Magnetic and neutron-diffraction investigations of reorientation transitions in cobalt-substituted yttrium orthoferrite

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Complex magnetic and neutron-diffraction investigations of the magnetic behavior and magnetic structure of cobalt-substituted yttrium orthoferrites have been carried out. Various types of reorientation transitions, both spontaneous and induced—by external magnetic fields of up to 250 kOe—have been studied. Concentration and field phase diagrams have been plotted and their characteristic properties considered. The second- and fourth-order anisotropy constants for Co^{2+} ions have been experimentally determined for the first time, and their temperature dependence has been plotted.

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It is well known that yttrium orthoferrite is a noncollinear antiferromagnet, exhibiting weak ferromagnetism along the c axis of the orthorhombic crystal,[1] the G_xF_z magnetic configuration being stable in the entire temperature range from 4.2 K to T_N.

In[2-4] it was shown that a small (~1%) substitution of the iron ions by cobalt ions in yttrium orthoferrite leads to the occurrence of the $G_xF_z \rightarrow G_zF_x$ temperature reorientation transition, and it has been suggested that to the spin reorientation leads the large magnitude of the Co^{2+} ions' anisotropy constant, which is strongly dependent on temperature. But the experimental determination of the anisotropy constants of cobalt ions has not been carried out, in view of which the interpretation of the magnetic behavior of the cobalt-substituted yttrium orthoferrites is difficult.

With the object of obtaining complete information about the character and nature of the reorientation transitions in these compounds, we undertook complex magnetic and neutron-diffraction investigations of their magnetic crystallographic anisotropy and their magnetic structure in the region of their spin-reorientation transition temperatures.

SAMPLES AND INVESTIGATION PROCEDURE

Neutron-diffraction investigations were carried out on polycrystalline samples of $YFe_{1-2X}Co_XTi_XO_3$ (X = 0.002; 0.003; 0.01) and $YFe_{1-X}Co_XO_3$ (X = 0.005; 0.01; 0.05; 0.1) prepared by the usual ceramic technology.

The magnetic measurements were made on single crystals containing Co^{2+} in amounts X = 0; 0.002; 0.0024; 0.003; 0.0031; 0.006. The crystals were grown by the method of spontaneous crystallization from a solution in a melt containing 50 molar percent of PbO, 40 molar percent of PbF_2, and 10 molar percent of B_2O_3. The quantitative content of Co^{2+} ions was monitored with the aid of x-ray spectral analysis to within 10^{-2} percent by weight.

The neutron-diffraction measurements were made on the Budapest type VVRS-M experimental reactor on a wavelength of 1.14 Å in the temperature range 6 to 700 K. We measured the temperature dependence of two magnetic reflections, (011) and (101), from which we determined the Néel points and the temperature range for the spin reorientation. From the neutron diffractogram taken below and above the reorientation temperature, we determined the magnetic structure before and after the reorientation. From the magnetic measurements we obtained the $H_r(T)$ phase diagrams and the temperature dependences of the second- and fourth-order anisotropy constants. We determined the threshold fields for each composition from the measurement of the field dependence of the magnetostriction and the rotating moment during the spin reorientation. The magnetostrictive distortions and the rotating moment of the samples were measured with the aid of piezoelectric transducers in the longitudinal and transverse pulsed solenoids with maximum magnetic field intensities of 250 and 180 kOe respectively.

RESULTS OF THE MEASUREMENTS

The magnetic and neutron-diffraction measurements showed that the substitution in yttrium orthoferrite of Fe^{3+} ions by Co^{3+} ions does not lead to the occurrence of spin reorientation, as was suggested in[2]. Spin reorientation was observed by us only in the case when the substituent cobalt ions were in the bivalent state.

The dependence, obtained with the aid of the magnetic and neutron-diffraction data, of the reorientation temperature T_r on the Co^{2+} concentration is shown in Fig. 1a. On the $T_r(X)$ curve are marked the spin-reorientation regions outside of which stable spin configurations existed (the T_r are the centers of these regions). The same figure shows the concentration dependence of the Néel temperature T_N. It can be seen that, as the Co^{2+} ion concentration increases, the Néel temperature decreases linearly, while the reorientation temperature rapidly increases.

For the $X \approx 0.02$ substitution, the reorientation temperature reaches the Néel temperature, and upon further increase of the Co^{2+} concentration the G_zF_x spin configuration becomes stable at all temperatures. For X = 0.001, we did not observe spin reorientation in co-

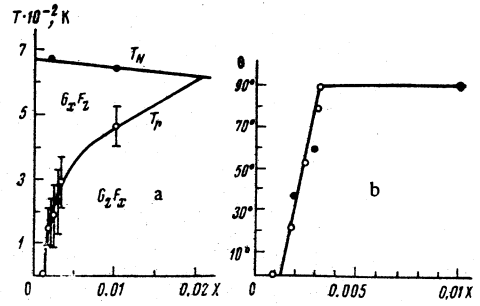

FIG. 1. The dependence of the Néel temperature T_N, the reorientation temperature T_r (Fig. a) and of the angle, θ, of stable orientation of the magnetic moment at low temperatures (Fig. b) on the Co^{2+} ion concentration (X) in cobalt-substituted yttrium orthoferrites: ●) the neutron-diffraction analysis data, ○) data obtained in the magnetic measurements.

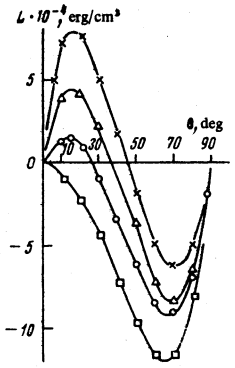

FIG. 3. Isotherms of the dependence of the magnitude, L, of the rotating moment on the angle, θ, between $\mathbf{m}$ and the c axis for $H=70$ kOe and $X=0.0024$ at the temperatures: ×) 120, △) 150, ○) 180, and □) 210 K.

balt-substituted yttrium orthoferrite. In the concentration range from $X=0.0013$ to $X=0.003$, we observed unusual—for unsubstituted orthoferrites—$G_xF_z \rightarrow G_{xz}F_{zx}$ reorientation transitions, when, as the temperature decreases, the weakly-ferromagnetic moment moves away from the c axis of the crystal and stably orientates at an angle of θ to it in the ac plane ($\theta < \pi/2$). Figure 1b shows the obtained—from the magnetic measurements—concentration dependence of the angle θ at which the magnetic moment at low temperatures stably orientates with respect to the c axis. The presence of a stable G_{zx} angular configuration in the case of a small Co^{2+} ion content in yttrium orthoferrite was confirmed also by the neutron diffraction measurements. In Fig. 2a we show the temperature dependences of the reflection intensities in samples with Co^{2+} ion contents $X=0.002$, 0.003, and 0.01 in the course of the reorientation. Besides the Néel points, the temperatures at which the spin reorientation begins and ends are indicated in Fig. 2a. The direction of the sublattice magnetizations can be determined from the ratio of the intensities of the (011) and (101) magnetic reflections (Fig. 2b).

If a spin configuration of the type G_xF_z is observed, then the ratio of the intensities of the magnetic reflections is roughly equal to three, while in the case of the G_zF_x structure the intensities of the (011) and (101)

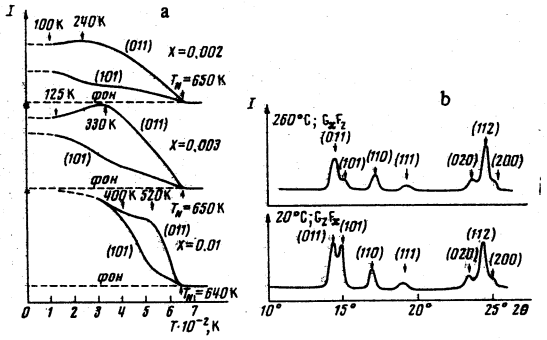

FIG. 2. The temperature dependence of the intensities of the (011) and (101) reflections in the orthoferrites $YFe_{1-2X}Co_XTi_XO_3$ for $X=0.002$, $X=0.003$, and $X=0.01$ (Fig. a) and the experimental neutron-diffraction pattern for the $X=0.01$ compound (Fig. b); I denotes the intensity and 2θ is the scattering angle.

magnetic reflections will be equal. As can be seen from Fig. 2a, for the concentrations $X=0.002$ and $X=0.003$, at temperatures respectively below 100 and 125 K the intensities of the (011) and (101) reflections have different magnitudes, the constancy of the intensities of the reflections upon further decrease of the temperature indicating that the process of rotation of the spins has already come to an end. The angle of inclination of the spins with respect to the a axis of the crystal, as determined from the intensity ratio, was, after the reorientation, 60° for the $X=0.003$ composition and 38° for the $X=0.002$ composition (Fig. 1b), which agrees with the data obtained in the magnetic measurements. For the $X=0.01$ composition the intensities of the (011) and (101) reflections below the reorientation temperature were equal, which indicates the total reorientation of the spins (the transition $G_xF_z \rightarrow G_zF_x$). For the purpose of explaining the occurrence of spin reorientation when Fe^{3+} ions are substituted by Co^{2+} ions, and also for the purpose of understanding a number of distinctive features of the magnetic behavior of the cobalt-substituted compounds—in particular, the unusual reorientation transitions $G_x \rightarrow G_{xz}$—we measured the torque curves $L(\varphi)$ (φ is the angle between the direction of the magnetic field H and the c axis of the crystal). The measurements were carried out in a field whose intensity was such that the difference $\theta - \varphi$ (θ is the angle between the weakly-ferromagnetic moment $\mathbf{m}$ and the c axis) was small (~10°). In this case we can easily obtain the curves $L(\theta)$ from the experimentally measured dependences $L(\varphi)$, using the relation

$$\theta - \varphi = \arcsin \frac{L}{H(m_0 + \chi_\perp H)}.$$

From the functions $L(\theta)$ we determined the second-order (K_u) and fourth-order (K_b) anisotropy constants[5] in accordance with the formula

$$L(\theta) = K_u \sin 2\theta + 4K_b \sin 4\theta.$$

Figure 3 shows the isotherms of the dependence of the rotating moment on the angle θ for $X=0.0024$ and $H=70$ kOe. It can be seen from the figure that the fourth-order anisotropy constant K_b for the cobalt-substituted compound is very large, and the relationship between K_u and K_b varies significantly with temperature.

We computed the second-order, K_1^{Co}, and fourth-or-

der, K_2^{Co}, anisotropy constants per Co^{2+} ion from the formulas

$$K_1=N[XK_1^{Co}+(1-X)K_1^{Fe}], \quad K_2=XNK_2^{Co},$$

where N is the number of Co^{2+} and Fe^{3+} ions in one gram, K_1^{Fe} is the anisotropy constant of the Fe^{3+} ions, X is the concentration, and K_1 and K_2 are the anisotropy constants of the cobalt-substituted orthoferrite in the free-energy expansion:

$$F=F_0+K_1\sin^2\theta+K_2\sin^4\theta, \quad K_1=-(K_u+8K_b), \quad K_2=8K_b.$$

The constant K_1^{Fe}, determined for unsubstituted yttrium orthoferrite, is equal to 0.14 cm^{-1} and is virtually temperature independent. The temperature dependences of K_1^{Co} and K_2^{Co} for the $X=0.002$, $X=0.0024$, and $X=0.003$ compounds are shown in Fig. 4. The good agreement between the anisotropy constants obtained from the measurements on the various compositions implies a linear dependence of K_1 and K_2 on X, which indicates the mono-ionic character of the anisotropy. As can be seen from Fig. 4, K_1^{Co} differed in sign from K_1^{Fe}, significantly exceeded it in magnitude, and exhibited considerable growth with decreasing temperature, which is the cause of the occurrence of spin reorientation in the cobalt-substituted orthoferrites.

The fourth-order anisotropy constant of cobalt ions is also large, positive, and strongly temperature dependent. The large K_1^{Co} and K_2^{Co} values can be explained by the fact that, for Co^{2+} ions, the orbital angular momentum is not quenched in the octahedral surroundings, and the spin–orbit coupling, which is responsible for the appearance of the anisotropy, appear already in first-order perturbation theory.

The large magnitude of the fourth-order anisotropy constant for the Co^{2+} ions explains a number of distinctive features of the magnetic behavior of the cobalt-substituted orthoferrites. In particular, for small Co^{2+} contents ($0.0013<X<0.003$), an unusual angular spin configuration is observed at low temperatures ($\theta<\pi/2$), since the orientation of the magnetic moment in the ac plane is determined (according to[6]) by the relation $\sin^2\theta=-K_1/2K_2$. With the large magnitude of the anisotropy constant K_2 is also connected the fact that the spin-reorientation transition for a cobalt-substituted orthoferrite extends over a temperature interval ~100°. The influence of K_2 also affected the character of the $H_r(T)$ phase diagrams.

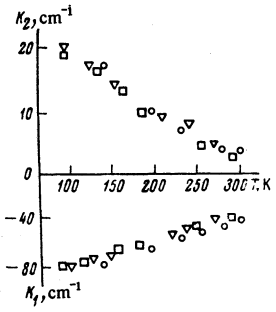

FIG. 4. Dependences of the magnitudes of the second-order, K_1, and fourth-order, K_2, anisotropy constants per Co^{2+} ion for samples with Co^{2+} ion contents: ○) $X=0.0031$; □) $X=0.0024$; △) $X=0.002$.

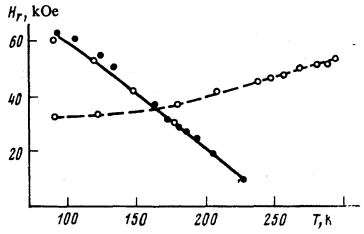

FIG. 5. The phase diagrams $H_r(T)$ for $H\parallel a$-axis (dashed curve) and $H\parallel c$-axis (continuous line): ○) H_r from isotherms of the rotating moment, ●) H_r from isotherms of the magnetostriction.

Figure 5 shows the $H_r(T)$ phase diagram ($H\parallel c$, $H\parallel a$) for the $X=0.0024$ compound, for which the G_xF_z spin configuration is observed above 240 K and the magnetic moment is stably orientated at an angle of 53° to the c axis of the orthorhombic crystal ($G_{xz}F_{zx}$) in the temperature interval from 80 down to 4.2 K. In contrast to the usually observed—in the orthoferrites—reorientation transitions $G_xF_z \rightleftarrows G_zF_x$, which are realized through two second-order phase transitions, in this case for $H=0$ we clearly have only one second-order phase transition, which occurs at the moment of departure of the spins from the c axis of the crystal. The magnetic field applied along the c axis shifts (Fig. 5) the $G_xF_z \rightarrow G_zF_x$ transition toward the region of lower temperatures. For $H\parallel a$-axis the transition $G_xF_z \rightarrow G_{xz}F_{zx}$ disappears and there arise the transitions $G_{xz}F_{zx} \rightarrow G_zF_x$ at $T<240$ K and $G_xF_z \rightarrow G_zF_x$ at $T>240$ K. The threshold fields of the transitions $G_xF_z \rightleftarrows G_zF_x$, $G_{xz}F_{zx} \rightarrow G_xF_z$, and $G_{xz}F_{zx} \rightarrow G_zF_x$ were determined from the isotherms $L(H)$[7] and from the isotherms of the field dependence of the magnetostriction $\Delta l/l$ for H parallel to the axes a and c. In both cases, as the value of H_r, we took the field in which the process of rotation of the spins is completed. The threshold fields determined from the H dependences of $\Delta l/l$ and L are in good agreement with each other (Fig. 5). The variation of the threshold fields with temperature is connected with the strong temperature dependence of the anisotropy constants of the Co^{2+} ions (Fig. 4). As can be seen from Fig. 5, the slopes of $H_r^a(T)$ and $H_r^c(T)$ are different; this is explained by the fact that, contrary to what is usually done in the analysis of the $G_xF_z \rightleftarrows G_zF_x$ transitions in the orthoferrites, we cannot neglect the temperature dependence of the fourth-order anisotropy constants K_2 in the case of the cobalt-substituted orthoferrites. Indeed, it follows from the thermodynamic analysis[8] that

$$H_r^c=\frac{2K_1}{m}, \quad H_r^a=\frac{2(K_1+2K_2)}{m}.$$

For the Co^{2+} ions, the derivative dK_2/dT is comparable to dK_1/dT (Fig. 4), which is responsible for the large differences in the slopes of $H_r(T)$ along the a and c axes of the orthorhombic crystal (Fig. 5).

Thus, it has been experimentally established that all the principal distinctive features of the magnetic behavior of the cobalt-substituted yttrium orthoferrites, to wit, the presence and considerable extent of reorientation transitions, the existence of unusual stable angu-

lar spin configurations, $\theta < \pi/2$, at low temperatures, as well as the different slopes of $H_\tau^c(T)$ and $H_\tau^a(T)$, are connected with the large magnitudes of the second- and fourth-order anisotropy constants measured by us and the strong dependence of these constants on temperature.

In conclusion, we consider it our pleasant duty to express our thanks to A. K. Gapeev for carrying out the x-ray spectral analysis of the compositions of the investigated samples and to A. K. Zvezdin and V. M. Matveev for fruitful discussions.

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Threshold piezoelectric instability in a liquid crystal

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The threshold characteristics of a new type of piezoelectric instability in a finite-thickness nematic layer are calculated as a function of the frequency of the applied electric field.

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1. As is well known,[1] a peculiar piezoelectric effect exists in nematic liquid crystals, caused by the linear coupling between the electric polarization and the orientation of the strains of the mesophase. The corresponding contribution to the free energy of a liquid crystal, placed in an external electric field **E**, can be expressed in the following form by starting out with the symmetry properties of the mesophase in the following manner:

$$\delta\mathcal{F} = -\int [e_1(\mathbf{En})\operatorname{div}\mathbf{n} + e_2\mathbf{E}(\mathbf{n}\nabla)\mathbf{n}]d^3\mathbf{r}, \quad (1)$$

where **n** is the "director" of the liquid crystal, and e_1 and e_2 are the piezomoduli. By minimizing the total free energy $\mathcal{F} = \mathcal{F}_0 + \delta\mathcal{F}$, where

$$\mathcal{F}_0 = \frac{1}{2}\int \left[K_{11}(\operatorname{div}\mathbf{n})^2 + K_{22}(\mathbf{n}\operatorname{rot}\mathbf{n})^2 + K_{33}[\mathbf{n}\operatorname{rot}\mathbf{n}]^2 - \frac{\varepsilon_a}{4\pi}(\mathbf{En})^2\right]d^3\mathbf{r}, \quad (2)$$

K_{jj} are the elastic moduli, and ε_a is the dielectric anisotropy, Meyer has shown that a periodic distribution $\mathbf{n}(\mathbf{r})$ is produced in an unbounded liquid crystal by an electric field. Here, if the director **n** in the unperturbed state is parallel to the x axis and the field **E** is directed along the z axis (Fig. 1), the angle of inclination θ of the director **n** to the x axis in the xz plane is given by the expression[1]

$$\theta = e_1 E x / K_{11} \quad (3)$$

at $e_2 = -e_1$, $K_{11} = K_{33}$, and $\varepsilon_a = 0$. We note that in the given case the effect is not a threshold one and that the angle θ changes by an amount π at a distance $x_0 = \pi K_{11}/e_1 E$, i.e., a domain picture periodic along the x axis and parallel to the y axis should appear. This effect was generalized in the work of Dmitriev[2] to the case of finite values of the dielectric anisotropy ε_a. In particular, it was shown that this type of instability can take place only upon satisfaction of the following inequality:

$$|\varepsilon_a| < e_1^2\pi^3/K_{11}. \quad (4)$$

We note that the absence of a threshold in the effect considered above is connected with the unboundedness of the medium. In the liquid-crystal layer of finite thickness, the role of the boundary conditions at the solid surfaces is decisive, and generally such a piezoeffect should have a threshold character. The distribution (3)

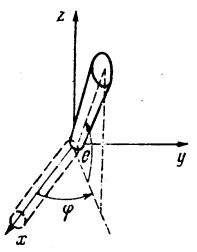

FIG. 1. Perturbations of the molecular orientation.