Distributions of the hyperfine interaction parameters in $(Er_{1-x}Sm_x)_2Fe_{14}B$ as seen by Mössbauer spectroscopy

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Abstract

The distributions of the hyperfine interaction parameters, caused by substitution of Sm for Er in the $(Er_{1-x}Sm_x)_2Fe_{14}B$ system, were studied by Mössbauer spectroscopy both at room and liquid nitrogen temperatures. It was proved that the random distribution of the rare earth atoms over their crystal sites and the additive contribution of the Sm atoms to the values of the hyperfine interaction parameters at the iron crystal sites lead to a linear dependence of the average values of the ^{57}Fe hyperfine magnetic field, isomer shift and quadrupole interaction on the Sm concentration in the present compounds. From these linear relations, the contributions Δ_H, Δ_{IS} and Δ_{QS} to the values of the hyperfine magnetic field, isomer shift and quadrupole interaction, caused by the presence of the Sm atom in the nearest neighbour shell of the Fe crystal sites, were derived. No distinct correlations were found between the Δ_H, Δ_{IS} and Δ_{QS} values and those of the nearest neighbours and/or their distances from the Fe crystal sites. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Although the $RE_2Fe_{14}B$-type compounds have been intensively studied during the last 15 years and many of their properties are well understood [1], they still attract attention due to their giant coercivities, large energy products and relatively high Curie temperature which lead to their increasing technical applications. The compounds crystallise in a tetragonal structure with the $P4_2/mnm$ space group. The iron atoms occupy six inequivalent crystal sites ($16k_1$, $16k_2$, $8j_1$, $8j_2$, $4c$, $4e$), the rare-earth atoms occupy two sites ($4f$ and $4g$) and one site ($4f$) only is occupied by the boron atoms [2–4]. For the notation of the sites we follow the Wyckoff convention. The numbers of the $3d$, rare earth and boron nearest neighbours 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).

Mössbauer spectroscopy has contributed greatly [5] to our understanding of the magnetic properties of these intermetallics since it has microscopic character and is sensitive to the electric and magnetic hyperfine interactions.

The purpose of this paper is to report on the results of investigations of the hyperfine interactions in the $(Er_{1-x}Sm_x)_2Fe_{14}B$ ($0.125 \leq x \leq 0.75$) system, performed at room and liquid nitrogen temperatures. Our attention has been focused on the distributions of the hyperfine interaction parameters caused by the substitution of Sm for Er. The contributions to the values of the hyperfine interaction parameters, caused by Sm ions present in the nearest neighbour rare earth shells of the different Fe crystal sites, have been derived from linear regressions of the averaged values of the hyperfine magnetic fields, isomer shifts and quadrupole interactions, as functions of the sample composition parameter x.

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 using X-ray diffraction analysis, thermal magnetic analysis and optical metallography. No phase other than that with the $P4_2/mnm$ space group has been detected.

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However, the Mössbauer absorption spectra indicate a small amount of iron impurities. The Curie temperatures were determined by plotting $M^2(T)$ and extrapolating the steep part of the curve to $M^2 = 0$.

The ^{57}Fe Mössbauer absorption spectra were recorded at room and liquid nitrogen temperatures using a ^{57}Co/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 iron Mössbauer spectrum. A least-squares computer program was used to derive from the Mössbauer absorption spectra the average values of the hyperfine interaction parameters for the $16k_1$, $16k_2$, $8j_1$, $8j_2$, $3c$ and $4e$ crystal sublattices. The spectra were numerically resolved into sets of six Zeeman sextets of intensities proportional to the site occupancies. Each sextet was characterised by its hyperfine magnetic field, isomer shift and electric quadrupole interaction. Common to all sextets were three different line widths and one line intensity ratio.

3. Average values of the hyperfine interaction parameters

Let us consider one of the Fe crystal sites $16k_1$, $16k_2$, $8j_1$, $8j_2$, $4c$ or $4e$ in $(Er_{1-x}Sm_x)_2Fe_{14}B$ and let us assume it
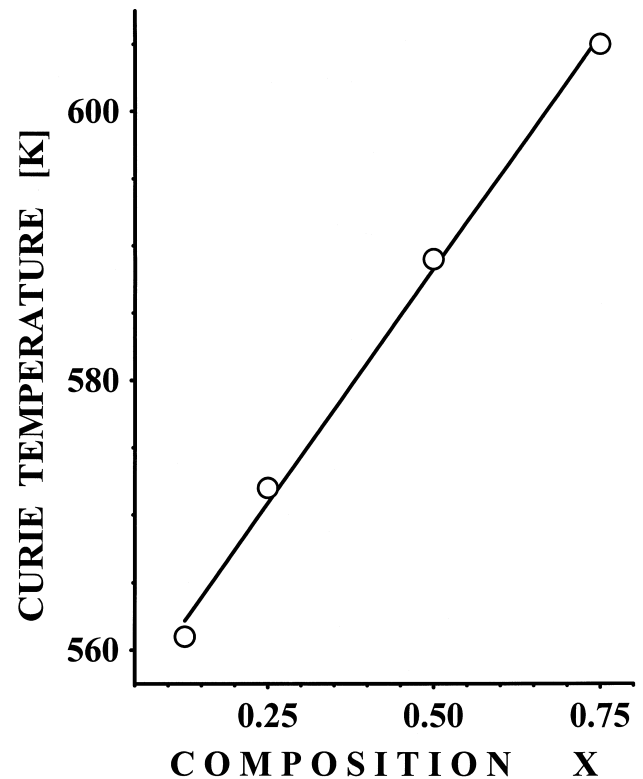

Fig. 1. Curie temperature of $(Er_{1-x}Sm_x)_2Fe_{14}B$ intermetallic compounds as a function of Sm content. The solid line represents a linear regression.

Table 1
^{57}Fe hyperfine interaction parameters of the $(Er_{1-x}Sm_x)_2Fe_{14}B$ intermetallic compounds[a]

x	T_C	T		$16k_1$	$16k_2$	$8j_1$	$8j_2$	$4c$	$4e$
0.125	561	78	IS	−0.041	−0.002	0.389	0.093	0.004	−0.039
			QS	−0.208	0.061	−0.088	−0.131	−0.047	0.126
			H	33.45	33.98	33.00	35.99	30.44	32.99
		295	IS	−0.192	−0.128	0.245	0.062	−0.094	−0.168
			QS	−0.177	0.046	−0.074	−0.145	−0.021	0.117
			H	29.29	29.28	28.67	31.56	26.12	28.34
0.25	572	78	IS	−0.037	0.005	0.393	0.097	−0.007	−0.035
			QS	−0.208	0.063	−0.093	−0.138	−0.034	0.128
			H	33.59	34.14	33.12	36.14	30.62	33.24
		295	IS	−0.189	−0.129	0.259	0.052	−0.081	−0.152
			QS	−0.182	0.053	−0.079	−0.139	−0.021	0.120
			H	29.54	29.61	28.91	31.82	26.34	28.54
0.50	589	78	IS	−0.035	0.006	0.397	0.078	−0.014	−0.040
			QS	−0.209	0.062	−0.090	−0.140	−0.033	0.154
			H	33.52	34.13	33.08	35.98	30.46	33.41
		295	IS	−0.177	−0.122	0.261	0.032	−0.092	−0.150
			QS	−0.186	0.061	−0.073	−0.135	−0.030	0.129
			H	29.95	30.19	29.37	32.22	26.78	29.06
0.75	605	78	IS	−0.023	0.018	0.407	0.066	0.002	−0.029
			QS	−0.213	0.070	−0.093	−0.144	−0.050	0.153
			H	33.58	34.26	33.15	36.03	30.28	33.42
		295	IS	−0.163	−0.115	0.274	−0.002	−0.091	−0.142
			QS	−0.192	0.069	−0.081	−0.125	−0.035	0.129
			H	30.22	30.62	29.70	32.53	26.95	29.42

[a] The parameters listed have the following meanings: x, the sample composition parameter; T_C (K), the Curie temperature; T (K), the temperature of measurement; IS (mm s^{-1}), the isomer shift with respect to metallic iron at room temperature; QS (mm s^{-1}), the quadrupole shift of the subspectra lines $[(V_6 − V_5) − (V_2 − V_1)]/2$; H (T), the hyperfine magnetic field. Errors: T_C (3 K), T (1 K), H (0.1 T), IS (0.008 mm s^{-1}), QS (0.008 mm s^{-1}).
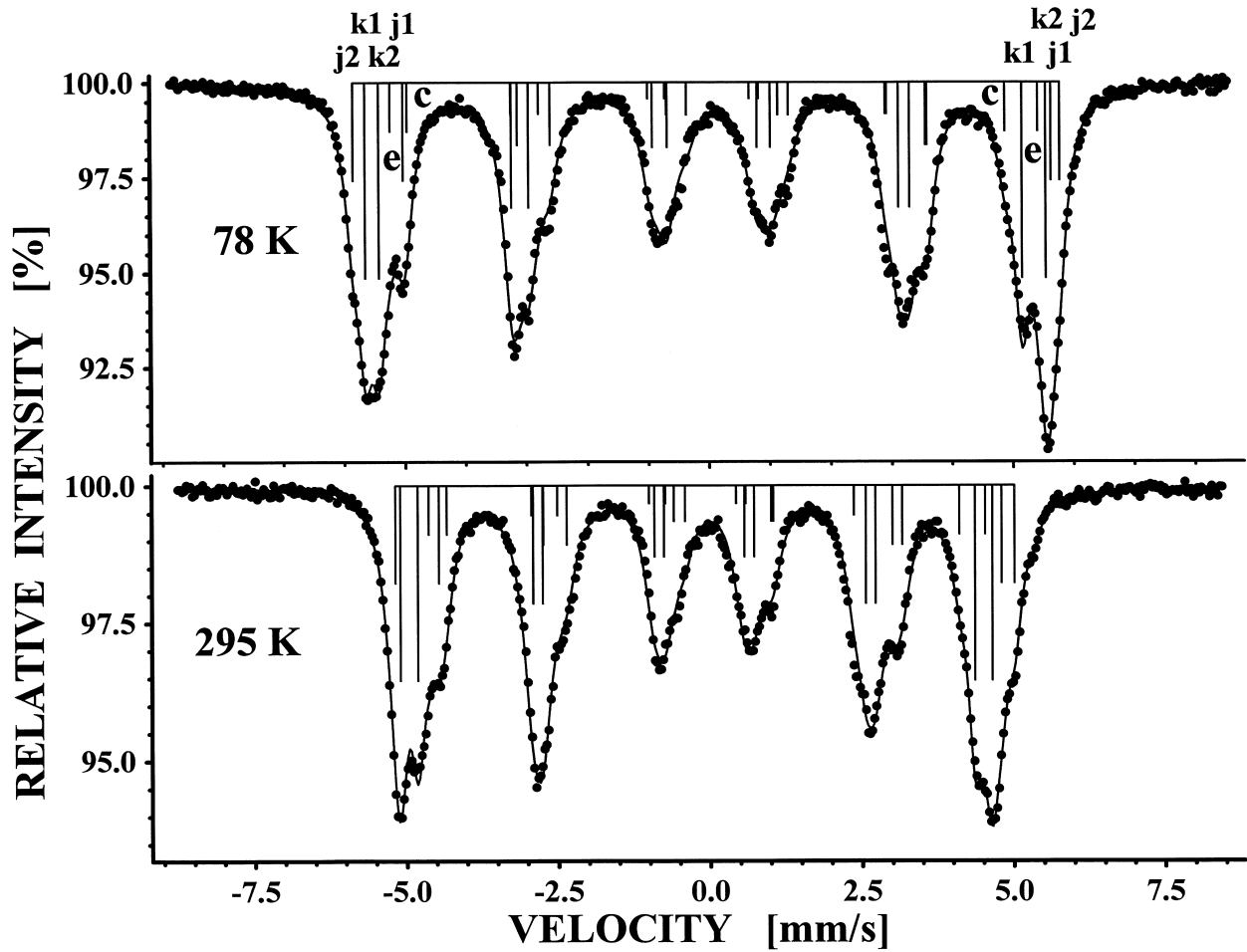
Fig. 2. Typical ^{57}Fe Mössbauer absorption spectra recorded at 78 K and 295 K for the $(Er_{0.875}Sm_{0.125})_2Fe_{14}B$ intermetallic compound. The spectra have been resolved into Zeeman sextets with relative intensities that are in accordance with the site populations: $16k_1$, $16k_2$, $8j_1$, $8j_2$, $4c$, $4e$.

has n nearest rare earth neighbours. We will not distinguish between $4f$ and $4g$ rare earth crystal sites because Mössbauer spectroscopy is unable to differentiate between their individual contributions to the hyperfine interaction parameters at the Fe sites. For a random distribution of Er and Sm ions over the rare earth sites, the probability $p(m, x)$ that the selected Fe ion will have a nearest neighbour rare earth configuration composed with m Sm ions and $(n − m)$ Er ions is given by the binomial formula

$$p(m, x) = \binom{n}{m} x^m (1 − x)^{n−m} \qquad (1)$$

where x is the sample composition parameter and m can vary in steps of 1 from 0 to n.

It is well known that a unique value of the hyperfine magnetic field $H(m, x)$ and, similarly, of the isomer shift $IS(m, x)$ and the quadrupole interaction $QS(m, x)$ is associated with each rare earth nearest neighbour configuration of a given Fe crystal site. This leads to $n + 1$ different Mössbauer subspectra for this Fe crystal site. In a first approximation we assume that any one of the m Sm ions present in the nearest neighbour shell of the selected

Fe ion, gives the same contribution Δ_H, Δ_{IS} and Δ_{QS}, to the value of the hyperfine magnetic field, isomer shift, and quadrupole interaction, respectively. This leads to the expressions

Table 2
Contributions Δ to the isomer shift (mm s^{-1}), quadrupole interaction (mm s^{-1}) and hyperfine magnetic field (T) in $(Er_{1-x}Sm_x)_2Fe_{14}B$ intermetallic compounds caused by Sm ions present in the nearest neighbour shell of various crystal sites occupied by Fe ions[a]

T		$16k_1$	$16k_2$	$8j_1$	$8j_2$	$4c$	$4e$
78	Δ_{IS}	0.013	0.014	0.009	−0.025	−0.001	0.006
	$\mp$	0.003	0.003	0.001	0.005	0.005	0.005
	Δ_{QS}	−0.004	0.006	−0.002	−0.009	−0.002	0.025
	$\mp$	0.002	0.003	0.002	0.003	0.005	0.008
	Δ_H	0.068	0.191	0.067	−0.019	−0.087	0.323
	$\mp$	0.067	0.065	0.035	0.091	0.062	0.120
295	Δ_{IS}	0.023	0.011	0.013	−0.050	−0.001	0.018
	$\mp$	0.002	0.002	0.003	0.005	0.004	0.006
	Δ_{QS}	−0.011	0.017	−0.002	0.015	−0.006	0.010
	$\mp$	0.002	0.002	0.003	0.002	0.001	0.003
	Δ_H	0.741	1.078	0.554	0.771	0.339	0.884
	$\mp$	0.062	0.063	0.033	0.056	0.050	0.051

[a] T, temperature (K). The errors of Δ are also presented.

$$H(m, x) = H_0 + m\Delta_H \tag{2}$$

$$IS(m, x) = IS_0 + m\Delta_{IS} \tag{3}$$

and

$$QS(m, x) = QS_0 + m\Delta_{QS} \tag{4}$$

H_0, IS_0 and QS_0 are the corresponding values of the hyperfine interaction parameters for $m = 0$.

Generally, the energy resolution of Mössbauer spectroscopy is not good enough to resolve uniquely a given Mössbauer spectrum into a set of subspectra corresponding to $n + 1$ different nearest neighbour configuration of each
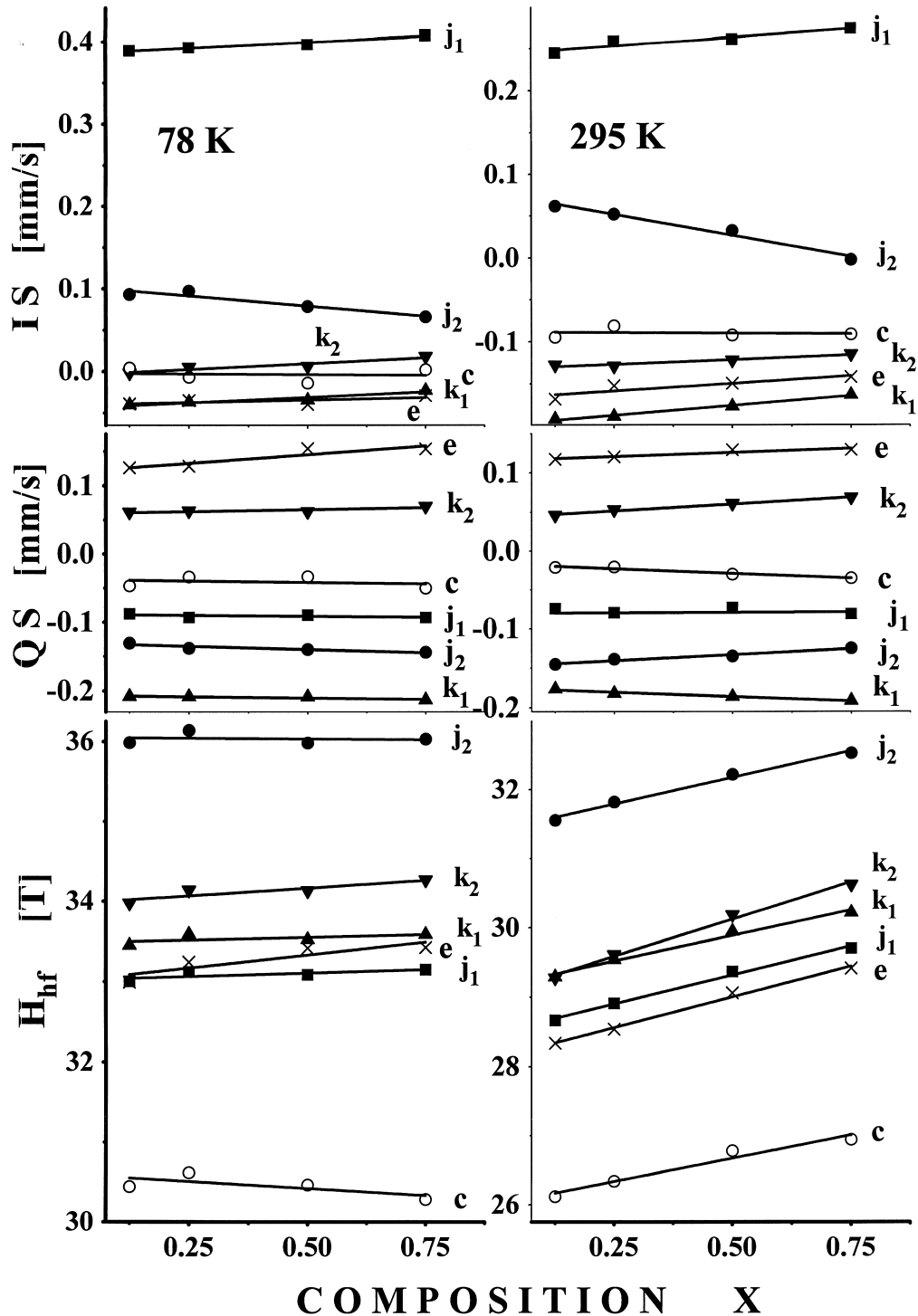

Fig. 3. Composition dependence of isomer shift, quadrupole interaction and hyperfine magnetic field for different crystal Fe sites of the $(Er_{1-x}Sm_x)_2Fe_{14}B$ intermetallic compounds. The solid lines represent the linear regression.

Fe crystal site in our compounds. Up to now such an approach [6] was applied successfully for compounds with simple crystal structure, mainly for ferrites, and almost exclusively for the values of the hyperfine magnetic fields. However, the values of Δ_H, Δ_{IS} and Δ_{QS} can be determined by Mössbauer spectroscopy, even for compounds with complex crystal structure, as in our case, if one notices that the binomial formula (1) and Eqs. (2)–(4) lead to the linear relations

$$\overline{H(x)} = H_0 + n\Delta_H x \tag{5}$$

$$\overline{IS(x)} = IS_0 + n\Delta_{IS}x \tag{6}$$

and

$$\overline{QS(x)} = QS_0 + n\Delta_{QS}x \tag{7}$$

between the averaged values of the hyperfine magnetic field $\overline{H(x)}$, isomer shift $\overline{IS(x)}$ and quadrupole interaction
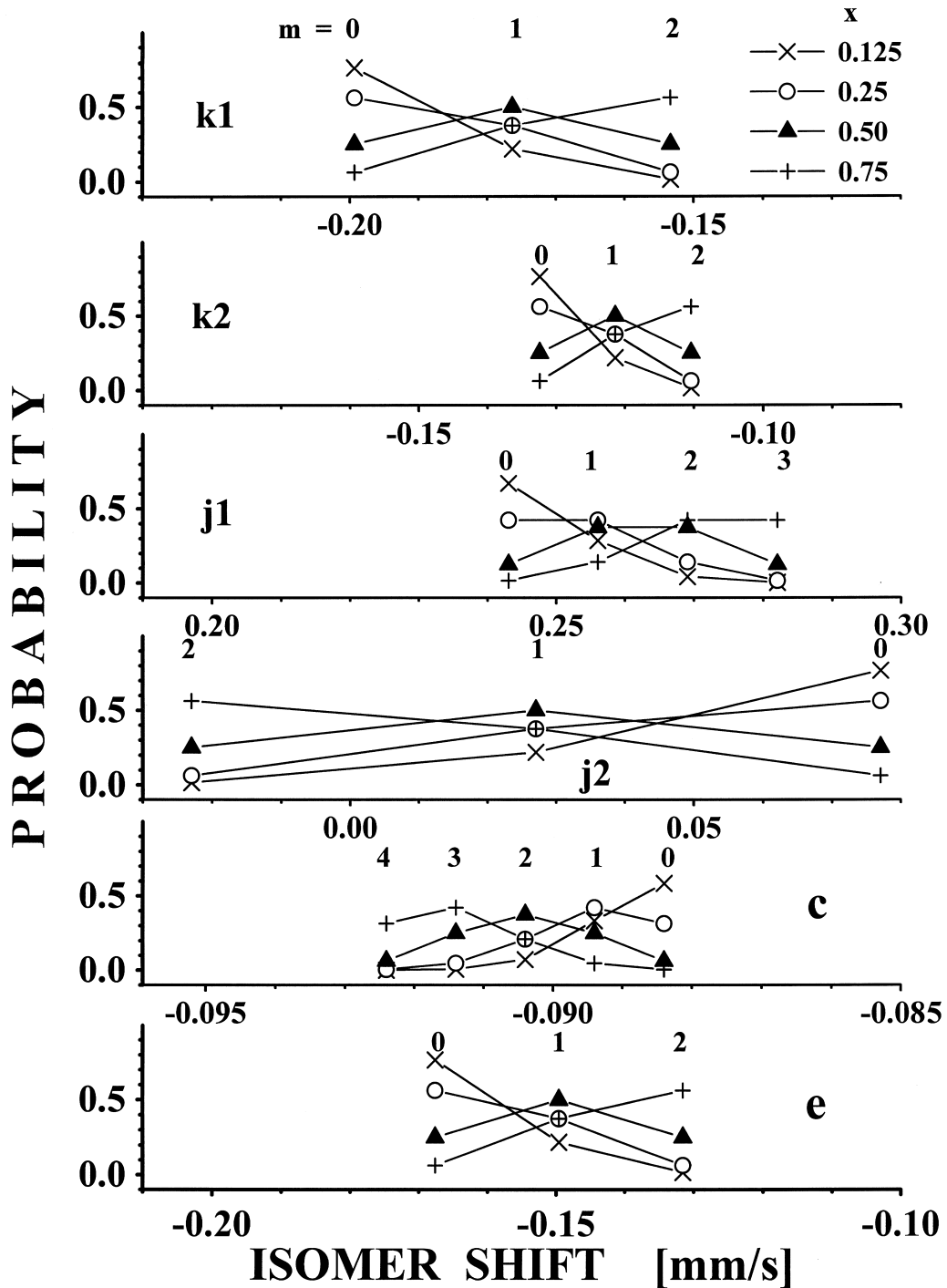

Fig. 4. Distribution diagrams of isomer shift at 295 K constructed for different Fe crystal sites of the $(Er_{1-x}Sm_x)_2Fe_{14}B$ intermetallic compounds. For each iron crystal site the probability is normalised to unity. Numbers (m) of Sm atoms as the nearest neighbours of the iron sites are indicated above each diagram.

$\overline{QS(x)}$ at a given Fe crystal site, and the sample composition parameter x. The Δ_H, Δ_{IS} and Δ_{QS} values can be derived from the slopes of these concentration dependencies.

4. Results and discussion

The substitution of Sm for Er in the $(Er_{1-x}Sm_x)_2Fe_{14}B$

system causes a linear increase of the values of the Curie temperature as a function of Sm concentration in the compounds (see Fig. 1), at a rate of 69.6 K per one substituted atom.

Typical Mössbauer spectra recorded for our system at 78 K and 295 K are shown in Fig. 2. Not taking into account the influence of nearest neighbours of the iron sites on the hyperfine interactions, the Mössbauer spectra were re-
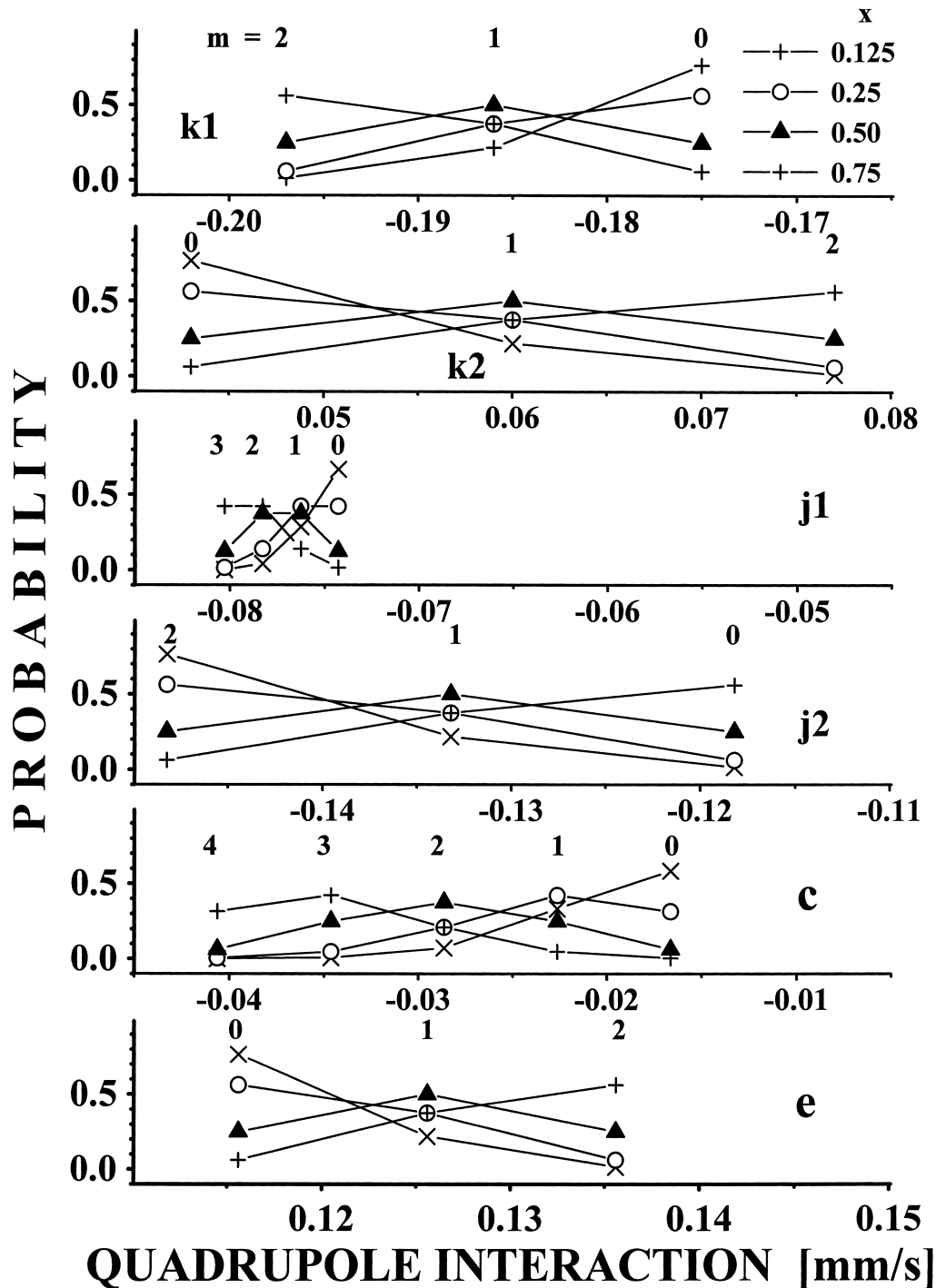

Fig. 5. Distribution diagrams of quadrupole interaction at 295 K constructed for different Fe crystal sites of the $(Er_{1-x}Sm_x)_2Fe_{14}B$ intermetallic compounds. For each iron crystal site the probability is normalised to unity. Numbers (m) of Sm atoms as the nearest neighbours of the iron sites are indicated above each diagram.

solved into a set of six Zeeman sextets. Each sextet corresponds to one of the six different Fe crystal site $16k_1$, $16k_2$, $8j_1$, $8j_2$, $4c$ and $4e$. The values of the hyperfine interaction parameters derived from the spectra are compiled in Table 1. Since all of them show only a minute dependence on the Sm concentration, each single subspectrum sufficiently well describes, in a first approximation, the averaged values of the hyperfine interaction parameters [Eqs. (5)–(7)] at a given crystal site. Thus, from the linear x dependence of the $H(x)$, $IS(x)$ and $QS(x)$ values (see Fig. 3), we could derive the contributions Δ_H, Δ_{IS} and Δ_{QS} to the values of the hyperfine magnetic field, isomer shift and quadrupole interactions caused by Sm ions present in the nearest neighbour rare earth shells of different iron crystal sites (see Table 2). Using the Δ_H, Δ_{IS} and Δ_{QS} data and the binomial formula (1) we have constructed the distribution
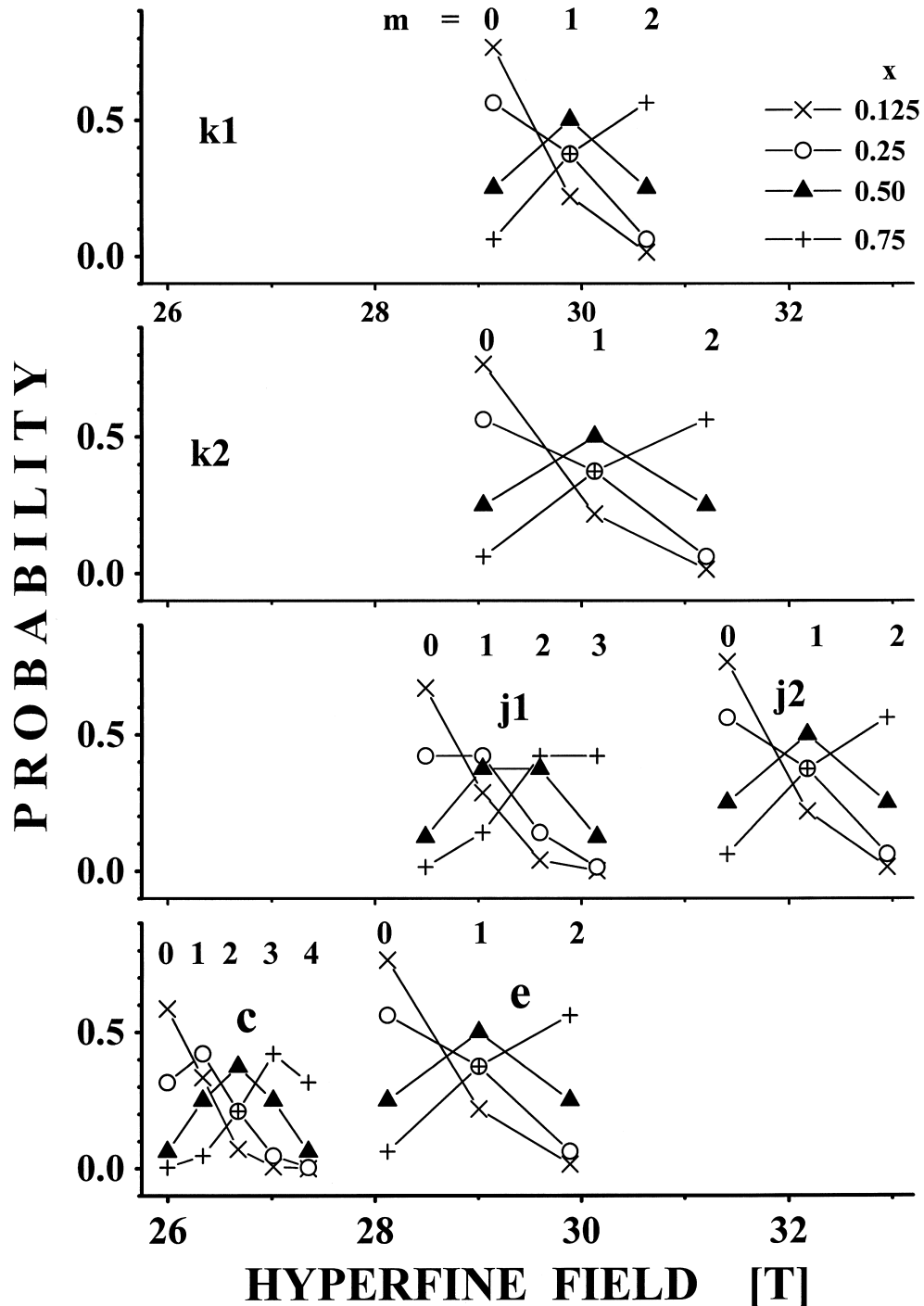

Fig. 6. Distribution diagrams of hyperfine magnetic field at 295 K constructed for different Fe crystal sites of the $(Er_{1-x}Sm_x)_2Fe_{14}B$ intermetallic compounds. For each iron crystal site the probability is normalised to unity. Numbers (m) of Sm atoms as the nearest neighbours of the iron sites are indicated above each diagram.

diagrams for the hyperfine magnetic fields, isomer shifts and quadrupole interactions. Those corresponding to room temperature are shown in Figs. 4–6 for the $(Er_{1-x}Sm_x)_2Fe_{14}B$ compounds.

A clearly pronounced linear change in the average values of hyperfine magnetic fields, isomer shifts and quadrupole interaction as a function of the sample composition parameter x, presented in Fig. 3, prove the assumptions (2)–(4) that each Sm near neighbour of the iron crystal site contributes additively to the values of the hyperfine magnetic field, isomer shift and quadrupole interaction. Substitution of Sm for Er in $(Er_{1-x}Sm_x)_2Fe_{14}B$ has a rather small influence on the values of the isomer shift and quadrupole splitting. The Δ_{IS} and Δ_{QS} values are either positive or negative depending on the particular crystal site. However, at room temperature, Sm causes a noticeable increase in the values of hyperfine magnetic fields for all iron sites, the most evident being that for k_2 site. No correlations were found between the Δ_H, Δ_{IS} and Δ_{QS} values and the kind of nearest neighbours, or their distances from the iron crystal sites.

5. Conclusions

The random distribution of rare earth atoms over their crystal sites in $(Er_{1-x}Sm_x)_2Fe_{14}B$ and the additive contri-

bution of Sm atoms to the values of the hyperfine interaction parameters lead to a linear dependence on Sm concentration of the average values of the hyperfine magnetic field, isomer shift and quadrupole interaction at the iron crystal sites. From these linear relations we derived the contributions Δ_H, Δ_{IS} and Δ_{QS} to the values of the hyperfine magnetic field, isomer shift and quadrupole interaction, caused by the presence of the Sm atom in the nearest neighbour shell of Fe crystal sites.

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