, the other takes the Lu compound for the heavy rare-earth compounds (Fig.9 in Herbst, 1991). Therefore, it is reasonable to obtain the value of  $T_{Fe-R}$  from the Curie temperatures of  $Er_2Fe_{17}$  and  $Lu_2Fe_{17}$ .

### 9.5.2 $Sm_2Fe_{17-x}Si_x$

The Curie temperatures of  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x$  (x=0, 0.5, 1, 2 and 3) have been calculated on the basis of (9.23) with  $T_0=733$  K,  $\alpha=0.016$ ,  $T_{Fe-Sm}=86$  K and the values of  $Z_-$  calculated by (9.24). The calculated results, as shown in Table 9.5, replicate the characteristics of the experimental data, which increase at first, reach a maximum at x=2, and then decrease with Si substitutions.

#### 9.5.3 R<sub>2</sub>Fe<sub>14</sub>Ga<sub>2</sub>

Mössbauer spectra at room temperature for  $R_2Fe_{14}Ga_2$  together with fitted subspectra are shown in Fig.9.8. The fitted subspectral areas are listed in Table 9.6. Fe atoms preferentially occupy the 9d and 18h site, whereas Ga atoms plus va-

	<u> </u>					$\overline{N_i(\text{Fe})}$			
	6c	9 <b>d</b>	18 <b>f</b>	18 <b>h</b>	6c	9 <b>d</b>	18 <i>f</i>	18h	
Ŷ	10.1	21.1	30.9	38.0	1.41	2.97	4.33	5.32	
Nd	10.6	20.8	30.1	38.6	1.48	2.91	4.21	5.40	
Sm	10.4	20.3	29.5	39.7	1.46	2.84	4.13	5.56	

Table 9.6: Relative areas A(%) of Mössbauer subspectra and the occupation number  $N_i$  (Fe) of Fe atoms on each site for for  $R_2$ Fe<sub>14</sub>Ga<sub>2</sub>.

Table 9.7: The Curie temperatures calculated with  $\alpha = 0.032$  and  $T_0 = 733$  K for  $R_2Fe_{14}Ga_2$ .

$\underline{Sm_2Fe_{17-x}Si_x}$								
x	Z	<i>T</i> <sub>+</sub> (K)	$T_{-}$ (K)	$T_{Fe-Sm}$ (K)	$T_{f}^{cal}$ (K)	$T_{f}^{exp}$ (K)		
<u> </u>	1.084	663	-231	0	432	478		
Nd	1.047	663	-223	3	443	526		
Sm	1.006	663	-215	86	534	541		

cancies occupy the 18f and 6c sites. This occupancy trends to elevate the Curie temperature, the same as the occupancy of the Fe and Si atoms in R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>.

The Curie temperatures of  $R_2Fe_{14}Ga_2$  are calculated from (9.23), where  $T_0=733$  K,  $\alpha$  is taken as 0.032 based on the literature for Fe-Ga alloys with low Ga concentration (Massalski, 1986) and  $Z_{-}$  is obtained from (9.24). The results are listed in Table 9.7. The calculated Curie temperatures are close to the experimental values.

## 9.6 Conclusions

Based on the mean field theory, the exchange integrals for  $Sm_2Fe_{17}$  and  $Sm_2Fe_{17}N_y$ , as a function of the distance between the Fe-Fe pairs, have been obtained by fitting the hyperfine field data at various temperatures for each Fe site. The results



Figure 9.8: Mössbauer spectra at room temperature for  $R_2Fe_{14}Ga_2$  together with fitted subspectra.

show that there are positive and negative exchange interactions for  $Sm_2Fe_{17}$  and  $Sm_2Fe_{17}N_y$ . When the interatomic distance is smaller than 2.45 Å, the exchange interactions between the Fe-Fe pairs are negative; when Fe atoms are located at a larger distance the interactions are positive. The positive and negative exchange integrals are 4.74 and -9.92 meV on the average, respectively.

For  $Sm_2Fe_{17}$ , the 6c-6c and the 9d-18f pairs have negative exchange interactions. This leads to a rather low Curie temperature for  $R_2Fe_{17}$ . For  $Sm_2Fe_{17}N_y$ , the negative exchange interaction between the 6c-6c pairs is weakened and that between the 9d-18f pairs is shifted to a positive interaction. Hence, the Curie temperatures are significantly elevated.

When Si atoms replace Fe in  $R_2Fe_{17}$ , Si atoms prefer the 18f/12j and 6c/4f sites which leads to a decrease in the negative interactions. Consequently, the Curie temperatures increase.

Based on a model that considers the competition between the positive and negative exchange interactions the Curie temperatures for some Y-Fe compounds and their nitrides and carbides as well as  $Sm_2Fe_{17-x}Si_x$ ,  $R_2Fe_{15}Si_2$  and  $R_2Fe_{14}Ga_2$  compounds have been calculated. The results are very consistent with the experimental values.

In summary, the negative exchange interactions play an important role in determining the Curie temperatures of the 2:17 type R-Fe compounds as well as their nitrides and carbides.

# Chapter 10 Conclusions

(1) The rare-earth iron nitrides and carbides,  $R_2Fe_{17}N_y$  and  $R_2Fe_{17}C_y$  made by a gas-phase reaction have attracted much attention because of their excellent intrinsic magnetic properties. However, these nitrides and carbides have a major drawback, namely their chemical or structural instability at high temperatures. They will completely decompose into  $\alpha$ -Fe and RN(RC). Because of this drawback, it is difficult for the nitrides or carbides to be made into anisotropic permanent magnets by normal techniques.

The author has discovered that Si substitution can elevate the gas-phasereaction temperature from 500°C to 700°C for the carbides and prevent the decomposition of the carbides into  $\alpha$ -Fe and RC. The carbides R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> with R=Nd, Gd and Er and Sm<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>C<sub>y</sub> with x=1, 2 and 3 have been prepared by heating fine-particle powders of their corresponding parents in CH<sub>4</sub> for 2 h at 700°C instead of the usual 500°C. All of these carbides have a high C concentration which is very close to the theoretical value of y=3.

(2) X-ray diffraction shows that the compounds  $R_2Fe_{15}Si_2$  and  $Sm_2Fe_{17-x}Si_xC_y$ have the rhombohedral structure for the light rare-earth compounds and the hexagonal structure for the heavy rare-earths. The carbides  $R_2Fe_{15}Si_2C_y$  and  $R_2Fe_{17-x}Si_xC_y$  retain the same structure as their corresponding parents, except for  $Gd_2Fe_{15}Si_2C_y$  which turns into the rhombohedral structure from the hexagonal structure. As compared to their parents, for  $R_2Fe_{15}Si_2C_y$ , the lattice parameter *a* increases by 2.3-2.7 %, the parameter *c* only increases by 0.2-0.8 %, and the cell volumes expand about 4.8-5.7 %. (3) The Curie temperatures are 496, 571 and 490 K for  $R_2Fe_{15}Si_2$  with R=Nd, Gd and Er, respectively. As compared to their parents, the Curie temperatures of the carbides are elevated by 127, 79 and 130°C, respectively. The Curie temperature of  $Sm_2Fe_{17}$  is rather low, only 410 K. With Si substitution, the Curie temperatures increase at first, reach a maximum of 530 K at x=2 and then decrease at x=3. The Curie temperatures of the carbides are 660, 630 and 595 K with Si concentrations of x=1, 2 and 3, respectively. They are raised by 170, 100 and 70°C, respectively, as compared to their corresponding parents.

Two methods are used to calculate the exchange interaction constants; the results are close. One is based on the values of the Curie temperature and the high-temperature approximation of the mean-field model; the other is based on the temperature dependences of the magnetization and the two-sublattice model. The average exchange interaction constants calculated from the Curie temperatures are  $J_{FeFe}=4.0(3)$  meV and  $J_{FeR}=0.6(2)$  meV for  $R_2Fe_{15}Si_2C_y$  and  $J_{FeFe}=3.1(2)$  meV and  $J_{FeR}=1.0(3)$  meV for the parents. As compared to their parents,  $J_{FeFe}$  for the carbides increases by about 30 %, whereas  $J_{FeR}$  decreases by about 40 %. Hence, an increase in the Curie temperatures of the carbides can be attributed to the enhanced interaction between the Fe-Fe pairs, but not to the interaction between the Fe-R pairs.

(4) The origin of the enhanced exchange interaction between the Fe-Fe pairs for the carbides has been studied based on the negative exchange interaction theory. The exchange integrals as a function of the distance between the Fe-Fe pairs have been obtained by fitting the hyperfine field data at various temperatures for each Fe site in terms of the mean-field theory. The results show that there are two types of exchange interactions; one is a positive interaction when the interatomic distance is larger than 2.45 Å and the other is a negative interaction when Fe atoms are located at a shorter distance. For  $Sm_2Fe_{17}$ , the 6c-6c and 9d-18f pairs have negative interactions. This leads to a rather low Curie temperature for  $R_2Fe_{17}$ . For  $Sm_2Fe_{17}N_y$  the negative integrals between the 6c-6c pairs is weakened and that between the 9d-18f is shifted to a positive value. Hence, the Curie temperature is significantly elevated. When Si atoms replace Fe in  $R_2Fe_{17}$ , Mössbauer spectra show that Si atoms prefer the 18f/12j and 6c/4f sites which leads to a decrease in the negative interaction. Consequently, the Curie temperatures are raised. Based on a model that considers the competition between the positive and negative exchange interactions, the Curie temperatures have been calculated for  $Y_2Fe_{17}N_y$ ,  $Y_2Fe_{17}C_y$ ,  $YTiFe_{11}N_y$ ,  $YTiFe_{11}C_y$ ,  $R_2Fe_{15}Si_2$  with R=Nd,Gd and Er,  $Sm_2Fe_{17-x}Si_x$  with x=0, 0.5, 1, 2 and 3 and  $R_2Fe_{14}Ga_2$  with R=Y, Nd and Sm. The results are very consistent with the experimental values. Hence, the negative interactions play an important role in determining the Curie temperature of the R-Fe compounds, nitrides and carbides.

(5) For aligned samples, the enhancement or disappearance of some characteristic x-ray diffraction lines and the ratio of intensities between the 2nd plus 5th and the 3rd plus 4th lines of the Mössbauer spectrum show that  $R_2Fe_{15}Si_2$  (R=Y, Nd, Sm, Gd and Er) and  $R_2Fe_{15}Si_2C_y$  (R=Nd, Gd and Er) have an easy c-plane anisotropy at room temperature; by contrast, the Sm carbides have an easy c-axis anisotropy. Based on the magnetization curves with the field applied parallel and perpendicular to the alignment direction, the anisotropy fields,  $H_a$ , are estimated to be larger than 140 kOe and 95 kOe at T=77 K and T=300 K, respectively, for  $Sm_2Fe_{16}SiC_y$ . In addition, the anisotropy fields of  $Sm_2Fe_{17-x}Si_xC_y$  decrease with increasing Si concentrations.

Mössbauer spectra of an aligned sample show that  $\text{Er}_2\text{Fe}_{15}\text{Si}_2\text{C}_y$  has an easy c-plane anisotropy at room temperature, whereas it has an easy c-axis anisotropy at T=77 K. The average isomer shifts, the average quadrupole splittings, hyperfine fields on each Fe site and the area ratios between the 2nd plus 5th and the 3rd plus 4th spectrum lines undergo an abrupt change in the interval T=90-100K. This implies that a spin-orientation transition from an easy c-plane to an easy c-axis anisotropy occurs between 90 and 100 K. By fitting the angles between the Fe moment and the c-axis at various temperature with using the two-sublattice model, the second order crystal-field coefficent,  $A_{20}=-180$  Ka<sub>0</sub><sup>2</sup> is obtained.

(6) The saturation magnetizations at room temperature are 22.4, 18.8, 13.5 and 15.8  $\mu B/f.u.$  for R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub> with R=Nd, Sm, Gd and Er, respectively. These values are smaller than 25.4, 24.0, 14.0 and 17.6  $\mu_B/f.u.$  for their corresponding

parents. Mössbauer spectra show that the average hyperfine fields are smaller for the carbides than for the parents. By using the conversion coefficient,  $\beta_F=150$ kOe/ $\mu_B$ , between the hyperfine field and the Fe moment, the Fe moments,  $\mu_{Fe}$ , are found to be about 1.3-1.4  $\mu_B$  for R<sub>2</sub>Fe<sub>15</sub>Si<sub>2</sub>C<sub>y</sub>, and 1.4-1.6  $\mu_B$  for the parents.

Mössbauer spectra further show that for  $R_2Fe_{15}Si_2C_y$  the hyperfine fields on the 6c/4f and 9d/6g sites increase, whereas the fields on the 18f/12j and 18h/12k sites decrease; on average there is a net decrease in the hyperfine field, as compared to their parents. The shortest distances of the C atom to the 6c/4f and 9d/6g sites are about 4.53 and 3.29 Å, respectively. However, the shortest distances to the 18f/12j and 18h/12k sites are only about 1.86 and 1.95 Å, respectively. The short bonds on the 18f/12j and 18h/12k sites lead to hybridizations between the 2p electrons of the C atom and the 3d electrons of the neighboring Fe atom, which may be responsible for the smaller hyperfine fields and the corresponding smaller Fe moments of the carbides.

(7) The saturation magnetizations are almost the same for  $Sm_2Fe_{15}Si_2$  and  $Nd_2Fe_{15}Si_2$ . However, the magnetization is significantly smaller for  $Sm_2Fe_{15}Si_2C_y$  than for  $Nd_2Fe_{15}Si_2C_y$  at T=300 or T=77 K. Based on the values of saturation magnetizations and hyperfine fields, the R moments are calculated; the results show that the Nd moments are positive for either  $Nd_2Fe_{15}Si_2$  or its carbide; the Sm moments are positive for  $Sm_2Fe_{17-x}Si_x$ , but are negative for the their carbides. An antiparallel coupling between the Sm and Fe moments is a strong possibility and leads to a relatively low saturation magnetization for  $Sm_2Fe_{17-x}Si_xC_y$ . This is a major drawback for the carbides  $Sm_2Fe_{17-x}Si_xC_y$ .

(8) For  $\text{Sm}_2\text{Fe}_{16}\text{SiC}_y$ , the Curie temperature is 660 K and the anisotropy field at room temperature is larger than 95 kOe; both are superior to those for  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . The saturation magnetization at room temperature is only 20.7  $\mu_B/\text{f.u.}$ . Further work includes two directions: (1) increase the saturation magnetization of  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  and (2) make  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  into a sintered anisotropic permanent magnet using two methods. One, the powders of  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x\text{C}_y$  after aligning and shaping are sintered at about 700°C. Two, the sintered anisotropic magnets  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x$  are carbonized in CH<sub>4</sub> at 700°C.

# **Bibliography**

Abache C and Oesterreicher H, 1986 J. Appl. Phys. 60 1114.

- Alp E E, Umarji A M, Malik S K and Shenoy G K, 1987 J. Magn. Magn. Mater. 68 305.
- Anagnostou M S, Panagiotopoulos L, Kostikas A, Niarchos D and Zouganelis G, 1994 J. Magn. Magn. Mater. 130 57.
- Andreev A V, Sechovsky V, Kudrevatykh N V, Sigaev S and Tarasov E N, 1988 J. Less-Common Met. 144 L21.
- Andreev A V, Bartashevich M, I, Kudrevatykh N V, Razgonyaev S M, Sigaev S and Tarasov E N, 1990 *Physica B* 167 139.
- Arthur H M, in *Mössbauer Effect Methodology*, Vol.4, ed. Gruverman I J, (Plenum Press, New York), 1968, p75.
- Asch L and Kalvius G M, 1981 Handbook of Spectroscopy vol.3, ed. Robinson J W, (CRC Press, Boca Raton, Florida), p404; p432.
- Atzmony U, Dariel M P, Bauminger E R, LeBenbaum D Nowik I and Ofer S, 1973 Phys. Rev. B 7 4220.
- Belorizky E, Frémy, Gavigan J P, Givord D and Li H S, 1987 J. Appl. Phys. 61 3971.
- Bernas H, Campbell I A and Fruchart F, 1967 J. Phys. Chem. Solids 28 17.
- Beuerle T, Braun P and Fähnle M, 1991 J. Magn. Magn. Mater. 94 L11.
- Beuerle T and Fähnle M, 1992 Phys. Status Solidi B 174 257,
- Brooks M S S, Eriksson O and Johansson B, 1989 J. Phys.: Condens Mater. 1 5861.
- Burzo E, Boltich E B, Huang M G and Wallace W E, 1985 Proceeding of the 8th International Workshop on Rare Earth Magnets and Their Applications, edited by K J Strnat (Dayton University Press, Dayton) p.771.

Buschow K H J, 1971 Phys. Stat. Sol. (a) 7 199.

- Buschow K H J, van Diepen A M and de Wijn H W, 1973 Phys. Rev. B 8 5134.
- Buschow K H J, 1977 Rep. Prog. Phys. 40 1179.
- Buschow K H J and de Mooij D B, 1989, Concerted European Action on Magnets (CEAM), eds Mitchell I V, Coey J M D, Givord D, Harris I R and Hanitsch R (Elsevier, London) p.63.
- Buschow K H J, DeMooij D B, DeWaard K and Jacobs T H, 1990 J. Magn. Magn. Mater. 92 L35.
- Buschow K H J, 1991 Rep. Prog. Phys. 51 1123.
- Cadogan J M, Coey J M D, Gavigan J, Givord D and Li H S, 1988 J. Phys. F: Metal 18 779.
- Cadogan J M, 1989 J. Less-Common Met. 147 L7.
- Cadogan J M, Li H S, Lavis R L, Margarian A, Dunlop J B and Gwan B, 1994a J. Appl. Phys. 75 7114.
- Cadogan J M, Li H S, Margarian A, Dunlop J B, Ryan D H, Collocott S J and Lavis R L, 1994 J. Appl. Phys. 76 6138.
- Callen H B and Callen E, 1966 J. Chem. Solids 27 1271.
- Campbell I A, 1972 J. Phys.F: Metal 2 L47.
- Cao L, Kong L S and Shen B G, 1992 J. Phys.: Condens Mater. 4 L515; 1993 J. Appl. Phys. 73 5887.
- Chappert J, Coey J M D, Lienard A and Rebouillat J P, 1981 J. Phys.F: Metal 11 2727.
- Chen X, Altounian Z and Ryan D H, 1993 J. Magn. Magn. Mater. 125 169.
- Chen X, Ryan D H, Altounian Z and Liao L X, 1993a J. Appl. Phys. 73 6038.
- Ching W Y, HuangM Zand Zhong X F, 1994 J. Appl. Phys. 76 6047.

- Coehoorn R, DeMooij D B, Duchateau J P W B and Buschow K H J, 1988 J de Phys. 49 C8-669.
- Coehoorn R, 1989 Phys. Rev. B 39 13072.
- Coene W, Hakkens F, Jacobs, deMooij D B and Buschow K H J, 1990 J. Less-Common Met. 157 255.
- Coey J M D and Sun H, 1990 J. Magn. Magn. Mater. 87 L251.
- Coey J M D, Lawler J F, Sun H and Allan J E M, 1991 J. Appl. Phys. 69 3007.
- Coey J M D, Sun H, Otani Y and Hurley D P F, 1991 J. Magn. Magn. Mater. 98 76.
- Coey J M D and Hurley D P F, 1992a J. Magn. Magn. Mater. 104-107 1098.
- Coey J M D, 1995 J. Magn. Magn. Mater. 140-144 1041.
- Collins R L and and Travis J C, in *Mössbauer Effect Methodology*, Vol.3, Ed. Gruverman I J, (Plenum Press, New York), 1967.
- Collocott S J, Day R K, Dunlop J B and Davis R L, 1992 Proceedings of the Seventh international Symposium on Magnetic Anisotropy and Coercivity in Rare-Earth Transition Metall Alloys, Canberra, (Rare-earth INformation Center, Ames, IA), p.437.
- Colucci C C, Gama S and Cabral F A O, 1992 IEEE Trans. Magn. 28 2578.
- Croat J J, Herbst J F, Lee R W and Pinkerton F E, 1984 J. Appl. Phys. Lett. 44 148; 1984 J. Appl. Phys. 55 2078.
- Cyrot M and Lavagna M, 1979 J. Phys. (Pairs) 40 763.
- Dariel M P, Atzmony U and Lebenbaum D, 1973 Phys. Status Solidi (b) 59 615.
- DeBore F R, Huang Y K, DeMooij D B and buschow K H J, 1987 J. Less-Common Met. 135 189.

- DeBore F R and Buschow K H J, 1992 Physica B 177 199.
- DeMooij D B and Buschow K H J, 1988 J. Less-Common Met. 142 349.
- Ding J and Rosenberg M, 1991 J. Less-Common Met. 168 335.
- Ding J, Street R, and McCormick P G, 1993 J. Magn. Magn. Mater. bf 115 211
- Ding J, McCormick P G and Street R, 1993 J. Magn. Magn. Mater. 124 1
- Ding J, Liu Y, Street R and McCormick P G, 1994 J. Appl. Phys. 75 1032.
- Dirken M W, Thiel R C, Coehoorn T H, Jacobs T H and Buschow K H J, 1989 J. Less-Common Met. 155 339.
- Dirken M W, Thiel R C, Jacobs T H and Buschow K H J, 1991 J. Magn. Magn. Mater. 94 L15.
- Eckert D, Muller K H, Handstein A, Schneider J, Grossinger R and Krewenka R, 1990 *IEEE Trans. Magn.* MAG-26 1990.
- Fischer H and Gonser U, 1981 Handbook of Spectroscopy vol.3, ed. Robinson J W, (CRC Press,Boca Raton, Florida), p451.
- Endoh M, Lwata M and Toknnaga M, 1991 J. Appl. Phys. 70 6030.
- Franse J J M, Kayzel F E, Marquina C, Radwanski R J and Verhoef R, 1992 J. Alloys Compounds 181 95.
- Frauenfelder H, "Mössbauer Effect", ed. Benjamin W A, New York, 1962.
- Friedt M, Vasquez A, Sanchez J P, L'Héritier P and Fruchart R, 1986 J. Phys. F: Metal 16 651.
- Fruchart D and Miraglia S, 1991 J. Appl. Phys. 69 5578.
- Fruchart P, L'Héritier P, de Réotier P. Dalmas, Fruchart D, Wolfers P, Coey J M D, Ferreira P, Guillen R, Vuliet P and Yaouanc A, 1987 J. Phys. F: Metal 17 483.

- Fuerst C D, Herbst J F and Alson E A, 1986 J. Magn. Magn. Mater. 54-57 567.
- Fuerst C D, Pinkerton F E and Herbst J F, 1994 J. Magn. Magn. Mater. 12 L115; 1994 J. Appl. Phys. 76 6144.
- Gavigan J P, Givord D, Li H S and Voiron J, 1988 Physica B 149 345.
- Givord D, Li H S and de la Bâthie Perrier R, 1984 Solid State Commun. 51 857.
- Gong H Y, Sheng B G, Kong L S Cao L Zhan W S Cheng Z H and Wang F W, 1994 J. Appl. Phys. 76 6711.
- Greenwood N N and Gibb T C, *Mössbauer spectroscopy*, (Chapman and Hall Ltd. London), 1971.
- Grössinger R, Kou X C, Jacobs T H and Buschow K H J, 1991 J. Appl. Phys. 69 5596.
- Gu Z Q, Lai W Y, Zhong X F and Ching W Y, 1993 J. Appl. Phys. 73 6928.
- Gubbens P C M, van Apeldoorn J H F, van der Kraan A M and Buschow K H J, 1974 J. Phys. F: Metal Phys. 4 921.
- Gubbens P C M, van der Kraan A M and Buschow K H J, 1976 Phys. Stat. Sol. (a) 34 729.
- Gubbens P C M, van der Kraan A N and Buschow K H J, 1978 Solid State Commun. 26 107.
- Gubbens P C M, van der Kraan A M, Jacobs T H and Buschow K H J, 1989 J. Magn. Magn. Mater. 80 265.
- Gubbens P C M, van der Kraan A M and Buschow K H J, 1989a *Phys. Rev. B* B39 12548.
- Gubbens P C M, Moolenaar A A, Boender G J, van der Kraan A M, Jacobs T H and Buschow K H J, 1991 J. Magn. Magn. Mater. 97 69.

- Gubbens P C M, Moolenaar A A, Jacobs T H and Bushow K H J, 1992 J. Magn. Magn. Mater. 104-107 1113.
- Gubbens P C M, Moolenaar A A and Bushow K H J, 1994 J Alloys Comp. 203 199.
- Hadjipanayis G C, Hazelton R C and Lawless K R, 1983 J. Appl. Phys. Lett. 43 797; 1984 J. Appl. Phys. 55 2073.
- Haije W G, Spijkerman A, deBoer F R, Bakker K and Buschow K H J, 1990 J. Less-Common Met. 162 285.
- Haije W G, Jacobs T H and Buschow K H J, 1990a J. Less-Common Met. 163 353.
- Helmholdt R B and Buschow K H J, 1989 J. Less-Common Met. 155 15
- Herbst J F, Croat J J, Pinkerton F E and Yelon W B, 1984 Phys. Rev. B 29
  4176. Herbst J F, Croat J J and Yelon W B, 1985 J. Appl. Phys. 57 4086.
- Herbst J F, 1991 Rev. Mod. Phys. 63 819.
- Hirosawa S, Kanekiyo H and Uehara M, 1990 J. Appl. Phys. 73 6488.
- Hu B P, Li H S, Gavigan J P and Coey J M D, 1989 J. Phys.: Condens Mater. 1 755.
- Hu B P, Li H S and Coey J M D, 1989a Hyperfine Interact. 45 233.
- Hu B P, Li H S Gavigan J P and Coey J M D, 1990 Phys. Rev. B 41 2221.
- Hu B P, Li H S, Sun Hong, Lawler J F and Coey J M D, 1990a Solid State Commun. 76 587.
- Hu B P, Li H S, Sun Hong and Coey J M D, 1991 J. Phys.: Condens Mater. 3 3983.
- Hu B P and Liu G C, 1991 Solid State Commun. 79 785.
- Hu B P,Rao X L, Xu J M, Liu G C, Cao F, Dong X L, Li H, Yin L and Zhao Z R, 1992 J. Magn. Magn. Mater. 114 138.

- Hu Z and Yelon W B, 1994 J. Appl. Phys. 76 6147.
- Huang M Q, Zhang L Y, Ma B M, Zhang Y, Elbicki J M, Wallance W E and Sankar S G, 1991 J. Appl. Phys. 70 6027.
- Hurley D P F and Coey J M D, 1991 J. Magn. Magn. Mater. 99 229.
- Hurley D P F and Coey J M D, 1992 J. Phys.: Condens Mater. 4 5573.
- Hutchings M T, 1964 Solid State Phys. 16 227.
- Ibberson R M, Moze O, Jacobs T H and Buschow K H J, 1991 J. Phys.: Condens Mater. 3 1219.
- Isnard O, Soubeyroux J L, Miraglia S, Fruchart D, Garcia L M and and Bartolomé, 1992 *Physica B* 180 624.
- Isnard O, Vulliet P, Blaise A, Sanchez J P, Miraglia S and Fruchart P, 1994 J. Magn. Magn. Mater. 131 83.
- Ivanova G V, Schcherbakova Y V, Belozerov Y V, Yermolen A S and Teytel Y I, 1992 J Alloys Compounds 182 199.
- Jaswal S S, Yelon W B, Hadjipanayis G C, Wang Y Z, and Sellmyer D J, 1991 Phys. Rev. Lett. 67 644.
- Jurczyk M and Wallace W E, 1987 J. Magn. Magn. Mater. 59 L182.
- Jurczyk M, Kowalczyk A and Wrzeciono A, 1987 Phys. Status Solidi A 101 K65.
- Kapusta Cz, Rosenberg M, Zukrowski J, Figiel H, Jacobs T H and Buschow K H J, 1990 J. Less-Common Met. 171 101.
- Kapusta Cz, Rosenberg M, Rau K V, Har Z H, Jacobs T H and Buschow K H J, 1990(a) J. Less-Common Met. 169 L5.
- Kasuya T, 1956 Prog. Theoret. Phys. (Kyoto) 16 45.
- Kato H, Yamada M, Kido G, Nakagawa T, Iriyama T and Kobayashi K 1993 J. Appl. Phys. 73 6931.

- Katter M, Wecker J, Schultz L and Grössinger R, 1990 J. Magn. Magn. Mater. 92 L14.
- Katter M, Wecker J and Schultz L, 1991 J. Appl. Phys. 70 3188.
- Katter M, Wecker J, Schultz L and Grössinger R, 1992 J. Magn. Magn. Mater. 114 35.
- Kong L S, Cao L and Shen B G, 1992 J. Magn. Magn. Mater. 115 L137;
- Kong L S, Cao L, Shen B G, Zhao J G, Gong H Y and Chen Y L, 1993 J Alloys Comp. 196 183.
- Koon N S and Das B N, 1984 J. Appl. Phys. 55 2063.
- Kou X C, Grössinger R, Jacobs T H and Buschow K H J, 1990 J. Magn. Magn. Mater. 88 1.
- Kou X C, Grössinger R, Katter M, Wecker J, Schultz L, Jacobs T H and Buschow K H J, 1991 J. Appl. Phys. 70 2272;
- Kou X C, Grössinger R, Jacobs T H and Buschow K H J, 1991 Physica B 168 181.
- Kuhrt C, Katter M, Wecker J, Schnitzke K and Schultz L, 1992 Appl. Phys. Letters 60 2029.
- Kündig W, 1967 Nucl. Instr. Methods 48 219.
- Koyama K, Mori Y, Asano M, Kamimori T, Tange H and Goto M, 1995 J. Magn. Magn. Mater. 140-144 979.
- Li H S, Zhang Z W and Dang M Z, 1988 J. Magn. Magn. Mater. 75 159.
- Li H S, Hu B P, Cadogan J M, Coey J M D and Gavigan J P, 1990 J. Appl. Phys. 56 868.
- Li H S, Li Y P and Coey J M D, 1990 J. Phys.: Condens Mater. 3 7277; 1991 J. Magn. Magn. Mater. 104-107 1444.

- Li H S and Cadogan J M, 1991 Solid State Commun. 80 905; 1992 J. Magn. Magn. Mater. 103 53; 1992a Solid State Commun. 82 121.
- Li H S and Coey J M D, 1992 J. Magn. Magn. Mater. 115 152.
- Li H S, Cadogan J M, Davis R L, Margarian A and Dunlop J B, 1994 Solid State Commun. 90 487.
- Li H S, Cadogan J M, Hu B P, Shen B G, Wang F H and Zhang W S, 1995 *IEEE* Trans. Magn. MAG-31 3716.
- Li X W, Tang N, Lu Z H, Zhao T Y, Lin W G, Zhao R W and Yang F M, 1993 J. Appl. Phys. 73 5890.
- Li Y P, Li, H S and Coey J M D, 1991 Phys. Status Solidi B 166 K107.
- Li Z W, Zhou X Z, and Morrish A H, 1990 Phys. Rev. B 41 8617.
- Li Z W, Zhou X Z, Morrish A H and Yang Y C, 1990a J. Phys.: Condens Mater. 2 4253
- Li Z W, Zhou X Z and Morrish A H, 1992a J. Phys.: Condens Mater. 4 10409.
- Li Z W, Zhou X Z and Morrish A H, 1992 Hyperfine Interact. 72 111.
- Li Z W, Zhou X Z and Morrish A H, 1993 J. Phys.: Condens Mater. 5 3027.
- Li Z W, Zhou X Z and Morrish A H, 1994 J. Phys.: Condens Mater. 6 L283.
- Li Z W, Zhou X Z and Morrish A H, 1995 Phys. Rev. B 51 2891.
- Li Z W and Morrish A H, 1995a J. Phys.: Condens Mater. 7 6727.
- Li Z W, Zhou X Z and Morrish A H, 1995b J. Magn. Magn. Mater. 150 57.
- Liao L X, Altounian and Ryan D H, 1991 J. Appl. Phys. 70 6006.
- Lin C, Sun Y X, Liu Z X, Jiang H W, Yang J L, Zhang B S and Deng Y F, 1992 Solid State Commun. 81 299

Lindgard P A and Danielsen O, 1975 Phys. Rev. B 11 351.

Liu J F and Luo H L, 1991 J. Magn. Magn. Mater. 94 43.

- Liu J P, Bakker K, DeBore F R, Jacobs T H, DeMooij D B and Buschow K H J, 1991 J. Less-Common Met. 170 109.
- Liu J P, Zeng D C, Tang N, Winkelman A J M, deBore F R and Buschow K H J, 1994 J. Appl. Phys. 75 6247.
- Long G J, Pringle O A, Grandjiean F and Buschow K H J, 1992 J. Appl. Phys. 72 4845.
- Long G J, Pringle O A, Grandjiean F, Yelon W B and Buschow K H J, 1993 J. Appl. Phys. 74 504.
- Manaf A, Buckley R A and Davies H A, 1993 J. Magn. Magn. Mater. 128 302.
- Manaf A, Al-Khafaji M, Zhang P Z, Davies H A, Buckley R A and Rainforth W M, 1993 J. Magn. Magn. Mater. 128 307.
- Marasinghe G K, Ezekwenna P C, James W J, Z Hu and Yelon W B, 41st Annual conference on Magnetism and Magnetic Materials 1996 (to be published).
- Marasinghe G K, Mishra S, Pringle O A, Long G J, Hu Z, Yelon W B Grandjean F, Middleton D P and Buschow K H J, J. Appl. Phys. **76** 6731.
- Malik S K, Sankar S G, Tao V U S and Wallace W E, 1976 *IEEE Trans. Magn.* MAG-12 1003.
- Marquina C, Kayzel F E, Anh T H, Radwanski R J and Franse J J M, 1992 J. Magn. Magn. Mater. 104-107 1323.
- Massalski T B, Binary Alloy Phase Diagrams, (American Society for Metals, Metals Park, OH, 1986) p1064.
- Matsuura Y, Hirosawa, S, Yamamoto H, Fujimura S and Sagawa M, 1985 J. Appl. Phys. Lett. 46 308.

Matthias E, Schneider W and Steffen R M, 1962 Phys. Rev. B 125 261.

- Middleton D P and Buschow K H J, 1994 J Alloys Comp. 203 217.
- Miraglia S, Soubeyroux J L, Kolbeck C, Isnard O, Fruchart D and Guillot M, 1991 J. Less-Common Met. 171 51.
- Mishra R K, Thomas G, Yoneyama T, Fukono A and Ojima T, 1981 J. Appl. Phys. 52 2517.
- Moriya T, Ino H, Fujita F E and Maeda Y, 1968 J. Phys. Soc. Japan 24 60.
- Mössbauer R L, 1958 Z. Physik 151 124; 1958 Naturwissenschaften 45 538.
- Mulder F M, Thiel R C, Coehoorn R, Jacobs T H and Buschow K H J, 1992 J. Magn. Magn. Mater. 117 413.
- Mukai T and Fujimoto K, 1992 J. Magn. Magn. Mater. 103 165.
- Ohno K, Saito T, Shinagawa K and Tsushima T, 1993 *IEEE Trans. Magn.* MAG-29 2854.
- Onodera H, Yamaguchi Y, Sagawa M, Matsuura Y and Yamamoto H, 1984 J. Magn. Magn. Mater. 46 151.
- Otani Y, Moukarika A, H Sun, Coey J M D, Devlin E and Harris I R, 1991 J. Appl. Phys. 69 6735
- Qi Q N, H Sun and Coey J M D, 1991 Hyperfine Interact. 68 27.
- Qi Q N, H Sun, Skomski R and Coey J M D, 1992 Phys. Rev. B B45 12278.
- Pedziwiatr A T, Wallace W E and Burzo E, 1987 *IEEE Trans. Magn.* MAG-23 1795.
- Popov A G, Belozerov E V, Kuchin A G, Ermolenko A S, Makarova G M, Gaviko V S and Khrabrov V I, 1990 *Phys. Status Solidi A* 121 K111.
- Pringle, O A, Long G J, Grandjean F and Buschow K H J, 1992 J. Magn. Magn. Mater. 104-107 1123.

Radwański R J and Franse J J M, 1988 J. Magn. Magn. Mater. 74 43.

- Rosenberg M, Zhou R J, Katter M, Schultz L and Filoti G, 1993 J. Appl. Phys. 73 6035.
- Ruderman M A and Kittel C, 1954 Phys. Rev. 96 99.
- Rudowicz C, 1985 J. Phys. C: Solid State Phys. 18 1415.
- Ryan D H, Altounian Z Strom-Olsen J O and Muir W B, 1989 Phys. Rev. B 39 4730.
- Sagawa M, Fujimura S, Yamamoto H and Matsuure Y, 1984 J. Appl. Phys. 55 2083.
- Sagama M, Hirosawa S, Yamamoto H, Fujimura S and Matsuure Y, 1987 Japan. J. Appl. Phys. 26 1123.
- Shen B G, Kong L S and Cao L, 1992 Solid State Commun. 83 753;
- Shen B G, Wang F W, Kong L S, Cao L and Guo H Q, 1993 J. Magn. Magn. Mater. 127 L267; Shen B G, Kong L S, Wang F W and Cao L, 1993 J. Appl. Phys. Lett. 63 2288. Shen B G, Wang F W, Kong L S, Cao L and Zhan, W S, 1994 J. Appl. Phys. 75 6253.
- Shen B G, Wang F W, Kong L S and Cao L, 1993a J. Phys.: Condens Mater. 5 L685.
- Shimzu M and Inoue J, 1986 J. Magn. Magn. Mater. 54-57 963; 1987 J. Magn. Magn. Mater. 70 61.
- Shirley D A, 1964 Rev. Rod. Phys. 36 339.
- Shoemaker C B, Shoemaker D P and Fruchart R, 1984 Acta Crystallogr. C 40 1665.
- Skomski R and Coey J M D, 1993 J. Appl. Phys. 73 7602.
- Slavic I A, 1976 Nucl. Instr. Methods 134 285. Skomski R, Murray C, Bernnan S and Coey J M D, 1993 J. Appl. Phys. 73 6940.

- Bernnan S, Skomski R, Qi Q N and Coey J M D, 1995 J. Magn. Magn. Mater. 140-144 999.
- Stearns M B 1987 Landolt-Börnstein, New Series Group III, vol.19a (Berlin:Springer) ed Hellwege K H and Madelung O.
- Steiner W and Haferl R, 1997 Phys. Status Solidi A: 42 739.
- Streever R L, 1979 Phys. Rev. B 19 2704.
- Strnat K J ferromagnetic Materials, vol 4, (1986), ed. Wohlfarth E P and Buschow K H J, North-Holland Physics Publishing, p132.
- Sun H, Coey J M D, Otani Y and Hurley D P F, 1990 J. Phys.: Condens Mater. 2 6465.
- Sun H, Hu B P and Coey J M D, 1990a Solid State Commun. 74 727.
- Sun H, Otani Y and Coey J D M, 1992 J. Magn. Magn. Mater. 104-107 1439.
- Sun H, Akayama M, Tatami K and Fujii H, 1992a Physica B 183 33.
- Szpunar B and Kozarzewski, 1977 Phys. Stat. Sol. (b) 82 205.
- Szpunar B, Wallace W E and Szpunar J, 1987 Phys. Rev. B 36 3782
- Tang N, Liu Y L, YU M J, Lu Y, Tegus O, Li Q A, JI S Q and Yang F M, 1992 J. Magn. Magn. Mater. 104-107 1086.
- Tang Z X, Singleton E W and Hadjipanayis G C, 1992 IEEE Trans. Magn. MAG-28 2572.
- Thomas M F and Grace M A, 1964 Phys. Letters 10 306.
- Trooster J M and Viegers M P A, 1981 Handbook of Spectroscopy vol.3, ed. Robinson J W, (CRC Press, Boca Raton, Florida), p465.

Valeanu M, Plugaru N and Burzo E, 1994 Solid State Commun. 89 519.

Van der Woude F, 1966 Phys. Statu Sol. 17 417.

Van Mens R, J. Magn. Magn. Mater. 61 24.

- Van Noort H M, deMooij D B and Buschow K H J, 1985 J. Appl. Phys. 57 5414.
- Van Vleck, 1962 Rev. Mod. Phys. 34 681.
- Vasquez A, Friedt M, Sanchez J P, L'Héritier and Fruchart R, 1985 Solid State Commun. 55 783.
- Verhoef R, deBore F R, Zhang Z D and Buschow K H J, 1988 J. Magn. Magn. Mater. 75 319.
- Verhoef R, DeBoer F R, Franse J J M, Denissen C J M, Jacobs T H and Buschow K H J, 1989 J. Magn. Magn. Mater. 80 41.
- Verhoef R, Radwanski R J and Franse J J M, 1990 J. Magn. Magn. Mater. 89 176.
- Verhoef R, DeBoer F R, Sinnema J J M, Franse J J M, Tomiyama F, Ono M, Date M and Yamagishi A, 1992a *Physica B* 177 223.
- Verhoef R, Quang P H, Radwanski R J, Marquina C and Franse J J M, 1992b J. Magn. Magn. Mater. 104-107 1473.
- Wallace W E, 1968, "Prog. Rare-Earth Sci. and Tech.", vol.III, 1968 p1-37.
- Wang Z and Dunlap R, 1993 J. Phys.: Condens Mater. 5 2047
- Williamson D L, Bukshpan S and Ingalls R, 1972 Phys. Rev. B 6 4194.
- Wolf M, Wirth S, Wendhausen P A P, Eckert D and Müller, 1995 J. Magn. Magn. Mater. 140-144 995.
- Wolfers P, Miraglia S, Fruchart D, Hirosawa S, Sagawa M, Bartolome J and Pannetier J, 1990 J. Less-Common Met. 162 237.
- Woods J P, Fernando A S, Jaswal S S, Pattersor. B M, Welipitiya D and Sellmyer D J, 1993 J. Appl. Phys. 73 6913.

- Xu X and Shaheen S A, 1993 J. Appl. Phys. 73 1892; 5896.
- Xu X and Shaheen S A, 1994 J. Appl. Phys. 76 6754.
- Yamada H and Shimizu M, 1982 J. Phys. F 12 2413.
- Yamada H and Shimizu M, 1986 J. Phys.F: Metal 16 1039.
- Yamada M, Kato H, Yamamoto H and Nakagawa Y, 1988 Phys. Rev. B 38 620.
- Yamada M, Kato H, Ido H and Nakagawa Y, 1995 J. Magn. Magn. Mater. 140-144 867.
- Yan Q W, Zhang P L, Wei Y N, Sun K, Hu B P, Wang Y Z, Liu G C, Gau C and Chen Y F, 1993 Phys. Rev. B 48 2878.
- Yang F M, Li Q N, Lu Y, Tang N, Tegus O, Yu M J, Zhao J G, Shen B G and Yang L Y, 1992 J. Magn. Magn. Mater. 114 255.
- Yang F M, Nasunjilegal B, Pan H Y, Wang J L, Zhao R W, Hu B P, Wang Y Z, Li H S and Cadogan J M, 1994 J. Magn. Magn. Mater. 135 298.
- Yang F M, Tang N, Wang J L, Zhong X P, Zhao R W and Lin W G, 1994a J. Appl. Phys. 75 3241.
- Yang F M, Nasunjilegal B, Wang J L, Zhu J J, Qin W D, Tang N, Zhao R W, Hu B P, Wang Y Z and Li H S, 1995 J. Phys.: Condens Mater. 7 1679.
- Yang Y C, Sun H, Kong L S, Yang J L, Ding Y F, Ye B S, Jin L and Zhou H M, 1988 J. Appl. Phys. 64 5968.
- Yang Y C, Zhang X D, Ge S L, Kong L S, Pan Q, Yang J L, Zhang B S, Ding Y F and Ye C T, 1991 J. Appl. Phys. 70 6001
- Yang Y C, Zhang X D, Kong L S, Pan Q, Ge S L, Yang J L, Ding Y F, Zhang B S, Ye C T and Jin L, 1991a Solid State Commun. 78 313
- Yelon W B and Hadjipanayis G C, 1992 IEEE Trans. Magn. MAG-28 2316.

Yosida K, 1957 Phys. Rev. 106 893.

- Zeng Z, Zheng Q Q, Lai W Y and Pan C Y, 1993 J. Appl. Phys. 73 6916.
- Zhang J X, Shen B G, Yang L Y and Zhan W S, 1990 Phys. Status Solidi A 122 651.
- Zhang Y D, Budnick J I, Shen N X, Hines W A, Fernando G W and Manzur T, 1995 J. Magn. Magn. Mater. 140-144 987.
- Zhao T S, Kou X C, Grössinger R and Kirchmayr H R, 1991 Phys. Rev. B 44 2846.
- Zhao T S, Pang K S, Lee T W and Lee J I, 1995 J. Magn. Magn. Mater. 140-144 989.
- Zhong X P, Radwanski R J, DeBore F R, Jacobs T H and Buschow H K J, 1990 J. Magn. Magn. Mater. 86 333.
- Zhou G F, de Bore D B and Buschow K H J, 1992 Physica B 176 288.
- Zhou R J, Rosenbegr M, Katter M and Schultz L, 1993 J. Magn. Magn. Mater. 118 110.
- Zhou Wei, Qu L J, Zhang Q M and Wang D S, 1989 Phys Rev. B 40 6393.
- Zouganelis, G M, Anagnostou M and Niarchos D, 1992 Solid State Commun. 77 11.