Nature of the anomalous magnetic properties of yttrium ferrite chromites

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The theoretical results of an analysis of Fe^{3+}–Fe^{3+}, Cr^{3+}–Cr^{3+}, and Fe^{3+}–Cr^{3+} exchange interactions are successfully used to explain the anomalous magnetic properties of single-crystal yttrium ferrite chromites. It is shown that these compounds are weak ferrimagnets with a mixed character of the Dzyaloshinskiĭ interaction. The complicated concentration and temperature dependences of the weakly ferromagnetic moment are qualitatively explained, and the nature and character of the spin reorientation phenomenon are discussed.

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INTRODUCTION

The compounds $YFe_{1-x}Cr_xO_3$ have interesting magnetic properties.[1] An increase in the Cr^{3+} ion concentration in $YFe_{1-x}Cr_xO_3$ leads to a decrease of the Neel temperature from 640 K in $YFeO_3$ to 140 K in $YCrO_3$. They behave like weak ferrimagnets in the entire interval of concentrations x. Even small admixtures of Cr^{3+} ions in $YFeO_3$ or of Fe^{3+} ions in $YCrO_3$ lead to a substantial decrease of the weak ferromagnetic moment (WFM). In addition, at intermediate concentrations x one observes a partial or complete reorientation of the WFM from the *c* axis (high-temperature region) to the *a* axis of the crystal (low temperature region).

The peculiar magnetic properties of mixed orthoferrites-orthochromites are explained on the basis of a study of the character and singularities of the superexchange Fe–Fe, Cr–Cr, and Fe–Cr interactions,

$$\hat{H}_{ex}=2\sum_{i,j} I_{ij}\mathbf{S}_i\mathbf{S}_j,$$

the antisymmetrical Dzyaloshinskiĭ–Morin exchange

$$\hat{H}_{ASE}=\sum_{i,j}\mathbf{d}_{ij}\,[\mathbf{S}_i\times\mathbf{S}_j],$$

in the corresponding pairs of ions, the magnetic-dipole interaction, and the single-ion crystallographic anisotropy of the ions Fe^{3+} and Cr^{3+}. These are also the main interactions in pure $YFeO_3$ and $YCrO_3$.

It will be shown below that the original properties of $YFe_{1-x}Cr_xO_3$ are due mainly to the following relations between the parameters I_{ij} and $\mathbf{d}_{ij}$[2]:

a) $I_{ij}(\mathrm{FeFe}) > I_{ij}(\mathrm{CrCr}) > I_{ij}(\mathrm{FeCr})$

(all the integrals are positive),

b) $\mathbf{d}_{ij}(\mathrm{FeFe}) \uparrow\uparrow \mathbf{d}_{ij}(\mathrm{CrCr}) \uparrow\downarrow \mathbf{d}_{ij}(\mathrm{FeCr})$, $d_{ij}(\mathrm{FeFe}) \sim d_{ij}(\mathrm{CrCr}) \sim d_{ij}(\mathrm{FeCr})$,

i.e., the Fe–Fe, Cr–Cr, Fe–Cr exchange interaction is antiferromagnetic, the "impurity–matrix" exchange integral being much less than the x "impurity–impurity" and "matrix–matrix" exchange integrals.3) Relation b) makes it possible to regard the compounds $YFe_{1-x}Cr_xO_3$ as weak ferromagnets with a mixed character of the antisymmetrical exchange—the vectors $\mathbf{d}_{ij}(\mathrm{FeFe})$, $\mathbf{d}_{ij}(\mathrm{CrCr})$, $\mathbf{d}_{ij}(\mathrm{FeCr})$ are collinear, but the directions of the vectors $\mathbf{d}_{ij}(\mathrm{FeFe})$ and $\mathbf{d}_{ij}(\mathrm{CrCr})$ are opposed to the direction of the vector $\mathbf{d}_{ij}(\mathrm{FeCr})$. As a result the WFM of the impurity system is always directed opposite to the WFM of the matrix. These compounds can in fact be called weak ferrimagnets.

The contemporary status of the statistical theory of binary magnetic systems is still incapable of providing a quantitative description of the concentration and temperature dependences; in addition, in our case we are dealing with subtle effects that are most sensitive to small distortions of the $YFe_{1-x}Cr_xO_3$ crystal due to the difference between the radii of the Fe^{3+} ions (0.67 Å) and the Cr^{3+} ions (0.64 Å). At the same time, the presence of a principal antiferromagnetic structure of the *G* type at $d_{ij} \ll I_{ij}$ and the relative simplicity of the Fe^{3+} and Cr^{3+} ions themselves facilitate the qualitative understanding of the singularities of the magnetic properties of $YFe_{1-x}Cr_xO_3$.

1. EXPERIMENTAL RESULTS

We investigated the magnetic properties of single crystals of the system $YFe_{1-x}Cr_xO_3$ (x equal to 0, 0.05, 0.15, 0.2, 0.5, 0.65, 0.85, 0.95 and 1) growth from the solution in the melt. The choice of the objects of investigation was governed, in particular, by the fact that, according to the semi-empirical rules of Goodenough and Kanamori,[3] the interaction of Fe^{3+} ions with half-filled t_{2g} shells can be ferromagnetic, and this should lead to a substantial change of the properties in a system of the $YFe_{1-x}Cr_xO_3$ type in comparison with the pure $YFeO_3$ and $YCrO_3$. The magnetic measurements have shown, however, that all the substituted compositions $YFe_{1-x}Cr_xO_3$ are weak ferromagnets, and their transverse WFM decreases sharply in comparison with the pure $YFeO_3$ and $YCrO_3$ (by approximately one order of magnitude (Fig. 1)) The exchange interaction energy decreases monotonically as the Fe^{3+} ions in the yttrium orthoferrite are replaced by Cr^{3+}, as is evidenced by the experimental dependence of the Neel point T_N on the concentration (Fig. 2).

Investigations of the Mössbauer effect on ^{57}Fe nuclei

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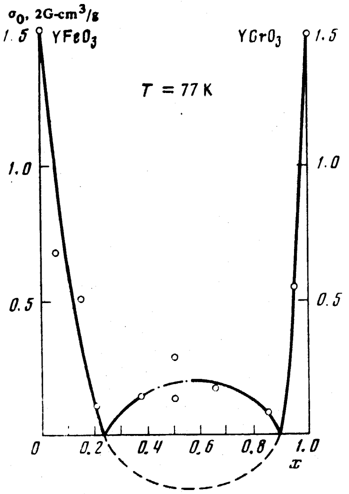

FIG. 1. Concentration dependence of the spontaneous magnetic moment of YFe$_{1-x}$Cr$_x$O$_3$ (T = 77K).

in RFe$_{1-x}$Cr$_x$O$_3$[4] have shown that the Fe–Cr exchange interaction depends strongly on the angle of the Fe—O—Cr bond, and that at the bond angle 146° characteristic of the YFe$_{1-x}$Cr$_x$O$_3$ system[5] this interaction is antiferromagnetic, just as the Fe–Fe and Cr–Cr interactions in YFeO$_3$ and YCrO$_3$. The temperature dependence of the hyperfine field at the ^{57}Fe nuclei in YFe$_{0,01}$Cr$_{0,99}$O$_3$ yielded for the exchange integral the value I(FeCr) = 6.7 K.[4] For pure YFeO^3 and YCrO$_3$ the molecular-field theory yields I(FeFe) = 18.3 K, I(CrCr) = 9.4 K.[4,5] The relatively small value of the exchange integral I(FeCr) explains the experimentally observed $T_N(x)$ dependence for the system YFe$_{1-x}$Cr$_x$O$_3$. Figure 2 shows a plot of $T_N(x)$ calculated at a constant value I(FeCr) = I(CrFe) = 6.7 K from formula (3) of Hashimoto's paper[6]:

$$(T_N-[1-x]T_{N_1})(T_N-xT_{N_2})=16S_1(S_1+1)S_2(S_2+1)x(1-x)I(\text{FeCr}), \quad (1)$$

where T_{N_1} and T_{N_2} are respectively the Néel temperatures of YFeO$_3$ and YCrO$_3$. As seen from Fig. 2, the agreement between the theoretical curve and the experimental values of $T_N(x)$ is perfectly satisfactory.

The weak exchange bond of Fe–Cr in comparison with Fe–Fe and Cr–Cr manifests itself also in the temperature dependence of the spontaneous magnetic moment. Figure 3 shows by way of example a plot of $\sigma_0(T)$ for $x = 0.15$ and $x = 0.65$. For the composition $x = 0.15$ below $T_N = 510$ K the weak ferromagnetic moment is oriented along the c axis of the rhombic crystal (spin configuration G_xF_z), and as the temperature is lowered, in the interval from 400 to 250 K, spin reorientation of the magnetic moment is observed from the c axis to the a axis of the crystal ($G_xF_z - G_zF_x$). With further decrease of temperature, the magnetic moment along the a axis first increases and then decreases, assuming a constant value 0.5 G-cm³/g below 120 K. For the composition $x = 0.65$ below $T_N = 240$ K the spin configuration G_xF_z is also observed, and the magnitude of the magnetic moment along the c axis of the crystal is exceedingly small (~0.01 G-cm³/g). When the temperature is lowered from 230 to 210 K, a spin reorientation $G_xF_z - G_zF_x$ takes place and is accompanied by a sharp increase of the magnetic moment along the crystal a axis, to a value $\sigma_a = 0.18$ G-cm³/g at 160 K, below which the magnetic moment hardly varies with changing temperature.

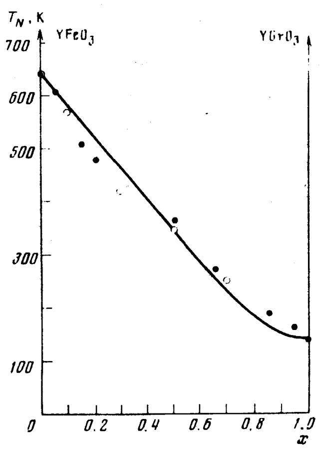

FIG. 2. Dependence of the Néel temperatures of mixed yttrium iron chromites on the composition: ● —single crystal, o —polycrystal.

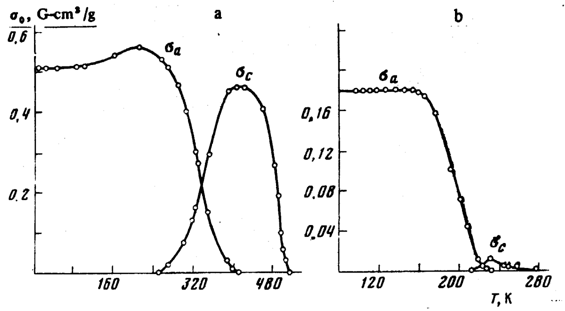

FIG. 3. Dependence of the spontaneous WFM on the temperature: a) $x = 0.15$, b) $x = 0.65$.

For compositions with x equal to 0.2, 0.38, 0.5, and 0.85 a complete or partial spin reorientation in the ac plane is also observed, although for pure YFeO$_2$ and YCrO$_3$ the spin configuration G_xF_z is stable at all temperatures. Figure 4 shows the temperature dependence of the WFM orientation angle θ relative to the c axis of a rhombic crystal. It is seen that for all compositions, at high temperatures the spin configuration is G_xF_z, but it goes over with decreasing temperature into G_zF_x or into $G_{xz}F_{zx}$, the spin reorientation process taking place smoothly in the temperature interval 10–100 K.

2. DISCUSSION OF RESULTS

1. Concentration and temperature dependences of WFM in YFe$_{1-x}$Cr$_x$O$_3$

The weak ferromagnetism of pure orthoferrites and orthochromites of yttrium is due mainly to the antisym-

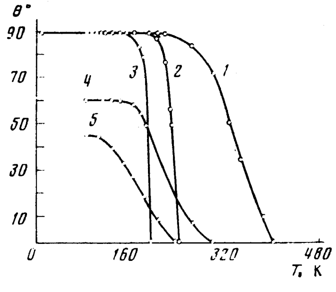

FIG. 4. Temperature dependence of the orientation angle of the spins in mixed ferrite chromites: x equal to 0.15 (curve 1); 0.65 (2); 0.85 (3); 0.5 (4); 0.38 (5).

metrical Dzyaloshinskiĭ-Morin exchange interaction in the ion pairs $Fe^{3+}-Fe^{3+}$ and $Cr^{3+}-Cr^{3+}$. In the mixed compounds $YFe_{1-x}Cr_xO_3$ it becomes necessary to consider three types of pairs, $Fe^{3+}-Fe^{3+}$, $Cr^{3+}-Cr^{3+}$ and $Fe^{3+}-Cr^{3+}$, with their antisymmetrical-exchange parameters, and this undoubtedly manifests itself in the original concentration and temperature dependences of the WFM. The antisymmetrical exchange interaction is described by the Hamiltonian[7]

$$\hat{V}_{ASE}=\sum_{i,j}\mathbf{d}_{ij}[\mathbf{S}_i\times\mathbf{S}_j], \tag{2}$$

and for the pair of ions Fe^{3+} and Cr^{3+} bound via an intermediate nonmagnetic ion of the O^{2-} type we have[2]

$$\mathbf{d}_{ij}=d(\theta)[\mathbf{r}_{i0}\mathbf{r}_{j0}],\quad d(\theta)=d_1+d_2\cos\theta, \tag{3}$$

where d_1 and d_2 are certain constants: for which microscopic expressions are given elsewhere,[2] $\mathbf{r}_{i0}$ and $\mathbf{r}_{j0}$ are unit radius vectors of the bonds M_i-O and M_j-O, and θ is the angle of the M_i-O-M_j bond. Moskvin and Bostrem[2] obtained a result of importance to us, namely, the parameters $d(\theta)$ for the pairs $Fe^{3+}-Fe^{3+}$, $Cr^{3+}-Cr^{3+}$ are of the same sigh, which is the opposite of the sign of the parameter $d(\theta)$ for the $Fe^{3+}-Cr^{3+}$ pair. An interesting possibility of verifying this result, as well as on the whole for an analysis of the role of antisymmetrical exchange, is offered by an analysis of the magnetic structure and the anisotropy energy of an yttrium orthoferrite with small admixture of Cr^{3+} ions. In the general case this is a complicated problem, and we confine ourselves to a somewhat idealized model in which it is assumed that:

1) No change of the crystallographic-structure parameters takes place when the Fe^{3+} ions are replaced by Cr^{3+}.

2) The impurity ion Cr^{3+} influences the magnetic configuration of the Fe^{3+} in the immediate surrounding only. Fe^{3+} ions that have no Cr^{3+} ions in their immediate surrounding retain a magnetic structure corresponding to pure $YFeO_3$.

The first of these approximations allows us to introduce a certain dimensionless parameter

$$\delta=\frac{\mathbf{d}_{ij}(\mathrm{CrFe})}{I(\mathrm{CrFe})}:\frac{\mathbf{d}_{ij}(\mathrm{FeFe})}{I(\mathrm{FeFe})}, \tag{4}$$

which characterizes the relative magnitude of the Cr–Fe and Fe–Fe antisymmetrical exchange. By using the second approximation, we formulate a system of molecular-field equations for the complex of the spins of the Cr^{3+} ions and of the six nearest Fe^{3+} ions, and take only the Dzyaloshinskiĭ field and the exchange field into account. The molecular-field equations are solved in an approximation wherein $d(\mathrm{CrFe})/I(\mathrm{CrFe})$ and $d(\mathrm{FeFe})/I(\mathrm{FeFe})$ are small. Without presenting the unwieldy calculations, we confine ourselves to a few of the most important results.

1) The spin angular momentum of the impurity ion Cr^{3+} can be represented in the form (the impurity is located at the site $(\frac{1}{2}, 0, 0)$[8])

$$\mathbf{S}_{\mathrm{Cr}}\cong S_{\mathrm{Cr}}\{-\mathbf{G}+(2\delta-1)\mathbf{F}-(2\delta+1)\mathbf{C}/3+(4\delta-1)\mathbf{A}/3\}, \tag{5}$$

where **G**, **F**, **C**, and **A** are the basis vectors of the magnetic structure of the pure $YFeO_3$.[9,10]

2) The combined spin momentum of the six Fe^{3+} ions from the immediate surrounding of the impurity remains the same as for the pure orthoferrite, although the direction of the spin of each separate ion does change.

The spin momentum of Fe^3—in the same position $(\frac{1}{2}, 0, 0)$ as the impurity (in pure $YFeO_3$ is given by[10]

$$\mathbf{S}_{\mathrm{Fe}}=S_{\mathrm{Fe}}(-\mathbf{G}+\mathbf{F}-\mathbf{C}+\mathbf{A}). \tag{6}$$

Consequently, at the theoretically predicted negative value of the parameter δ the weak ferromagnetic moment of the impurity Cr^{3+} (with value $2\mu_B S_{\mathrm{Cr}}(2\delta-1)\mathbf{F}$) will have a direction opposite to that of the weak ferromagnetic moment of the matrix ion (with value $2\mu_B S_{\mathrm{Fe}}\mathbf{F}$), and the introduction of the Cr^{3+} into $YFeO_3$ leads to a decrease of the total WFM by an amount

$$\Delta\sigma_{\mathrm{Cr}}=2\mu_B[S_{\mathrm{Fe}}-(2\delta-1)S_{\mathrm{Cr}}]\mathbf{F}. \tag{7}$$

An Fe^{3+} impurity in $YCrO_3$ can be treated in exactly the same manner. Introducing the parameter

$$\delta'=\frac{\mathbf{d}_{ij}(\mathrm{FeCr})}{I(\mathrm{FeCr})}:\frac{\mathbf{d}_{ij}(\mathrm{CrCr})}{I(\mathrm{CrCr})}, \tag{8}$$

we obtain for the spin moment of the impurity Fe^{3+} ion and for the change of the WFM in $YCrO_3$ following implantation of one Fe^{3+} ion relationa analogous to (5) and (7), with the substitutions $\delta\rightarrow\delta'$ and $S_{\mathrm{Cr}}\leftrightarrow S_{\mathrm{Fe}}$.

For pure $YFeO_3$ and $YCrO_3$, the WFM are close in magnitude, i.e.,

$$\frac{d_{ij}(\mathrm{FeFe})}{I(\mathrm{FeFe})}S_{\mathrm{Fe}}\approx\frac{d_{ij}(\mathrm{CrCr})}{I(\mathrm{CrCr})}S_{\mathrm{Cr}}, \tag{9}$$

whence we obtain, taking into account (4), (8), and the equality $d_{ij}(\mathrm{FeCr})=d_{ij}(\mathrm{CrFe})$, a relation between δ and δ':

$$S_{\mathrm{Cr}}|\delta|\approx S_{\mathrm{Fe}}|\delta'|. \tag{10}$$

If the signs of δ and δ' are the same (i.e., if the vectors $\mathbf{d}_{ij}(\mathrm{FeFe})$ and $\mathbf{d}_{ij}(\mathrm{CrCr})$ are parallel) we have

$$S_{\mathrm{Cr}}-(2\delta'-1)S_{\mathrm{Fe}}=S_{\mathrm{Fe}}-(2\delta-1)S_{\mathrm{Cr}}; \tag{11}$$

$$\Delta\sigma_{\mathrm{Fe}}/\Delta\sigma_{\mathrm{Cr}}=F_{\mathrm{YFeO_3}}/F_{\mathrm{YCrO_3}}=S_{\mathrm{Fe}}/S_{\mathrm{Cr}}={}^5/_3, \tag{12}$$

i.e., the Fe^{3+} impurity in $YCrO_3$ leads to a larger change of the WFM than the Cr^{3+} impurity in $YFeO_3$.

At low impurity concentrations, i.e., of Cr^{3+} in $YFeO_3 (x\ll 1)$ or of Fe^{3+} in $YCrO_3 (1-x\ll 1)$, the concentration dependence of the WFM in $YFe_{1-x}Cr_xO_3$ will be determined by the relations

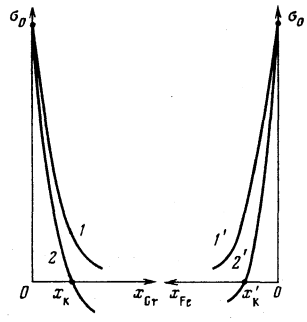

FIG. 5. Possible variants of the $\sigma_0(x)$ dependence at low impurity concentrations.

$$\sigma(x)=\sigma_{Fe}-[S_{Fe}-(2\delta-1)S_{Cr}]\sigma_{Fe}x/S_{Fe},\quad x\ll 1,$$
$$\sigma(x)=\sigma_{Cr}-[S_{Cr}-(2\delta'-1)S_{Fe}]\sigma_{Cr}(1-x)/S_{Cr},\quad 1-x\ll 1. \tag{13}$$

Comparison with the experimental data of Fig. 1 shows that both δ and δ' should be negative, with

$$\delta\approx{}^5/_3\delta'\approx-8, \tag{14}$$

i.e., the Dzyaloshinskiĭ vectors $\mathbf{d}_{ij}$(FeFe) and $\mathbf{d}_{ij}$(CrCr) should be parallel, whereas the Dzyaloshinskiĭ vector $\mathbf{d}_{ij}(\mathrm{FeCr})=\mathbf{d}_{ij}(\mathrm{CrFe})$ (impurity–matrix) has the opposite direction, in full agreement with the predictions of the theory,[2] and

$$d_{ij}(\mathrm{FeCr})\approx 3d_{ij}(\mathrm{FeFe}). \tag{15}$$

The WFM of the impurity ion is antiparallel here to the WFM of the matrix, and is larger by almost one order of magnitude than the WFM of the matrix ion.

With increasing impurity concentration, the linear law (13) ceases to hold, and complexes containing 1, 2, ... impurity ions in the immediate surrounding of the impurity assume an appreciable role. The Dzyaloshinskiĭ interaction in such complexes is weakened by the decrease of the number of impurity–matrix bonds with the large value of d_{ij}(FeCr), and this slows down greatly the growth of the WFM of the impurity. In fact, the contribution of impurity ions having in their immediate surrounding only matrix ions to the WFM of $YFe_{1-x}Cr_xO_3$ will be maximal at $x=\frac{1}{7}$(Cr^{3+} ions) and $x=\frac{6}{7}$(Fe^{3+} ions). The probability that an impurity ion will also be present among the nearest neighbors of the impurity is, however, almost 40%. It appears that the validity of the linear approximation (13) is restricted to concentrations on the order of several per cent. We note also that the theoretical prediction that the Fe^{3+} ions in $YCrO_3$ exert a stronger influence on the decrease of the WFM than the Cr^{3+} ions in $YFeO_3$($\Delta\sigma_{Fe}>\Delta\sigma_{Cr}$) has been experimentally confirmed.

In the general case of the WFM of $YFe_{1-x}Cr_xO_3$ can be represented in the form

$$\sigma(x)=x\bar{\sigma}_{Cr}+(1-x)\bar{\sigma}_{Fe}, \tag{16}$$

where $\bar{\sigma}_{Cr}$ and $\bar{\sigma}_{Fe}$ are the average WFM of the corresponding ions and depend in turn on the concentration x. At small x (or $1-x$) the quantity $|\bar{\sigma}_{Cr}|$ (or $|\bar{\sigma}_{Fe}|$) greatly exceeds $|\bar{\sigma}_{Fe}|$ (or $|\bar{\sigma}_{Cr}|$). With increasing x (or $1-x$) the value of $\bar{\sigma}_{Cr}$ (or $\bar{\sigma}_{Fe}$) decreases to its value in pure $YCrO_3$ (or $YFeO_3$). The quantities $\bar{\sigma}_{Cr}$ and $\bar{\sigma}_{Fe}$ are of equal sign in practically the entire region of the concentrations x (with the exception of the region where these quantities reverse sign). In addition, the pairs of quantities x, $\bar{\sigma}_{Cr}$ and $1-x$, $\bar{\sigma}_{Fe}$ vary in opposite directions. It can therefore be assumed that in the region of intermediate concentrations ($0.3\lesssim x\lesssim 0.7$) the value of $\sigma(x)$ changes little. The experimental data show that in this region σ is extremely small, $\sigma(x)\sim 0.1$.

We can propose approximately two variants of the $\sigma(x)$ dependence in the region of small impurity concentrations in $YFe_{1-x}Cr_xO_3$($x<0.2$) (Fig. 5), differing in the fact that in case 2(2′) at $x=x_c(x'_c)$ cancellation of the WFM is observed and that at $x_c<x<1-x'_c$ the combined WFM of the impurity system exceeds the WFM of the matrix, and the direction of the WFM reverses sign on going through $x_c(x'_c)$. We note in this connection that in the experimental data the sign of the WFM is chosen to be positive in the entire region of x, i.e., the experimental points for σ at $x_c<x<1-x'_c$ will lie on the curves shown dashed in Fig. 1.

The most complicated region for the analysis of the behavior of the WFM is the concentration region near $x\approx 0.5$, where the meaning of the impurity–matrix concepts is completely lost. In this region we can expect also an irregular dependence of the WFM on the concentration, as is indicated also by the experimental data. For two samples with a composition close to $x=0.5$ we obtained noticeably different values of the weak ferromagnetism at 77 K (Fig. 1, dash-dot curve), although the values of T_N are practically the same in both cases.

It is easy to obtain a qualitative explanation of the peculiar dependence of the WFM in $YFe_{1-x}Cr_xO_3$ on the temperature if the following circumstance is taken into account. The exchange integral I(FeCr) is smaller in magnitude than the exchange integrals between the ions of the matrix, i.e., I(FeFe) or I(CrCr). As a result, the effective field acting on the impurity ions (Cr^{3+} in $YFeO_3$ or Fe^{3+} in $YCrO_3$) is less than the effective magnetic field acting on the matrix ions. This means that the magnetic moment of the impurity ion saturates at lower temperatures than the moment of the matrix ion, and the relative contribution of the impurity system to the WFM increases with decreasing temperature.

By way of illustration Fig. 6 shows the temperature dependence of the reduced magnetic moment $M_{Cr}(T)$ of the impurity ion Cr^{3+} on $UFeO_3$, calculated by the mo-

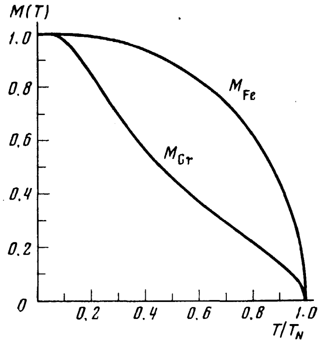

FIG. 6. Temperature dependence of the reduced magnetic moments of the ions Cr^{3+} and Fe^{3+} in $YFeO_3:Cr^{3+}$.

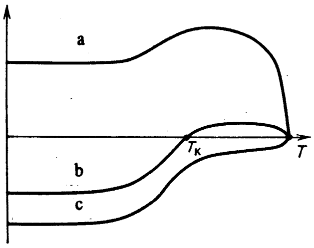

FIG. 7. Possible variants of the $\sigma_0(T)$ dependence in $YFe_{1-x}Cr_xO_3$.

lecular-field method, and for comparison the value of $M_{Fe}(T)$ for pure $YFeO_3$. The measured reduced magnetic moment $M_{Fe}(T)$ of the impurity ion Fe^{3+} in certain orthochromites are given in[4]. The temperature dependence of the WFM can be approximately written in the form

$$\sigma(T)=\alpha_1 M_{Cr}(T)+\beta_1 M_{Fe}(T), \qquad (17)$$

where $M_{Cr,Fe}(T)$ are the reduced average magnetic moments of the $Cr^{3+}(Fe^{3+})$ions. Since the coefficients α_1 and β_1 have opposite signs in practically the entire range of the concentration x, several types of $\sigma(T)$ dependence are possible in practice, as shown schematically in Fig. 7. The dependence of type *a* is realized at low impurity concentrations, when the contribution of the impurity system to the WFM does not exceed the matrix contribution in the entire temperature interval. The dependence *c* is realized at sufficiently high impurity concentrations, when the contribution of the impurity system below T_N exceeds immediately the contribution of the matrix. The type-*b* dependence is characterized by the presence of compensation point at which $\alpha_1 M_{Cr}(T) = -\beta_1 M_{Fe}(T)$, and the contribution of the impurity or of the matrix predominates below or above T_c, respectively.

Thus, an investigation of the qualitative variation of $\sigma(T)$ makes it possible to determine the direction of the WFM in $YFe_{1-x}Cr_xO_3$ at various concentrations relative to the direction of the WFM in pure $YFeO_3$ and $YCrO_3$. The measurements of $\sigma(T)$ show that at x equal to 0.05, 0.15, 0.2, and 0.95 dependences of the type *a* are observed, and dependences of the type *b* or *c* at x equal 0.5, 0.65, and 0.85, i.e., at low temperatures (in the saturation region of $\sigma(T)$) we have $\sigma > 0$ in the former case and $\sigma < 0$ in the latter. The function $\sigma(x)_{T\to 0}$ takes the form shown in Fig. 1 (solid curves), i.e., a plot of the type 2 (see Fig. 5) with two compensation points at $x \approx 0.24$ and $x \approx 0.9$.

Near the Néel temperature, the laws governing the variation of the relative magnetic moment of the impurity ion and of the matrix are similar in the molecular-field model, and can be very roughly approximated by a power-law dependence

$$M(T)\sim(1-T/T_N)^\beta, \qquad (18)$$

where $\beta \sim 0.5$. Then the expression for $\sigma(T, x)$ at $T \lesssim T_N$ takes the form

$$\sigma(T, x)\cong[x\bar{\sigma}_{Cr}'+(1-x)\bar{\sigma}_{Fe}'](1-T/T_N)^\beta. \qquad (19)$$

In the case of $YFe_{1-x}Cr_xO_3$, the value of $x\bar{\sigma}_{Cr}' + (1-x)\bar{\sigma}_{Fe}$ in the concentration region $0.3 \lesssim x \lesssim 0.85$ turns out to be close to zero also in the temperature region where relation (18) is satisfied, and the WFM turns out to be negligibly small. With further decrease of the temperature, however, relation (18) is not satisfied. The faster growth of the WFM of the impurity leads to decompensation and to a rapid growth of the absolute value of the WFM (Fig. 3b). It is interesting that in some $YFe_{1-x}Cr_xO_3$ compositions the WFM becomes reoriented from the *c* axis to the *a* axis or, in analogy with pure orthoferrites such as $ErFeO_3$ and $SmFeO_3$, a phase transition is observed from the high-temperature configuration of the type Γ_4 to a low-temperature configuration of the Γ_2 type.

2. Spin reorientation in $YFe_{1-x}Cr_xO_3$

The magnetic-anisotropy in mixed orthoferrites-orthochromites of yttrium is determined by three principal interactions: antisymmetric exchange, magnetic-dipole interaction, and single-ion crystallographic anisotropy. It was shown[11,12] that antisymmetric exchange and magnetic-dipole interaction in pure orthoferrites (this is apparently valid also for orthochromites) stabilize the magnetic structure $\Gamma_4(G_xF_z)$. The role of these interactions in mixed compositions can be illustrated with the very simple example of an impurity Cr^{3+} ion in $YFeO_3$, which was considered above. The energy of the magnetic-dipole interaction of the Cr^{3+} ion with the surrounding F^{3+} ions is $\frac{3}{5}$ of the Fe^{3+} ion energy in YFO_3 and is minimal for a configuration of the G_x type.

In the molecular field approximation, we calculated the change ε_Γ of the energies of the magnetic configurations Γ_1, Γ_2, and Γ_4 of $YFeO_3$ following introduction of the Cr^{3+} ion, due only to antisymmetric exchange. Figure 8 shows the calculated values of ε_Γ as functions of the parameter δ that characterizes the relative role of the antisymmetric exchange $Fe^{3+}-Cr^{3+}$ and $Fe^{3+}-Fe^{3+}$. If the Fe^{3+} ion in pure $YFeO_3$, with account taken of the antisymmetrical exchange only, behaves effectively like an ion for which the easy axis is the *a* axis, then the Cr^{3+} impurity ion in $YFeO_3$ "prefers" under these conditions the *c* axis for δ values in the range -0.4 to -3 and the *a* axis at $\delta < -3$. The value $\delta \approx -8$, obtained from data on the concentration dependence of the WFM in $YFe_{1-x}Cr_xO_3$, indicates that the antisymmetrical exchange between the impurity and the matrix stabilizes the G_x structure.

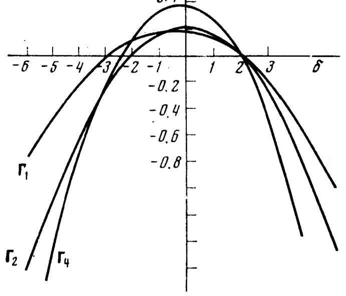

FIG. 8. Variation of the energy of the magnetic configurations Γ_1, Γ_2, Γ_4 (G_y, G_z, G_x) in $YFeO_3$ following implantation of a Cr^{3+} ion, as a function of the parameter δ.

The most complicated is the analysis of the one-ion crystallographic anisotropy of the Fe^{3+} and Cr^{3+} ions. On the one hand, the microscopic theory is still incapable at present to propose a method of obtaining a reliable estimate of the magnitude and sign of the crystallographic-anisotropy parameters. On the other hand, it is possible to obtain in experiment only the constants of the effective magnetic anisotropy, which contains various contributions. In this sense, definite interest attaches to measurements of the crystallographic-anisotropy parameters in experiments on ESR if impurity Fe^{3+} and Cr^{3+} ions in ortho-aluminates, which are isostructural to $YFeO_3$ and $YCrO_3$. Approximating the second-order anisotropy by the axial term DS_z^2, Taylor *et al.*[13] have shown that in $LaAlO_3$ the sign of the parameter D is different for the Fe^{3+} and Cr^{3+} ions, and the two parameters are close in order of magnitude:

$$LaAlO_3{:}Fe^{3+}, \quad D=4.90\cdot 10^{-2}\ \mathrm{cm}^{-1},$$

$$LaAlO_3{:}Cr^{3+}, \quad D=-5.55\cdot 10^{-2}\ \mathrm{cm}^{-1}.$$

It is therefore natural to suggest that the sign of the single-ion anisotropy for the Fe^{3+} and Cr^{3+} ions in an identical matrix with structure of the $YFeO_3$ type will be different, i.e., the easy axis for the matrix ion can be the difficult axis for the impurity ions, and vice versa.

Single-ion fourth-order anisotropy differs from zero only for the Fe^{3+} ions and can be approximated sufficiently reliably by the so-called cubic anisotropy

$$F_{\text{cub}}={}^1/_6 a[S_x^4+S_y^4+S_z^4-{}^1/_5 S(S+1)(3S^2+3S-1)], \tag{20}$$

where the constant a is not very sensitive to the noncubic distortions of the surrounding of the Fe^{3+} ion. The quantity $a=4\times 10^{-2}$ cm^{-1}, obtained from measurements of the ESR of Fe^{3+} ions in $LaAlO_3$ can be regarded as a good estimate for $YFeO_3$.

The expression for the free anisotropy energy of $YFe_{1-x}Cr_xO_3$ in the region of the transition between the phases$^{4)}$—we shall arbitrarily call them Γ_4 and Γ_2—can be written in the form[14]

$$F={}^1/_2 k_u \cos 2\theta+k_b \cos 4\theta, \tag{21}$$

where θ is the angle between the directions of the WFM and the c axis of the crystal, and k_u and k_b are the first and second anisotropy constants. The quantity k_u can be approximately represented as a sum of three terms:

$$k_u \approx \alpha_2 M_{\text{imp}}^2+\beta_2 M_{\text{m}}^2+\gamma_2 M_{\text{imp}} M_{\text{m}}, \tag{22}$$

where M_{imp} and M_{m} are the relative mean magnetic moments of the impurity and matrix ions. The first two terms are determined by single-ion anisotropy of the impurity and matrix ions, as well as by the Dzyaloshinskiĭ interaction and the magnetic-dipole Cr–Cr and Fe–Fe interaction. The last term is due mainly to the Dzyaloshinskiĭ Fe–Cr interaction. In pure $YFeO_3$ and $YCrO_3$, the configuration Γ_4 is realized in the entire temperature interval; this enables us to assume that, at least at low concentrations of Cr^{3+} in $YFeO_3$ or of Fe^{3+} in $YCrO_3$, the second term is always negative ($\beta_2<0$), i.e., it stabilizes the Γ_4 phase, and increases with decreasing temperature. Consequently, the reorientation Γ_4–Γ_2 will take place if either $\alpha_2>0$ or $\gamma_2>0$, or else both α_2 and γ_2 are positive, i.e., if the single-ion anisotropy of the impurity or the antisymmetrical exchange contribute to the Γ_4–Γ_2 reorientation. In fact, with decreasing temperature, the ratio

$$M_{\text{imp}}^2 < M_{\text{imp}} M_{\text{m}} < M_{\text{m}}^2 \tag{23}$$

goes over into

$$M_{\text{imp}}^2 \approx M_{\text{imp}} M_{\text{m}} \approx M_{\text{m}}^2, \tag{24}$$

which leads to an increase of the relative role of the first and third terms at low temperatures.

Near T_N, the quantity k_u can be represented in the form

$$k_u \approx \text{const}(1-T/T_N)^{2\beta}, \tag{25}$$

and consequently if the configuration Γ_4 is realized directly below T_N, then this configuration will remain stable at least down to temperatures fo which the power-law (25) is still satisfied. With further decrease of temperature, the magnetic moment of the impurity begins to increase more rapidly than the moment of the matrix ion, and at a positive sign of α_2 (and/or γ_2), this can lead to a Γ_4–Γ_2 reorientation.

Two circumstances allow us to regard precisely the single-ion impurity anisotropy as the cause of the Γ_4–Γ_2 reorientation in $YFe_{1-x}Cr_xO_3$. First, when the temperature is lowered the first term of (22) increases more rapidly than the third, meaning that if the configuration Γ_2 is not realized directly below T_N, then at negative α_2 it can likewise not be realized also at lower temperatures. Second, the calculated energies of various magnetic configurations of pure $YFeO_3$ with Cr^{3+} impurity show that the antisymmetrical Cr–Fe exchange at values $\delta \approx -8$ leads to stabilization of the configuration Γ_4, i.e., $\gamma_2<0$.

A quantitative analysis of single-ion crystallographic anisotropy of the Cr^{3+} impurity ion in $YFeO_3$ or of Fe^{3+} in YCr_3 comes up against the estimate of the local deformations of the environment, which reach apparently values on the order of several percent. An important role would be played here also by the knowledge of the crystallographic positions of the O^{2-} ions in the lattice of pure $YCrO_3$.

A characteristic feature of spin reorientation in $YFe_{1-x}Cr_xO_3$ compositions at $x=9.65$ is the abrupt increase of the WFM on going from the phase Γ_4 to Γ_2. In the Γ_4 configuration, the WFM of the impurity and the matrix practically cancel each other (Fig. 3b). The WFM of the matrix ($YCrO_3$) in the Γ_4–Γ_2 transition will decrease by approximately 10%, as is unequivocally indicated by the data of Sanina *et al.*,[15] who cite the values of the Dzyaloshinskiĭ parameters and anisotropy constants obtained for pure $YCrO_3$ from measurements of the field dependence of the AFMR frequencies. The relative changes of the WFM of the Fe^{3+} ion in $YFeO_3$

and in $YCrO_3$, due only to antisymmetric exchange, can be connected by the relation

$$\Delta\sigma_{\text{imp}}(\Gamma_4-\Gamma_2)/\sigma_{\text{imp}} \approx \delta(\Delta\sigma_{\text{m}}(\Gamma_4-\Gamma_2)/\sigma_{\text{m}}), \tag{26}$$

where δ is determined by expression (4). Recognizing that $\delta \cong -8$ and $\Delta\sigma_M(\Gamma_4-\Gamma_2)/\sigma_M = -1\%$,[2] we find that allowance for the antisymmetric Fe^{3+}–Cr^{3+} exchange makes it possible to predict theoretically the increase of the WFM of the impurity (Fe^{3+} in $YCrO_3$) following a Γ_4–Γ_2 reorientation on the order of 10%.

Thus, a Γ_4–Γ_2 transition in compositions with $x=0.65$ causes a decompensation of the WFM, the direction of the WFM in the Γ_2 phase being determined by the moment of the impurity (Fe^{3+}).

One of the distinguishing features of the Γ_4–Γ_2 transition in $YFe_{1-x}Cr_xO_3$ is the usually rather large width of the temperature interval in which the spin rotation takes place; moreover, in some mixed orthoferrites-orthochromites the reorientation does not terminate at $T\to 0$, and the so-called canted structure (Fig. 4) is formed. To interpret these features of the reorientation in $YFe_{1-x}Cr_xO_3$, lets consider the relation for the temperature dependence of the angle θ in the spin rotation process,[14]

$$\sin^2\theta=(k_u+8k_b)/16k_b. \tag{27}$$

The second anisotropy constant k_b or cubic anisotropy in $YFe_{1-x}Cr_xO_3$ is small and positive, and can be represented in the form

$$k_b\approx k_b^{(0)}(1-x)\bar{M}_{Fe}^4, \tag{28}$$

where $k_b^{(0)}$ is the cubic-anisotropy constant in pure $YFeO_3$ as $T\to 0$, and $\bar{M}_{Fe}$ is the average relative magnetic moment of the iron ion in $YFe_{1-x}Cr_xO_3$.

The start (T_{r1}, $\theta=0$) and end (T_{r2}, $\theta=\pi/2$) of the reorientation are determined from the conditions

$$k_u(T_{r1})=-8k_b(T_{r1}), \quad k_u(T_{r2})=+8k_b(T_{r2}). \tag{29}$$

It is necessary here to take into account also the saturation of the magnetic moment of the impurity and matrix ions at low temperatures. Let us introduce conditionally a certain saturation temperature $T_{sat}(x)$, below which the values of k_u and k_b are practically independent of temperature. If

$$k_u(T_{sat})\geqslant 8k_b(T_N),$$

then the reorientation is completed at a temperature $T_{r2}\geqslant T_{sat}$, but if

$$k_u(T_{sat})<8k_b(T_{sat}),$$

then the reorientation is incomplete: a canted structure is realized below T_{sat}, with the angle θ_{sat} determined from (27) at $T=T_{sat}$.

In any case, when T_{sat} is approached, the temperature dependences of k_u and k_b become weak, and this hinders the satisfaction of the second condition (29), i.e., it broadens the reorientation region.

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3) Here and below the term "impurity" is arbitrarily used for the Cr^{3+} ions at $x<0.5$ or the Fe^{3+} ions at $x>0.5$.

4) We assume coherent rotation of the matrix and impurity spins in the spin-flip region.

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