SPINTRONICS

ON THE CHEMICAL STABILITY OF THE STRUCTURE AND PHYSICAL CHARACTERISTICS OF THE HIGH-TEMPERATURE SPINTRONIC COMPOSITE EuO:Fe UNDER NORMAL CONDITIONS

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Abstract. **The possibility of forming a limited solid solution $Eu_{1-x}Fe_xO$ in the structure of a spintronic composite material EuO:Fe obtained by the high-temperature solid-phase reduction method of a mixture of higher metal oxides is discussed. Its prevailing role in the formation of outstanding physical properties of this composite as a high-temperature spin injector is described from experimental and theoretical data.**

CONTENTS

1. INTRODUCTION

It is considered [1] that metallic iron does not dissolve in europium monoxide and does not form an independent crystalline phase with it as a solid solution (SS) $Eu_{1-x}Fe_xO$. However, this does not mean that such SSs are not able to originate at least partially or in limited regions of compositions in more complex multiphase composites containing europium and iron oxides. In particular, in the spintronic composite material synthesized from higher oxides of europium (Eu_2O_3) and iron (Fe_2O_3) by the high-temperature solid-phase reduction method [2]. It has been experimentally

confirmed [3] that several more independent crystalline phases co-exist in such composite in addition to the above-mentioned SS: from nano sized super paramagnetic particles of metallic iron to oxides of both metals in different oxidation states. However, it is the presence of this SS that determines the outstanding physical characteristics of this composite - its high specific magnetization (40-60 emu/g at room temperatures, Tr) and the Curie temperature, $T_c = 480$ K. Under the conditions of its inherent semiconductor conductivity at the range of compositions $0.15 < x < 0.25$, this composite material is promising in the creation of semiconductor spintronic devices capable of stable operation at the room temperature, while ensuring an increased degree of spin current transfer, P $\approx 60\%$ [4]. To the latter in a great extent contributes the chemical stability of this composite, located both in bulk and

in thin-film states in normal environmental conditions. This is evidenced by the complete identity of the experimental data obtained on samples of different synthesis series after long (several years) time intervals of their storage. The data are presented below.

2. EXPERIMENTAL DATA

In support of the above, we present the results of the experimental studies of resonance (nuclear magnetic resonance, NGR) and magnetic parameters of this composite, according to data from [5, 6]. Moreover, NGR spectroscopy of composite samples was studied using a standard SM-2201 spectrometer with ^{57}Fe and ^{151}Sm$_2$O$_3$ sources. Their magnetic parameter at low temperatures was studied on a SQUID magnetometer of MPHS-XL7 type, and at elevated temperatures - on a magnetic balance using the Faraday method.

Thus, the spectra of nuclear magnetic resonance (or the Mössbauer effect) of a bulk sample of the EuO:Fe composite for the ^{57}Fe isotope, taken at room temperature are presented in **Fig. 1**. It's characterized by a typical ferromagnetism and contain at least two sixes of Zeeman lines: one with H_{eff} = 32.8Tl, δ = 0, ΔE = 0, the other with H_{eff} = 19.2Tl, δ = +0.20 mm/s, ΔE = 0.005 mm/s.

They relate to α-Fe nanoparticles and Eu-Fe-O clusters, respectively. The relative intensity of the sextets $I(\alpha$-Fe$) \approx$ 0.72; $I($Eu-Fe-O$) \approx$ 0.28. From which it may be concluded that the presence of iron in the composite, basically,

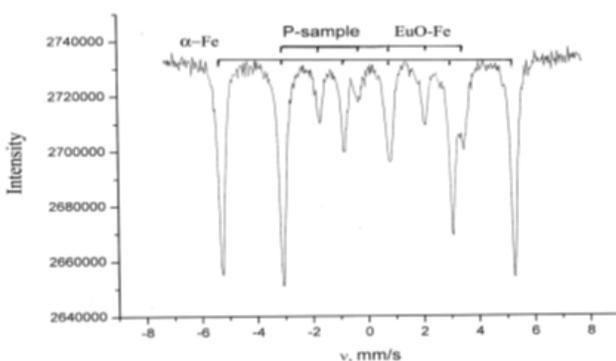corresponds to its free (metallic) state. The fraction of ferromagnetic clusters in it is much smaller, which agrees with the impossibility of formation of solid substitution solutions of Eu on Fe at the EuO lattice. The display of the ionic state of iron in the composite should be considered as impurity centers forming Eu-Fe-O clusters as a result of a possible chemical interaction of them with an europium cations at accordance by the mechanism of indirect *d-f-*exchange [7].

In the same conditions the Mössbauer spectra of ^{57}Fe of the composite films (**Fig. 2**) represent a singlet with an isomeric shift of δ = +0.20 mm/s and with a very weak splitting, typical for the display of super paramagnets of α-Fe nano particles. This data exemplifies that the high-temperature magnetism of the composite is caused by the presence of the ferromagnetic ordering of Eu-Fe-O clusters and super paramagnetic α-Fe nanoparticles in it. As shown below, this is fully confirmed by magnetic studies of the composite.

The cation state of the europium atoms in the composite illustrates the NGR spectrum of ^{151}Eu, **Fig. 3**. It is an overlap of two lines characterized by isomeric shifts of δ = 12.6 mm/s and δ = +0.02 mm/s, and width at half height of 3.7 mm/s and 4.1 mm/s, respectively. The
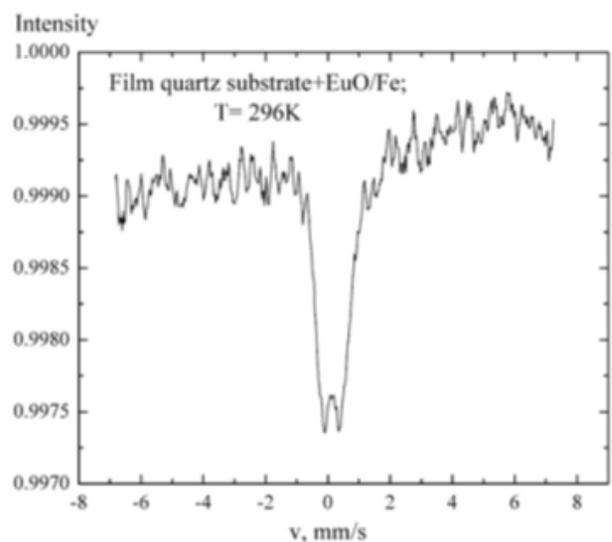

Fig. 1. *NGR spectra of ^{57}Fe powder of the EuO:Fe composite at room temperature.*

Fig. 2. *Mössbauer spectra of ^{57}Fe thin films of a composite on Quartz.*

SPINTRONICS

ON THE CHEMICAL STABILITY OF THE STRUCTURE AND PHYSICAL
CHARACTERISTICS OF THE HIGH-TEMPERATURE SPINTRONIC COMPOSITE...

405
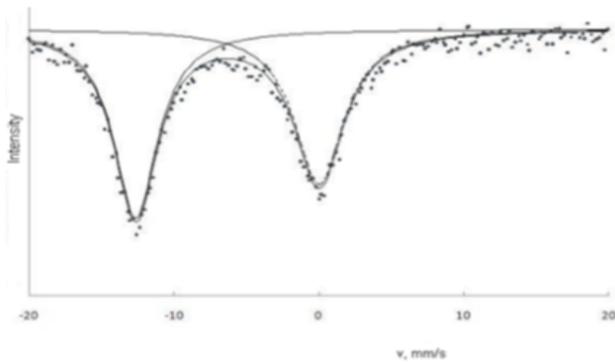
Fig. 3. *The Mossbauer spectrum of ^{151}Eu powder of the composite at room temperature.*

Fig. 4. *Dependence of the magnetic saturation moment of the $(EuO)_{0.75}Fe_{0.25}$ composite by H.*

first line corresponds to the paramagnetic ion of the Eu^{2+} matrix; the second line is responsible for the manifestation of the valence state of Eu^{3+}. Note that such isomeric shifts of NGR spectra of ^{151}Eu at the composite correspond to the positions of these cations in the lattices of EuO and Eu_2O_3 [8]. The obtained spectra and the position of the isomeric shifts of the Eu^{2+} and Eu^{3+} ions in them agree well with the NGR investigation of the micro crystals of the magnetic semiconductor EuS interspersed in thin films of the TiO_2, Al_2O_3 and SiO_2 oxides [9].

The presence of Eu^{3+} ions in the composite, on the one hand, can be considered as an impurity phase of Eu_2O_3 due to the conditions of its synthesis – high temperature reduction of a sesquioxide or a mixture $(Eu_2O_3 + Fe_2O_3)$ by carbon. Based on the results of chemical and X-ray spectral analysis, the presence of this phase in the composite did not exceed 1% by weight.

On the other hand, comparison of state line intensities of the Eu^{3+} ions (~0.55) in the spectrum with that for the ion state Eu^{2+} (~ 0.45) may indicate the appearance in the composite of some "inductive" effect associated with the effect of iron atoms on the electron density on ^{151}Eu nuclei. This, as noted above, can correspond to the manifestation of an indirect (via the *p*-state of oxygen) *d-f* exchange between iron and europium to form Eu-Fe-O clusters. A possible transfer of the electron density from Eu^{2+} to the iron (even partial) will lead to the
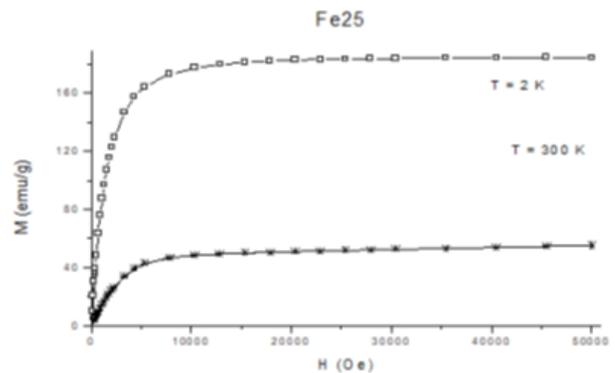
polarization of the spins of these ions, which under these conditions is equivalent to the manifestation of their ionic state in the cluster as Eu^{3+}, and the states of the iron ion as Fe^+. As a result, the ferromagnetic moment of such an $Eu^{3+}Fe^+O$ cluster at T > 70 K (the temperature of the ferromagnetic disordering of the EuO phase) caused by the spin polarization of the paramagnetic europium ions from the nearest environment of the impurity Fe^+ ion and localized on might become increased comparing to magnetic moment of atomic iron.

Let us now analyze the magnetic characteristics of the samples of the composite, measured for a wide range of temperatures and magnitudes of the external magnetic field. **Fig. 4** shows the field dependence from the ferromagnetic saturation moment $M(H)$ of a composite composition $(EuO)_{0.75}Fe_{0.25}$ at $T = 2$ K and $T = 300$ K, and in **Fig. 5** (a, b) its temperature dependences, $M(T)$.

From these data, it follows that the composite is actually a heterogeneous mixture at least of three ferromagnetic ally ordered phases. In this case, the value of the magnetization of the
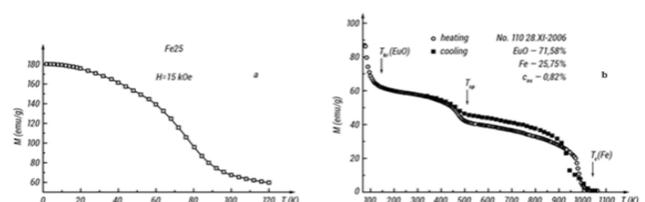

Fig. 5. *Temperature dependences of the magnetization of a composite at low (a) and elevated temperatures (b).*

Fe-component for this concentration range almost linearly corresponds to its share presence in the composite [2].

At the room temperature, the ferromagnetic saturation moment of this composition composite is close to the value of $M \approx 60$ emu/g, which completely corresponds to the Fe-component, although it exceeds it in absolute terms by approximately 10÷15 units. At low temperatures the ferromagnetic moment predominates mainly due to the contribution of the divalent europium ion in the composite against which the contribution of iron to M is $\leq 30\%$. Throughout the temperature range the samples of the composite exhibit the properties of magnetically soft ferromagnetism. A feature of the $M(T)$ dependence in Fig. 5(b) is its inflection in the region of $T \approx 480$ K which is characteristic of the ferromagnetic disordering of the magneto-structural phase. If a transition of the "ferro-para" of the EuO phase takes place in the region of $T \approx 70$ K, and a similar for the Fe-component of the composite observed at $T \approx 1000$ K, then a certain ferromagnetic (super paramagnetic) constituent (i.e., ferromagnetic phase) of the composite must undergo a disorder in the above temperature range. It should be responsible for the increased value of its specific magnetization (magnetic saturation moment) at the room temperature range and above (up to 480 K). As follows from the above NMR-spectra of a composite, such a ferromagnetically ordered structural phase can only be the presence of a cluster (solid solution) of $Eu^{3+}Fe^{+}O$ with a Curie temperature in it, $T_c = 480$ K.

The behavior of the magnetization of the composite films received "flash technique" in the way [3], correlates well with the data in Fig. 5 - the characteristic features of the $M(T)$ dependences also appear in the films. Their magnetization reversal curve under normal conditions in the easy direction is close to rectangular, saturation is achieved in fields of $H \approx 0.5$Tl. However, the opening of the hysteresis loop is not observed. The magnitude of the magnetic moment of the

composite thus reaches $M \approx 4\mu_B$ and correlates in these conditions with magnetically active Fe-centers in it. This value of M exceeds the characteristic value of the magnetic moment of pure iron almost by $\approx 20\%$, which completely corresponds to the contribution made to it from the environment of the paramagnetic moments of europium ions.

At the same time, studies of the $M(T)$ dependence upon cooling of the composite films at low temperatures in an external magnetic field (the FC condition) and without a field ($H = 0$, the ZFC condition) revealed another feature. Namely, the presence of an inflection of this dependence in the temperature region of $T = 25÷30$ K (**Fig. 6**) in the latter case. This so-called "blocking temperature" (T_{bl}) - is the transition from the anti ferromagnetically ordered state (at $T < T_{bl}$) to super paramagnetic (at $T > T_{bl}$) of α-iron nanoparticles in the composite. Physically this means that the magnetic moments of such nanoparticles at $T \leq T_{bl}$ are anti ferromagnetically in relation to ferromagnetically ordered state of the ions of the Eu^{2+} matrix. This leads to a general decrease in the magnetic moment of the composite at $T = 0$ K to a value of $M = 180$ emu/g. For comparison: under the same conditions, "pure" EuO monoxide has a record value of $M = 240$ emu/g for ferromagnets. However, at $T > T_{bl}$, the situation changes to the directly opposite – super paramagnetic of α-Fe nanoparticles
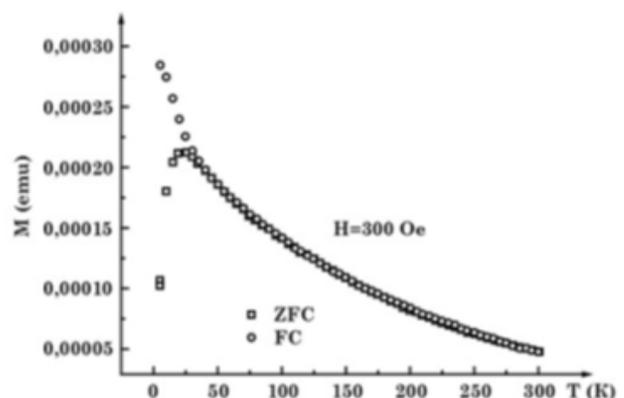

Fig. 6. *The magnetization of the $(EuO)_{0.75}Fe_{0.25}$ composite film on a silicon substrate under conditions of ZFC and FC.*

SPINTRONICS

ON THE CHEMICAL STABILITY OF THE STRUCTURE AND PHYSICAL **407**
CHARACTERISTICS OF THE HIGH-TEMPERATURE SPINTRONIC COMPOSITE...

promotes the growth of the magnetic moment of the EuO:Fe cluster (solid solution) in the composite with decreasing magnetization and disordering of the Eu^{2+} cations of the matrix. According to the magnetic data presented, the total ferromagnetic moment of such a cluster (solid solution) at room temperature is numerically more than 10 emu/g exceeding the ferromagnetic moment inherent in pure iron at these temperatures. Due to this, in general, taking into account a last parameter, this composite is the record among all known ferromagnetic materials, especially semiconductor materials, which are recommended for spintronics. When using a composite as a spin injector, these qualities will, in particular, contribute to an increase of the degree of spin current transfer in spintronic structures created with his participation [4].

3. THEORY

For a possible theoretical justification and understanding of the regularities behavior of the EuO:Fe composite experimental parameters, a model calculation of the electronic band structure of the $Eu_{1-x}Fe_xO$ solid solution, which is structurally included at the composite composition, was performed [10]. The calculation method included the use of the linear method of associated plane waves (FLAPW, code WIEN2k) with the generalized gradient approximation (GGA) of the exchange-correlation potential [11]. In recent years, a similar calculation method has been applied to the EuO and a EuS phase doped with rare earth metals and provides good correlation with experiment [12, 13]. At the calculations a super lattice, obtained by translating the unit cell of EuO along the crystallographic axes when one of the europium cations is replaced by an iron ion, was constructed. Without going into here, especially in carrying out such calculations of systems with strongly correlated electrons, such as Europium compounds, and performing certain corrections of the band-state spectrum [14], we will analyze only the results of the theoretically modeling of

the band states density of iron-doped europium oxide, indicating their good agreement with the above experimental data presented. These results are illustrated in **Fig. 7**, where along with the final picture of the spectrum of the solid solution, the partial density of the electronic 3d states of iron is allocated.

It follows that zone states formed mainly by the 2p orbitals of oxygen atoms are located below the energies -2eV, whereas at states above 0.5 eV there are band states formed by the 5d orbital's of europium atoms (the energy of states is relative to the Fermi level). The band states formed by the 4f-orbitals of europium are situated at the near Fermi region. Wherein the activation energy of the conductivity, ΔE, between the Fermi level near the 4f-zone ceiling and the bottom of the 5d band is 0.8 eV, which agrees well with the experimental value of ΔE = 0.75 eV [3]. Also the calculations reproduce well the interval between the maxima of the 2p O- and 4f Eu-states, equal to 2.5 eV [15].

The most significant changes in the spectrum of the EuO band states when doped with iron are the appearance of two bands of states with a positive spin-up direction at the energy near -6 eV and one band with a negative spin down direction at Fermi level. The magnetic moments values obtained on Fe ions were 3.74 μ_B, and on Eu^{2+} cations, they were from 6.86 to 6.88 μ_B. To explain these values, we consider the partial density of the 3d states of iron atoms
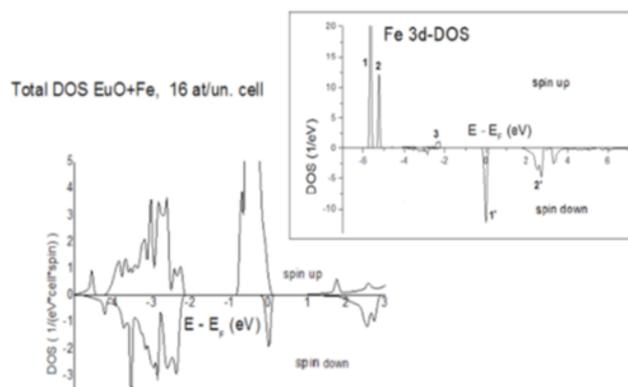

Fig. 7. *The density of electronic states of TP $Eu_{1-x}Fe_xO$ with the separation of the partial density of the electronic 3d-states of iron.*

which additively enters the band spectrum of this SS. The bands of spin-up band states noted on Fig. 7 by the numerals 1 and 2 have the type of local symmetry t_{2g} and e_g and contain 3+2 electrons. Another peak of the density of $3d$ Fe- states (peak 3) is located at the top of the valence $2p$ O - band, but it is a consequence of the hybridization of $2p$ O- and $3d$ Fe - states. Band 1' corresponds to spin down $3d$ Fe-states with e_g-type local symmetry: it contains one electron. Band 2' corresponds to the empty zone of spin-down 3d Fe states. It follows that the iron ions in the monoxide structure retain 6 electrons, i.e. they are in the charge state 2^+ and will have a magnetic moment equal to 4 μ_B which corresponds to the data given above. The spin up band of the $4f$-states in the near Fermi region contains ~ 7 electrons, i.e., the magnetic moment of the Eu atoms is ~ 7 μ_B, which also corresponds to the values given above.

The reason for the presence of large magnetic moments on iron atoms is a large exchange splitting of the states of iron ions – at around 5 eV (Fig. 7), so that the majority of spin-down states of iron are not populated by electrons. As a result, the magnetic moment on Fe^{2+} cations is ~$1.7\mu_B$ higher than the magnetic moment of pure iron. Accordingly, at room temperature, the numerical value of the saturation magnetization of the composite due to doping reaches values of $40\div60$ emu/g [2]. Since the $3d$ orbitals of iron are much less localized in space than the $4f$ states of europium, the appearance of iron atoms in the structure of the monoxide leads to an increase in the exchange interaction between the f- and d-cations and, as a consequence, to an increase in the Curie temperature of the composite. Note also that in the energy range from about 0.9 to 1.3 eV, i.e., near the bottom of the conduction band, there are no spin-down band states. This may mean that even in the presence of iron atoms a 100% spin polarization of the charge carriers is possible what corresponds to the previously indicated values of the spin polarization P in pure EuO

[16]. Thus, the existence of a ferromagnetically ordered phase in the form of a similar SS in the EuO:Fe composite is completely responsible for the experimental observation in it at room temperature of a record-breaking degree of spin current transfer.

Let us also trace the possible correspondence of the performed calculation of the band spectrum of the solid solution to the electronic parameters of the composite, related to the manifestations of its other structural components. First, this concerns the data of the NGR-studies of the composite and the possibility of carrying out in it an "induction" effect - transfer of the electron density from Eu^{2+} ions to impurity ions Fe^{2+} introduced in the matrix lattice. The presence of such a transfer, which can be interpreted as the transition of a part of the europium ions Eu^{2+} to the Eu^{3+} state, and some iron ions to the Fe^+ state, does not contradict the results of calculations of the electronic band structure of the solid solution, although they do not directly follow from them. Approximately 0.03 of the $4f$-states (per europium atom) remain empty. On the other hand, it can be noted that the band of $3d$-states of iron (with a negative value of the spin projection, spin-down) is asymmetric relative to the Fermi level. I.e., the number of states occupied by electrons (to the left of the Fermi energy) is somewhat larger (their zeroing corresponds to an energy of -0.15 eV) than the number of empty states in this zone (to the right of the Fermi energy, zeroing at 0.1 eV). Both of these circumstances indicate that there is actually a slight transfer of the electron density from the $4f$ Eu^{2+} state to the $3d$ Fe^{2+} state (about 0.03 electron per impurity Fe-node).

These calculations, like the vast majority of similar calculations by the methods of the electron density functional theory, correspond to the temperature of $T = 0$ K. Obviously, a certain "smearing" of the Fermi level with an increase in the temperature can be accompanied by a somewhat higher transfer of the electron density from $4f$ Eu- states to $3d$ Fe-states wherein.

SPINTRONICS

ON THE CHEMICAL STABILITY OF THE STRUCTURE AND PHYSICAL **409**
CHARACTERISTICS OF THE HIGH-TEMPERATURE SPINTRONIC COMPOSITE...

The second example concerns the experimental data of Fig. 6 – the presence of a "blocking" temperature – the spin reorientation of the magnetic moments of free iron nanoparticles in the composite structure and its transition from an antiferromagnetic to a superparamagnetic state at $T > 25$ K. Such a spin reorientation is in many ways analogous to spin-orientation transitions in rare-earth metals observed at low temperatures [17]. Nevertheless, the very indication of the theory of the antiparallelity of the spins of iron nanoparticles at the SS with respect to the spin state of the Eu^{2+} - cations at T = 0 K implies the presence of T_{bl} at $T > 0$ K. What also can be attributed to the merit of these calculations.

4. CONCLUSION

Thus, the comparison of the calculation results of electronic band structure of the $Eu_{1-x}Fe_xO$ SS with the experimental data of the EuO:Fe spintronic composite, which is one of its structural constituents, is indicative of both surprisingly good agreement between each other and a correct and justified choice of theoretical model for doping a monoxide lattice, and the method used at calculating its electronic band structure. It is shown that the presence of this SS in the composite provides its elevated Curie temperature. At the same time, iron cations are in a high-spin state, on the $1.7\mu_B$ higher than the intrinsic magnetic moment of pure iron. It is also shown that iron and europium cations in the monoxide structure have an oxidation degree close to 2^+. Both in pure and in Fe-doped monoxide, the states near the bottom of the conduction band (the $5d$-state of europium) are 100% spin-polarized. What is quite possible to provide, as already noted, an increased (record-to-date) degree of spin current transfer from the composite when it is used as an injector of spin carriers in semiconductor devices of spin electronics. It is shown that in Fe-doped monoxide there is an insignificant electron density transfer from Eu^{2+} ions to Fe^{2+} ions,

but the main factor ensuring the presence of Eu^{3+} ions observed in the experiments - iron nanoparticles, apparently provides is apparently the presence of Eu_2O_3 nanoclusters in the composite structure. Their presence, as well as the presence of superparamagnetic α-iron nanoparticles, apparently provides the samples of this composite in the bulk and thin-film states with long-term chemical stability of their physical parameters under normal conditions. As evidenced by the available experience with this spintronic material [18]. Its further advancement in high-temperature spintronics and the creation of appropriate devices, in particular, a spin transistor, is possible with the development of thin-film composite technology in the method of molecular epitaxy from higher oxides of europium and iron. As the most economically justified and corresponding to industrial production of films of composites of a given composition with a corresponding set of physical and physical-chemical characteristics. In contrast from the less effective and a more costly of the "flash technique" method of synthesis of the thin films of such a composite, based on the preliminary synthesis of bulk material - a precursor [3].

In conclusion, we note that this combination of phase components, which form the outstanding properties of this composite as a high-temperature spintronic material, may be reproduced only when it is synthesized from the higher oxides of metals. Attempts to synthesize the aforementioned single-phase SS from the metals corresponding to the properties of this composite have so far been unsuccessful.

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