The *f-d* exchange interaction in heavy-rare-earth RCo$_2$ compounds

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The magnetization of the intermetallic compounds $(R_tY_{1-t})(Co_{1-x}Al_x)_2$ with heavy rare earths from Tb to Tm was measured in pulsed magnetic fields up to 240 kOe. The f-d exchange interaction parameters of these compounds were determined from the magnetization curves of the field-induced noncollinear phase. It was shown that the f-d exchange interaction integral in RCo$_2$ intermetallides with a heavy rare earth is virtually independent of the number of the rare earth. © *1995 American Institute of Physics.*

1. INTRODUCTION

Magnetism of rare-earth intermetallic compounds with iron-group $3d$ transition metals is caused by two different magnetic subsystems, one of which is formed by localized $4f$ electrons and the other by the itinerant $3d$ electrons of the transition metal which are hybridized with the $5d$ electrons of the rare earth R (or the yttrium $4d$ electrons). One of the main parameters determining the properties of R $3d$-intermetallides is the f-d exchange interaction between these magnetic subsystems.[1,2] For this reason, a great deal of attention has been devoted in recent years to the experimental and theoretical investigation of this interaction in different classes of intermetallic compounds.[3–8] The f-d exchange interaction parameter in heavy-rare-earth intermetallides, in which antiparallel collinear ordering of the magnetic moments M_f and M_d of the f and d-subsystems is realized (f-d exchange is negative), can be determined most directly by observing field-induced noncollinear magnetic structures, since this method, in contrast to other methods (on the basis of the magnetic-ordering temperatures, magnetic-compensation points, and others), does not require knowledge of any additional parameters determined from other experiments.

In the exchange approximation the noncollinear magnetic structure of a ferrimagnet exists in fields (see, for example, Ref. 1)

$$H_{c1}<H<H_{c2}, \tag{1}$$

where

$$H_{c1}=-\lambda|M_f-M_d|, \quad H_{c2}=-\lambda(M_f+M_d), \tag{2}$$

and the magnetization in the noncollinear phase $M=|\mathbf{M}_f+\mathbf{M}_d|$ is a linear function of the magnetic field:

$$M=-H/\lambda, \tag{3}$$

where $\lambda<0$ is the molecular field f-d exchange interaction constant.

The molecular field constant λ can be calculated from both the values of the critical fields H_{c1} and H_{c2} [Eq. (2)] and the values of the susceptibility in the noncollinear phase [Eq. (3)].

This method, however, is not applicable for all rare-earth intermetallides with ferrimagnetic structure. In particular, the field-induced noncollinear magnetic structures are in principle impossible to observe in the cubic Laves phases of RCo$_2$ (fcc structure of the MgCu$_2$ type) with heavy rare earths. This is because the itinerant d subsystem of these compounds is magnetically unstable: In YCo$_2$ and LuCo$_2$ intermetallides with nonmagnetic rare earths the d subsystem is paramagnetic and switches abruptly from the paramagnetic into the ferromagnetic state under the action of an external magnetic field, when it reaches the critical field H_m of the metamagnetic transition.[9,10] This magnetic instability of the d subsystem is caused by the behavior of the density of states $N(E_F)$ of the itinerant d electrons near the Fermi level. To a first approximation, it can be regarded as being identical for all RCo$_2$ compounds with heavy rare earths and yttrium.

In all RCo$_2$ intermetallides with magnetic rare earths the molecular field exerted by the rare-earth subsystem on the d subsystem is stronger than the metamagnetic transition field H_m, i.e., this subsystem is in a magnetically ordered state, and the collinear ferrimagnetic structure with antiparallel orientation of the moments f and d of the subsystems is realized in RCo$_2$.[11] Since all of these compounds have $M_f > M_d$, the magnetic moment of the d subsystem is oriented antiparallel to the external field and the total effective field acting on the d subsystem with increasing external field

$$H_{\text{eff}}=-\lambda M_f-H. \tag{4}$$

Therefore, a transition of the d subsystem into the paramagnetic phase can occur in the external field

$$H'_m=-\lambda M_f-H_m. \tag{5}$$

It is obvious that the field-induced noncollinear structure will arise in RCo$_2$ only if $H_{c1} < H'_m$. Comparing Eqs. (2) and (5), we find the condition under which the field-induced noncollinear phase exists in a ferrimagnet with one magnetically unstable subsystem:

$$M_d(H_m)>-H_m/\lambda. \tag{6}$$

According to Refs. 9 and 10, the magnetizations of YCo$_2$ and LuCo$_2$ are $M_d(H_m)\simeq 1\mu_B$ per formula unit (f.u.), and H_m

$\simeq$ 700 kOe. Simple estimates show that in $GdCo_2$(λ = − 620 kOe·f.u./μ_B [Ref. 12] the left-handed side of Eq. (6) is less than the right-hand side and a field-induced noncollinear phase will not appear, i.e., in this case the transition from the ferrimagnetic to the ferromagnetic phase in a field will occur via demagnetization and then magnetization of the d subsystem.[8] The relation (6) will be violated even more for other RCo_2 with heavy rare earths in which the quantity $|\lambda|$ is less than in $GdCo_2$.[1]

Under certain conditions it is nonetheless possible to observe field-induced noncollinear magnetic structures in RCo_2 compounds. This is because trace substitutions of aluminum for cobalt in the $Y(Co_{1-x}Al_x)_2$ and $Lu(Co_{1-x}Al_x)_2$ systems decrease sharply the metamagnetic transition fields H_m, while the values of $M_d(H_m)$ do not change much.[11] Therefore, in aluminum-substituted compounds $R(Co_{1-x}Al_x)_2$ the relation (6) can be satisfied and, therefore, field-induced noncollinear magnetic structures can be observed.

This fundamental possibility is very difficult to realize experimentally, however, since in the compounds $R(Co_{1-x}Al_x)_2$ the difference $M_f - M_d$ and therefore H_{c1} [see Eq. (2)] is large. Even for the most favorable case R=Tm, calculations based on the data of Ref. 13 give $H_{c1} \simeq 600$ kOe, i.e., noncollinear structures arise in these compounds only in very weak magnetic fields.

The critical field H_{c1} can be lowered to experimentally achievable fields by substituting a rare earth for yttrium in the $(R_tY_{1-t})(Co,Al)_2$ systems, since in this case the magnetic moment M_f of the rare-earth subsystem and therefore the difference $M_f - M_d$ decrease with decreasing concentration t of the rare earth ($M_f = t\mu_f$, where μ_f is the rare-earth magnetic moment per atom).

We previously investigated the field-induced noncollinear magnetic structures in the compounds $(Gd_{1-t}Y_t)(Co_{1-x}Al_x)_2$,[12] $(Gd_{1-t}Lu_t)(Co_{1-x}Al_x)_2$,[14] and $(Tm_{t-1}Lu_t)(Co_{0.88}Al_{0.12})_2$.[13] In the present work, these investigations are extended to the system $(R_tY_{1-t})(Co_{1-x}Al_x)_2$ with different heavy rare earths.

2. SAMPLES AND MEASUREMENT PROCEDURE

The compositions $(R_tY_{t-1})(Co_{1-x}Al_x)_2$ with $x=0.12$ were chosen to investigate the noncollinear magnetic structures, since preliminary estimates based on Eq. (6) showed that for all heavy rare earths noncollinear magnetic structures should arise in an external field in such compositions. The choice of rare-earth concentration was made on the basis of approximate values of λ (Ref. 7), in a manner so that the compositions investigated fell into the region of the concentration compensation point $M_d \simeq M_f = t\mu_f$, and the field H_{c1} would be located in the region of magnetic fields which are experimentally accessible to us.

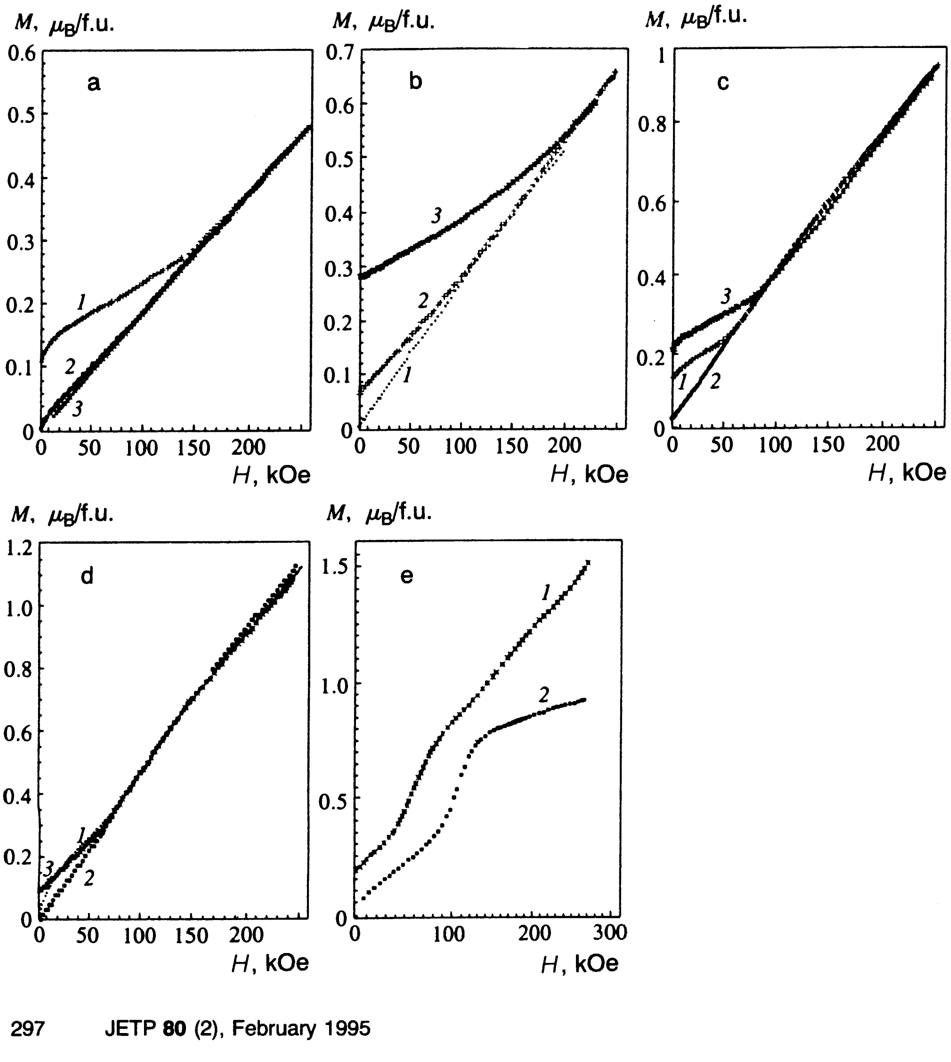

FIG. 1. Magnetization curves of $(R_tY_{t-1})(Co_{0.88}Al_{0.12})_2$ at 4.2 K for R=Tb (a), Dy(b), Ho(c), Er(d); curve *1* corresponds to $t=0.1$ (a,b) and $t=0.08$ (c,d); curve *2* corresponds to $t=0.12$; curve *3* corresponds to $t=0.14$.

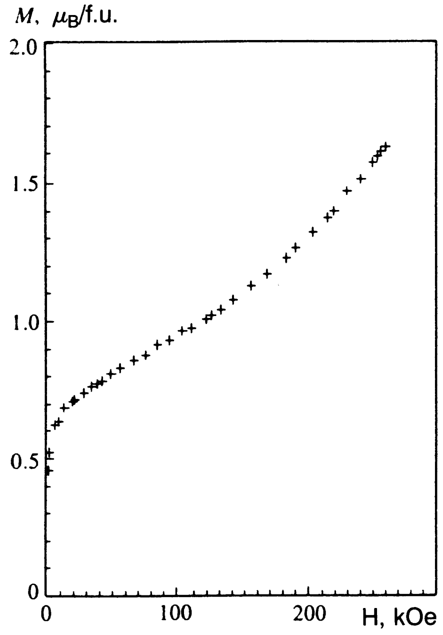

FIG. 2. Magnetization curve of the compound $(Tm_{0.4}Y_{0.6})(Co_{0.87}Al_{0.13})_2$ at 4.2 K.

The samples were synthesized from the initial components in an electric-arc furnace by the standard technique, followed by homogenizing annealing. X-ray diffraction investigations showed that the experimental samples were single-phase (the content of impurity phases in the samples obtained was less than 3%). Magnetization measurements were conducted at 4.2 K in pulsed magnetic fields up to 240 kOe on spherical polycrystalline samples.

3. EXPERIMENTAL DATA

Figure 1 displays the magnetization curves of the intermetallides $(R_tY_{t-1})(Co_{0.88}Al_{0.12})_2$ for R=Tb, Dy, Ho, Er, and Tm. One can see that the field-induced noncollinear magnetic structure arises in all experimental compounds, except for the compound with thulium: Above the critical field H_{c1} the magnetization increases almost linearly with the field (the small deviation of $M(H)$ from linearity is probably due to magnetic anisotropy[15]).

Note that both the spontaneous magnetization and the critical field H_{c1} of the transition into the noncollinear phase depend nonmonotonically on the rare-earth concentration and vanish at the composition compensation point: $t_{\text{comp}} =$ 0.14, 0.10, 0.12, and 0.12 for compounds with Tb, Dy, Ho, and Er, respectively.

The field dependence of the magnetization of the compound $(Tm_{0.25}Y_{0.75})(Co_{0.88}Al_{0.12})_2$ (curve *1*, Fig. 1e) is qualitatively different for the $M(H)$ curves for intermetallides with other rare earths. The field-induced noncollinear phase is not observed in this compound, and as the field increases, a metamagnetic transition occurs. Comparison with data for the intermetallide $Y(Co_{0.88}Al_{0.12})_2$ (see curve *2* in Fig. 1e) shows that in the thulium intermetallide demagnetization of the itinerant *d* subsystem occurs in an external field: The system switches from the strongly ferromagnetic state into a weakly magnetic state. In summary, our measurements show that for intermetallic compounds of thulium with aluminum concentration $x = 0.12$, in contrast to intermetallides of other heavy rare earths, the relation (6) for the appearance of the noncollinear phase is not satisfied. It should be noted that in this case the composition compensation point for thulium compounds, analogous to the compensation point observed for intermetallides with other rare earths, is absent (a more detailed discussion is given in Ref. 16).

In the compounds $(Tm_tY_{t-1})(Co, Al)_2$ field-induced noncollinear magnetic structures can be observed by decreasing the metamagnetic transition field H_m by increasing the aluminum concentration. This is clearly seen in Fig. 2 , which displays the magnetization curve of $(Tm_{0.25}Y_{0.75})(Co_{0.87}Al_{0.13})_2$. In this compound, the relation (6) holds and a magnetic field induces a transition into the noncollinear phase.

4. DISCUSSION

Using Eq. (3) we calculated, from the experimental curves $M(H)$ obtained in the noncollinear phase, the molecular field *f-d* exchange interaction constants (when $M(H)$ deviated from a linear function the average slope of the curves $M(H)$ in fields above H_{c1} was used in the calculations). The quantity λ for $(Tm_{0.25}Y_{0.75})(Co_{0.88}Al_{0.12})_2$ was determined, using Eq. (5), from data on the metamagnetic-transition fields in this compound and in the basic compound $Y(Co_{0.88}Al_{0.12})_2$. The magnetic moment of thulium $\mu_{\text{Tm}} = 4.3\ \mu_B$ was taken from Ref. 13. Both methods gave identical results within the limits of experimental error.

The values obtained for λ for our experimental compounds (R, Y)(Co, Al)$_2$ with heavy rare earths are presented in Table I together with data for (Gd, Y)(Co, Al)$_2$,[12] (Lu, Gd)(Co, Al)$_2$,[14] and (Tm, Lu)(Co, Al)$_2$,[13] as well as the field-induced noncollinear magnetic structures determined from the investigations.

It is interesting that the values of λ for lutetium compounds with gadolinium and thulium are lower than for the corresponding compounds with yttrium. It has been shown recently that the band structure of the *d* electrons of the compounds Lu(Co, Al)$_2$ is different from that of other compounds R(Co, Al)$_2$ and Y(Co, Al)$_2$[17,18] (so-called "lutetium paradox"), and this is apparently when the molecular-field *f-d* exchange coefficient of intermetallides containing lutetium changes.

There arises the question of whether the values of $|\lambda|$ obtained for the substituted compounds explain *f-d* exchange in RCo_2. Although this question has not been completely solved, existing data[12] show that as the concentration of the rare earth changes in the system (Gd, Y)(Co, Al)$_2$ up to 20% gadolinium, the value of λ does not change much. Comparing the value $\lambda = -215$ kOe·f.u./μ_B for the compounds (Er, Y)(Co, Al)$_2$ to the value 200 kOe·f.u./μ_B for $ErCo_2$, determined from the demagnetization field 1100 kOe[1)] of the *d* subsystem in this compound, gives the most convincing indication that λ is virtually independent of the rare-earth concentration.

TABLE I. *f-d* Exchange interaction constants λ and the exchange parameters A of the intermetallides RCo_2 with heavy rare earths. The values were determined by analyzing the magnetic field dependences $M(H)$ and from indirect measurements.

R	Direct Measurements				Indirect Measurements		
	$(R, Y)(Co, Al)_2$		$(R, Lu)(Co, Al)_2$		RCo_2		
	$kOe\cdot f.u./\mu_B$	$A\cdot 10^{-23}$, J	$kOe\cdot f.u./\mu_B$	$A\cdot 10^{-23}$, J	$A\cdot 10^{-23}$, J [3, 19, 7]		
Gd	-620 ± 20	-19.6 ± 0.7 [12]	-400 ± 100 [14]	12.5 ± 3	19.4,	23.3,	20.1
Tb	-537 ± 30	-24.9 ± 1.4	-	-	27.1,	26.5,	20.2
Dy	-373 ± 20	-23.0 ± 1.2	-	-	33.6,	23.3,	20.1
Ho	-258 ± 15	-19.9 ± 1.2	-	-	39.1,	23.3,	20.4
Er	-215 ± 12	-19.9 ± 1.1	-	-	39.1,	20.0,	20.0
Tm	-170 ± 10	-18.4 ± 1.1	-135 ± 10 [13]	14.6 ± 0.6	-	-	24.0
$ErCo_2$			-200^*	21.6			

*Data obtained by T. Goto (private communication).

In the nearest-neighbor approximation the molecular field constant λ is related to the *f-d* spin exchange interaction parameter A by the relation[7]

The values of λ calculated in Refs. 3, 7, and 20 from the Curie temperatures of the isostructural compounds RCo_2 and RNi_2, the magnetic susceptibility of $LuCo_2$, and so on are also given in Table I. Comparing the results shows that the values of λ which we determined by the direct method from investigations of the noncollinear phase are identical in order of magnitude to the values determined by indirect methods, though there is a large spread between the numerical values of λ obtained in different works.

In our opinion, the quantities λ determined from indirect measurements are approximate, since they are based on the assumption that the *f-f* interaction is identical in RCo_2 and RNi_2. Moreover, the main point is that the equations employed in Refs. 3–7 and 19 to calculate λ presuppose that a second-order phase transition occurs at the Curie temperature, while it is well known that in most compounds RCo_2 with heavy rare earths R = Dy–Tm the transition is a first-order transition.[11]

$$-\lambda(Z_f/N_d)A\mu_f^S/\mu_f\mu_B^2=(Z_f/N_d)A(g_f-1)/g_f\mu_B^2, \quad (7)$$

where μ_f^S and μ_f are, respectively, the spin and total magnetic moments of the rare-earth ion, Z_f is the number of f atoms closest to the d atom, and N_d is the number of d atoms in a formula unit ($Z_f/N_d=6$ for RCo_2), and g_f is the g-factor of the f atom. Using the experimental data obtained for λ, we calculated the parameter A for heavy rare earths.

The dependence of the exchange parameter A on the number of the rare earth has recently been discussed in the literature. In many works this parameter is assumed to be constant, but in a number of works[3,7,19] data on the dependence of A in RCo_2 on the number of the rare earth were presented. This conclusion was drawn on the basis of indirect methods for determining A from the magnetic characteristics, which, as we have already mentioned, must be regarded as being only approximate. According to our data, A increases somewhat from Tm to Tb, but the data for gadolinium compounds do not fit this pattern: For them A is less than for compounds with Tb and Dy and is comparable to the values of A for compounds with Ho and Er. The reasons for the nonmonotonic dependence of the exchange parameter on the rare earth are not clear.

We call attention to the fact that gadolinium is an s ion (its orbital angular momentum $L = 0$), so that the gadolinium subsystem in a compound $GdCo_2$ exhibits a weak magnetic anisotropy. In other compounds RCo_2 which we investigated, the rare-earth ions have a nonzero orbital angular momentum and their magnetic anisotropy is high: Although no systematic investigations of the magnetic anisotropy of the compound RCo_2 have been performed, according to existing data on the magnetic anisotropy of $HoCO_2$[20] and the isostructural compounds RFe_2,[21] the cubic anisotropy constant K_f is of the order of several 10^7 ergs/cm^3.

It is possible that the observed nonmonotonic dependence of the exchange parameter A on the rare-earth element arises because the effect of the magnetic anisotropy was neglected in the calculations of the value of λ (and therefore the value of A also) from the susceptibility in the noncollinear phase.

Theoretical estimates according to the equations presented in Ref. 15 show that the correction to the susceptibility produced in an isotropic ferrimagnet as a result of magnetic anisotropy is

$$\frac{\Delta\chi}{\chi}\approx-\frac{bK_f}{\lambda|M_f^2-M_d^2|}. \quad (8)$$

The coefficient $b\approx 1$, and its value and sign depend on the orientation of the field with respect to the crystallographic axes. For a polycrystal the quantity b is unknown, and it can be only asserted that it must be less than 1, since contributions of different signs will cancel one another on averaging.

Calculations using Eq. (8) show that if we have $b=1$, then $\Delta\chi/\chi\geqslant 0.1$ holds for most compositions which we investigated. According to the experimental data, however, this estimate is very rough and the effect of the anisotropy on the susceptibility in the noncollinear phase is much smaller. This can be seen from the fact that according to our data the quantity λ determined for the compounds with Tm and Er from the susceptibility in the noncollinear phase according to formulas which do not take into account the magnetic anisotropy is identical, within the limits of error (3–5%), to the value of λ determined from the critical metamagnetic-transition field (in the latter case the effect of the anisotropy is much weaker).

For a final answer to the question of the dependence of the f-d exchange parameter on the rare-earth element, measurements must be performed for RCo_2 with light rare earths, in which according to Ref. 7 the exchange parameter is much larger than in compounds with heavy rare earths.

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[1)] Data obtained by T. Goto (private communication).

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[1] P. E. Brommer and J. J. M. Franse in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow, North-Holland, Amsterdam, 1993, Vol. 7, p. 307.

[2] K. H. J. Buschow, J. Less-Common Metals **43**, 55 (1975).

[3] E. Belorizky, M. A. Fremy, J. P. Gavigan, D. Givord, and H. S. Li, J. Appl. Phys. **61**, 3971 (1987).

[4] N. H. Duc, Phys. Status Solidi B **164**, 545 (1991).

[5] N. H. Duc, T. D. Hien, P. E. Brommer, and J. J. M. Franse, J. Magn. Magn. Mater. **104–107**, 1252 (1992).

[6] N. H. Duc, T. D. Hien, and D. Givord, J. Magn. Magn. Mater. **104–107**, 1344 (1992).

[7] N. H. Duc, T. D. Hien, D. Givord, J. J. M. Franse, and F. R. de Boer, J. Magn. Magn. Mater. **124**, 305 (1993).

[8] A. K. Zvezdin, Pis'ma Zh. Eksp. Teor. Fiz. **58**, 744 (1993) [JETP Lett. **58**, 719 (1993)].

[9] T. Goto, K. Fukamichi, T. Sakakibara, and H. Komatsu, Solid State Commun. **72**, 945 (1989).

[10] T. Sakakibara, T. Goto, K. Yoshimura, and K. Fukamichi, J. Phys.: Condens. Matter **3**, 3381 (1990).

[11] R. Z. Levitin and A. S. Markosyan, Usp. Fiz. Nauk **155**, 623 (1988) [Sov. Phys. Usp. **31**, 730 (1988)].

[12] R. Ballou, Z. M. Gamishidze, R. Lemaire, R. Z. Levitin, A. S. Markosyan, and V. V. Snegirev, J. Magn. Magn. Mater. **118**, 159 (1993).

[13] P. E. Brommer, I. S. Dubenko, J. J. M. Franse, R. Z. Levitin, A. S. Markosyan, R. J. Radwanski, V. V. Snegirev, and A. Yu. Sokolov, Physica B **183**, 363 (1993).

[14] Z. M. Gamishidze, *Author's Abstract of Candidate's Dissertation in Physical-Mathematical Sciences*, Moscow State University, Moscow, 1993.

[15] K. P. Belov, A. K. Zvezdin, A. M. Kademtseva, and R. Z. Levitin, *Orientational Transitions in Rare-Earth Magnets* [in Russian], Nauka, Moscow, 1979, p. 243.

[16] P. E. Brommer, I. S. Dubenko, J. J. M. Franse *et al.*, Phys. Lett. A **189**, 253 (1994).

[17] I. S. Dubenko, R. Z. Levitin, A. S. Markosyan, and H. Yamada, J. Magn. Magn. Mater. **135**, 326 (1994).

[18] I. S. Dubenko, R. Z. Levitin, and A. S. Markosyan, J. Magn. Magn. Mater. **111**, 146 (1992).

[19] D. Bloch and R. Lemaire, Phys. Rev. B **2**, 2648 (1970).

[20] D. Gignoux, F. Givord, and R. Lemaire, Phys. Rev. B **12**, 2648 (1975).

[21] K. P. Belov, *Rare-Earth Magnets and Their Applications* [in Russian], Nauka, Moscow, 1980, p. 103.

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