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ABSTRACT

The magnetic phase diagram for the Co^{2+} substituted $ErFeO_3$ in the concentration range up to 5 at% was obtained from magnetic and neutron diffraction measurements. From the low temperature magnetostriction measurements the temperature dependence of the threshold field along the a axis induced by the spin reorientation $G_{yz} \rightarrow G_z F_x$ was measured and an estimation was made for the anisotropy energy of the iron sublattice in the /bc/ plane, resulting in K_{bc}^{Fe} = 0.2 K. The calculations for the magnetic anisotropy originating from the Co^{2+} ions give K_{bc}^{Co} = 0.2 K, which is considerably less than the anisotropy constant in the /ac/ plane: K_{ac}^{Co} = -120 K.

АННОТАЦИЯ

Из магнитных и нейтрондифракционных измерений получена магнитная фазовая диаграмма Co^{2+}, замещенного $ErFeO_3$ в области концентрации до 5 ат%. Из измерений магнитострикции в области низких температур определена температурная зависимость порогового поля и оценена энергия анизотропии железной подрешетки в /bc/ плоскости, оказавшаяся равной K_{bc}^{Fe} = 0,2 К. Вычисления магнитной анизотропии, вносимой ионами Co^{2+}, дали ту же самую величину K_{bc}^{Co} = 0,2К, которая значительно меньше константы анизотропии в /ac/ плоскости: K_{ac}^{Co} = -120 К.

KIVONAT

Mágneses és neutrondiffrakciós módszerrel végzett mérések alapján megadjuk a Co^{2+} helyettesitésü $ErFeO_3$ /max. koncentráció 5 at%/ mágneses fázisábráját. Alacsony hőmérsékletü magnetostrikciós mérésekből meghatároztuk a küszöb tér hőmérsékletfüggését és megbecsültük a vas alrács anizotrópia terét a /bc/ sikban, amelyre K_{bc}^{Fe} = 0.2 K érték adódott. A Co^{2+} ionok mágneses anizotrópiájára K_{bc}^{Co} = 0.2 K értéket kaptuk, amely jóval kisebb, mint az /ac/ sikban az anizotrópia: K_{ac}^{Co} = -120 K

INTRODUCTION

Erbium orthoferrite is the only orthoferrite in which the decrease of temperature leads to two types of spin reorientation transition of the Fe^{3+} ions, namely: $G_xF_z \rightarrow G_zF_x/\Gamma_4 \rightarrow \Gamma_2/$ near 90 K and $G_zF_x \rightarrow G_{zy}F_x/\Gamma_2 \rightarrow \Gamma_{12}/$ near 4 K, whereby the latter transition is accompanied by an ordering of the spins of the erbium ions at mode $C_z/\Gamma_1/$.

It is interesting to reflect on the character and the temperature of the spin reorientation transition /SRT/ in $ErFeO_3$, substituting the Fe^{3+} ions by ions having a strong effect on the magnetic anisotropy of the orthoferrites, e.g. for Co^{2+} ions [1,2,3]. In spite of the great number of papers devoted to the study of cobalt substituted orthoferrites, the effect of Co^{2+} ions on SRT in $ErFeO_3$ has not been investigated intensively. In particular, there are no data on the low-temperature magnetic transition or on transitions induced by external magnetic fields, etc.

EXPERIMENTAL

Polycrystalline $ErFe_{1-2x}Co_xTi_xO_3$ /x=0, 0.005, 0.01, 0.05/ orthoferrites and single crystals in which the electronic neutrality of the molecules was maintained by substituting Ti^{4+} ions instead of Fe^{3+} or F^- ions instead of O^{2-} with nearly the same Co^{2+} ion content were investigated. The single crystals were grown by the flux method. The concentration of Co^{2+}, Ti^{4+} and F^- ions was determined by X-ray fluorescence analysis. The polycrystalline samples were obtained by the usual ceramic technique.

In the samples of single crystalline Co^{2+} substituted erbium orthoferrites, the temperature dependence of magnetization and magnetostriction were measured in the temperature range between 2 and 350 K. The spontaneous magnetization was determined by extrapolating the magnetization isotherms recorded with the help of differential coils and by measuring the torque curves with the help of a strain-gauge anisometer. The magnetostriction was measured by using a special strain-gauge in fields up to 60 kOe.

Neutron diffraction measurements were performed on the powder samples in the temperature range 80 - 700 K at the WWRS-M reactor in Budapest using a monochromated neutron beam of 1.14 Å wavelength.

RESULTS

Neutron scattering provides a sensitive method for investigating the antiferromagnetic order of the iron sublattice [4]. The spin reorientation can be observed by measuring the intensity of the magnetic reflections /011/ and /101/ - indexed in the P_{bnm} space group -, the intensity of which depends on the direction of the magnetic moments of the Fe^{3+} ions. *Fig. 1* shows the temperature dependence of the magnetic reflections /011/ and /101/ for the $ErFe_{1-2x}Co_xTi_xO_3$ system with different Co^{2+} concentration. In pure $ErFeO_3$ the reorientation takes place at T_r = 100 K within a temperature range of 12 K, whereas in the presence of Co^{2+} ions the spin reorientation is shifted towards higher temperatures and the range of reorientation is broadened. In the case of compounds with x = 0.005 and 0.01 the initial T_1 and final T_2 temperatures of the reorientation were found to be T_1 = 180 K, T_2 = 320 K and T_1 = 280 K, T_2 = 400 K, respectively. The magnetic phase diagram of the studied system as shown in *Fig. 2* describes the two different phases with the antiferromagnetic moment along the $\underline{a}$ axis /G_xF_z/ and along the $\underline{c}$ axis /G_zF_x/ of the orthorhombic crystal, respectively. For the composition with x = 0.05 the spin configuration G_zF_x is observed at all temperatures up to Néel temperature.

The results of the magnetic measurements carried out on single crystals are shown in *Fig. 3*. It is apparent that the substitution of the Fe^{3+} ions by Co^{2+} ions, similarly to the case of polycrystalline samples, strongly influence the magnetic anisotropy and increases the temperature of the spin reorientation; however, the temperature range determined by neutron diffraction for powder samples is somewhat wider than in the case of single crystals. The strong influence of the Co^{2+} ions on the magnetic anisotropy of the orthoferrites and on the SRT temperatures /see ref. [4]/ is due to the extremely high constant of anisotropy of the Co^{2+} ions: K_{ac}^{Co} = -120 K, which is considerably higher than the anisotropy constant of Fe^{3+} ions: K_{ac}^{Fe} = 0.21 K and has an opposite sign.

On decreasing the temperature below the SRT, the magnetic behaviour of cobalt substituted erbium orthoferrites is like that of the pure $ErFeO_3$ in many respects. The magnetic moment along the a axis of the crystal decreases first: it equals zero at the compensation point, after which it begins to increase and reaches a maximum at the ordering temperature of the erbium ions. A further decrease in temperature causes the magnetic moment to decrease again. *Fig. 4* shows the temperature dependence of the ferromagnetic moment along the a axis for the compositions with x = 0 and x = 0.01. For Co substituted erbium orthoferrite, the temperature of compensation agrees with that observable for pure $ErFeO_3$ /T_K = 45 K/, and the magnetic moment reaches its maximum σ_a = 9.5 emu/g at 3.4 K then it decreases with decreasing temperature down to 7.8 emu/g at T = 2.1 K. This decrease of the magnetic moment is apparently connected with the reorientation of the iron spins from the G_zF_x to the $G_{zy}F_x$ mode just as in the case of the pure erbium orthoferrite. Note that the SRT in the Fe sublattice takes place simultaneously with the ordering of the spins of the Er^{3+} ions /$T_{R2} = T_{N2}$/, because for $T<T_{R2}$ the spin configuration of the Fe^{3+} ions is the G_{zy} mode, of the Er^{3+} ions it is the C_z mode, and they are compatible, i.e. the appearance of one mode induces the formation of the other. Magnetostriction measurements support the presence of reorientation transitions in the investigated single crystals. *Fig. 5* shows

the field dependence of the magnetostriction isotherms recorded for $ErFeO_3$ below T_{R2}. It is seen that, the application of an external magnetic field parallel to the a axis of the crystal leads to magnetostriction deformations, whose measure and sign correspond to the spin reorientation $G_{zy} \rightarrow G_z F_x$ [5,6]. The break points observed on the magnetostriction curves /H_{thresh}/ correspond to the end of the SRT. The temperature dependence of the threshold field for $ErFeO_3$ is observable in *Fig. 6*.

DISCUSSION

As was shown in refs. [7] and [8] the value of the threshold field and its temperature dependence considerably depend on the ratio of the interactions between Er-Er ions and Er-Fe ions an they show the best agreement with the experimentally observed $H/T/_{threshold}$ curve for $\Delta_{1Er-Er} = 3.2$ K and $\Delta_{1Er-Fe} = 1.3$ K where Δ_1 represents the splitting of the basic doublet of the Er^{3+} ions in the C_z phase. The estimation of the Er-Er and Er-Fe interactions eneables us to determine such important parameters as the anisotropy energy of the Fe sublattice in the (bc) plane of the crystal resulting, $K_{bc}^{Fe} = 0.2$ K. We obtained similar phase diagrams indicating the transition $G_{zy} \rightarrow G_z$ for the Co^{2+} substituted erbium orthoferrites as well. From the value of T_{N2} observed in the substituted $ErFeO_3$ - supposing that small amounts of impurities /Co^{2+}, Ti^{4+}/ do not change significantly the parameters of the interactions between Er-Er and Er-Fe ions -, one can estimate the anisotropy caused by the impurities and separate the magnetic anisotropy of the Co^{2+} ions themselves. It is remarkable, however, that the substitution of non-magnetic ions /in our case the Ti ions/ into the orthoferrite lattice, which can be considered as magnetic vacancies, may lead to essential changes in the magnetic anisotropy [9,10]. The presence of a magnetic vacancy leads to decompensation of the isotropic component of the Er-Fe interaction and to the appearance of a strong exchange field H^{vac}, acting on the Er^{3+} ions surrounding

the vacancy splace. It is apparent that H^{vac} has a direction parallel to the vector of the antiferromagnetism $\underline{G}$ and thus the energetically most advantageous orientation will be parallel to the direction of the maximum susceptibility of Er^{3+}, i.e. to the $\underline{c}$ axis of the crystal /configuration Γ_2/. The additional anisotropy stabilizing Γ_2 which appears in the presence of vacancies of x concentration, has the form:

$$E_{an} \approx 4.x \frac{\chi_c - \chi_b}{2} (H^{vac})^2 . \qquad (1)$$

By using the values of ref. [11] for the susceptibility data $\chi_c = 6.10^{-3}$, $\chi_b = 10^{-3}$ and taking into account that $H^{vac} \approx$ $\approx 10^4 - 10^5$ Oe [9], we obtain for the anisotropy caused by the titan ions:

$$E_{an}^{vac} \approx 2.10^6 \text{ erg cm}^{-3} = 0.5 \text{ K} . \qquad (2)$$

To determine the total anisotropy energy caused by the impurities Co^{2+} and Ti^{4+} ions in the (bc) plane, we can write using the analogy of $ErFeO_3$ after ref.[7], that

$$(1-8x)[2K_{bc}^{Fe} - f(\frac{\Delta_1^2}{1-\lambda g^2 f} - \Delta_2^2)] + 2.K_{eff}^{imp} = 0 \qquad (3)$$

where K_{bc}^{Fe} denotes the anisotropy of the Fe^{3+} sublattice in the (bc) plane; $2\Delta_1$ and $2\Delta_2$ are the splitting of the basic doublet of the Er^{3+} ion caused by the Er-Fe interaction in the configurations Γ_1 and Γ_2, respectively; λ is the constant of the Er-Er interactions, $2\lambda g^2$ means the splitting of the basic doublet by the Er-Er interaction at T=0; the quantity f is connected with the temperature of reorientation (T = 3.4 K). From eq.(3) we get for the effective anisotropy constant due to the impurities the value of $K_{eff}^{imp} = 0.7$ K. The magnetic anisotropy originating from the Co^{2+} ions /single ion + exchange $Co^{2+} - Er^{3+}$/ can be obtained by subtracting $K_{eff}^{vac} = 0.5$ K from $K_{eff}^{imp} = 0.7$ K resulting $K_{bc}^{Co} = 0.2$ K. This value is considerably less than the anisotropy constant of the Co^{2+} ions in the (ac) plane, being $K_{ac}^{Co} = -120$ K.

The above considerations are valid for concentrations less than 1 %. For high concentrations /above 10 %/ the Er^{3+} ions will be placed in a random field of the vacancies H^{vac} and the influence of H^{vac} will be distributed almost throughout the whole crystal which leads to a completely non-ordered state in the rare earth sublattice. The non-ordered Er^{3+} ions do not induce a C_z phase and the strong anisotropy of the magnetic vacancies can maintain the Γ_2 configuration of the crystal down to the lowest temperatures.

FIGURE CAPTIONS

Fig. 1. *Temperature dependence of the (011) and (101) magnetic reflections for the* $ErFe_{1-2x}Co_xTi_xO_3$ *powder samples with x=0, 0.005 and 0.01*

Fig. 2. *Magnetic phase diagram of the* $ErFe_{1-2x}Co_xTi_xO_3$ *system in the temperature range 80 - 650 K*

Fig. 3. *Temperature dependence of the weak ferromagnetic moment along the c direction (•) and along the a direction (o) for* Co^{2+} *substituted* $ErFeO_3$ *single crystals in the temperature range 80 - 360 K*

Fig. 4. *Temperature dependence of the magnetic moment along the a direction for* $ErFeO_3$ *(•) and* $ErFe_{0.99}Co_{0.01}O_3$ *(o) crystals in the low temperature range*

Fig. 5. *Magnetostriction isotherms for* $ErFeO_3$ *in magnetic field parallel to a axis*

Fig. 6. *Temperature dependence of the threshold field along the a axis in* $ErFeO_3$ *induced by the SRT* $G_{yz} \rightarrow G_zF_x$

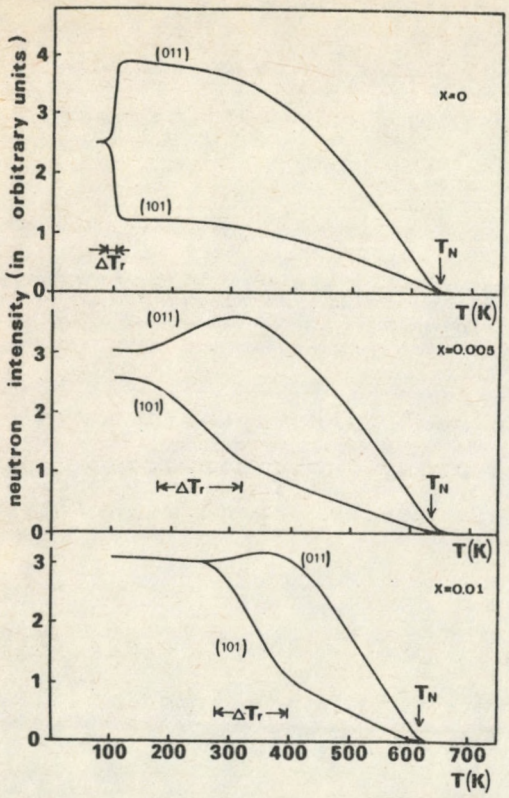

Fig. 1.

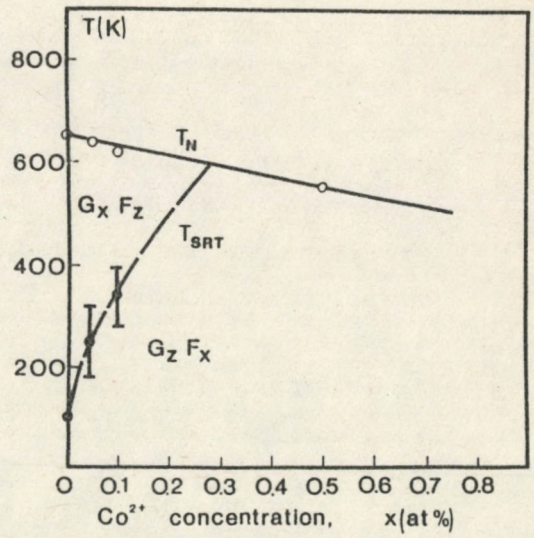

Fig. 2.

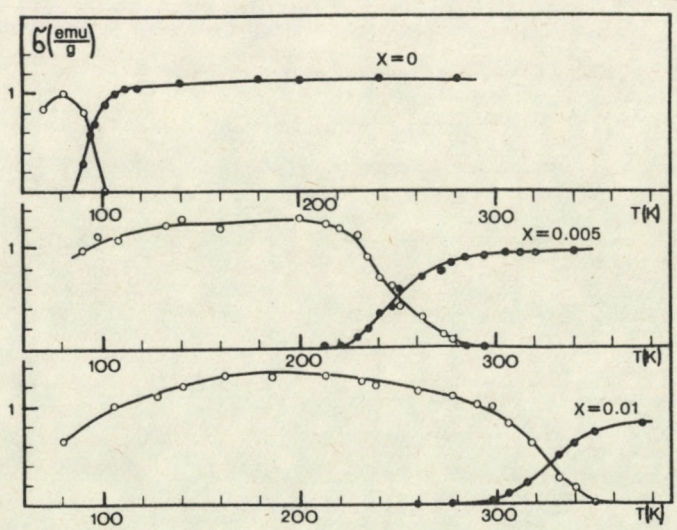

Fig. 3.

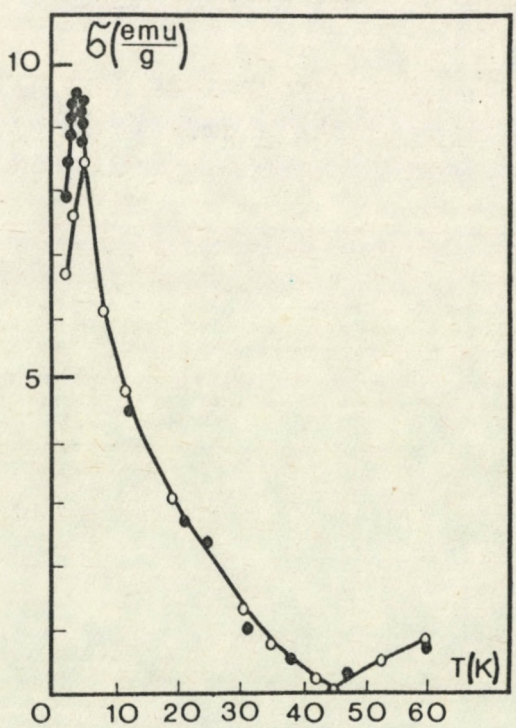

Fig. 4.

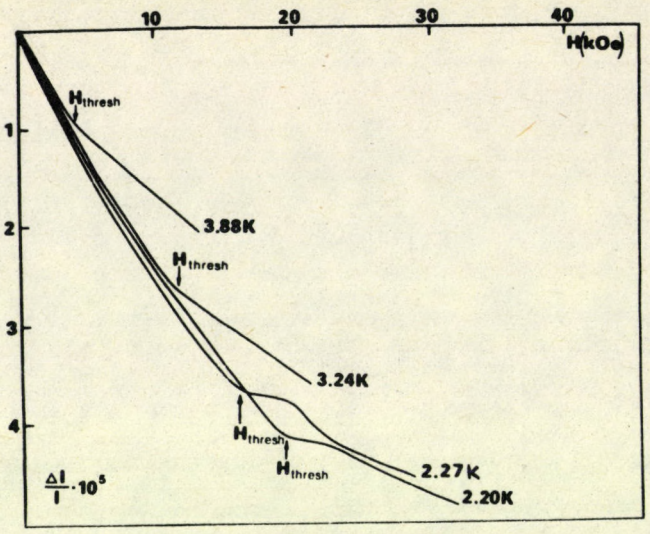
10
20
30
40
H(kOe)
H thresh
3.88K
H thresh
3.24K
H thresh
H thresh
2.27K
2.20K
1
2
3
4
Δl/l · 10⁵

Fig. 5.

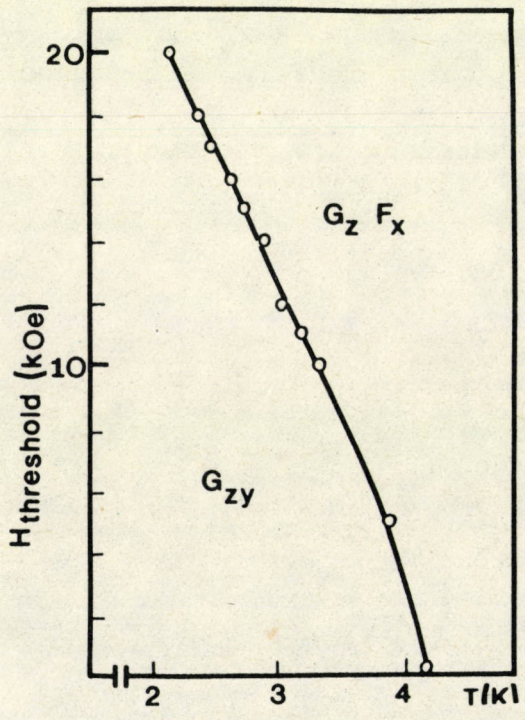
20
10
H threshold (kOe)
G_z F_x
G_zy
2
3
4
T(K)

Fig. 6.

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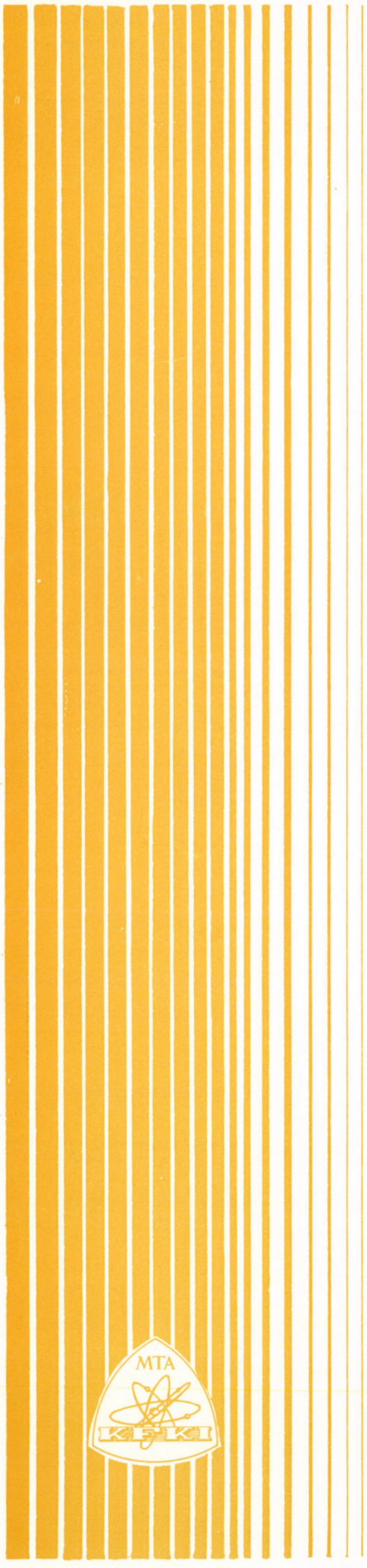

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