

A Mössbauer spectral study of $\text{Nd}_6\text{Fe}_{13}\text{X}$, where X is Cu, Ag, and Au and of the spin reorientation in $\text{Nd}_6\text{Fe}_{13}\text{Si}$

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The Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{X}$, where X is Si, Cu, Ag, and Au, have been measured between 80 and 500 K. A model corresponding to a basal alignment of the magnetic moments leads to excellent, internally consistent, fits for the Cu, Ag, and Au compounds. The resulting temperature dependences of the spectral hyperfine parameters are uniform and reveal for each Fe site the expected correlations between the isomer shift and the Wigner-Seitz cell volume and the hyperfine field and the number of Fe near neighbors. For $\text{Nd}_6\text{Fe}_{13}\text{Si}$, a different model must be used because of the presence of a spin reorientation below 155 K. Above 155 K, because of the axial alignment of the moments, and in agreement with the 295 K powder neutron diffraction results, the spectra can be analyzed with four sextets. Below 155 K, five additional sextets are required to fit the spectra because of a progressive transition towards a basal alignment of the Fe moments. At 80 K the mixed magnetic phase is 75% basal and 25% axial, whereas at 110 K the mixture is 50:50. The hyperfine parameters of the basal and axial sextets found for $\text{Nd}_6\text{Fe}_{13}\text{Si}$ are consistent with those found for the basal Cu, Ag, and Au compounds and those observed for basal $\text{Nd}_6\text{Fe}_{13}\text{Sn}$. The lattice properties of the compounds, obtained from the temperature dependences of the isomer shift and the spectral absorption area, are consistent with the Wigner-Seitz cell volumes and the bonding of each crystallographically distinct Fe site. The magnetic anisotropy of a variety of $\text{Nd}_6\text{Fe}_{13}\text{X}$ compounds is controlled by the *s-p* hybridization of the Nd-X bonds, a hybridization which is very sensitive to the electronic configuration of X. © 1998 American Institute of Physics.

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I. INTRODUCTION

In the search for magnetic materials suitable for hard permanent magnet applications, the ternary rare-earth-iron-metal systems have been systematically investigated and a new phase, $\text{R}_6\text{Fe}_{13}\text{X}$, where R is a light rare-earth and X is a metametal, such as Si and Ge, has recently been identified.^{1,2} The compounds studied herein, where R is Nd and X is Si, Cu, Ag, and Au, crystallize in the tetragonal *14/mcm* $\text{Nd}_6\text{Fe}_{13}\text{Si}$ structure^{3,4} which may be envisioned³ as a succession of layers perpendicular to the tetragonal *c*-axis, with the sequence, C, B, A_1 , S, A_2 , B, forming one-half of the unit cell. Layer C contains Fe on the *16k* and *4d* sites, layer B contains Fe on the *16l*₁ and *16l*₂ sites and Nd on the *8f* site, layers A_1 and A_2 contain Nd on the *16l* site, and layer S contains X on the *4a* site. Hence, the Fe atoms occupy the *4d*, *16k*, *16l*₁, and *16l*₂ crystallographic sites, with 12, 10, 9, and 7 iron near neighbors, respectively, sites which have no X near-neighbors.

The magnetic properties of the $\text{Nd}_6\text{Fe}_{13}\text{X}$ compounds have been investigated³⁻⁹ by several groups. $\text{Nd}_6\text{Fe}_{13}\text{Si}$ was first³ reported to be antiferromagnetic with a Néel temperature, T_N , of 725 K, but subsequently was found⁵ to be ferromagnetic with a Curie temperature, T_C , of 441 K and a compensation temperature of 357 K. A complex noncollinear ferrimagnetic structure, with a T_C first⁶ of 463 K and

subsequently⁴ of 335 K, was found for $\text{Nd}_6\text{Fe}_{13}\text{Cu}$. A T_C of 340 K was found⁴ for $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ and $\text{Nd}_6\text{Fe}_{13}\text{Au}$. However, recent measurements on $\text{Nd}_6\text{Fe}_{13}\text{Au}$ found⁷ it to be antiferromagnetic with a T_N of 408 K. These conflicting magnetic results are most likely due to traces of ferromagnetic $\text{Nd}_2\text{Fe}_{17}$ impurity.

The magnetic structure of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ has been studied⁵ by neutron diffraction at 295 K and the reported lattice parameters agree reasonably well with those obtained from x-ray diffraction.³ At 295 K the Fe and Nd magnetic moments are parallel to the tetragonal *c*-axis with an antiferromagnetic coupling between the Fe magnetic moments, i.e., the *4d* and *16l*₂ moments are up whereas the *16k* and *16l*₁ moments are down. Further, there is a ferromagnetic coupling between the Fe *4d* and *16l*₂ moments and the Nd moments. The accuracy of the Fe magnetic moments of 1.3, 0.9, 0.5, and 0.8 μ_B , for the *4d*, *16k*, *16l*₁, and *16l*₂ sites, respectively, is low because the magnetic contribution to the total neutron scattering is small. The smallest moment of 0.5 μ_B , assigned to the *16l*₁ site, does not agree with the smallest hyperfine field which is assigned^{4,7-11} to the *16l*₂ site in the Mössbauer spectra of related $\text{Nd}_6\text{Fe}_{13}\text{X}$ compounds. This disagreement cannot be explained as the result of an incorrect assignment of the *16l*₁ and *16l*₂ sextets in the Mössbauer spectra, as was suggested by Yan *et al.*⁵ and will be discussed below.

Because of the unusual spin reorientation observed⁸ in $\text{Nd}_6\text{Fe}_{13}\text{Si}$, it is essential to have a good understanding of the Mössbauer spectra of the various $\text{Nd}_6\text{Fe}_{13}\text{X}$ compounds, where X is Cu, Ag, and Au. Further, in view of the controversial magnetic behavior³⁻⁷ of the $\text{Nd}_6\text{Fe}_{13}\text{X}$ compounds, and the conflicts present in previous Mössbauer spectral studies,^{4,6,10,11} we have extended our earlier studies^{7,8} to some additional compounds and to a wider range of temperatures.

II. EXPERIMENT

The samples of $\text{Nd}_6\text{Fe}_{13}\text{X}$, where X is Si, Cu, Ag, and Au, were prepared by arc melting starting materials of at least 99.9% purity. After arc melting the samples were wrapped in tantalum foil, sealed in an evacuated quartz tube, annealed for four weeks at 900 K, and quenched to room temperature. The x-ray diffraction patterns indicated that all the annealed samples crystallized in the tetragonal $\text{Nd}_6\text{Fe}_{13}\text{Si}$ structure.³ The likely impurity in these samples is $\text{Nd}_2\text{Fe}_{17}$, whose x-ray diffraction pattern is very difficult to detect when it overlaps with the complex $\text{Nd}_6\text{Fe}_{13}\text{Si}$ pattern. Hence, the presence of $\text{Nd}_2\text{Fe}_{17}$ was not detected in the x-ray diffraction patterns, but the Mössbauer spectra discussed in Sec. III and the magnetization data discussed in Sec. IV indicate that $\sim 10\%$ of $\text{Nd}_2\text{Fe}_{17}$ are present in $\text{Nd}_6\text{Fe}_{13}\text{Si}$.

The Mössbauer spectra were obtained between 85 and 500 K on a constant acceleration spectrometer which utilized a room temperature rhodium matrix cobalt-57 source and was calibrated at room temperature with α -iron foil. The Mössbauer spectral absorbers, which contained 26 to 29 mg/cm^2 of compound, were prepared from pieces of samples pulverized under liquid toluene and sieved to particle diameters of approximately 0.045 mm or smaller. The Mössbauer spectra above room temperature were measured under vacuum. The accuracy of the hyperfine parameters obtained from Lorentzian lineshape fits is estimated to be ± 0.005 mm/s for the isomer shift, ± 0.05 mm/s for the quadrupole shift, and ± 2 kOe for the hyperfine field. Variations of the hyperfine parameters within these limits lead to minor and insignificant increases in MISFIT,¹² which is of the order of 0.5% for all fits reported herein.

The temperature dependence of the magnetization of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ was measured in a field of 0.1 T on a locally built magnetometer based on the Faraday method.

III. MÖSSBAUER SPECTRA

There have been several earlier Mössbauer studies of $\text{Nd}_6\text{Fe}_{13}\text{X}$, where X is Cu,⁶ Ag,^{4,9} Au,^{4,7} Ge,¹⁰ In,¹¹ Tl,¹¹ Sn,^{9,11} and Pb.¹¹ The spectra have been analyzed in terms of two basic models, with either four sextets, with relative areas in the ratio 4:16:16:16 assigned to the four, $4d$, $16k$, $16l_1$, and $16l_2$, crystallographically inequivalent Fe sites, or five sextets, with relative areas in the ratio 4:8:8:16:16 assigned to the five, $4d$, $16k$, $16k'$, $16l_1$, and $16l_2$, magnetically inequivalent Fe sites. The four sextet model can be applied to the spectra^{9,11} of $\text{Nd}_6\text{Fe}_{13}\text{Sn}$, which shows a uniaxial c -axis magnetization. The five sextet model can be applied to the spectra of $\text{Nd}_6\text{Fe}_{13}\text{X}$, where X is Ag,^{4,9} Au,^{4,7} In,¹¹ Tl,¹¹ and

Pb.¹¹ Because the latter compounds have a basal orientation of the magnetization, the dipolar contribution to the field at the Fe $16k$ site removes the magnetic degeneracy of this site and two sextets of equal areas, herein labelled $16k$ and $16k'$, are observed. The fits of the spectra^{6,10} of $\text{Nd}_6\text{Fe}_{13}\text{Cu}$ and $\text{Nd}_6\text{Fe}_{13}\text{Ge}$ with four sextets are, at best, only first order approximations, because, as indicated by the authors,^{6,10} both of these compounds present complex noncollinear magnetic structures in which the spins are not oriented along the c -axis.

There are some common features in the models and the assignment of the Mössbauer spectral sextets reported by different authors.^{4,6,7,9,11} The assignment to the $4d$ site of the sextet with the smallest relative area and the largest hyperfine field is obvious on the basis of its crystallographic degeneracy and its highest number of Fe near neighbors. In the four sextet model, the assignment of the three sextets with the same relative area is based on the relationship between the hyperfine field and the number of Fe near neighbors for a given site, i.e., the hyperfine fields are assigned in the sequence $16k > 16l_1 > 16l_2$. In the five sextet model, the assignment to the $16k$ and $16k'$ sites of the two sextets with relative area of eight is straightforward and the remaining two sextets of relative area 16 are assigned to the $16l_1$ and $16l_2$ sites on the same basis as in the four sextet model. In contrast, there are more variations in the hyperfine parameters, particularly the isomer shifts, obtained^{4,7,9} for $\text{Nd}_6\text{Fe}_{13}\text{Au}$ and $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ with the five sextet model. Indeed, the isomer shifts reported⁴ for the two magnetically inequivalent but crystallographically equivalent $16k$ and $16k'$ sites differ by 0.01 and 0.04 mm/s, respectively, a difference which is physically unreasonable. In contrast, in the fits⁸ of $\text{Nd}_6\text{Fe}_{13}\text{Au}$, the isomer shifts of the $16k$ and $16k'$ sites have been constrained to be equal. Furthermore, as noted by Weitzer *et al.*⁴ their isomer shifts for $\text{Nd}_6\text{Fe}_{13}\text{Au}$ and $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ do not follow the usual relation between hyperfine field and isomer shift, i.e., a larger hyperfine field is accompanied by a more negative isomer shift. Finally, the isomer shifts reported earlier⁴ do not correlate with the Wigner-Seitz volumes of the four crystallographic sites, a correlation which holds^{12,13} for many related rare-earth Fe compounds. These difficulties are not present with the set of hyperfine parameters discussed in detail below.

A. Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{X}$, where X is Cu, Ag, and Au

The Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Cu}$ and $\text{Nd}_6\text{Fe}_{13}\text{Au}$, obtained at several temperatures, are shown in Figs. 1 and 2. The spectra of $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ are virtually identical to those of $\text{Nd}_6\text{Fe}_{13}\text{Cu}$ and are not shown. All these spectra have been analyzed with a five sextet model, indicating^{4,9} that the Fe magnetic moments are oriented in the basal plane of the tetragonal unit cell. The isomer shifts of the $16k$ and $16k'$ sites were constrained to be equal, a constraint which was not imposed in earlier work.⁴ In our initial⁸ 16 parameter fits of $\text{Nd}_6\text{Fe}_{13}\text{Au}$, the relative areas of the five sextets were constrained to the magnetic degeneracies of the Fe sites, i.e., 4:8:8:16:16, and no effect of texture was introduced. In the fits shown in Figs. 1 and 2 the effect of texture, which is

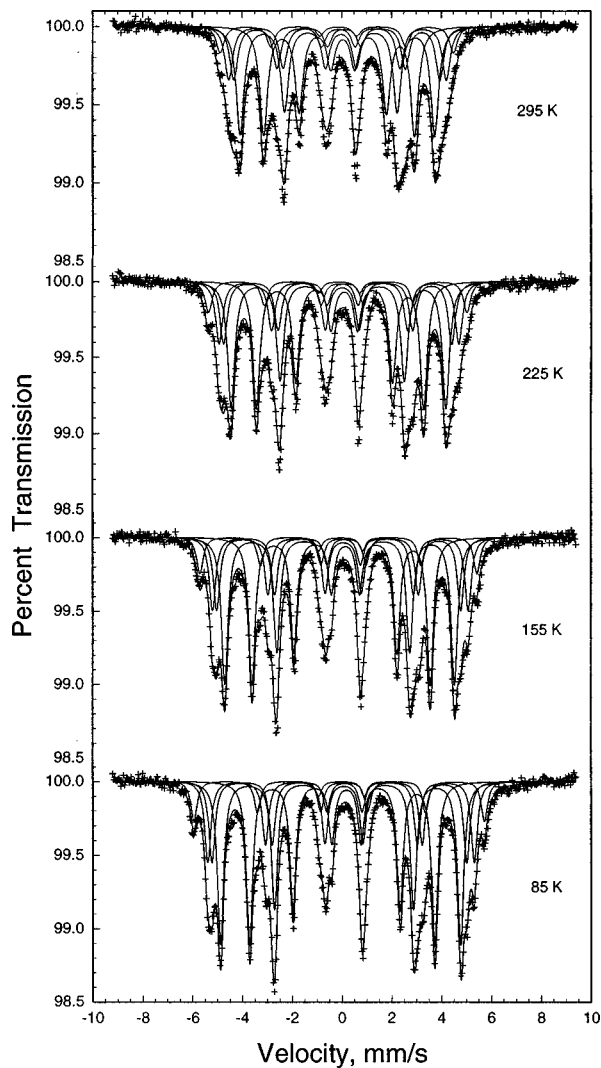


FIG. 1. The Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Cu}$ obtained at the indicated temperatures.

clearly visible⁸ in the large relative areas of the second and fifth lines, was included as the variable x in the ratio of the relative component areas, $3:x:1:1:x:3$, in each of the five sextets. Further, the relative areas of the five sextets were adjusted, with the constraint that the area of the $16k$ and $16k'$ sextets were equal. The additional number of adjustable parameters was four, i.e., three relative absorption areas and one texture parameter, for a total of 20 adjustable parameters. Of those 20 parameters, at most ten were simultaneously adjusted. The fits obtained under these conditions are excellent, as is shown in Figs. 1 and 2, and the corresponding 295 and 85 K hyperfine parameters are summarized in Table I. The complete details of these fits will be published separately.

For $\text{Nd}_6\text{Fe}_{13}\text{Cu}$, the relative areas of the five sextets do not significantly depart from the relative magnetically inequivalent Fe site degeneracies, i.e., 4:8:8:16:16. For $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ and $\text{Nd}_6\text{Fe}_{13}\text{Au}$, the relative areas of the five sextets depart by at most 3% from this theoretical ratio. The difference between experimental and theoretical values increases as the temperature increases from 85 to 295 K. This increase results from the inequivalent temperature depen-

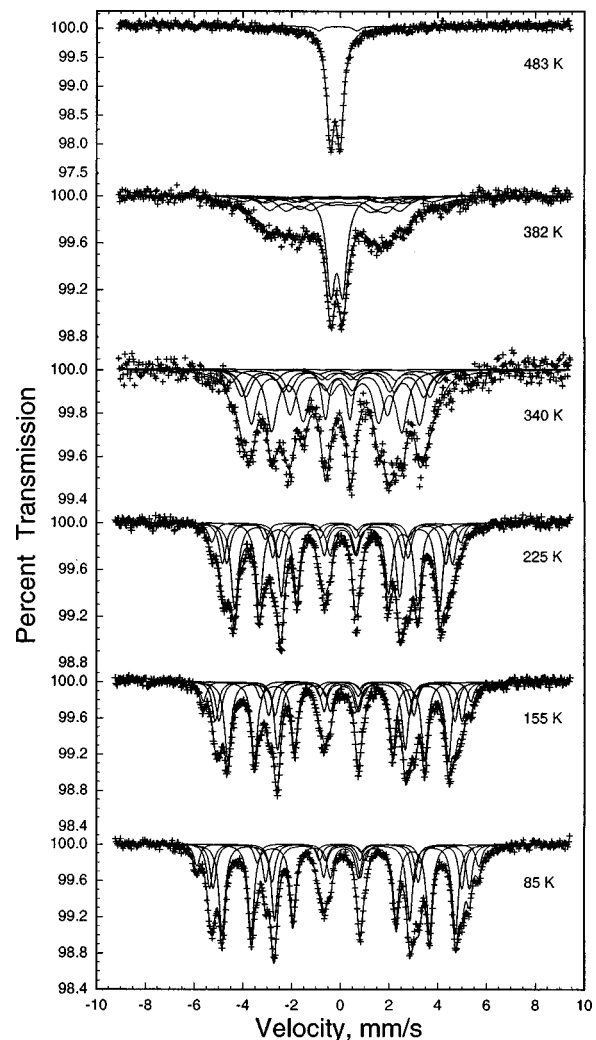


FIG. 2. The Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Au}$ obtained at the indicated temperatures.

dences of the recoil free fractions of the four different Fe sites. The $16l_2$ relative area tends to be systematically smaller than the theoretical value by $\sim 1.5\%$ in agreement with its large Wigner-Seitz cell volume. In contrast, the $16l_1$ relative area is larger than the theoretical value by as much as 3%. The texture parameter, x , is, as expected, temperature independent and amounts to 2.35, 2.08, and 2.55 for the spectra of $\text{Nd}_6\text{Fe}_{13}\text{Cu}$, $\text{Nd}_6\text{Fe}_{13}\text{Ag}$, and $\text{Nd}_6\text{Fe}_{13}\text{Au}$, respectively.

The assignment of the five sextets to the five magnetically inequivalent sites has been carried out as explained above. In all three compounds, the sequence of hyperfine fields, $4d > 16k > 16l_1 > 16l_2$, completely agrees with the sequence of Fe near neighbors, $12 > 10 > 9 > 7$. The hyperfine fields obtained at 295 K for $\text{Nd}_6\text{Fe}_{13}\text{Cu}$, see Table I, are in excellent agreement with the preliminary values obtained⁶ at 293 K from a four sextet fit, because the difference between the $16k$ and $16k'$ hyperfine fields is only 2 kOe. The hyperfine fields obtained at 85 K for $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ and $\text{Nd}_6\text{Fe}_{13}\text{Au}$, are completely compatible with the values measured⁴ at 4.2 K and the temperature dependence of the hyperfine fields for $\text{Nd}_6\text{Fe}_{13}\text{Cu}$, $\text{Nd}_6\text{Fe}_{13}\text{Ag}$, and $\text{Nd}_6\text{Fe}_{13}\text{Au}$ is perfectly smooth.

TABLE I. Mössbauer spectral hyperfine parameters^a for Nd₆Fe₁₃X.

Parameter	<i>T</i> , K	X	4 <i>d</i>	16 <i>k</i>	16 <i>k</i> '	16 <i>l</i> ₁	16 <i>l</i> ₂	Wt. Ave.
H, kOe	295	Cu	292	267	265	243	189	237
	85		362	327	323	300	231	291
	295	Ag	288	263	257	238	184	232
	85		362	327	323	300	231	291
	295	Au	284	258	254	233	181	228
	85		358	326	321	297	227	288
δ , ^b mm/s	295	Cu	-0.164	-0.097	-0.097	-0.100	-0.028	-0.082
	85		-0.059	0.019	0.019	0.019	0.101	0.038
	295	Ag	-0.161	-0.085	-0.085	-0.079	-0.010	-0.066
	85		-0.062	0.022	0.022	0.025	0.102	0.041
	295	Au	-0.180	-0.094	-0.094	-0.099	-0.025	-0.081
	85		-0.067	0.021	0.021	0.017	0.099	0.037
QS, mm/s	295	Cu	-0.06	0.06	-0.40	-0.14	-0.16	—
	85		-0.09	0.07	-0.40	-0.14	-0.18	—
	295	Ag	-0.06	0.04	-0.39	-0.13	-0.16	—
	85		-0.08	0.07	-0.37	-0.14	-0.16	—
	295	Au	-0.04	0.06	-0.38	-0.14	-0.17	—
	85		-0.04	0.06	-0.39	-0.14	-0.17	—

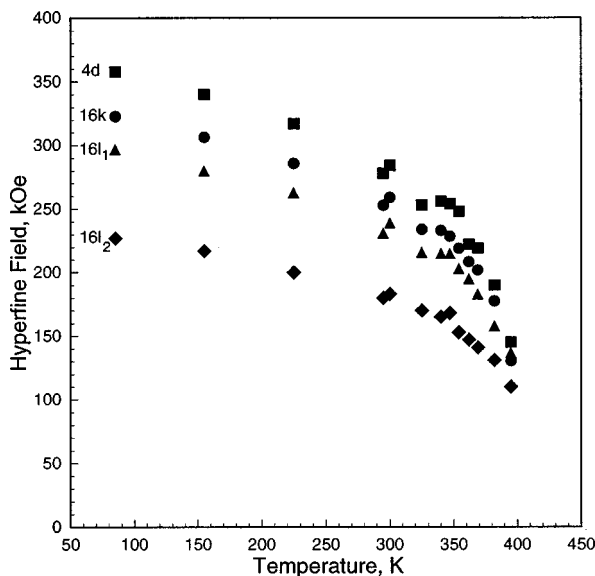
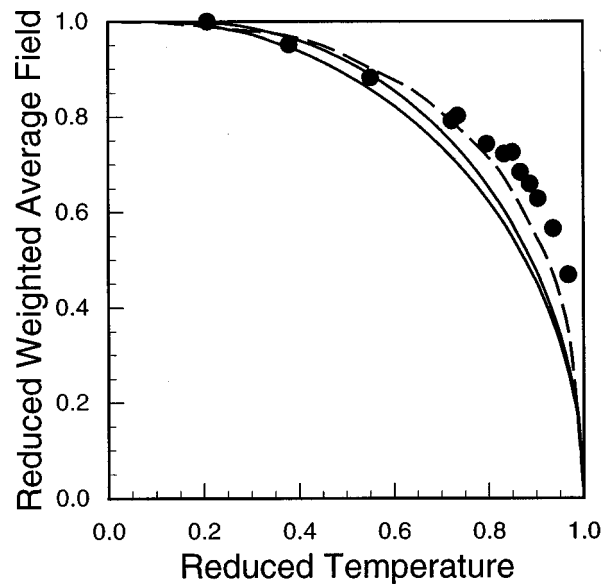
^aThe linewidths are 0.30 mm/s at 85 K and 0.38, 0.41, and 0.42 mm/s at 295 K for X=Cu, Ag, and Au, respectively. The values *x* are 2.35, 2.08, and 2.55 for X=Cu, Ag, and Au, respectively.

^bRelative to α -iron foil at room temperature.

Figure 3 shows the temperature dependence of the four hyperfine fields in Nd₆Fe₁₃Au, where the average of the 16*k* and 16*k*' fields has been plotted. It is clear from this figure that Nd₆Fe₁₃Au is magnetically ordered above the previously reported *T_C* of 340 K and the *T_N* of 408 K is confirmed by the Mössbauer spectra measured at 411 K. As is shown in Fig. 4, the reduced weighted average hyperfine field versus the reduced temperature does not follow a Brillouin curve for spin 3/2 or 5/2, but does follow a curve similar to those calculated by Bean and Rodbell¹⁴ for the temperature dependence of the magnetization in a magnetostrictive system. The experimental values for Nd₆Fe₁₃Au agree rather well with the calculated curve for a spin 3/2 and $\eta=0.5$. The η parameter measures how much the magnetic transition departs

from second order, for which η is 0, or from first order, for which η is 1. Hence, in Nd₆Fe₁₃Au there is evidence for magnetostriction but it is not strong enough to lead to a first-order transition.

The previously reported⁴ isomer shifts of Nd₆Fe₁₃Ag and Nd₆Fe₁₃Au were not very satisfactory because they did not follow the expected variation with near-neighbor environment and the Wigner-Seitz cell volume. These difficulties have been resolved herein, and the largest field, that of the 4*d* site, is always associated with the most negative isomer shift, and the smallest field, that of the 16*l*₂ site, is always associated

FIG. 3. The temperature dependence of the hyperfine fields in Nd₆Fe₁₃Au.FIG. 4. The reduced weighted average hyperfine field, relative to 288 kOe, versus the reduced temperature, relative to 408 K, for Nd₆Fe₁₃Au. The two solid lines are the Brillouin function for spin 5/2, lower, and 3/2. The dashed line is the curve calculated for spin 3/2 and $\eta=0.5$ (See Ref. 14).

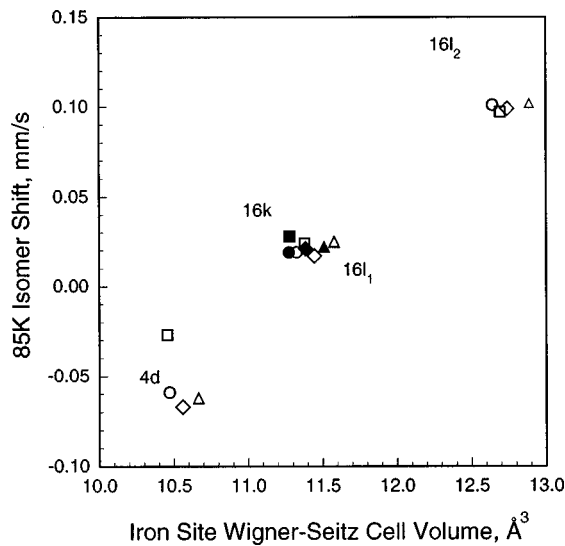


FIG. 5. The correlation between isomer shift and Wigner-Seitz cell volume in $\text{Nd}_6\text{Fe}_{13}\text{X}$, where X is Si, \square , Cu, O, Ag, Δ , and Au, \diamond , and the solid symbols refer to the 16k site.

with the most positive isomer shift. Furthermore, as is expected,¹³ see Fig. 5, there is a virtually perfect linear correlation between the isomer shifts and the Wigner-Seitz cell volumes^{15,16} for the three compounds.

The temperature dependence of the isomer shifts of $\text{Nd}_6\text{Fe}_{13}\text{Au}$ are shown in Fig. 6. The plots for $\text{Nd}_6\text{Fe}_{13}\text{Cu}$ and $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ between 85 and 295 K are very similar. The temperature dependence of the isomer shifts and the natural logarithm of the total absorption areas, and the derived¹⁷ effective masses, M_{eff} , and the Mössbauer or Debye temperatures, θ_M , are given in Table II. There is no significant variation in the weighted average isomer shifts at zero Kelvin with X, in agreement with the absence of the X atom in the first neighbor shell of each of the Fe sites. Equally, there is little variation in the Mössbauer temperature for the Cu, Ag, and Au compounds, indicating the similarity in the

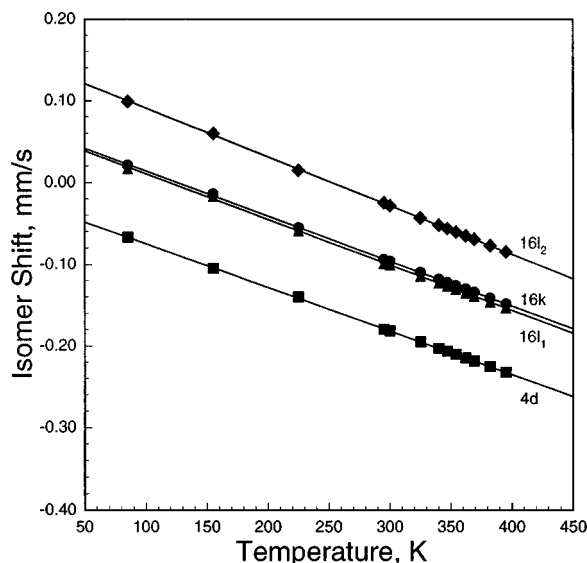


FIG. 6. The temperature dependence of the isomer shifts in $\text{Nd}_6\text{Fe}_{13}\text{Au}$.

TABLE II. The lattice properties^a of $\text{Nd}_6\text{Fe}_{13}\text{X}$.

X	Sites	δ_0 , mm/s	$10^4 d\delta/dT$, (mm/s)/K	M_{eff} , g/mol	$10^4 d(\ln A)/dT$, K ⁻¹	θ_M , K
Cu	Wt. Ave.	0.091(8)	-5.7(4)	72(5)	-10.9(7)	314(20)
	4d		-5.1(3)	82(4)		
	16k		-5.6(5)	75(6)		
	16l ₁		-5.7(4)	74(5)		
	16l ₂		-6.2(3)	67(3)		
Ag	Wt. Ave.	0.086(3)	-5.2(1)	81(2)	-8.5(4)	337(12)
	4d		-4.73(4)	88(1)		
	16k		-5.1(1)	81(2)		
	16l ₁		-5.0(1)	83(2)		
	16l ₂		-5.4(2)	77(2)		
Au	Wt. Ave.	0.086(1)	-5.66(3)	73.5(3)	-10.8(8)	312(12)
	4d		-5.36(2)	77.7(3)		
	16k		-5.51(3)	75.5(4)		
	16l ₁		-5.57(4)	74.7(5)		
	16l ₂		-5.95(2)	69.9(3)		
Si	Wt. Ave.	0.099(1)	-6.44(8)	65(1)	-8.9(3)	368(8)
	4d		-5.75(8)	72(1)		
	16k		-6.26(5)	66.5(5)		
	16l ₁		-6.37(3)	65.3(3)		
	16l ₂		-6.8(2)	61(2)		

^aThe errors associated with the final digits are given in parentheses for each value.

average binding of the Fe in the lattices of the three compounds. The temperature dependence of the isomer shifts and the effective masses for the different sites are also given in Table II. In all three compounds, the effective masses of the individual sites correlate well with the Wigner-Seitz cell volumes. The smallest 4d site is characterized by the largest effective mass, a mass which indicates that the Fe atom is more tightly bound in this small site. In contrast, the largest site 16l₂ is characterized by the smallest effective mass, corresponding to a weaker covalent bonding of the Fe atom in this site.

B. Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$

The Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$, obtained at several temperatures, are shown in Fig. 7. Because the Fe moments are parallel⁵ to the tetragonal *c*-axis at room temperature, the 295 K Mössbauer spectrum of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ was first fit with four sextets. A reasonable but not fully satisfactory fit was obtained with parameters⁹ similar to those of $\text{Nd}_6\text{Fe}_{13}\text{Sn}$. A close examination of the spectra obtained at 155 K and above, reveal additional weak components whose hyperfine parameters are equivalent to those expected¹² of $\text{Nd}_2\text{Fe}_{17}$ or of $\text{Nd}_2\text{Fe}_{17}$ containing a small amount of Si.¹⁸ Indeed a neutron diffraction¹⁹ study of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ at 295 and 17 K has revealed the presence of 10 and 12%, respectively, of a $\text{Nd}_2\text{Fe}_{17}$ phase. Hence the fit of all of these spectra has included 11% of $\text{Nd}_2\text{Fe}_{17}$, an impurity which accounts for the weak absorptions shown in Fig. 7.

A careful examination of the temperature dependence of the Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ obtained between 130 and 80 K, reveals that the spectra are slowly changing with decreasing temperature. The most obvious changes occur at

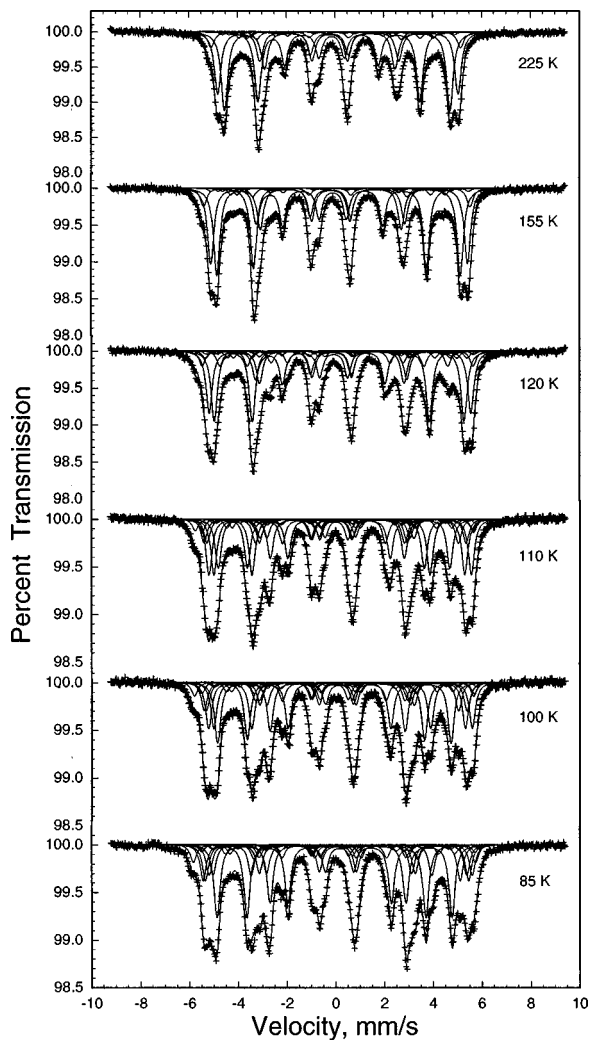


FIG. 7. The Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ obtained at the indicated temperatures.

$\sim -3, 4$, and 5 mm/s. Below 100 K the spectra closely resemble those of $\text{Nd}_6\text{Fe}_{13}\text{Cu}$, $\text{Nd}_6\text{Fe}_{13}\text{Ag}$, and $\text{Nd}_6\text{Fe}_{13}\text{Au}$. Hence a fit with five sextets was attempted, a fit which was not fully satisfactory. The slow changes occurring in the spectrum with decreasing temperature indicate the coexistence of two phases, a high-temperature phase with a c -axis magnetization requiring four sextets, and a low-temperature phase with a basal magnetization requiring five sextets. Hence, we have fit the Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ obtained below 155 K, with nine sextets, in which the isomer shifts of the two or three sextets, corresponding to the high-temperature and low-temperature phases of the $4d$, $16l_1$, and $16l_2$ or $16k$ sites, respectively, were constrained to be equal. The relative areas of the two sextets representing the $16k$ and $16k'$ sites in the low-temperature phase were also constrained to be equal. The initial hyperfine parameters of the low-temperature phase were chosen to be similar to those of $\text{Nd}_6\text{Fe}_{13}\text{Cu}$, and the initial hyperfine parameters of the high-temperature phase were taken from the four sextet fit of the room temperature spectrum of $\text{Nd}_6\text{Fe}_{13}\text{Si}$. The relative areas were constrained to the ratio of the magnetic degeneracies. Only one linewidth was adjusted. Hence, there was a

maximum of 31 adjustable parameters, of which at most ten were simultaneously adjusted. In a second step of the fitting procedure, a texture parameter, x , was adjusted. Because the magnetization rotates by 90 degrees between the high- and the low-temperature phase, x is expected to be different in the two phases. Indeed, x is ~ 2.4 in the low-temperature phase and 1.4 in the high-temperature phase. As is shown in Fig. 7, the fits obtained with this complex model are excellent. The resulting hyperfine parameters are given in Table III. The temperature dependences of the individual isomer shifts and hyperfine fields are perfectly uniform as indicated by the values given in this table.

The lattice parameters of $\text{Nd}_6\text{Fe}_{13}\text{Si}$, obtained¹⁷ from the temperature dependences of the isomer shifts and the natural logarithm of the total experimental absorption area are given in Table II. There is no clear significant difference between $\text{Nd}_6\text{Fe}_{13}\text{Si}$ and the other three compounds, except for the Mössbauer temperature which is larger and the effective mass which is smaller for $\text{Nd}_6\text{Fe}_{13}\text{Si}$.

The quadrupole shift values, QS, given in Table III and shown in Fig. 8 for the axial and basal phases, particularly their signs, reflect the rotation of the magnetic easy axis through the change of the factor $3 \cos^2 \theta - 1$, where θ is the angle between the principal axis of the electric field gradient tensor and the hyperfine field. If we assume that the QS values for the $16l_1$ and $16l_2$ sites in the axial phase correspond to $\theta = 0^\circ$, then the QS values in the basal phase are exactly what is expected for $\theta = 90^\circ$ and a rotation of 90° of the magnetic easy axis.

In conclusion, the Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ indicate that a spin reorientation occurs over a wide range of temperatures below 150 K. The temperature dependence of the percentage of the high- and low-temperature phases is shown in Fig. 9. At 110 K the mixed magnetic phase is $\sim 50:50$ axial and basal magnetization and at 80 K, 75% of the spins are aligned in the basal plane.

IV. MAGNETIZATION STUDIES

The temperature dependence of the magnetization of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ measured in a field of 0.1 T is shown in Fig. 10. The cusp anomaly observed at 420 K is very similar to that observed⁵ at ~ 410 K in a field of 0.04 T and to that observed⁷ in $\text{Nd}_6\text{Fe}_{13}\text{Au}$ at 410 ± 3 K in a field of 0.1 T. This similarity suggests an antiferromagnetic behavior of the Fe sublattice in $\text{Nd}_6\text{Fe}_{13}\text{Si}$. A moderate increase of magnetization is observed in $\text{Nd}_6\text{Fe}_{13}\text{Si}$ below 340 K. This increase in the magnetization is attributed to the presence¹⁹ of 11% of $\text{Nd}_2\text{Fe}_{17}$ in $\text{Nd}_6\text{Fe}_{13}\text{Si}$.

V. DISCUSSION AND CONCLUSIONS

It should be noted that many alternative models may adequately fit the complex Mössbauer spectra of the type reported herein. However, the internal correlation of the hyperfine parameters as a function of X and temperature can often highly restrict the number of these models. In this article, we have developed an internally consistent model which has been applied to four different compounds over a range of temperatures and magnetic anisotropies. Thus, al-

TABLE III. Mössbauer spectral hyperfine parameters^a for Nd₆Fe₁₃Si.

Parameter	T , K	Axial						Basal						
		$4d$	$16k$	$16l_1$	$16l_2$	W. Av.	%A	$4d$	$16k$	$16k'$	$16l_1$	$16l_2$	W. Av.	%A
H, kOe	295	289	277	257	187	244	100	—	—	—	—	—	—	0
	225	317	305	286	206	270	100	—	—	—	—	—	—	0
	155	339	326	309	219	289	100	—	—	—	—	—	—	0
	135	340	329	315	223	293	96	350	331	318	293	220	285	4
	120	344	332	317	225	295	77	354	332	320	290	225	286	23
	110	345	333	319	226	297	49	352	329	323	294	225	287	51
	100	346	335	319	227	298	40	354	331	323	297	225	288	60
	90	347	335	320	231	299	28	361	336	325	300	229	292	72
	85	347	334	322	230	299	26	358	334	326	299	227	291	74
80	347	334	322	230	299	25	361	336	326	300	228	292	75	
δ , ^b mm/s	295	-0.148	-0.103	-0.110	-0.039	0.089	100	—	—	—	—	—	—	0
	225	-0.110	-0.060	-0.064	-0.008	-0.050	100	—	—	—	—	—	—	0
	155	-0.070	-0.015	-0.020	0.050	-0.001	100	—	—	—	—	—	—	0
	135	-0.057	-0.002	-0.007	0.067	0.013	96	-0.057	-0.002	-0.002	-0.007	0.067	0.013	4
	120	-0.050	0.008	0.003	0.077	0.023	77	-0.050	0.008	0.008	0.003	0.077	0.023	23
	110	-0.045	0.012	0.008	0.081	0.028	49	-0.045	0.012	0.012	0.008	0.081	0.028	51
	100	-0.039	0.020	0.016	0.089	0.035	40	-0.039	0.020	0.020	0.016	0.089	0.035	60
	90	-0.030	0.024	0.021	0.094	0.040	28	-0.030	0.024	0.024	0.021	0.094	0.040	72
	85	-0.027	0.028	0.024	0.097	0.044	26	-0.027	0.028	0.028	0.024	0.097	0.044	74
80	-0.024	0.031	0.027	0.100	0.047	25	-0.024	0.031	0.031	0.027	0.100	0.047	75	
QS, mm/s	295	0.28	0.35	0.30	0.28	—	100	—	—	—	—	—	—	0
	225	0.28	0.35	0.30	0.30	—	100	—	—	—	—	—	—	0
	155	0.28	0.35	0.32	0.32	—	100	—	—	—	—	—	—	0
	135	0.28	0.36	0.30	0.29	—	96	-0.040	0.060	-0.038	-0.140	-0.130	—	4
	120	0.28	0.36	0.30	0.29	—	77	-0.040	0.060	-0.038	-0.140	-0.130	—	23
	110	0.28	0.36	0.30	0.29	—	49	-0.040	0.060	-0.038	-0.135	-0.131	—	51
	100	0.28	0.36	0.30	0.29	—	40	-0.040	0.060	-0.038	-0.137	-0.145	—	60
	90	0.28	0.36	0.30	0.29	—	28	-0.040	0.060	-0.038	-0.146	-0.140	—	72
	85	0.28	0.36	0.30	0.29	—	26	-0.040	0.060	-0.038	-0.145	-0.134	—	74
80	0.28	0.36	0.30	0.29	—	25	-0.040	0.060	-0.038	-0.148	-0.134	—	75	

^aThe linewidths are 0.30 mm/s at 80, 85, 90, 100, 110, and 120 K, 0.32, 0.31, 0.32, and 0.34 mm/s at 135, 155, 225, and 295 K, respectively, and x is 2.4 and 1.4 for the basal and axial phases, respectively.

^bRelative to α -iron foil at room temperature.

though our model may not be unique, we do believe it is the best available for understanding the Mössbauer spectra of the Nd₆Fe₁₃X compounds. Further this model provides an excellent correlation between the isomer shifts and the hyperfine fields or the Wigner-Seitz cell volumes of the different crystallographic iron sites, as discussed above. Indeed, by using this internally consistent model, it is possible to understand the magnetic interactions in a variety of related compounds.

From the low temperature hyperfine fields given in Tables I and III, magnetic moments for all four compounds of 2.4, 2.2, 2.0, and 1.5 μ_B can be computed for the 4d, 16k, 16l₁, and 16l₂ sites, respectively, assuming an empirical conversion factor^{20,21} of 148 kOe/ μ_B . These values, and the weighted average value of 1.92 μ_B , are in excellent agreement with the average magnetic moment of 1.9 μ_B obtained^{7,22} from magnetization measurements at 4.2 K in Nd₆Fe₁₃Au and at 15 K in Nd₆Fe₁₃X, where X is Cu, Sb, and Bi. The room temperature hyperfine fields give magnetic moments of 1.9, 1.7, 1.6, and 1.2 μ_B for the 4d, 16k, 16l₁, and 16l₂ sites, respectively, values which are substantially larger than the moments of 1.3, 0.9, 0.5, and 0.8 μ_B , obtained from neutron diffraction measurements⁵ on Nd₆Fe₁₃Si. The disagreement between the Mössbauer and neutron diffraction results for the 16l₁ site cannot be explained as a misassign-

ment of the 16l₁ sextet as was suggested by Yan *et al.*⁵ In the R₂Fe₁₄B compounds, the agreement between the magnetic moments computed from hyperfine field measurements and those obtained from neutron diffraction measurements is much better.²³ The relationship between the hyperfine field and the iron magnetic moment is more accurately described by the linear relationship, $H = A\mu_{Fe} + B\mu_{orb}$, where μ_{Fe} is the spin only contribution and μ_{orb} is the orbital contribution to the Fe magnetic moment. The orbital contribution to the field in a series of Y-Fe compounds has been estimated²¹ to be similar to the value of 38 kOe measured in α -iron. If we assume the same orbital contribution in Nd₆Fe₁₃X, we obtain spin only moments of 1.7, 1.5, 1.4, and 1.0 for the 4d, 16k, 16l₁, and 16l₂ sites, respectively. These values are still significantly larger than the moments obtained from neutron diffraction measurements.⁵ We believe that this discrepancy is due to the inaccuracy of the magnetic moments obtained from neutron diffraction measurements,⁵ an inaccuracy which results from the very small contribution¹⁹ the magnetic scattering makes to the total neutron scattering.

The variation of the four hyperfine fields as a function of X in Nd₆Fe₁₃X is shown in Fig. 11. This figure uses the 85 K hyperfine fields when X is Cu, Ag, Au, and Si, the previously

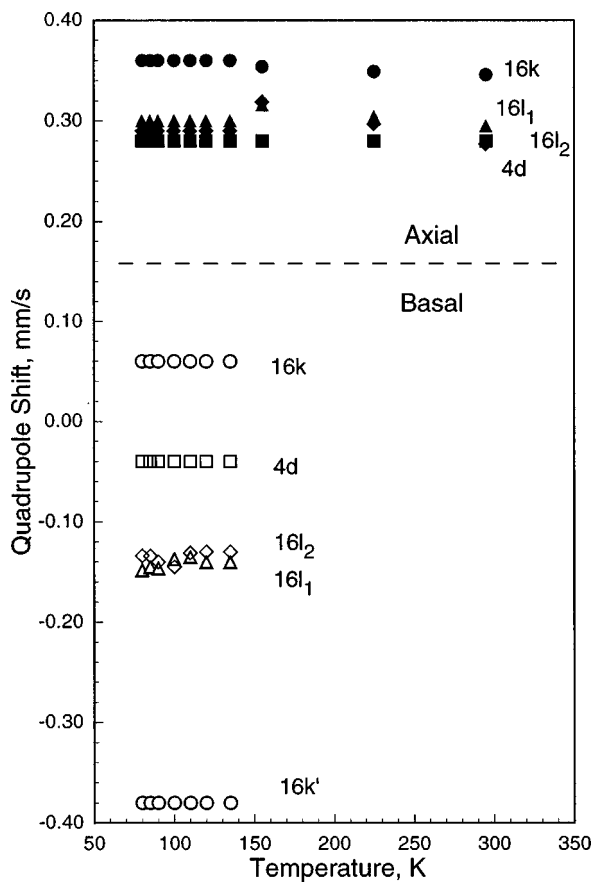


FIG. 8. The temperature dependence of the quadrupole shifts, QS, in the Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$.

reported¹¹ 4.2 K hyperfine fields when X is In, Tl, Sn, Pb, and Sb, and the previously reported^{10,18} 15 K hyperfine fields when X is Ge and Bi. The X atoms have been grouped according to their electronic structure and the dotted lines separate columns in the periodic table. As is indicated by our five sextet Mössbauer spectral analysis, the $\text{Nd}_6\text{Fe}_{13}\text{X}$ com-

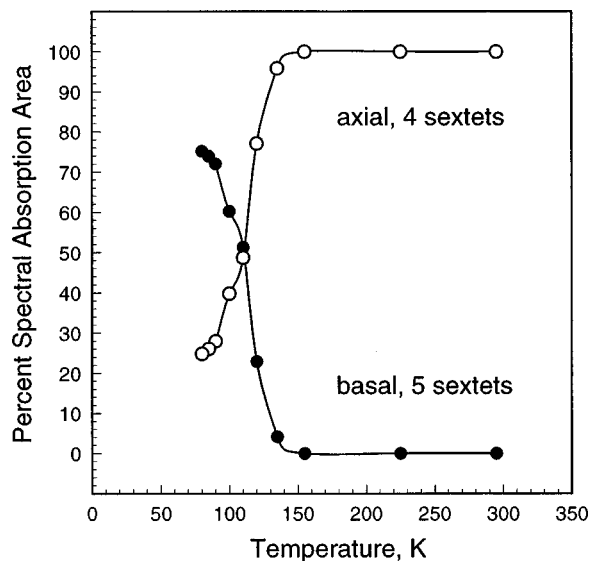


FIG. 9. The temperature dependence of the percentage of the high-temperature phase in the Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$.

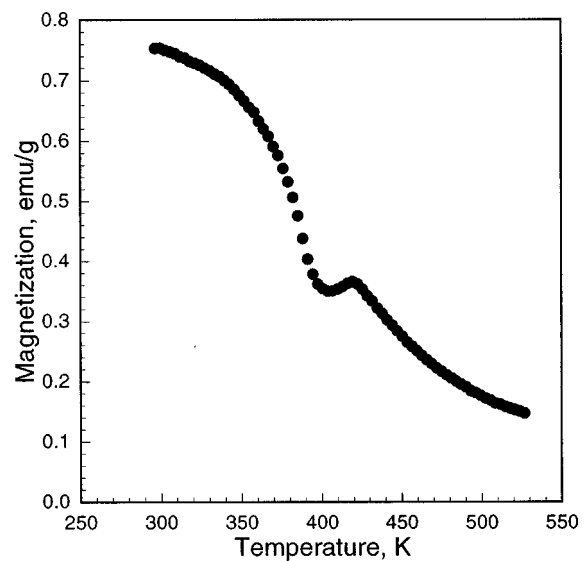


FIG. 10. The temperature dependence of the magnetization of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ measured in a field of 0.1 T.

pounds, where X is Cu, Ag, Au, and Si, exhibit basal magnetic anisotropy. In contrast, as is indicated by a four sextet spectral analysis,¹¹ the $\text{Nd}_6\text{Fe}_{13}\text{X}$ compounds, where X is In, Tl, Sn, and Pb, exhibit axial magnetic anisotropy. The shape²² of the Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Sb}$ and $\text{Nd}_6\text{Fe}_{13}\text{Bi}$, particularly between -4 and -2 mm/s, suggests that these spectra should have been analyzed with five rather than four sextets, and thus it would appear that these two compounds also exhibit basal magnetic anisotropy. Finally the spectra¹⁰ at 290 and 15 K of $\text{Nd}_6\text{Fe}_{13}\text{Ge}$ are very similar to the 295 and 85 K spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ and probably should have been analyzed with four and five sextets, respectively. Hence, we believe that $\text{Nd}_6\text{Fe}_{13}\text{Ge}$ shows a spin-reorientation similar to that observed herein for $\text{Nd}_6\text{Fe}_{13}\text{Si}$.

The successive changes from basal to axial magnetic anisotropy are clearly apparent in Fig. 11. The X atoms of group IB or 11, i.e., Cu, Ag, and Au, with an electronic

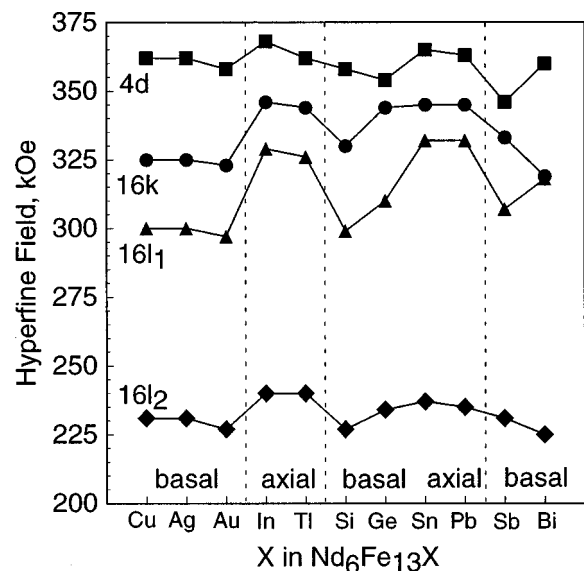


FIG. 11. The compositional dependence of the hyperfine fields in $\text{Nd}_6\text{Fe}_{13}\text{X}$.

structure $nd^{10}(n+1)s^1$, give rise to a basal anisotropy, whereas the X atoms of group IIIA or 13, i.e., In and Tl, with an electronic structure $nd^{10}(n+1)s^2(n+1)p^1$, give rise to an axial anisotropy. The lighter X atoms of group IVA or 14, i.e., Si and Ge, with an electronic structure $nd^{10}(n+1)s^2(n+1)p^2$, give rise to a basal anisotropy at low temperature but to an axial anisotropy at room temperature. In contrast, the heavier X atoms of group IVA or 14, i.e., Sn and Pb, with an electronic structure $nd^{10}(n+1)s^2(n+1)p^2$, give rise to an axial anisotropy. The X atoms of group VA or 15, i.e., Sb and Bi, with an electronic structure $nd^{10}(n+1)s^2(n+1)p^3$, give rise to a basal anisotropy. The influence of the nature of the non-magnetic X atom on the direction of the magnetic anisotropy is rather surprising and has not been addressed to date. Because the X atom has no Fe near neighbors, this influence can only take place through the ten Nd near neighbors of X and we believe that the valence electrons of X play a major role in determining the nature of the magnetic anisotropy, perhaps through hybridization with the Nd valence electrons. A model describing how this hybridization can lead to either axial or basal magnetization in the $R_6\text{Fe}_{13}\text{X}$ compounds will be presented elsewhere.²⁴ This model assumes that the magnetic anisotropy is crystal field induced and controlled mainly by the second order crystal field parameter, which in turn depends upon the electron density at the edge of the Wigner-Seitz cell of the rare-earth atom. The competition between the electron density at this edge contributed the Fe and by X explains the differing axial and basal anisotropies noted in Fig. 11.

It is obvious from Fig. 11 that on average the hyperfine fields are higher in the compounds showing axial magnetic anisotropy, i.e., for In, Tl, Sn, and Pb. Such an enhancement of the hyperfine field by the axial alignment of the spins has also been observed²⁵ in $\text{Sm}_2\text{Fe}_{17}\text{N}_3$. Because the 4d Fe atom has no Nd or X near neighbors, its hyperfine field is essentially independent of X as is shown in Fig. 11. We believe that the slightly low value reported¹⁰ for Ge is due to the four sextet approximation used to fit this spectrum. The very low value reported²² for Sb is obviously related to a misfit of the spectrum at ~ -6 mm/s, a misfit which leads to an underestimated hyperfine field for the iron on the 4d site. The 16k, 16l₁, and 16l₂ Fe atoms have two, three, and five Nd near neighbors, respectively, and their hyperfine fields show significant increases of ~ 10 to 15 kOe between the compounds exhibiting basal anisotropy and those exhibiting axial anisotropy.

As indicated by the values given in Table II, the effective masses of the Fe 4d and 16l₂ site are respectively the largest and the smallest in the four compounds studied herein. This observation correlates well not only with the small and the large Wigner-Seitz cell volumes of the 4d and 16l₂ sites, respectively, but also with the number and the nature of the 4d and 16l₂ near neighbors. Indeed, the Fe 4d site is bonded to twelve Fe atoms whereas the Fe 16l₂ site is bonded to five Nd and seven Fe atoms, as is indicated by the Wigner-Seitz cell analysis.^{15,16} Because the Fe-Fe bonds are expected to be stronger than the Fe-Nd bonds, the 4d Fe

atoms are more tightly bound in the lattice and have a larger effective mass.

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