Magnetism of ordered and disordered alloys of R$_2$Fe$_{14}$B (R = Nd, Er) type


Abstract

Magnetic susceptibility, magnetization and neutron diffraction measurements have been performed to study structure and magnetic states of crystalline and amorphous Nd$_2$Fe$_{14}$B and Er$_2$Fe$_{14}$B alloys. In the crystalline state there exists a large (about 20%) anisotropy of Er-sublattice magnetization. Values of the magnetic anisotropy constant of Er ions and the Er–Fe exchange-coupling parameter were estimated using temperature dependence of the Er- and Fe-sublattice magnetizations. Amorphous state of the samples was obtained by irradiation of fast (E$_{nx}$ ≥ 1 MeV) neutrons with a fluence up to the 1.2 × 10$^{20}$ n/cm$^2$ at 340 K. It is shown that antiferromagnetic coupling between the rare-earth and iron spins is kept in the amorphous state. Amorphization of the samples is found to result in reduction of the Curie temperature ($T_C$) by about 200 K and almost total absence of coercivity. We suggest that the strong decrease of $T_C$ is a consequence of enhancement of negative Fe–Fe interactions as a result of interatomic distance changes, which is a characteristic feature of the amorphous state.

1. Introduction

Permanent magnets produced on the base of Nd$_2$Fe$_{14}$B compound possess record values of maximal magnetic energy product, $(BH)_{max} > 470$ kJ m$^{-3}$ [1]. These $(BH)_{max}$ values are achieved due to a large magnetocrystalline anisotropy (MCA) and relatively high spontaneous magnetization of Nd$_2$Fe$_{14}$B.

Despite of a great technological progress, the coercive field of Nd$_2$Fe$_{14}$B compound possess record values of maximal magnetic energy product, $(BH)_{max} > 470$ kJ m$^{-3}$ [1]. These $(BH)_{max}$ values are achieved due to a large magnetocrystalline anisotropy (MCA) and relatively high spontaneous magnetization of Nd$_2$Fe$_{14}$B.

Magnetic susceptibility, magnetization and neutron diffraction measurements have been performed to study structure and magnetic states of crystalline and amorphous Nd$_2$Fe$_{14}$B and Er$_2$Fe$_{14}$B alloys. In the crystalline state there exists a large (about 20%) anisotropy of Er-sublattice magnetization. Values of the magnetic anisotropy constant of Er ions and the Er–Fe exchange-coupling parameter were estimated using temperature dependence of the Er- and Fe-sublattice magnetizations. Amorphous state of the samples was obtained by irradiation of fast (E$_{nx}$ ≥ 1 MeV) neutrons with a fluence up to the 1.2 × 10$^{20}$ n/cm$^2$ at 340 K. It is shown that antiferromagnetic coupling between the rare-earth and iron spins is kept in the amorphous state. Amorphization of the samples is found to result in reduction of the Curie temperature ($T_C$) by about 200 K and almost total absence of coercivity. We suggest that the strong decrease of $T_C$ is a consequence of enhancement of negative Fe–Fe interactions as a result of interatomic distance changes, which is a characteristic feature of the amorphous state.

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powder particle size of the Nd$_2$Fe$_{14}$B phase. However, they could not obtain a high degree of alignment by applying of external magnetic field.

One can guess [6] that the high degree of alignment is possible to obtain in Nd–Fe–B material in fully amorphous state with successive heat treatment for formation of multi-phase nanograin structure of soft (α-Fe and FeB) and hard (Nd$_2$Fe$_{14}$B) phases. Synthesis of exchange-spring nanocomposite magnets was also realized by spark erosion [7], hot pressing at 600–800 °C under pressure of 100–200 MPa in vacuum [8] and some other methods.

It is important to search for new ways to amorphize Nd–Fe–B materials, to study their structure state and their magnetic properties in the amorphous state. According to Refs. [9,10], the amorphous Nd–Fe–B materials could be synthesized via severe plastic deformation by torsion. Authors of Ref. [11] reported that they achieved an amorphous state of Nd$_2$Fe$_{14}$B magnet using irradiation with high-energy electrons. It should be noted that the conclusion about structure state of these materials has been made on the base of X-ray diffraction data. However, the X-ray radiation penetrates only into thin layer near the grain surface of the Nd$_2$Fe$_{14}$B alloys, and therefore, their bulk structure remains unclear. Reliable data on the realization of amorphous state can be obtained only from the neutron-diffraction experiment.

In literature there are numerous studies, devoted to influence of fast neutron [12–14], X-ray, γ-ray [15–17] and electron irradiations [18,19] on properties of the Nd–Fe–B magnets. The aim of these works was to study the radiation resistance of Nd–Fe–B magnets. These permanent magnets are used in a high-energy storage ring of current, third-generation synchrotron light sources and, therefore, are subjected to irradiation by the synchrotron radiation, high-energy bremsstrahlung, and bremsstrahlung-produced neutrons. A fluence attained in previous studies by means of neutron irradiation [12,13] did not exceed $6.1 \times 10^{16}$ n/cm$^2$, which resulted in significant remanence losses though was not enough to achieve a fully disordered state of the Nd–Fe–B magnet. Next-generation light sources will exceed present the third-generation sources in terms of brightness, coherence, beam power, and energy of radiation by several orders of magnitude [20]. Hence, it is important to know detailed information about neutron irradiation effects on Nd–Fe–B magnets.

In the present work, the Nd$_2$Fe$_{14}$B and Er$_2$Fe$_{14}$B alloys (hereinafter NFB and EFB, respectively) have been irradiated by the fluence up to $1.2 \times 10^{17}$ n/cm$^2$ and transformed into the amorphous state. We studied the atomic structure state and the magnetic properties of these alloys by means of magnetic measurements and neutron diffraction prior and after the irradiation. Among magnetic properties, we have measured magnetization of R- and Fe-ion sublattices in the above alloys, their coercivity, the MCA constant $K$ of Er ions and a function of spin-density distribution in the Er$_2$Fe$_{14}$B compound.

2. Experimental

The NFB and EFB ingots were smelt in an induction furnace in quartz crucibles under the atmosphere of high-purity argon in a mass of 50 g. Each ingot has been then treated via melt-spinning procedure. Rapidly quenched NFB and EFB alloys were prepared at the wheel surface velocity $V = 20$ m/s as pieces (flakes) of metallic ribbons 30–50 μm thick, 2–5 mm wide and up to 40 mm long. Flakes were milled into powder to measure the magnetic properties and perform the neutron diffraction experiment.

In order to obtain the amorphous state, the powder NFB and EFB samples were irradiated with fast neutrons ($E_n > 1$ MeV) to a fluence $1.2 \times 10^{18}$ n/cm$^2$ at temperatures below 340 K using sealed aluminum ampoules placed in the water pool of the IVV-2M reactor. Magnetic measurements were carried out by means of a vibrating-sample magnetometer over the temperature range 5–400 K in field up to 2 T. The errors in the determination of magnetization and temperature were ±1.5% and ±1 K, respectively.

Neutron powder diffraction (NPD) patterns were recorded on the EFB sample with the HRPD diffractometer on the HANARO reactor (Korea) in the temperature range 9–650 K prior to the melt-spinning procedure. The wave length of incident neutron beam in HRPD diffractometer was $\lambda = 1.835$ Å. When the measurements were performed in a cryostat, the temperature stability was ±0.5 K, and if we used a high temperature device, ±1 K.

The neutron diffraction experiments on the rapidly quenched EFB and NFB samples were carried out prior and after the neutron irradiation with the D-2 and D-3 diffractometers, mounted on the reactor IVV-2M (Zarechny, Russia). The wave lengths $\lambda$ were 1.805 Å and 2.43 Å, respectively. The NPD patterns were calculated by means of Fullprof software [21].

A vanadium standard has been used to convert intensity (in counts) of scattered neutrons on the amorphous EFB sample to units (in cm$^{-2}$) of the cross section. Corrections for neutron adsorption and multiple scattering were considered according to [22,23].

3. Experimental results

3.1. Crystalline state

As example, Fig. 1 shows the NPD pattern of the EFB sample, recorded with the HRPD diffractometer at 200 K; NPD patterns measured at other temperatures differ from this one only by intensities of reflections. In the temperature region 10–650 K, the EFB sample possesses the tetragonal Nd$_2$Fe$_{14}$B-type structure (space group $P4_{2}mnm$) as the main phase and contains about 2% of the additional χ-Fe phase.

Fig. 2 presents the temperature dependencies of the $a$ and $c$ lattice parameters. At $T > 600$ K experimental values of the $a$ and $c$ parameters are taken from Ref. [24]. Above $T_C$, the thermal expansion has only a phonon contribution from the lattice and its temperature dependence is practically linear. Below $T_C$, the thermal expansion becomes nonlinear because of a contribution from a spontaneous magnetostriction. We extrapolated the $a(T)$ and $c(T)$ dependencies below $T_C$ using Debye approximation and assuming that the Debye temperature is equal to 450 K as it is pointed in [25]. These dependencies are shown in Fig. 2 by dashed lines. As one can see from comparison of experimental data and calculated lines, the EFB sample exhibits a large spontaneous magnetostriction at low temperatures, $\Delta V/V(10\,K) = 2.4\%$. Our results are in good agreement with previous studies [25–27]. Nevertheless, it is worth to note that we observed an additional anomaly like a jump on the $a(T)$ and $c(T)$ dependencies at $T_{1p} = 298$ K (see insert in Fig. 2).

In the Nd$_2$Fe$_{14}$B-type structure the Er ions occupy two (4f and 4g) positions, while the Fe atoms are located at five (4c, 4e, 8j, 16k$_1$, 16k$_2$) sites and the B atoms form only one (4g) sublattice

![Fig. 1. Observed (circles) and calculated (solid lines) neutron powder diffraction patterns of the crystalline Er$_2$Fe$_{14}$B sample at (a) 600 K and (b) 200 K. Vertical bars indicate the positions of nuclear and magnetic Bragg reflections. Difference between the observed and calculated intensities is given at the bottom of the patterns.](image-url)
magnetizations are mutually antiparallel within the error (±10°) of a determination of magnetization directions. In our calculations we supposed that magnetizations of the Er ions at the 4f and 4g positions were the same, and the Fe-ion moments at the 4c, 4e, 8j, 16k, and 16l sites were assumed independent on the crystallographic positions. Magnetic moments of all the Er and Fe sublattices are oriented parallel to the basal plane at temperatures below 325 K and they are arranged along the c-axis at temperatures above 327 K, so, the spontaneous spin-reorientation transition (SRT) takes place between these temperatures. This is the first order transition of the "easy plane–easy axis" type. Therefore, we considered that in our EFB sample the Er- and Fe-sublattice magnetizations are rotated from the basal plane to the c-axis at the temperature of the spin-reorientation transition at Tc = 326 K. According to study of the specific heat [28] the SRT occurs at 323 K in the EFB single crystal, in good agreement with our results. The SRT becomes apparent on the temperature dependency of the Er-ion magnetization (μEr(T)) as a jump at the Tc (see Fig. 3). One can see from Fig. 3 that the μEr value decreases by about ΔμEr = 0.8 μB in the SRT region, so, the anisotropy of Er-ion magnetization ΔμEr/μ Er (327 K) = 20%. In comparison with the μEr(T) dependence the temperature evolution of the Fe-ion magnetization (μFe(T)) is rather smooth (see Fig. 3).

It would be tempting to relate the SRT with the jumps on a(T) and c(T) dependencies at Tc = 298 K (see inset in Fig. 2). But, we cannot explain the difference in 28 K between the Tc and TcP.

To make unambiguous decision about the change of the crystal structure and magnetic states in the result of a fast neutron irradiation, we measured NPD patterns of the rapidly quenched EFB sample with the D-2 diffractometer before and after irradiation. This diffractometer was also used for recording NPD patterns obtained prior and after neutron irradiation of the rapidly quenched NFB sample. The NPD patterns of non-irradiated samples are presented in Figs. 4a and 5a; calculated lines have been obtained with parameters, which are given in Table 1. Both samples contain the crystalline Nd2Fe14B-type phase as the main phase, whereas content of the amorphous phase does not exceed 10% in each sample. It is worth to note that prior irradiation the content of the α-Fe phase was about 7% in the NFB sample.

### 3.2. Amorphous state

Figs. 4b and 5b show NPD patterns of the NFB and EFB samples after irradiation with fast neutrons up a fluence of 1.2 × 1020 n/cm². Both patterns include narrow half-width peaks at angles 2θ = 53°.

### Table 1

Lattice constants a, b, c and volume of unit cell V, coordinates of positions (space group P42/mnm), the average Nd-, Er- and Fe-ion magnetic moments μNd, μEr and μFe, contents of the Nd2Fe14B and α-Fe phases, agreement factor and χ² for the Nd2Fe14B and Er2Fe14B samples at room temperature.

<table>
<thead>
<tr>
<th>Structural parameter</th>
<th>Nd2Fe14B</th>
<th>Er2Fe14B</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>8.816(1)</td>
<td>8.744(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>2.120(2)</td>
<td>1.1968(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>951.4(2)</td>
<td>914.3(5)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>914.3(5)</td>
<td>12.240(2)</td>
</tr>
<tr>
<td>R, 4f, x</td>
<td>0.267(1)</td>
<td>0.273(1)</td>
</tr>
<tr>
<td>R, 4g, x</td>
<td>0.113(1)</td>
<td>0.112(1)</td>
</tr>
<tr>
<td>Fe, 4e, z</td>
<td>0.098(1)</td>
<td>0.097(1)</td>
</tr>
<tr>
<td>Fe, 8j, x</td>
<td>0.204(1)</td>
<td>0.201(1)</td>
</tr>
<tr>
<td>Fe, 8j2, x</td>
<td>0.318(1)</td>
<td>0.318(1)</td>
</tr>
<tr>
<td>Fe, 16k, x</td>
<td>0.224(1)</td>
<td>0.222(1)</td>
</tr>
<tr>
<td>Fe, 16l, x</td>
<td>0.567(1)</td>
<td>0.567(1)</td>
</tr>
<tr>
<td>z</td>
<td>0.128(1)</td>
<td>0.127(1)</td>
</tr>
<tr>
<td>Fe, 16k2, x</td>
<td>0.037(1)</td>
<td>0.036(1)</td>
</tr>
<tr>
<td>Fe, 16l2, x</td>
<td>0.361(1)</td>
<td>0.360(1)</td>
</tr>
<tr>
<td>z</td>
<td>0.176(1)</td>
<td>0.170(1)</td>
</tr>
<tr>
<td>B, 4g, x</td>
<td>0.625(2)</td>
<td>0.636(2)</td>
</tr>
<tr>
<td>μ²Nd (μB)</td>
<td>1.5(1)</td>
<td>1.9(1)</td>
</tr>
<tr>
<td>μ²Er (μB)</td>
<td>4.1(1)</td>
<td>1.3(1)</td>
</tr>
<tr>
<td>Nd2Fe14B, mass%</td>
<td>93.0(5)</td>
<td>58.0(2)</td>
</tr>
<tr>
<td>Fe, mass%</td>
<td>7.0(5)</td>
<td>2.0(2)</td>
</tr>
<tr>
<td>Rmax (%)</td>
<td>3.19</td>
<td>5.53</td>
</tr>
<tr>
<td>χ²</td>
<td>4.50</td>
<td>4.46</td>
</tr>
</tbody>
</table>
78° and 101° and also wide maximum at 2θ = 53°. The narrow peaks are originated from neutron scattering on the α-Fe lattice, and the wide maximum is evidence of that we have achieved the amorphous state of the Nd2Fe14B phase in both samples.

Fig. 6 presents magnetization curves and hysteresis loop for the NFB sample at room temperature before and after irradiation, i.e., in crystalline and amorphous states. One can see that the magnetization at the field μ0H = 2 T is almost the same in both states, but, a coercitivity decreases noticeably in the amorphous state. Magnetization curves are changed substantially in the low-field region.

Fig. 7 shows experimental temperature dependence of the magnetization of the amorphous NFB sample below Tc = 300 K at the field μ0H = 1 T. We extrapolated this dependence to higher temperatures using the Stoner’s law M(T) = M(0) (1 − (T/Tc)2)1/2 and estimated the Tc in the amorphous state as Tc ≈ 450 K, this is by about 150 K lower than Tc in the crystalline state.

Fig. 8 presents the magnetization curves for the EFB sample in the crystalline and amorphous states at room temperature. It is seen that the amorphization of the sample is accompanied by the lowering of the magnetization by two times in comparison with that in the crystalline state. The coercitivity is very small in the amorphous state.

Fig. 9 shows temperature dependence of the magnetization of the amorphous EFB sample when it was cooled at zero field and at various fields up to 0.7 T. As one can see, a sudden change of the magnetization takes place at about Tf ≈ 70 K at the minimal field. Below this temperature the magnetization irreversibility is observed: the field-cooled magnetization curve and the zero-field cooled one are different. The Tc value decreases with increasing field and the anomaly disappears at μ0H = 0.7 T. Such magnetization behavior is a typical for the systems with competitive exchange interactions in reentrant spin glass state [29]. At the same time the sample possesses a spontaneous magnetization. Therefore, the sample shows properties, which are characteristic for the ferrimagnets and spin glass systems, so we may classify such magnetic state as the mixed state.

Fig. 10 presents temperature dependence of the magnetization of the amorphous EFB sample at μ0H = 1 T. Tc of the sample was measured at the low field, μ0H = 5 mT. We determined the Tc to be equal to 314(2) K, which is noticeably lower that in the crystalline sample. According to our AC-susceptibility measurements the Tc value of crystalline sample was 570(1) K. Thus, the amorphization of the EFB sample results in reduction of Tc by ~250 K, this is the reason, why the magnetization of the amorphous sample is much lower that of crystalline one at room temperature.

To find a saturation magnetization of the EFB sample we extrapolated a high field part of M(H) dependencies to the infinite magnetic field making M = f(1/H2) plots. Using such extrapolation results and taking into account the amount of α-Fe phase, we calculated the magnetic moments of the formula unit for the EFB sample in crystalline and amorphous states (Mcr and Mad, respectively) at 5 K. Following values were obtained: Mcr = 10.7 µB and Mad = 10.1 µB. The obtained Mcr value agrees well with μLω deter-
and 4.0 T. This maximum is the result of a strong Fe–Fe interaction; a slow fall of the Fe magnetization with temperature. The difference between models concerns mainly a procedure of Hamiltonian minimalizing. In our model the angle between the c-axis and the Fe-sublattice magnetization (ψFe) is an independent parameter while the angle between the c-axis and the Er-sublattice magnetization (ψEr) should be found by Hamiltonian minimalizing.

In order to obtain the MCA constants and the parameter Er–Fe exchange interaction in the EFB sample we write Hamiltonian in following view:

\[
H_{\text{Er}} = (g_{\text{Er}} - 1) \cdot I_{\text{Er}} \cdot (J_{fz} + J_{gz}) \cdot \cos(\psi_{\text{Er}}) + (\cos(\psi_{\text{Er}})(J_{fz} + J_{gz}) + \sin(\psi_{\text{Er}})(J_{fz} + J_{gz})) \cdot \sin(\psi_{\text{Er}}) + k_{f}^{1} \cdot J_{fz}^{2} + k_{f}^{2} \cdot J_{gz}^{2} + k_{f}^{2} \cdot J_{fz}^{2} + k_{f}^{2} \cdot J_{gz}^{2}
\]

\[
+ k_{f}^{2} \cdot J_{fz}^{2} - g_{\mu_{B}}HJ_{fz} + J_{fz} + J_{gz} \cdot \cos(\psi_{\text{Er}}) - (\mu_{\text{Er}}H), \tag{1}
\]

where \(g_{\text{Er}}\) is the Landé factor; \(I_{\text{Er}}\) is the parameter of Er–Fe exchange interaction; \(J\) is the operator of a full mechanical moment of the Er ion; \(J_{fz}, J_{gz}, J_{fz}, J_{gz}\) and \(J_{fz}\) are the projections of \(J\) of the Er ions at the 4f and 4g positions to the x, y and z axes; \(k_{f}^{1}, k_{f}^{2}, k_{f}^{2}\) and \(k_{f}^{2}\) are the first and second microscopic MCA constants of the Er ions at the 4f and 4g positions. We assumed that \(k_{f}^{1} = k_{f}^{1} = k_{1},\) and \(k_{f}^{2} = k_{f}^{2} = k_{2}.\) Calculation curve describing the experimental \(\mu_{\text{Er}}(T)\) dependence is presented in Fig. 3 by the dashed line. At minimalization procedure we obtained values of the \(I_{\text{Er}}\) parameter and the first and second microscopic MCA constants for the Er ions at the 4f and 4g positions, which are given in Table 2. Information about \(I_{\text{Er}}\) and \(I_{\text{Fe}}\) allows us to estimate energies of the Er–Fe exchange and magnetic anisotropy by means of following equations:

\[
K_{1}^{\text{Er}} = N_{\text{Er}}k_{1} \cdot J \cdot (J - 1/2), \tag{2}
\]

\[
E_{\text{ErFe}} = I_{\text{ErFe}} \cdot J. \tag{3}
\]

Table 2

<table>
<thead>
<tr>
<th>(I_{\text{Er}}(J/kg))</th>
<th>(E_{\text{ErFe}}(J/kg))</th>
<th>(K_{1}^{\text{Er}}(J/kg))</th>
<th>(K_{2}^{\text{Er}}(J/kg))</th>
<th>(K_{1}^{\text{Fe}}(J/kg))</th>
<th>(K_{2}^{\text{Fe}}(J/kg))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.2 \times 10^{3})</td>
<td>(1.6 \times 10^{4})</td>
<td>(-26)</td>
<td>(-1390)</td>
<td>(3)</td>
<td></td>
</tr>
</tbody>
</table>
where \( N_{\text{Er}} \) is number of the Er ions per cubic meter. The values of \( K_{\text{Er}}^r \) and \( E_{\text{ErFe}} \) are given in Table 2. As one can see, these energies are close together in their values. This factor causes the large magnetization anisotropy of the Er ions at the SRT. The obtained values of \( K_{\text{Er}}^r \) and \( E_{\text{ErFe}} \) agree with those found in [32] but differ from values presented in [33].

5. Amorphous state of the EFB sample

The NPD patterns of the EFB amorphous sample have been recorded at \( T = 6, 150, 295 \) and \( 360 \) K. The NPD patterns measured at \( T = 6 \) K (below \( T_C \) ) and \( 360 \) K (above \( T_C \) ) are presented in Fig. 11 as example. It is seen that the pattern at \( 6 \) K differs from that obtained at \( 360 \) K and this difference arises from a magnetic scattering. It is worthy to note the intensive small angle neutron scattering (see inset in Fig. 11), which is absent in the crystalline sample. The magnetic scattering at \( 360 \) K originates may be from ferromagnetic correlations which exist in paramagnetic region close to \( T_C \). Using Guinier asymptotic we found that the length of the correlations is about \( 8–15 \) Å. The presence of the small angle scattering at \( 6 \) K in the interval \( q = 2n\sin\theta/2 = 0.08–0.18 \) Å\(^{-1}\) is the evidence of existence of the magnetic fluctuations in the ferromagnetic amorphous sample. These fluctuations are fluctuations of the \( z \)-projection of the magnetic moments. Apparently, the fluctuations originate from the competition between ferro- and antiferromagnetic exchange interactions in the regions with nanometer scale. Our estimations show the length of these fluctuations is about \( 20 \) Å.

Now we try to get a quantitative information from the observed NPD patterns of the EFB amorphous sample. As it is well known, the intensity of unpolarized neutron scattering involves the following main contributions: instrumental background, nuclear (coherent, incoherent and multiple) and magnetic scattering. As it was pointed above, the EFB amorphous sample is paramagnetic at \( 360 \) K. In this case the paramagnetic scattering presents in a diffraction pattern. The cross section of this scattering is [34]:

\[
d\sigma_p/d\Omega = 2/3(r_0)^2\gamma^2{c_{\text{Fe}}s_{\text{Fe}}(s_{\text{Fe}} + 1)f_{\text{Fe}}^2(q)} + c_{\text{Er}}s_{\text{Er}}(s_{\text{Er}} + 1)f_{\text{Er}}^2(q),
\]

(4)

where \( r_0 \) is the classical radius of the electron; \( \gamma \) is the magnetic moment of the electron; \( c_{\text{Fe}}, c_{\text{Er}} \) are the Fe-atom and Er-atom concentrations in the sample, respectively; \( s_{\text{Fe}} \) and \( s_{\text{Er}} \) — the effective spin-quantum numbers of the Fe atoms and Er ions, respectively, (we consider \( s_{\text{Fe}} = g_s/2 \); \( f_{\text{Fe}}(q) \) and \( f_{\text{Er}}(q) \) are the magnetic form-factors of the Fe atoms and Er ions, respectively, \( q = 4\pi \sin(\theta/2) \) is the vector scattering. The temperature decrease below \( T_C \) results in a modulation of the paramagnetic scattering. If the instrumental background and nuclear scattering do not change visibly with temperature, we can obtain a magnetic contribution to NPD patterns. The pattern obtained in such a way may be used for description of magnetic properties of the amorphous sample.

We may write the magnetic structure factor for the amorphous state in the form as in [35):

\[
S_M(q) = (d\sigma_M/d\Omega - d\sigma_p/d\Omega)/d\sigma_p/d\Omega,
\]

(5)

where \( d\sigma_M/d\Omega \) is the differential cross section of the magnetic scattering in the magnetically ordering state. Physical sense of Eq. (5) is clear enough: the \( S_M(q) \) is the normalized difference of magnetic scattering intensities in the magnetically ordered and the paramagnetic states.

In order to characterize the magnetic ordering in the real space of isotropic amorphous solid state, the so-called function of magnetic distribution is usually used [36]:

\[
G_M(r) = 4\pi[\rho_M(r) - \rho_{\text{g}}^2(r)],
\]

(6)

where \( \rho_M(r) = \rho_{\text{Fe}}(r) < s(0)s(r) > /s(s + 1) \); \( \rho_{\text{g}}^2(r) \) is the density of the Fe-ion magnetic moments in \( r \)-distance from the atom which is taken as the first atom; \( \rho_{\text{g}}^2(r) \) is the average value of \( \rho_M(r) \). \( \rho_M(r) \) may have both positive and negative values in dependence on the orientation of \( \mathbf{s}(r) \) relative to the spin of the first atom. In such an approach, the veritable three-dimensional distribution of spins is replaced by the one-dimensional arrangement. The \( G_M(r) \) function can be expressed by the \( S_M(q) \) factor in following view (see, for example, [35]):

\[
G_M(r) = 2/\pi \left[ \int_0^{\infty} qS_M(q)\Phi(q)\sin(qr) dq \right],
\]

(7)

where \( \Phi(q) \) is the modified function which reduces influence of breaking off the integration by \( q \) at the \( q_{\text{max}} \) achievable in the experiment. The \( q_{\text{max}} \) equals to be about \( 5 \) Å\(^{-1}\) because the \( f(q) \) form-factor falls fast with \( q \). We choose the \( \Phi(q) \) function as \( F(q) \). In the experiment it is more convenient to use the other function instead of the \( S_M(q) \) factor:

\[
S_{\text{ML}}(q) = F(q)S_M(q) \equiv \Phi(q)S_M(q),
\]

(8)

since determination of \( S_M(q) \) does not demand information about an explicit view of the \( f(q) \) form-factor. We found the \( S_{\text{ML}}(q) \) function by following equation:

\[
S_{\text{ML}}(q) = [J_{\text{BSK}} - J_{\text{GROK}}/D(q)/(2/3)(r_0\gamma)^2]c_{\text{Fe}}s_{\text{Fe}}(s_{\text{Fe}} + 1) + c_{\text{Er}}s_{\text{Er}}(s_{\text{Er}} + 1),
\]

(9)

where \( J_{\text{BSK}} \) and \( J_{\text{GROK}} \) are normalized intensities of scattered neutrons at 6 and 360 K, respectively; \( D(q) \) is a correction for change of the nuclear intensity with temperature. To reduce the statistical error in the determination of \( S_{\text{ML}}(q) \) we made averaging-out in three nearest 2\( \theta \) points. The temperature correction has been taken in the view as Debye–Waller factor: \( D = \exp[-2k\sin(\theta/2)^2] \). The value of \( B \) was determined from measuring in the high 2\( \theta \) angle region where the magnetic scattering is practically absent. An increase in \( B \) by 0.35 Å\(^2\) is obtained when the temperature increases from 6 to 360 K. Correction for the thermal expansion has been carried out too, for that we used the temperature dependence of angle position of the (110) reflection resulting from \( \alpha \)-Fe (see Fig. 5b). In the same manner we obtained the \( S_{\text{ML}}(q) \) factor at 150 K. Unfortunately, we did not succeed in determination of \( S_{\text{ML}}(q) \) at 295 K because the magnetic contribution in the NPD pattern at 295 K was low and comparable with a statistical error.

Thus, we obtained the \( S_{\text{ML}}(q) \) values for the amorphous EFB sample. They are presented in Fig. 12a. The \( S_{\text{ML}}(q) \) maxima decrease appreciably with increasing temperature from 6 K up to 150 K. Calculated arbitrary intensity of the magnetic scattering at

![Fig. 11. Neutron diffraction patterns of the ErFe_{2}B amorphous sample at 6 K (open symbols) and 360 K (filled symbols). Small angle parts of the patterns are presented in insert.](image-url)
6 K is shown for the crystalline sample in Fig. 12b for comparison. It is seen that $S_{M}(q)$ maxima are located at about the same $q$ values as magnetic Bragg reflections for the crystalline Er$_2$Fe$_{14}$B sample at 6 K. This means that the main character of the magnetic structure is kept in the amorphous state.

Results of numerical integration of Eq. (7) are presented in Fig. 13 which shows the $G_{M0}(r)$ function at 6 and 150 K. The $G_{M0}(r)$ function gives information about the space distribution the magnetic atoms and the magnetic moment orientations in the amorphous sample. As can be seen from Fig. 13, the distinct maxima are located in the positive region at $r_0 = 0.53$ Å, $r_1 = 2.26$ Å, and a maximum (in absolute value) is situated in the negative field at $r_2 = 3.25$ Å. Positive maxima point to predominantly ferromagnetic orientation of moments in the distance $r$ from the first atom. Negative maxima indicate the antiferromagnetic arrangement of moments. The $G_{M0}(r)$ maximum at $r_0$ is originated apparently from a distribution of magneto-active electrons around the first atom.

Let us compare the $G_{M0}(r)$ function of the amorphous sample with the picture of the magnetic structure of the crystalline EFB specimen. As was shown above, in the crystalline EFB sample the Fe atoms occupy six crystallographic positions and the Er ions are located at two sites. Distances between Fe atoms change from 2.32 to 2.75 Å while the Fe atoms and Er atoms are positioned from each other at distances between 2.99 to 3.39 Å depending on the Fe (Er) atom positions. Taking into account the multiplicity of the positions, we calculated the average weighted distances between the Fe atoms as $\langle r_{Fe-Fe} \rangle = 2.54$ Å and between the Fe atoms and Er ions as $\langle r_{Fe-Er} \rangle = 3.18$ Å. These values are close to pointed above distances $r_1 = 2.26$ Å and $r_2 = 3.25$ Å, at which the negative and positive $G_{M0}(r)$ maxima are located. In the EFB crystal the Fe-atom moments are coupled ferromagnetically, whereas, the Fe-atom and Er-ion moments are oriented antiferromagnetically. Therefore, positive maxima at $r_1$ and negative maxima at $r_2$ agree with ferromagnetic and ferrimagnetic arrangements of the Fe–Fe-Fe and Fe–Er–Er moments at 6 K. Thus, the ferrimagnetic character of magnetic ordering is kept in the amorphous sample though the translation symmetry is absent. When the temperature increases, atomic vibrations increase and destroy the magnetic arrangement that results in the lowering of the intensity of the $G_{M0}(r)$ maxima at 150 K.

### 6. Conclusions

The structural state and magnetic properties of the crystalline and amorphous NFB and EFB samples have been studied by means of neutron diffraction and magnetic measurements. Amorphous state of the NFB and EFB samples was produced by the fast ($E_{\text{eff}} > 1$ MeV) neutron irradiation up to $1.2 \times 10^{20}$ n/cm$^2$ fluence.

The evaluation of the Er-sublattice magnetization temperature behavior shows the distinct ($\Delta H_{\text{vis}}/H_{\text{field}}(320 \, K) \approx 20\%$) dependence of the magnetization value on its orientation in the crystal. Using neutron diffraction data and our model, we estimated the values of the MCA constant of the Er-sublattice and the parameter of the Er–Fe exchange interaction. The energy of the Er-sublattice magnetic anisotropy is closed to the Er–Fe–Fe exchange interaction energy that causes the clear magnetization anisotropy effect at the spin-reorientation transition.

The amorphization of the NFB and EFB samples results in strong decrease of $T_c$ and almost total collapse of coercivity.

For the EFB amorphous sample the magnetic structure factors are calculated from the NPD patterns, obtained at 6 and 150 K. The magnetic distribution function is reestablished by means of Fourier transform from neutron data. This function characterizes a space distribution of magnetic atoms and mutual orientations of their magnetic moments in the amorphous EFB sample.

A local magnetic ordering in the EFB amorphous sample is similar in general to the ferrimagnetic structure in the crystalline specimen. However, the magnetization anomalies are observed in low temperature region, that it is typical for the reentrant transition in spin glasses. These anomalies originate, on our opinion, from the fluctuations of z-projection of the magnetic moments. Existence of the fluctuations is the sequence of a competition of positive and negative interactions between the Fe atoms.

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References