

HYPERFINE INTERACTIONS IN $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ COMPOUNDS

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Résumé. — Nous présentons les résultats d'une étude par effet Mössbauer des composés $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ dans un large domaine des températures. Les directions des axes de facile aimantation ont été déterminées en fonction de la température et de la composition. Nous discutons le diagramme de réorientation du spin, en considérant la compétition entre l'anisotropie du sous-réseau du fer et celle des interactions d'échange. Nous analysons la dépendance avec la composition des paramètres hyperfins. La variation thermique des champs internes suggère que la plupart des électrons 3d du fer forment une bande étroite et peuvent être considérés comme localisés.

Abstract. — We present the results of ME measurements on $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ compounds in a large temperature range. The direction of the easy axis of magnetization have been determined as function of temperature and composition. The spin reorientation diagram is discussed considering the competing influences of the anisotropy of the iron sublattice and that of the exchange interactions. The composition dependence of the hyperfine parameters is analysed. The thermal variation of the hyperfine fields suggests that the largest part of 3d electrons of iron are in the narrow band and can be considered localized.

1. Introduction. — The cubic rare-earth iron Laves phases, RFe_2 have been in the last years the subject of extensive investigations. The Mössbauer effect (ME) studies on Fe^{57} in these alloys have pointed out that although these compounds have the same crystalline structure, they present different types of spectra [1]. This behaviour is attributed to the different orientations of the easy axis of magnetization relative to the crystallographic axes. The ME studies on pseudobinary $(\text{R}'_x\text{R}''_{1-x})\text{Fe}_2$ compounds, where R' and R'' is a non-S-state rare-earth, evidenced that the direction of the easy axis of magnetization is temperature and composition dependent [2]. Assuming that the contribution to the magnetic crystalline anisotropy is mainly due to the interaction of the rare-earth ions with the crystalline field, the theoretical calculations are in agreement with the experimental results [2]. Other minor sources like the anisotropy of the iron sublattice and that due to the exchange interactions seem also to contribute to the magnetic anisotropy of the system.

It is also of interest to study the compounds with a S-state ion as gadolinium or the non-magnetic rare-earth or yttrium. For these systems one expects the easy direction of magnetization to be determined only by the anisotropy of the iron sublattice or that of the exchange interactions.

In this paper we present the results of ME measurements on the $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ compounds. These compounds crystallize in MgCu_2 -type structure. The iron atoms occupy the $(\bar{3}m)$ sites, while gadolinium and yttrium are randomly distributed in the $(\bar{4}3m)$ positions.

Magnetic measurements on $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ system were made both in the ordered and paramagnetic range [3, 4]. The gadolinium sublattice magnetization is antiparallel oriented to that of the iron atoms. Substituting gadolinium by yttrium, the relative magnitude of the two sublattices magnetization changes. Thus, various curves characteristic to the ferrimagnetic ordering are evidenced [3, 4]. The iron saturation moment is almost linearly dependent on composition [4]: $M_{\text{Fe}}(x) = (1.44 + 0.18x) \mu_B$. A compensation of the magnetization of the two sublattices at 4.2 K is observed for $x \approx 0.44$.

Various point of views are expressed in connection with the direction of the easy axis of magnetization in GdFe_2 . Bowden *et al.* [1] concluded that it is not along any symmetry axis of the Laves phase structure. Atzmony *et al.* [5] showed only a six-lines hyperfine pattern and concluded that the easy direction of magnetization is along [001] axis. Later, Van der Velden *et al.* [6] decomposed the GdFe_2 Mössbauer spectra at 78 K into three different subspectra.

2. Experimental. — The samples were prepared by melting the constituents in an arc-furnace, in helium gas atmosphere. The samples were thermally treated at 950 °C for one week. The X-ray analysis showed the purity of the samples. The lattice parameters are found to lay between those of GdFe_2 (7.389 Å) and YFe_2 (7.356 Å).

The ME measurements were performed between 78 K and the Curie temperatures. The GdFe_2 and YFe_2 compounds were also studied at 4.2 K. A ^{57}Co source in copper matrix was used. The data storage

was done for the velocity range ± 10 mm/s by means of a DIDAC-4000 analyser. The spectra were fitted by using a FFORTRAN program assuming a Lorentzian line shape.

3. Experimental results and discussions. — We present in figures 1 and 2 some characteristic spectra obtained at 78 K and 300 K. The GdFe_2 spectrum may be decomposed in two six line patterns [7] with the intensity ratio 1 : 1, suggesting that the easy axis of magnetization is the [011] direction. The ratio of the quadrupole shifts ($\frac{1}{4} e^2 Qq$) of the two iron sublattices, in this case, is expected to be 1 : -1. This is in agreement with the experimental data as shown in table I. The spectra of YFe_2 may be decomposed in two six-line patterns with the intensity ratio 3 : 1, in agreement with the previous results [1, 8]. In this case, the easy direction of magnetization is the [111] axis.

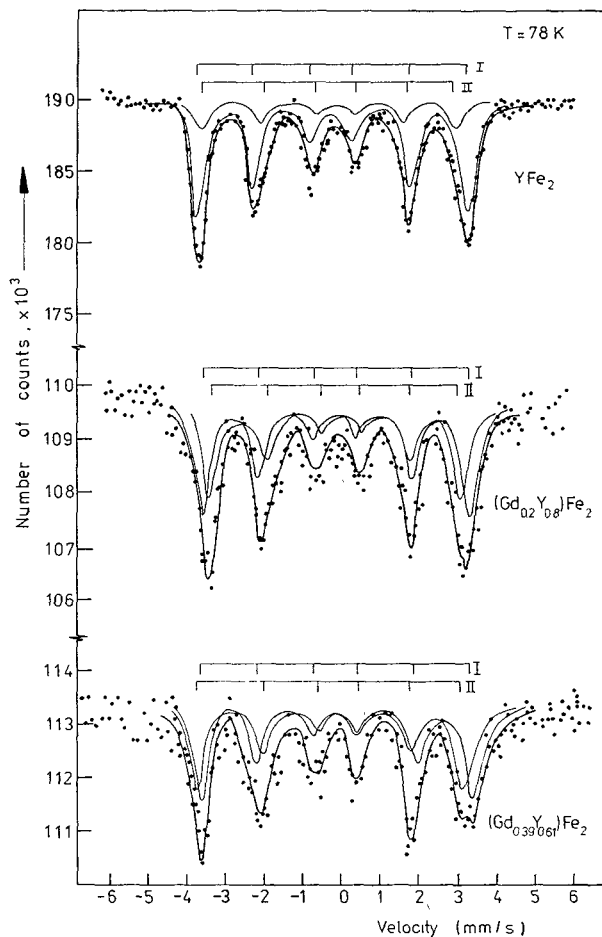


FIG. 1. — Mössbauer spectra at 78 K for $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ compounds with $x = 0.00$; 0.20 and 0.39 .

As the temperature and composition vary, a change in the easy direction of magnetization becomes apparent. At 78 K the transitions from the [111] direction to the [011] direction appear for $0 < x < 0.2$. At 300 K

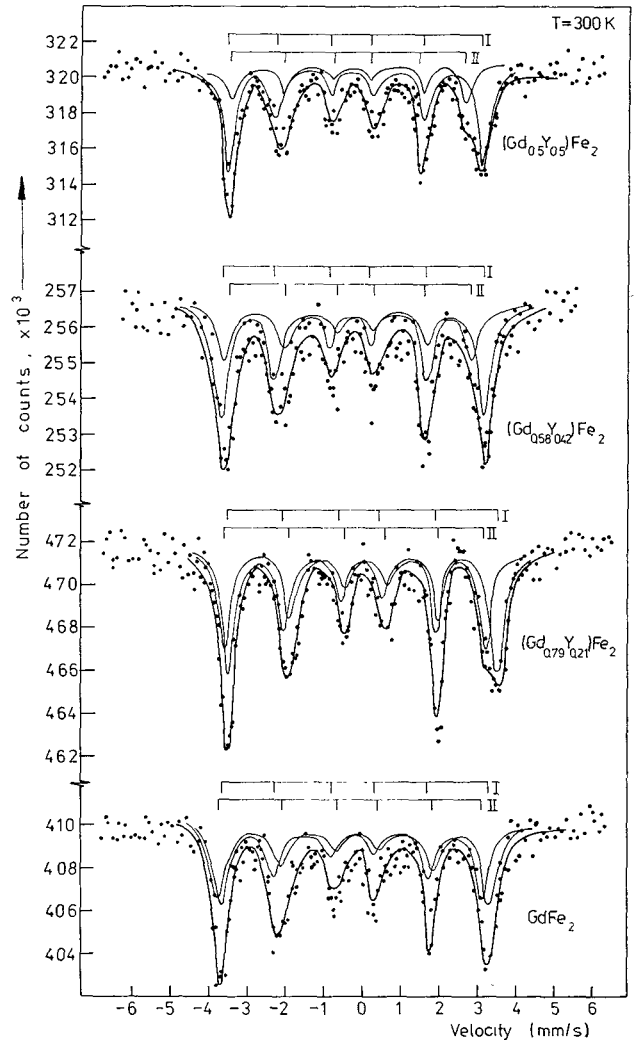


FIG. 2. — Mössbauer spectra at 300 K for $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ compounds with $x = 0.50$; 0.58 ; 0.79 and 1.00 .

this transition takes place for $0.6 < x < 0.8$ as demonstrated in figures 1 and 2. The transitions between the different regions of the spin-orientation diagram are not sharp, however, they occur in a definite range of composition and temperature. The analysis of the Mössbauer spectra allows to determine the easy direction of magnetization as function of composition and temperature. A synthesis of the results is presented in figure 3. The open circles and open triangles correspond to the Mössbauer spectra with the intensity ratio 3 : 1 and 1 : 1, respectively. Intermediate types of spectra are also presented.

The ratio between the quadrupole shifts of the two iron sublattices, for the systems where [011] is the easy direction of magnetization is approximately 1 : -1 (Table I). The quadrupole shifts decrease by increasing the yttrium content or the temperature.

The thermal variation of the hyperfine fields for some of the studied compounds is presented in figures 4 and 5. As seen from these figures, at high temperatures

TABLE I

Hyperfine parameters at 78 K and 300 K

Composition (x)		1.00	0.79	0.58	0.50	0.39	0.20	0.00		
Hyperfine fields (kOe) $H_n \pm 2$	78 K (4.2 K)	I	238 (239)	230	230	229	220	219	215 (218)	
		II	225 (227)	226	216	215	205	202	199 (200)	
	300 K	I	223	218	215	207	205	201	190	
		II	215	210	201	191	191	184	180	
	Quadrupole shifts ($\frac{1}{2} e^2 qQ$) (mm/s) ± 0.03	78 K	I	0.110	0.083	0.050	0.054	0.028	0.024	0.018
			II	-0.098	-0.070	-0.060	-0.040	-0.021	-0.040	-0.096
300 K		I	0.080	0.060	0.071	0.033	0.014	0.055	0.048	
		II	-0.070	-0.070	-0.055	-0.043	-0.039	-0.094	-0.088	
78 K		I	-0.165	-0.147	-0.140	-0.171	-0.133	-0.164	-0.196	
		II	-0.159	-0.161	-0.174	-0.181	-0.149	-0.139	-0.204	
300 K	I	-0.269	-0.280	-0.317	-0.281	-0.284	-0.288	-0.290		
	II	-0.308	-0.237	-0.278	-0.337	-0.264	-0.290	-0.254		
The iron magnetic moment at 4.2 K $M_{\text{Fe}} (\mu_B)$		1.62	1.58	1.54	1.52	1.51	1.47	1.44		
The hyperfine field per unit spin A at 4.2 K (kOe μ_B^{-1})		144.3	145.5	144.2	145.4	143	146.5	148		

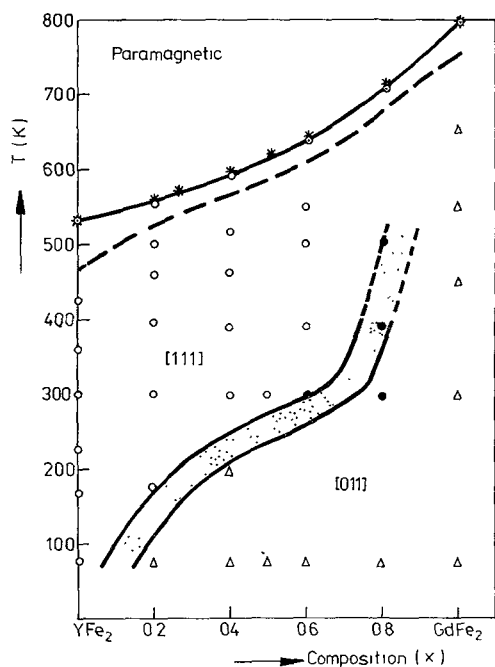


FIG. 3. — Spin-orientation diagram of the $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ system. Open circles, open triangles and filled circles correspond to experimentally determined spectra characteristic to the [111], [011] directions and intermediate types spectra, respectively. By broken lines we plotted the temperatures where the two sextets collapse in a single six-line pattern. By solid line we represent the Curie temperatures, T_c . We noted by (O) the T_c values determined by ME studies and by (*) those obtained by magnetic measurements.

($T \geq T_1$), the two sextets collapse in an one six-line pattern. The variation of T_1 temperatures along the

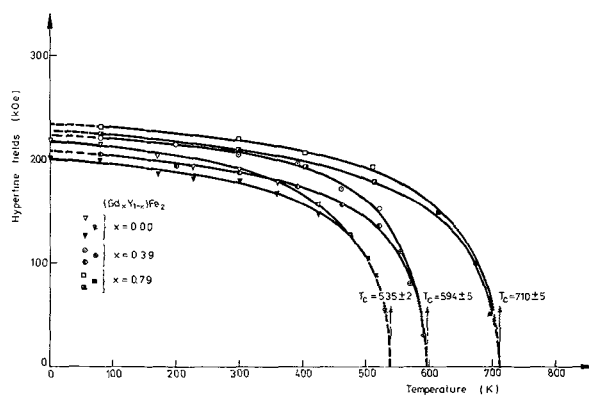


FIG. 4. — Thermal variation of the hyperfine fields at Fe^{57} nucleus for $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ compounds with $x = 0.00$; $x = 0.39$ and $x = 0.79$.

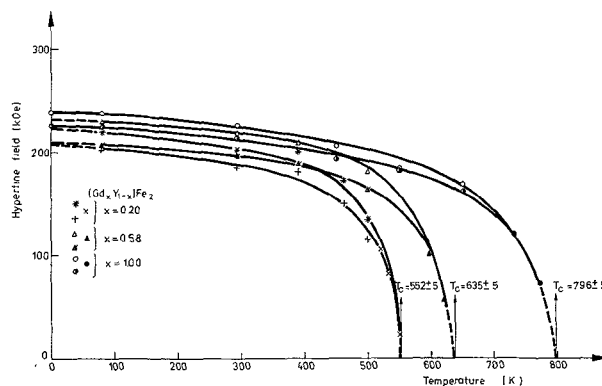


FIG. 5. — Thermal variation of the hyperfine fields at Fe^{57} nucleus for $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ compounds with $x = 0.20$; $x = 0.58$ and $x = 1.00$.

system is represented in the spin-reorientation diagram by the broken line. The composition dependence of the Curie temperatures, T_c is plotted in figure 3 as a solid line.

The magnetic anisotropy in YFe_2 may be ascribed to the anisotropy of iron sublattice. The magnetic anisotropy in GdFe_2 is due to the competition between the magnetic anisotropy of the iron sublattice and that of Gd-Fe and Gd-Gd exchange interactions. Since the Gd-Gd exchange interactions are about one order of magnitude smaller than those between Gd-Fe sublattices, as shown by magnetic measurements [9], the latter seems to be the dominant one in determining the direction of the easy axis of magnetization at low temperatures. The contribution to the magnetic anisotropy due to the exchange interaction varies more rapidly with the temperature than that due to the iron sublattice. Thus, by increasing the temperature, the region of composition where the [111] direction is the easy axis of magnetization becomes greater (see Fig. 3). In this manner may be also justified the composition and temperature dependence of the quadrupole shifts (Table I).

The composition dependence of the hyperfine fields at 78 K and 300 K is presented in figure 6. The values

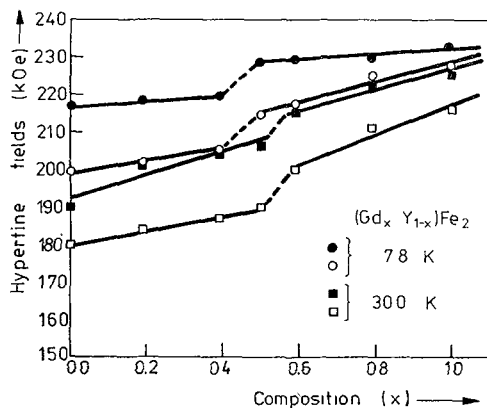


FIG. 6. — Composition dependence of the hyperfine fields at 78 K and 300 K.

obtained at 78 K are close to those shown at 4.2 K (see Table I). By increasing the gadolinium content, the Fe^{57} hyperfine fields increase also. At a certain composition a sudden, but small change, ΔH_n , in the hyperfine field values is apparent ($\Delta H_n \approx 9$ kOe at 78 K). A similar behaviour was observed by NMR studies on the same system [10]. This behaviour is attributed to the change of the polarization of 4s conduction electrons at the composition where the magnetizations of the two sublattices are compensated. At this composition the sign of the polarization of the conduction electrons must change [10]. Because the 4s electrons have a small but finite density at nucleus, this change is reflected in the hyperfine field values.

The d-like itinerant electrons have zero probability of being at the nucleus and therefore do not contribute to the hyperfine field [11].

The composition at which the jump in H_n is observed, is a function of temperature, shifting towards the high gadolinium content as the temperature increases. The thermal variation of the gadolinium sublattice magnetization is more pronounced than that of the iron. Thus, the compensation takes place at a higher gadolinium content as the temperature is higher.

Part of the hyperfine field acting on the iron nuclei is due to the polarization of inner core 1s, 2s and 3s electrons by the magnetic interactions. Previously, a linear relationship has been suggested between the hyperfine field H_n and the effective spin of rare-earth. These polarization effects contribute to the hyperfine fields approximately 7 kOe/unit spin [12, 13]. As observed from table I, the magnetic interactions modify the density of states at the Fermi level and, consequently, change the iron d-band polarization [4]. The iron moments increase also with the increase of the gadolinium content, and thus the core polarization due to the iron 3d electrons is also influenced.

In order to characterize the magnetic interactions in the system, we use the exchange field H_{ex} in the molecular field approximation. On the iron sublattice magnetization acts $H_{ex}(\text{Fe})$ as given by :

$$H_{ex}(\text{Fe}) = J_{\text{Fe-Fe}} M_{\text{Fe}} + J_{\text{Gd-Fe}} M_{\text{Gd}}. \quad (1)$$

We denote by $J_{\text{Fe-Fe}}$ and $J_{\text{Gd-Fe}}$, the molecular field coefficients characterizing the magnetic interactions between the iron moments, gadolinium-iron, respectively. The $H_{ex}(\text{Fe})$ values take into account the polarization of core electrons by both the gadolinium (M_{Gd}) and the iron (M_{Fe}) magnetization. If we assume that $J_{\text{Gd-Fe}}$ and $J_{\text{Fe-Fe}}$ are constant along series, it follows that the induced hyperfine field is proportional to the effective spin. But the above assumption is not valid, as proved by the magnetic measurements [4].

Using the magnetic data [4] we have calculated the $H_{ex}(\text{Fe})$ values. As seen from figure 7 a linear depen-

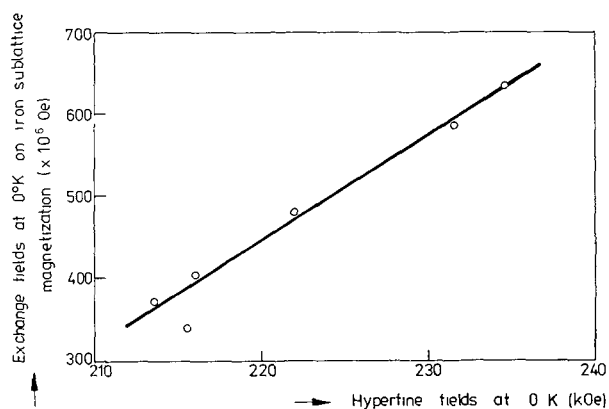


FIG. 7. — Dependence of the hyperfine fields (extrapolated at 0 K) with the exchange interactions.

dence between the exchange fields and hyperfine fields is observed. The proportionality constant is $H_n/H_{\text{ex}}(\text{Fe}) \simeq 0.78 \times 10^{-2}$.

The hyperfine field per unit spin in $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ system is

$$A = (145 \pm 3) \text{ kOe } \mu_B^{-1},$$

for all the compositions (see Table I). The analysis of the temperature dependence of A for iron showed that the fractional change of A is less than 1 % between 4.2 and 400 K [14]. It seems therefore reasonable to analyse the behaviour of the iron sublattice magnetization using the mean hyperfine field values, \bar{H}_n . To compare the shapes of the thermal variation of $\bar{H}_n(x, T)/\bar{H}_n(x, 0)$ values we use the parameter $h(x, T)$ previously defined [15]

$$h(x, T) = \bar{H}_n(x, T)/\bar{H}_n(x, 0) - \bar{H}_n(x = 1, T)/\bar{H}_n(x = 1, 0). \quad (2)$$

The $h(x, T)$ values are negative as observed from figure 8 and increase in absolute magnitude as x

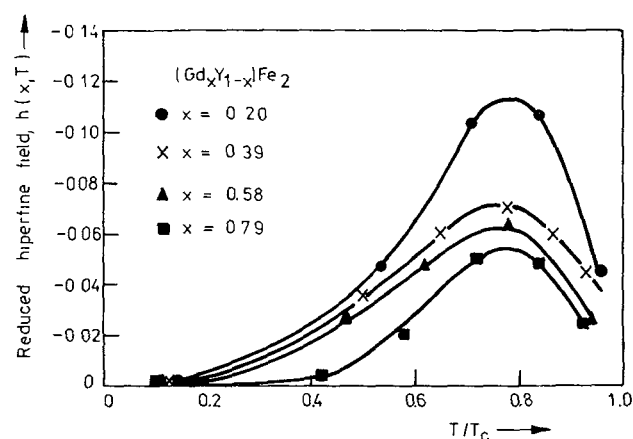


FIG. 8. — Plot of $h(x, T)$ as function of the reduced temperatures T/T_c .

decrease. The temperature dependence of $h(x, T)$ values [15] is characteristic for the localized moments, showing the decrease of the exchange coupling felt by the iron spin. This decrease is also reflected by the composition dependence of the Curie temperatures (Fig. 3).

Probably, the magnetic behaviour of iron in these compounds can be considered in the model proposed by Stearns [16] which assumes that the greatest part of d electrons is in a narrow d-band and only a small part of these electrons is itinerant. Because of the experimental errors we cannot estimate accurately the number of itinerant d-electrons, starting from the composition dependence of the hyperfine field values as suggested by Stearns [16]. It seems that this number is near 10 % as shown also from the magnetic measurements [4].

The isomer shifts $\delta(x)$, for a fixed temperature, are not dependent on the composition, in the limit of the experimental errors (see Table I). The substitution of gadolinium by yttrium does not change the electronic concentration of the system. On the other hand, the lattice parameters of GdFe_2 and YFe_2 are nearly the same and thus the volume effects on $\delta(x)$ values are negligible.

4. Conclusions. — The easy axis of magnetization changes in $(\text{Gd}_x\text{Y}_{1-x})\text{Fe}_2$ compounds by varying the temperature and composition. The spin reorientation diagram may be analysed considering the competing influences between the anisotropy of the iron sublattice and that of the exchange interactions, the latter decreasing more rapidly by increasing the temperature.

The thermal variation of the hyperfine field values suggests that the iron moments are largely localized.

The small jump in the composition dependence of the hyperfine field values is due to the change of the sign in the polarization of 4s electrons. A correlation between the exchange fields acting on the iron magnetization and the Fe^{57} hyperfine field values was put into evidence.

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