Negative exchange interactions and Curie temperatures for Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$

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Mössbauer spectra of Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$ in a temperature range between 77 K and the Curie temperature have been studied. The exchange integrals, as a function of the distances between the Fe-Fe pairs, have been found by fitting the hyperfine field data at various temperatures for each Fe site. The results show that there exist both positive and negative exchange interactions for Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$. The magnitude of the negative interaction leads to a significant difference in the Curie temperature for the two materials. Based on a model that considers the competition between the positive and negative exchange interactions, the Curie temperatures of some 2:17-type compounds have been calculated; the results agree well with the experimental values. [S0163-1829(97)01106-5]

I. INTRODUCTION

The magnetic 2:17-type compounds possess many interesting properties. One of them is abnormalities in their 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 temperatures.[1–6] In addition, it was recently discovered that when N or C is introduced interstitially into the lattice of R_2Fe_{17} compounds, the Curie temperatures are elevated by about 400 °C.[7,8] The increase in the Curie temperatures is usually attributed to an expansion of the lattice. However, for Si-substituted R_2Fe_{17}, the cell volume actually decreases,[4–6] instead of increasing. Interstitial N or C atoms do not lead to an increase in the Curie temperature for martensite Fe-N and Fe-C alloys. Therefore, the origin of this increase in the Curie temperature for the substituted $R_2(Fe,M)_{17}$ compounds and $R_2Fe_{17}Z_y$ (Z=N or C) is still a problem that remains to be solved.

The above problems involve the magnitude and the sign of the exchange interactions in the 2:17-type compounds. A hypothesis that negative exchange interactions exist for some Fe-Fe pairs in R-Fe compounds was proposed by Givord and Lemaire.[9] Since then, this hypothesis has been extensively used to interpret the abnormalities in Curie temperatures and thermal expansions. For example, Narasimhn *et al.*[10] suggested that the short distances between the $4f$-$4f$ or $6c$-$6c$ Fe atom pairs may lead to a low Curie temperature for the R_2Fe_{17} compounds. Also, Li *et al.*[11] interpreted an increase in the Curie temperature when Si atoms replace Fe in R_2Fe_{17} in terms of a decrease in the negative exchange interactions. However, direct experimental evidence for the negative interaction hypothesis is needed.

It is known that many ways can be used to find the exchange integrals of the Fe-Fe or Fe-R pairs for R-Fe compounds. Based on the high-temperature approximation of the mean-field theory, the exchange integrals J_{FeFe} and J_{FeR} can be obtained from the Curie temperatures.[12] In terms of the two-sublattice model, J_{FeFe}, J_{FeR}, and J_{RR} can be found from the temperature dependence of the saturation

magnetizations.[13] In addition, J_{FeR} can be derived directly from the kinks or the slope of the magnetization curve in the high-field region.[14] However, all these methods only give an average value for the exchange interactions, and not the magnitude and the sign of the interactions for each Fe site.

Mössbauer spectroscopy is a powerful experimental way to study the magnetic properties at each iron site in the R-Fe compounds. In the present paper, Mössbauer spectra in a temperature range of 77 K to the Curie temperature for Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$ are reported and analyzed. The experimental temperature dependences of the hyperfine fields have been used to calculate the magnitude and sign of the exchange integrals between Fe pairs for all the sites. The Fe-Fe exchange integrals as a function of distance between the Fe atoms have also been determined. The exchange integrals so deduced are negative for Fe pairs between the $6c$-$6c$ and $9d$-$18f$ sites of Sm_2Fe_{17}. These results establish the validity of the hypothesis of the negative interactions for some pairs. As far as we know, this is the first time that Mössbauer spectroscopy has been used to obtain the sign and magnitude of the exchange integrals between the Fe-Fe pairs in the R-Fe compounds. In addition, the negative interaction model turns out to be useful for many other R-Fe compounds, such as $R_2Fe_{14}B$, $RTiFe_{11}$, and $R_2(Fe,M)_{17}$.

II. EXPERIMENT

The Sm_2Fe_{17} compound was prepared by arc melting under an Ar atmosphere. The purities of the starting materials were 99.8% Sm and 99.9% Fe. The ingot was remelted three times in order to achieve homogeneity and then was annealed at 1200 K for 4 h. $Sm_2Fe_{17}N_y$ nitride was made by heating the ground fine-particle powders of Sm_2Fe_{17} in a N_2 atmosphere at 480 °C for 1 h. The N concentration was determined to be about $y=2.7$ by weighing.

X-ray diffraction with CuK_α radiation indicated that Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$ are primarily single phases with the Th_2Zn_{17} structure; a small amount of α-Fe is also present. The Curie temperatures were found to be 410 and 740 K for Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$, respectively.

Mössbauer absorbers were made by immobilizing the powdered samples in benzophenone for measurements below

Sm$_2$Fe$_{17}$
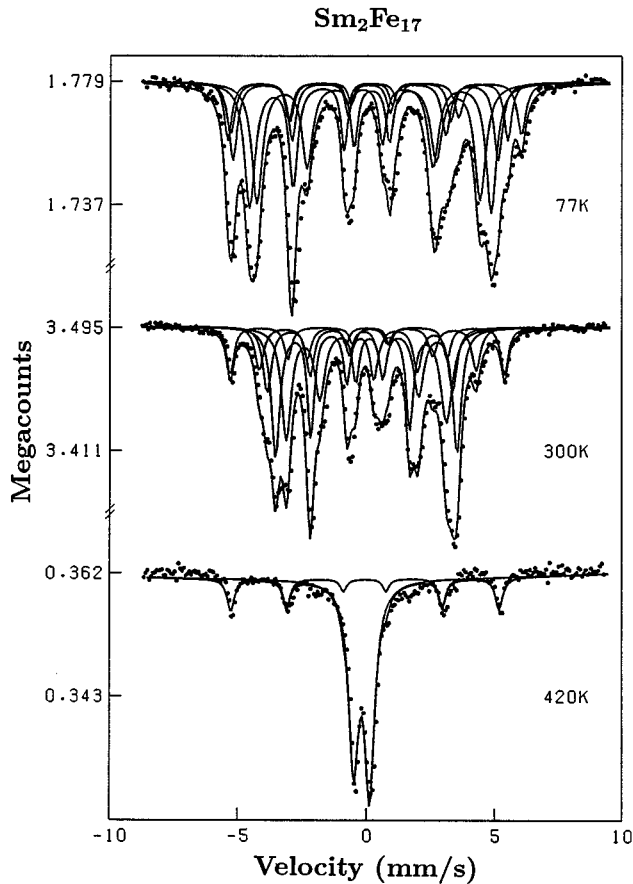

FIG. 1. Mössbauer spectra of Sm$_2$Fe$_{17}$ at $T=77$, 300, and 420 K, as well as the curves for the subspectra obtained by a computer fitting.

Sm$_2$Fe$_{17}$N$_y$

FIG. 2. Mössbauer spectra of Sm$_2$Fe$_{17}$N$_y$ at $T=77$, 300, and 700 K, as well as fitted subspectrum curves.

room temperature and in boron-nitride powders for high temperatures. The absorbers contained about 8 mg/cm^2 of natural iron. ^{57}Fe Mössbauer spectra of Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_y$ were taken between 77 K and the Curie temperature with a conventional constant-acceleration spectrometer. The γ-ray source was ^{57}Co in a Rh matrix. Calibration was made using the spectrum of α-Fe at room temperature. The Mössbauer spectra of Sm$_2$Fe$_{17}$ were fitted with four subspectra, corresponding to the four crystallographically inequivalent Fe sites, the $6c$, $9d$, $18f$, and $18h$ sites, of the Th$_2$Zn$_{17}$ structure. The Mössbauer spectra of Sm$_2$Fe$_{17}$N$_y$ were fitted with five subspectra, with two subspectra assigned to the $9d$ site.[15] Some constraints were used in the fitting procedure. The quadrupole interaction was treated as a perturbation on the magnetic-dipole interaction. The area ratios of the six absorption lines in each subspectrum were assumed to be 3:2:1:1:2:3. The areas ratios amongst the subspectra at various temperatures were kept the same as those at room temperature. In addition, a sextet, corresponding to an α-Fe phase, was incorporated into the fit for both Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_y$; a double-line spectrum appears above room temperature for Sm$_2$Fe$_{17}$N$_y$, which may be attributed to superparamagnetism of the fine particles.[16]

III. RESULTS

Some Mössbauer spectra and computer-fitted subspectra for Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_y$ are shown in Figs. 1 and 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 Sm$_2$Fe$_{17}$ and 10.7:17.8:35.7:35.8=1.8:3.0:6.1:6.1 for Sm$_2$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 has the sequences $H_{hf}(6c)>H_{hf}(9d)>H_{hf}(18f)>H_{hf}(18h)$. The Mössbauer parameters at $T=77$ K from the fittings are listed in Table I.

The average spectrum shifts and quadrupole splittings between 77 K and the Curie temperature are shown in Figs. 3(a) and 3(b), respectively. The average spectrum shifts decrease with increasing temperature for both Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$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$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_y$.

The dependences of the hyperfine fields on temperature are shown in Figs. 4 and 5 for Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_y$, respectively. With increasing temperature, the hyperfine fields decrease at different rates for the four Fe sites. For Sm$_2$Fe$_{17}$ the hyperfine field decreases 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 $T=300$ K
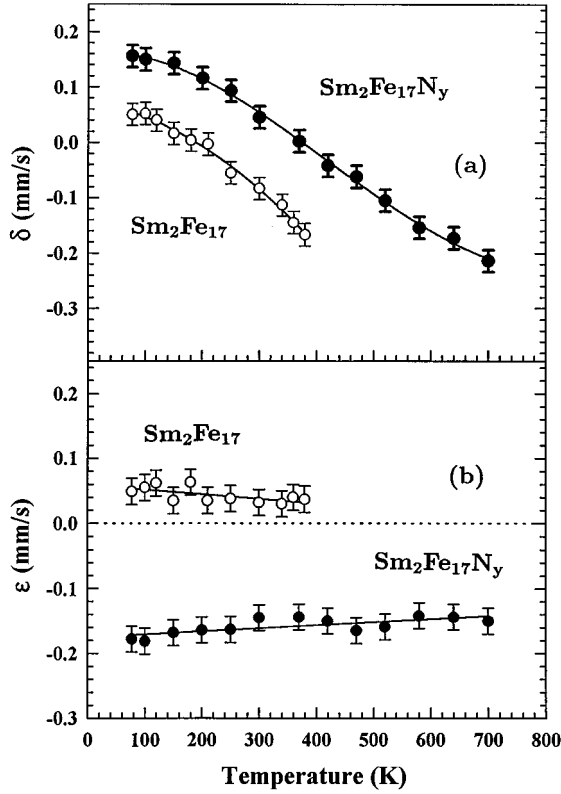
FIG. 3. The dependences of (a) the average spectrum shift, δ, and (b) the average quadrupole splitting, ϵ, on the temperature. The open circles are for Sm_2Fe_{17} and the solid circles are for $Sm_2Fe_{17}N_y$.

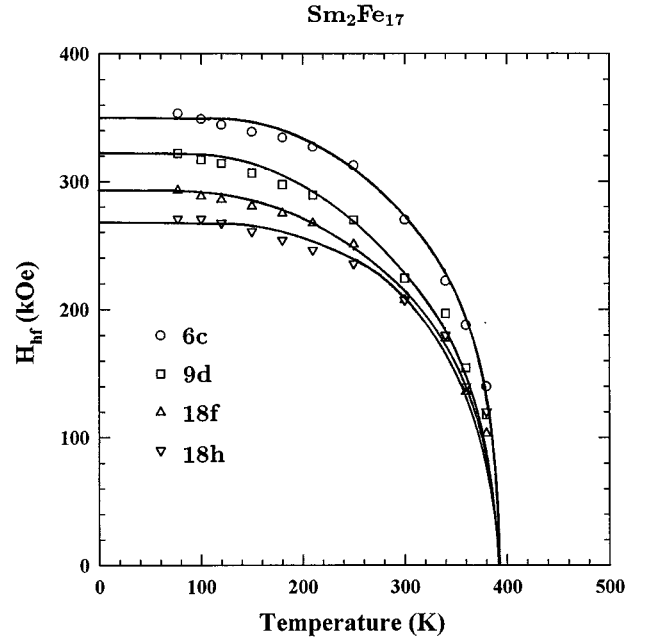

FIG. 4. The dependences of the hyperfine fields, H_{hf}, on the temperature for each Fe site in Sm_2Fe_{17}. The solid lines are the theoretical curves calculated by Eq. (6).

IV. DISCUSSION

A. Exchange interactions

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

$$\mathcal{H} = -2\sum_{i<j} J_{\mathrm{FeFe}}^{ij} \mathbf{S}_{\mathrm{Fe}}^i \cdot \mathbf{S}_{\mathrm{Fe}}^j - 2\sum_{i<j} J_{\mathrm{Fe}R}^{ij} \mathbf{S}_{\mathrm{Fe}}^i \cdot \mathbf{S}_R^j$$

$$= -\sum_{i<j} \mathbf{S}_{\mathrm{Fe}}^i (2J_{\mathrm{FeFe}}^{ij} \langle \mathbf{S}_{\mathrm{Fe}}^j \rangle + J_{\mathrm{Fe}R}^{ij} \langle \mathbf{S}_R^j \rangle) - \sum_{i<j} J_{\mathrm{Fe}R}^{ij} \mathbf{S}_R^i \langle \mathbf{S}_{\mathrm{Fe}}^j \rangle,$$

$$(1)$$

where J_{AB}^{ij} is the exchange integral between the ith A atom and the jth B atom, $\mathbf{S}_A^i$ is the spin operator of the ith A atom, and $\langle \mathbf{S}_{\mathrm{Fe}} \rangle$ and $\langle \mathbf{S}_R \rangle$ are given by

$$\langle \mathbf{S}_{\mathrm{Fe}} \rangle = -\mu_{\mathrm{Fe}}(T)/g_{\mathrm{Fe}}, \qquad (2)$$

$$\langle \mathbf{S}_R \rangle = \langle (g_R - 1)\mathbf{J}_R \rangle = -\gamma\mu_R(T), \qquad (3)$$

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

In Sm_2Fe_{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, $J_{\mathrm{Fe}R}^{ij} = J_{\mathrm{Fe}R}$, and (3) the magnitude of the exchange integrals, J_{FeFe}^{ij}, are related to the distances of Fe-Fe pairs, i.e., the integral of Fe-Fe pairs is the same if their distances are equal or very close.

After substituting Eqs. (2) and (3) into Eq. (1), the Heisenberg Hamiltonians are given by

these lines overlap. For $Sm_2Fe_{17}N_y$ 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 Sec. IV.

TABLE I. Hyperfine parameters of Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$ at 77 K. H_{hf} is the hyperfine field; ϵ is the quadrupole splitting, δ is the spectrum shift, relative to α-Fe at room temperature, and S is the spectral area. The numbers in parentheses are the errors in the last significant digit.

Site	H_{hf} (kOe)	ϵ (mm/s)	δ (mm/s)	S (%)
Sm_2Fe_{17}
$6c$	353(3)	0.07(2)	0.29(2)	11.9(8)
$9d$	322	-0.13	-0.02	17.9(11)
$18f$	293	0.29	-0.04	35.7(23)
$18h$	271	-0.11	0.09	34.5(22)
$Sm_2Fe_{17}N_y$
$6c$	415(3)	$-0.06(2)$	0.28(2)	10.7(10)
$9d$	380	-0.05	0.04	17.8(17)
$18f$	356	-0.26	0.12	35.7(34)
$18h$	313	-0.20	0.21	35.8(34)

Sm$_2$Fe$_{17}$N$_y$
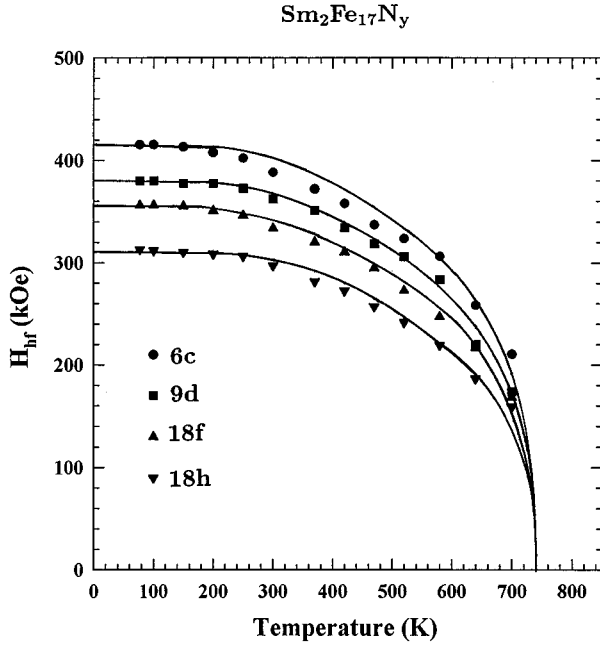

FIG. 5. The dependences of the hyperfine fields, H_{hf}, on the temperature for each Fe site of Sm$_2$Fe$_{17}$N$_y$. The solid lines are the theoretical curves calculated by Eq. (6).

$$\mathcal{H}^i_{Fe} = -\mathbf{S}^i_{Fe}\left(\sum_j 2J^{ij}_{FeFe}Z^{ij}_{FeFe}\mu^j_{Fe}(T)/g_{Fe} + J_{FeR}Z^i_{RFe}\gamma\mu_R(T)\right), \quad (4)$$

$$\mathcal{H}_R = -\mathbf{S}_R J_{RFe}\sum_j Z^j_{FeR}\mu^j_{Fe}(T)/g_{Fe}, \quad (5)$$

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

The magnetic moments (or hyperfine fields) of Fe and R can be expressed as a Brillouin function, B_S, with $S=1$ for Fe and $S=5/2$ for Sm, respectively,

$$H^i_{hf}(T) = H^i_{hf}(0)B_S\left[\frac{S_{Fe}}{k_BT}\left(\sum_j 2J^{ij}_{FeFe}Z^{ij}_{FeFe}\beta H^j_{hf}(T)\right)\middle/ g_{Fe}\right.$$
$$\left. - J_{FeR}Z^i_{RFe}\gamma\mu_R(T)\right], \quad (6)$$

$$\mu_R(T) = \mu_R(0)B_S\left(\frac{S_R}{k_BT}J_{RFe}\sum_j Z^j_{FeR}\mu^j_{Fe}(T)/g_{Fe}\right), \quad (7)$$

where $\beta = 1/150\mu_B/\text{kOe}$ is the proportionality coefficient between an Fe magnetic moment and its hyperfine field. $H^i_{hf}(0)$ are taken as H^i_{hf} (77 K) and $\mu_R(0)$ as $1.6\mu_B$.

Based on Eqs. (6) and (7), the exchange integrals, J^{ij}_{FeFe}, of the Fe-Fe pairs can be found. First of all, the numbers of adjacent atoms, Z^{ij}_{FeFe} and Z^i_{FeR}, and their interatomic distances are listed in Table II. Because no exact determination of the parameters of the atomic positions could be found for Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_y$ in the literature, the atomic positions[17] for Nd$_2$Fe$_{17}$ and Nd$_2$Fe$_{17}$N$_y$ were used instead to calculate the interatomic distances. However, the lattice parameters for Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_y$ were used.

Second, the values of $J_{RFe}(=J_{FeR})$ are calculated to be 16.6 and 16.3 K for Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_y$, respectively, based on the Curie temperatures, T_R and T_Y, of Sm and Y compounds and the formula

$$J_{FeR} = \frac{3}{2}k_B$$
$$\times\sqrt{\frac{T_R(T_R-T_Y)}{\langle Z_{RFe}\rangle\langle Z_{FeR}\rangle S_{Fe}(S_{Fe}+1)(g_R-1)^2 J_R(J_R+1)}}, \quad (8)$$

where $\langle Z_{RFe}\rangle = 6$ is the number of neighboring Fe atoms for a given R atom and $\langle Z_{FeR}\rangle = 5.41$ is the number of neighboring R atoms for a given Fe atom.

Then, the values of $\mu_R(T)$ are found from Eq. (7). Finally, a nonlinear least-squares method is applied to Eq. (6), where the exchange integrals, J^{ij}_{FeFe}, are the fitted parameters. By iteration a set of optimum exchange integrals is

TABLE II. The interatomic distances (in Å) and the numbers of adjacent atoms for each site.

Site	6c	9d	18f	18h		R	
			Sm$_2$Fe$_{17}$				
6c	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	
18f	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	2.467×2	2.553×2	2.508×2	3.085×1	3.203×1	3.255×1
			2.657×2		4.877×2		
			Sm$_2$Fe$_{17}$N$_y$				
6c	2.427×1	2.674×3	2.760×6	2.620×3	3.065×1	5.170×3	5.200×3
9d	2.674×2		2.473×4	2.469×4	3.327×2	4.875×4	
18f	2.760×2	2.473×2	2.479×2	2.583×2	3.148×2	4.945×2	5.312×1
				2.724×2			
18h	2.620×1	2.469×2	2.583×2	2.650×2	3.147×1	3.246×1	3.423×1
			2.724×2		4.939×2		

TABLE III. The fitted exchange integrals, J_{FeFe}, and the interatomic distances, d.

				Sm_2Fe_{17}					
			$18f\text{-}18f$			$6c\text{-}18h$		
Fe-Fe pair	$6c\text{-}6c$	$9d\text{-}18f$	$9d\text{-}18h$	$18h\text{-}18h$	$18f\text{-}18f$	$18f\text{-}18f$	$18f\text{-}18h$	$6c\text{-}18f$
d (Å)	2.392	2.438	2.467	2.508	2.553	2.625	2.657	2.742
J_{FeFe} (K)	$-201(19)$	$-20(5)$	31(5)	29(17)	58(5)	78(9)	53(7)	16(4)

				$Sm_2Fe_{17}N_y$				
		$9d\text{-}18f,9d\text{-}18h$						
Fe-Fe pair	$6c\text{-}6c$	$18f\text{-}18f$	$18f\text{-}18h$	$6c\text{-}18h$	$18h\text{-}18h$	$6c\text{-}9d$	$18f\text{-}18h$	$6c\text{-}18f$
d (Å)	2.427	2.469–2.479	2.583	2.620	2.650	2.674	2.724	2.760
J_{FeFe} (K)	$-49(7)$	39(4)	44(6)	65(8)	53(9)	45(13)	26(5)	22(4)

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 III. By substituting the fitted J_{FeFe}^{ij} into Eq. (6), the hyperfine fields for each Fe site as a function of temperatures are calculated; the results are shown by the solid curves of Figs. 4 and 5. 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. 6. The two sets of data (for $Sm_2Fe_{17}N_y$ and $Sm_2Fe_{17}N_y$) 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 Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$. 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; 4 of 10 pairs of the $9d$ atoms associated with its neighboring Fe atoms, 2 of 10 pairs of the $18f$ atoms and 1 of 13 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.

The exchange integrals for $Sm_2Fe_{17}N_y$ are different in two significant ways as compared to Sm_2Fe_{17}. First, the exchange integrals are elevated to $J = -49$ K from $J = -201$ K for the $6c\text{-}6c$ sites and second, the negative exchange interaction is turned into a positive one for the $9d\text{-}18f$ site. Consequently, with increasing temperature the hyperfine fields decrease most rapidly for the $6c$ site; more importantly, the Curie temperatures are greatly elevated for $Sm_2Fe_{17}N_y$.

B. Curie temperatures

1. Y-Fe compounds and their nitrides and carbides

Gavigan et al.[18] state that the mean local Fe coordination numbers play an important role in determining the Curie temperatures for R-Fe 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 IV, 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.

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 distances 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 distance, the interactions are positive. Then, based on Fig. 6 the positive exchange integral is taken as $J_+ = 55$ K on the average and the negative exchange integral is taken as $J_- = -115$ K. Finally, for Y-Fe com-
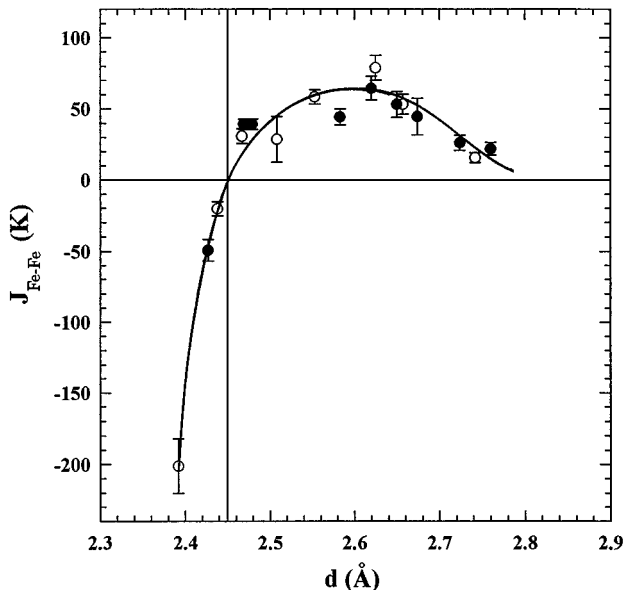

FIG. 6. The exchange integrals, J_{FeFe}, as a function of the distances between the Fe-Fe pairs. The open circles are for Sm_2Fe_{17} and the solid circles are for $Sm_2Fe_{17}N_y$.

TABLE IV. The Curie temperatures calculated from Eqs. (9)–(11) for some Y-Fe compounds and their nitrides and carbides. ($J_+ = 55$ K and $J_- = -115$ K.)

	Z	Z_-	$d_{\text{Fe-Fe}}$ (Å)	T_+ (K)	T_- (K)	T_f^{calc} (K)	T_f^{expt} (K)
Y_2Fe_{17}	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
$YFe_{11}Ti$	9.96	0.92	2.61	730	-208	522	524
$YFe_{11}TiN_y$	9.96	0.25	2.63	730	-57	673	713
$YFe_{11}TiC_y$	9.96	0.25	2.63	730	-57	673	708
$Y_2Fe_{14}B$	9.64	0.71	2.58	707	-162	545	571

pounds, mean-field theory gives the Curie temperatures as

$$T_f = \frac{2S_{\text{Fe}}(S_{\text{Fe}}+1)}{3}(Z_+J_+ + Z_-J_-)$$

$$= \frac{2S_{\text{Fe}}(S_{\text{Fe}}+1)}{3}[ZJ_+ + Z_-(J_- - J_+)]$$

$$= T_+ + T_- , \tag{9}$$

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 Eq. (9),

$$T_+ = \frac{2S_{\text{Fe}}(S_{\text{Fe}}+1)}{3}ZJ_+ , \tag{10}$$

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.

The second term,

$$T_- = \frac{2S_{\text{Fe}}(S_{\text{Fe}}+1)}{3}Z_-(J_- - J_+), \tag{11}$$

is the contribution of the negative interactions on 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 $J_- - J_+ = -170$ K, the values of T_- found from Eq. (11) are also listed in Table IV. For Y_2Fe_{17}, $Z_- = 1.53$ and $T_- = -346$ K, however, for $Y_2Fe_{17}N_y$ and $Y_2Fe_{17}C_y$, $Z_- = 0.12$ 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}. Consequently, 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 Eqs. (9)–(11), with $J_+ = 55$ K, $J_- = -115$ K and the parameters, Z and Z_-, listed in Table IV. The calculated Curie temperatures, T_f^{calc} agree well with the experimental data, as shown in Table IV.

2. Si-substituted 2:17-type compounds

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 Eq. (9), therefore, can be expressed as

$$T_+ = T_0(1 - \alpha x), \tag{12}$$

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 α is a coefficient. In addition, the contribution of the R-Fe interaction on the Curie temperatures, $T_{R\text{-Fe}}$, should be considered. Hence, for $R_2Fe_{15}Si_2$, the Curie temperatures, T_f^{calc}, are given by

$$T_f^{\text{calc}} = T_0(1 - \alpha x) + \frac{2S_{\text{Fe}}(S_{\text{Fe}}+1)}{3}Z_-(J_- - J_+) + T_{R\text{-Fe}}, \tag{13}$$

where the value of α is taken as 0.016 for Si,[11] the values of Z_- are derived from the areas of the Mössbauer subspectra, and the values of $T_{R\text{-Fe}}$ are obtained from the Curie temperature of R_2Fe_{17} minus that of Y_2Fe_{17}. The calculated Curie temperatures are listed in Table V; they are close to the experimental data.

For $Er_2Fe_{17-x}Si_x$, a negative value of $T_{\text{Fe-}R}$ is unreasonable. However, if the value of $T_{\text{Fe-}R}$ is derived from the Curie temperatures of Er_2Fe_{17} and Lu_2Fe_{17} (268 K), one obtains

TABLE V. The Curie temperatures calculated by Eq. (13) with $\alpha = 0.016$ and $T_0 = 733$ K for $R_2Fe_{17-x}Si_x$ (R=Y,Nd,Sm,Gd,Er). (The value of $T_{R\text{-Fe}}$ with the superscript is deduced from the Curie temperatures of Er_2Fe_{17} and Lu_2Fe_{17} and the corresponding T_f^{calc} is also marked with the superscript.)

R	Z_-	T_+ (K)	T_- (K)	$T_{\text{Fe-}R}$ (K)	T_f^{calc} (K)	T_f^{expt} (K)
Y	1.13	710	-255	0	455	490
Nd	1.18	710	-268	3	445	500
Sm	1.21	710	-274	86	522	530
Gd	1.12	710	-255	149	604	570
Er	1.19	710	-269	$-19,37^*$	$422,478^*$	480

TABLE VI. The Curie temperatures calculated by Eq. (13) with $\alpha=0.016$ and $T_0=733$ K for $Sm_2Fe_{17-x}Si_x$.

x	Z_-	T_+ (K)	T_- (K)	T_{Fe-Sm} (K)	T_f^{calc} (K)	T_f^{expt} (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

$T_{Fe-R}=37$ K and $T_f^{calc}=478$ K; this latter value agrees very well with the experimental value of 490 K. It has been shown that the dependences of the Curie temperatures on $\sqrt{G}$ $[G=(g-1)^2J(J+1)]$ 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 Ref. 13). Therefore, it is reasonable to obtain the value of T_{Fe-R} from the Curie temperatures of Er_2Fe_{17} and Lu_2Fe_{17}.

The Curie temperatures of $Sm_2Fe_{17-x}Si_x$ ($x=0$, 0.5, 1, 2, and 3) have been calculated on the basis of Eq. (13) with $T_0=733$ K, $\alpha=0.016$, $T_{Fe-Sm}=86$ K, and the values of Z_- taken from Ref. 11. The calculated results, as shown in Table VI, replicate the characteristics of the experimental data, which increase at first, reach a maximum at $x=2$, and then decrease with Si substitutions.

V. 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 be-tween the Fe-Fe pairs, have been deduced by fitting the Mössbauer hyperfine field data at various temperatures for each Fe site. The results show that there are positive and negative exchange interactions in 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. These results establish that the hypothesis of negative interactions in the 2:17-type compounds is valid.

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 into a positive interaction. When Si atoms replace Fe in R_2Fe_{17}, Si atoms prefer the $18f/12j$ and $6c/4f$ sites[11] which leads to a decrease in the negative interactions. Hence, the elevation of the Curie temperature for $Sm_2Fe_{17}N_y$ and $R_2(Fe,Si)_{17}$ is identified with the negative exchange interactions, a microscopic origin, instead of a volume effect, a macroscopic origin, as concluded in many earlier investigations.

The negative interaction model is useful in predicting the Curie temperatures for many R-Fe compounds, such as $Y_2Fe_{14}B$, $YTiFe_{11}$, and $R_2(Fe,Si)_{17}$. The Curie temperatures calculated by this model are consistent with the experimental data.

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