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Simple Realistic Model of Spin Reorientation in 4f-3d Compounds

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Abstract: This is a simple but realistic microscopic theory of spontaneous spin reorientation in rare-earth perovskites, orthoferrites $R\text{FeO}_3$ and orthochromites $R\text{CrO}_3$, induced by the 4f-3d interaction, namely, the interaction of the well-isolated ground-state Kramers doublet or non-Kramers quasi-doublet of the 4f ion with an effective magnetic field induced by 3d sublattice. Both the temperature and the nature of the spin-reorientation transition are the result of competition between the second- and fourth-order spin anisotropy of the 3d sublattice, the crystal field for 4f ions, and 4f-3d interaction.

Keywords: 4f-3d interaction; (quasi)doublets; spin reorientation

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1. Introduction

Rare-earth orthorhombic perovskites, orthoferrites $R\text{FeO}_3$ and orthochromites $R\text{CrO}_3$ (where R is a rare-earth ion and yttrium), exhibit many important features, such as weak ferro- and antiferromagnetism, which are an overt and hidden canting of magnetic sublattices, magnetization reversal, anomalous circular magnetooptics and the phenomenon of spontaneous spin reorientation (see, e.g., review article [1]). Spin reorientation (SR) is one of their unique properties that attracted a lot of attention back in the 1970s [2,3], though their exact microscopic origin is still a challenge to theorists and experimentalists.

The revival of interest in the mechanism of the spontaneous spin reorientation and magnetic compensation in rare-earth perovskites in recent years is related to the discovery of the magnetoelectric and exchange bias effects, which can have a direct application in magnetoelectronics. Along with the emergence of new experimental studies (see, e.g., [4,5]), there have also appeared theoretical works claiming to modify the mean-field theory of spontaneous spin-reorientation transitions [6] or to scrutinize the microscopic mechanism responsible for spin reorientations and magnetization reversal [7]. In fact, these results are not directly related to the microscopic theory of spontaneous spin reorientation in rare-earth orthoferrites and orthochromites. For instance, the authors of the most recent paper [7] did not take into account a number of interactions, such as the fourth-order anisotropy for the 3d sublattice of orthoferrites and the crystal field for R-ions, which play fundamental roles in determining spontaneous spin reorientation. The spin anisotropy of the second order in the 3d sublattice of orthorhombic orthoferrites and orthochromites is generally not reduced to an effective uniaxial form as adopted in [7]. Furthermore, the density functional theory does not allow, in principle, to give an adequate description of such effects of higher orders of perturbation theory as spin anisotropy or antisymmetric exchange [8,9].

In this paper, we present the results of a simple but realistic microscopic model of the spontaneous spin reorientation in rare-earth orthoferrites and orthochromites, which takes into account all the main relevant interactions. This model was developed back in the 1980s [10], but has not been published until now.

2. Model Formulation

The most popular examples of systems with spontaneous SR transitions are magnets based on 3d and 4f elements, such as rare-earth orthoferrites $R\mathrm{FeO_3}$, orthochromites $R\mathrm{CrO_3}$, intermetallic compounds $R\mathrm{Co_5}$, $R\mathrm{Fe_2}$, etc. In all cases, an important cause of the spontaneous SR is the 4f-3d interaction. Usually this interaction is taken into account by introducing an effective field of the magnetically ordered 3d sublattice acting on the 4f ions.

To consider the contribution of the rare-earth sublattice to the free energy at low temperatures, we are developing a model that takes into account either the well-isolated lower Kramers doublet of the 4f ions (with an odd number of the 4f electrons) or the well-isolated two lower Stark sublevels with close energies that form a quasi-doublet.

Within the framework of such "single–doublet" approximation, we consider the spontaneous SR transition in orthorhombic weak ferromagnets $R\mathrm{FeO_3}$ and $R\mathrm{CrO_3}$, where the free energy per ion can be represented as follows

$$\Phi(\theta) = K_1 \cos 2\theta + K_2 \cos 4\theta - kT \ln 2 \cosh \frac{\Delta(\theta)}{2kT}, \quad (1)$$

where K_1 and K_2 are the first and second anisotropy constants of the 3d sublattice, respectively, which are temperature-independent (at least in the SR region), θ is the orientation angle of the main antiferromagnetic, or Néel vector $\mathbf{G}$ of the 3d sublattice (e.g., in the *ac* plane), and $\Delta(\theta)$ is the lower doublet (quasi-doublet) splitting of the 4f ion in a magnetic field induced by the 3d sublattice. The last term in (1) is the 4f doublet contribution to the free energy: $\Delta\Phi(\theta) = -kT \ln Z$, where Z is the statistical sum and k is the Boltzmann constant.

Theoretical estimations [10–12] of the different contributions to the first constants of the magnetic anisotropy for orthoferrites $R\mathrm{FeO_3}$ point to competition between several main mechanisms with relatively regular (Dzyaloshinskii-Moriya (DM) coupling, magnetodipole interaction) or irregular (single-ion anisotropy, SIA) dependence on the type of R-ion. For instance, the microscopic theory predicts an unexpectedly strong increase in values of the constant $K_1(ac)$ for $\mathrm{LuFeO_3}$ as compared with $\mathrm{YFeO_3}$. The SIA contribution to $K_1(ac)$ partially compensates for the large contribution of the DM interaction in $\mathrm{YFeO_3}$, whereas in $\mathrm{LuFeO_3}$, they add up. This result is confirmed by experimental data on the measurement of the threshold field H_{SR} of spin reorientation $\Gamma_4 \to \Gamma_2$ $(G_x \to G_z)$ in the orthoferrite $\mathrm{Lu_{0.5}Y_{0.5}FeO_3}$, in which $H_{SR} = 15$ T as compared to $H_{SR} = 7.5$ T in $\mathrm{YFeO_3}$ [12]. Thus, one can estimate $K_1(ac)$ in $\mathrm{LuFeO_3}$ as around three times as much as $K_1(ac) \approx 2 \times 10^5$ erg/cm^3 ≈ 1 K/ion in $\mathrm{YFeO_3}$ [11,12].

Let us pay attention to recent work on the determination of the parameters of the spin-Hamiltonian in $\mathrm{YFeO_3}$ from measurements of the spin–wave spectrum by inelastic neutron scattering [13,14] and terahertz absorption spectroscopy [15]. However, these authors started with a simplified spin-Hamiltonian that took into account only Heisenberg exchange, DM interaction, and single-ion anisotropy. Obviously, disregarding the magnetic dipole and exchange-relativistic anisotropy, the "single-ion anisotropy" constants found by the authors are some effective quantities that are not directly related to the SIA.

Unfortunately, despite numerous, including fairly recent, studies of the magnetic anisotropy of orthoferrites, we do not have reliable experimental data on the magnitude of the contributions of various anisotropy mechanisms.

As shown by theoretical calculations [10,11,16], the constants K_2 of fourth-order spin anisotropy in $R\mathrm{FeO_3}$ rather smoothly decrease in absolute value, changing by no more than two times when going from La to Lu, in $\mathrm{YFeO_3}$, $K_2(ac) \approx 1.5 \times 10^4$ erg/cm^3 ≈ 0.1 K/ion. But the most interesting was the conclusion about the different signs of these constants, positive for the *ac* and *bc* planes and negative for the *ab* plane, thus indicating a different character of spin-reorientation transitions in the corresponding planes, i.e., second-order transitions in the *ac* and *bc* planes and first-order transitions in the *ab* plane [3]. Indeed, all currently known spin-reorientation transitions of the $\Gamma_4 - \Gamma_2$ $(G_x - G_z)$ type in orthoferrites $R\mathrm{FeO_3}$ (R = Pr, Nd, Sm, Tb, Ho, Er, Tm, Yb) are smooth, with two characteristic temperatures of the second-order phase transitions to be a start and finish of the spin reorientation, and the only known jump-like first-order SR transition for these crystals is the SR transition $\Gamma_4 - \Gamma_1$ ($G_x - G_y$) in the *ab* plane in $DyFeO_3$ [3]. A unique example that confirms the conclusions about the sign of the second anisotropy constant is a mixed orthoferrite $Ho_{0.5}Dy_{0.5}FeO_3$ [3] in which two spin-reorientation transitions, $G_x - G_y$ ($T = 46$ K) and $G_y - G_z$ ($18 \div 24$ K), are realized through one phase transition of the first order in the *ab* plane and two phase transitions of the second order in the *bc* plane, respectively.

The splitting value $\Delta(\theta)$ for the Kramers doublet in a magnetic field $\mathbf{H}$ has the well-known form

$$\Delta(\theta) = \mu_B \left[\left(g_{xx} H_x + g_{xy} H_y \right)^2 + \left(g_{xy} H_x + g_{yy} H_y \right)^2 + g_{zz}^2 H_z^2 \right]^{1/2}, \tag{2}$$

where it is taken into account that for the $4f$ ions in $RFeO_3$, the $\hat{g}$-tensor, which reflects both the local point symmetry C_s and the strength of the crystal field, has the form

$$\hat{g} = \begin{pmatrix} g_{xx} & g_{xy} & 0 \\ g_{xy} & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix}. \tag{3}$$

The effective field $\mathbf{H}$ for the SR transition $G_x \to G_z$ in the *ac* plane can be represented as follows

$$H_x = H_x^{(0)} \cos\theta, \;\; H_y = H_y^{(0)} \cos\theta, \;\; H_z = H_z^{(0)} \sin\theta, \tag{4}$$

so in the absence of an external magnetic field, for $\Delta(\theta)$ we have the rather simple expression:

$$\Delta(\theta) = \left(\frac{\Delta_a^2 - \Delta_c^2}{2} \cos 2\theta + \frac{\Delta_a^2 + \Delta_c^2}{2} \right)^{1/2}, \tag{5}$$

where $\Delta_{a,c}$ are doublet splitting for the cases of $\theta = 0$ (G_z-phase) and $\theta = \pi/2$ (G_x-phase), respectively. The dependence $\Delta(\theta)$ from (5) is also valid in the case of quasi-doublet.

A contribution of splitting Δ to the free energy $\Phi(\theta)$ for the rare-earth sublattice is usually considered in the "high-temperature" approximation, when $kT \gg \Delta$ and the influence of the $4f$ sublattice is reduced only to renormalization of the first anisotropy constant K_1:

$$K_1^* = K_1 \left(1 - \frac{1}{\tau} \right), \tag{6}$$

where $\tau = T/T_{SR}$ is the reduced temperature and $T_{SR} = (\Delta_a^2 - \Delta_c^2)/16kK_1$ is the characteristic transition temperature.

Below we will consider a specific situation when $K_1 > 0$ and $\Delta_a > \Delta_c$, i.e., when the configuration G_x ($\theta = \pi/2$) is realized at high temperatures and a decrease in temperature can lead to the spin reorientation $G_x \to G_z$ or $G_x \to G_{xz}$ (transition to an angular spin structure). The type of phase transition of the spin reorientation in the "high-temperature" approximation is determined by the sign of the second constant K_2: at $K_2 < 0$ it will be realized by one first-order phase transition at $T = T_{SR}$, i.e., $\tau = 1$, or at $K_2 > 0$ by two second-order phase transitions at $\tau_s = (1+\gamma)^{-1}$ and $\tau_f = (1-\gamma)^{-1}$, where τ_s and τ_f are the reduced temperatures of the beginning and end of the SR phase transition and $\gamma = 4K_2/K_1$.

Analysis of the "Single-Doublet" Model

A behavior of a system described by the free energy (1) can be analyzed rigorously. The condition $\partial\Phi/\partial\theta = 0$ reduces in this case to two equations:

$$\sin 2\theta = 0, \tag{7}$$

$$\alpha\mu + \beta\mu^3 = \tanh\frac{\mu}{\tau}; \tag{8}$$

where the following notations are introduced:

$$\alpha = 1 - \gamma\frac{\Delta_a^2 + \Delta_c^2}{\Delta_a^2 - \Delta_c^2},\ \beta = \frac{2\gamma}{\mu_f^2 - \mu_s^2},\ \mu = \frac{\Delta(\theta)}{2kT_{SR}},\ \mu_s = \frac{\Delta_c}{2kT_{SR}},\ \mu_f = \frac{\Delta_a}{2kT_{SR}}. \quad (9)$$

This corresponds to three possible magnetic configurations:

- The configuration G_x: $\theta = \pm\pi/2$, stable at $\tanh \mu_s/\tau \le \alpha\mu_s + \beta\mu_s^3$.
- The configuration G_z: $\theta = 0,\ \pi$, stable at $\tanh \mu_f/\tau \ge \alpha\mu_f + \beta\mu_f^3$.
- The angular configuration G_{xz}: the temperature dependence of $\theta(\tau)$ is determined by solving the Equation (8) (see Figure 1), the state is stable at $\partial\mu/\partial\tau \le 0$.

The peculiar μ–τ phase diagram representing solutions of the master Equation (8) given a fixed value for α and different values for β is shown in Figure 1, where areas with different character of the SR transition are highlighted in different colors. For the solutions in the FO region, the SR goes through one first-order phase transition; in the SO region, we arrive at one or two second-order phase transitions; in the $MO_{1,2}$ regions, we arrive at a "mixture" of the first- and second-order phase transitions. All the lines $\mu(\tau)$ on the right side converge to $\sqrt{|\alpha/\beta|}$ at $\tau \to \infty$; on the left side, when $\tau \to 0$, the branch point $\mu = \frac{3}{2\alpha}$ is obtained at $\beta = -\frac{4}{27}\alpha^3$, and the point $\mu = 1/\alpha$ at $\beta = 0$; all the solutions where μ can reach zero converge to $\tau = 1/\alpha$.

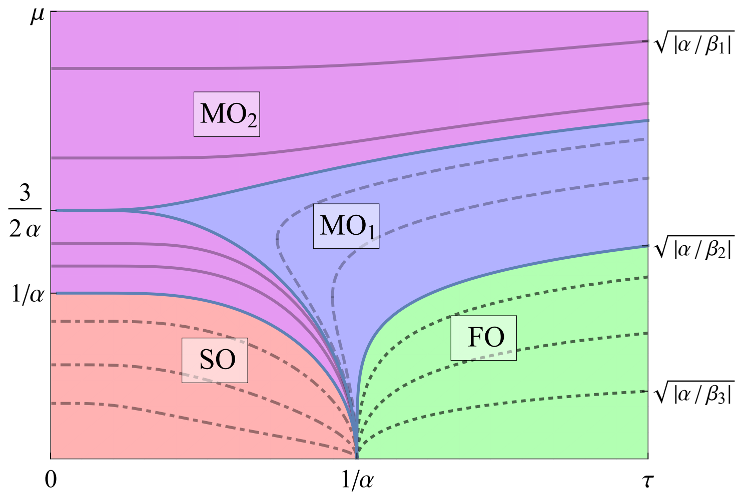

Figure 1. (Color online) The peculiar μ–τ phase diagram representing solutions of the master Equation (8) given a fixed value for α and different values for β (see text for details).

The character of the SR transition will be determined by the form of the solution of Equation (8) in the region $\mu_s \le \mu \le \mu_f$. Let us analyze this equation starting with the simplest case: $K_2 = 0$, i.e., $\alpha = 1$, $\beta = 0$. In this case, the main equation transforms into the molecular field equation well known in the basic theory of ferromagnetism:

$$\mu = \tanh\frac{\mu}{\tau} = B_{\frac{1}{2}}\left(\frac{\mu}{\tau}\right), \quad (10)$$

where $B_{1/2}(x)$ is the Brillouin function. The equation has only one non-trivial solution at $0 \le \tau \le 1$, $0 \le \mu \le 1$, and the function $\mu(\tau)$ has the usual "Weiss" form. Thus, with the absence of cubic anisotropy ($K_2 = 0$) in the "single-doublet" model, the SR will be realized either through two second-order phase transitions at $\mu_f \le 1$ (the complete spin-reorientation $G_x \to G_z$), or through one second-order phase transition at $\mu_f > 1$, but in this case the SR will be incomplete, i.e., it will end with a transition to the angular spin structure G_{xz}. The spin reorientation will begin at a temperature $T_s \le T_{SR}$, and T_s is equal to T_{SR} only in the case $\mu_s = 0$ ($\Delta_c = 0$), which can be realized in the general case only for Ising ions (e.g., Dy^{3+} in $DyFeO_3$). For this type of ions, the temperature dependence of the "order parameter" μ (in fact the splitting $\Delta(\theta)$ of the doublet) in a close range of T_{SR} will be very sharp: $\mu(T) \sim (T - T_{SR})^{-1/2}$. Nevertheless, the SR will be continuous, and the temperature range of the SR $\Delta T = T_s - T_f$ at $\mu \ll 1$ can theoretically reach arbitrarily small values.

Thus, the results of the rigorous analysis of the "single-doublet" model are fundamentally different from the conclusions of the simplified model (the "high-temperature" approximation), according to which, for $K_2 = 0$, the spin reorientation always occurs as the first-order phase transition at $T = T_{SR}$.

For a positive second anisotropy constant ($K_2 > 0$, $\beta > 0$), the main Equation (8) has one non-trivial solution in the region $0 \leq \tau \leq 1/\alpha$, $0 \leq \mu \leq \mu_0$ at $\alpha > 0$, and one in the region $0 \leq \tau \leq \infty$, $\sqrt{|\alpha/\beta|} \leq \mu \leq \mu_0$ at $\alpha \leq 0$, where μ_0 is determined from the solution of the equation $\alpha\mu_0 + \beta\mu_0^3 = 1$. The situation in this case is very similar to the previous one, i.e., the beginning of the SR will always be a second-order phase transition, and the reorientation will be complete ($G_x \to G_z$) or incomplete ($G_x \to G_{xz}$). Note that under the condition $(\mu_f^2 - \mu_s^2)/(\mu_f^2 + \mu_s^2) \geq \gamma$, i.e., $\alpha \leq 0$, the width of the reorientation region becomes very large, even if μ_s differs slightly from μ_f.

For Ising ions at $\Delta_c = 0$, the SR beginning temperature is determined in exactly the same way as in the "high-temperature" approximation $T_s = T_{SR}/(1+\gamma)$.

For a negative second anisotropy constant ($K_2 < 0$, $\beta < 0$), several fundamentally different solutions to the main Equation (8) are possible. For $K_2^* \geq K_2$, where K_2^* is determined from the condition $\beta = -\frac{1}{3}\alpha^3$, i.e.,

$$\frac{2\gamma}{\mu_f^2 - \mu_s^2} = -\frac{1}{3}\left(1 - \gamma\frac{\mu_f^2 + \mu_s^2}{\mu_f^2 - \mu_s^2}\right)^3, \tag{11}$$

there is one non-trivial solution of Equation (8) in the region $1/\alpha \leq \tau < \infty$, $\mu \leq \sqrt{\alpha/\beta}$, but here $\mu(T)$ decreases with decreasing temperature, i.e., $\partial\mu/\partial\tau > 0$. This solution is unstable, and there is no fundamental possibility for a smooth rotation of spins—the SR is always realized through the first-order phase transition.

In the intermediate range of values K_2 ($K_2^* < K_2 < 0$ or $-\frac{1}{3}\alpha^3 < \beta < 0$), the main equation has two non-trivial solutions, and for one of them, $\partial\mu/\partial\tau > 0$ (corresponding to bigger values of μ), and for the second, $\partial\mu/\partial\tau < 0$ (corresponding to smaller values of μ). It is convenient to consider separately three areas of variation β.

1. $-\frac{4}{27}\alpha^3 < \beta < 0$:
   (a) the first solution: $0 \leq \tau < \infty$, $\mu_> \leq \mu < \sqrt{|\alpha/\beta|}$,
   (b) the second solution: $0 \leq \tau \leq 1/\alpha$, $0 \leq \mu \leq \mu_<$,
   where $\mu_>$ and $\mu_<$, respectively, are the bigger and smaller positive solutions of the equation $\alpha\mu + \beta\mu^3 = 1$.
2. $\beta = -\frac{4}{27}\alpha^3$:
   (a) the first solution: $0 \leq \tau < \infty$, $3/(2\alpha) \leq \mu < \sqrt{|\alpha/\beta|}$,
   (b) the second solution: $0 \leq \tau \leq 1/\alpha$, $0 \leq \mu \leq 3/(2\alpha)$;
   moreover, in this case we have a branch point of the main equation solution at $\tau = 0$, $\mu = 1$.
3. $-\frac{1}{3}\alpha^3 < \beta < -\frac{4}{27}\alpha^3$:
   (a) the first solution: $\tau_0 \leq \tau < \infty$, $\mu_0 \leq \mu < \sqrt{|\alpha/\beta|}$,
   (b) the second solution: $\tau_0 \leq \tau \leq 1/\alpha$, $0 \leq \mu \leq \mu_0$,
   where the quantities μ_0 and τ_0 correspond to the branch points of the main equation solutions.

Illustrations of typical (a,b) and unconventional (c,d) SR transitions predicted by simple (quasi)doublet model are shown in Figure 2. Figure 2a, built with $K_1 = 1$, $\gamma = 0.05$, $\Delta_a = 30.84$, $\Delta_c = 14.82$, which corresponds to $T_{SR} = 45.73$, $\mu_s = 0.162$, $\mu_f = 0.337$, $\tau_s = 1.04$, $\tau_f = 0.91$, describes a typical smooth SR transition with two second-order phase transitions $G_x - G_{xz}$ at the beginning (τ_s) and $G_{xz} - G_z$ at the end (τ_f) of the spin reorientation.

Figure 2b, built with $K_1 = 1$, $\gamma = -0.1$, $\Delta_a = 33.19$, $\Delta_c = 27.1$, which corresponds to $T_{SR} = 22.95$, $\mu_s = 0.59$, $\mu_f = 0.72$, $\tau_s = 0.762$, $\tau_f = 0.93$, describes an abrupt first-order SR transition. For $\tau > \tau_f$ there is the G_x-phase, which can remain stable up to τ_s when cooled. For $\tau < \tau_s$ there is the G_z-phase, which can remain stable up to τ_f when heated. Point A marks a phase transition point when the phases G_x and G_z have equal energies.

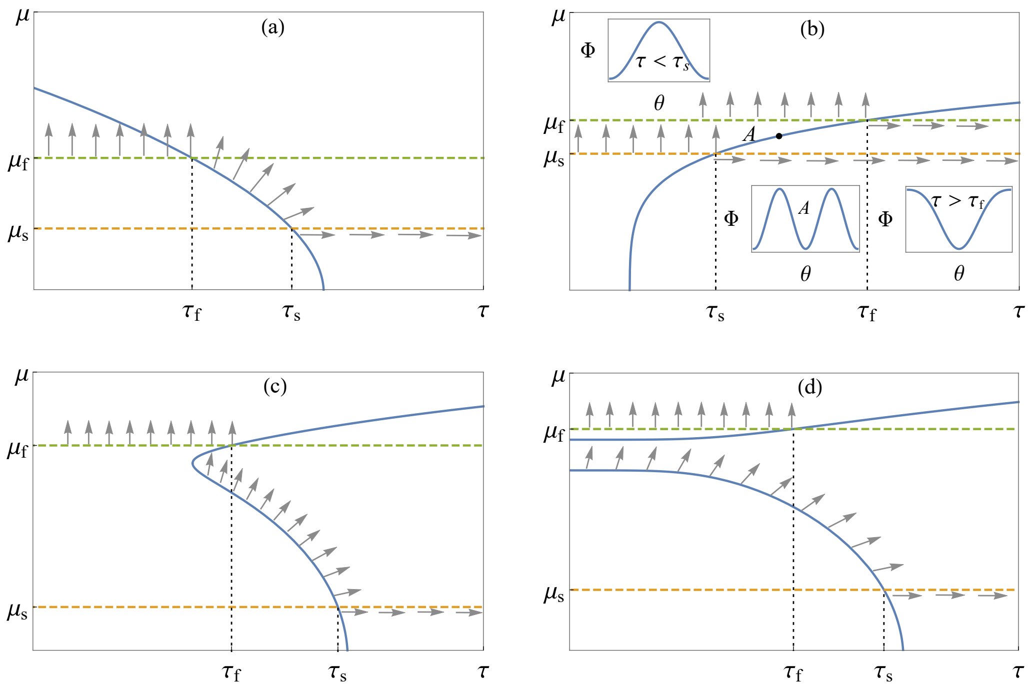

Figure 2. Illustrations of typical (**a**,**b**) and unconventional (**c**,**d**) SR transitions predicted by simple (quasi)doublet model (see text for detail). The arrows indicate the direction of the antiferromagnetic vector **G** in the *ac* plane. The insets in panel (**b**) show the θ-dependence of the free energy.

Figure 2c, built with $K_1 = 1$, $\gamma = -0.222$, $\Delta_a = 6.72$, $\Delta_c = 1.63$, which corresponds to $T_{SR} = 2.65$, $\mu_s = 0.307$, $\mu_f = 1.266$, $\tau_s = 0.778$, $\tau_f = 0.523$, and Figure 2d, built with $K_1 = 1$, $\gamma = -0.25$, $\Delta_a = 6.71$, $\Delta_c = 2.02$, which corresponds to $T_{SR} = 2.56$, $\mu_s = 0.396$, $\mu_f = 1.31$, $\tau_s = 0.73$, $\tau_f = 0.545$, describe unconventional "mixed" SR transitions. At τ_s, there is the smooth second-order phase transition $G_x - G_{xz}$. At $\tau \leq \tau_f$, we have two stable phases, G_z and G_{xz}: at those temperatures the sharp first-order phase transition $G_{xz} - G_z$ can happen, or the system could stay in the angular G_{xz}-phase.

Thus, there are not only the smooth and abrupt SR transitions—a characteristic feature of the range of intermediate values of K_2 is the fundamental possibility of the existence of "mixed" SR transitions, in which the spins first smoothly rotate through a certain angle and then jump to the position with $\theta = 0$. For this, it is sufficient that μ_f corresponds to a point on the upper branch of solutions, and μ_s to a point on the lower branch of solutions at $\tau_f < \tau_s$. In this case, the spin reorientation begins with the single second-order transition $G_x \to G_{xz}$ and then ends with the first-order phase transition $G_{xz} \to G_z$. In contrast to the "high-temperature" approximation, the "single-doublet" model claims the nature of the phase transition is determined not simply by the sign of the second anisotropy constant, but also it depends on the ratio between K_1 and K_2 and the doublet splitting in both phases. Nevertheless, if we apply the simplified model to describe the SR transition, we have to renormalize both the first and the second anisotropy constant, giving the last one sometimes a rather complicated temperature dependence, in particular with a change in sign when considering transitions of the "mixed" type. Of course, in this case, Fe sublattice alone is not enough to provide the value of the effective second constant.

3. Conclusions

A simple model of spin-reorientation transitions induced by the 4f-3d interaction with well-isolated ground-state Kramers doublet or non-Kramers quasi-doublet of the 4f ion in rare-earth orthoferrites and orthochromites has been investigated. It is shown that both the temperature and the nature of the spin-reorientation transition, which follow from the solution of the transcendental Equation (8), are the results of competition between the second- and fourth-order spin anisotropy of the 3d sublattice, the crystal field for 4f ions, and the 4f-3d interaction. At variance with the well-known "high-temperature" approximation, the "single-doublet" model, along with typical smooth and sharp SR transitions, predicts the appearance of mixed-type SR transitions with an initial second-order transition and a final sharp first-order transition.

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