GENERAL CHARACTERISTICS OF SPIN-REORIENTATION TRANSITIONS IN ORTHOFERRITES

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UDC 537.622.5

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Viktor Bar'yakhtar turns 75:
"Everywhere and always he looks for the roots
to get acquainted with the flower"
(*Stefan Zweig*)

The temperature dependences of the magnetization absolute value $|\mathbf{M}|(T)$ and its rotation angle $\theta(T)$ during the $\Gamma_4 \to \Gamma_{24} \to \Gamma_2$ spin-reorientation transition in $YbFeO_3$, $ErFeO_3$, and $TmFeO_3$ single crystals are measured and found to be incompatible with the conventional Landau mean-field theory. A modified mean-field theory describing experimental data with no fitting parameters was proposed. Its key point is the account of the anisotropic rare earth contribution to the total magnetization. The successful fitting of experimental data for several materials with a wide range of magnetic parameters demonstrates the generality of the proposed description of the $\Gamma_4(G_x, F_z) \to \Gamma_{24}(G_{xz}, F_{xz}) \to \Gamma_2(G_z, F_x)$ orientation phase transitions in orthoferrites.

1. Introduction

Being noncollinear antiferromagnets with unique magnetic properties, rare earth orthoferrites attract attention of the scientific community for the last half of the last century. Their chemical formula is $RFeO_3$, where R is a rare-earth ion, or yttrium ion, and their crystallographic structure is the one of perovskite $CaTiO_3$ with a space group $D_{2h}^{16} - P_{bnm}$ [1]. By itself, $CaTiO_3$ has simple cubic structure and the elementary cell containes one formula unit (see Fig. 1,*a*). In rare-earth orthoferrites the perovskite structure has significant rhombic distortions. The degree of distortion is different for different orthoferrites and is determined by the ratio of ion radii for R^{3+} and Fe^{3+}. Distortions grow as the radius of the rare earth ion decreases.

The elementary cell of an orthoferrite consists of four distorted perovskite elementary cells and contains four iron and four rare-earth ions. The crystallographic and magnetic cells of orthoferrites coincide. The ions of iron occupy positions shown on Fig. 1,*b*. Oxygen and rare-earth ions are displaced from their ideal positions by a fraction of an Angstrom. Rare-earth orthoferrites are characterized by a strongly temperature-dependent anisotropy [2].

The crystal structure of orthoferrites implies the presence of two magnetic subsystems: iron ions and rare-earth ions. In a number of orthoferrites, e.g. in $YbFeO_3$, $ErFeO_3$, $TmFeO_3$, two possible spin configurations are compatible with the P_{bnm} space group and can be realized in nature (see Fig. 2). The *d*-subsystem of iron ions orders into a slightly canted antiferromagnetic structure exhibiting a weak ferromagnetic moment **F**. The rare-earth ions subsystem is paramagnetic. For all orthoferrites, the antiferromagnetic structure directly below the Neel temperature T_N ($T_N = 620 \div 740$K) corresponds to the $\Gamma_4(G_x, F_z)$ irreducible representation with the magnetic vector **F** pointing along the **c** axis of the crystal and the antiferromagnetic vector **G** pointing along the **a** axis. The coordinates are chosen so that $c = z$ and $a = x$. In orthoferrites with non-magnetic rare-earth ions R = La, Lu, or Y, the $\Gamma_4(G_x, F_z)$ configuration persists to the lowest temperatures. For other rare-earth ions, the interaction between magnetic subsystems and the dependence of the effective anisotropy constants on external parameters, such as temperature, field, or elastic strain, leads to a series of orientation phase transitions. Most often they happen upon cooling (for R = Yb, Er, Tm, Nd, Sm) according to the sequence

$$\Gamma_4(G_x, F_z) \to \Gamma_{24}(G_{xz}, F_{xz}) \to \Gamma_2(G_z, F_x)$$

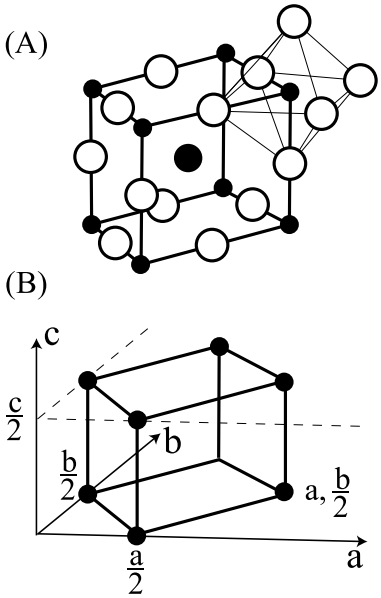

Fig. 1. *a* — elementary cell of a perovskite. Large filled circle — Ca ion, small filled circles — Ti ions, empty circles — O ions: *b* — positions of Fe ions (filled circles) in the elementray cell of an orthoferrite

with a reorientation happening as a continuous rotation of F with decrease in temperature. The magnetic vector rotates in the $(\mathbf{a}, \mathbf{c})$ plane from the $\mathbf{c}$ axis to the $\mathbf{a}$ axis in the temperature interval $[T_1 \div T_2]$ $(T_2 < T_1 < T_N)$. As the temperature reaches T_2, the system enters the $\Gamma_2(G_z, F_x)$ phase with $\mathbf{F}||\mathbf{a}$. The temperatures T_1, T_2 are the points of orientation phase transitions of the second order.

The spin reorientation region $[T_2 \div T_1]$ has been studied for many orthoferrites by different experimental techniques, but not enough is known about the specifics of the rotation. Relevant experimental results are often incomplete and do not correspond to either conventional Landau theory [3—5] or its suggested modifications. Presently, the studies of spin-reorientation in orthoferrites are returned into the spotlight due to the finding of the extremely fast dynamics of the antiferromagnetic vector in this region [6].

The purpose of this work is an analysis of the detailed measurements of the absolute value of the magnetization $M(T)$ and its rotation angle $\theta(T)$ with respect to the $\mathbf{c}$ axis in the $[T_2, T_1]$ temperature interval at zero external magnetic field. Experiments were done on single crystals of $YbFeO_3$, $ErFeO_3$, and $TmFeO_3$ [7—10], which exhibit the same $\Gamma_4 \to \Gamma_{24} \to \Gamma_2$ transition.

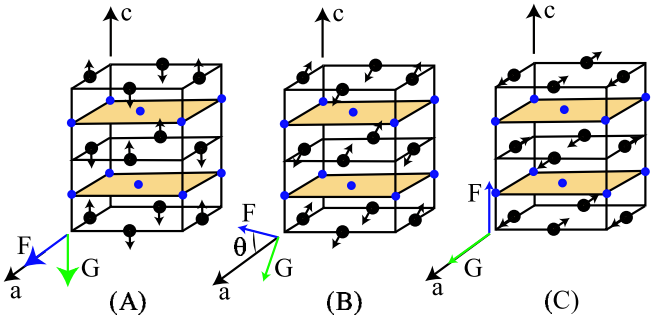

Fig. 2. Elementary cell of an orthorhombic orthoferrite showing ideal positions of iron (filled black circles), reare earth ions (filled blue circles), and their spin directions for $T > T_1$ (c), $T_2 < T < T_1$ (b), and $T < T_2$ (a)

It is shown that the experimental results are in very good agreement with the proposed modified mean-field theory [7, 8], that emphasized the anisotropy of the paramagnetic susceptibility of rare-earth ions. The theory, originally developed for $ErFeO_3$, describes the behavior of orthoferrites with vastly different transition temperatures: $T \approx 8$ K for $YbFeO_3$, and $T \approx 90$ K for $ErFeO_3$ and $TmFeO_3$. Note that the Neel temperatures in these magnetodielectrics remain roughly the same: $T_N \approx 627$K for $YbFeO_3$, $T_N \approx 636$ K for $ErFeO_3$, and $T_N \approx 632$ K for $TmFeO_3$. It was conjectured that this model would be suitable for all orthoferrites with $\Gamma_4 \to \Gamma_{24} \to \Gamma_2$ phase transitions.

2. Experimental Results

All measurements of the spontaneous magnetization of $YbFeO_3$, $TmFeO_3$, and $ErFeO_3$ were performed on samples prepared from single crystals. The results obtained on crystals grown by different methods are in a good agreement.

The magnetic moments were measured using a Superconducting Quantum Interference Device (SQUID) magnetometer Quantum Design MPMS-5S. Measurements of the magnetic moment as a function of temperature were performed both in zero magnetic field (through the analysis of hysteresis loops) and at the weak field. Indeed, knowing the shape of the loops, a simpler and faster procedure to measure M_a and M_c can be implemented. It was observed that in a rather weak field, $H = 50 \div 250$ Oe, the magnetization value is approximately equal to bulk $M_{a,c}$ for all temperatures. Thus, simple temperature sweeps at a fixed weak field directed along the $\mathbf{a}$- or $\mathbf{c}$-axis give the corresponding components of $\mathbf{M}$. Fig. 3 shows $M_{a,c}$ measured in this

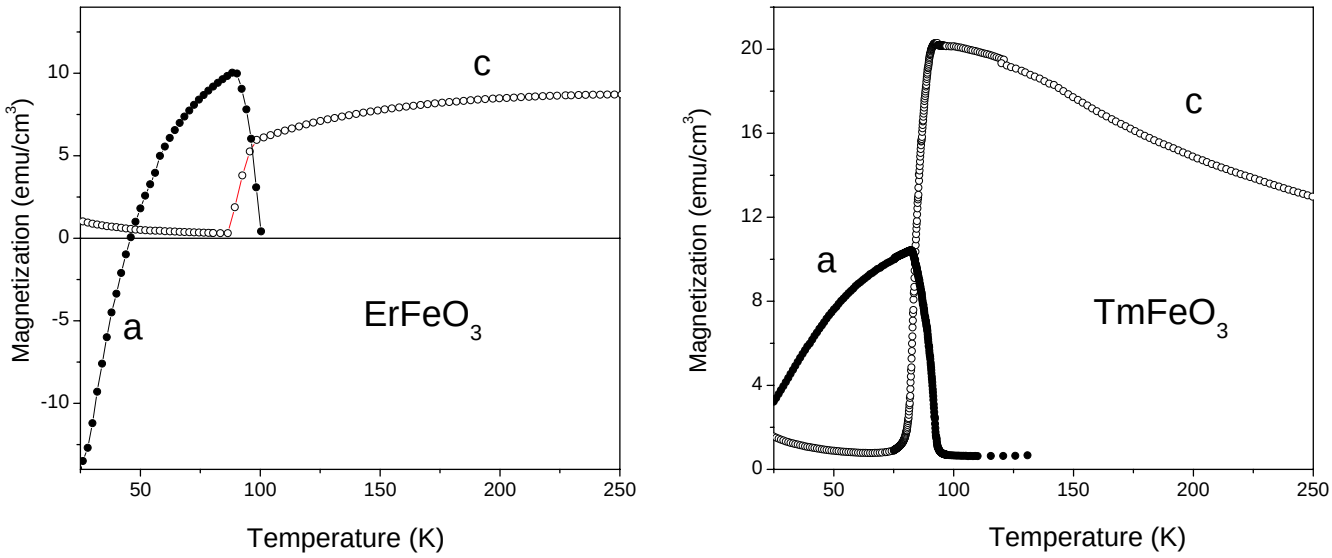

Fig. 3. Magnetic moment projections $M_{a,c}$ of $ErFeO_3$ and $TmFeO_3$ in a wide temperature range

manner for $ErFeO_3$ and $TmFeO_3$ over the temperature interval 25—250 K. The difference between such measured values and those obtained on the basis of the analysis of loops is insignificant. Fig. 3 shows how the overall magnetization behavior can be substantially different even for materials with similar spin-reorientation temperatures.

Knowing M_a and M_c, one can reconstruct the temperature dependence of $|\mathbf{M}|$ and the rotation angle θ:

$$|\mathbf{M}| = \sqrt{M_a^2 + M_c^2}, \quad \theta = \arctan\left(\frac{M_a}{M_c}\right).$$

The results are shown in Figs. 4 and 5. Fig. 4 clearly shows that, in the tilted phase of all the investigated orthoferrites, a dramatic change of the magnetization in the narrow (T_1—T_2) interval is observed. This shows a marked difference from the usually assumed [5] constancy of magnetization in the reorientation process. Next, Fig. 5 demonstrates that the rotation angle in the (T_1—T_2) interval is changed continuously from 0 to 90 degrees, but the temperature dependence of the rotation angle is also incompatible with the Landau mean-field theory usually applied to the spin-reorientation transition.

The temperatures T_1 and T_2 were extracted from experimental data using several procedures. The determination is based on the measurements of the quantities that have singularities at second-order phase transitions. These are: ultrasound attenuation, RF absorbtion, and ferromagnetic resonance. In real crystals, the reorientation interval changes with purity, perfection, and growth conditions and changes slightly from sample to sample. Reorientation temperatures are controlled by the behavior of the anisotropy constants. Thus, it is understandable that the processes, e.g. chemical and thermal ones, that influence the anisotropy will also change the transition temperatures. The quantitative analysis of experimental data requires the determination of T_1 and T_2 for each crystal under study.

3. Discussion

The $\theta(T)$ dependence in orthoferrites is considered to be well described by the mean-field Landau theory [5]. In the usual approach, a free energy functional of the form

$$\mathcal{F} = \mathcal{F}_0 + \frac{1}{2}K_u(T)\cos(2\theta) + K_b\cos(4\theta) \qquad (1)$$

is used. The reorientation region is defined by the inequalities

$$-8K_b < K_u(T) < 8K_b$$

and, within them, the rotation angle is given by

$$\tan^2\theta(T) = \frac{8K_b + K_u(T)}{8K_b - K_u(T)}.$$

It is also assumed that, within this interval, $K_u(T)$ has an approximately linear dependence on T:

$$K_u(T) = 8K_b\xi(T), \quad \xi(T) = \frac{(T_1+T_2)/2 - T}{(T_1-T_2)/2}.$$

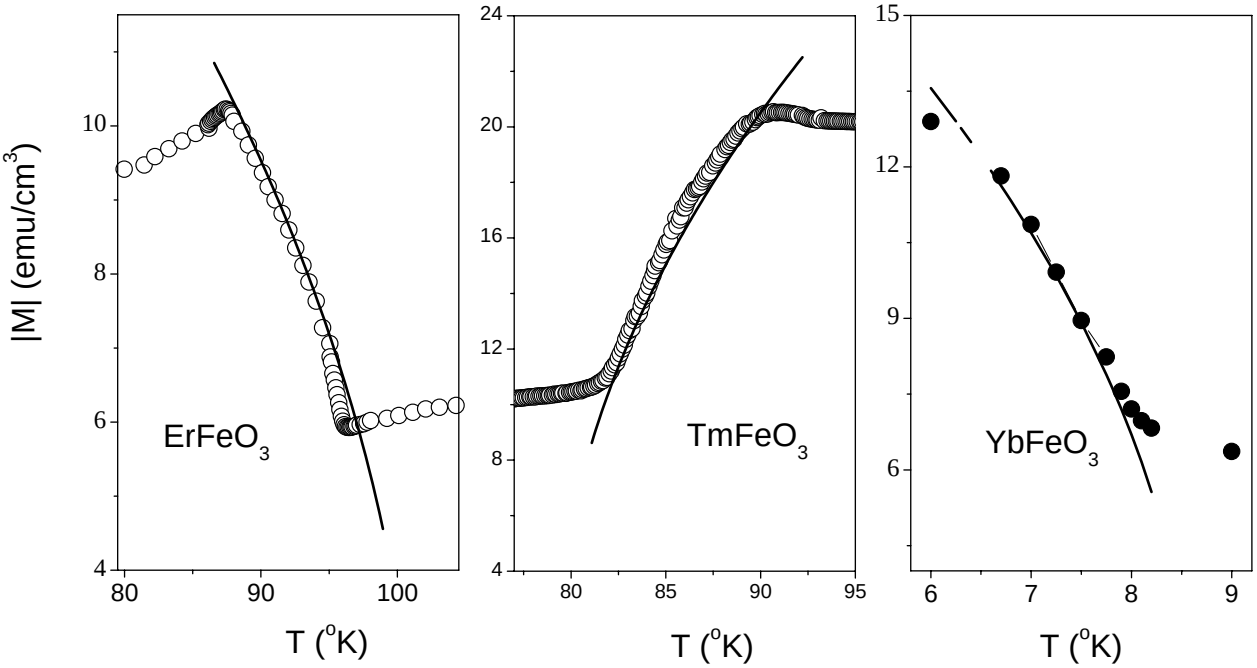

Fig. 4. Absolute value of magnetization $|\mathbf{M}|(\mathbf{T})$ in the reorientation region $T \in [T_1, T_2]$ at zero external field for all measured materials. The magnetization was calculated from the $\mathbf{M}$ components measured at weak field, as explained in the text. Solid curves are drawn according to relation (8)

Then the angle is given by

$$\tan\theta = \sqrt{\frac{1+\xi}{1-\xi}}. \tag{2}$$

When the orientation phase transition temperatures are known, this formula has no fitting parameters. The resulting $\theta(T)$ is shown in Fig. 5 as a dotted line. It is seen that relation (2) does not describe the experimental results. This is not very surprising, since the measurements show (see Fig.4) that the magnetic moment is not the same in phases, but rather changes during the reorientation. From T_1 to T_2, it changes by the factors $M_a(T_2)/M_c(T_1) \approx 1.72$ for $ErFeO_3$, $M_a(T_2)/M_c(T_1) \approx 0,47$ for $TmFeO_3$, and $M_a(T_2)/M_c(T_1) \approx 1.78$ for $YbFeO_3$. Thus, at least the assumption of constant M which leads to (2) is violated in these materials.

How can the magnetization of a rare-earth orthoferrite change by about (70—100)% in the temperature interval of several Kelvin degrees if the reorientation happens so far below the Neel temperature of the material? This change in the magnitude of $|\mathbf{M}|$ is assumed to be due to the change of the rare earth magnetization $\mathbf{m}$, while the iron magnetization $\mathbf{F}$ indeed does not change. In the reorientation interval, rare-earth ions are paramagnetic and only partially magnetized by the molecular field of the iron subsystem. Phenomenologically, the angle dependence of $|\mathbf{M}|$ can be reproduced by assuming that the susceptibilities of the R-ions to the molecular field in the **a**- and **c**-directions are different

$$m_a = \chi_a^{\mathrm{R}} F_a,$$
$$m_c = \chi_c^{\mathrm{R}} F_c \tag{3}$$

For $\chi_c^{\mathrm{R}} \neq \chi_a^{\mathrm{R}}$, $|\mathbf{m}|$ (and accordingly $|\mathbf{M}|$) will change as $\mathbf{F}$ rotates. It should be underscored that, in this approach, a change of $|\mathbf{m}|$ is not due to the temperature dependence of $\hat{\chi}$, but because different components of the susceptibility tensor are relevant for the high and low ends of the interval.

To describe this mechanism in the mean-field theory, we consider the free energy functional

$$\tilde{\mathcal{F}} = \tilde{\mathcal{F}}_0 + \frac{1}{2}K_u(T)\cos(2\theta_F) + K_b\cos(4\theta_F) -$$
$$-\beta(F_a\chi_a^{\mathrm{R}}m_a + F_c\chi_c^{\mathrm{R}}m_c) + \frac{\beta}{2}\mathbf{m}^2 \tag{4}$$

where θ_F is the rotation angle of $\mathbf{F}$: $F_a = F\sin\theta_F$, $F_c = F\cos\theta_F$. The third term in (4) describes the

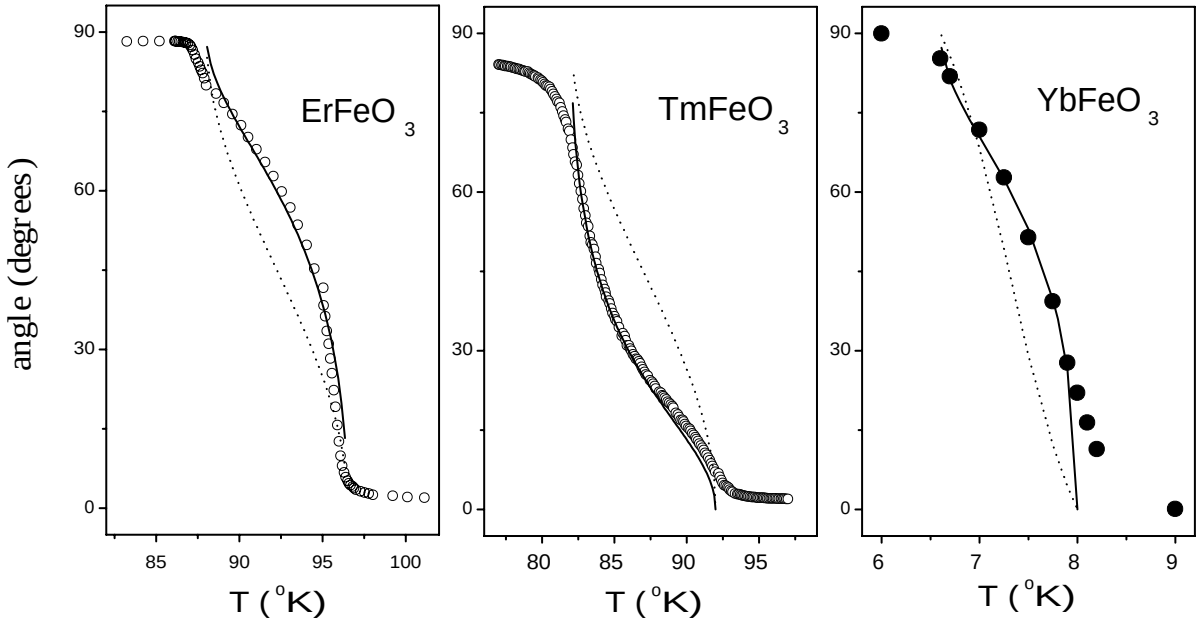

Fig. 5. Rotation angle $\theta(T)$ of the magnetization in the reorientation region $T \in [T_1, T_2]$ at zero external field. The angle is calculated from the **M** components measured at weak field, as explained in the text. The dotted line represents a conventional mean-field theory result given by relation (2). Solid curves correspond to relation (7)

influence of the iron molecular field on the erbium magnetization and the fourth term with $\beta > 0$ ensures that the erbium subsystem is paramagnetic.

The minimization of $\tilde{\mathcal{F}}$ with respect to m_a and m_c indeed gives relations (3). When evaluated at the equilibrium values of **m**, relation (4) gives

$$\tilde{\mathcal{F}} = \tilde{\mathcal{F}}_0 + \frac{1}{2}K_u(T)\cos(2\theta_F) + K_b\cos(4\theta_F) -$$

$$-\frac{\beta}{2}((\chi_a^{\mathrm{R}})^2F_a^2 + (\chi_c^{\mathrm{R}})^2F_c^2) =$$

$$= \tilde{\mathcal{F}}_0' + \frac{1}{2}K_u'(T)\cos(2\theta_F) + K_b\cos(4\theta_F) \qquad (5)$$

with new coefficients defined as

$$\tilde{\mathcal{F}}_0' = \tilde{\mathcal{F}}_0 - \frac{\beta F^2}{4}((\chi_a^{\mathrm{R}})^2 + (\chi_c^{\mathrm{R}})^2),$$

$$K_u' = K_u - \frac{\beta F^2}{2}((\chi_c^{\mathrm{R}})^2 - (\chi_a^{\mathrm{R}})^2). \qquad (6)$$

Relation (5) has the same form as (1) and thus leads to the same picture of the two phase transitions. Due to the renormalization of K_u (6), the OPT temperatures are now different, but in terms of the actual T_1, T_2 known from experiment, the angle θ_F is given by the same relation (2) as before. The angle of rotation of the total magnetization **M** is obtained from

$$\tan\theta = \frac{M_a}{M_c} = \left(\frac{1+\chi_a^{\mathrm{R}}}{1+\chi_c^{\mathrm{R}}}\right)\frac{F_a}{F_c} = \left(\frac{1+\chi_a^{\mathrm{R}}}{1+\chi_c^{\mathrm{R}}}\right)\tan\theta_F.$$

Taking into account that $M(T_1) = M_c(T_1) = (1+\chi_c^{\mathrm{R}})F$ and $M(T_2) = M_a(T_2) = (1+\chi_a^{\mathrm{R}})F$, this formula can be rewritten as

$$\tan\theta = \frac{M_a(T_2)}{M_c(T_1)}\tan\theta_F.$$

As a result, the modified mean-field theory predicts

$$\tan\theta = r\sqrt{\frac{1+\xi}{1-\xi}}, \quad r = \frac{M_a(T_2)}{M_c(T_1)} \qquad (7)$$

and

$$|M| = M_c(T_1)\sqrt{\frac{r^2(1+\xi)+(1-\xi)}{2}}. \qquad (8)$$

Again, for these formulas, there are no adjustable parameters that are not determined from the experiment. Using the relation $M_a(T_2)/M_c(T_1)$ the theoretical curves (the full line in Fig. 5) and the observed data are in a very good agreement.

Note that the analysis of experimental data in terms of the model introduced in [7, 8] is only valid inside the reorientation region. However, it is important that,

inside the region of its validity, such a analysis is independent of the driving mechanism of the transition, be it the interactions in the iron subsystem, the R-Fe interactions, the behavior of the rare-earth magnetic succeptibility, or any other process. The approach developed in [7, 8] only requires the effective anisotropy constant $K_u(T)$ to be a linear function of temperature. Since precisely that behavior of $K_u(T)$ was measured in [11, 12] and work [13] showed that such a behavior follows from the microscopic model of [14], the modified mean-field theory [7, 8] can be applicable for a wide variety of orthoferrites.

The work at O.Galkin Physics & Technology Institute National Academy of Sciences of Ukraine was partially supported by the State Fund for Fundamental Research of Ukraine, project F7/203-2004. Ya.B. was supported by DARPA/ARO, Contract No. DAAD19-01-C-006.

1. *Marezio M., Remeika J. P., Dernier P. D.* // Acta cryst. — 1970. — **B26**.— P.2008
2. *White R. L.* // J Appl.Phys. — 1969. — **40**.— P.1061.
3. *Shane J.R.* // Phys. Rev. Lett. — 1968. — **20**.— P.728; *H. Horner, C. M. Varma* // Phys. Rev. Lett. — 1968. — **20**.— P.845.
4. *Sirvardiere J.* //Solid State Communs. — 1969. — **7**.— P.1555.
5. *Belov K.P., Zvezdin A.K., Kadomtseva A.M., Levitin R.Z.* Orientation Phase Transitions in Rare-Earth Magnetic Materials.— Moscow: Nauka, 1979 (in Russian).
6. *Kimel A.V., Kirilyuk A., Tsvetkov A. et al.* // Nature. — 2004.— **429**.— P.850.
7. *Bazaliy Ya.B., Tsymbal L.T., Kakazei G.N. et al.* // Phys. Rev. B. — 2004. — **69**.— P.104429.
8. *Bazaliy Ya.B., Tsymbal L.T., Kakazei G.N., Wigen P.E*// J. Appl. Phys. — 2004. — **95**.— P.6622.
9. *Tsymbal L.T., Bazaliy Ya.B., Kakazei G.N. et al.* // Fiz. Nizk. Temp. — 2005. — **31**.— P.367.
10. *Bazaliy Ya.B., Tsymbal L.T., Kakazei G.N. et al.* // Preprint. — 2005. — cond-mat/0503060.
11. *Abe M., Gomi M., Shono K. et al.* // Jap. J. Appl. Phys. — 1977. — **16**.— P.279.
12. *Belov K.P., Volkov R.A., Goranskii B.P. et al.* // Soviet Physics Solid State. — 1969. — **11**.— P.935.
13. *W. J. Schaffer, R. W. Bene, and R. M. Walser* // Phys. Rev. B. — 1974 — **10**. — P.255
14. *Levinson L.M., Luban M., Shtrikman S.* // Phys. Rev. — 1969. — **187**.— P.715.

ЗАГАЛЬНІ ВЛАСТИВОСТІ СПІН-РЕОРІЄНТАЦІЙНИХ ПЕРЕХОДІВ В ОРТОФЕРИТАХ

Л.Т. Цимбал, Я.Б. Базалій, Г.М. Каказей, П.Є. Віген

Р е з ю м е

Виміряно температурні залежності намагніченості $|\mathbf{M}|(T)$ та кута її повороту $\theta(T)$ при орієнтаційних фазових перетвореннях $\Gamma_4 \to \Gamma_{24} \to \Gamma_2$ в монокристалах $YbFeO_3$, $ErFeO_3$ та $TmFeO_3$. Встановлено невідповідність їх поведінки загальноприйнятій теорії середнього поля Ландау. Запропоновано модифіковану теорію середнього поля, яка не містить невідомих з експерименту параметрів. Ключовим моментом моделі є враховування анізотропного рідкісноземельного внеску у загальну намагніченість. Чітке узгодження з експериментом для ряду матеріалів зі значною відмінністю магнітних параметрів демонструє загальність запропонованого опису орієнтаційних фазових перетворень $\Gamma_4 \to \Gamma_{24} \to \Gamma_2$ в ортоферитах.

ОБЩИЕ СВОЙСТВА СПИН-РЕОРИЕНТАЦИОННЫХ ПЕРЕХОДОВ В ОРТОФЕРРИТАХ

Л.Т. Цымбал, Я.Б. Базалий, Г.Н. Каказей, П.Е. Виген

Р е з ю м е

Измерены температурные зависимости намагниченности $|\mathbf{M}|(T)$ и угла её поворота $\theta(T)$ при ориентационных фазовых переходах $\Gamma_4 \to \Gamma_{24} \to \Gamma_2$ в монокристаллах $YbFeO_3$, $ErFeO_3$ и $TmFeO_3$. Установлено несоответствие их поведения общепринятой теории среднего поля Ландау. Предложена модифицированная теория среднего поля, не включающая неизвестных из эксперимента параметров. Ключевым моментом модели является учёт анизотропного редкоземельного вклада в общую намагниченность. Убедительное совпадение с экспериментом для ряда материалов со значительно отличающимися магнитными параметрами демонстрирует общность предложенного описания ориентационных фазовых превращений $\Gamma_4 \to \Gamma_{24} \to \Gamma_2$ в ортоферритах.