PHASE TRANSITIONS IN ErFe$_{1-x}$Al$_x$O$_3$ SYSTEM 
($x \leq 0.1$)*

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The magnetic measurements for some representatives of ErFe$_{1-x}$Al$_x$O$_3$ system were performed. The obtained results indicate an essential influence of nonmagnetic substitution on physical behaviour of examined compounds.

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1. Introduction

The rare-earth orthoferrites RFeO$_3$ (R — rare-earth element) crystallise in an orthorhombically distorted perovskite structure belonging to the space group $D^{18}_{2h}$ ($Pbnm$). The unit cell contains four chemical formulae and the rare-earth ions centre a polyhedron formed by eight Fe$^{3+}$ ions. These compounds exhibit a great and sometimes bewildering array of magnetic and other physical properties. A member of this family is typically, though not necessarily a weak ferromagnet up to $T_{N_1}$ (620–740 K). The magnetic moments of the rare-earth sublattice begin to be in order at temperature $T_{N_2}$ ($\leq 10$ K).

In the temperature range 80–130 K the spin reorientation process, during which the weak ferromagnetic moment of ferrite sublattice switches from the c-axis to the a-axis, is observed. From the point of view of symmetry this process consists of two successive second-order phase transitions. The beginning and end of the spin-flop process determine the transitions temperatures $T_{t_1}$, $T_{t_2}$ respectively. The strong exchange Fe–Fe and a much weaker R–Fe interaction are responsible for the magnetic properties of the discussed family of compounds. The weakness of the second one is a result of an annulment of the isotropic part of the exchange R–Fe interaction in the centre of the iron polyhedron occupied by R$^{3+}$ ion. The remaining part of the exchange interaction, an isotropic and antisymmetric one,

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causes the rare-earth ions to polarise quasiparamagnetically in the “exchange field” generated by the weak magnetic moment of ferrite sublattice. The rare-earth moments may have either the same or opposite polarization to the Fe\(^{3+}\) net moments.

In the second case a compensation point, i.e. the temperature \(T_{\text{com}}\) at which the weak magnetic moment of the iron sublattice and the net magnetic moment of R sublattice are annulled, can be observed. A review of works on these problems can be found in the article of White [1] and in the monograph of Belov et al. [2].

The isotropic exchange R–Fe interaction may be included in the system by substitution of one or some Fe\(^{3+}\) ions from R\(^{3+}\) neighbourhood by nonmagnetic ions like: Al\(^{3+}\), Ga\(^{3+}\), etc. (Fig. 1). For these configurations, the isotropic part of

![Fig. 1. Neighbourhood of R\(^{3+}\) ion in the substituted compound.](image)

R–Fe interaction is not annulled any more. It has been shown for DyFe\(_{1-x}\)Al\(_x\)O\(_3\) and for some representatives of TbFe\(_{1-x}\)Al\(_x\)O\(_3\) and HoFe\(_{1-x}\)Al\(_x\)O\(_3\) system [3, 4] that substitution plays a role of an additional anisotropy which may be controlled (for small \(x\)) by changing the amount of nonmagnetic ions in the system. This additional “configuration anisotropy” influences very strongly not only the magnetic but also the optical, mechanical and other physical properties of the substituted compounds. For instance, this anisotropy noticeably moves the Moriya point in DyFe\(_{1-x}\)Al\(_x\)O\(_3\) and modifies spin-flop transitions in TbFe\(_{1-x}\)Al\(_x\)O\(_3\) and HoFe\(_{1-x}\)Al\(_x\)O\(_3\) systems. It has been suggested that nonmagnetic substitutions can even change the sign of anisotropy constant in those systems [5].

Inspired by the works mentioned above we undertook the investigation of the phase diagram of ErFe\(_{1-x}\)Al\(_x\)O\(_3\). Simple ErFeO\(_3\) compound has been examined intensively by diverse methods [6–8] but no information about substituted ErFe\(_{1-x}\)Al\(_x\)O\(_3\) system has been found up to now. The aim of our research is to determine how the sort and the quantity of substitution modify anisotropy and, as a result, change physical behaviour of orthoferrites.
2. Experimental

The ultrafine powders of $\text{ErFe}_{1-x}\text{Al}_x\text{O}_3$ were prepared by co-precipitation of Er, Fe, Al oxalates and thermal decomposition at 850°C. The mixed oxide powders were pressed (370 MPa) into disc of 13 mm diameter and about 2 mm thickness and heat roasted at 1350-1360°C for 4 h in air atmosphere. This preparation procedure was chosen to assure proper homogeneity of material which is especially important when low values of $x$ are concerned.

For the first magnetic measurements the following compositions of $\text{ErFe}_{1-x}\text{Al}_x\text{O}_3$ system were selected: $x = 0, 0.03, 0.05$ and 0.10. Magnetization measurements were performed on a Faraday-type Cahn RG electrobalance equipped with a flow liquid helium cryostat. A typical dependence of magnetization on temperature is shown in Fig. 2. As it turned out, the experimental results depend on the value of the magnetic field and on the history of the sample. All measurements were performed for a relatively low magnetic field (450 Oe) and for both increasing and decreasing temperatures.

It must be emphasised that for non-single-crystal samples characteristic points: $T_{N_2}$, $T_{\text{com}}$, $T_{t_1}$, $T_{t_2}$ are detectable. These points are especially visible on the net curve obtained by subtraction of decreasing and increasing temperature magnetization curves (upper insertion in Fig. 2). What is really surprising is the similarity of this curve to the one achieved in investigation of a single crystal [1]. A very illustrative example of this is the distinct mark of the compensation point and its hysteresis.

![Fig. 2. Temperature dependence of the magnetization. The upper insertion shows the difference between the curves for the decreasing and the increasing temperatures.](image-url)
3. Conclusions

General conclusions of this work can be stated as follows:

a) All characteristic temperatures of the presented system can be determined by examining powder samples;

b) The magnetization process is more complicated than it seemed;

c) Concentration of $\text{Al}^{3+}$ ions at the examined range $x$ moves slightly the $T_{N_2}$ temperature;

d) Substitution of $\text{Fe}^{3+}$ ions by $\text{Al}^{3+}$ ones rises the compensation point;

e) The temperature interval of the spin reorientation process is narrowed by increasing concentration of $\text{Al}^{3+}$ in the system.

References