# Diversity of orientational transitions in the $Dy_xEr_{1-x}CrO_3$ system

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Spontaneous orientational transitions between the main magnetic configurations $\Gamma_2(G_zF_x) \to \Gamma_4(G_xF_z) \to \Gamma_1(Gy)$ were discovered during cooling of orthochromites of the system $Dy_xEr_{1-x}CrO_3$ ($x = 0.2$ and $0.3$). A study was made of various orientational transitions in a magnetic field **H** applied along the **a** and **c** axes. The corresponding $H$-$T$ phase diagrams were constructed. The $H_x$-$T$ phase diagram had a bicritical point of convergence of two lines representing second-order phase transitions $\Gamma_{12} \rightleftarrows \Gamma_2$ and $\Gamma_{24} \leftrightarrows \Gamma_2$, and a line representing a first-order phase transition between canted phases $\Gamma_{24} \rightleftarrows \Gamma_{12}$. An allowance for the nature of the anisotropy of the exchange splitting of the ground doublet of the $Dy^{3+}$ and $Er^{3+}$ ions was made in an analysis of the mechanisms of the observed phase transitions, and the calculated $H_x$-$T$ and $H_z$-$T$ phase diagrams were in agreement with the experiments.

## INTRODUCTION

Magnetic properties of dysprosium and erbium orthochromites are very different. At all temperatures below $T_N = 142$ K dysprosium orthochromite has a stable magnetic structure $\Gamma_2(G_zF_x)$ (Refs. 1 and 2). In the case of erbium orthochromite below $T_N = 133$ K there is a magnetic structure $\Gamma_4(G_xF_z)$, but cooling to $T_M = 9.3$ K results in a spin-reorientation transition to an antiferromagnetic state $\Gamma_1(G_y)$, known as the Morin transition.[3,4] Such a difference in the behavior of these orthochromites is due to the anisotropy of the R-Cr exchange interaction, particularly the anisotropy of splitting of the ground-state doublet of the $Er^{3+}$ and $Dy^{3+}$ ions because of the R-Cr exchange. This stabilizes different magnetic structures in these compounds. It would be of interest to vary the concentrations of the $Dy^{3+}$ and $Er^{3+}$ ions in orthochromites and obtain a composition in which the competition between the Dy-Cr and Er-Cr anisotropic exchange processes would induce different types of spontaneous and field-induced spin-reorientation transitions providing an opportunity to check and understand better the nature of the mechanisms responsible for the magnetic anisotropy of orthochromites.

## EXPERIMENTAL RESULTS

We investigated $Dy_\varkappa Er_{1-\varkappa}CrO_3$ ($\varkappa = 0.2$, $0.3$) single crystals grown from a molten solution by isothermal evaporation and we measured the magnetization (using a vibrating magnetometer) and the magnetostriction (using strain gauges) at temperatures 1.5–150 K in the field of a superconducting solenoid ranging up to 60 kOe. Measurements of the magnetization curves along different crystallographic axes established that in the case of the investigated crystals there were two types of spin-reorientational transitions: $\Gamma_2 \rightleftarrows \Gamma_4$ and $\Gamma_4 \rightleftarrows \Gamma_1$.

Figure 1 shows the temperature dependence of the spontaneous magnetization $m$ for the composition with $\varkappa = 0.3$ found by extrapolation of the magnetization isotherms to zero field. We can see that below $T_N = 127$ K the weak ferromagnetic moment was oriented along the **a** axis of an orthorhombic crystal with the $\Gamma_2(G_zF_x)$ magnetic structure. Cooling resulted in reorientation at $T_R = 14$ K from the **a** to the **c** axis (orientational transition $\Gamma_2 \rightleftarrows \Gamma_4$) and further cooling to $T_M = 5.9$ K destroyed the weak ferromagnetism so that the crystal became antiferromagnetic (Morin-type transition $\Gamma_4 \rightleftarrows \Gamma_1$); the latter orientational transition $\Gamma_4 \rightleftarrows \Gamma_1$ was abrupt representing a first-order phase transition. Similar transitions at $T_R = 17$ K and $T_M = 7.8$ K were observed also for the composition with $\varkappa = 0.2$. Therefore, cooling of the $Dy_\varkappa Er_{1-\varkappa}CrO_3$ system ($\varkappa = 0.2, 0.3$) revealed all three types of the magnetic structure, $\Gamma_1$, $\Gamma_2$, and $\Gamma_4$, compatible with the crystal symmetry.

The application of an external magnetic field $\mathbf{H}\|\mathbf{c}$ induced at temperatures $T < T_M$ an orientational transition $\Gamma_1 \rightleftarrows \Gamma_4$, as demonstrated clearly by the magnetization curves and those representing the magnetostriction $\lambda$, which were typically of the kind shown in Fig. 2. Clearly, in low fields the magnetization (curve 1) and the magnetostriction were practically equal to zero and only after passing through a threshold field $H^{th} \approx 0.7$ kOe did we find that the $m(H)$ and $\lambda(H)$ curves exhibited inflections followed by a rapid rise of the magnetization and magnetostriction, which was completed in fields of the order of several kilo-oersted. An allowance for a demagnetizing field had the effect that the $\Gamma_1 \rightleftarrows \Gamma_4$ transition occurred abruptly in a field corresponding to a lower inflection of the magnetization and magnetostriction curves.

The extended nature of the transition, demonstrated in Figs. 2a and 2b, was clearly associated with the presence of an intermediate state which appeared as a result of a first-order phase transition. The width of the transition on the field scale was less for a sample used to investigate the magnetization. This sample was a plate of $3.6 \times 2.7 \times 0.8$ mm dimensions with the long side parallel to the field (demagnetization factor $N_z \approx 2$). The magnetostriction was investigated employing a more complex sample ($N_z \approx 4.6$); the range of existence of the intermediate state was wider. We determined the temperature dependences of the fields corresponding to the onset and completion of a reorientational transition ($H_z$-$T$ phase diagram) for a sample with $N_z = 4.6$ (Fig. 3) and identified the region of the intermediate state. Clearly, the field corresponding to the onset of the phase transition vanished at the point $T_M$, whereas the field corresponding to the completion of the transition remained finite and similar in value to the demagnetizing field. We also in-

  

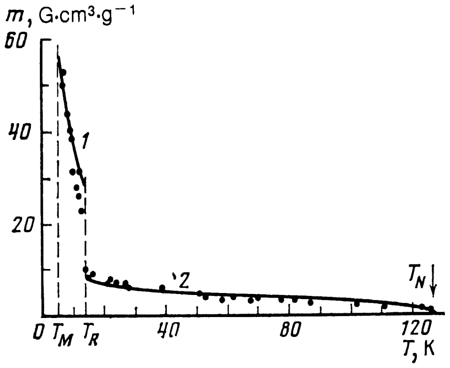


FIG. 1. Temperature dependences of the spontaneous magnetization along the **a** and **c** axes obtained for a $Dy_{0.3}Er_{0.7}CrO_3$ single crystal: 1) $m_z$; 2) $m_x$. The continuous curve calculated in the one-doublet approximation and the points are the experimental values.

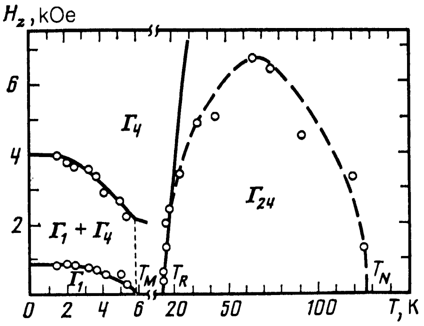


FIG. 3. Phase ($H_z$-$T$) diagram for the composition with $\varkappa = 0.3$. The continuous curves are calculated; the circles and the dashed line are the experimental results; the dotted line represents the position of $T_M$.

cluded in Fig. 3 (on the right) the $H_z$-$T$ phase diagram for a spin-reorientational transition $\Gamma_{24} \rightleftarrows \Gamma_4$ induced by a field **H**||**c** at temperatures $T > T_R = 14$ K. The threshold field for this transition was deduced from an inflection of the magnetization curves corresponding to completion of the process of spin reorientation (curve 3 in Fig. 2a). A similar phase diagram was also obtained for the sample with $\varkappa = 0.2$.

The greatest diversity of the orientational transitions was exhibited by $Dy_\varkappa Er_{1-\varkappa}CrO_3$ in fields **H**||**a**. The field dependence of the magnetostriction was then more complex (Fig. 4). At temperatures $T < T_M = 5.9$ K the composition with $\varkappa = 0.3$ exhibited in fields **H**||**a** a positive magnetostriction corresponding to smooth rotation of the spins in the *bc* plane as a result of an orientational transition $\Gamma_{12} \rightleftarrows \Gamma_2$, completed when the field reached $H^{\text{th}} \approx 20$–30 kOe. The magnetostriction isotherms were most complex in the temperature range $T_M = 5.9\text{ K} < T < T_Q = 6.4$ K ($T_Q$ is the temperature corresponding to the bicritical point) where in the range of low fields of the order of several kilo-oersted there was an abrupt change of the magnetostriction to the negative range followed by an increase with the field up to $H^{\text{th}} \approx 20$ kOe, when the spin reorientation was completed. We shall show below that the negative jump of the magnetostriction was due to rotation of the spins in a field **H**||**a** from the *ac* plane to the *bc* plane ($\Gamma_{12} \rightleftarrows \Gamma_{24}$), and the subsequent rise was due to further reorientation of the spins toward the **c** axis creating the $\Gamma_2(G_z F_x)$ magnetic structure. At temperatures above 6.4 K the magnetostriction was negative and corresponded to the $\Gamma_{24} \rightleftarrows \Gamma_2$ orientational transition. The $H_x$-$T$ phase diagram is shown in Fig. 5. The magnetostriction curves and the phase diagram for the composition with $\varkappa = 0.2$ obtained in fields **H**||**a** were qualitatively the same as those shown in Figs. 4 and 5 for the composition with $\varkappa = 0.3$.

## THEORY AND DISCUSSION OF RESULTS

In describing the phase transitions observed in the $Dy_\varkappa Er_{1-\varkappa}CrO_3$ system at low temperatures ($T < 50$ K) it is sufficient to consider only the ground-state doublets of the $Er^{3+}$ and $Dy^{3+}$ ions separated from excited states by intervals $\approx 50$ K for $ErCrO_3$ (Ref. 5) and $\approx 75$ K according to the data for $Dy^{3+}$ in $DyFeO_3$ (Ref. 6). We shall represent the energy levels of the ground-state doublet in the form[7,8]

$$E_{Ri}^{(1,2)} = \Delta E_{Ri}^{VV}(\mathbf{H}, \mathbf{G}) \pm \Delta_R^i(\mathbf{H}, \mathbf{G}), \tag{1}$$

where $i = \pm$ distinguishes two inequivalent positions of the rare-earth ions and $\Delta E_{Ri}^{VV}$ is the shift (of the Van Vleck type) of the center of gravity of the ground-state doublet due to mixing of excited states as a result of the R-Cr exchange

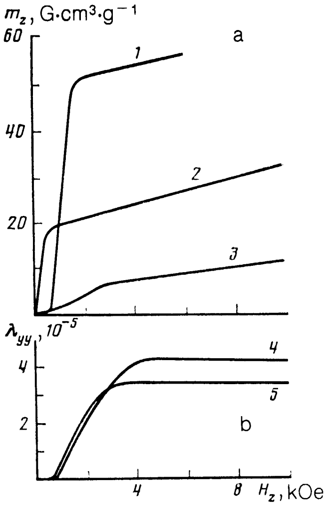


FIG. 2. Isotherms of the magnetization (a) and the magnetostriction (b) in **H**||**c**: 1), 5) $T = 4.2$ K; 2) 10.6 K; 3) 25.6 K; 4) $T = 1.5$ K.

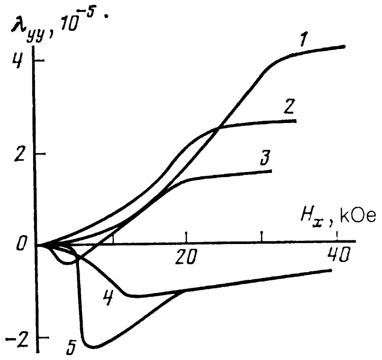


FIG. 4. Isotherm of the magnetostriction of $Dy_{0.3}Er_{0.7}CrO_3$ in **H**||**a**: 1) $T = 1.5$ K; 2) 5.4 K; 3) 5.9 K; 4) 7.1 K; 5) 6.1 K.

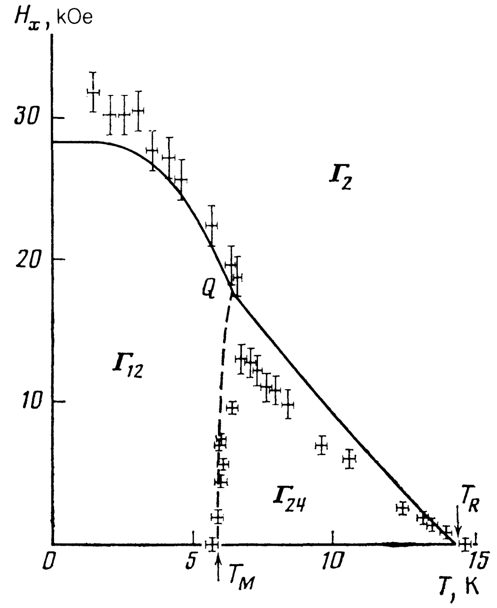


FIG. 5. Phase ($H_x$-$T$) diagram of $Dy_{0.3}Er_{0.7}CrO_3$. The points are the experimental values, whereas the continuous and dashed curves are calculated (the continuous curves correspond to a second-order phase transition and the dashed line corresponds to a first-order transition); $Q$ is the bicritical point.

interaction and the interaction with an external field. Without specifying the explicit form of $\Delta E^{VV}_{Ri}$, we shall allow for it by renormalization of the thermodynamic potential of Cr subsystem. The quantities $\Delta_R^i$ governing the half-splitting of the ground-state doublets of the $Dy^{3+}$ and $Er^{3+}$ ions are

$$\Delta_{Dy}^{\pm}=\mu_x^0 H_x+\Delta_z^0 G_z \pm \mu_y^0 H_y, \qquad (2)$$

$$(\Delta_{Er}^{\pm})^2=(\mu_{xx}H_x+\Delta_z' G_z\pm\mu_{xy}H_y)^2+(\mu_{yy}H_y\pm\Delta_z'' G_z\pm\mu_{yx}H_x)^2+(\mu_{zz}H_z+\Delta_x G_x\pm\Delta_y G_y)^2, \qquad (3)$$

where $\Delta_x$, $\Delta_y$, $\Delta_z = [(\Delta_z')^2+(\Delta_z'')^2]^{1/2}$, and $\Delta_z^0$ represent the half-splitting of the doublets due to the R-Cr interaction in the $\Gamma_4(G_x)$, $\Gamma_1(G_y)$, and $\Gamma_2(G_z)$ phases; the effective magnetic moments are $\mu_{\alpha\beta}=\mu_B g_{\alpha\beta}/2$, where $g_{\alpha\beta}$ is the $g$ tensor of the doublet. The difference between $\Delta_{Dy}^{\pm}$ and $\Delta_{Er}^{\pm}$ is due to the fact that the $Dy^{3+}$ ion is of the Ising type,[2] i.e., it becomes magnetized only parallel or antiparallel to a specific axis lying in the *ab* plane and oriented at an angle $\alpha_{\pm}=\pm\tan^{-1}(\mu_y^0/\mu_x^0)$ relative to the **a** axis. For simplicity, Eq. (3) is derived ignoring the R-R interaction, which is not of fundamental importance in the effects under consideration.

According to Ref. 2, in the case of $DyCrO_3$, we have

$$\Delta_z^0=0.84\ \text{K},\ \mu_x^0=4.13\mu_B, \qquad (4a)$$

whereas the results of Ref. 3 give for $ErCrO_3$

$$\Delta_x=4.45\ \text{K},\ \Delta_y=4.8\ \text{K},\ \Delta_z=3.2\ \text{K},\ \mu_{zz}=5.65\mu_B,$$
$$\mu_x=(\mu_{xx}^2+\mu_{yx}^2)^{1/2}=2.95\mu_B,\ \bar{\mu}_x=(\mu_{xx}\Delta_z'+\mu_{yx}\Delta_z'')/\Delta_z=1.0\mu_B. \qquad (4b)$$

The thermodynamic potential of the system per one formula unit can be represented in the form[7,8]

$$\Phi=\tilde{\Phi}_{Cr}-\frac{T}{2}\sum_{i=\pm}\left[\varkappa\ln\left(2\,\mathrm{ch}\frac{\Delta_{Dy}^i}{T}\right)+(1-\varkappa)\ln\left(2\,\mathrm{ch}\frac{\Delta_{Er}^i}{T}\right)\right], \qquad (5)$$

where

$$\tilde{\Phi}_{Cr}=\Phi_{Cr}+\frac{1}{2}\sum_i[\varkappa\Delta E^{\mathrm{B\Phi}}_{Dy\,i}+(1-\varkappa)\Delta E^{\mathrm{B\Phi}}_{Er\,i}]=\frac{1}{2}K_{ac}^0G_z^2+\frac{1}{2}K_{ab}^0G_y^2-m_x^0H_xG_z-m_z^0H_zG_x-\frac{1}{2}\chi_\perp[H^2-(\mathbf{HG})^2] \qquad (6)$$

is the thermodynamic potential of the Cr subsystem renormalized by the Van Vleck corrections: $K^0_{ac,ab}=K^{Cr}_{ac,ab}+\varkappa K^{Dy}_{ac,ab}+(1-\varkappa)K^{Er}_{ac,ab}$, where $m^0_{x,z}$ are the weak ferromagnetic moments, and $\chi_\perp$ is the transverse susceptibility of the Cr subsystem. The majority of the observed properties of the $Dy_\varkappa Er_{1-\varkappa}CrO_3$ system can be described simply by adopting the high-temperature approximation ($\Delta_R \ll T$) for $\Phi$, where

$$\Phi=\Phi_0-{}^1/_2\chi_\perp[H^2-(\mathbf{HG})^2]-m_xH_xG_z-m_zH_zG_x+{}^1/_2K_{ac}G_z^2+{}^1/_2K_{ab}G_y^2+{}^1/_2K_{ab}'G_x^2G_y^2+\Delta\Phi(\mathbf{G}), \qquad (7)$$

where the term $\Phi_0$ is independent of **G**,

$$m_z=m_z^0+(1-\varkappa)\mu_{zz}\Delta_x/T,$$
$$m_x=m_x^0+\varkappa\mu_x^0\Delta_z^0/T+(1-\varkappa)\bar{\mu}_x\Delta_z/T,$$
$$K_{ac}=K_{ac}^0-\varkappa(\Delta_z^0)^2/T+(1-\varkappa)(\Delta_x^2-\Delta_z^2)/T,$$
$$K_{ab}=K_{ab}^0+(1-\varkappa)(\Delta_x^2-\Delta_y^2)/T,\quad K_{ab}'=2\Delta_x^2\Delta_y^2/3T^3,$$
$$\Delta\Phi(\mathbf{G})=\{\varkappa(\Delta_z^0)^4G_z^4+(1-\varkappa)[(\Delta_x^2-\Delta_y^2)G_z^2-(\Delta_y^2-\Delta_x^2)G_y^2]^2\}/12T^3. \qquad (8)$$

In the subsequent analysis, allowing for the smallness of $\Delta_z^0$ in the case of $Dy^{3+}$ ($\approx 0.84$ K) and for the relatively weak anisotropy of the exchange splitting in the case of $Er^{3+}$ ($|\Delta_{y,z}{}^2-\Delta_x^2|\ll\Delta_x^2$) [see Eq. (4)], we shall ignore the term $\Delta\Phi(\mathbf{G})$ in Eq. (7), but retain the term $K_{ab}'G_x^2G_y^2$ which is sufficiently large and determines the nature of the process of spin reorientation in the *ab* plane.

We shall first analyze the spontaneous orientational transitions ($H=0$). The $\Gamma_2(G_z)\rightleftarrows\Gamma_4(G_x)$ reorientation at $T_R=14$ K occurs when the sign of $K_{ac}$ is reversed see Eq. (7)] as a result of competition between the exchange splitting anisotropy of the doublets and the anisotropy energy $K_{ac}^0$ stabilizing the $\Gamma_2$ phase. It follows from the condition $K_{ac}(T_R)=0$ and from Eq. (4) that $K_{ac}^0=-0.432$ K ($\varkappa=0.3$). Since $K_{ac}^{Cr}>0$ (Ref. 9), the negative value of $K_{ac}^0$ is clearly due to the large Van Vleck contribution, as in the case of $DyCrO_3$ (Ref. 2).

The nature of the $\Gamma_2\rightleftarrows\Gamma_4$ transition is governed by the sign of the coefficient in front of $G_z^4$ which occurs in the expression for $\Delta\Phi$ in the system (8); this term is positive but very small. Hence it follows that the $\Gamma_2\rightleftarrows\Gamma_4$ reorientation occurs smoothly via an intermediate canted phase $\Gamma_{24}$, but this happens in a very narrow temperature interval ($\Delta T\approx 0.2$ K), which is manifested experimentally (Fig. 1) as an abrupt change in the spontaneous weak ferromagnetic moments $m_x$ and $m_z$ at $T\approx T_R$.

The $\Gamma_4(G_x)\rightleftarrows\Gamma_1(G_y)$ transition in the *ab* plane, which occurs because of the anisotropy of the exchange splitting of the $Er^{3+}$ doublet in the phases $\Gamma_1$ and $\Gamma_4$, is a clear first-order phase transition and it occurs when $K_{ab}(T_M)=0$. The formal reason for this nature of the reorientation process is the relatively large positive value of the fourth-order anisotropy constant $K'_{ab}$, which suppresses the canted phase $\Gamma_{14}$. The physical reason is the special nature of the behavior of the splitting of the $Er^{3+}$ doublet. Since $\Delta_y-\Delta_x \ll \Delta_{x,y}$, it follows from Eq. (3) that in the case of smooth reorientation the splitting of the doublets of the $Er^{3+}$ ions occupying one of the inequivalent positions with

$$\varphi=\mathrm{arctg}(G_y/G_x)=\mathrm{arctg}(\Delta_x/\Delta_y)\approx 45^\circ$$

passes through zero, which is not favored by energy considerations so that an abrupt ФП $\Gamma_4 \rightleftarrows \Gamma_1$ phase transition takes place.

We shall first consider the field-induced orientational transitions.

**H**$\|$**a**. Both $\Gamma_{24}(G_xG_z)\rightleftarrows\Gamma_2(G_z)$ and $\Gamma_{12}(G_yG_z)\rightleftarrows\Gamma_2(G_z)$ transitions occur smoothly in the relevant $ac$ $(T>T_Q)$ and $bc$ $(T<T_Q)$ planes, and their fields are given by the expressions

$$\Gamma_{24}\rightleftarrows\Gamma_2:\ \left.\frac{\partial^2\Phi}{\partial\theta^2}\right|_{\theta=0,\,\varphi=0}=0,\quad \chi_\perp H_x^2+m_xH_x=K_{ac}, \tag{9}$$

$$\Gamma_{12}\rightleftarrows\Gamma_2:\ \left.\frac{\partial^2\Phi}{\partial\theta^2}\right|_{\theta=0,\,\varphi=\pi/2}=0,\quad m_xH_x=K_{ac}-K_{ab}, \tag{10}$$

where $\theta$ and $\varphi$ are the angles governing the orientation of the vector $\mathbf{G}=(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$.

In the direct vicinity of the Morin point within the interval $T_M<T<T_Q$ there is a characteristic first-order transition between the phases $\Gamma_{12}$ and $\Gamma_{24}$ in the course of which the antiferromagnetic vector is reoriented abruptly from the $bc$ to the $ac$ plane. If we find the orientation of the vector $\mathbf{G}$ for these phases

$$\Gamma_{24}:\ \varphi=0,\ \cos\theta=m_xH_x/(K_{ac}-\chi_\perp H_x^2),$$

$$\Gamma_{12}:\ \varphi=\pi/2,\ \cos\theta=m_xH_x/(K_{ac}-K_{ab}), \tag{11}$$

and equate the corresponding thermodynamic potentials obtained for the field of the $\Gamma_{12}\rightleftarrows\Gamma_{24}$ transition,[10,11] we obtain

$$\chi_\perp H_x^2=K_{ab}. \tag{12}$$

This a spin-flop transition (but not in a plane as is usually observed, but in space), i.e., it is due to the difference between the susceptibility of the Cr system along the **a** axis in the $\Gamma_{12}$ and $\Gamma_{24}$ phases and not due to the interaction of the weakly ferromagnetic moment $m_x$ with the external field.

Figure 5 shows the experimental and theoretical $H_x$-$T$ phase diagrams of $Dy_\varkappa Er_{1-\varkappa}CrO_3$ $(\varkappa=0.3)$. Calculations of the theoretical temperature dependences of the threshold fields were carried out using Eqs. (9), (10), and (12), but allowing for the demagnetizing field characterized by $N_x=5$. At low temperatures and in high fields, when the approximation of Eq. (7) is no longer valid, we obtain equations of the (10) type for the field of the $\Gamma_{12}\rightleftarrows\Gamma_2$ transition when $m_x$ and $K_{ac}-K_{ab}$ depend on the field:

$$m_x=m_x^0+\varkappa\mu_x^0\Delta_z^0/T_0(H_x)+(1-\varkappa)\bar{\mu}_x\Delta_z/T_1(H_x),$$

$$K_{ac}-K_{ab}=K_{ac}^0-K_{ab}^0-\varkappa(\Delta_z^0)^2/T_0(H_x)$$

$$+(1-\varkappa)(\Delta_y^2-\Delta_z^2)/T_1(H_x), \tag{13}$$

where

$$T_0=\Delta_{Dy}/\mathrm{th}(\Delta_{Dy}/T),\quad T_1=\Delta_{Er}/\mathrm{th}(\Delta_{Er}/T),$$

$$\Delta_{Dy}=\mu_x^0H_x+\Delta_z^0,\quad \Delta_{Er}^2=\mu_x^2H_x^2+2\bar{\mu}_xH_x\Delta_z+\Delta_z^2.$$

At high temperatures $T$ $(T\gg\Delta_R)$ the system (13) reduces to the system (10).

It follows from the condition for the best match between the theoretical and experimental $H_x$-$T$ phase diagrams and from a comparison of the calculated and experimental temperature dependences of the weakly ferromagnetic moments (Fig. 1) that the main parameters of the magnetic interactions are as follows:[1]

$$\Delta_x=4.5\ \mathrm{K},\quad \Delta_y=5.5\ \mathrm{K},\quad \Delta_z=2.5\ \mathrm{K},$$

$$K_{ab}^0=0.93\ \mathrm{K},\quad K_{ac}^0=-0.67\ \mathrm{K},\quad m_x^0=0.18\mu_B,\quad m_z^0=0.13\mu_B. \tag{14}$$

The values of $K^0_{ab}$ and $K^0_{ac}$ were determined in terms of $\Delta_i$ $(i=x, y, z)$ using the conditions $K_{ab}(T_M)=0$ and $K_{ac}(T_R)=0$. The quantities $\mu_{x,zz}$ and $\bar{\mu}_x$, and the center of gravity of the splitting of the doublet $\Delta_{Er}=\frac{1}{3}\Sigma_i\Delta_i=4.15$ K were taken from the published data[3] [see Eq. (4b)], the susceptibility was taken to be $\chi_\perp=2.5\times10^{-5}$ cm$^3$/g, and the differences $\Delta_x-\Delta_y$ and $\Delta_x-\Delta_z$ were varied. It is clear from Figs. 1 and 5 that on the whole a satisfactory description could be provided of the $H_x$-$T$ diagram and of the temperature dependences $m_{m,z}(T)$. A characteristic feature of the $H_x$-$T$ diagram was the bicritical point $Q$, where two second-order phase transition lines and a first-order phase transition line converged. Such a point had been observed earlier for $DyFe_{1-x}Al_xO_3$ (Ref. 12) and discussed in Refs. 11 and 13 for $DyFeO_3$; judging by the data of Ref. 4, it should appear also in the $H_x$-$T$ phase diagram of pure $ErCrO_3$.

**H**$\|$**c**. If $T>T_R$, then in this geometry a smooth reorientation $\Gamma_{24}\rightleftarrows\Gamma_4$ takes place in a field found from the condition

$$\left.\frac{\partial^2\Phi}{\partial\theta^2}\right|_{\varphi=0,\,\theta=\pi/2}=0,\quad \chi_\perp H_z^2+m_zH_z=-K_{ac}. \tag{15}$$

At temperatures $T<T_M$ in a field **H**$\|$**c** there is a first-order transition $\Gamma_{14}\rightleftarrows\Gamma_4$. The abrupt change in the angle $\varphi$, governing the orientation **G** in the $ab$ plane, is shown by an analysis to be close to 90°, which is a consequence of the suppression of the canted phase $\Gamma_{14}$ mentioned above. On the assumption of a 90° abrupt change in the angle $\varphi$, we can use the condition of equality of the corresponding values of the thermodynamic potential of Eq. (4) to deduce the following equation:

$$H_z=\mu_{zz}^{-1}\{T\mathrm{arch}[\mathrm{ch}(\Delta_y/T)e^{-k}(1+\varepsilon^2)^{1/2}]-\Delta_x\}, \tag{16}$$

where

$$k=\frac{K_{ab}^0/2+m_z^0H_z}{(1-\varkappa)T}\qquad \varepsilon=\frac{\mathrm{sh}(\mu_{zz}H_z/T)}{\mathrm{ch}(\Delta_y/T)}\ll 1$$

At temperatures $T\lesssim T_M$ it follows from Eq. (16) that on approach to $T\to T_M$ the threshold field becomes

$$H_z^{\mathrm{th}}\approx -K_{ab}(T)/2m_z(T)\to 0,$$

whereas in the limit $T\to 0$ we obtain (for $\varkappa=0.3$)

$$H_z^{\mathrm{th}}\approx[(1-\varkappa)(\Delta_y-\Delta_x)-K_{ab}^0/2][(1-\varkappa)\mu_{zz}+m_z^0]^{-1}\approx 0.9\ \mathrm{kOe}.$$

Figure 3 shows the temperature dependence $H_z(T)$ calculated allowing for the demagnetizing field and for the existence of a region of an intermediate state, using the parameters given above which describe well the independent experimental data obtained at low temperatures. In view of the fact that the sample was of irregular shape, the demagnetization factor $N_z$ was deduced from the condition of the best match between the upper limit of the intermediate state $\widetilde{H}_z^{\text{th}} = H_z^{\text{th}} + N_z \Delta M_z$ and the experimental result, where $H_z^{\text{th}}$ is the threshold field found from Eq. (16) and $\Delta M_z$ is the abrupt change in the magnetization on transition to the $\Gamma_4$ phase. The discrepancy between the theory and experiment relatively high ($T > 30$ K) temperature is clearly due to the influence of the excited states of the $Er^{3+}$ and $Dy^{3+}$ ions on the anisotropy energy.

## CONCLUSIONS

We shall now summarize the main results of the investigation. Cooling of $Dy_{x}Er_{1-x}CrO_3$ ($x = 0.2, 0.3$) crystals in the absence of an external magnetic field induced consecutively all three main spin configurations: $\Gamma_2(G_z)$, $\Gamma_4(G_x)$, and $\Gamma_1(G_y)$, which had not been observed before for orthochromites. An investigation was made of the various orientational transitions induced by a magnetic field $\mathbf{H}\|\mathbf{c}$ and the corresponding $H$-$T$ phase diagrams were obtained. In particular, for $\mathbf{H}\|\mathbf{a}$ near the Morin point $T_M$ we observed in addition to the usual reorientation in the *ac* and *bc* planes, also a first-order transition (of the spatial spin-flop type) between canted phases $\Gamma_{12}$ and $\Gamma_{24}$. The $H_x$-$T$ phase diagram had a bicritical point corresponding to convergence of two second-order phase transition lines ($\Gamma_{24} \rightleftarrows \Gamma_2$ and $\Gamma_{12} \rightleftarrows \Gamma_2$) and one first-order phase transition line ($\Gamma_{12} \rightleftarrows \Gamma_{24}$).

The $H_x$-$T$ and $H_z$-$T$ phase diagrams found by calculation agreed with the experimental results. The parameters of the main magnetic interactions in the system were determined. It was established that the nature of the $\Gamma_1 \rightleftarrows \Gamma_4$ abrupt Morin transition, involving a first-order phase transition (both in $ErCrO_3$ and $Dy_xEr_{1-x}CrO_3$), was related to a special feature of the splitting of the ground-state doublet of $Er^{3+}$ on rotation of $\mathbf{G}$ in the *ab* plane, namely its reduction at $\varphi \approx 45°$ for one of the inequivalent positions of the $Er^{3+}$ ions.

[1)] In the calculation of $m_x(T)$ at $T \sim T_N$ we allowed (using the molecular field theory) for a reduction in the magnetic moment of the $Cr^{3+}$ sublattices or the modulus of the antiferromagnetic vector $\mathbf{G}$.


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