Mössbauer effect evidence of influence of thorium on the spin reorientation in $(Er_{1-x}Th_x)_2Fe_{14}B$ intermetallic compounds

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Abstract

The spin reorientation in the $(Er_{1-x}Th_x)_2Fe_{14}B$ system was observed by ^{57}Fe Mössbauer spectroscopy and magnetic measurements. The phenomenon originates from a competition between the magnetic anisotropies of the iron and rare earth sublattices, the latter being altered by substitution of thorium for erbium. The spin transition temperature was derived from magnetic measurements. Its value is lowered by magnetic dilution of the rare earth crystal sublattice, due to substitution of thorium for erbium. The ^{57}Fe Mössbauer effect measurements were carried out at room and liquid nitrogen temperatures. Owing to the influence on the shape of Mössbauer spectra of the combined electric quadrupole and magnetic dipole hyperfine interactions, it was possible to show, in a simple manner, that a spin reorientation phenomenon had taken place between 78 and 295 K in the investigated compounds. There is also evidence that the spin reorientation process proceeds not at a discrete temperature but in a wide temperature range. The discrete values of the ^{57}Fe hyperfine interaction parameters, derived from Mössbauer absorption spectra, are consistent with localised interactions of iron atoms with their nearest neighbours. It was found that substitution of thorium for erbium slightly reduces the hyperfine magnetic fields at iron sites and has only a minute influence on the values of the isomer shifts and quadrupole interactions.

Keywords: Mössbauer effect; Spin reorientation in $(Er_{1-x}Th_x)_2Fe_{14}B$

1. Introduction

The $RE_2Fe_{14}B$-type compounds have been studied intensively using many methods over the last decade [1]. Some of them are used in manufacturing of high quality permanent magnets, since they possess large coercivities, large energy products and relatively high Curie temperature. The compounds crystallize 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 boron atoms [2–4]. For the notation of the sites we follow the convention of Wyckoff. 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).

In $RE_2Fe_{14}B$-type compounds one can distinguish two magnetic sublattices: the iron sublattice, constituting six sets of inequivalent iron sites, and the rare earth sublattice, composed of two sets of inequivalent

crystal sites. The magnetic properties of the compounds depend on the rare earth constituent. The iron and rare earth sublattice magnetic moments couple ferromagnetically in the case of the light rare earth elements and antiferromagnetically for the heavy rare earth elements.

Of particular interest, both from a fundamental point of view and for permanent magnet applications, are spin transitions, originating from substitution or temperature dependences of the iron and rare earth sublattice magnetic anisotropies. The iron sublattice has uniaxial anisotropy along the crystal c-axis, while that of the rare earth sublattice 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 rare earth elements Pr, Nd, Tb, Dy and Ho, for which the Stevens factor is negative. It is planar, however, perpendicular to the c-axis, in the compounds with rare earth elements Sm, Er and Tm, for which the Stevens factor is positive.

The spin transition phenomena in the $RE_2Fe_{14}B$-

type compounds have been studied with many methods [1,5,6], among which Mössbauer spectroscopy has proved very useful [7–14] due to its microscopic character and sensitivity to combined electric and magnetic hyperfine interactions.

In an ongoing program of studies we report in this paper the results of investigations of the hyperfine interactions in the $(Er_{1-x}Th_x)_2Fe_{14}B$, $0.25 < x < 0.75$ system, performed at room and liquid nitrogen temperatures. Our attention has been focused on the distinct influence on Mössbauer spectra of the spin reorientation phenomenon, induced by substitution of thorium for erbium. Thorium is not a lanthanide, yet it forms the $Nd_2Fe_{14}B$-type structure [15] and behaves in a manner similar to yttrium.

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 two 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 metallography. No other phase but that with space group $P4_2/mnm$ has been detected. However, the Mössbauer absorption spectra indicate a small amount of iron impurities at 295 K for the $x = 0.50$ and 0.75 samples.

The spin transition temperatures were derived from magnetic measurements performed with the method described elsewhere [16].

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 Mössbauer absorption spectra the values of the hyperfine interaction parameters.

3. Results and discussion

The magnetic properties of the $(Er_{1-x}Th_x)_2Fe_{14}B$ system follow those of their parent $Er_2Fe_{14}B$ intermetallic compound. It was shown [17] that in $Er_2Fe_{14}B$ the easy direction of magnetisation is parallel to [001] above 316 K, but changes to [100] at room temperature and below. The observed spin reorientation phenomenon has been interpreted as originating

from a different temperature dependence of the iron and rare earth sublattice magnetic anisotropies. The former prefer a spin orientation along the c-axis, the latter along a direction perpendicular to it. Above 316 K the iron magnetic anisotropy predominates the rare earth one, and therefore spins are oriented along the c-axis. At lower temperatures the spins are plane oriented, perpendicular to the c-axis, because at those temperatures the rare earth magnetic anisotropy prevails over that of the iron sublattice. In $Th_2Fe_{14}B$, as in $Y_2Fe_{14}B$, the easy direction of magnetisation, being along the c-axis, is determined by the iron sublattice anisotropy.

The spin reorientation in the $RE_2Fe_{14}B$-type compounds can be induced not only by temperature but also by magnetic dilution of the rare earth sublattice, or by a partial substitution of a rare earth element with positive Stevens factor for one characterized by a negative Stevens factor, or vice versa. Substitution of thorium for erbium in our $(Er_{1-x}Th_x)_2Fe_{14}B$ system causes weakening of the rare earth magnetic anisotropy. This results in a lowering of the temperature at which the spins rotate from a direction parallel to the c-axis to a direction perpendicular to the c-axis. Thus the spin transition temperature is composition dependent. Such dependence is shown in Fig. 1, where the spin transition temperatures derived for our system from the bulk magnetic measurements are presented. On cooling from an elevated temperature, the investigated compounds $(Er_{1-x}Th_x)_2Fe_{14}B$, $x = 0.25$, 0.5, 0.75, undergo spin transition at their individual spin transition temperatures. With increasing thorium content the transition temperature decreases almost linearly from about 330 K, for $x = 0$, to 0 K, for $x = 1$. This can be expected, since the rare earth magnetic anisotropy of the $(Er_{1-x}Th_x)_2Fe_{14}B$ system is roughly dependent on the number of erbium ions in the rare
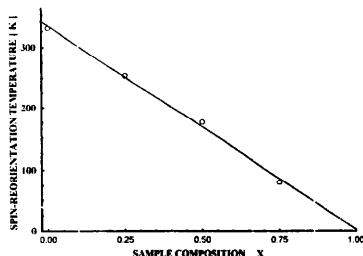

Fig. 1. Spin reorientation temperatures in $(Er_{1-x}Th_x)_2Fe_{14}B$ intermetallic compounds as a function of Th content. The solid line represents a linear regression.

earth sublattice which are successively replaced by thorium ions when the dilution proceeds.

Owing to its high energy resolution, Mössbauer spectroscopy can provide a variety of useful information, basically of local character, concerning the magnetic structure of the materials studied. The Mössbauer spectra recorded for the $(Er_{1-x}Th_x)_2Fe_{14}B$ system at room and liquid nitrogen temperatures are shown in Fig. 2 and Fig. 3 respectively. Owing to six non-equivalent crystal sites occupied by iron atoms, the Mössbauer absorption spectra of the investigated compounds are very complex. In order to derive the hyperfine parameters, the spectra were numerically

resolved into Zeeman sextets. Each sextet in any given spectrum is characterized by its hyperfine magnetic field, isomer shift and electric quadrupole interaction. Common to all sextets are three different linewidths and one line intensity ratio. For all investigated compositions the number of Zeeman subspectra, six for each composition, and their relative intensities are completely in accord with the site population. This is shown by the bar diagrams in Figs. 2 and 3. The values of the hyperfine interaction parameter, derived from the Mössbauer spectra, are compiled in Table 1. A small amount of iron impurities, found at 295 K for the $x = 0.50$ and 0.75 samples, manifests itself in the form
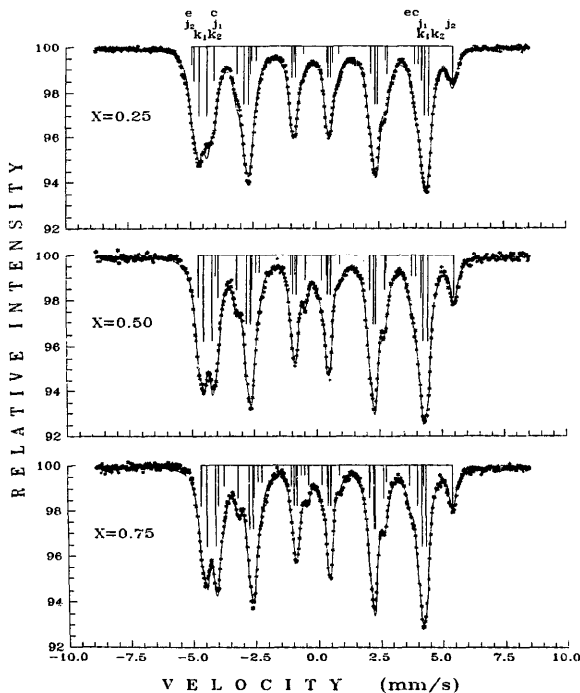

Fig. 2. ^{57}Fe Mössbauer absorption spectra recorded at 295 K for the $(Er_{1-x}Th_x)_2Fe_{14}B$ intermetallic compounds. The spectra have been resolved into Zeeman sextets with relative intensities that are in accord with the site populations: $16k_1$, $16k_2$, $8j_1$, $8j_2$, 4c, 4e. The quadrupole doublet, seen near zero velocity for the $x = 0.50$ and 0.75 samples, indicates a small amount of impurities of unknown origin. In the $x = 0.25$ sample the spin transition is already in progress at 295 K.
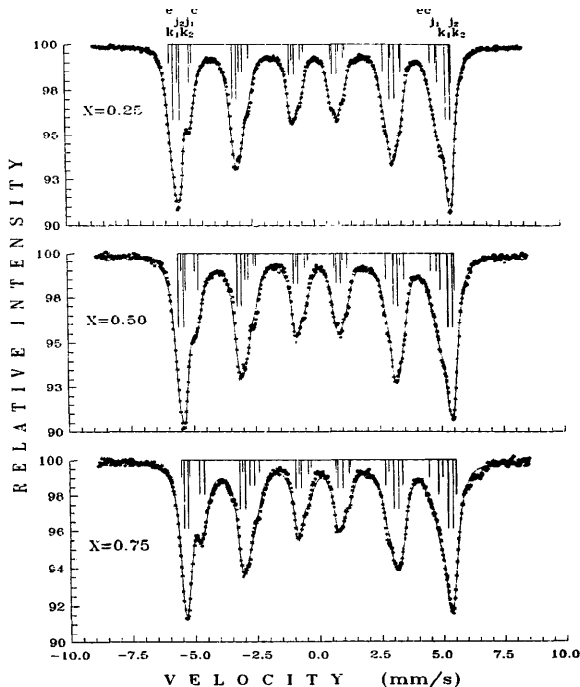
Fig. 3. ⁵⁷Fe Mössbauer absorption spectra recorded at 78 K for the $(Er_{1-x}Th_x)_2Fe_{14}B$ intermetallic compounds. The spectra have been resolved into Zeeman sextets with relative intensities that are in accord with the site populations: $16k_1$, $16k_2$, $8j_1$, $8j_2$, $4c$, $4e$. In the $x = 0.75$ sample the spin transition has not been completed at 78 K.

of a quadrupole doublet located near zero velocity (see Fig. 2). At low temperature the impurities become magnetic phases that cannot be seen in spectra recorded at 78 K.

Magnetic dilution of the rare earth sublattice, caused by substitution of thorium for erbium, slightly diminishes the hyperfine magnetic fields at all iron sites, both at room and liquid nitrogen temperature. The decrease in field value per substituted atom is 1.2 T, both at room and liquid nitrogen temperatures. 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. The isomer shifts and quadrupole splittings depend very little on substitution. All quadrupole shifts of subspectra lines, excepting that of 4e sites, are positive at room temperature, e.g. for the samples with spin orientation along the c-axis. At liquid nitrogen temperature the $16k_2$ and $8j_1$ positions give rise to positive quadrupole shifts of the corresponding subspectra lines for all compositions. The change in sign of the quadrupole shifts for the other positions may be interpreted as evidence of spin reorientation taking place between room and liquid nitrogen temperature.

The spin transition in the $(Er_{1-x}Th_x)_2Fe_{14}B$ system

Table 1

Fe hyperfine interaction parameters of the (Er₁₋ₓThₓ)₂Fe₁₄ intermetallic compounds. The parameters listed have the following meaning: H, hyperfine magnetic field; $\langle H \rangle$, averaged hyperfine magnetic field; IS, isomer shift with respect to metallic iron at room temperature; QS, quadrupole shift of the subspectra lines $[(U_1 + U_4) - (U_2 + U_3)]/2$. Errors: H (0.1 T), $\langle H \rangle$ (0.1 T), IS (0.008 mm s⁻¹), QS (0.008 mm s⁻¹)

Sample x	Parameter	Temperature (K)	Crystal site					
			16k	16k	8j	8j	4e	4e
0.25	H	78	34.2	33.9	31.1	34.3	30.7	32.7
		295	27.0	27.4	25.7	32.0	25.3	27.6
	$\langle H \rangle$	78				33.5		
		295				27.8		
	IS	78	0.012	0.027	0.005	0.231	0.190	0.002
		295	0.189	0.005	0.056	0.089	0.084	0.145
	QS	78	0.120	0.084	0.049	0.147	0.110	0.483
		295	0.047	0.100	0.151	0.233	0.102	0.351
0.50	H	78	33.7	33.6	30.3	33.5	30.2	31.2
		295	27.2	26.8	25.1	31.6	24.2	27.1
	$\langle H \rangle$	78				32.7		
		295				27.2		
	IS	78	0.004	0.010	0.040	0.270	0.135	0.024
		295	0.190	0.03	0.049	0.070	0.148	0.058
	QS	78	0.130	0.061	0.075	0.123	0.164	0.444
		295	0.065	0.135	0.168	0.315	0.020	0.336
0.75	H	78	33.0	33.0	29.2	32.0	31.5	30.9
		295	26.6	26.1	24.6	31.1	22.9	27.5
	$\langle H \rangle$	78				32.1		
		295				26.6		
	IS	78	0.015	0.005	0.032	0.384	0.109	0.024
		295	0.177	0.020	0.085	0.070	0.032	0.017
	QS	78	0.112	0.077	0.079	0.009	0.014	0.509
		295	0.060	0.149	0.126	0.326	0.031	0.202

has a pronounced influence on the shape of the Mössbauer spectra, since they are very sensitive to combined electric quadrupole and magnetic dipole hyperfine interactions. Even visual inspection of the spectra shows that all those recorded at room temperature are very similar to each other. The same can be said about the spectra recorded at liquid temperature. These similarities in spectral shapes are due to the minute influence of the substitution of thorium in the two erbium sites on the hyperfine magnetic fields at the iron lattice sites. However, the room temperature spectra are distinctly different from those recorded at liquid nitrogen temperature. This is due to spin rotation phenomena taking place between room and liquid nitrogen temperature in the investigated samples.

The most obvious visual difference between the two groups of spectra discussed is the lack of a well-resolved satellite line (about +5.45 mm s⁻¹) in the spectra recorded at liquid nitrogen temperature. This line is the sixth line of the $8j_2$ sublattice Zeeman sextet. Among six crystal sites occupied by iron, the $8j_2$ site has the largest magnetic 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 by 90° from the c-axis, the quadrupole parameter is reduced by a factor of approximately −2. Owing to this the line is shifted

towards 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). Its shift of approximately 0.45 mm s⁻¹ towards lower velocities (see Fig. 3) indicates a reorientation of the spins from a direction parallel to the c-axis to a direction perpendicular to the c-axis.

In the room temperature spectrum of the $x = 0.25$ sample, the sixth line of the $8j_2$ sublattice Zeeman sextet is slightly disturbed, while in the liquid nitrogen spectrum of the $x = 0.75$ sample a small remainder of this line is still present. These observations indicate that in the $x = 0.25$ sample the spin rotation is already in progress at room temperature, while in the $x = 0.75$ sample it has not been completed even at liquid nitrogen temperature, although the former is higher while the latter is 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 temperature range. This is not surprising from a magnetic microscopic point of view, if one assumes that two different elements, erbium and thorium, are statistically distributed on the 4f and 4g rare earth sites. One of them (Er) favours a spin orientation perpendicular to the c-axis, while the other one (Th) is weakening this

effect, causing the spin transition temperature to be composition dependent, also on a microscopic scale.

The spectra of the samples in which the spin reorientation was not completed at the temperature of investigation show 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, a physical meaning of the spectral parameters derived, since the spectral deconvolution may not be unique.

In conclusion, magnetic dilution of the rare earth sublattice in the $(Er_{1-x}Th_x)_2Fe_{14}B$ system, due to substitution of thorium for erbium, does not influence the hyperfine interactions significantly. It affects, however, the spin reorientation, which takes place between room and liquid nitrogen temperature. Mössbauer spectroscopy has proved to be useful in studying this phenomenon.

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