

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

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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 85 and 435 K. An analysis of the spectra of $\text{Nd}_6\text{Fe}_{13}\text{X}$, where X is Cu, Ag, and Au in terms of five sextets, indicates that the iron moments lie in the basal plane of the unit cell. The assignment of the five sextets to the five magnetically inequivalent sites in the structure is based on a correlation between the isomer shift and the Wigner-Seitz cell volume for all iron sites, between the isomer shift and the hyperfine field for each site, and the relationship between the hyperfine field at a given iron site and its number of iron near-neighbors. An analysis of the spectra of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ reveals that a high temperature magnetic phase, with its moments parallel to the c axis, coexists between 295 and 85 K with a low temperature magnetic phase, with its moments oriented in the basal plane. Hence, $\text{Nd}_6\text{Fe}_{13}\text{Si}$ shows a continuous magnetic spin-reorientation from axial towards basal alignment upon cooling. © 1997 American Institute of Physics. [S0021-8979(97)22908-7]

I. INTRODUCTION

The compounds $\text{Nd}_6\text{Fe}_{13}\text{X}$, where X is Si, Cu, Ag, and Au crystallize in the tetragonal $\text{Nd}_6\text{Fe}_{13}\text{Si}$ structure.¹ $\text{Nd}_6\text{Fe}_{13}\text{Au}$ was first reported² to be ferromagnetic below 340 K and later³ to be antiferromagnetic below 413 K. $\text{Nd}_6\text{Fe}_{13}\text{Si}$ was first¹ reported to be antiferromagnetic below 725 K and later⁴ to be ferrimagnetic with a Curie temperature of 441 K, a compensation point of 357 K, and to have iron magnetic moments parallel to the tetragonal c axis at room temperature. $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ shows² ferromagnetic behavior below 340 K. $\text{Nd}_6\text{Fe}_{13}\text{Cu}$ has⁵ a complex noncolinear magnetic structure with a Curie temperature of 463 K. This range of controversial magnetic behaviors has prompted us to extend our earlier³ Mössbauer spectral study of $\text{Nd}_6\text{Fe}_{13}\text{Au}$.

II. EXPERIMENT

The samples were prepared as described³ previously and their x-ray diffraction patterns indicate that they are essentially single phase.¹ The preparation of the absorbers and the description of the Mössbauer spectral measurements have been given earlier.³ It is very difficult to obtain accurate error limits for the hyperfine parameters but we estimate that the hyperfine fields are valid to ± 1 kOe, the isomer shifts to ± 0.005 mm/s, and the quadrupole shifts to ± 0.02 mm/s, when X is Cu, Ag, and Au, and probably double these values for Si.

III. RESULTS AND DISCUSSION

The Mössbauer spectra of $\text{Nd}_6\text{Fe}_{13}\text{Ag}$, obtained at 85 and 295 K, are shown in Fig. 1. These spectra and those of $\text{Nd}_6\text{Fe}_{13}\text{Cu}$ are very similar to those³ of $\text{Nd}_6\text{Fe}_{13}\text{Au}$ and have been analyzed in a similar fashion. Because the iron magnetic moments are oriented in the basal plane of the unit cell, the $16k$ sites are magnetically inequivalent and, because of

their point symmetry, are subdivided into two eightfold populated sites, labelled $16k$ and $16k'$ herein. As a consequence, five sextets, with relative areas in the ratio 4:8:8:16:16, are necessary to fit the spectra and are assigned to the $4d$, $16k$, $16k'$, $16l_1$, and $16l_2$ iron sites. In addition, the isomer shifts of the two magnetically inequivalent $16k$ and $16k'$ sites were constrained to be equal and one linewidth was used for all spectral lines. Hence, 16 parameters, five hyperfine fields, four isomer shifts, five quadrupole shifts, one linewidth, and the total absorption area, have to be fit. A more detailed analysis of the absorber texture, clearly visible in the intensities of the second and fifth absorption peaks, involves an additional parameter, x , defined by the six line area ratio, $3:x:1:1:x:3$, within each sextet.

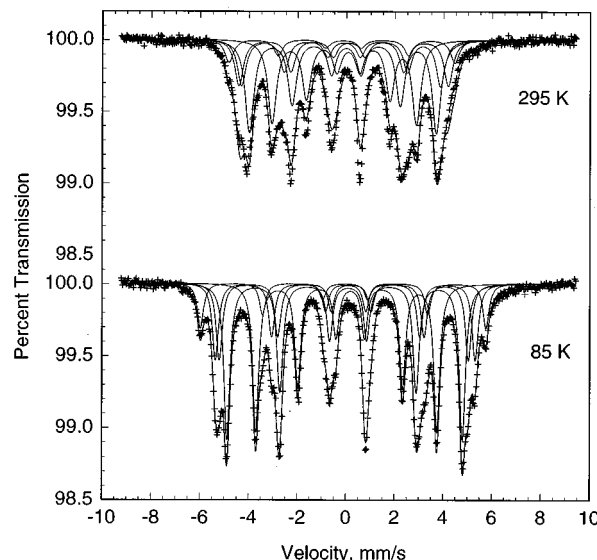


FIG. 1. Mössbauer spectra measured at 85 and 295 K for $\text{Nd}_6\text{Fe}_{13}\text{Ag}$.

TABLE I. Mössbauer spectral hyperfine parameters for Nd₆Fe₁₃X, where X is Si, Cu, Ag, and Au.

T (K)	Site	δ^a (mm/s)				H (kOe)				QS (mm/s)			
		Si ^b	Cu	Ag	Au	Si ^b	Cu	Ag	Au	Si ^b	Cu	Ag	Au
296	4d	-0.148	-0.164	-0.161	-0.180	286	292	290	278	0.29	-0.60	-0.04	-0.04
	16k	-0.103	-0.097	-0.085	-0.100	276	267	262	254	0.40	0.06	0.057	0.06
	16k'	...	-0.097	-0.085	-0.100	...	265	259	252	...	-0.40	-0.40	-0.37
	16l ₁	-0.110	-0.100	-0.079	-0.100	256	243	238	231	0.26	-0.14	-0.14	-0.14
	16l ₂	-0.039	-0.028	-0.010	-0.025	188	189	185	180	0.37	-0.16	-0.16	-0.15
	Average	-0.089	-0.082	-0.066	-0.083	244	237	233	225
85	4d	-0.027	-0.059	-0.073	-0.070	360	362	364	358	-0.04	-0.09	-0.07	-0.04
	16k	0.028	0.019	0.022	0.028	333	327	326	325	0.04	0.07	0.07	0.06
	16k'	0.028	0.019	0.022	0.028	322	323	322	321	-0.43	-0.40	-0.37	-0.39
	16l ₁	0.024	0.019	0.024	0.024	298	300	300	297	-0.12	-0.14	-0.14	-0.14
	16l ₂	0.097	0.101	0.101	0.115	229	231	231	227	-0.16	-0.18	-0.16	-0.17
	Average	0.044	0.038	0.040	0.046	291	291	291	288

^aRelative to room temperature α -iron foil.

^bFor this compound, at 295 K only the parameters for the high temperature components are given, whereas at 85 K only the parameters for the low temperature components are given.

Table I gives the hyperfine parameters obtained from the fits of the Nd₆Fe₁₃Cu and Nd₆Fe₁₃Ag spectra at 85 and 295 K, together with those obtained³ for Nd₆Fe₁₃Au. Between 85 and 295 K, the four isomer shifts decrease linearly with temperature. The quadrupole shifts are virtually independent of temperature and the hyperfine fields decrease smoothly with increasing temperature. It is obvious that there are only very small differences between the three compounds. This similarity is not surprising because in the Nd₆Fe₁₃X structure the iron atoms have no X, i.e., no Cu, Ag, or Au, near neighbors. Hence differences in the hyperfine parameters result mainly from differences in the lattice parameters upon changing X.

The hyperfine parameters and the site assignments for Nd₆Fe₁₃Ag and Nd₆Fe₁₃Au, given in Table I, are different from those reported by Weitzer *et al.*^{2,6} and are, we believe, more valid.⁷ Furthermore, the earlier⁵ analysis of the Mössbauer spectra of Nd₆Fe₁₃Cu in terms of four sextets is not valid in view of the noncollinear⁵ magnetic structure of this compound. Because the lines of equivalent areas in the pair of sextets, 16k and 16k', as well as those of the 16l₁ and 16l₂ sites, have been coupled differently in our fits and the earlier fits,^{2,6} the resulting isomer shifts are different.⁸ As a consequence of these different assignments, our analysis yields the expected correlation between the hyperfine fields and the isomer shifts, i.e., a large hyperfine field is associated with a more negative isomer shift, whereas this correlation was not observed in the earlier fits.² In our analysis the isomer shifts of the four iron sites correlate linearly, as expected,⁹ with the Wigner-Seitz cell volumes,^{10,11} see Fig. 2, a correlation that was not observed in the earlier work.² However, there are no substantial differences between our hyperfine fields and those reported earlier.^{2,5} Finally the assignment of the hyperfine fields to the sites is in agreement⁶ with the number of iron near neighbors of each site, namely, 12, 10, 9, and 7, for the 4d, 16k, 16l₁, and 16l₂ sites, respectively.

Figure 3 shows the Mössbauer spectra of Nd₆Fe₁₃Si obtained at various temperatures between 295 and 85 K. It is obvious that the spectra are dramatically different at 295 and

85 K. Below 155 K additional weak absorption lines are clearly present at ~ -2.6 , -2 , 3.9 , and 4.5 mm/s, lines whose intensities increase dramatically upon further cooling. Because Nd₆Fe₁₃Si exhibits⁴ an axial magnetization at room temperature, we attempted to fit its 295 K spectrum with four sextets. A less than adequate, although reasonable, fit was obtained because some structure in the 1, 2, 4, and 6 lines was unaccounted for and because the absorption in the 2 and 5 lines was lower than expected for a random absorber. In contrast, at 85 K the spectrum of Nd₆Fe₁₃Si resembles those of Nd₆Fe₁₃Ag and Nd₆Fe₁₃Au, but is more complex and could not be adequately fit with five sextets. A close examination of the experimental spectra reveals that the intensities of the lines at -2 and 3.9 mm/s are increasing below 155 K, whereas the intensities of the lines at -2.2 and 4.1 mm/s are decreasing. Hence, we concluded that the spectrum at 85 K is the superposition of nine sextets, four of which are similar to those observed at 295 K and typical of the high temperature magnetic phase, and five of which are similar to those ob-

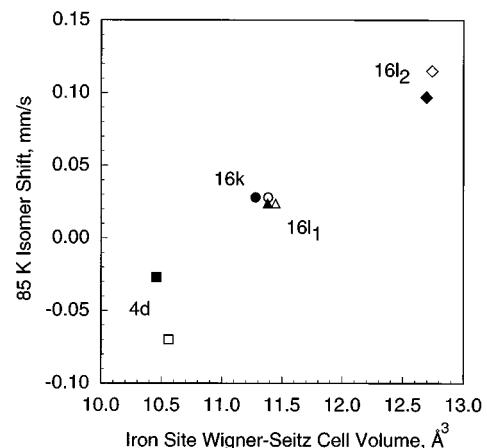


FIG. 2. The correlation between the isomer shifts measured at 295 K and the Wigner-Seitz cell volumes for Nd₆Fe₁₃Si, closed symbols, and for Nd₆Fe₁₃Au, open symbols.

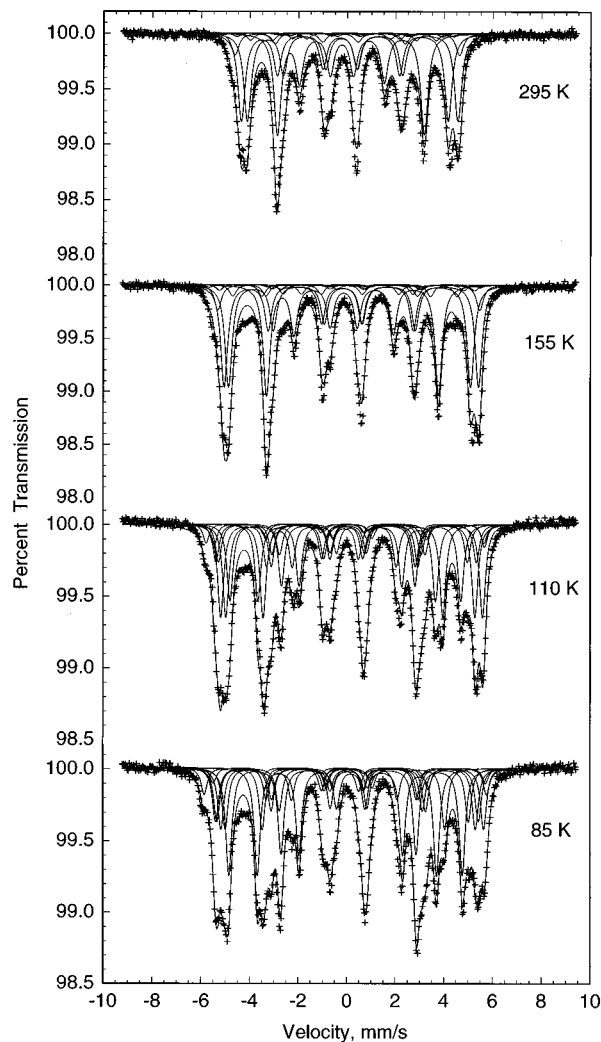


FIG. 3. Mössbauer spectra measured at the indicated temperatures for $\text{Nd}_6\text{Fe}_{13}\text{Si}$.

served in $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ and $\text{Nd}_6\text{Fe}_{13}\text{Au}$ and typical of the low temperature magnetic phase. Thus, we analyzed the 85 K spectrum of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ with nine sextets with equal isomer shifts for the same crystallographic sites and quadrupole shifts which agree with those observed in $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ and $\text{Nd}_6\text{Fe}_{13}\text{Au}$ for the low temperature magnetic phase and with those obtained from the preliminary four sextet fit of its 295 K spectrum. Although the resulting preliminary fit is adequate, see Fig. 3, it may not be unique because of the large number of adjustable parameters. At 85 K the preliminary hyperfine parameters, given in Table I, are for the low temperature magnetic phase which represents $\sim 70\%$ of the total absorption area.

The same nine sextet fit was used for the 295 K spectrum and yielded the preliminary fit shown in Fig. 3, a fit in which the high temperature magnetic phase accounts for $\sim 90\%$ of the total absorption area. The preliminary hyperfine parameters of the high temperature phase at 295 K are given in Table I. The isomer shifts compare well with those measured for $\text{Nd}_6\text{Fe}_{13}\text{Ag}$ and $\text{Nd}_6\text{Fe}_{13}\text{Au}$, and correlate well

with the Wigner–Seitz cell volume, as is shown in Fig. 2. Although at 295 K the weighted average hyperfine field is larger than those measured in $\text{Nd}_6\text{Fe}_{13}\text{X}$, when X is Cu, Ag, and Au, probably because the spins are aligned along the c axis, at 85 K it is the same. Furthermore, at 295 K the hyperfine parameters are very similar to those measured² in $\text{Nd}_6\text{Fe}_{13}\text{Sn}$, in which the spins are also aligned along the c axis.

From the preliminary fits of the spectra between 295 and 85 K, we conclude, in agreement with the neutron diffraction results,⁴ that $\sim 90\%$ of the iron moments are oriented along the c axis above 155 K. Below 155 K the moments rotate away from the c axis and tend to align in the basal plane. At 85 K $\sim 70\%$ of the iron magnetic moments are aligned in the basal plane. The two different orientations of the spins coexist over an $\sim 100^\circ$ temperature range and at 110 K have an equal probability. In contrast to the Néel temperature¹ of 725 K and the Curie temperature⁴ of 441 K, the temperature dependence of the magnetization of $\text{Nd}_6\text{Fe}_{13}\text{Si}$ measured¹² in a field of 1 T indicates a Néel temperature of ~ 425 K.

In order to further investigate the spin reorientation discovered in this study of $\text{Nd}_6\text{Fe}_{13}\text{Si}$, neutron diffraction studies at low temperature and Mössbauer spectral studies at lower temperatures and in an applied field are in progress.

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¹J. Allemand, A. Letant, J. M. Moreau, J. P. Nozières, and R. Perrier de la Bathie, *J. Less-Common Met.* **166**, 73 (1990).

²F. Weitzer, A. Leithe-Jasper, P. Rogl, K. Hiebl, A. Rainbacher, G. Wiesinger, W. Steiner, J. Friedl, and F. E. Wagner, *J. Appl. Phys.* **75**, 7745 (1994).

³C. H. de Groot, F. R. de Boer, K. H. J. Buschow, D. Hautot, G. J. Long, and F. Grandjean, *J. Alloys Compd.* **233**, 161 (1996).

⁴Q. W. Yan, P. L. Zhang, X. D. Sun, B. P. Hu, Y. Z. Wang, X. L. Rao, G. C. Liu, C. Gou, D. F. Chen, and Y. F. Cheng, *J. Phys. Condens. Matter*, **6**, 3101 (1994).

⁵K. G. Knoch, A. Le Calvez, Q. Qi, A. Leithe-Jasper, and J. M. D. Coey, *J. Appl. Phys.* **73**, 5878 (1993).

⁶F. Weitzer, A. Leithe-Jasper, P. Rogl, K. Hiebl, H. Noël, G. Wiesinger, and W. Steiner, *J. Solid State Chem.* **104**, 368 (1993).

⁷The quadrupole shift, QS , given in Table I, has been defined differently than the parameter noted as E_Q in Ref. 2 and ΔE_Q in Ref. 6. In Table I QS is defined as $e^2Qq(3\cos^2\theta - 1)/4$, where e^2Qq and θ are not determined separately, whereas E_Q and ΔE_Q are not clearly defined (see Refs. 2 and 6) but apparently use a different sign convention.

⁸It should be noted that there is a typographical error in Table 1 of Ref. 3. The average isomer shifts at 155 and 85 K should be 0.00 and 0.05 mm/s, respectively.

⁹G. J. Long, O. A. Pringle, F. Grandjean, and K. H. J. Buschow, *J. Appl. Phys.* **72**, 4845 (1992); G. J. Long, S. Mishra, O. A. Pringle, F. Grandjean, and K. H. J. Buschow, *ibid.* **75**, 5994 (1994).

¹⁰L. Gelato, *J. Appl. Crystallogr.* **14**, 141 (1981).

¹¹The Wigner–Seitz cell volume calculations used twelve coordinate metallic radii of 1.82, 1.26, 1.32, and 1.46 Å for Nd, Fe, Si, and Au, respectively.

¹²C. H. de Groot and K. H. J. Buschow (unpublished results).