



Spin reorientation process in $\text{Er}_2\text{Fe}_{14}\text{C}$ magnetic material

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ABSTRACT

The $\text{Er}_2\text{Fe}_{14}\text{C}$ intermetallic compound has been synthesized and studied by ^{57}Fe Mössbauer spectroscopy and differential scanning calorimetry (DSC). The spin reorientation phenomenon was investigated in this compound in the temperature range 80–330 K by narrow step temperature scanning in the neighborhood of the reorientation temperature 316 K. Spin arrangement in this compound was determined. Experimental Mössbauer spectra were analyzed by fitting six Zeeman subspectra according to six iron occupations of the crystallographic sublattices, except for spin reorientation region, where each subspectrum splits additionally into two Zeeman sextets. A consistent description of Mössbauer spectra below, during and above the spin reorientation temperature – was established. Parameters of hyperfine interactions, their temperature dependencies in transition region and spin reorientation temperature were obtained from consistent fits. DSC studies proved that the spin reorientations were accompanied by thermal effects. The spin reorientation temperature was established to be $T_{\text{SR}} = 313 \pm 2$ K and the enthalpy of the transition $\Delta H = 0.26 \pm 0.04$ J/g.

A comparison of spin reorientation process in $\text{Er}_2\text{Fe}_{14}\text{C}$ and $\text{Er}_2\text{Fe}_{14}\text{B}$ is presented.

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1. Introduction

The $\text{Er}_2\text{Fe}_{14}\text{C}$ intermetallic compound belongs to the $\text{R}_2\text{Fe}_{14}\text{B}$ structure (R—rare earth) type and has a tetragonal crystal lattice of the $P4_2/mmm$ space group, where Fe atoms occupy six different positions in elementary cell: $16k_1$, $16k_2$, $8j_1$, $8j_2$, $4e$, $4c$; rare earth atoms occupy two different positions: $4f$ and $4g$; and carbon atom has $4g$ position [1,2].

We are specially interested in a spin reorientation process, the result of a competition between axial and planar tendency in Fe and Er sublattice [3], which occurs at the certain temperature, called the spin reorientation temperature, T_{SR} . In this process, the direction of easy magnetization vector is changing from planar (in basal plane) to axial (along the c -axis) with increasing temperature, without intermediate conical arrangement. The change of spin orientation from planar to axial arrangement is an important phenomenon which determines temperature region of axial anisotropy and gives information about the suitability of this type of compounds for the production of permanent magnets.

This phenomenon was studied previously by several groups for different rare earth ions [4–12].

It was confirmed by neutron diffraction investigations on single crystals [13].

The study of $\text{Er}_2\text{Fe}_{14}\text{B}$ compound [10] revealed that reorientation process takes part in the temperature range of 12 K and established the reorientation temperature $T_{\text{SR}} = 324$ K.

This study involves the investigation of the spin reorientation phenomenon in $\text{Er}_2\text{Fe}_{14}\text{C}$ magnetic material (with carbon, instead of boron, which does not influence negatively on health and environment during processing) using ^{57}Fe Mössbauer spectroscopy and DSC. We have studied Mössbauer spectra by narrow step temperature scanning, trying to establish T_{SR} and temperature range of the transition process. Our purpose was also to investigate the influence of this process on hyperfine parameters and to study related thermal effects. Additionally, we have compared spin reorientation process in $\text{Er}_2\text{Fe}_{14}\text{C}$ and $\text{Er}_2\text{Fe}_{14}\text{B}$ compounds.

2. Experimental methods

The $\text{Er}_2\text{Fe}_{14}\text{C}$ was produced by a standard procedure of induction melting under flowing high purity argon and the subsequent annealing at 900°C for two weeks. The X-ray and thermomagnetic analysis proved the single-phase integrity of the material.

The $\text{Er}_2\text{Fe}_{14}\text{C}$ absorber for Mössbauer investigations, was prepared in the form of thin layer of powdered material. This ensured a random distribution of orientation of magnetic moments, which – for a thin absorber – would give 3:2:1 ratio for line intensities in a single Zeeman pattern.

The Mössbauer spectra of $\text{Er}_2\text{Fe}_{14}\text{C}$ were recorded in the temperature range 80–330 K, with 1 K step in the vicinity of reorientation temperature T_{SR} , using a ^{57}Co (Rh) source and a computer driven constant acceleration mode spectrometer. The velocity scale was calibrated with a high purity iron foil. Isomer shift was established with respect to the center of the room temperature iron Mössbauer spectrum.

$\text{Er}_2\text{Fe}_{14}\text{C}$ has also been investigated by differential scanning calorimeter Pyris 1 – DSC method. The compound has been studied in the temperature range 93–373 K

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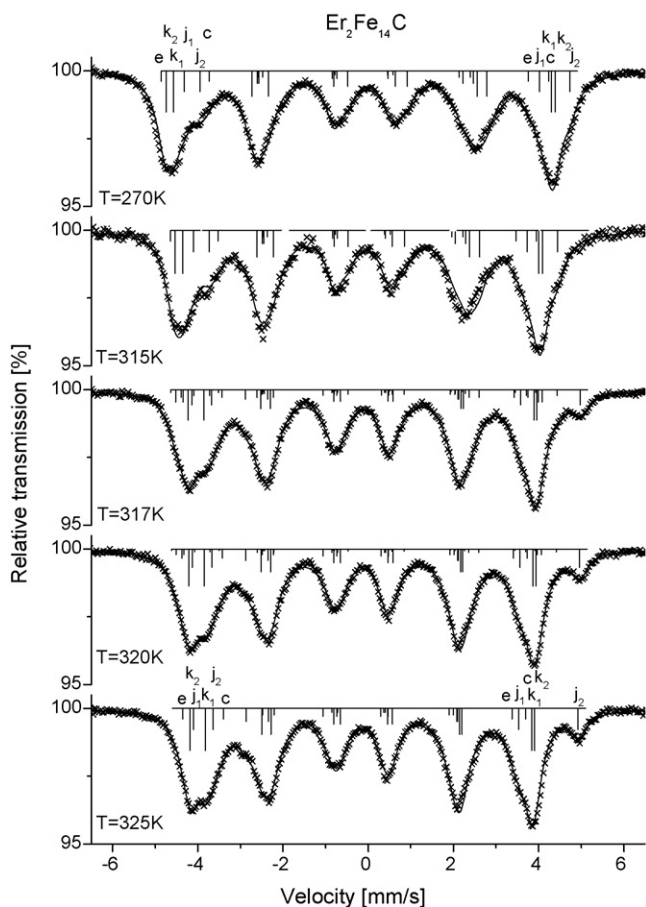


Fig. 1. The exemplary Mössbauer spectra showing the transition process for $\text{Er}_2\text{Fe}_{14}\text{C}$ compound. The solid lines are the fits to the data. The bar diagrams show the line positions and relative intensities. Positions of the first and sixth line of all sextets are marked with letters related to the particular subspectra, in the first and last spectrum.

with different scanning rates (60–10 K/min) for heating and cooling cycles of measurements.

3. Results and discussion

3.1. Mössbauer spectroscopy method

Mössbauer spectra were obtained in the temperature region 80–330 K, which includes temperature range below, above and during the transitions process. Spectra were analyzed with a transmission integral approach [14] by fitting six Zeeman subspectra according to six iron occupations of the crystallographic sublattices.

Each subspectrum was characterized by the three hyperfine interaction parameters: isomer shift – IS, quadrupole splitting – QS, define as $[(V_6 - V_5) - (V_2 - V_1)]/2$, where V_i are velocities corresponding to Mössbauer line positions, and hyperfine magnetic field – B. One common set of three line widths was used for all Zeeman subspectra. The “exponential” approximation [14] of the transmission integral was used to describe obtained Mössbauer spectra. This method takes into account the influence of sample thickness on the ratio of line intensities in Mössbauer spectrum. A procedure of simultaneous fitting of several spectra with interconnected parameters [10–12] was applied in order to get a consistent description of spectra throughout the series. This method gave us possibility to establish the temperature dependence of hyperfine parameters.

Exemplary spectra for $\text{Er}_2\text{Fe}_{14}\text{C}$ compound are presented in Fig. 1. The spectrum at the top of the figure is related to the tem-

perature below the spin reorientation (planar spin arrangement), whereas the bottom one – to the temperature above the transition process (axial spin arrangement). The spectra below and above the reorientation region were described with six Zeeman sextets called “low” and “high temperature”, respectively with relative intensities according to iron occupations of the crystallographic sublattices (4:4:2:2:1:1).

The three intermediate spectra represent the spectra measured at temperatures inside the spin reorientation region, where the coexistence of both types of sextets was assumed with contributions C_l and C_h to spectrum. This gives twelve Zeeman sextets in the spectrum.

In comparison with single crystal investigations for Er–Fe based compounds [15], for polycrystalline material there is no possibility to use the change in the ratio of line intensities of Zeeman spectrum for observing reorientation process. However, line positions related to the sublattices slightly change due to changes of hyperfine interaction parameters during the reorientation. The most visible effect is the appearing of the sixth line for the $8j_2$ sublattice sextet and its separation from other lines. Its intensity has a clearly visible temperature dependence, hence it was possible to establish precisely the contribution of “high temperature” part of $8j_2$ sublattice to the spectrum. This facilitated the observation of reorientation process.

In the reorientation region Mössbauer spectra below the reorientation (described by “low temperature” Zeeman sextets) and above (described by “high temperature” Zeeman sextets) have different values of B and QS. The systematic changes of B with temperature were taken into account assuming the possibility of a shift of this dependence during reorientation process.

The temperature dependencies of hyperfine magnetic field derived from the spectra are shown in Fig. 2. For all sublattices, the hyperfine field decreases with the increasing temperature below and above region of spin reorientation. During the transition each Zeeman sextet splits into two subspectra. Similar as in the case of $\text{Er}_2\text{Fe}_{14}\text{B}$, the “high temperature” Zeeman sextet for $8j_2$ sublattice, has larger hyperfine field than in the case of basal arrangement. For all other subspectra we observed smaller values of B.

Quadrupole splitting QS is related to the angle between the easy axis of magnetization and the electric field gradient direction [16], and change of QS is connected with the change of this angle during spin reorientation process. There are two different values of QS in the transition region related to “high temperature” and “low temperature” Zeeman sextets, respectively. The difference of QS values is significant for $8j_2$ crystal site. Above and below the transition process QS is almost independent of temperature (Fig. 3).

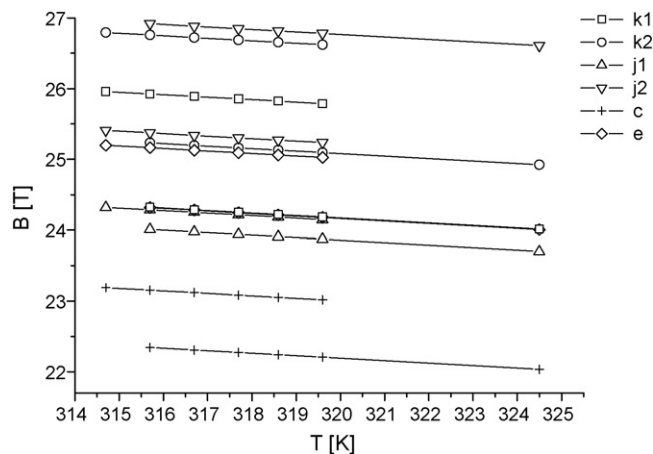


Fig. 2. The temperature dependence of hyperfine field, B, for different crystal sites of $\text{Er}_2\text{Fe}_{14}\text{C}$, with a change in the value of B during reorientation process. The average error is 0.1 T.

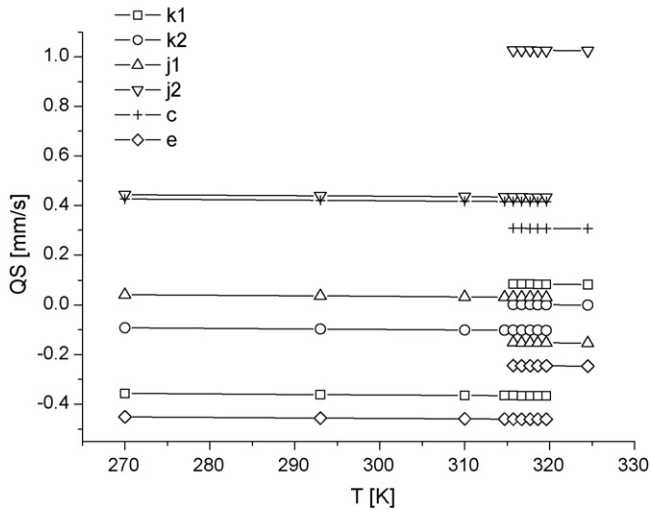


Fig. 3. The temperature dependence of the quadrupole splitting, QS, for different crystal sites of $\text{Er}_2\text{Fe}_{14}\text{C}$, with a change in the value of QS during reorientation process. The average error is 0.01 mm/s.

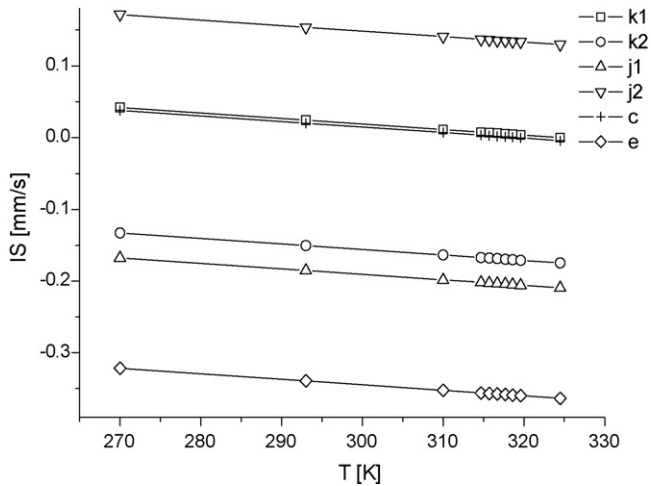


Fig. 4. The temperature dependence of isomer shift, IS, for different crystal sites of $\text{Er}_2\text{Fe}_{14}\text{C}$. The average error is 0.01 mm/s.

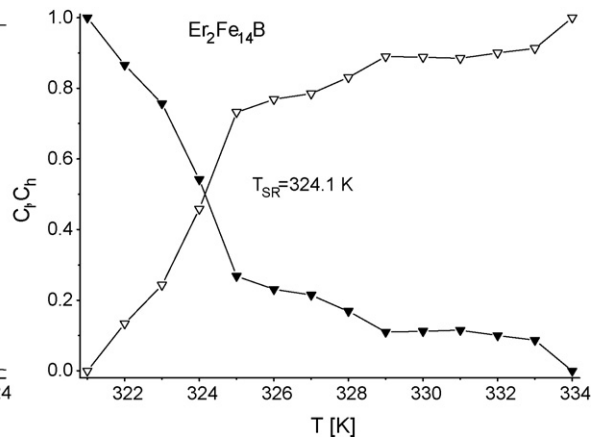
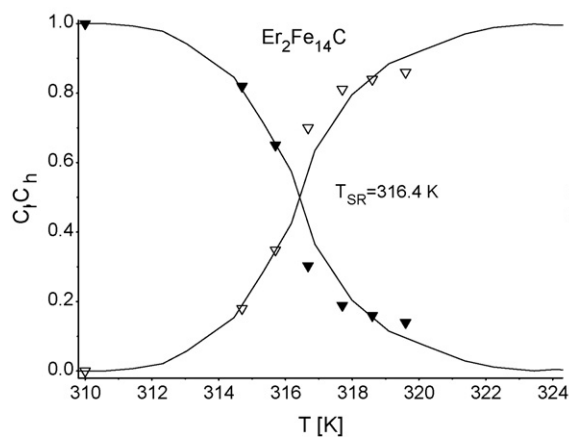


Fig. 5. The temperature dependences of subpectra contributions for C_l – “low temperature” (solid triangle) and C_h – “high temperature” (open triangle) Zeeman sextets for $\text{Er}_2\text{Fe}_{14}\text{C}$ and $\text{Er}_2\text{Fe}_{14}\text{B}$ [10] compounds.

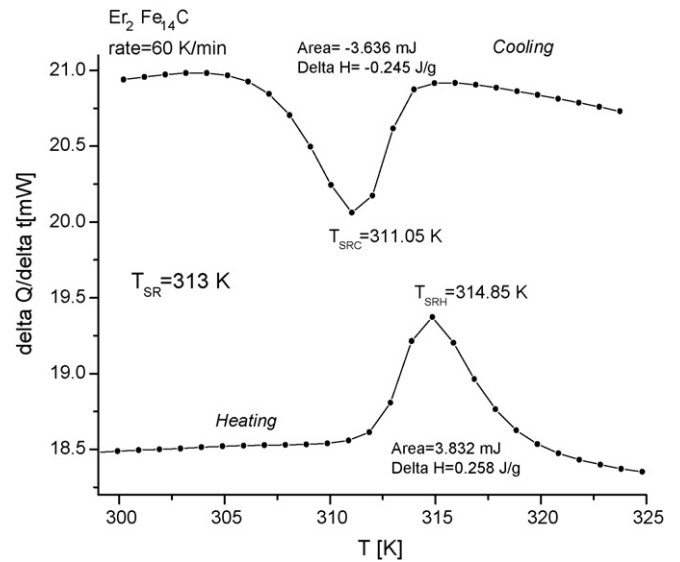


Fig. 6. DSC curves for the $\text{Er}_2\text{Fe}_{14}\text{C}$ compound. Peaks correspond to the heat emission/absorption of sample during the transition process. Measurements performed on heating and cooling with the rate of 60 K/min.

A common linear temperature dependence of IS caused by second-order Doppler shift effect was assumed for “low” and “high temperature” Zeeman sextets (Fig. 4).

During the transition process “low” and “high temperature” Zeeman sextets exchange gradually (between themselves) their contributions C_l and C_h ($C_l + C_h = 1$) to the spectrum (Fig. 5). The spin reorientation temperature value T_{SR} , taken as the intersection point of C_l and C_h curves (when both contribution are 50%), is 316 ± 1 K, and it is about 8 K lower than in the case of $\text{Er}_2\text{Fe}_{14}\text{B}$ compound ($T_{SR} = 324.1$ K) [10]. Reorientation region has a range of about 10 K, which is close to the range for $\text{Er}_2\text{Fe}_{14}\text{B}$.

3.2. Differential scanning calorimetry (DSC) method

Considering thermal effects, such as the absorption and emission of heat, towards the reorientation process, we had observed the endo- and exothermic curves for $\text{Er}_2\text{Fe}_{14}\text{C}$ compound, using the DSC calorimetry (Fig. 6).

The experiment shows well defined endo- and exothermic peaks which correspond to the change of easy magnetization direction in the crystal due to increasing/decreasing temperature.

The spin reorientation temperature derived from this method $T_{\text{SRC}} = 313 \pm 2$ K was taken as an arithmetic average of temperatures obtained for heating and cooling cycles. The temperature range of the peak is about 10 K degrees region. This is close to the results obtained from Mössbauer measurements. The area under the DSC peak is defined as the transformation enthalpy, $\Delta H = 0.26 \pm 0.04$ J/g.

For $\text{Er}_2\text{Fe}_{14}\text{B}$ compound spin reorientation temperature obtained from DSC measurement is $T_{\text{SR}} = 325.5 \pm 0.5$ K and transition range is about 10 K. Thus, we can see that the substitution of C for B in $\text{Er}_2\text{Fe}_{14}\text{B}$ compound shifts the reorientation process to lower temperatures by about 12 K.

4. Conclusions

We conclude that arrangement of magnetic moments in $\text{Er}_2\text{Fe}_{14}\text{C}$ is similar to that in the rare earth iron borides, studied before [17]. For the $\text{Er}_2\text{Fe}_{14}\text{C}$ compound axial spin arrangement dominates at high temperatures while planar arrangement is present at low temperature. Comparing the spin reorientation process for $\text{Er}_2\text{Fe}_{14}\text{C}$ with process for $\text{Er}_2\text{Fe}_{14}\text{B}$, it is visible that the substitution of C for B in $\text{Er}_2\text{Fe}_{14}\text{B}$ compound shifts the reorientation process to lower temperatures by about 10 K. This only slightly influences the physical parameters of the process, but does not change its character in general. From ^{57}Fe Mössbauer spectroscopy analysis the spin reorientation temperature was established to be $T_{\text{SR}} = 316 \pm 1$ K while the result obtained from calorimetric measurements is $T_{\text{SR}} = 313 \pm 2$ K.

$\text{Er}_2\text{Fe}_{14}\text{C}$ is a compound synthesized with carbon, which does not carry health hazard during processing. This feature can be useful for the production of permanent magnets.

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