## SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Europium Valence State in Europium Monoxide–Iron (Cobalt) Magnetic Composites

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Abstract—Composite magnetic powders EuO/Fe(Co) were synthesized. These composites are candidates for use as materials for spintronics devices operating at room temperature. The composites synthesized by carbothermal reduction of oxide mixtures  $Eu_2O_3$  and  $Fe_2O_3$  (or  $Co_3O_4$ ) contain not only europium in the main valence state (2+) but also europium in the state 3+, its content increasing with the content of the *d* metal and depending on technological parameters of the reduction process. The content of the trivalent europium in the composites was estimated by chemical analysis and  $L_{111}$ -edge X-ray absorption spectroscopy (XAS). The results obtained by these methods correlate with each other. XAS is considered to be a quantitative express method of certification of materials containing europium in various valence states.

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The development of a new field in microelectronics-spin electronics-is based on realization of electron transport between the working elements of electronic devices in which the information carrier is the spin of an electron. In solid heterostructures, the source (injector) of spin-polarized electrons can be wide-gap ferromagnetic semiconductors. These conditions are completely met by composites based on europium monoxide, a ferromagnetic semiconductor ( $\rho = 10^8$ –  $10^{10} \Omega$  cm, the bandgap  $E_g = 1.2$  eV,  $T_c = 69$  K, chemically stable at ambient temperatures) [1, 2]. It is precisely europium monoxide that is currently believed to be the best candidate for film heterostructures of the FS/S type (ferromagnetic semiconductor/nonmagnetic semiconductor) in which both solid solutions based on europium monoxide and its composites with 3d- and 4f metals can act as spin injectors [3, 4]. Composite materials EuO/Fe(Co), composed of two phases differing in ferromagnetic ordering temperatures and conductivity, meet the requirements of operation of spin devices at room temperature. To realize spin transport in such systems, the content of the metal phase should fall within the range where direct M-M interaction is absent and the material retains the properties of the ferromagnetic semiconductor at a rather high magnetic moment (up to 25 wt % metal). On the other hand, the content of trivalent europium in the material should be controlled since the presence of paramagnetic Eu<sup>3+</sup> ions sharply deteriorates the ferromagnetic characteristics of the composite. Chemical methods of quantification of valence states of rare earth metals (Ce, Sm, Eu, Yb) are rather complicated even when voltammetry, polarography, EPR, and other methods are invoked. As a rule, in natural and technical objects, the total content of these

metals is determined. In the present work, in addition to traditional chemical analysis methods, we used  $L_{111}$  edge X-ray absorption spectroscopy (XAS) developed at the Institute of Metal Physics, Ural Division of the RAS, which makes it possible to determine, to a rather high accuracy, the quantitative ratio of the Eu<sup>2+</sup> and Eu<sup>3+</sup> ions in EuO/Fe(Co) composites of different compositions.

#### **EXPERIMENTAL**

To obtain composite materials with phases containing low valence states of metals (Fe<sup>0</sup>, Co<sup>0</sup>, and Eu<sup>2+</sup>) iron or cobalt metals and europium monoxide, the known methods of reduction of their highest oxides with carbon (carbothermy) can be used. The reduction of Fe<sub>2</sub>O<sub>3</sub> to the metal is a well-documented physicochemical process. It proceeds by the indirect reduction mechanism involving the gas phase (carbon monoxide CO) at temperatures on the order of 1100°C. The highest europium oxide  $Eu_2O_3$ , in contrast to 3*d*-metal oxides, is not reduced by CO. The main role in the reduction of Eu<sub>2</sub>O<sub>3</sub> with carbon is played by oxygen diffusion from the bulk of the sample to its surface while the reagents are in direct contact, and the synthesis of lower europium oxides occurs at ~1300°C producing CO.

Taking into account the differences in the reduction mechanisms and temperatures of the highest iron, cobalt, and europium oxides by carbon, we selected high-temperature carbothermal reduction of a mixture of  $Eu_2O_3$ ,  $Fe_2O_3$ , and  $Co_3O_4$  as the simplest and most available method of synthesis of composites [5, 6]. The synthesis was carried out at reduced pressures of the



**Fig. 1.** X-ray powder diffraction patterns of (a) EuO and (b) the composite EuO/Fe.

gas phase, which is necessary for stabilization of the divalent europium by the reactions

$$Eu_2O_3 + Fe_2O_3 + 4C = 2EuO + 2Fe + 4COT$$
, (1)

$$Eu_2O_3 + Co_3O_4 + 5C = 2EuO + 3Co + 5COT$$
. (2)

Reactions (1) and (2) are basic for calculation of the weights of corresponding oxides and carbon required to obtain a specified amount of a composite with an iron (or cobalt) content within 5–40 wt %. The initial mixture was prepared from 3d metal oxides (chemically pure grade), Eu<sub>2</sub>O<sub>3</sub> of class 0 (99.999% purity), and acetylene black (pure for analysis). The powder blend prepared by thorough mixing was placed into a molybdenum crucible and heated in two stages (at 1100 and 1300°C) in an SNV-1500 vacuum furnace, while the pressure of the gas phase was maintained at  $10^2-10^{-1}$  Pa. The first stage of the reduction process (1100°C, pressure in the system  $10^2$  Pa) leads to the appearance of Fe and Co metal particles in the system. At the second stage (1300°C, 10<sup>-1</sup>Pa), Eu<sub>2</sub>O<sub>3</sub> is reduced to europium monoxide. The phase composition of the reduction products was monitored by X-ray powder diffraction on a DRON-2 diffractometer (Cu $K_{\alpha}$ radiation). The weight percentage of Eu, Fe, and Co was determined by gravimetric and volumetric chemical analysis: from hydrochloric acid solutions, europium was isolated as oxalate; iron was determined trilonometrically and cobalt, by atomic emission spectroscopy. Carbon was determined by burning a sample in oxygen. The content of oxygen was determined by calculation. The valence state of europium in the oxide phase of composites and the quantitative ratio between the  $Eu^{2+}$  and  $Eu^{3+}$  ions were determined from chemical analysis data and from the results of processing the Eu absorption spectra obtained by the XAS method [7, 8]. This method is based on excitation by X-rays of the electronic transition  $2p_{3/2} \longrightarrow 5d$  in atoms of rare earth elements, in particular, in europium atoms. The energies of this transition for the  $Eu^{2+}$  and  $Eu^{3+}$  ions differ by 7 eV, which makes it possible to determine the content of these europium ions from the intensities of two signals. An advantage of this method is its selectivity; i.e., the result is independent of the presence of other chemical elements.

The Eu  $L_{111}$  X-ray absorption spectra were recorded on an ARS-KD-2 vacuum X-ray spectrometer with the use of a coordinate detector. The  $(13\overline{4}\,0)$  plane of a bent quartz single crystal with a curvature radius of 1.940 m was used as the crystal analyzer. Dispersion near the  $L_{111}$  edge was 2.6 eV/mm, the spectrometer resolution was ~8000. To determine the valence, a composite spectrum was routinely decomposed into a combination of Lorentzian and arctangent functions in order to model the process of electron transfer, after X-ray quantum absorption, to coupled states and continuous spectrum, respectively. The areas under the curves described by Lorentzian functions ( $S_{Eu^{2+}}$  and  $S_{Eu^{3+}}$ ) are proportional to the number of atoms with different valences. The europium valence  $(V_{Eu})$  was calculated by the formula  $V_{\text{Eu}} = 2 + [S_{\text{Eu}^{2+}}/(S_{\text{Eu}^{2+}} + S_{\text{Eu}^{3+}})].$ 

### **RESULTS AND DISCUSSION**

The products of high-temperature reduction of mixtures of europium and 3*d*-metal oxides by carbon are fine powders composed of the oxide matrix of EuO (an NaCl structure) and  $\alpha$ -Fe or Co metal particles 200– 300 nm in size uniformly distributed over the matrix. Figure 1 shows the X-ray powder diffraction patterns of the composite (b) in which, in addition to the EuO line (a), the lie of Fe metal is observed (20 44.8 °). According to our magnetic measurements, the composites consist of two ferromagnetic phases that differ in magnetization and Curie temperature (Fig. 2).

The valence state of europium and the quantitative ratio of the Eu<sup>2+</sup> and Eu<sup>3+</sup> ions in the europium monoxide phase were estimated from the results of chemical analysis of the EuO/Fe and EuO/Co composites. With allowance for the fact that all oxygen in the composite



Fig. 2. Temperature dependence of the saturation ferromagnetic moment of the composite EuO/25 wt % Fe in the magnetic field H = 15 kOe.

is bound only to europium to form  $EuO_x$  phases nonstoichiometric with respect to oxygen, the formula of this phase can be calculated from the weight percentages of oxygen and europium in the composite reduced to their atomic weights (16 and 152, respectively). The content of europium in the di- and trivalent state in the composite was calculated from the derived formula of monoxide. There is an example of calculation of the oxide formula and the contents of  $Eu^{2+}$  and  $Eu^{3+}$  ions for sample no. 1 (table): 8.35 : 16 = 0.52, 76.04 : 152 = 0.5. Hence, the oxide formula is  $EuO_{1.04}$ . Assuming that the  $EuO_x$ oxide with an oxygen excess is a mixture of the oxides EuO and  $EuO_{1.5}$ , we calculate the atomic percentage of the  $Eu^{2+}$  and  $Eu^{3+}$  ions in the oxide  $EuO_{1.04}$  by the equa-

No.	Chemical composition, wt %				$EuO_x$ formula by chemical	Content, at % of the total Eu content, according to chemical analysis		Content, at % of the total Eu content, according to XAS data	
	М	Eu	С	0	anarysis	Eu <sup>2+</sup>	Eu <sup>3+</sup>	Eu <sup>2+</sup>	Eu <sup>3+</sup>
EuO–Fe system									
1	13.75	76.04	1.86	8.35	EuO <sub>1.04</sub>	92	8	87	13
2	25.75	64.78	2.00	7.47	EuO <sub>1.09</sub>	82	18	79	21
3	34.70	56.10	2.08	7.12	EuO <sub>1.20</sub>	60	40	58	42
4	40.24	50.70	2.20	6.86	EuO <sub>1.28</sub>	44	56	45	55
EuO–Co system									
5	6.28	84.32	Traces	9.40	EuO <sub>1.05</sub>	86	14	84	16
6	14.97	76.23	Traces	8.80	EuO <sub>1.07</sub>	80	20	77	23
7	35.00	56.90	0.20	7.90	EuO <sub>1.33</sub>	33	64	34	66

Contents of Eu<sup>2+</sup> and Eu<sup>3+</sup> in various composites as determined by chemical analysis and X-ray absorption spectroscopy

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**Fig. 3.** Eu  $L_{111}$ -edge X-ray absorption spectra of composites with iron: (1) EuO<sub>1.04</sub> + 13.75 wt % Fe, (2) EuO<sub>1.09</sub> + 25.75 wt % Fe, (3) EuO<sub>1.28</sub> + 40.24 wt % Fe, (4) EuS, and (5) Eu<sub>2</sub>O<sub>3</sub>.

tion 1.04 = 1.0y + 1.5(1 - y), hence y = 0.92. Thus, the oxide EuO<sub>1.04</sub> contains 92 at % Eu<sup>2+</sup> and 8 at % Eu<sup>3+</sup>.

The Eu  $L_{111}$  X-ray absorption spectra are shown in Figs. 3 and 4. Europium(II) sulfide EuS and europium(III) oxide Eu<sub>2</sub>O<sub>3</sub> were used as the references. Maxima A and B correspond to the Eu<sup>2+</sup> and Eu<sup>3+</sup> absorption signals, respectively.

The table summarizes the results of determination of the europium valence state on the basis of chemical analysis and XAS data.

Analysis of the data in the table shows the results of determination of the content of europium in different valence states in magnetic composites by the chemical analysis and XAS methods are consistent (the discrepancy is no more than 5 at %). With allowance for the fact that all used chemical analytical methods implying the destruction of considerable samples of a material are indirect methods of determination of the europium valence state and that each of the procedures introduces a definite error to the overall result, the XAS method should be considered preferable for certification of the synthesized magnetic powders. We found that the content of Eu<sup>3+</sup> increases with the content of the metal in the EuO/Fe and EuO/Co composites. This is presumably due to different mechanisms of reduction of 3d and 4f elements with carbon. An increase in the percentage of iron or cobalt oxides in the initial mixture leads to that the mechanism involving the gas phase becomes



**Fig. 4.** Eu  $L_{111}$ -edge X-ray absorption spectra of composites with cobalt: (1) EuO<sub>1.05</sub> + 6.28 wt % Co, (2) EuO<sub>1.07</sub> + 14.97 wt % Co, (3) EuO<sub>1.33</sub> + 35 wt % Co, (4) EuS, and (5) Eu<sub>2</sub>O<sub>3</sub>.

dominating over the process of solid-phase reduction, and this leads to a considerable consumption of the reducing agent at the stage of reduction of Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> to the metal and to its deficiency at the stage of phase transitions Eu<sub>2</sub>O<sub>3</sub>  $\longrightarrow$  Eu<sub>3</sub>O<sub>4</sub>  $\longrightarrow$  EuO. Therefore, for the development of technological parameters of synthesis (reductant consumption, temperature, gasphase pressure, heating and cooling regimes) and certification of magnetic composites based on lower europium oxide, the L<sub>111</sub>-edge XAS method can be recommended as a reliable express method for quantification of the europium valence state in the materials under consideration.

We found that, with the use of the suggested method of synthesis of EuO/M composites, the content of trivalent europium in the oxide phase can be stabilized at the level of 20 at % of the total Eu content when as much as 25% of the metal is introduced into the composite.

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