

# Mössbauer effect evidence of spin reorientation in $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$ intermetallic compounds

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## Abstract

Spin reorientation in  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  system, originating from competition between the magnetic anisotropies of the erbium and iron sublattices, was observed by the  $^{57}\text{Fe}$  Mössbauer spectroscopy below room temperature. The spin transition temperature is lowered by non-magnetic dilution within the rare earth crystal sublattice, caused by substitution of cerium for erbium. There is evidence that the process proceeds not at a discrete temperature but in a wide temperature range. The discrete values of the  $^{57}\text{Fe}$  hyperfine interaction parameters, derived from Mössbauer absorption spectra, are consistent with localized interactions of iron atoms with their nearest neighbours. It was found that substitution of cerium for erbium slightly reduces hyperfine magnetic fields at iron sites and it only has a minute influence on the values of the isomer shifts and quadrupole interactions.

*Keywords:* Spin reorientation; Ternary rare earth compounds; R-Fe-B compounds; Mössbauer effect

## 1. Introduction

Some of the  $\text{RE}_2\text{Fe}_{14}\text{B}$ -type compounds (RE = rare earth) possess the outstanding permanent magnet properties which result from the large saturation magnetization, strong uniaxial anisotropy and relatively high Curie temperatures [1]. They crystallize in a tetragonal structure with the  $P4_2/mnm$  space group. As determined independently by several groups [2–4], there are six inequivalent crystal sites ( $16k_1$ ,  $16k_2$ ,  $8j_1$ ,  $8j_2$ ,  $4c$  and  $4e$ ) occupied by iron atoms, two ( $4f$  and  $4g$ ) occupied by rare earth atoms and one ( $4f$ ) occupied by boron atoms. The numbers of the 3d, rare earth and boron nearest neighbors of the 3d-metal sites are given in parentheses as follows:  $16k_1$  (10,2,1),  $16k_2$  (10,2,0),  $8j_1$  (9,3,0),  $8j_2$  (12,2,0),  $4c$  (8,4,0) and  $4e$  (9,2,2).

The magnetic properties of the  $\text{RE}_2\text{Fe}_{14}\text{B}$  compounds depend on the type of the rare earth constituent. The iron sublattice, which consists of six sets of inequivalent iron sites, has uniaxial anisotropy along the crystal  $c$ -axis while that of the rare earth sublattice, composed of two sets of inequivalent crystal sites, varies according to the nature of the rare earth cations. At elevated temperatures the overall anisotropy of the rare earth sublattice is uniaxial, along the

$c$ -axis, in the compounds with RE elements for which the Stevens factor  $\alpha_j$  is negative (Pr, Nd, Tb, Dy, Ho). It is planar, however, perpendicular to the  $c$ -axis, in the compounds with RE elements for which  $\alpha_j$  is positive (Sm, Er, Tm). Owing to a strong magnetic coupling between the 3d and 4f elements, the iron and the rare earth sublattices are collinearly oriented in the  $\text{RE}_2\text{Fe}_{14}\text{B}$  compounds: ferromagnetically for light RE or antiferromagnetically for heavy RE elements.

At elevated temperatures the iron sublattice magnetization predominates over the rare earth one. The easy direction of magnetization of all  $\text{RE}_2\text{Fe}_{14}\text{B}$  compounds is parallel to the crystal  $c$ -axis except for those containing samarium. With lowering temperature the magnetizations of both the rare earth and the iron sublattices increase; this is faster with the rare earths. At the same time, the magnetocrystalline anisotropy of the rare earth sublattice develops rapidly, as the temperature decreases, becoming larger at certain temperatures than that of the iron sublattice. The spin orientation does not change in materials having RE elements with the negative Stevens factor. They are still oriented parallel to the  $c$ -axis. This is not the case in compounds in which RE elements have a positive Stevens factor. They undergo spin reorientation from

a direction parallel to the *c*-axis (uniaxial orientation) to a direction perpendicular to it (planar orientation) as the result of competition between the two sublattice magnetocrystalline anisotropies. At low temperatures the rare earth anisotropy is dominant.

The spin reorientation can also be induced at a constant temperature. This can be done, for instance, by non-magnetic dilution within the rare earth crystal sublattice or by a partial substitution of the rare earth elements with a positive Stevens factor for one characterized by a negative Stevens factor, or vice versa.

The spin transition phenomena in the  $\text{RE}_2\text{Fe}_{14}\text{B}$  compounds have been studied with many methods [5,6] among which the Mössbauer spectroscopy has proved very useful [7–13] due to its microscopic character. The sophisticated approach of the method, including monocrystals, magnetically oriented samples or polarized Mössbauer  $\gamma$ -rays, can provide most valuable information on the spin reorientation phenomenon.

The purpose of this paper is to report on the results of the Mössbauer spectroscopy investigations of the hyperfine interactions in the  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$ ,  $0.125 < x < 0.75$  system, at room and liquid nitrogen temperatures, and to give an indication of the spin reorientation phenomenon induced by substitution of cerium for erbium.

## 2. Experimental

The samples were produced by melting stoichiometric proportions of the constituent elements (99.9% purity or better) in a water-cooled copper boat by induction heating under flowing high purity argon. The as-cast ingots were annealed at 900 °C for 2 weeks and then rapidly cooled to room temperature. The phase integrity of the samples was verified by X-ray diffraction analysis, thermal magnetic analysis and optical metallographic microscope. No other phase but the one with  $P4_2/mnm$  space group has been detected.

The  $^{57}\text{Fe}$  Mössbauer absorption spectra were recorded at room and liquid nitrogen temperatures using a  $^{57}\text{Co}/\text{Cr}$  source, kept at room temperature, and a constant acceleration Mössbauer spectrometer. A high purity metallic iron foil was used for calibration of the velocity scale. Isomer shifts were established with respect to the centre of gravity of the metallic iron Mössbauer spectrum recorded at room temperature. A least squares computer program was used to derive the values of the hyperfine interaction parameters from Mössbauer absorption spectra.

## 3. Results and discussion

The investigated system,  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  ( $x =$

0.125, 0.25, 0.5 and 0.75), possesses two different magnetic sublattices. One is composed of iron cations, occupying six inequivalent crystal sites, while the other one is formed by rare earth cations, situated in two inequivalent crystal sites. Magnetocrystalline anisotropy of the iron sublattice prefers spin orientation along the *c*-axis while that of the erbium sublattice prefers orientation in the plane perpendicular to it. At elevated temperatures (above 325 K) the iron sublattice wins the competition with the erbium sublattice in non-magnetically diluted  $\text{Er}_2\text{Fe}_{14}\text{B}$  samples and, as a result of this, spins are oriented along the *c*-axis. At lower temperatures the spins are plane oriented, perpendicularly to the *c*-axis in the  $\text{Er}_2\text{Fe}_{14}\text{B}$  sample, since at those temperatures the erbium magnetocrystalline anisotropy predominates that of the iron sublattice. Non-magnetic dilution in the rare earth sublattice, caused by substitution of cerium for erbium in  $\text{Er}_2\text{Fe}_{14}\text{B}$  samples, weakens the rare earth magnetocrystalline anisotropy and hence lowers the spin transition temperature, which then becomes composition dependent. This is shown in Fig. 1 where the spin transition temperatures, derived from magnetic measurements performed with the method described elsewhere [14], are presented. Going down from elevated temperatures, the investigated compounds  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  ( $x = 0.125, 0.25, 0.5, 0.75$ ), undergo spin transition, from a direction parallel to the *c*-axis to plane perpendicular to it.

In order to get some insight into the local magnetic properties of iron in its six crystal sites in the  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  system and to get direct evidence for spin reorientation, induced by substitution of cerium for erbium, we used the Mössbauer spectroscopy. This distinguishes the non-equivalent crystal sites and follows their individual magnetizations. The

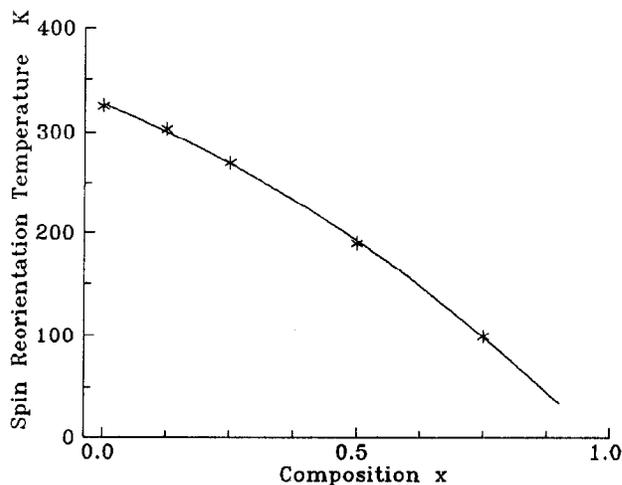


Fig. 1. Spin reorientation temperatures in  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  intermetallic compounds as a function of Ce content. The solid line guides the eye.

influence on the shape of Mössbauer spectra of the combined electric quadrupole and magnetic dipole interactions makes it possible to observe, in a simple manner, the spin reorientation phenomenon.

The Mössbauer absorption spectra recorded for our samples at room and at liquid nitrogen temperatures are shown in Figs. 2 and 3 respectively, while the values of the hyperfine interaction parameters derived from the spectra are compiled in Table 1 and shown in Figs. 4 and 5. Owing to the six non-equivalent crystal sites occupied by iron atoms, the Mössbauer absorption spectra of the investigated compounds are very complex. Even visual inspection of the spectra shows that all those recorded at room temperature, except for  $x = 0.125$ , are very similar to each other. The same can be stated about the spectra recorded at liquid nitrogen temperature, except that for  $x = 0.75$ . These similarities in spectra shapes at a given temperature are due to the minute influence of substitution of

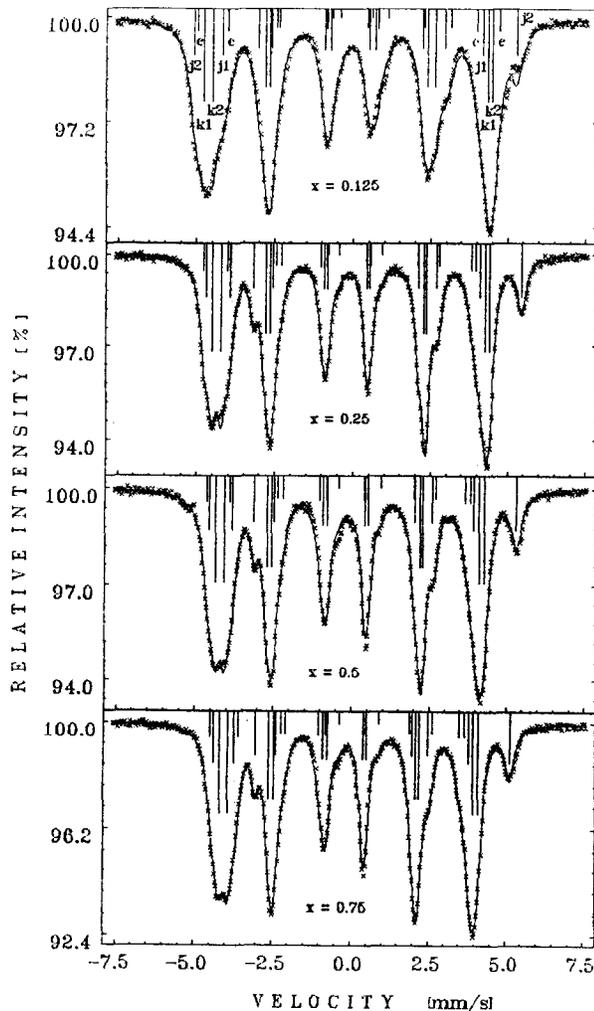


Fig. 2. The  $^{57}\text{Fe}$  Mössbauer absorption spectra recorded at 295 K for the  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  intermetallic compounds. The spectra have been resolved into Zeeman sextets with the relative intensities which are in accord with site populations,  $16k_1:16k_2:8j_1:8j_2:4c:4e$ . In the  $x = 0.125$  composition the spin transition has not been completed at 295 K.

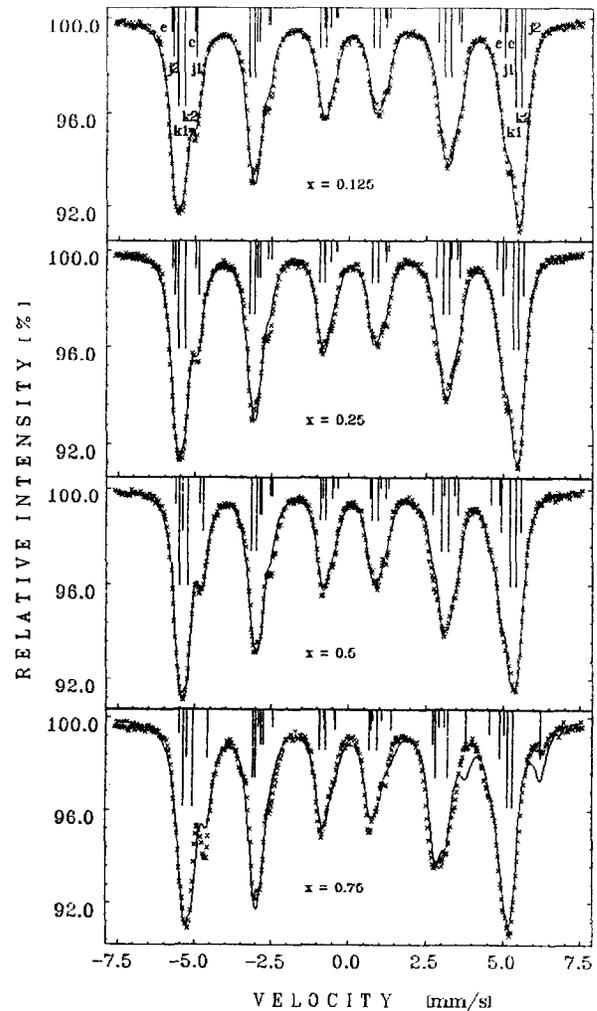


Fig. 3. The  $^{57}\text{Fe}$  Mössbauer absorption spectra recorded at 78 K for the  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  intermetallic compounds. The spectra have been resolved into Zeeman sextets with the relative intensities which are in accord with site populations,  $16k_1:16k_2:8j_1:8j_2:4c:4e$ . In the  $x = 0.75$  composition the spin transition has not been completed at 78 K.

cerium for erbium in the two rare earth sites on the hyperfine interaction parameters at the iron lattice sites. However, excluding the two above-mentioned spectra, the room temperature spectra are distinctly different from those recorded at liquid nitrogen temperature; this is due to a spin rotation phenomenon which takes place between room and liquid nitrogen temperatures in the investigated samples. This process was not completed at room temperature for the  $x = 0.125$  sample nor at liquid nitrogen temperature for the  $x = 0.75$  sample.

The most obvious visual difference between the two groups of spectra discussed is the lack of the well-resolved satellite line, seen at 295 K at the velocity of about  $+5.3 \text{ mm s}^{-1}$ , in the spectra of the  $x = 0.125$ , 0.25 and 0.5 samples recorded at liquid nitrogen temperature. This line is the sixth line of the  $8j_2$  sublattice Zeeman sextet. Among the six crystal sites occupied by iron, the  $8j_2$  site has the largest magnetic

Table 1  
The  $^{57}\text{Fe}$  hyperfine interaction parameters of the  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  intermetallic compounds

Sample $x$	Parameter <sup>a</sup>	Measurement temperature (K)	Crystal site						
			16k <sub>1</sub>	16k <sub>2</sub>	8j <sub>1</sub>	8j <sub>2</sub>	4c	4e	
0.125	H	295	28.3	27.9	25.9	32.0	24.9	30.0	
		78	34.0	33.9	31.0	35.4	31.4	33.0	
	⟨H⟩	295				28.3			
		78				33.5			
	IS	295	-0.112	-0.104	-0.100	0.030	-0.030	0.100	
		78	0.019	0.019	0.033	0.152	0.213	0.022	
QS	295	-0.200	0.206	0.200	0.138	0.020	-0.494		
	78	-0.208	0.196	0.064	-0.326	-0.312	-0.910		
0.25	H	295	27.2	26.8	24.9	31.5	24.3	27.1	
		78	33.7	33.6	30.6	35.1	31.2	32.7	
	⟨H⟩	295				27.2			
		78				33.2			
	IS	295	-0.185	-0.018	-0.074	0.066	-0.136	-0.085	
		78	0.004	0.010	0.030	0.164	0.225	-0.004	
QS	295	0.130	0.232	0.290	0.614	0.084	-0.662		
	78	-0.204	0.184	0.098	-0.310	-0.354	-0.920		
0.50	H	295	26.2	25.9	24.1	30.6	23.4	26.3	
		78	33.3	33.1	30.0	34.0	30.1	31.7	
	⟨H⟩	295				26.3			
		78				32.5			
	IS	295	-0.191	-0.019	-0.077	0.059	-0.150	-0.078	
		78	-0.013	0.014	0.027	0.233	0.159	-0.018	
QS	295	0.128	0.232	0.274	0.648	0.058	-0.654		
	78	-0.272	0.174	0.180	-0.252	-0.256	-0.992		
0.75	H	295	25.2	24.9	23.4	29.5	22.0	25.2	
		78	33.1	31.6	29.4	35.6	29.7	31.2	
	⟨H⟩	295				25.2			
		78				32.1			
	IS	295	-0.189	-0.022	-0.091	0.053	-0.114	-0.079	
		78	0.039	-0.049	0.066	0.476	0.272	-0.235	
QS	295	0.134	0.218	0.242	0.662	0.124	-0.686		
	78	-0.122	0.174	0.172	0.004	-0.094	-0.470		

<sup>a</sup> H, the hyperfine magnetic field; ⟨H⟩, the averaged hyperfine magnetic field; IS, the isomer shift with respect to metallic iron at room temperature; QS, the quadrupole shift of the subspectra lines:  $[(v_6 - v_5) - (v_2 - v_1)]/2$ . Errors: H (0.1 T), ⟨H⟩ (0.1 T), IS (0.005 mm s<sup>-1</sup>), QS (0.008 mm s<sup>-1</sup>).

hyperfine field and for samples with spin orientation along the  $c$ -axis it has the largest positive quadrupole interaction (Table 1). When spins are rotated 90° from the  $c$ -axis the quadrupole parameter is reduced by a factor of approximately  $-2$ . Thus the line is shifted towards the lower velocity and is no longer resolved. The sixth line of the  $8j_2$  sublattice Zeeman sextet is always present in Mössbauer spectra recorded for samples with spins orientated along the  $c$ -axis (see Fig. 2,  $x = 0.25, 0.50$  and  $0.75$ ). Its shift of approximately  $0.6 \text{ mm s}^{-1}$  (compare spectra  $x = 0.5$  and  $x = 0.75$  in Fig. 3) towards lower velocities indicates reorientation of spin from a direction parallel to the  $c$ -axis to perpendicular to it (Fig. 3,  $x = 0.125, 0.25$  and  $0.50$ ). A small remnant of this line, observed in the two excluded spectra (Fig. 2,  $x = 0.125$  and Fig. 3,  $x = 0.75$ ), indicates that the spin rotation phenomenon has not been completed at the given temperatures, although

they are somewhat lower than the appropriate spin transition temperatures (see Fig. 1). Thus, the spin transition in the investigated compounds must take place not at a discrete temperature for each sample but over some wide range of temperature. This is not surprising from the magnetic microscopic point of view since two different rare earth elements are statistically distributed among 4f and 4g rare earth sites. One of them (Er) forces spin orientation perpendicular to the  $c$ -axis while the other one (Ce) is weakening that process, causing the spin transition temperature to be composition dependent on the microscopic scale.

The spectra recorded for the  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  ( $x = 0.125, 0.25, 0.5$  and  $0.75$ ) system were resolved into Zeeman sextets. Each sextet in any given spectrum is characterized by its hyperfine magnetic field, isomer shift and electric quadrupole interaction. Common for all sextets are three different linewidths and one line

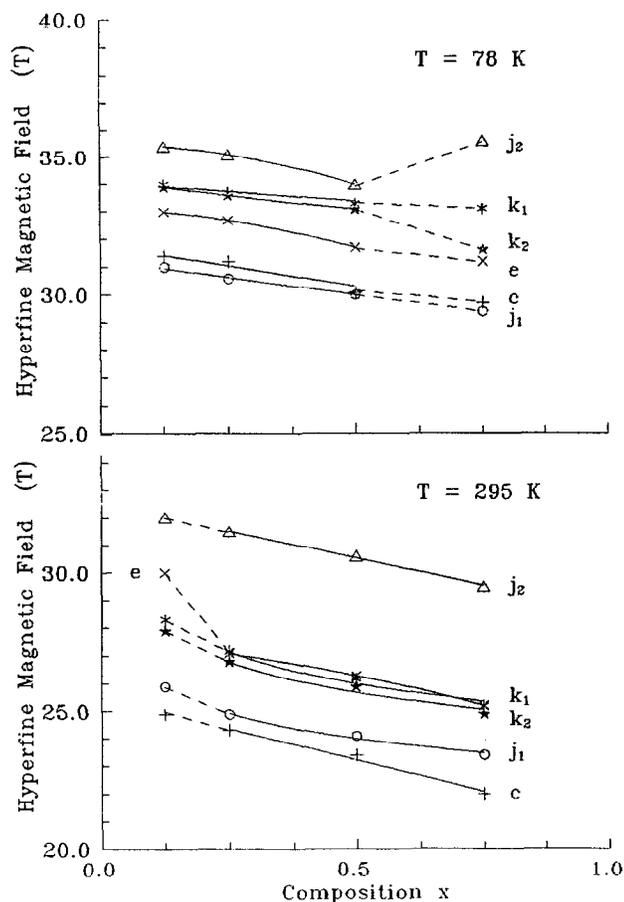


Fig. 4. Composition dependence of hyperfine magnetic field for different crystal sites. the solid lines guide the eye. In the  $x = 0.125$  composition at 295 K and  $x = 0.75$  composition at 78 K, the spin transition has not been completed.

intensity ratio. For all investigated compositions the number of Zeeman subspectra, six for each composition, and their relative intensities are completely in accord with site populations. This is shown by the line diagrams in Figs. 2 and 3. These diagrams also demonstrate an identical sequence of the six subspectra line positions on the velocity scale in the spectra recorded for all compositions, at a given temperature, except for those in which spin transition has not been completed. This proves the correctness of the spectra resolution and demonstrates the usefulness of Mössbauer spectroscopy in investigating such complex systems.

Non-magnetic dilution within the rare earth sublattice, caused by substitution of cerium for erbium, slightly diminishes the hyperfine magnetic fields at all iron sites, both at room and liquid nitrogen temperatures. The decrease in average field value per one-substituted-atom is 2.0 T and 1.3 T at room and liquid nitrogen temperatures respectively. The values of the hyperfine magnetic fields reflect the populations of magnetic cations in the nearest neighbour configurations of the iron sites, thus confirming localized interactions of iron atoms with their nearest neighbours.

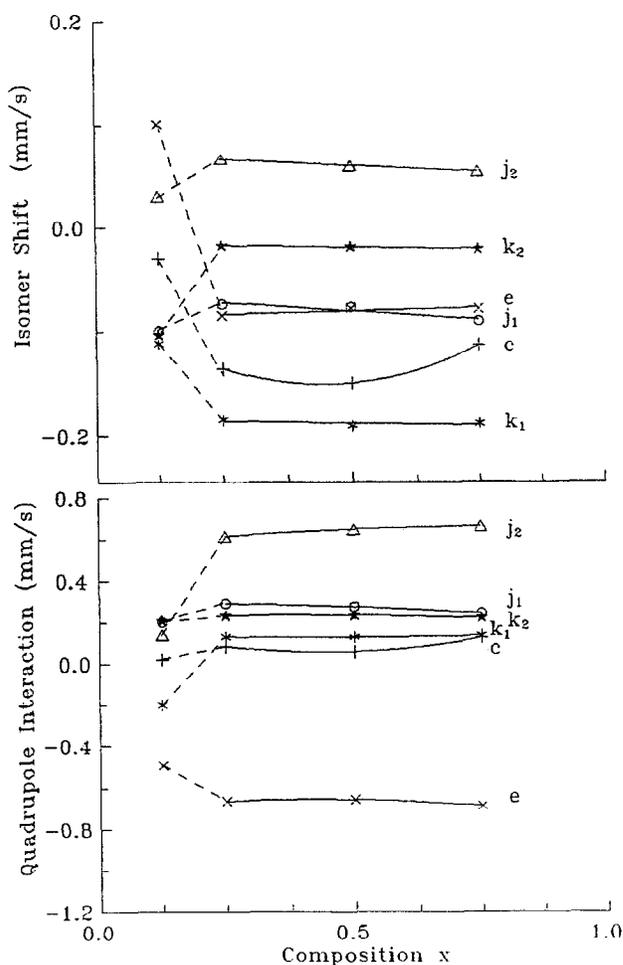


Fig. 5. Composition dependence of isomer shift and quadrupole interaction for different crystal sites at 295 K. The solid lines guide the eye. In the  $x = 0.125$  composition the spin transition has not been completed at 295 K.

The isomer shifts and quadrupole splittings are very slightly substitution dependent. All quadrupole shifts of subspectra lines, except that of  $4e$  sites, are positive at room temperature for the samples with spin orientation along the  $c$ -axis. At liquid nitrogen temperature only  $16k_2$  and  $8j_1$  positions exhibit positive quadrupole shifts of the subspectra lines. The change in sign of quadrupole shifts is interpreted as evidence of spin reorientation which takes place between room and liquid nitrogen temperatures.

The spectra of the samples in which spin reorientation was not completed at the temperature of investigation shows some deviation from the overall trends. They should be resolved into more subspectra than the number of inequivalent crystal sites occupied by iron cations. This procedure may not guarantee, however, physical meaning of derived spectra parameters, since spectra resolution may not be unique.

In conclusion, the non-magnetic dilution within the rare earth sublattice of the  $(\text{Er}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$  system, caused by substitution of cerium for erbium does not

influence the hyperfine interaction parameters greatly. It induces, however, the spin reorientation, which takes place between room and liquid nitrogen temperatures. Mössbauer spectroscopy proved to be useful in studying this phenomenon.

## References

- [1] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto and Y. Matsuura, *J. Appl. Phys.*, **55** (1984) 2083.
- [2] J.F. Herbst, J.J. Croat and F.E. Pinkerton, *Phys. Rev. B*, **29** (1988) 4176.
- [3] D. Givord, H.S. Li and J.M. Moreau, *Solid State Commun.*, **50** (1984) 497.
- [4] C.B. Shoemaker, D.P. Shoemaker and R. Fruchart, *Acta Crystallogr. C*, **40** (1984) 1665.
- [5] J. Bartolome, in G.J. Long and F. Grandjean (eds.), *Supermagnets, Hard Magnetic Materials*, NATO ASI Series, Kluwer, 1990, p. 261.
- [6] J. Bartolome, in F. Grandjean, G.J. Long and K.H.J. Buschow (eds.), *Interstitial Intermetallic Alloys*, NATO ASI Series, Kluwer, 1994, p. 559.
- [7] A. Vasquez, J.M. Friedt, J.P. Sanchez, P. L'Héritier and R. Fruchard, *Solid State Commun.*, **55** (1985) 783.
- [8] D.C. Price, R.K. Day and J.B. Dunlop, *J. Appl. Phys.*, **59** (1986) 3585.
- [9] N.C. Koon, M. Abe, E. Callen, N.B. Das, S.H. Liou, A. Martinez and R. Segnan, *J. Magn. Magn. Mater.*, **54–57** (1986) 593.
- [10] R. Fruchart, P. L'Héritier, P. Dalmas de Réotier, D. Fruchart, P. Wolfers, J.M.D. Coey, L.F. Ferreira, R. Guillen, P. Vulliet and A. Yaouanc, *J. Phys. F*, **17** (1987) 483.
- [11] A. Simopoulos and D. Niarchos, *Hyp. Inter.*, **40** (1988) 425.
- [12] M. Rosenberg, P. Deppe and Th. Sinnemann, *Hyp. Inter.*, **45** (1989) 3.
- [13] J.J. Bara, B.F. Bogacz and A.T. Pędzwiatr, *J. Magn. Magn. Mater.*, **99** (1991) 204.
- [14] A.T. Pędzwiatr and W.E. Wallace, *J. Magn. Magn. Mater.*, **65** (1987) 139.