Mossbauer effect in alloys of variable composition (Tb$_{1-x}$Y$_x$)$_{0.8}$Sm$_{0.2}$Fe$_2$

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Abstract. The paper presents the results of studying the Mossbauer effect on alloys of the multicomponent system (Tb$_{1-x}$Y$_x$)$_{0.8}$Sm$_{0.2}$Fe$_2$ (substitution parameter $x = 0, 0.2, 0.4, 0.6, 0.8, 1$). This system is based on the TbFe$_2$ compound, which has a cubic crystal structure and the highest magnetostriiction constants among rare-earth intermetallic compounds of the RF$_2$ type. Substitution of atoms magnetic terbium for weakly magnetic samarium (20%) and nonmagnetic yttrium leads to exchange interactions altering in the system which should affect the magnitude of hyperfine interactions on $^{57}$Fe nuclei in alloys of this system. The studies were carried out at room temperature. All parameters of the Mossbauer spectrum being isotropic and anisotropic hyperfine fields, quadrupole shift of the components of the spectrum hyperfine structure, and isomeric shift of the Mossbauer line have been determined. Their dependences on the concentration of yttrium have been established.

1. Introduction

Exchange interactions are one of the main reasons for magnetic ordering in ferromagnetic materials. As is commonly known, exchange interactions can have different signs. They can be both positive and negative. Depending on the sign of the exchange interaction integral [1], a ferro- or ferrimagnetic atomic magnetic moment arrangement that make up one or another magnet is realized in magnets. Intermetallic compounds of rare earth metals (REM) with metals of the iron group are convenient objects for studying the interaction of two types of magnetoactive atoms being REM atoms with a 4f-electron shell, lying deep and screened by overlying electron layers and slightly changing under the action of surrounding atoms, and atoms of 3d-elements, in which the electron shell is strongly influenced by crystal and exchange fields [2]. The so-called Laves phases of stoichiometry RM$_2$, where R is a rare-earth ion and M is a 3d ion of a metal are important objects for studying the nature of magnetism of rare-earth alloys and compounds. This stoichiometry has a crystal structure of the MgCu$_2$ type [3,4].

When it comes to multicomponent alloys, the presence of rare-earth ions, whose exchange interactions with the atoms of the iron group can have different signs, in them will lead to the fact that
as the concentration of one of the alloy components increases, a transition from one type of interaction to another (for example, from ferromagnetism to ferrimagnetism or vice versa) can be observed. Herewith, if the signs of the magnetic anisotropy and magnetostriction constants for the initial alloys are different, then we can observe new phenomena such as the phenomena of spin reorientation, magnetic compensation, and the inversion of the magnetostriction constants sign. All these phenomena were observed by the authors of this work on alloys of the multicomponent system \((\text{Tb}_{1-x}\text{Y}_x)_{0.8}\text{Sm}_{0.2}\text{Fe}_2\) [5,6].

Hyperfine interactions (HFI), which are usually studied using the Mossbauer effect, are a sensitive parameter to the change in the sign and type of exchange interactions. In addition, the Mossbauer effect is one of the finest tools for studying the magnetic and nuclear magnetic characteristics of a matter.

Therefore, in this work, the goal is to study the Mossbauer effect, determine the main parameters of the Mossbauer spectrum, and also establish the relationship between exchange and hyperfine interactions in the \((\text{Tb}_{1-x}\text{Y}_x)_{0.8}\text{Sm}_{0.2}\text{Fe}_2\) alloy system depending on the value of the substitution parameter \(x\).

For this purpose, for the first time we have synthesized alloys of the new quasi-ternary system \((\text{Tb}_{1-x}\text{Y}_x)_{0.8}\text{Sm}_{0.2}\text{Fe}_2\) with the substitution parameter \(x = 0, 0.2, 0.4, 0.6, 0.8, 1.0\). The system is based on the \(\text{TbFe}_2\) and \(\text{SmFe}_2\) compounds having record values of the magnetostriction constants [7]. In this system, there will be competition between the exchange interactions of \(\text{Tb-Fe}\) and \(\text{Sm-Fe}\) depending on the concentration of yttrium introduced into the rare-earth sublattice. Therefore, the study of the alloys of this system will make it possible to study not only the intersublattice exchange interaction of \(\text{R-Fe}\) when the rare-earth sublattice is diluted with non-magnetic yttrium atoms but also the exchange interaction in the rare-earth sublattice itself. As is well known, hyperfine interactions are sensitive parameters to exchange interactions altering.

2. Materials and methods
We synthesized alloys \((\text{Tb}_{1-x}\text{Y}_x)_{0.8}\text{Sm}_{0.2}\text{Fe}_2\) on the basis of high-purity rare-earth metals and Fe in an arc furnace with a non-consumable tungsten electrode on a copper water-cooled hearth of a special design in an atmosphere of purified inert gas (argon) at normal pressure. Then the samples were subjected to homogenizing annealing for 2 weeks.

X-ray structural analysis was carried out for all samples on a Panalytical Empyrean diffractometer in the Bragg-Brentano geometry (operating mode \(I = 40\) mA, \(U = 40\) kV) in the angle range from 5 to 140 degrees. The phase was identified by reflexes \((222)\), \((311)\) and \((220)\). The diffraction patterns were analyzed using the FullProf software. The X-ray diffraction analysis showed that only the extreme alloys in this system being \(\text{Tb}_{0.8}\text{Sm}_{0.2}\text{Fe}_2\) and \(\text{Y}_{0.8}\text{Sm}_{0.2}\text{Fe}_2\), for which the substitution parameter \(x\) is equal to 0 and 1.0, respectively, are single-phase and have the C15-type structure of the Laves phase. C15 is a structure of the MgCu2 type. It has cubic symmetry and belongs to the spatial group \(\text{Fd}3\text{m-O}_h^7\). The unit cell of stoichiometry \(\text{RM}_2\) contains 8 formula units or 24 atoms located in two nonequivalent positions [8], specifically, 8 (a) and 16 (d).

In more complex compositions \((\text{Tb}_{0.8}\text{Y}_{0.2})_{0.8}\text{Sm}_{0.2}\text{Fe}_2\), \((\text{Tb}_{0.6}\text{Y}_{0.4})_{0.8}\text{Sm}_{0.2}\text{Fe}_2\), \((\text{Tb}_{0.4}\text{Y}_{0.6})_{0.8}\text{Sm}_{0.2}\text{Fe}_2\), \((\text{Tb}_{0.2}\text{Y}_{0.8})_{0.8}\text{Sm}_{0.2}\text{Fe}_2\) (the value of the substitution parameter for which is \(x = 0.2, 0.4, 0.6, \) and 0.8, respectively), a small content of the second phase was observed. Its amount varied from 5 to 15%.

The Mossbauer effect was studied on an MS-1104m nuclear-gamma resonance spectrometer in the range of room temperatures. The spectra were recorded in the constant acceleration mode.

3. Experimental findings
As indicated above, the \(\text{TbFe}_2\) compound possesses enormous values of magnetostriction and magnetic anisotropy [9, 10]. As a result of spontaneous magnetostriction, its crystal lattice is deformed along the easy magnetic axis [111]. Nuclear hyperfine interactions are the parameters sensitive to the features of the crystallographic and magnetic structure of matter. It is of considerable interest to study
the Mössbauer effect on $^{57}$Fe nuclei in the system $(\text{Tb}_{1-x}\text{Y}_x)_{0.8}\text{Sm}_{0.2}\text{Fe}_2$ for obtaining quantitative information on hyperfine interactions and effective magnetic fields $H_{\text{I,II}}$ on nuclei $^{57}$Fe.

Figure 1 shows the Mössbauer spectra of multicomponent alloys of the system $(\text{Tb}_{1-x}\text{Y}_x)_{0.8}\text{Sm}_{0.2}\text{Fe}_2$ where the substitution parameter takes the following values: $x = 0; 0.1; 0.2; 0.8; 0.9; 1$.

![Figure 1. Mossbauer spectra of alloys of the system $(\text{Tb}_{1-x}\text{Y}_x)_{0.8}\text{Sm}_{0.2}\text{Fe}_2$ at room temperatures](image)

As can be seen, the Tb atoms are replaced by Y atoms, the shape of the Mössbauer spectra changes insignificantly. The spectra presented are of the magnetically ordered type and represent a set of Zeeman sextets. It is known that Fe atoms in the Laves phases RFe$_2$ occupy crystallographic positions that do not have cubic symmetry [11, 12]. The spectra obtained by us were a superposition of two Zeeman sextets with an intensity ratio of 1:3, corresponding to two types of sites of $^{57}$Fe nuclei that are not magnetically equivalent.

Using the tensor approach to describe the hyperfine interactions of $^{57}$Fe nuclei in compounds of this type, the isotropic $H_i$ and anisotropic $H_{\text{an}}$ fields, the magnitude of the Mössbauer line $\delta$ shift and the
quadrupole shift of the components of the spectra Q hyperfine structure were obtained using the LAVES program.

Figure 2 shows the values of hyperfine fields, isotropic $H_{\text{is}}$ and anisotropic $H_{\text{an}}$, on $^{57}$Fe nuclei depending on the concentration of yttrium.

![Figure 2](image)

**Figure 2.** Dependences of isotropic $H_{\text{is}}$ (dark points) and anisotropic $H_{\text{an}}$ (light points) hyperfine fields on $^{57}$Fe nuclei on the yttrium concentration for the (Tb$_{1-x}$Y$_x$)$_{0.8}$Sm$_{0.2}$Fe$_2$ system

The hyperfine fields for the extreme compositions Tb$_{0.8}$Sm$_{0.2}$Fe$_2$ и Y$_{0.8}$Sm$_{0.2}$Fe$_2$ correspond well with the literature data for the TbFe$_2$ and YFe$_2$ compounds [13, 14]. Despite the anisotropy of hyperfine interactions and due to the Fermi interaction of electrons with the nucleus the isotropic contribution of $H_S$ is the same for both iron sublattices and equal to $H_S = 210$ kOe for TbFe$_2$. As can be seen from figure 2, alloy 20% of terbium atoms in the Tb$_{0.8}$Sm$_{0.2}$Fe$_2$ are replaced by atoms of weakly magnetic samarium $H_S = 205$ kOe. As terbium is replaced by yttrium, there is a slight increase in the anisotropic hyperfine field on $^{57}$Fe nuclei. In this case, a noticeable decrease in the isotropic field is observed. It is known that the effective spin of the trivalent ion of the rare earth element Tb$^{3+}$, in accordance with its electronic configuration ($4f^85d^6s^2$), is much larger than the corresponding spins of the yttrium ion Y$^{3+}$ and Sm$^{3+}$. Then it can be assumed that there is a noticeable contribution to the isotropic field caused by the exchange interaction of the spins of localized 4f-electrons of rare earth elements with conduction electrons of the 4s- and 6s- bands. A detailed analysis of the mechanisms of conduction electrons polarization has shown that this contribution is always opposite to the main contribution to the hyperfine field due to the contact Fermi interaction with localized s-electrons of iron [11]. Therefore, an increase in the spin of the rare earth element leads to a decrease in the value of the isotropic field $H_S$.

As a result of processing the Mossbauer spectra of the system (Tb$_{1-x}$Y$_x$)$_{0.8}$Sm$_{0.2}$Fe$_2$ samples, the average values of the hyperfine parameters were determined. Specifically, they are as follows: the isomeric shift of the Mossbauer line $\delta$ and the quadrupole shift of the spectral components Q. The results are shown in Figures 3 and 4. It is known that the isomeric boyer or the chemical shift of the Mossbauer overlap line is proportional to the same electron density in the area of the nucleus, and its total value is an important infrared characteristic of isotopes of the chemical bond of atoms in solids [15].

The magnitude of the quadrupole shift of the spectrum components describes the interaction of the quadrupole moment of the nucleus with inhomogeneous energies in the electric field on the nucleus. The study of the quadrupole interaction enables to obtain information not only about the electronic
configurations of atoms and ions but also covalent information about the quadrupole moments of atomic nuclei.

![Figure 3. Dependence of isomeric shift of Mossbauer line of the (Tb₁ₓYₓ)₀.₈Sm₀.₂Fe₂ alloys on yttrium concentration](image)

![Figure 4. Dependence of quadrupole displacement of hyperfine structure components of Mossbauer spectra of system (Tb₁₋ₓYₓ)₀.₈Sm₀.₂Fe₂ alloys on yttrium concentration](image)

4. Conclusion

Analyzing the results of processing the Mossbauer spectra, it is possible to note a positive correlation between the shift of the Mossbauer line δ and the quadrupole shift of the Q components of the spectrum. This means that their behavior qualitatively coincides with an increase in yttrium concentration (figures 3 and 4). In addition, the average value of the isomeric shift is δ = - 0.86 ± 0.04 mm/s and it does not change within the indicated limits. As mentioned above, fluctuations in the magnitude of the isomeric shift around this average value may be due to a small amount of impurity phase in the intermediate compositions.

Firstly, if we assume that the average value of the isomeric shift is constant when the terbium atoms are replaced by yttrium atoms, which has a practically similar electronic structure as rare earths, then it follows that when the ratio of atoms Tb and Y surrounding the Fe atom changes, the density of s-electrons charge on the ⁵⁷Fe nucleus remains constant.

Secondly, the closest environment of iron atoms in compounds of this type consists of iron atoms. A certain constancy of the average value of the isomeric shift makes it possible to assert that the degree of overlap of the iron atoms wave functions also does not change.

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