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MAGNETOELASTIC PROPERTIES OF RARE-EARTH ORTHOFERRITES

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INTRODUCTION

THERE has been great interest in recent years in investigations of the magnetic properties of rare-earth orthoferrites in connection with the revealed possibilities of using these substances as highly effective magnetic materials, especially for computer technology.[1]

The study of the magnetic properties of rare-earth orthoferrites was initiated by French scientists[2,3] on polycrystalline samples and was continued by Americans[4,5] on single crystals. It was established in these investigations that rare-earth orthoferrites are weakly-magnetic substances with antiferromagnetic behavior.

A more intense stage in the development of research on the magnetic properties of rare-earth orthoferrites began after the Soviet scientists Borovik-Romanov[6] and Dzyaloshinskiĭ[7] discovered a new class of magnetically ordered substances—noncollinear antiferromagnets ("weak" ferromagnets). It was shown in [4,8] that rare-earth orthoferrites are "weak" ferromagnets with very interesting properties. For many years, this approach to research on rare-earth orthoferrites attracted the persistent interest of many researchers.

In spite of the great present interest in research on orthoferrites, many of their properties are only just beginning to be studied. In particular, there have been practically no studies of the elastic and magnetoelastic properties of orthoferrites, knowledge of which is essential for dynamic measurements and for their practical utilization.

In the present review we present data on the magnetoelastic properties of rare-earth orthoferrites, which the present authors and their co-workers were the first to study. We discuss in detail the behavior of these properties following spin reorientation. We present also results of an investigation of the influence of unilateral and hydrostatic pressure on the temperature of the reorientation. To understand the presented results, let us stop first to discuss in greater detail the nature of magnetic transitions connected with spin reorientation.

1. SPIN REORIENTATION IN RARE-EARTH ORTHOFERRITES

Rare-earth orthoferrites with the general formula $MFeO_3$, where M is an ion of a rare-earth element or of yttrium (space group P_{bnm}-D_{2h}^{16}) are complex compounds where an antiferromagnetic structure ordered in first approximation can be formed both by the spins of the iron ions and by the rare-earth ions. At high temperatures, the weak ferromagnetism of the orthoferrites is due to the noncollinear arrangement of the spins of the iron ions, and the rare-earth ions are in a disordered paramagnetic state. According to neutron-diffraction data,[9] the spins of the iron ions form an antiferromagnetic structure of type G (checkerboard order) with an antiferromagnetism vector oriented at high temperatures along the a-axis of the rhombic crystal. With decreasing temperature there is observed in a large number of orthoferrites a spontaneous reorientation of the antiferromagnetism vector towards the c-axis of the crystal, and the weak ferromagnetic moment goes over from the c axis to the a axis of the crystal. The reorientation of the magnetic moment is observed also upon application of an external magnetic field along the antiferromagnetism axis.[10,11] From such experiments one can determine the values of the internal effective fields, an important factor for the theory of antiferromagnetism.

It was shown in [12,13] that spin reorientation in orthoferrites does not occur instantaneously, but extends over a temperature interval on the order of several times 10°. The first anisotropy constant of orthoferrites for which the spin reorientation phenomenon is observed depends strongly on the temperature,[11,13] reversing sign upon reorientation of the spins (Fig. 1). In the temperature region where the first anisotropy constant is small, the second anisotropy constant may exert a significant influence. The expansion of the free energy with allowance for the anisotropy terms of higher

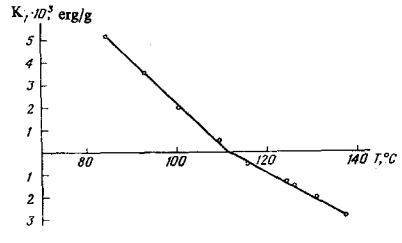

FIG. 1. Temperature dependence of the first anisotropy constant of the single crystal $Eu_{0.25}Sm_{0.75}FeO_3$.

order can be written in the following manner:

$$F=\frac{1}{2}Am^2+\frac{1}{2}b_1l_x^2+\frac{1}{2}b_3l_z^2+d_1m_xl_z-d_3m_zl_x+\frac{1}{4}e_1l_x^4+\frac{1}{4}e_2l_x^2l_z^2+\frac{1}{4}e_3l_z^4, \quad (1)$$

where m is the magnetic-moment vector, l the antiferromagnetism vector [(m·l) = 0, $l^2 + m^2 = 1$], A the exchange-interaction constant, b_1 and b_3 the constants of the relativistic interactions of second order, e_1, e_2, and e_3 the constants of relativistic interactions of order IV, and d_1 and d_3 the constants of the exchange-relativistic interactions. Introducing the angle θ between the vector m and the c-axis of the crystal, assuming that the rotation occurs in the ac plane, and substituting in (1) the equilibrium values of m, we obtain for the energy an expression analogous to that obtained empirically in [12]:

$$F=F_0+\frac{K_u}{2}\cos 2\theta+K_b\cos 4\theta, \quad (2)$$

where F_0 is the part of the free energy independent of the orientation of the magnetic moment,

$$K_u=\frac{1}{2}\left(b_1-b_3+\frac{1}{2}e_1-\frac{1}{2}e_3+\frac{d_1^2-d_3^2}{A}\right),\qquad K_b=\frac{1}{16}\left[-\frac{(d_1-d_3)^2}{A}+\frac{e_1}{2}+\frac{e_2}{2}+\frac{e_3}{2}\right]. \quad (3)$$

Minimizing the energy with respect to the angle θ, we obtain three equilibrium states of the system:

$$\left.\begin{array}{lll} \text{I.} & \sin\theta=0 & \text{for temperatures } T\gg T_2,\\ \text{II.} & \cos\theta=0 & \text{for temperatures } T\ll T_1,\\ \text{III.} & \sin^2\theta=\frac{K_u+8K_b}{8K_b} & \text{for temperatures } T_1<T<T_2. \end{array}\right\} \quad (4)$$

The temperatures T_1 and T_2 are determined from the condition

$$K_u(T_1)=8K_b, \quad (5)$$

$$K_u(T_2)=-8K_b. \quad (6)$$

The quantity K_b can be determined from the torque curves. For the orthoferrite $Sm_{0.75}Eu_{0.25}FeO_3$, K_b is positive and depends little on the field, and its magnitude is 0.5×10^3 erg/g.[13] Positiveness of the second anisotropy constant is observed also for other orthoferrites, leading to certain distinguishing features in the character of the transition following the spin reorientation. When the orthoferrites are cooled below T_2 there appear, in place of one easy-magnetization direction along the c axis (solution I), two directions that are symmetrically disposed about the c-axis at an angle θ to it (solution III), and during the course of the cooling of the crystal the splitting angle increases, reaching 45° at $K_u = 0$, after which, on approaching T_1, both directions contract to the a-axis, i.e., a state corresponding to solution II is realized. The splitting of the direction of the easy magnetization can be seen easily on the torque curves of compositions where the anisotropy of the susceptibility of the rare-earth ions is small.[12,13] It was shown in [13] that at temperatures T_1 and T_2 in orthoferrites, in the absence of a field, there exist two second-order phase transitions, corresponding to the beginning and the end of the reorientation process.

It should be noted that in the presence of an external magnetic field, the character of the phase transitions following the spin reorientation in the orthoferrites changes. According to [14], the expression for the free energy in the presence of an external field is written, after minimization, in the following manner:

$$F=F_0+\frac{M_0H^2}{2A}\sin^2(\varphi-\theta)+\frac{d_3-d_1}{2A}M_0H\cos(\varphi-\theta)+\frac{(d_1+d_3)M_0H}{2A}\cos(\varphi-\theta)\cos 2\theta+\frac{K_u}{2}\cos 2\theta+K_b\cos 4\theta, \quad (7)$$

where H is the external magnetic field, M_0 is the magnetization of the sublattice, φ the angle between the direction of the magnetic field and the c axis, and the remaining symbols are the same as in formula (1). Minimization of the energy for a field parallel to the c axis of the crystal results in two classes of solutions:

$$\left.\begin{array}{l} \text{I. } \sin\theta=0,\\ \text{II. } \cos^3\theta-\frac{3(\sigma_3-\sigma_1)}{4K_2}\cos^2\theta-\left(1-\frac{K_1}{2K_2}+\frac{\chi_\perp H^2}{4K_2}\right)\cos\theta-\frac{\sigma_1 H}{4K_2}=0; \end{array}\right\} \quad (8)$$

Here $\sigma_1 = M_0d_1/A$ and $\sigma_3 = M_0d_3/A$ are the spontaneous magnetizations along the a and c axes, $\chi_\perp = M_0^2/A$ is the transverse susceptibility, $K_1 = -(K_u + 8K_b)$, and $K_2 = 8K_b$. The first solution corresponds to the minimum of the energy at any value of the magnetic field H for temperatures $T > T_2$, and also for $T < T_2$ if $H \geq H_n(T)$, where

$$H_n(T)=-\frac{3\sigma_3-2\sigma_1}{3\chi_\perp}+\sqrt{\frac{(3\sigma_3-2\sigma_1)^2}{4\chi_\perp^2}+\frac{2(K_u+8K_b)}{\chi_\perp}}. \quad (9)$$

The second solution is realized for $T < T_2$ if $H \leq H_n(T)$. Formula (9) coincides with that obtained in [10] for orthoferrites, where the condition $\sigma_1 = \sigma_3$ is satisfied. The relation $\theta = \theta(T, H)$ for samarium orthoferrite was calculated from Eq. (8).[14] Figure 2 shows the temperature dependence of the polar angle, which determines the orientation of the magnetization of the orthoferrite in the ac plane, in dimensionless units $\theta/(\pi/2)$ against $(T - T_1)/(T_1 - T_2)$ at several values of the parameter $x = \chi_\perp H/(3\sigma_3 - 2\sigma_1)$, for a field directed along the c axis. In the absence of a field, when the temperature decreases from the value T_2, the magnetic moment gradually turns from the c axis to the a axis of the crystal, and at temperatures $T < T_1$ it becomes parallel to the a axis. As mentioned above, at the temperatures T_1 and T_2, in the absence of a field, there exist two second-order phase transitions, corresponding to the start and the end of the reorientation process. For

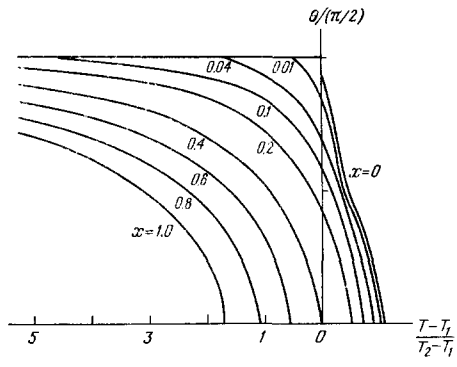

FIG. 2. Temperature dependence of the polar angle θ for a field applied along the c axis at several values of the parameter $x = \chi_\perp H/(3\sigma_3 - 2\sigma_1)$.

a field parallel to the c axis, when the temperature decreases from the value

$$T_2(H)=T_2(0)-\frac{H\{T_2(0)-T_1(0)\}(3\sigma_3-2\sigma_1+\chi_\perp H)}{32K_b} \qquad (10)$$

the magnetic moment gradually turns from the c axis to the a axis, but does not reach the latter, and the larger H, the smaller the angle from the c axis to which the rotation of the magnetic moment takes place at a fixed temperature. It was shown in [14] that when a magnetic field is applied along the c axis, there remains one phase transition at the temperature $T_2(H)$, instead of the two second-order phase transitions observed in the absence of the field. Assuming that $\sigma_1 = \sigma_3 = \sigma_0$, which agrees with the experimental results for certain orthoferrites, we can assume that the shift of the temperature T_2 under the influence of the external magnetic field H is equal to

$$\Delta T_2(H)=\frac{H\Delta T(0)(\sigma_0+\chi_\perp H)}{32K_b} \qquad (11)$$

Analogously, upon application of an external magnetic field along the a axis of the crystal, there should be observed one second-order phase transition at a temperature $T_1(H)$ given by the formula

$$T_1(H)=T_1(0)+\frac{H\Delta T(0)(\sigma_0+\chi_\perp H)}{32K_b}. \qquad (12)$$

2. ELASTIC PROPERTIES OF ORTHOFERRITES AND FEATURES OF THEIR BEHAVIOR NEAR THE SPIN-REORIENTATION TEMPERATURE

The first investigation of the elastic properties of orthoferrites was undertaken in [15], where a study was made of the temperature dependence of the Young's modulus of single-crystal thulium orthoferrite along the a, b, and c axes of the crystal in the temperature interval from 4.2 to 300°K. Measurements of Young's modulus were made by the compound-vibrator method at a frequency of 150 kHz. The results of the measurements are shown in Figs. 3 and 4. The values of Young's modulus along different axes of the crystal differ little from one another (at 78°K, $E_a = 1.89 \times 10^{12}$, $E_b = 1.83 \times 10^{12}$, and $E_c = 1.92 \times 10^{12}$ erg/cm^3). With increasing temperature there is observed, against the background of the monotonic decrease of Young's modulus, a sharp drop in the value of the modulus in the temperature interval 80–92°K. It is known that a spontaneous reorientation of the spins takes place in thulium orthoferrite in the indicated temperature interval, and the two jumps of Young's modulus at $T_1 = 80$°K and $T_2 = 92$°K correspond apparently to two second-order phase transitions. The observed anomaly of Young's modulus in $TmFeO_3$ can be explained by starting from a thermodynamic analysis. When an external stress is applied along the c axis of the crystal, the total free energy of the crystal, which includes, besides the magnetic energy, also the elastic and magnetoelastic energies and the energy of the external stresses in the spin-reorientation region, in the ac plane, can be written as follows:

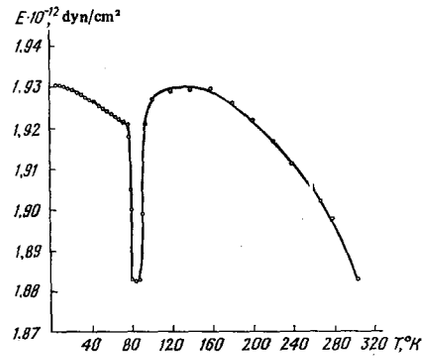

FIG. 3. Temperature dependence of the Young's modulus of single-crystal thulium orthoferrite, measured along the c axis of the crystal.

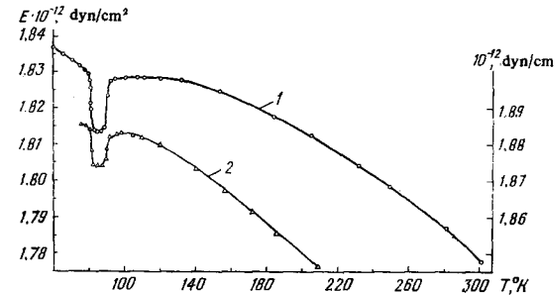

FIG. 4. Temperature dependence of Young's modulus of single-crystal thulium orthoferrite, measured along the a axis (curve 1, scale on the left) and along the b axis (curve 2, scale on the right) of the crystal.

$$F=F_0+K_1\sin^2\theta+K_2\sin^4\theta+L_z\xi_z\sin^2\theta+\frac{1}{2}M_z\xi_z^2\sin^2\theta+\frac{E_{0z}}{2}\xi_z^2+\xi_z p_z. \qquad (13)$$

where F_0 is the part of the energy that does not depend on the orientation of the antiferromagnetism vector and on the strain ξ_z, K_1 and K_2 are the first and second magnetic-anisotropy constants ($K_1 = -(K_U + 8K_b)$, $K_2 = 8K_b$), L_z and M_z are the constants of the magnetoelastic energy, E_{0z} is Young's modulus, p_z is the external stress, and ξ_z is the relative strain along the c axis of the rhombic crystal. Then the equilibrium values of ξ_z and θ can be obtained from the condition of the energy minimum:

$$\frac{\partial F}{\partial\xi_z}=0,\quad \frac{\partial F}{\partial\sin^2\theta}=0, \qquad (14)$$

$$L_z\sin^2\theta+p_z+[E_{0z}+M_z\sin^2\theta]\xi_z=0, \qquad (15)$$

$$K_1+2K_2\sin^2\theta+L_z\xi_z+\frac{1}{2}M_z\xi_z^2=0. \qquad (16)$$

Substituting the value obtained from (8) and (7) for $\sin^2\theta = -K_1/2K_2 - L_z\xi_z/2K_2$ and neglecting terms quadratic in ξ_z, we obtain

$$\xi_z=\frac{L_zK_1}{E_z2K_2}-\frac{p_z}{E_{0z}-\frac{K_1M_z}{2K_2}-\frac{L_z^2}{2K_2}}. \qquad (17)$$

At temperatures $T < T_1$, when $\sin\theta = 1$, we have

$$E_z=E_{0z}+M_z, \qquad (18)$$

At $T > T_2$, when $\sin\theta = 0$, we have

$$E_z=E_{0z}. \qquad (19)$$

In the temperature region $T_1 < T < T_2$, where the spontaneous spin reorientation is observed, Young's modulus decreases in accordance with (17) and becomes equal to

$$E_z=E_{0z}-\frac{K_1M_z}{2K_2}-\frac{L^2}{2K_2}. \qquad (20)$$

Consequently, at the temperatures T_1 and T_2 there should be observed two jumps of Young's modulus, corresponding to two second-order phase transitions. According to (13), the jump of Young's modulus on the right at the temperature T_2 = 92°K should be equal to

$$\Delta E_2 = \frac{L_z^2}{2K_2}, \qquad (21)$$

since the first anisotropy constant K_1 vanishes at T_2. Thus, knowing the second anisotropy constant ($K_2 = 4 \times 10^3$ erg/g $\approx 30 \times 10^3$ erg/cm^3) we can determine, from the value of the jump of Young's modulus along the c axis (see Fig. 3), the absolute value of the magnetoelastic constant L_Z, which turns out to equal $5 \times 10^7 \pm 0.5 \times 10^7$ erg/cm^3. As seen from Fig. 3, the values of Young's modulus at the temperatures T_1 and T_2 are somewhat different from each other. According to relations (18) and (19), it is possible to determine the second magnetoelastic constant $M_Z = (6 \pm 0.6) \times 10^9$ erg/cm^3 from the difference in the values of Young's modulus at T_1 and T_2. We also observed analogous anomalies in the temperature dependence of Young's modulus following spin orientation upon application of stresses along the a and b axes of the crystal (see Fig. 4). From the values of the jumps of the Young's modulus we determined the values of the first magnetoelastic constants along the a and b axes.

$|L_x| = (2.2 \pm 0.2) \cdot 10^7$ erg/cm^3, $|L_y| = (2.8 \pm 0.3) \cdot 10^7$ erg/cm^3,

and from the difference of the values of Young's modulus at the temperatures T_1 and T_2 we determined the second magnetoelastic constants $M_X = -(3 \pm 0.3) \times 10^9$ erg/cm^3 and $M_Y = -(3.5 \pm 0.4) \times 10^9$ erg/cm^3.

The magnetoelastic constants $L_{X,y,z}$ and the elastic moduli $E_{X,y,z}$ can be expressed in terms of the constants δ_i and λ_i with the aid of which the magnetoelastic and elastic energies of the orthoferrites were expressed in [16]. In [14], measurements were made of the temperature dependence of Young's modulus of single-crystal thulium orthoferrite in the absence of a field and with a magnetic field applied along the c and a axes of the crystal. Figure 5 shows the temperature dependence of Young's modulus measured along the c axis of the crystal. It is seen that whereas in the absence of the field two jumps of the Young's modulus are observed at temperatures T_1 = 80°K and T_2 = 92°K, in a field parallel to the c axis only one jump is observed at $T_2(H)$ = 90°K, and the second transition becomes smeared out. The experimentally observed decrease of the temperature T_2 in a field of 1.5 kOe ($\Delta T_2 \approx 2°$) is in good agreement with the value calculated from formula (11).

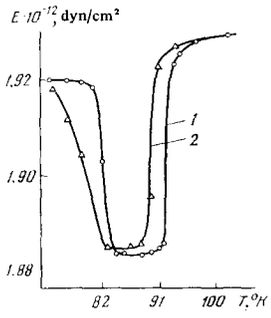

FIG. 5. Temperature dependence of Young's modulus of single-crystal thulium orthoferrite measured along the c axis in the absence of a magnetic field (curve 1) and in a field applied along the c axis of the crystal (curve 2).

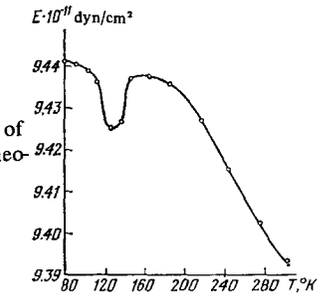

FIG. 6. Temperature dependence of Young's modulus of polycrystalline neodymium orthoferrite.

In the field applied along the a axis of the crystal there was observed an increase of the temperature T_1; the character of the transition at this temperature remained the same, while the second phase transition at the temperature T_2 vanished.

In connection with the presence of a distinct anomaly in the spontaneous reorientation of the spins, it is possible to determine the region of reorientation more accurately from the temperature dependence of Young's modulus than from magnetic measurements, in which the presence of the magnetic field changes the character of the transition and shifts the reorientation temperature. In addition, from the temperature dependence of Young's modulus it is possible to determine the temperature region where the reorientation of the spins is observed, not only in single crystals but also in polycrystalline samples, something impossible to do in magnetic measurements. This is connected with the fact that, as seen from Figs. 3 and 4, Young's modulus decreases along the three principal axes of the crystal upon reorientation of the spins, giving grounds for expecting a decrease of Young's modulus following spin reorientation in polycrystals, too. Figure 6 shows the temperature dependence of Young's modulus for a polycrystalline sample of neodymium orthoferrite. We see that in a definite temperature interval centered at ~130°K there is observed a noticeable anomaly of Young's modulus, and the region of the reorientation amounts to approximately 40°.

The phenomenon of spin reorientation in single-crystal neodymium orthoferrite was observed relatively recently in torque-curve measurements.[17]

The process of reorientation in the neodymium single crystal was gradual and spanned a temperature interval ~40° with center at 145°K. Some difference in the temperature of the center of the reorientation region for poly- and single-crystal neodymium orthoferrite can be explained as being due to the fact that Fe^{2+} ions, which, according to the published data, can change the reorientation temperature, can appear in single crystals grown from a melt of lead compounds. Thus, from the temperature dependence of Young's modulus of orthoferrites it is possible to determine reliably the temperature region where spin reorientation is observed, and the indicated method is almost the only simple method with the aid of which it is possible to observe the reorientation of spins in polycrystals. We have also measured Young's modulus in torsional vibrations in the three principal planes of a rhombic crystal, i.e., perpendicular to the a, b, and c axes. The obtained values of the shear modulus G_{XY}, G_{YZ}, and G_{XZ} differed by not more than 10%, which is within the limits of the

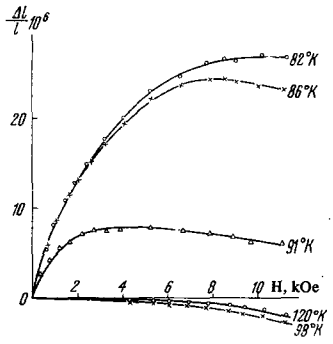

FIG. 7. Variation of the longitudinal magnetostriction of thulium orthoferrite along the c axis of the crystal.

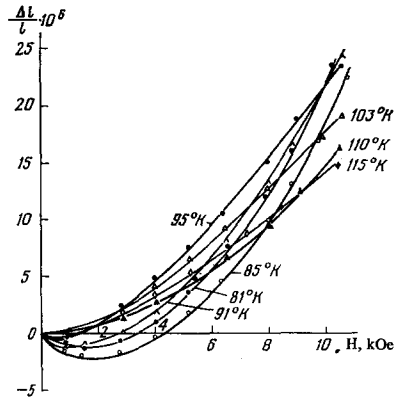

FIG. 8. Magnetostriction of thulium orthoferrite along the b axis at H parallel to the c axis.

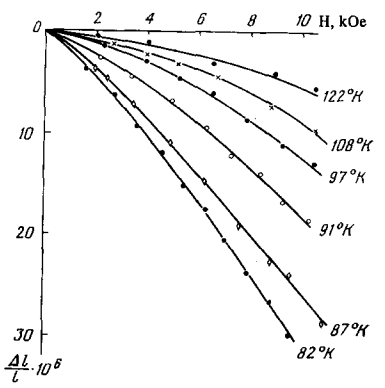

FIG. 9. Magnetostriction of thulium orthoferrite along the a axis with H parallel to the c axis.

experimental accuracy, and were equal to $(0.67 \pm 0.07) \times 10^{12}$ erg/cm^3.

Magnetostriction of Certain Rare-earth Orthoferrites

The first measurement of the longitudinal magnetostriction along the c axis of a thulium orthoferrite crystal was carried out in [18]. The measurements were made on single crystals grown by V. A. Timofeeva at the Institute of Crystallography of the USSR Academy of Sciences, by the method of spontaneous crystallization from the solution in a melt of lead compounds. The magnetostriction was measured in the temperature interval from 70 to 300°K in magnetic fields up to 15 kOe. It was shown that an external magnetic field applied along the c axis of the crystal causes an appreciable positive magnetostriction in the temperature interval from 86 to 70°K. The magnitude of the magnetostriction in a field of 15 kOe reached a maximum at 78°K ($\sim 20 \times 10^{-6}$), and then decreased with decreasing temperature. The occurrence of magnetostriction upon application of a field along the c axis of the crystal, which is the antiferromagnetism axis at low temperatures, was explained as being due to the deformation of the crystal following the turning of the antiferromagnetic iron sublattices. The relatively low value of the threshold field (~ 15 kOe) at 78°K was attributed to the small value of the first anisotropy constant, which goes through zero in the temperature region where the spontaneous spin reorientation is observed. The decrease of the magnetostriction in a field of 15 kOe with decreasing temperature is obviously connected with the fact that the anisotropy constant, and consequently also the value of the threshold field, increase with increasing distance from the reorientation temperature.

The longitudinal magnetostriction along the a, b, and c axes of a thulium orthoferrite single crystal [19] grown by the crucible-less zone melting method in the problem laboratory of the Moscow Power Engineering Institute, was measured recently in our laboratory. The measurements of the longitudinal magnetostriction along the c axis of the crystal (Fig. 7) agree qualitatively with the results described above, although the magnitude of longitudinal magnetostriction was somewhat larger ($\sim 27 \times 10^{-6}$).

The magnetostrictions of thulium orthoferrite along the a, b, and c axes of the crystal with the field applied along the c axis of the crystal (Figs. 7, 8, and 9) differ both in magnitude and in sign. At temperatures below 95°K the magnetostriction has a complicated dependence on the field. Thus, the magnetostriction along the b axis of the crystal in a weak field is negative, and then reverses sign with increasing field and increases rapidly in magnitude. At higher temperatures, the magnetostriction depends quadratically on the field, thus evidencing that at these temperatures it is due mainly to the paramagnetism of the rare-earth ions. As seen from Figs. 7, 8, and 9, the magnetostriction due to the paramagnetism of the rare-earth ions along different axes of the crystal is anisotropic. The anisotropy of the paramagnetic magnetostriction was observed by us also upon application of a field along the a and b axes of the crystal.

The results obtained on the magnetostriction of the rare-earth ions can be discussed within the framework of the phenomenological analysis. The expression for the magnetoelastic energy [16,19] connected with the magnetization of the rare-earth ions with allowance for the symmetry of the crystal can be written as follows:

$$\begin{aligned} F_{\text{m.e.}} = {} & [\Lambda_1 (M_x^2 - M_z^2) + \Lambda_2 (M_y^2 - M_z^2)] U_{xx} \\ & + [\Lambda_3 (M_x^2 - M_z^2) + \Lambda_4 (M_y^2 - M_z^2)] U_{yy} \\ & + [\Lambda_5 (M_x^2 - M_z^2) + \Lambda_6 (M_y^2 - M_z^2)] U_{zz} \\ & + 2\Lambda_7 M_y M_x U_{xy} + 2\Lambda_8 M_x M_z U_{xz} + 2\Lambda_9 M_y M_z U_{xz}; \end{aligned} \tag{22}$$

Here Λ_i are the magnetoelastic constants, $M_{x,y,z} = \chi_{x,y,z} H$ (χ_i —susceptibility of the rare-earth ions), and U_{ij} are the components of the strain tensor of the crystal. Upon application of a field H along the c axis (the z direction) of the crystal, we have

$$M_z = \chi_z H, \quad M_x = M_y = 0,$$

and the expression for the magnetoelastic energy takes the form

$$F_{\text{m.e.}} = -(\Lambda_1 + \Lambda_2) M_z^2 U_{xx} - (\Lambda_3 + \Lambda_4) M_z^2 U_{yy} - (\Lambda_5 + \Lambda_6) M_z^2 U_{zz}. \quad (23)$$

Drawing an analogy between the obtained expression and the expression for the energy of the external stresses[16]

$$F_{\text{e.s.}} = -\sum \sigma_{ij} U_{ij},$$

we can assume that

$$\left.\begin{aligned} U_{xx} &= \frac{(\Lambda_1+\Lambda_2)}{E} M_z^2 - \frac{\mu}{E}(\Lambda_3+\Lambda_4) M_z^2 - \frac{\mu}{E}(\Lambda_5+\Lambda_6) M_z^2, \\ U_{yy} &= -\frac{\mu(\Lambda_1+\Lambda_2)}{E} M_z^2 + \frac{(\Lambda_3+\Lambda_4)}{E} M_z^2 - \frac{\mu(\Lambda_5+\Lambda_6)}{E} M_z^2, \\ U_{zz} &= -\frac{\mu(\Lambda_1+\Lambda_2)}{E} M_z^2 - \frac{\mu(\Lambda_3+\Lambda_4)}{E} M_z^2 + \frac{(\Lambda_5+\Lambda_6)}{E} M_z^2, \end{aligned}\right\} \quad (24)$$

where U_{XX}, U_{YY}, and U_{ZZ} can be regarded as magnetostriction deformations along the a, b, and c axes following application of a field along the c axis of the crystal. In the consideration of the strains we have neglected here the anisotropy of the Poisson coefficient μ and of Young's modulus, since, as indicated above, according to our experimental results from measurement of Young's modulus this anisotropy is small in the case of longitudinal and torsional vibrations.

Analogously, for a field applied along the a axis of the crystal we have

$$F_{\text{m.e.}} = \Lambda_1 M_x^2 U_{xx} + \Lambda_3 M_x^2 U_{yy} + \Lambda_5 M_x^2 U_{zz}, \quad (25)$$

from which we can calculate the magnetostriction strains along the a, b, and c axes of the crystal.

Substituting in the obtained relations our measured values of the magnetostriction along the a, b, and c axes with the field applied along the c and a axes of the crystal, we can calculate for a definite temperature the values of the magnetoelastic constants:

$$\Lambda_1 = (6 \pm 1)\cdot 10^6, \quad \Lambda_2 = (-8.5 \pm 2)\cdot 10^6,$$
$$\Lambda_3 = (-14 \pm 2)\cdot 10^6, \quad \Lambda_4 = (15 \pm 2)\cdot 10^6,$$
$$\Lambda_5 = (0.5 \pm 0.5)\cdot 10^6, \quad \Lambda_6 = (-0.5 \pm 0.5)\ 10^6$$

(Λ_i are given in erg-g^2/cm^{9}G^2). In accordance with [15], we assumed that the Young's modulus is equal to $E = 1.9 \times 10^{12}$ dyne/cm^2 and the Poisson coefficient is $\mu = 0.3$.

Knowing the magnetoelastic constants, it is possible to calculate the paramagnetic magnetostriction upon application of a magnetic field along the b axis, assuming that the magnetoelastic energy has in this case the form

$$F_{\text{m.e.}} = \Lambda_2 M_y^2 U_{xx} + \Lambda_4 M_y^2 U_{yy} + \Lambda_6 M_y^2 U_{zz}. \quad (26)$$

The calculated and directly measured values of the magnetostriction are in good agreement, thus indicating that the assumed analysis is correct. We thus find, in accord with the experimental results, that even if the elastic energy is assumed to isotropic, the magnetoelastic energy of the orthoferrites is strongly anisotropic, owing to the paramagnetism of the rare-earth ions. We consider now the behavior of the orthoferrites at lower temperatures, when, as noted above, the dependence of the magnetostriction on the field has a more complicated character. As mentioned earlier, in thulium orthoferrite in the temperature region 80–90°K there is observed a spontaneous reorientation of the spins of the iron ions. In this connection, upon application of a sufficiently strong magnetic field along the c axis of the crystal, which is the antiferrimagnetism axis of the iron ions at low temperatures, there should be observed, besides the magnetostriction due to the paramagnetism of the rare-earth ions, also magnetostriction due to the turning of the antiferromagnetic iron sublattices. The "turning" magnetostriction is best observed along the c axis of the crystal (see Fig. 7), since the magnetostriction due to the paramagnetism of the rare-earth ions is small along this axis. The presence of a weakly ferromagnetic moment along the c axis of the crystal at high temperatures likewise does not make a noticeable contribution to the magnetostriction, so that the magnetostriction along the c axis is the result mainly of rotation of the vector of antiferromagnetism of the iron ions. To determine the magnitude of the "turning" magnetostriction along the different axes of the crystals it is necessary to subtract from the total magnetostriction the part due to the paramagnetism of the rare-earth ions. The result yields the following values of the magnetostriction due to the turning of the sublattices along the c, a, and b axes of the crystal:

$$\lambda_c = (27 \pm 3)\cdot 10^{-6}, \quad \lambda_a = -(11 \pm 2)\cdot 10^{-6}, \quad \lambda_b = -(11 \pm 2)\cdot 10^{-6}.$$

Assuming the obtained values of the magnetostriction along the a, b, and c axes of the crystal to be equal to the deformations of the lattice along the corresponding axes upon spontaneous reorientation of the spins, we can determine, in accordance with [15], the values of the three magnetoelastic constants in thulium orthoferrite:

$$L_x = \lambda_a E_x = -(2.2 \pm 0.4)\cdot 10^7 \text{ erg/cm}^3,$$
$$L_y = \lambda_b E_y = -(2.2 \pm 0.4)\cdot 10^7 \text{ erg/cm}^3,$$
$$L_z = \lambda_c E_z = (5.4 \pm 0.6)\cdot 10^7 \text{ erg/cm}^3.$$

The obtained values of the magnetoelastic constants agree well with those obtained in [15] from the formula $L_i = \sqrt{\Delta E_i K_2}$, where ΔE_i is the jump of Young's modulus along the a, b, and c axes of the crystal following the reorientation of the spins and K_2 is the second anisotropy constant (see Sec. 2). The determination of the magnetoelastic constants from magnetostriction measurements has the advantage over the method described in [15] that it makes it possible to determine both the magnitude and the sign of the magnetoelastic constants. Knowing the magnetoelastic and elastic constants, we can estimate the contribution of the magnetoelastic and elastic energies to the anisotropy energy. Far from the temperature where the spin reorientation is observed, the anisotropy energy ($\sim 10^5$ erg/cm^3) greatly exceeds the magnetoelastic and elastic energies due to the iron ions ($\sim 10^2$ erg/cm^3). The magnetoelastic energy due to the thulium ions is also small near the reorientation temperature ($\sim 0.5 \times 10^2$ erg/cm^3). However, following the spin reorientation the anisotropy constant passes through zero and the influence of the magnetoelastic and elastic energies becomes appreciable

Together with V. V. Uskov, we also carried out a measurement of the longitudinal magnetostriction along the a, b, and c axes of the crystal at liquid-helium temperature in superconducting-solenoid fields up to 50 kOe (Fig. 10). It is seen from the figure that at 4.2°K the

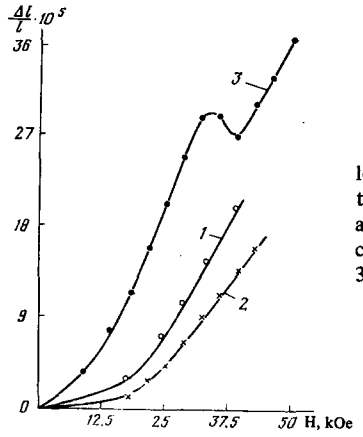

FIG. 10. Dependence of the longitudinal magnetostriction on the field for thulium orthoferrite along the a, b, and c axes of the crystal at 4.2°K, (curves 1, 2, and 3, respectively).

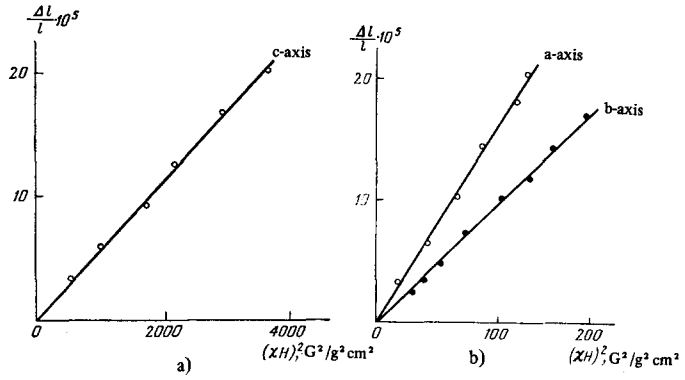

FIG. 11. Dependence of the longitudinal magnetostriction on $(\chi H)^2$ at 4.2°K for single-crystal thulium orthoferrite: a) along the c axis of the crystal, b) along the a and b axes of the crystal.

magnitude of the magnetostriction increased strongly. The maximum value of the magnetostriction was observed along the c axis of the crystal, where a value $\lambda_c \approx -4 \times 10^{-4}$ was observed in a field ~45 kOe. The magnitude of the longitudinal magnetostriction along the a, b, and c axes of the crystal is negative and has an approximately linear dependence on $(\chi H)^2$ (Fig. 11), indicating that it is due mainly to the paramagnetism of the rare-earth ions. The magnetostriction along the c axis of the crystal in a strong magnetic field revealed a strong kink connected apparently with the fact that the c axis is the antiferromagnetism axis at low temperatures, and a field of ~30 kOe is sufficient to cause the turning of the iron sublattices. This assumption is confirmed by the fact that the magnitude of the magnetostriction observed by us earlier along the c axis upon turning of the sublattices in the temperature region where the spin reorientation takes place (Fig. 7) coincides with the value of the magnetostriction jump at 4.2°K at the point of the kink of the $\lambda_c = f(H)$ curve, and has the same sign.

The lattice deformation which is observed upon application of a threshold field along the antiferromagnetism axis of the iron ions should also occur in the absence of the field in the temperature region where the spontaneous spin reorientation takes place. For the purpose of measuring directly the lattice deformation occurring during the spin reorientation, M. M. Umanskiĭ and A. S. Kononenko (see [19]) measured the temperature dependence of the lattice parameters in the orthoferrite $Tm_{0.5}Sm_{0.5}FeO_3$, for which the region of reorientation of the spins has a center at 223°K. It should be noted that for thulium and samarium orthoferrites and for mixed compositions $Tm_xSm_{1-x}FeO_3$ we do not know to this very day the causes of the spin reorientation. It follows from magnetic measurements that in these compounds the spin reorientation is not connected with the interaction between the rare-earth and iron ions, as is the case, for example, for the orthoferrites of holmium, erbium, and ytterbium.[20]

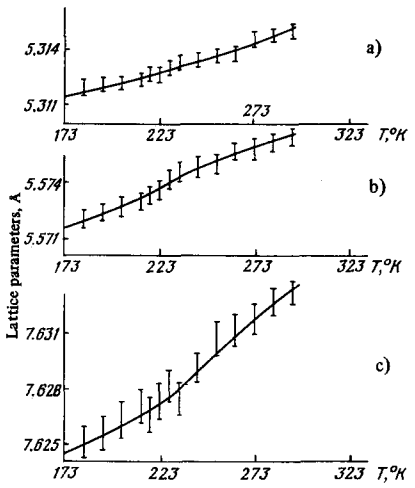

FIG. 12. Temperature dependence of the lattice parameters of single-crystal $Tm_{0.5}Sm_{0.5}FeO_3$.

In the measurement of the temperature dependence of the lattice parameters of $Tm_{0.5}Sm_{0.5}FeO_3$ in the temperature interval 173–300°K it was found that the lattice parameters along the a, b, and c axes of the crystal vary anisotropically with the temperature (Fig. 12). It is possible that the anisotropic variation of the lattice parameters with temperature leads to reversal of the sign of the anisotropy constant and is the cause of the reorientation of the spins in this compound, all the more since, according to the published data,[21] the lattice parameters of lanthanum orthoferrite, for which no spin reorientation is observed, vary with the temperature practically isotropically. As to the jump in the lattice parameters following the spin reorientation, we see from Fig. 12 that its magnitude lies within the limits of the experimental errors and consequently cannot be determined from our measurements. Thus, the magnitude of the deformations following spin reorientation is apparently determined most reliably by measurements of the magnetostriction resulting from the turning of the antiferromagnetic ion sublattices, especially for those orthoferrites where the magnetostriction is small because of the paramagnetism of the rare-earth ions.

3. INFLUENCE OF PRESSURE ON THE SPIN-REORIENTATION TEMPERATURE

The influence of unilateral and hydrostatic pressure on the spin-reorientation temperature in thulium orthoferrite was investigated in our laboratory. To this end, torque curves in the ab plane were obtained without and with pressure. The hydrostatic pressure was produced

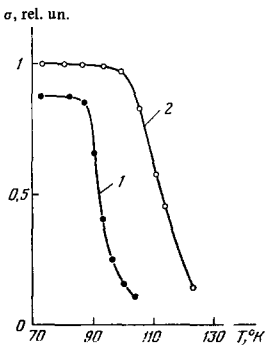

FIG. 13. Temperature dependence of the magnetization of $TmFeO_3$ along the a axis without pressure (curve 1) and under unilateral pressure of 1.5 kbar (curve 2).

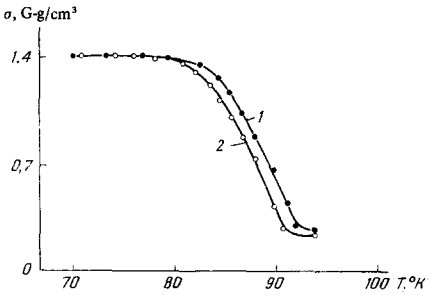

FIG. 14. Temperature dependence of the spontaneous magnetization of thulium orthoferrite along the a axis of the crystal in the absence of pressure (curve 1) and under hydrostatic pressure of 1.5 kbar (curve 2).

by freezing water inside a beryllium bomb. The unilateral pressure was produced by mechanically compressing the sample with a special stopper which was screwed into the body of the bomb. The previously oriented crystal was secured inside the bomb, and the bomb was suspended on bracing wires from the quartz filament of the balance.

Figure 13 shows the temperature dependence of the spontaneous magnetization of thulium orthoferrite along the a axis of the crystal, determined from the torque curves in the ab plane without pressure and under unilateral pressure along the c axis of the crystal $P_Z \approx 1.5$ kbar. We see that the indicated pressure shifts the temperature of the center of the region of reorientation (taken to be the temperature at which a maximum decrease of magnetization is observed) by about 10°. It follows also from the thermodynamic analysis that the application of the unilateral pressure should shift the reorientation temperature. According to (16), recognizing that $K_1 = a(T - T_2)$, where $a = 2K_2/(T - T_2)$, we find that the reorientation temperature for a pressure along the c axis should shift by an amount

$$\Delta T = \frac{L_z p_z}{a E_z}. \qquad (27)$$

If we substitute in this formula the values determined by us

$$L_z = 5 \cdot 10^7 \text{ erg/cm}^3\text{-deg}, \quad E_z = 1{,}9 \cdot 10^{12} \text{ erg/cm}^3\text{-deg},$$

$$a = 5 \cdot 10^3 \text{ erg/cm}^3\text{-deg},$$

then we get $\Delta T \approx 10°$, which is in good agreement with the experimentally observed shift. The influence of hydrostatic pressure on the reorientation temperature was analyzed thermodynamically in [16]. A formula was derived for the critical pressure p_c causing the reorientation of the spins:

$$p_c = \frac{b_3 - b_1}{\frac{2}{\Delta}[(s_1' + s_2' + s_3') - (s_1 + s_2 + s_3)]}. \qquad (28)$$

Taking into account the temperature dependence of the first anisotropy constant $K_1 = (b_3 - b_1)/2 = a(T - T_2)$, we obtain an expression for the reorientation-temperature shift

$$\Delta T = \frac{\frac{1}{\Delta}[(s_1' + s_2' + s_3') - (s_1 + s_2 + s_3)]}{a}. \qquad (29)$$

The difference in the numerator $(s_i' - s_i)/\Delta$, where i = 1, 2, 3, represents the deformation along the corresponding axis of the crystal upon reorientation of the spins, which we measured as magnetostriction upon turning of the iron sublattices by the field. It is easy to see that for unilateral pressures, formula (29) goes over into formula (27), since

$$\frac{1}{\Delta}(s_i' - s_i) = \frac{L_i}{E_i}.$$

If we take into account the fact that the magnetostriction was negative along the a and b axes of the crystal and positive along the c axis, one should expect hydrostatic compression to exert a smaller influence on the reorientation temperature than unilateral compression.

We attempted to measure the reorientation-temperature shift under the influence of hydrostatic pressure. The results of the experiment are shown in Fig. 14, from which it is seen that the reorientation temperature changed insignificantly, by ~1–1.5°, at a pressure ~1.7 kbar, with the sign of the shift being opposite to that observed for unilateral pressure. This result is somewhat unexpected, but if we consider the value of $(s_i' - s_i)/\Delta$ obtained by substituting the deformations determined from the jumps of the Young's modulus, then we obtain

$$(-1.4 \pm 0.1) + (-1.1 \pm 0.1) + (2.5 \pm 0.3) \cdot 10^{-5} = (0 \pm 0.5) \cdot 10^{-5}.$$

It follows therefore that the shift of the reorientation temperature under hydrostatic pressure should be negligibly small and could be either positive or negative, in accord with the experimental results.

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