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Simple spin-reorientation model for rare-earth orthoferrites and orthochromites

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A simple theory of spontaneous spin reorientation in rare-earth orthoferrites $RFeO_3$ and orthochromites $RCrO_3$ induced by 4f−3d-interaction is presented. It is shown that both the temperature and the nature of the spin reorientation are the result of the competition between the second- and fourth-order spin anisotropy of the 3d-sublattice, the crystal field for 4f-ions, and also the 4f−3d interaction. A case of the substitution of the rare-earth ions with a non-magnetic impurity is also considered.

Keywords: spin reorientation, 4f−3d interaction, weak ferromagnetism, orthoferrites, orthochromites.

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1. Introduction

The rare-earth orthoferrites $RFeO_3$ and the orthochromites $RCrO_3$ (where R — rare-earth ion or yttrium) are of interest due to their unique magnetic properties such as weak ferro- and anti-ferromagnetism, magnetic reversal, magnetoelectric effect and spontaneous spin-reorientation (SR) phenomenon. Rare-earth magnetics, as well as their orientation phase transitions, have been extensively studied in the past [1], but their exact microscopic description is still a pressing problem for theorists and experimentalists. The discovery of the multiferroicity and the exchange bias effect in many $RFe_xCr_{1-x}O_3$ magnetics (see e.g. [2]), which is of great importance in the field of magnetoelectronics, has led to a renewed interest in recent years.

Orthoferrites and orthochromites have a perovskite structure with slight rhombic distortions. Below the Néel temperature T_{N_1} (620−740 K for $RFeO_3$ and 100−300 K for $RCrO_3$) the 3d subsystem orders into a slightly canted antiferromagnetic structure $\Gamma_4(G_x, F_z)$ with antiferromagnetic moment **G** and weak ferromagnetic moment **F**, where $F \ll G$ [1,3]. With the decrease in temperature, or under external magnetic field, various SR transitions to structures of the $\Gamma_2(G_z)$ or $\Gamma_1(G_y)$ type may occur, with the 4f-subsystem in a rather wide temperature range being in a paramagnetic state (for R-ions $T_{N_2} < 10$ K). Note also, that due to the relations between **G** and **F**, we only need to consider one vector, e.g., **G**.

Various theoretical papers have emerged to describe spin-reorientation, such as those related to mean-field modification [4] or to the study of the microscopic mechanism [5]. But, strictly speaking, these results are not directly related to the microscopic theory of SR transitions in rare-earth orthoferrites and orthochromites. For example, the authors [5] have not considered a number of interactions, such as fourth order anisotropy for the 3d-sublattice of orthoferrites and the crystal field for R-ions, which play a fundamental role. In addition, density functional theory in principle does not allow one to adequately describe the effects of the high order perturbation theory, such as spin anisotropy or antisymmetric exchange [6,7].

In the present paper, a simple model of spontaneous spin-reorientation in rare-earth orthoferrites and orthochromites is studied, which takes into account all basic interactions in the system.

2. Basics of the „single-doublet“ model

For a wide class of compounds such as rare-earth orthoferrites $RFeO_3$, orthochromites $RCrO_3$, intermetallic compounds RCo_5, RFe_2 and so forth, the nature of the spontaneous SR transition is related to the 4f−3d interaction. This interaction is usually accounted for by introducing an effective field of a magnetically ordered 3d-sublattice acting on 4f-ions.

To account for the contribution of the 4f-sublattice to the free energy at low temperatures, we propose a model taking into account either a well isolated lower Kramers doublet of 4f-ions (with an odd number of 4f-electrons), or two well isolated lower Stark sub-levels with close energies forming a quasi-doublet. It is also assumed that all R-ion positions in the crystal are equivalent. In such a „single-doublet“ approximation for a spontaneous SR-transition in a certain crystallographic, for example, ac-plane, one can introduce the free energy per ion as follows:

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

where K_1 and K_2 are the first and second anisotropy constants for the 3d-sublattice, θ is the deviation angle of

the antiferromagnetic vector **G** in the 3d-sublattice from the c-direction. The last term is the contribution of the (quasi)doublet of the 4f-ion to the free energy, $\Delta(\theta)$ is the splitting of the (quasi)doublet in the magnetic field induced by the 3d-sublattice.

According to the theory, the effective anisotropy of K_1 depends in a complex way on the Dzyaloshinskii–Moriya (DM) interaction, the magnetic dipole interaction, and the single-ion anisotropy [3,8]. For example, in $YFeO_3$, the single-ion contribution is partially compensated by the DM contribution, whereas in $LuFeO_3$, they should, on the contrary, add up. These predictions are confirmed in experimental studies of the threshold fields of spin-reorientation H_{SR} for $\Gamma_4(G_x) \to \Gamma_2(G_z)$ transition: $H_{SR} = 15\,\mathrm{T}$ in $Lu_{0.5}Y_{0.5}FeO_3$, whereas in $YFeO_3$ $H_{SR} = 7.5\,\mathrm{T}$. Thus, while the anisotropy constant $K_1(ac) \approx 2 \cdot 10^5\,\mathrm{erg/cm^3}$ in $YFeO_3$, in the case of $LuFeO_3$ $K_1(ac)$ should be three times larger [3,8].

In accordance with theoretical calculations [3,9], in the series from $LaFeO_3$ to $LuFeO_3$ the second anisotropy constant K_2 smoothly decreases in modulo, and on average we have $K_2(ac) \approx 1.6 \cdot 10^4\,\mathrm{erg/cm^3}$, $K_2(bc) \approx 2.5 \cdot 10^4\,\mathrm{erg/cm^3}$, $K_2(ab) \approx -2.8 \cdot 10^4\,\mathrm{erg/cm^3}$. Generally speaking, the sign of K_2 is of a great importance for the character of the SR-transition. Indeed, in most orthoferrites, the SR follows the $\Gamma_4(G_x) \to \Gamma_2(G_z)$ scenario with two smooth phase transitions of the second order in the ac-plane, where $K_2 > 0$. But in $DyFeO_3$, the SR occurs through one sharp phase transition of the first order $\Gamma_4(G_x) \to \Gamma_1(G_y)$ in the ab-plane, where $K_2 < 0$, while in $Ho_{0.5}Dy_{0.5}FeO_3$, two SR transitions [1] are observed: one sharp $\Gamma_4(G_x) \to \Gamma_1(G_y)$ at $T = 46\,\mathrm{K}$ and one smooth transition $\Gamma_1(G_y) \to \Gamma_2(G_z)$ at $T = 18{-}24\,\mathrm{K}$.

3. Phase diagram for the „single-doublet“ model

$\Delta(\theta)$ splitting for a Kramers doublet in a magnetic field **H** has the following form:

$$\Delta(\theta) = \mu_B \Big[(g_{xx}H_x + g_{xy}H_y)^2 + (g_{xy}H_x + g_{yy}H_y)^2 + g_{zz}^2 H_z^2 \Big]^{1/2}. \qquad (2)$$

In the case of the $G_x \to G_z$ SR-transition, the effective molecular field $\mathbf{H}_m$ consists of components: $H_x, H_y \propto \cos\theta$, $H_z \propto \sin\theta$, i.e. in the absence of an external magnetic field, the expression for $\Delta(\theta)$ can be written as follows

$$\Delta(\theta) = \left(\frac{\Delta_a^2 - \Delta_c^2}{2} \cos(2\theta) + \frac{\Delta_a^2 + \Delta_c^2}{2} \right)^{1/2}, \qquad (3)$$

where $\Delta_{a,c}$ is the doublet splittings at low (G_z-phase) and high (G_x-phase) temperatures, respectively.

The standard way to account for the contribution from energy splitting Δ — is to approximate the form $\ln(\cosh \frac{\Delta}{k_B T}) \approx 0.5\Delta^2/(k_B T)^2$ (see, for example, [10]). However, for a potential (1) with splitting (3) the spontaneous SR-transition problem can already be solved exactly.

Phase stability conditions

Angle θ	Phase	Stability
$\pm\pi/2$	G_x	$\tanh(\mu_s/\tau) \le \alpha\mu_s + \beta\mu_s^3$
$0, \pi$	G_z	$\tanh(\mu_f/\tau) \ge \alpha\mu_f + \beta\mu_f^3$
$\theta(\tau)$	G_{xz}	$\partial\mu/\partial\tau < 0$

Assuming that $\Delta_a > \Delta_c$, from the free energy minimum condition we arrive at a system of equations describing the SR-transition [11]:

$$\sin 2\theta = 0, \quad \alpha\mu + \beta\mu^3 = \tanh\frac{\mu}{\tau}, \qquad (4)$$

where the following notation is introduced:

$$\alpha = 1 - \gamma\frac{\Delta_a^2 + \Delta_c^2}{\Delta_a^2 - \Delta_c^2},\ \beta = \frac{2\gamma}{\mu_f^2 - \mu_s^2},\ \gamma = 4\frac{K_2}{K_1}, \qquad (5)$$

$$\mu = \frac{\Delta(\theta)}{2k_B T_{SR}},\ \mu_s = \frac{\Delta_c}{2k_B T_{SR}},\ \tau = \frac{T}{T_{SR}},\ T_{SR} = \frac{\Delta_a^2 - \Delta_c^2}{16 k_B K_1}.$$

The system of equations (4) corresponds to the following magnetic configurations: $\Gamma_4(G_x)$, $\Gamma_2(G_z)$, and the angular phase $\Gamma_{24}(G_{xz})$, where the temperature dependence of the angle $\theta(\tau)$ is found from the solution of equations (4). These phases are stable when the inequalities shown in the table are met.

The SR-transition nature is determined by the type of solution to the master equation (4) in the region $\mu_s \le \mu \le \mu_f$, where μ_s corresponds to the start of the SR-transition at high temperature τ_s, and μ_f — the end of the transition at low temperature τ_f. By varying the values of the parameters α and β, we can obtain different solutions to the equation. The lines of each type of solution are represented in the phase diagram (Fig. 1).

In the simple case ($K_2 = 0$), the basic equation transforms into a molecular field equation: $\mu = \tanh(\mu/\tau) = B_{1/2}(\mu/\tau)$, where $B_{1/2}(x)$ is the Brillouin function. Thus, in the absence of K_2 anisotropy in the „single-doublet“ model, the SR will be realized either through two second-order phase transitions at $\mu_f \le 1$ (complete spin-reorientattion $G_x \to G_z$), or through one second-order transition at $\mu_f > 1$, but in this case, the SR will not be complete and will end in a transition to an angular spin structure G_{xz}.

Similar behavior, but with a more complex $\mu(\tau)$ relationship, will be realized with $K_2 > 0$ (SO-region in Fig. 1).

When the second anisotropy constant $K_2 < 0$ is negative, several fundamentally different solutions to the basic equation (4) are possible. With $K_2^* \ge K_2$, where K_2^* is defined from the condition $\beta = -\alpha^3/3$, there is one nontrivial solution of the equation. This solution is unstable, and there is no principal possibility of smooth rotation of

the spins: SR is always realized through a phase transition of the first order (FO region in Fig. 1).

In the intermediate range of $K_2^* < K_2 < 0$ values, the basic equation has two nontrivial solutions, simultaneously. It can be shown that the „mixed“ type SR transitions must be realized here (Fig. 1, $MO_{1,2}$ areas). For example, at temperature τ_s, a smooth phase transition of the second order $G_x \to G_{xz}$ occurs (Fig. 2), but on subsequent cooling below temperature τ_f the phases G_{xz} and G_z will already be stable (see table); in other words, the system can either remain in the angular G_{xz}-phase, or a transition of the first order $G_{xz} \to G_z$ can take place.

4. Influence of nonmagnetic substitution in 4f-sublattice

Given the non-magnetic substitution of rare-earth ions in the „single-doublet“ model, the nature of the SR-transition will be determined by solving an equation like (4):

$$\alpha(x)\mu + \beta(x)\mu^3 = \tanh\frac{\mu}{\tau}, \qquad (6)$$

where $\alpha(x) = \alpha/x$, $\beta(x) = \beta/x$, α and β are parameter values in the unsubstituted composition, x is concentration of 4f-ions in the substituted composition (for example, $N_{1-x}R_xFeO_3$, where N is a non-magnetic ion like La, Y, Lu). It is interesting to compare the results of the „single-doublet“ model with the „high-temperature“ approximation, where 4f-contribution in (1) is considered with the $k_BT \gg \Delta$ condition.

Without fourth order spin anisotropy ($K_2 = 0$), $\tau - x$-phase diagram in the „high temperature“ approximation includes a straight line separating the phases G_x and G_z (Fig. 3, bold black line), the SR will occur through a first order phase transition and the critical temperature will depend linearly on the concentration of R-ions. In the case of a non-zero positive $K_2 > 0$ constant, the SR will occur through two second-order phase transitions, and the SR start and end temperatures and the width of the SR region will decrease linearly with decreasing R-ion concentration (Fig. 3, thin grey lines).

A very different situation would occur in the „single-doublet“ model (Fig. 3, colored dashed lines). Firstly, the SR start and end temperatures are, in general, nonlinearly concentration dependent (e.g., the effect is observed in $Er_{1-x}Y_xFeO_3$ [12]), secondly, the transition region width increases as the concentration of paramagnetic R-ions decreases. And thirdly, the SR will be incomplete at concentration $x < x_{crit} = \mu_f$, i.e. at $T \approx 0$ the SR will end in a transition to an angular spin configuration G_{xz}.

Also of interest is the analysis of the effect of non-magnetic substitution in compositions where there is a sharp SR-transition (FO-region in Fig. 1). Indeed, the condition $\beta(x) \le -\alpha(x)^3/3$, at which SR is possible only by first order phase transition, will be fulfilled up to a certain critical concentration $x_{crit} = \alpha\sqrt{\alpha/|3\beta|}$, below which SR can either proceed smoothly, or it will have a „mixed“ character.

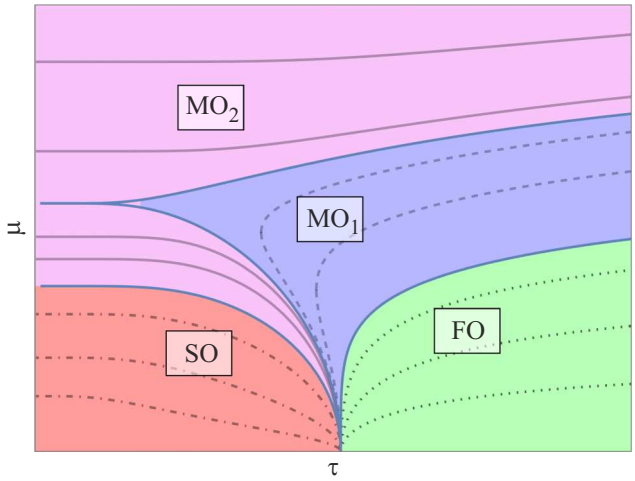

Figure 1. Phase diagram $\mu - \tau$ with solutions of equation (4); here the region FO — is an SR with a phase transition of the first order, SO — with a transition of the second order, MO_1 (MO_2) — is an SR that starts with a transition of the second order and ends with a transition of either the first or second order.

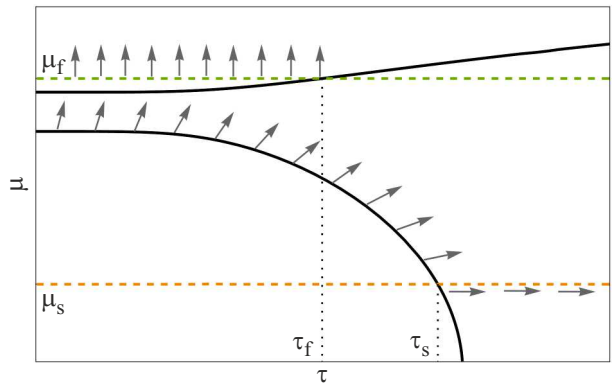

Figure 2. Example of an unusual spontaneous „mixed“ spin-reorientation. The arrows indicate the direction of vector **G** in the ac-plane.

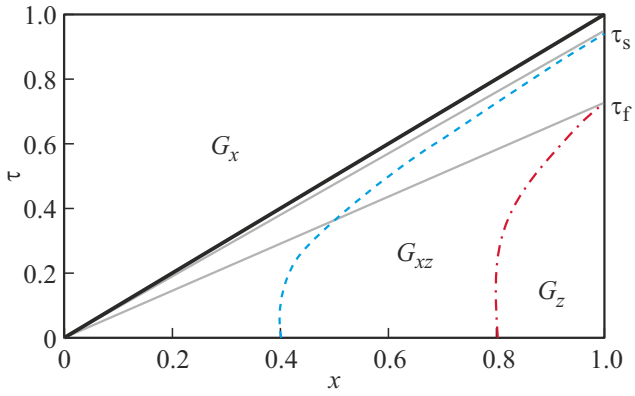

Figure 3. Phase diagram in coordinates $\tau - x$ for the „high temperature“ approximation (straight lines) and for the „single-doublet“ model (colored dashed lines).

5. Conclusion

A simple model of spontaneous spin-reorientation transitions in rare-earth orthoferrites and orthochromites has been studied. The interaction of the well-isolated lower (quasi)doublet of the R-ion with the 3d-sublattice acts as the main mechanism. It is shown that both the temperature and the character of spin-reorientation transition are the results of a competition between the second and fourth-order anisotropy of the 3d-sublattice, the crystal field and the 4f−3d interaction.

The „single-doublet“ model accurately accounts for the contribution from the splitting of the lower (quasi)doublet of the R-ion. In this model, along with typical smooth and abrupt SR-transitions, we arrive at unique „mixed“ SR-transitions, in which the spins first rotate smoothly to a particular angle, and then, abruptly reorient to another angle.

It is shown that when R-ions are replaced by the non-magnetic ones, the temperatures of the beginning and the end of the SR-transition can behave nonlinearly with concentration, and furthermore, a critical concentration is possible at which the nature of the SR-transition changes.

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Conflict of interest

The authors declare that they have no conflict of interest.

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