thin layers adjacent to the negatively charged cleavage plane. The density n_h referred to one hole layer is then 7×10^{12} cm^{-2} and the ratio is $n_h/n_l = 10$, in accord with the ratio of the effective-mass ratio of the heavy and light holes in germanium.

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Translated by J. G. Adashko

Magnetic phase transitions in terbium orthoferrite

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(Submitted 7 September 1978)
Zh. Eksp. Teor. Fiz. **76**, 1100–1110 (March 1979)

Spin-reorientation transitions in TbFeO$_3$ are investigated. It is shown that they may be regarded as transitions of the Jahn-Teller type. The parameters of isotropic and of anisotropic R–Fe exchange are determined ($a \approx 70$ kOe, $b \approx 19$ kOe). It is shown that the R–Fe interaction shifts the antiferromagnetic ordering point of the Tb^{3+} ions and has a considerable effect on the cant angle of the magnetic sublattices of the Fe^{3+} ions (at $T \sim 5$ K, the change of the cant angle ~40%). The importance is noted of the Van Vleck interaction of the quasidoublet ground state of the Tb^{3+} ion with the excited states.

PACS numbers: 75.30.Kz, 71.70.Ej, 75.50.Gg, 75.30.Et

1. INTRODUCTION

There have recently been intensive investigation of mangetic phase transitions of the spin-reorientation type (SR transitions) in rare-earth orthoferrites (ROF).[1] The variety of the magnetic properties observed in these compounds is determined, as a rule, by the peculiarities of the magnetism of the rare-earth ion (RI) in the orthoferrite structure and by the anisotropy of the exchange interaction of the rare-earth and iron ions. At low temperatures, the magnetic behavior of the RI depends substantially on the character of the wave functions of its lower energy levels. A good material for study of the influence of the ground state of the RI on the magnetic properties of a crystal is terbium orthoferrite, in which two phase transitions are observed at low temperatures; during them the weakly ferromagnetic moment, which at high temperatures is directed along the c axis of the crystal, with lowering of the temperature deviates to the a axis, and then again returns to its original state.[2]

In Refs. 3–5, phase transitions and H-T diagrams were investigated in TbFeO$_3$ at low temperatures, and the important role of dipole R-Fe interaction and of specimen shape in the phenomena considered was demonstrated. But in the theoretical investigation,[3-5] the nonisotropic part of the exchange R-Fe interaction was neglected, and this led to difficulties in the interpretation of the magnetic properties [in particular, of the $m_c(T)$ relation].

The present paper is devoted chiefly to explanation of the mechanisms of SR transitions in TbFeO$_3$ on the basis of microscopic ideas regarding the energy spectrum and the wave functions of the Tb^{3+} ion in TbFeO$_3$. It is shown that the high-temperature transition[1)] $\Gamma_4 - \Gamma_2$ can be regarded as a magnetic phase transition of Jahn-Teller type.[6] The low-temperature transition is more complicated. It occurs in two stages. First, at $T_N \approx 3.3$ K antiferromagnetic ordering occurs in the rare-earth subsystem ($\Gamma_2 \to \Gamma_{82}$); then at $T_{R2} \approx 3.1$ K this produces a reverse SR transition $\Gamma_2 - \Gamma_4$ in the subsystem of the Fe^{3+} ions, in which the RI go over to the purely antiferromagnetic configuration $\Gamma_8(A_x' G_y')$.

During the comparison of the results of the theory with experiment, the R-Fe exchange-interaction constants are estimated.

2. Tb^{3+} IONS IN RARE-EARTH ORTHOFERRITES

In orthoferrites, the elementary cell contains four RI, which are located at crystallographic positions having local environmental symmetry C_s[2)]. The ground multiplet $^7F_6$ of the free non-Kramers Tb^{3+} ion splits, in the crystalline field, into singlets, the nomenclature of whose wave functions is determined by the irreducible representations of the point group C_s: A and B. The lowest two singlets of the Tb^{3+} ion, quite clearly separated from the excited states ($E_1 \gtrsim 10^2$ cm^{-1}), form a quasidoublet (the energy gap between the levels in the quasidoublet is $\Delta_0 \lesssim 1$ cm^{-1}), whose wave functions belong to different representations of the group C_s (A and B).[7] This leads to the result that the magnetic moment of the Tb^{3+} ion lies, at low temperatures, in the ab plane of the crystal (since $\langle A|J_z|B\rangle = 0$), displaying an extremely anisotropic (Ising) behavior in the ab plane itself.[4] Its Ising axis lies at an angle $\alpha = \pm 36°$ to the a axis[3)] (Fig. 1), and the magnetic moment along this axis is close to the maximum possible value $m_0 \approx 9\ \mu_B$. We take the Ising axis as the z' axis of a local system of RI coordinates, and the y' axis along the c axis. Then the wave functions of the ground quasidoublet, corresponding to the maximum moment of the Tb^{3+} ion, are (in the local RI axes)

$$|A\rangle,\ |B\rangle = (|J=6,\ M_J=6\rangle \pm |J=6,\ M_J=-6\rangle)/\sqrt{2}. \tag{1}$$

Such a ground state of the Tb^{3+} ion in $TbFeO_3$ leads to the result that its magnetic moment lies in the ab plane for any orientation of the external field. But a considerable susceptibility ($\chi_c \sim 10^{-4}$ cm^3/g) and magnetization ($m_c \sim 2.6$ G cm^3/g) have been detected[4,9] along the c axis of the crystal. The susceptibility χ_c in $TbFeO_3$ is independent of temperature (for $T < E_1$) and evidently has a Van Vleck origin; that is, it is caused by admixture of the excited states of the Tb^{3+} ion to the ground state on application of a magnetic field and can be represented in the form (per RI)

$$\chi_c = \chi_{VV} = g_L^2 \mu_B^2 \left[\sum_n \frac{|\langle A|J_{y'}|A^{(n)}\rangle|^2}{E_A^{(n)}} + \sum_n \frac{|\langle B|J_{y'}|B^{(n)}\rangle|^2}{E_B^{(n)}} \right]. \tag{2}$$

The value of the susceptibility χ_c can be explained if we suppose that in the expansion of the wave functions of the first excited quasidoublet $|A^{(1)}\rangle$, $|B^{(1)}\rangle$, the state

$$|A^{(1)}\rangle,\ |B^{(1)}\rangle = (|J=6,\ M_J=5\rangle \mp |J=6,\ M_J=-5\rangle)/\sqrt{2}, \tag{3}$$

is represented with appreciable weight (~ 1). In this case, on setting $E_A^{(1)} \approx E_B^{(1)} \approx 10^2$ cm^{-1}, we get $\chi_{VV} = 2(g_L\mu_B\sqrt{3})^2/E_A^{(1)} \approx 1.3 \cdot 10^{-4}$ cm^3/g, which agrees fairly well with experimental data.

Thus in order to explain the magnetic properties of $TbFeO_3$, it is necessary to take into account the excited states of the Tb^{3+} ion. Then as will be shown below, an important role is acquired by asymmetric, anisotropic R-Fe exchange interaction, because of which, for example, an appreciable weakly ferromagnetic moment appears along the c axis.

In order to calculate the energy levels of the Tb^{3+} ion in the crystalline field and in the effective field produced by the R-Fe and R-R interaction, we represent the Hamiltonian of the Tb^{3+} ion in the form

$$\mathscr{H}_0 = \mathscr{H}_c - g_L\mu_B \mathbf{J}\mathbf{H}_{\text{eff}}, \tag{4}$$

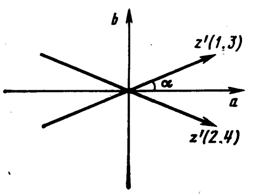

FIG. 1. Directions of the Ising axes of the Tb^{3+} ions in $TbFeO_3$.

where $\mathbf{J}$ is the operator of the total moment of the RI, $\mathscr{H}_c$ is the operator of the crystalline field, $\mathbf{H}_{\text{eff}} = \mathbf{H} + \mathbf{H}_{\text{R-E}} + \mathbf{H}_{\text{R}}$ is the operator of the total effective field acting on the RI; $\mathbf{H}$ is the external magnetic field, $\mathbf{H}_{\text{R}}$ is the effective field exerted on the given RI by the others (it will be determined below), and $\mathbf{H}_{\text{R=Fe}}$ is the operator of the effective field produced by the Fe^{3+} ions, which consists of two contributions, dipole and exchange. The dipole contribution to the effective field can be represented in the form $\mathbf{H}_{\text{R-Fe}}^{\text{dip}} = \hat{P}^{\pm}\mathbf{G}$, where the nonvanishing elements of the matrix $\hat{P}^{\pm}$ are $p_{xz}^{\pm} = p_{zx}^{\pm} = p_1,\ p_{yz}^{\pm} = p_{zy}^{\pm} = \pm p_2$ (the constants p_1 and p_2 are determined through dipole sums, calculation of which for $TbFeO_3$ gives $p_1 = 811.95$ Oe, $p_2 = 2956.12$ Oe).[4)] We represent the exchange contribution to the effective field, in the standard two-sublattice approximation, as[10]

$$\mathbf{H}_{\text{R-Fe}}^{\text{ex}} = A(\mathbf{L})\mathbf{F} + B(\mathbf{L})\mathbf{G}, \tag{5}$$

where $\mathbf{F}$ and $\mathbf{G}$ are, respectively, the ferromagnetism and antiferromagnetism vectors of the Fe^{3+} ions; $\mathbf{L}$ is the orbital moment of the RI; $A(\mathbf{L})$ is a symmetric and $B(\mathbf{L})$ an antisymmetric function with respect to reflection in the plane C_s. The first term of this expression describes isotropic R-Fe exchange with small anisotropic corrections; the second describes anisotropic, asymmetric exchange.[5)]

At low temperatures, the principal contribution to the free energy comes from the lowest two levels of the Tb^{3+} ion, but in calculating them it is necessary to allow for their interaction with the excited states. As a result, the behavior of the Tb^{3+} ion can be described by the following spin Hamiltonian:

$$\begin{gathered}
\mathscr{H}_0 = \begin{pmatrix} \mathscr{H}_{11} & \mathscr{H}_{12} \\ \mathscr{H}_{21} & \mathscr{H}_{22} \end{pmatrix}, \\
\mathscr{H}_{11} = -\frac{\Delta_0}{2} - \sum \frac{|\langle A|V|k\rangle|^2}{E_k}, \\
\mathscr{H}_{12} = \langle A|V|B\rangle - \sum \frac{\langle A|V|k\rangle\langle k|V|B\rangle}{E_k}, \\
\mathscr{H}_{21} = \langle B|V|A\rangle - \sum \frac{\langle B|V|k\rangle\langle k|V|A\rangle}{E_k}, \\
\mathscr{H}_{22} = \frac{\Delta_0}{2} - \sum \frac{|\langle B|V|k\rangle|^2}{E_k},
\end{gathered} \tag{6}$$

where $V = -g_L\mu_B \mathbf{J} \cdot \mathbf{H}_{\text{eff}}$. The eigenvalues of the spin Hamiltonian (6) can be represented in the form

$$E_{1,2} = -\Delta E \pm \Delta, \quad \Delta E = -(\mathscr{H}_{11} + \mathscr{H}_{22})/2,$$
$$\Delta^2 = (\mathscr{H}_{11} - \mathscr{H}_{22})^2/4 + |\mathscr{H}_{12}|^2.$$

On using as the wave functions of the ground state the functions (1) and of the first excited state the functions (3), we get

$$\Delta E={}^1/{}_2\chi_{VV}[(H_{\text{eff}}^{x'})^2+(H_{\text{eff}}^{y'})^2],$$

$$\Delta^2=(\Delta_0/2)^2+(m_0H_{\text{eff}}^{z'})^2, \tag{7}$$

where $m_0=g_LJ\mu_B=9\mu_B$, $\mathbf{H}_{\text{eff}}=\mathbf{H}+a\mathbf{F}+(p^{\pm}+B^{\pm})\mathbf{G}+\mathbf{H}_{\text{R}}$ is the total effective field acting on the RI, and $\hat{B}^{\pm}$ is the matrix of asymmetric R-Fe exchange, whose nonvanishing elements are

$$b_{zx}{}^{\pm}=b\cos\alpha,\quad b_{zy}{}^{\pm}=\pm b\sin\alpha,\quad b=i\langle A|B(\mathbf{L})J_{z'}|A^{(1)}\rangle/\sqrt{3}.$$

In calculating the matrix elements of the operator (5), we have neglected small anisotropic corrections to $A(\mathbf{L})$ and have set $A(\mathbf{L})=A(0)\equiv a$.

3. THE THERMODYNAMIC POTENTIAL

We represent the Hamiltonian of the Tb^{3+} ions in $TbFeO_3$ in the form

$$\mathcal{H}=\sum_i[\mathcal{H}_c{}^i-g_L\mu_B(\mathbf{H}+\mathbf{H}_{\text{R-Fe}}^i)\mathbf{J}]-{}^1/{}_2g_L{}^2\mu_B{}^2\sum_{i\neq j}\mathbf{J}_i\hat{T}_{ij}\mathbf{J}_j, \tag{8}$$

where $\hat{T}_{ij}$ is the R-R interaction matrix of the ith and jth ions, the contributions to which come from dipole and exchange interactions between the RI.

In order to obtain the thermodynamic potential of a system of RI interacting with each other, we use a variational principle of statistical physics in the form proposed by Bogolyubov.[11] We represent the Hamiltonian of the system (8) in the form

$$\mathcal{H}=\mathcal{H}_1+\mathcal{H}_2, \tag{9}$$

where

$$\mathcal{H}_1=\sum_i[\mathcal{H}_c{}^i-g_L\mu_B\mathbf{H}_{\text{eff}}^iJ_i],\quad \mathcal{H}_2=\mathcal{H}-\mathcal{H}_1,$$

$$\mathbf{H}_{\text{eff}}^i=\mathbf{H}+\mathbf{H}_{\text{R-Fe}}^i+\mathbf{H}_{\text{R}}{}^i.$$

The effective fields $\mathbf{H}_{\text{R}}^i$ are determined by minimization of the following free energy[11]:

$$\mathcal{F}=-T\ln\operatorname{Sp}(e^{-\mathcal{H}_1/T})+\operatorname{Sp}(\mathcal{H}_2e^{-\mathcal{H}_1/T})/\operatorname{Sp}(e^{-\mathcal{H}_1/T}), \tag{10}$$

which in our case reduces to the form

$$\mathcal{F}=-T\ln\operatorname{Sp}(e^{-\mathcal{H}_1/T})+\sum_i\mathbf{m}_i\mathbf{H}_{\text{R}}{}^i-\frac{1}{2}\sum_{i\neq j}\mathbf{m}_i\hat{T}_{ij}\mathbf{m}_j, \tag{11}$$

where $\mathbf{m}_i$ is the magnetic moment of the ith RI,

$$\mathbf{m}_i=\frac{\partial}{\partial\mathbf{H}_{\text{eff}}^i}[T\ln\operatorname{Sp}(e^{-\mathcal{H}_1/T})]. \tag{12}$$

On minimizing (11) with respect to $\mathbf{H}_{\text{R}}^i$, we find

$$\mathbf{H}_{\text{R}}{}^i=\sum_{i\neq j}\hat{T}_{ij}\mathbf{m}_j.$$

On substituting $\mathbf{H}_{\text{R}}^i$ in (11), we get the equilibrium free energy of the Tb^{3+} ions with respect to the $\mathbf{m}_i$. As a result, the total free energy of $TbFeO_3$, in the approximation of four rare-earth sublattices, will be (per RI)

$$\mathcal{F}=\frac{A\mathbf{F}^2}{2}+\frac{1}{2}\sum_{i=xyz}b_iG_i{}^2+d(F_zG_x-F_xG_z)-\mu_{\text{Fe}}\mathbf{F}\mathbf{H}-\frac{1}{4}\sum_\alpha\Delta E_\alpha$$
$$-\frac{1}{4}T\sum_\alpha\ln\operatorname{ch}\left(\frac{\Delta_\alpha}{T}\right)+\frac{1}{8}\sum_{\alpha,\beta}\mathbf{m}_\alpha\hat{T}_{\alpha\beta}\mathbf{m}_\beta, \tag{13}$$

where $\alpha,\beta=1,2,3,4$ are the indices of the rare-earth sublattices; $\hat{T}_{\alpha\beta}$ are the interaction matrices of the rare-earth sublattices, whose symmetry properties for ROF have been expounded quite completely.[8]

The magnetic moments of the rare-earth sublattices are determined by the equation

$$\mathbf{m}_\alpha=\frac{\partial\Delta E_\alpha}{\partial\mathbf{H}_\alpha}+\frac{\partial\Delta_\alpha}{\partial\mathbf{H}_\alpha}\operatorname{th}\left(\frac{\Delta_\alpha}{T}\right), \tag{14}$$

where the first term determines a temperature-independent Van Vleck contribution to the magnetization, while the second is caused by Zeeman splitting of the ground quasidoublet. In our case, with allowance for (7), the components of the magnetic moment of the Tb^{3+} ion in the local axes will be

$$m_\alpha{}^{x'}=\chi_{VV}H_\alpha{}^{x'},\quad m_\alpha{}^{y'}=\chi_{VV}H_\alpha{}^{y'},\quad m_\alpha{}^{z'}=\frac{m_0{}^2H_\alpha{}^{z'}}{\Delta_\alpha}\operatorname{th}\frac{\Delta_\alpha}{T}.$$

By using the linear character of the dependence of $m_\alpha^{x',y'}$ on $H_\alpha^{x',y'}$, one can eliminate them from the expression for the free energy and represent the latter as a function solely of $m_\alpha\equiv m_\alpha^{z'}$, the components of the RI magnetic moments along the easy axis. This procedure leads to an inconsequential (by virtue of the smallness of χ_{VV}) renormalization of $T_{\alpha\beta}^{z'z'}$ and of the effective fields $H_\alpha^{z'}$ along the corresponding RI axes.

On minimizing this free energy with respect to $\mathbf{F}$, with allowance for the relations $\mathbf{F}\cdot\mathbf{G}=0$ and $\mathbf{G}^2=1-\mathbf{F}^2\approx1$, we get

$$\mathbf{F}=\frac{\mathbf{H}_t+\Delta\mathbf{H}_t-((\mathbf{H}_t+\Delta\mathbf{H}_t)\mathbf{G})\mathbf{G}}{A}, \tag{15}$$

$$\mathcal{F}=-\frac{\mathbf{H}_t{}^2-(\mathbf{H}_t\mathbf{G})^2}{2A}+\frac{\Delta\mathbf{H}_t{}^2-(\Delta\mathbf{H}_t\mathbf{G})^2}{2A}+\frac{1}{2}\sum_i\tilde{b}_iG_i{}^2-\frac{1}{2}\sum_i\chi_{VV}{}^iH_i{}^2$$
$$-\tau_1H_zG_x-\tau_2H_xG_z-\frac{1}{4}T\sum_\alpha\ln\operatorname{ch}\left(\frac{\Delta_\alpha}{T}\right)+\frac{1}{8}\sum_{\alpha,\beta}m_\alpha T_{\alpha\beta}m_\beta, \tag{16}$$

where

$$\mathbf{H}_t=(dG_z+\eta_xH_x,\ \eta_yH_y-dG_x+\eta_zH_z),\quad \Delta\mathbf{H}_t=(aM_x{}^{\text{R}},\ aM_y{}^{\text{R}},\ 0)$$
$$M_x{}^{\text{R}}={}^1/{}_4(m_1+m_2+m_3+m_4)\cos\alpha,\quad M_y{}^{\text{R}}={}^1/{}_4(m_1-m_2+m_3-m_4)\sin\alpha,$$
$$\tilde{b}_1=b_1-\chi_{VV}(b\cos a+p_1)^2,\ \tilde{b}_2=b_2-\chi_{VV}(b\sin\alpha+p_2)^2,\ \tilde{b}_3=b_3-\chi_{VV}p'^2,$$
$$\eta_x=\mu_{\text{Fe}}+\chi_{VV}a\sin^2a,\ \eta_y=\mu_{\text{Fe}}+\chi_{VV}a\cos^2\alpha,\ \eta_z=\mu_{\text{Fe}}+\chi_{VV}a,$$
$$\tau_1=\chi_{VV}(b\cos\alpha+p_1),\ \tau_2=\chi_{VV}p',\ p'=p_1\sin\alpha-p_2\cos\alpha,$$
$$\chi_{VV}{}^x=\chi_{VV}\sin\alpha,\ \chi_{VV}{}^y=\chi_{VV}\cos\alpha,\ \chi_{VV}{}^z=\chi_{VV}.$$

The magnetic moments m_α of the RI are determined by the system of nonlinear equations $m_\alpha=(m_0^2H_\alpha/\Delta_\alpha)\operatorname{th}(\Delta_\alpha/T)(\alpha=1,2,3,4)$.

$$H_\alpha=H_\alpha{}^{z'}=(H_x+aF_x)\cos\alpha+pG_z\pm(H_y+aF_y)\sin\alpha+\sum_\beta T_{\alpha\beta}m_\beta,$$
$$p=p_1\cos\alpha+p_2\sin\alpha.$$

The R-R interaction constants ($T_{\alpha\beta}=T_{\alpha\beta}^{z'z'}$) possess the following symmetry properties[8]:

$$T_{\alpha\beta}=T_{\beta\alpha},\ T_{\alpha\alpha}\equiv T_1,\ T_{12}=T_{34}\equiv T_2,\ T_{13}=T_{24}\equiv T_3,\ T_{14}=T_{23}\equiv T_4.$$

4. SPONTANEOUS PHASE TRANSITIONS IN TbFeO$_3$

Before passing on to a detailed analysis of the phase transitions determined by the free energy (16), we shall consider a simplified phenomenological model that reflects the basic features of the phase transitions observed in TbFeO$_3$.

According to experimental data,[5,9] at $T>6.5$ K the spins of the Fe^{3+} ions are in phase $\Gamma_4(G_xF_z)$, and at $T_{R1}=6.5$ K they change to phase $\Gamma_2(G_zF_x)$, polarizing the Tb^{3+} ions along the a axis of the crystal according to mode $F_x'C_y'$. At $R_{R2}\approx 3.1$ K the spins of the Fe^{3+} ions return to their high-temperature configuration G_xF_z, while the Tb^{3+} ions change to the antiferromagnetic phase $\Gamma_8(A_x'G_y')$. Thus the behavior of the system during the phase transitions may be described by a multidimensional order parameter, containing F_x, F_z, G_x, and G_z (of the Fe subsystem and F_x', C_y', A_x', and G_y' (of the R subsystem).

But after minimization of the free energy with respect to **F**, the components F_x and F_z may be eliminated; and in the rare-earth subsystem, because of the fact that the Tb^{3+} ions are of Ising nature, the number of components of the order parameter shrinks to two, for which we may choose

$$m=(m_1+m_2+m_3+m_4)/4m_0 \qquad l=(m_1-m_2-m_3+m_4)/4m_0.$$

Now m describes the mode $F_x'C_y'$, l the mode $A_x'G_y'$. Then by minimizing the free energy with respect to m and eliminating m, we decrease the number of components of the order parameter to three: G_x, G_z, and l. Taking into account that $G_x^2+G_z^2=1$, one can use, instead of two variables, one, for example the angle θ between **G** and the c axis of the crystal. Thus we have $\mathcal{F}=\mathcal{F}(\theta,l)$. Expanding $\mathcal{F}$ in $\cos\theta$ and l, we get

$$\mathcal{F}=\frac{\alpha_1}{2}l^2+\frac{\alpha_2}{2}\cos^2\theta+\frac{\beta}{4}l^4+\frac{\delta}{2}l^2\cos^2\theta. \tag{17}$$

Angular phases are here unimportant to us, therefore for the time being we neglect terms of higher order in $\cos\theta$. The coefficients α_1, α_2, β, and δ are functions of temperature and can be calculated from (16). It is important that the coefficients α_1 and α_2 change sign near T_N^0 and T_{R1}. Therefore they may be represented in the form $\alpha_1=\alpha_1^0(T-T_N^0)$, $\alpha_2=\alpha_2^0(T-T_{R1})$; we shall suppose that β and δ are temperature-independent and positive.

Minimization of (17) with respect to θ and l gives the following phases:

$$A\left(l=0;\ \theta=\pm\frac{\pi}{2}\right),\quad B(l=0;\ \theta=0,\pi),\quad C\left(l^2=-\frac{\alpha_1+\delta}{\beta};\ \theta=0,\pi\right),$$
$$D\left(l^2=-\frac{\alpha_1}{\beta};\ \theta=\pm\frac{\pi}{2}\right).$$

In phase A, the rare-earth subsystem is in the paramagnetic state,[6] whereas the magnetic structure of the Fe sublattice is described by the irreducible representation $\Gamma_4(G_xF_z)$ of the group D_{2h}^{16}. At $T=T_{R1}$, phase A transforms to phase B, in which the magnetic structure of the Fe and R sublattices is described by the single irreducible representation $\Gamma_2(G_z, F_x, F_x', C_y')$. At $T=T_N=T_N^0-\delta/\alpha_1^0$, the system transforms to phase C, where the R sublattice is described by the reducible representation Γ_{82} and the iron, as before, by the irreducible representation Γ_2. Phase C is stable until temperature $T_{R2}''=(T_N-\varepsilon T_{R1})/(1-\varepsilon)$, where $\varepsilon=\beta\alpha_2^0/\delta\alpha_1^0$. In phase D, the magnetic structure of the Fe sublattice is described by the irreducible representation Γ_4 and that of the rare-earth by Γ_8. This phase is stable in the temperature interval $0<T<T_{R2}'$, where $T_{R2}'=(T_N^0-\varepsilon T_{R1})/(1-\varepsilon)$. Since, the regions of existence of phases C and D overlap, a phase transition of the first kind between them occurs at $T=T_{R2}=(T_{R2}'+T_{R2}'')/2$. Thus this model reflects qualitatively the principal features of the phase transformations observed in TbFeO$_3$.

For a more detailed, quantitative description of these phase transitions, we shall start from the free energy (16) obtained earlier for TbFeO$_3$; when $H=0$, this is

$$\mathcal{F}=\frac{K_1^0G_z^2}{2}+\frac{K_2^{Fe}G_z^4}{4}+\frac{km^2G_z^2}{2}-\frac{T}{2}\ln\left(\operatorname{ch}\frac{\Delta_1}{T}\operatorname{ch}\frac{\Delta_2}{T}\right)+\frac{T_Q^0m^2}{2}+\frac{T_N^0l^2}{2}, \tag{18}$$

where $\Delta_{1,2}=\lambda m_0G_z+(kG_z^2+T_Q^0)m\pm T_N^0l$ are the splittings of the lowest levels of RI occupying, respectively, positions 1, 4 and 2, 3;[7]

$$\lambda=p+da\cos\alpha/A,\quad k=(am_0\cos\alpha)^2/A,$$
$$K_1^0=K_1^{Fe}+K_1^{VV}>0,\ K_1^{VV}=\chi_{VV}[(b\cos\alpha+p_1)^2-p'^2],\ K_2^{Fe}>0,$$
$$T_Q^0=m_0^2(T_1+T_2+T_3+T_4),\qquad T_N^0=m_0^2(T_1-T_2-T_3+T_4).$$

The values of θ, m, and l that determine the equilibrium states of the system are found from the condition that the free energy (18) shall be a minimum; they satisfy the following system of nonlinear equations:

$$\sin\theta[K_1^0\cos\theta+K_2^{Fe}\cos^3\theta-\lambda m_0m-km^2\cos\theta]=0.$$
$$m=\frac{1}{2}\left(\operatorname{th}\frac{\Delta_1}{T}+\operatorname{th}\frac{\Delta_2}{T}\right),\quad l=\frac{1}{2}\left(\operatorname{th}\frac{\Delta_1}{T}-\operatorname{th}\frac{\Delta_2}{T}\right). \tag{19}$$

The results of solution of these equations are shown in Fig. 2 and are interpreted as follows.

A. Reorientational transiton $\Gamma_4\to\Gamma_2$

In this case $l=0$, and we may set $\Delta_1=\Delta_2$. The temperature at which instability of the phase $\Gamma_4(G_xF_z)$ occurs is determined by the condition

$$\left.\frac{d^2\mathcal{F}}{d\theta^2}\right|_{\substack{\theta=\pi/2\\ m=0}}=0$$

and is

$$T_{R1}=\lambda^2m_0^2/K_1^0+T_Q^0. \tag{20}$$

It is essentially the point where there is a change of sign of the anisotropy constant $K_1(T)$ determined by the expansion of the free energy in $\cos\theta$:

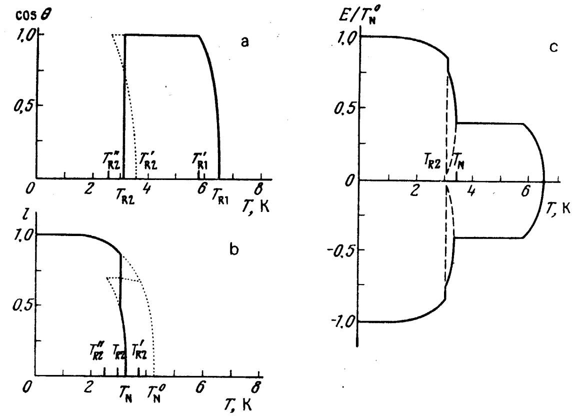

FIG. 2. Temperature dependence of the angle θ between the vector **G** and the c axis of the crystal (a), of the antiferromagnetism vector l of the RI (b), and of the lowest two levels of Tb^{3+} ions located in different nonequivalent positions (c): solid line, positions 1, 4 (2,3); dashed line, positions 2, 3 (1, 4). The dotted lines correspond to metastable or unstable states. Numerical calculation for $K_1^0 = 0.656 \cdot 10^{-16}$ erg/ion, $K_2^{\mathrm{Fe}} = 0.4\,K_1^0$, $T_N^0 = 4.3$ K, $T_Q^0 = -0.9$ K.

$$\mathcal{F} = {}^1/_2 K_1 \cos^2\theta + {}^1/_4 K_2 \cos^4\theta + \ldots, \tag{21}$$

where

$$K_1 = K_1^0 - \chi_T\lambda^2, \quad K_2 = K_2^{\mathrm{Fe}} - 2k\left(\frac{\chi_T\lambda}{m_0}\right)^2 + \frac{T}{3}\left(\frac{\chi_T\lambda}{m_0}\right)^4, \quad \chi_T = \frac{m_0^2}{T - T_Q^0}.$$

It is evident that the change of sign of $K_1(T)$ with lowering of temperature occurs because of magnetization of the RI in the effective field λ (the term $-\chi_T\lambda^2$ in K_1). The temperature T_{R1}, at which the process of rotation of the vector **G** is completed, and the system changes to phase Γ_2, is

$$T_{R1}' = [\lambda m_0 + (T_Q^0 + k)\,m^*]/\mathrm{arth}\, m^*,$$

$$m^* = \frac{\lambda m_0}{2k}\left[\left(1 + \frac{4(K_1^0 + K_2^{\mathrm{Fe}})\,k}{(\lambda m_0)^2}\right)^{1/2} - 1\right]. \tag{22}$$

In order to explain the mechanism of the phase transition $\Gamma_4 \to \Gamma_2$, we consider the behavior of the lowest energy levels of the Tb^{3+} ions during the reorientation process (Fig. 2c). In the high-temperature phase $\Gamma_4(G_x F_z)$, which is stabilized by the anisotropy energy of the Fe^{3+} ions, their splitting is zero; that is, the ground state of the Tb^{3+} ions is degenerate. The degeneracy can be removed as a result of deformation of the magnetic structure of the Fe^{3+} ions, *i.e.* deviation of the vector **G** from the a axis of the crystal. The energy of the ground state of the RI is thereby lowered. On the other hand, deformation of the magnetic structure entails an energy disadvantage (because of the anisotropy energy). Competition of these two mechanisms determines the phase transition $\Gamma_4 \to \Gamma_2$, during which the degeneracy of the ground state of the Tb^{3+} ions is removed. Thus the phase transition $\Gamma_4 \to \Gamma_2$ in $\mathrm{TbFeO_3}$ may be regarded as a cooperative phase transition of the Jahn-Teller type.[6]

B. Antiferromagnetic ordering of the RI and the reserve reorientational transition $\Gamma_2 \to \Gamma_4$

On further lowering of the temperature, as is shown by analysis of equations (19), the state of the RI with $l = 0$ becomes unstable, and the system acquires a nonzero antiferromagnetic RI moment (Fig. 2b). The antiferromagnetic ordering point T_N is distinct from the Néel temperature T_N^0, which is determined by the internal interactions of the RI, and is found from the equation

$$\lambda m_0 + (T_Q^0 + k)\,(1 - T_N/T_N^0)^{1/2} = T_N\, \mathrm{arth}\,(1 - T_N/T_N^0)^{1/2}, \tag{23}$$

whose solution in the case $\eta = \lambda m_0/(T_N^0 - T_Q^0 - k) \ll 1$ is

$$T_N = T_N^0\left\{1 - \eta^2\left[1 - \frac{4}{3}\,\frac{T_N^0}{T_N^0 - T_Q^0 - k}\,\eta^2 + \frac{2}{45}\,T^{\circ}\,\frac{83T_N^0 - 6(T_Q^0 + k)}{(T_N^0 - T_Q^0 - k)^2}\,n^4 + \ldots\right]\right\}. \tag{23a}$$

Thus the R-Fe interaction shifts the antiferromagnetic ordering point of the RI. An estimate of the amount of the shift of the Néel point for the parameters indicated in Fig. 2 gives $T_N \approx 0.8\, T_N^0$.

To determine the stability range of the low-temperature phase, in which $\cos\theta = 0$, we expand the free energy in $\cos\theta$, representing it in the form (21). The corresponding expansion coefficients K_1 and K_2, which have the meaning of anisotropy constants, depend on the antiferromagnetism vector l of the RI, which is determined by the equation $l = \tanh(T_N^0 l/T)$. The expression for $K_1(T, l)$ has exactly the same form as in (21), but in it the susceptibility χ_T of the RI, in consequence of their antiferromagnetic ordering, is decreased and is

$$\chi_T(l) = m_0^2\left(\frac{T}{1 - l^2} - T_Q^0\right)^{-1}. \tag{24}$$

The decrease of χ_T with lowering of temperature (because of increase of l) leads to a second change of sign of K_1, at T'_{R2}, and stabilization of the phase Γ_4 (Fig. 3). The point T'_{R2} of loss of stability of the low-temperature phase is determined by the condition $K_1(T, l) = 0$ and satisfies the equation

$$\left(1 - \frac{T_{R2}'}{T_{R1}}\right)^{1/2} = \frac{T_{R2}'}{T_N^0}\,\mathrm{arth}\left(1 - \frac{T_{R2}'}{T_{R1}}\right)^{1/2}, \tag{25}$$

whose solution for $\xi = (T_{R1} - T_N^0)/2T_{R1} \ll 1$ is

$$T_{R2}' = T_{R1}\left[1 - 3\xi + \frac{3^2}{5}\xi^2 + \frac{3^3}{5^2 \cdot 7}\xi^3 + \frac{3^3}{5^2 \cdot 7}\xi^4 + \ldots\right]. \tag{25a}$$

From the relations obtained and from experimental

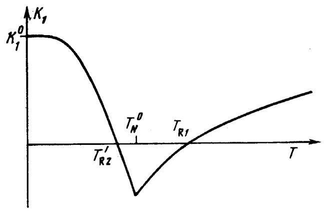

FIG. 3. Temperature dependence of the second-order anisotropy constant of the crystal in the *ac* plane (schematic).

data we shall estimate the constants of antisymmetric and of isotropic R-Fe exchange (b and a). As has already been indicated above, an appreciable value of the magnetic moment m_c along the c axis of the crystal is produced by polarization of the RI as a result of antisymmetric R-Fe exchange. From the expression (16) for the free energy, it is easy to obtain the value of m_c in phase Γ_4:

$$m_c \approx m_{Fe} + \chi_{VV}(b\cos\alpha + p_1), \qquad (26)$$

where $m_{Fe} = -\mu_{Fe}\, d/A$. On setting $m_c = 2.6$ G cm^3/g, $m_{Fe} \approx 1$ G cm^3/g, and $\chi_{VV} = 10^{-4}$ cm^3/g, we get $b \approx 19$ kOe. The constant a of isotropic R-Fe exchange will be estimated from the relation (20). Supposing that K_1^{Fe} has, as in YFeO$_3$,[12] the value $K_1^{Fe} = 0.556 \cdot 10^{-16}$ erg/ion, and that $K_1^{VV} = 0.1 \cdot 10^{-16}$ erg/ion, $T_{R1} \approx 6.5$ K, and $T_Q^0 \sim 0$, we get $\lambda \approx 3$ kOe. Hence it follows that the isotropic field on the Tb^{3+} ions, which appears because of canting of the sublattice of Fe^{3+} ions, is $ad/A = (\lambda - p)/\cos\alpha \approx 700$ Oe ($p = 2394$ Oe); and for $|d/A| \sim 10^{-2}$, we have $|a| \approx 70$ kOe.

We note that such an appreciable value of the constant of isotropic R-Fe exchange can lead, at low temperatures, to a substantial change of the cant angle of the magnetic moments of the Fe sublattice. We shall estimate, for example, the value of the weakly ferromagnetic moment in the phase Γ_2. According to (15) we have $F_x = F_x^0 + aM_x^R/A$, where $F_x^0 = d/A$ and $M_x^R \approx \chi_T\lambda$. As a result, at $T \sim 5$ K and $H_D = d/\mu_{Fe} \approx 10^3$ Oe we get $\Delta F_x/F_x^0 \approx 40\%$.

5. CONCLUSION

The analysis presented shows that the spin-reorientation transition $\Gamma_4 \rightarrow \Gamma_2$ in TbFeO$_3$ can be regarded as a cooperative transition of the Jahn-Teller type (Fig. 2c). In such a transition, polarization of the Tb^{3+} ions occurs under the influence of R-Fe interaction according to the mode $F_x' C_y'$. In this phase, under the influence of the R-Fe interaction, there occurs an additional change of the cant angle of the iron sublattices (at $T \sim 5$ K the cant angle changes by 40%). The low-temperature phase transition is more complicated and is accomplished in two stages. First there occurs, at $T = T_N$, an ordering of the Tb^{3+} ions according to the representation Γ_{82} (by a phase transition of the second kind). Antiferromagnetic ordering of the Tb^{3+} ions produces, at $T = T_{R2}$, the reverse transition $\Gamma_2 \rightarrow \Gamma_4$ in the Fe subsystem and the transition $\Gamma_{82} \rightarrow \Gamma_8$ in the R subsystem. It has been shown that the R-Fe interaction shifts the Neel point of the Tb^{3+} ions (~20%). We have noted the important role of asymmetric R-Fe interaction and of Van Vleck susceptibility of the Tb^{3+} ions in the shaping of the magnetic properties of TbFeO$_3$ at low temperatures. From a comparison of the results of the theory with experimental data, we have determined the constants of R-Fe exchange interaction ($a \approx 70$ kOe, $b \approx 19$ kOe).

The authors express their thanks to A. M. Kadomtseva for valuable comments during discussion of the results of the research.

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[1] The indices Γ_i denote the magnetic configurations possible in orthoferrites. Thus, for example, the modes F_x, G_z, C_y of the Fe^{3+} ions and the modes F_x', C_y' of the Tb^{3+} ions (in Bertaut's notation) exist in the configuration Γ_2. We recall that to each configuration Γ_i corresponds an irreducible representation of the space group D_{2h}^{16} that determines the symmetry of orthoferrites. Indices Γ_{ik} denote reducible representations containing the representations Γ_i and Γ_k. To them correspond angular magnetic configurations.

[2] There is only one symmetry element, a mirror reflection plane parallel to the ab plane of the crystal.

[3] The signs + and − pertain to the positions 1, 3 and 2, 4, respectively, of the RI in the elementary cell.[8]

[4] These values are close to the corresponding parameters for HoFeO$_3$ calculated in Ref. 8.

[5] In Refs. 3-5 only the first term of the R-Fe interaction was taken into account, although in orthoferrites the antisymmetric R-Fe interaction dominates.

[6] We note that in this phase the R-Fe interaction (mainly its asymmetric part) leads to a weak polarization of the RI along the c axis of the crystal because of the Van Vleck sysceptibility of the Tb^{3+} ions.

[7] Here we set $\Delta_0 = 0$, since its value is small[4] ($\Delta_0 \lesssim 1$ K) and has practically no influenece on the subsequent results.

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Translated by W. F. Brown, Jr.