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A new mechanism of first-order magnetization in multisublattice rare-earth compounds

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Abstract

First-order field-induced spin-reorientation transitions in multisublattice intermetallic compounds are considered within an anisotropic Heisenberg model. Unlike in previous works, only leading-order anisotropy constants of the sublattices are included. The exchange interactions both between the rare-earth (RE) and transition metal (TM) sublattices and within the RE sublattice play an important role in the model. The latter interaction results in the occurrence of metastable states. One of the minima corresponds to the non-collinear magnetic structure where the RE subsystem is divided into two sublattices, and their moments deviate in opposite directions from the TM moment direction. The possible first-order magnetization process scenarios for R_2Fe_{17}, $HoFe_{11}Ti$, and $TbMn_6Sn_6$ systems are discussed.

1. Introduction

The phenomenon of a FOMP (first-order magnetization process) has been discovered in recent years in many intermetallic compounds. These include a number of practically important compounds of transition metals with rare earths (RE), such as $R_2Fe_{14}B$ [1, 2], $Nd_2Co_{14}B$ [3], R_2Fe_{17} [4–8], $RFe_{11}Ti$ [9–11], RMn_6Sn_6 [12], $Sm_{1-x}Nd_xCo_5$ [13, 14], and also some ferrites [15]. In some directions, magnetization jumps with increasing external magnetic field are observed in these systems. Usually, this effect is treated phenomenologically as a result of the competition of magnetic anisotropy (MA) constants $K^{(n)}$ of different orders [16, 17]. The presence of large high-order constants enables one to obtain local minima of free energy and thereby first-order transitions. However, such an approach meets with a number of difficulties. The large values of $K^{(n>1)}$ required are not confirmed by crystal-field calculations (see [1, 2, 18]). Also, high-order $K^{(n)}$ are proportional to high powers of magnetization and should decrease rapidly with increasing temperature T. This effect should be stronger in the case where the $K^{(n)}$ come mainly from the RE sublattice: the RE moments can become rather small at T well below the Curie temperature T_C. The reason is that the exchange interaction

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J_{RT}, which acts on RE ions from the transition metal (TM) system, may be considerably smaller than the interaction J_{TT} which determines T_C [19]. Thus, the local minima explaining the FOMP should exist only at low temperatures. However, the FOMP is observed as a rule over a wide temperature region [7, 12]. The dependences $K^{(n)}(T)$ fitted from magnetization curves turn out to be rather complicated and sometimes seem to be artificial.

The data discussed lead one to the conclusion that the effects of the many-sublattice structure are important in systems demonstrating the FOMP [17]. It is known that in a number of intermetallic RE systems (Tm_2Fe_{17}, $RFe_{11}Ti$, $TbMn_6Sn_6$) temperature-induced orientational transitions are caused by competing anisotropy of RE and TM sublattices (in the hexaferrites $BaZn_{2-x}Co_xFe_{16}O_{27}$ [15], competition of the Fe and Co sublattices plays a similar role). It is natural to suppose that this factor is essential for the field-induced transitions too. Although the many-sublattice case has already been considered [20], the earlier treatments were also based on the idea of competition of high-order constants.

In the present work we propose a new mechanism of the FOMP in a multisublattice magnet, which is connected with the formation of a non-collinear spin structure. The corresponding theoretical model is formulated in section 2. In section 3 we consider the FOMP picture in various cases and discuss experimental situations.

2. The theoretical model

We start from the Heisenberg model of a uniaxial multisublattice crystal with inclusion of magnetic anisotropy. The MA constants in the problem are usually treated as phenomenological parameters which are obtained by fitting magnetization curves. When describing the FOMP, one introduces as a rule large high-order constants, $K^{(3)} \sim K^{(2)} \sim K^{(1)}$. To avoid the difficulties discussed above, we include only leading-order MA constants for different magnetic sublattices, $K_i = K_i^{(1)}$. Using the mean-field approximation we write down the expression for the total energy:

$$E = \sum_{i>j} J_{ij} \cos(\theta_i - \theta_j) + \sum_i (K_i \sin^2 \theta_i - \boldsymbol{H} \cdot \boldsymbol{M}_i). \tag{1}$$

Here i, j are sublattice indices, $\boldsymbol{M}_i$ are the corresponding magnetic moments which make angles θ_i with the z-axis, J_{ij} are exchange parameters, $\boldsymbol{H}$ is the external magnetic field. For the sake of convenience, we have included the dimensionless factors of $M_i = \langle \boldsymbol{M}_i \rangle$ into J_{ij}, so that $J_{ij} \propto M_i M_j$. The crystal and magnetic structures contain TM and RE sublattices which are coupled by the exchange interaction J_{RT}. The TM subsystem usually yields the main contribution to the magnetic moment, and the RE one that to the MA. The strongest interaction J_{TT} plays the role of a mean field in the TM subsystem and need not be included explicitly.

Crystal-field considerations indicate that formation of non-collinear magnetic structures is possible in multisublattice structures, e.g., for the systems $R_2Fe_{14}B$ [1, 2]. The simplest case of a two-sublattice magnet was analysed earlier in [19]. It was shown that, in the case where K_T and K_R have opposite signs (competing anisotropy), the sublattice moments become non-parallel provided that

$$|J_{RT}(1/K_R + 1/K_T)| < 2. \tag{2}$$

If the absolute values of K_T and K_R are close, this condition can hold even for rather strong exchange J_{RT}.

The two-sublattice problem with non-collinear magnetic structure enables one to obtain a local energy minimum including a magnetic field, but for one field direction only. To avoid this

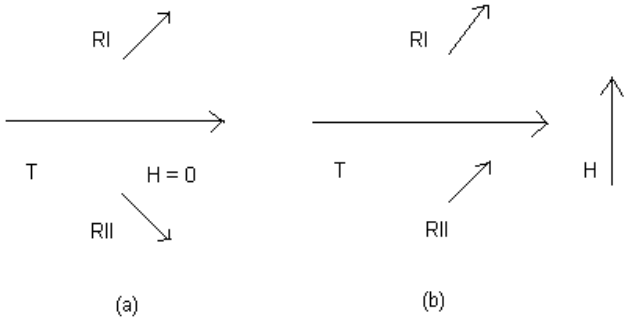

Figure 1. A schematic picture of the FOMP in a simple toy model with ferromagnetic exchange J_{RT}, $K_R > 0$, and a large easy-plane $K_T < 0$: (a) the spin configuration in zero magnetic field; (b) the spin configuration after the transition induced by the magnetic field in the x-direction.

difficulty, we have to introduce, instead of one RE subsystem, *two* equivalent RE sublattices, RI and RII, with $K_{RI} = K_{RII} = K_R$, $J_{RIT} = J_{RIIT} = J_{RT}$. This model preserves the correct axial symmetry and yields the energy minimum for both field directions. Of course, for real compounds with complicated crystal structures, each 'sublattice' corresponds to several crystal positions. To stabilize the non-collinear structure with the split RE sublattice, we include the antiferromagnetic exchange interaction between the sublattices, $J_{RR} > 0$. The values of J_{RT} and J_{RR} cannot be reliably obtained from existing experimental data, but for the long-range RKKY exchange interaction, $|J_{RR}|$ may be assumed not to be small. The essential property of such a model is that metastable states are already present at $H = 0$. Owing to this fact, first-order phase transitions are possible, which occur at energy level crossings in the external magnetic field.

3. FOMP scenarios for various experimental situations

The idea of the FOMP mechanism can be illustrated using a simple toy model where the TM moment is rigidly fixed by strong MA in the x-direction (or in the xy-plane for the three-dimensional problem). The RE ions which possess weaker easy-axis MA tend to incline in the z-direction, each ion having two local minima. The interaction J_{RR} results in the degeneracy of the minima being lifted, so the moments of the RE sublattices deviate in opposite directions (figure 1(a)). With increasing magnetic field along the z-axis, a first-order transition occurs to the configuration where the RE moments are almost parallel (figure 1(b)). A smooth transition does not occur because of the influence of the MA of the RE ions.

Now we pass to a more realistic situation of finite (and even small) MA of the TM subsystem. First we consider the situation where $K_R > 0$, $K_T < 0$, and the easy-axis MA of the RE sublattice predominates. This is the case for the systems Tm_2Fe_{17} and $TbMn_6Sn_6$, as follows from the existence of easy-axis–easy-plane spin-reorientation transitions with increasing temperature ($|K_R|$ decreases more rapidly than $|K_T|$). Two possible metastable states are shown in figure 2, the exchange J_{RT} being supposed antiferromagnetic, which corresponds to heavy RE ions, e.g., to Tb and Tm. In the case where $J_{RT} < 0$, which occurs for light REs, e.g., for Nd and Pr, the picture differs by the RE moments having opposite direction.

In the zero magnetic field the first state (figure 2(a)) is realized with the collinear spin configuration along the z-axis (the easy direction for the RE sublattice). On increasing the field $\boldsymbol{H} \parallel \boldsymbol{x}$, the magnetization vector starts to rotate, retaining the nearly antiparallel orientation

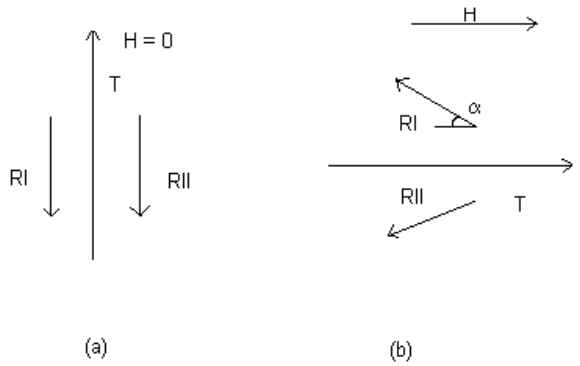

Figure 2. A schematic picture of FOMP in the case of antiferromagnetic exchange $J_{RT}, K_R > 0$: (a) the spin configuration in zero field; (b) the non-collinear spin configuration after the magnetization jump induced by the magnetic field $\boldsymbol{H} \parallel \boldsymbol{x}$.

of the TM and RE moments. For simplicity, we neglect in the analytical treatment the non-collinearity of TM and RE moments for this state, which is weak due to the large value of $|J_{RT}|$. Then the energy in the state (a) is expressed in terms of the angle θ between the TM moment and the z-axis:

$$E_a = -2|J_{RT}| + J_{RR} - H(M_T \pm 2M_R)\sin\theta + (K_T + 2K_R)\sin^2\theta$$
$$= -2|J_{RT}| + J_{RR} - \frac{(M_T \pm 2M_R)^2}{4(2K_R + K_T)}H^2 \tag{3}$$

the sign + (−) corresponding to $J_{RT} < 0$ ($J_{RT} > 0$). The second state (figure 2(b)) possesses a non-collinear spin configuration with a split RE sublattice owing to the gain in the MA energy for the RE subsystem, and also due to the interaction J_{RR}. In this state the spin configuration depends weakly on the magnetic field and the TM moment remains parallel to the x-axis, so

$$E_b = -2|J_{RT}|\cos\alpha + J_{RR}\cos 2\alpha - H(M_T \pm 2M_R\cos\alpha) + K_T + 2K_R\cos^2\alpha$$
$$= K_T - HM_T - J_{RR} - \frac{(J_{RT} - HM_R)^2}{4(J_{RR} + K_R)} \tag{4}$$

where α ($0 < \alpha < \pi/2$) is the angle of the RE moment deviation from the x-axis. The total energy in the state (b) has an almost linear field dependence and decreases more rapidly than that for the state (a) with rotating moment (figure 3). The angles θ and α are obtained by minimization of equations (3), (4):

$$\sin\theta = \frac{H(M_T \pm 2M_R)}{2(2K_R + K_T)}, \qquad \cos\alpha = \frac{|J_{RT} - HM_R|}{2(J_{RR} + K_R)}. \tag{5}$$

Thus the local minimum (non-collinear state) occurs at

$$J_{RR} + K_R > |J_{RT} - HM_R|/2. \tag{6}$$

Note that the minimum can occur including a magnetic field, even if it is absent at $H = 0$. The transition field and the angle α (but not the magnetization jump) turn out to be small provided that $2|J_{RR} + K_R| \simeq |J_{RT}|$. Since J_{RR} and K_R are proportional to $M^2(T)$ (unlike the constants $K^{(n>1)}$ in standard FOMP considerations, which decrease rapidly with increasing T), the criterion (6) depends rather weakly on T. Therefore the mechanism discussed enables one to obtain the FOMP over a wide temperature region.

The numerical calculations were performed by direct minimization of total energy (1) without the approximations discussed above. The moment values were taken to be $M_T = 4$,

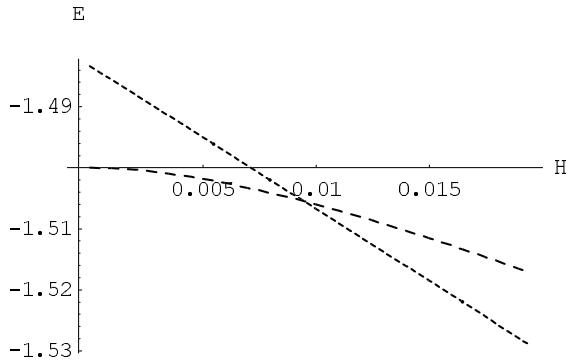

Figure 3. The field dependence of the total energy in units of $J_{RT} = 1$. Other parameter values are: $K_R = 0.1$, $K_T = -0.15$, $J_{RR} = 0.5$. The long-dashed curve corresponds to the state (a) in figure 2, and the short-dashed line to the state (b).

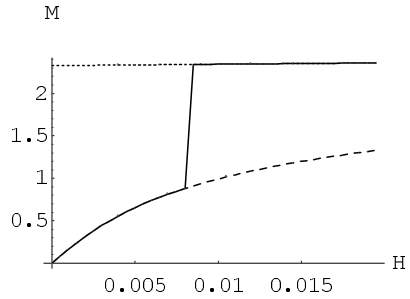

Figure 4. The field dependence of the magnetization in the x-direction for the same parameters as for figure 3. The observable dependence demonstrating the FOMP (vertical jump) is shown by the solid line.

$M_{RI} = M_{RII} = M_R/2 = 1$, which corresponds roughly to R_2Fe_{17} compounds (e.g., for Tb_2Fe_{17} the moment of the Fe subsystem is more than double that of the RE subsystem, $M_{Tb} = 18.6\,\mu_B$, $M_{Fe} = 36.6\,\mu_B$ per formula unit [5]). At some critical field, E_a becomes equal to E_b (figure 3), and the magnetization demonstrates a vertical jump (figure 4). It should be noted that the transition field is much smaller than the exchange interaction J_{RR}, unlike the situation of figure 1. After the jump, the magnetization increases rather slowly because of the large value of J_{RT}. On the other hand, the magnetization depends very weakly on the field $\boldsymbol{H} \parallel \boldsymbol{z}$ because of the strong interaction J_{RT}. Owing to the deviation from the antiparallel alignment, the magnetization in the hard direction $\boldsymbol{x}$ after the transition turns out to be larger than the zero-field magnetization in the easy direction $\boldsymbol{z}$ ($M_x > M_z = 4-2 = 2$). Such behaviour is demonstrated by the experimental dependences $M(H)$ of a number of systems, e.g., in Tm_2Fe_{17} [7, 8].

The zero-field canting angle α of the RE sublattice for the parameters of figure 3 makes up about 20°. Such small values do not contradict reliable experimental data. Indications of formation of the non-collinear structure after the transition are given by neutron scattering data on Tm_2Fe_{17} [8] and $TbMn_6Sn_6$ [21]. Non-collinear structures with the split RE sublattice were also observed for $R_2Fe_{14}B$ systems [22].

In the system Tb_2Fe_{17} [5, 7] the Fe sublattice has the easy-plane magnetic anisotropy, as does the Tb sublattice (although Tb ions in different positions are supposed to have MA of different signs). Thus, the competing anisotropy situation does not occur. Nevertheless, in

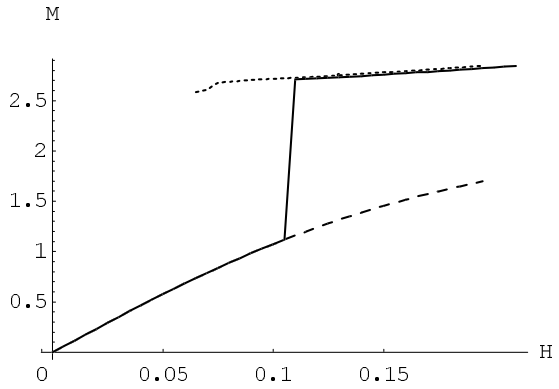

Figure 5. The magnetization curve in the x-direction for $J_{RT} = 1$, $K_R = 0.1$, $K_T = 0.1$, $J_{RR} = 0.6$.

this case our approach also enables one to obtain FOMP, but the transition field turns out to be somewhat larger. Figure 5 shows the result of a calculation of the magnetization for constants of the same sign, $K_R > 0$, $K_T > 0$ (the easy-plane and easy-axis problems are equivalent provided that we restrict ourselves to the xz-plane model). One can see that before the jump the field dependence of the magnetization is nearly linear, unlike in figure 4. The state with split RE sublattices occurs only with increasing magnetic field.

The curves obtained exhibit a similarity to experimental ones. Let us try to perform a more detailed comparison with experimental data. The critical FOMP field is determined by the overall scale of the anisotropy parameters. Unfortunately, MA constants are usually fitted from magnetization curves including high-order constants, which contradicts our model. Therefore we shall concentrate on the cases where the parameters of the model can be determined from independent experiments. Using the data for Tm_2Fe_{17} from [8], $M_{Tm} \simeq 12\ \mu_B$, $M_{Fe} \simeq 30\ \mu_B$ per formula unit; $J_{TmFe} = 60$ J cm^{-3}, $K_{Fe} = -2.5$ J cm^{-3}, $K_{Tm} = 7$ J cm^{-3}, we can fit the experimental FOMP field, $\mu_0 H = 5$ T, by taking $J_{RR}/J_{RT} \simeq 0.5$. Unfortunately, the value of the magnetization jump cannot be reliably determined from the results of [7, 8].

The values of the MA constants of Tb_2Fe_{17} can be estimated from NMR data [23] (see [24]): $K_{Tb} = -10$ J cm^{-3} and $K_{Tb} = 3$ J cm^{-3} for the positions 2b and 2d respectively, $K_{Fe} = -3$ J cm^{-3}. Of course, the accuracy of these values is rather poor. After averaging the values of K_{Tb} over sublattices, the relation between MA constants corresponds roughly to the parameters of figure 5. The rescaled FOMP critical field from this figure turns out to be about double the experimental value, i.e. $\mu_0 H \simeq 4$ T. The agreement can be made better, provided that we take somewhat smaller values of $|K_{Fe}|$ and increase the ratio J_{RR}/J_{RT}. Also, the situation in Tb_2Fe_{17} is complicated because of the existence of two FOMP-type transitions [7].

Now we treat the case where the easy-axis anisotropy K_T dominates over the MA of the RE sublattice, which has the opposite sign (such a situation arises, e.g., for the compound $HoFe_{11}Ti$). Then the qualitative picture of FOMP turns out to be different from that of figure 2. As shown in figure 6(a), at $H = 0$ RE moments deviate from the z-axis (the easy direction for the TM sublattice) by the angle

$$\alpha = \arccos\left[\frac{|J_{RT}|}{2(J_{RR} - K_R)}\right]. \tag{7}$$

This configuration begins to rotate on including a small magnetic field in the x-direction. On further increasing the field, the nearly collinear spin configuration shown in figure 6(b)

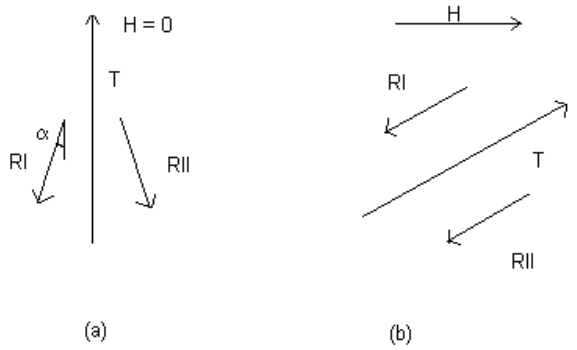

Figure 6. A schematic picture of the FOMP in the case of antiferromagnetic exchange J_{RT}, $K_R < 0$. The spin configuration is non-collinear before the jump (a) and becomes almost collinear after the jump (b).

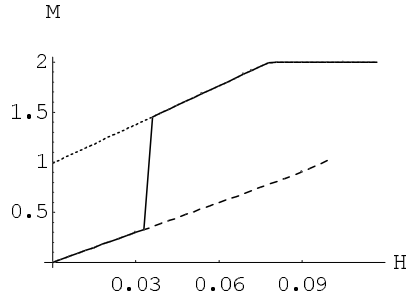

Figure 7. The magnetization curve in the x-direction for $J_{RT} = 1$, $K_R = -0.2$, $K_T = 0.4$, $J_{RR} = 0.45$. The long-dashed line corresponds to the state (a) in figure 6, and the short-dashed line to the state (b).

becomes favourable. As follows from (7), the FOMP is possible at $J_{RR} - K_R > |J_{RT}|/2$. Note that the solution (local minimum) corresponding to the non-collinear structure can vanish with increasing H somewhat above the critical field of the FOMP. A structure of the type shown in figure 6(a) (but with ferromagnetic interaction $J_{RT} < 0$) was proposed for $Y_{1-x}Nd_xCo_5$ on the basis of magnetic measurements [25].

After the jump, the magnetization in the x-direction continues to increase rather rapidly due to rotation of the TM moments (figure 6(b)), and becomes saturated only when the moments lie along the x-axis ($M_x = 2$). Absence of saturation immediately after the jump corresponds to FOMP-II according to the classification of [16, 17]. The result of the magnetization calculation is shown in figure 7. For simplicity, we restrict ourselves again to the planar problem (the xz-plane model). The parameter values are chosen to demonstrate the existence of the saturation region, although a FOMP can be obtained for smaller $|K_i/J_{RT}|$ and at smaller H too. The dependence obtained is in qualitative agreement with that for $HoFe_{11}Ti$ [11]. This system is close to instability with respect to the formation of the 'easy-cone' structure [11], owing to the competing MA of the Ho and Fe sublattices with $K_R < 0$, $K_T > 0$.

4. Conclusions

To conclude, we have proposed a simple model which reproduces qualitatively the FOMP pictures in some RE systems with different sign combinations of sublattice MA constants. It should be noted that the field-induced transitions considered are similar in some respects to the spin-flop transitions in anisotropic antiferromagnets. In the latter situation, formation of metastable states and magnetization jumps are possible too (see, e.g., [26]). However, our picture is more complicated, since it includes the TM sublattice.

The consideration enables one to avoid some difficulties and reduce the number of fitting parameters in comparison with the treatments that use high-order MA constants. Further experimental investigations of magnetic structures, especially with the use of neutron scattering, would be of interest to verify the FOMP scenarios proposed.

When considering the situation in other compounds, we meet some problems. The description of the FOMP for the systems $Pr_2Fe_{14}B$, $Nd_2Fe_{14}B$ should also include non-collinear structures [2], but this problem is more difficult. In the compound $Nd_2Fe_{14}B$ a conical structure occurs in zero field, although the signs of the MA for the Nd and Fe sublattices coincide. Usually such behaviour is attributed to the influence of higher-order anisotropy constants; the possibility of different roles of various Nd positions is also discussed. It should be noted that the FOMP picture is similar for the compound $Nd_2Co_{14}B$ [3] where the Co ions have easy-plane MA. For the system $Sm_{1-x}Nd_xCo_5$ [13] the RE sublattice already includes two subsystems with opposite MA signs. However, to obtain a FOMP in spirit of our mechanism, one still has to divide this sublattice into two symmetric parts.

Acknowledgments

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