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## Magnetocaloric effect in $(\text{Tb,Dy},R)(\text{Co,Fe})_2$ ( $R = \text{Ho, Er}$ ) multicomponent compounds

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**Abstract.** The magnetic, magnetocaloric, and magnetoelastic properties of  $\text{Tb}_x\text{Dy}_y\text{R}_z(\text{Co,Fe})_2$  ( $R = \text{Ho, Er}$ ;  $x + y + z = 1$ ) single-phase alloys prepared by arc melting were investigated. The high-purity samples with various compositions were used for the study, and a comprehensive investigation of the properties was performed. The measurements of the magnetocaloric effect (MCE) were carried out by a direct method; and the magnetostriction was determined using the strain-gauge technique. In the vicinity of the magnetic phase transition, an abrupt change of the magnetization, a large MCE, and the maxima of volume magnetostriction were observed for the compounds studied. Obtained results of MCE in  $(\text{Tb,Dy})\text{Co}_2$  agree well with available theoretical calculations.

### 1. Introduction

Owing to the relatively simple crystallographic and magnetic structures, the Laves phase intermetallic compounds  $R\text{Co}_2$  ( $R$  is the rare earth element) remain an attractive subject for testing various physical models in the field of the Solid State Physics [1,2].  $R\text{Co}_2$  crystallize in the  $\text{MgCu}_2$ -type structure (Laves C15 phase, space group  $Fd\bar{3}m$ ). The compounds with non-magnetic  $R$ ,  $\text{YCo}_2$  and  $\text{LuCo}_2$ , are Pauli paramagnets. The magnetic state of the Co-sublattice can be stabilized by applying the magnetic field higher than  $\sim 70$  T or by the molecular field arising from the magnetic  $R$ -sublattice. The  $R\text{Co}_2$  with  $R = \text{Gd} - \text{Er}$  are ferrimagnets. As the temperature is varied,  $\text{GdCo}_2$  and  $\text{TbCo}_2$  pass through the second-order magnetic phase transition from ferri- to the paramagnetic state while the first-order magnetic phase transition takes place for  $\text{DyCo}_2$ ,  $\text{HoCo}_2$  and  $\text{ErCo}_2$  [3]. It is known that the highest values of the magnetocaloric effect (MCE) are usually observed in the vicinity of the magnetic phase transitions [4], particularly of the first-order, where the magnetization and other characteristics change drastically upon the temperature or magnetic field variation, suggesting the potential application of the compounds as magnetic refrigerants.

In the present work, the search for new materials with a large MCE was carried out among the multicomponent alloys of the  $R\text{Co}_2$  type. Though during the past decade numerous investigations of MCE performed on  $R\text{Co}_2$  with different substitutions either in the rare-earth  $(RR')\text{Co}_2$  [5-8] or in the

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Co sublattices  $R(\text{Co},T)_2$  [9-12] ( $T$  is another transition metal) were carried out, we are not familiar with the works on MCE of the multicomponent compounds of the  $(RR'R'')(Co,T)_2$  type.

Among the  $(RR')\text{Co}_2$  alloys,  $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$  system deserves a special attention.  $\text{TbCo}_2$  and  $\text{DyCo}_2$  with the neighboring  $R$  and different disorder-order transition types have similar lattice parameters. According to Refs. [13,14], the change of the transition type from the first to the second-order in  $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$  occurred at  $0.1 < x < 0.3$ . The compounds were shown to have the compensated magnetic anisotropy (MA) within the rare-earth sublattice due to the opposite sign of the single-ion MA constants of Terbium and Dysprosium [15]. (It should be mentioned that the Fe-containing analogue of  $(\text{Tb},\text{Dy})\text{Co}_2$ ,  $\text{Tb}_{0.23}\text{Dy}_{0.73}\text{Fe}_2$ , also known as terfenol-D, possesses giant values of magnetostriction and is widely used in practice.) In Ref. [16], the magnetocaloric properties of  $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$  were discussed in terms of the theoretical model using the treatment of the  $4f$  spin-spin interaction with respect to the rare earth ion type.

The aim of the present work was to investigate the magnetic, magnetothermal and magnetoelastic properties of the multicomponent compounds  $(\text{Tb},\text{Dy},R)(\text{Co},T)_2$  ( $R = \text{Ho}, \text{Er}; T = \text{Fe}$ ) with the compensated magnetic anisotropy, selected on the account of theoretical predictions based on the single-ion model of magnetic anisotropy, as well as to compare the experimental data on MCE with known theoretical values. Partial substitution of Fe atoms for Co was performed in order to bring the Curie temperatures ( $T_C$ ) of the compounds under study towards the room temperature [17].

## 2. Experimental details

The rare-earth metals purified by a double vacuum distillation (Tb) and sublimation (Dy, Ho, Er) with the use of original furnace designed at Baikov Institute of Metallurgy and Materials Science RAS [18] were used as starting materials. The purified metals (99.956-99.983 wt. %) were characterized by low content of metallic and interstitial elements. An Armco iron and Co with the purity of 99.9% were also used. The following alloys have been prepared:  $\text{Tb}_{0.27}\text{Dy}_{0.73}\text{Co}_2$ ,  $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Co}_2$ ,  $(\text{Tb}_{0.45}\text{Dy}_{0.55})_{1-x}\text{Ho}_x\text{Co}_2$  ( $x = 0.1, 0.2, 0.3$  and  $0.5$ ),  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_{1.8}\text{Fe}_{0.2}$  and  $(\text{Tb}_{0.45}\text{Dy}_{0.55})_{1-x}\text{Er}_x\text{Co}_2$  ( $x = 0.1, 0.2, 0.3$ ). Details of the sample preparation and quality control have been described earlier [19].

The MCE measurement was conducted by a direct method. The specific-heat measurements in 0 T were carried out by a standard relaxation method on PPMS installation (Quantum Design). The field and temperature dependencies of magnetization were measured by the standard SQUID magnetometer and the magnetostriction and thermal expansion was determined using the strain-gauge technique.

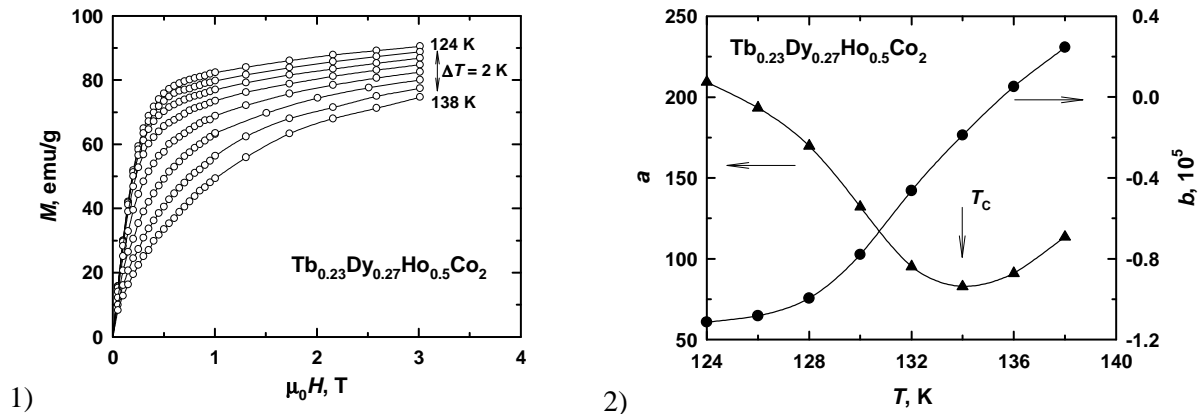
## 3. Results and discussion

The magnetic anisotropy constants are known to have non-zero values at the Curie point. In general, the MA constant of the rare-earth sublattice is an additive superposition of the product of single-ion anisotropy constants of the  $R$  ions multiplied by their concentrations [20]. The total  $l$ th-order MA constant can be calculated from the relation [11]

$$K_l = \sum X_n K_{nl}^0 \hat{I}_{l+(1/2)} \{L_m^{-1}\}, \quad (1)$$

where  $K_{nl}^0$  is the  $l$ th-order single-ion anisotropy constant at 0 K,  $\hat{I}$  is the reduced hyperbolic Bessel function,  $L_m^{-1}(m)$  is the inverse Langevin function of reduced magnetization  $m = I_s(T)/I_s(0)$  ( $I_s(0)$  and  $I_s(T)$  are the spontaneous magnetizations at 0 K and at a temperature  $T$ , respectively). In order to attain the compensation of MA within the rare-earth sublattice, the compositions with the  $R$  ions having different signs of the single-ion MA constants (of the first and higher orders) were chosen. So that we defined and prepared the multicomponent compounds with general formulas  $\text{Tb}_x\text{Dy}_y\text{R}_z\text{Co}_2$  ( $R = \text{Ho}$  or  $\text{Er}$ ,  $x+y+z = 1$ ). From the analysis of X-ray diffraction patterns, it was concluded that the samples were single phase with the cubic  $\text{MgCu}_2$  structure. The prepared alloys were also examined by the X-ray fluorescent microanalysis in order to determine the exact compositions.

The magnetization curves for the compounds under study were measured (see, for example Fig.1(1)). A weak magnetic hysteresis (not more than 10% of magnetization value) was observed in fields below



**Figure 1.** Magnetization isotherms (1) and the temperature dependence of Landau coefficients  $a$  and  $b$  (2) for  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$ . The units for  $a(T)$  and  $b(T)$  are  $\text{T}^2\text{kg/J}$  and  $\text{T}^4\text{kg/J}$ , respectively.

0.05 T, which disappeared at higher applied fields (such a small hysteresis can be explained by the compensated MA constants near  $T_C$ ). The magnetic phase transitions were examined in terms of Landau theory by analyzing the temperature dependencies of Landau coefficients in the magnetic free energy ( $F$ ) equation as a function of total magnetization (in case of neglecting the higher order terms):

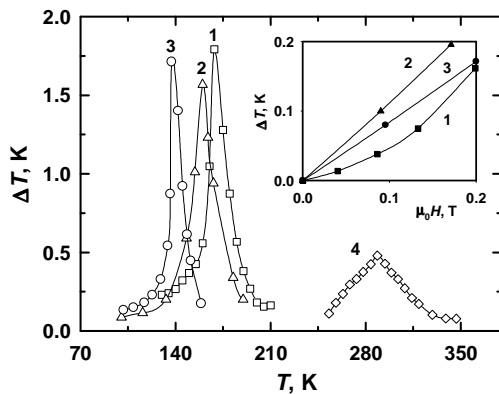
$$F = (1/2)a(T)M^2 + (1/4)b(T)M^4 + (1/6)c(T)M^6 - \mu_0MH. \quad (2)$$

The description of magnetization near  $T_C$  follows from the equilibrium condition  $(\partial F / \partial M) = 0$ . The  $a(T)$  dependence was used to determine the Curie temperatures of the compounds. A group of alloys demonstrating the first-order transition defined in accordance with the sign of  $b(T_C)$  (negative at  $T_C$  while the parameters  $a(T_C)$  and  $c(T_C)$  are positive) was revealed [8,21]. The lattice parameters, the refined alloys compositions, the Curie temperatures and the type of order of magnetic phase transition are listed in Table 1.

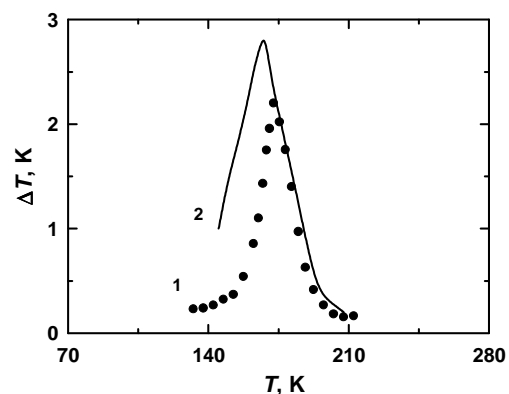
**Table 1.** Lattice parameters, Curie temperatures and the types of magnetic phase transition in  $(\text{Tb,Dy,R})(\text{Co,Fe})_2$  ( $R = \text{Ho, Er}$ ).

Compounds	$a, \text{\AA}$	$V, \text{\AA}^3$	$T_C, \text{K}$	Transition type
$\text{Tb}_{0.27}\text{Dy}_{0.73}\text{Co}_2$	7.1930	372.11	168	First-order
$\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Co}_2$	7.1937	372.27	170	First-order
$\text{Tb}_{0.4}\text{Dy}_{0.5}\text{Er}_{0.1}\text{Co}_2$	7.1917	371.96	168	First-order
$\text{Tb}_{0.35}\text{Dy}_{0.45}\text{Er}_{0.2}\text{Co}_2$	7.1878	371.36	162	First-order
$\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$	7.1820	370.46	134	First-order
$\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_{1.8}\text{Fe}_{0.2}$	7.2126	375.21	290	Second-order

Figure 2 shows the temperature dependence of MCE of selected  $(\text{Tb,Dy,R})(\text{Co,Fe})_2$  compounds. For  $\text{Tb}_{0.27}\text{Dy}_{0.73}\text{Co}_2$ ,  $\text{Tb}_{0.35}\text{Dy}_{0.45}\text{Er}_{0.2}\text{Co}_2$  and  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$ , MCE is observed in the 130 – 170 K temperature range and consists of 1.6 – 1.8 K adiabatic temperature change under the variation of magnetic field from 0 up to 1.2 T. The partial substitution of Fe for Co has allowed us to move the transition temperature towards the room temperature, however, resulting in a change of the transition type from the first to the second order in  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_{1.8}\text{Fe}_{0.2}$ . Such substitution has also led to a threefold decrease in the MCE value (curve 4 in Fig. 2). As it is seen from the field dependence of MCE presented in the inset in Fig. 2, and in contrast with  $\text{Tb}_{0.27}\text{Dy}_{0.73}\text{Co}_2$ , the  $\text{Tb}_{0.35}\text{Dy}_{0.45}\text{Er}_{0.2}\text{Co}_2$  and  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$  compounds demonstrate an almost linear behavior and higher MCE values in a



**Figure 2.** Adiabatic temperature change  $\Delta T$  vs. absolute temperature for  $\text{Tb}_{0.27}\text{Dy}_{0.73}\text{Co}_2$  (1),  $\text{Tb}_{0.35}\text{Dy}_{0.45}\text{Er}_{0.2}\text{Co}_2$  (2),  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$  (3) and  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_{1.8}\text{Fe}_{0.2}$  (4) near  $T_C$  upon the  $\mu_0\Delta H = 1.2$  T field change. The inset: field dependence of  $\Delta T$  for the same samples.

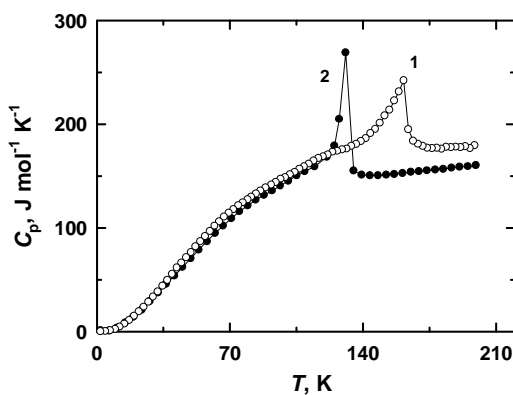


**Figure 3.** Adiabatic temperature change  $\Delta T$  vs. absolute temperature in  $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Co}_2$  as measured upon the magnetic field variation from 0 to 1.5 T (1). Solid line (2) shows theoretical predictions adopted from Ref. [17].

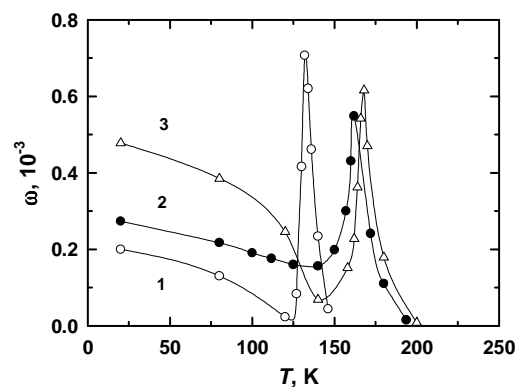
rather weak ( $< 0.2$  T) magnetic field. On our point of view, the latter fact is connected with a total compensation of magnetic anisotropy in the studied compounds.

The theoretical predictions on the magnetocaloric potential of  $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$  were given in Ref. [17] with the  $H = H_d + H_f$  model Hamiltonian used for the MCE calculation ( $H_d$  and  $H_f$  describe the subsystems of itinerant  $3d$ -electrons of Co and the localized  $4f$ -electrons of the  $R$  ions, respectively (see the corresponding formulas (1) and (2) in Ref. [17])). The exchange, magnetoelastic, anisotropic and magnetic energy contributing to the observed effects are also taken into account. Experimental adiabatic temperature change upon the magnetic field variation from 0 to 1.5 T in  $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Co}_2$  compound is shown in Fig. 3 in comparison with the theoretical data adopted from Ref. [17]. The obtained results agree rather well with calculations for  $T > T_C$ , whereas a small deviation from the calculated curve at lowered temperatures may be connected with the domain structure formation.

The zero-field specific heat data for  $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Co}_2$  and  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$  is shown in Fig. 4. The sharp peak in the temperature dependence of  $C_p$  is observed at  $T = 134$  K for  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$ ,



**Figure 4.** Temperature dependence of specific heat of  $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Co}_2$  (1) and  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$  (2) compounds in zero magnetic field.



**Figure 5.** Volume magnetostriction vs. temperature for  $\text{Tb}_{0.27}\text{Dy}_{0.73}\text{Co}_2$  (1),  $\text{Tb}_{0.35}\text{Dy}_{0.45}\text{Er}_{0.2}\text{Co}_2$  (2) and  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$  (3) in field of 1.2 T.

whereas for  $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Co}_2$  it is somewhat reduced and broadened at  $T = 170$  K. Nevertheless, the obtained values of  $b(T_C)$  for  $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Co}_2$  were found to be negative, confirming an occurrence of the first order magnetic phase transition, though with the magnitude rather close to zero.

In addition to aforesaid, the investigation of the magnetostriction of  $(\text{Tb,Dy,R})\text{Co}_2$  alloys with  $R = \text{Ho}$  and  $\text{Er}$  was carried out in the present work in the temperature range from 5 to 200 K and in magnetic fields up to 1.2 T. Figure 5 presents the temperature dependencies of the volume magnetostriction  $\omega$  for  $\text{Tb}_{0.27}\text{Dy}_{0.73}\text{Co}_2$ ,  $\text{Tb}_{0.35}\text{Dy}_{0.45}\text{Er}_{0.2}\text{Co}_2$  and  $\text{Tb}_{0.23}\text{Dy}_{0.27}\text{Ho}_{0.5}\text{Co}_2$  compounds. In the vicinity of the magnetic phase transition, the observed volume magnetostriction reaches the range of “giant” values of  $(0.55-0.7) \times 10^{-3}$ . As a result of the conducted comprehensive research on magnetic, magnetoelastic and magnetothermal properties, the estimation of various energy contributions (namely, the exchange, magnetoelastic, anisotropic and magnetic energy) to the thermodynamic potential [22,23] of the  $(\text{Tb,Dy,R})\text{Co}_2$ -type compounds with the first order magnetic phase transitions was carried out (will be published elsewhere). At the Curie temperature, the ratio between the values of exchange and the magnetoelastic energies accounts for 3:1. The energy of magnetic anisotropy is found to affect insignificantly the magnetic phase transition.

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## References

- [1] Duc N C , Brommer P E Formation of 3d-moments and spin fluctuations in some rare-earth-cobalt compounds , in: *Handbook of Magnetis Materials* K.H.J. Buschow (Ed.) 1999 vol. 12 (Amsterdam, Elsevier Science)
- [2] Gratz E and Markosyan A S 2001 *J. Phys.:Condens. Matter* **13** R385
- [3] Khmelevski S and Mohn P 2000 *J. Phys.:Condens. Matter* **12** 9453
- [4] Tishin A M Magnetocaloric effect in the vicinity of phase transitions in: *Handbook of Magnetis Materials* K.H.J. Buschow (Ed.), 1999 vol. 12 (Amsterdam, Elsevier Science).
- [5] Liu X B and Altounian Z 2005 *J. Magn. Magn. Matter.* **292** 83
- [6] Gomes A M , Reis M S, Oliveira I S , Guimaraes A P , Takeuchi A Y 2002 *J. Magn. Magn. Matter.* **242-245** 870
- [7] Ouyang Z W , Rao G H , Yang H F, Liu W F , Liu G Y , Feng X M , Liang J K 2004 *J. Alloys Compd.* **372** 76
- [8] Balli M, Fruchart D, Gignoux D 2007 *J. Magn. Magn. Matter.* **314** 16
- [9] Liu H, Wang D, Tang S, Cao Q, Tang T, Gu B, Du Y 2002 *J. Alloys Compd.* **346** 314
- [10] Prokleska J, Vejpravova J, Vasylyev D, Danis S, Sechovsky V 2005 *J. Magn. Magn. Matter.* **290-291** 676
- [11] Chen X, Zhuang Y, Yan J, Zhou K, Li K. 2008 *J. Rare metals* **27** 350
- [12] Wada H, Tanabe Y, Shiga M, Sugawara H, Sato H 2001 *J. Alloys Compd.* **316** 245
- [13] Gu K, Li J, Ao W, Jian Y, Tang J 2007 *J. Alloys Compd.* **441** 39
- [14] Zhuang Y, Chen X, Zhou K, Li K 2008 *J. Rare metals* **26** 749
- [15] Klimker H, Dariel M P, Rosen M 1980 *J.Phys.Chem.Solids* **41** 215
- [16] Han Z, Hua Z, Wang D, Zhang C, Gu B, Du Y 2006 *J. Magn. Magn. Matter.* **302** 109
- [17] de Oliveira N A 2008 *J. Magn. Magn. Matter.* **320** e150
- [18] Chistyakov O D, Burkhanov G S, Kol'chugina N B 1994 *Vysokochistye veshchestva* **3** 57 (in Russian)
- [19] Tereshina I, Politova G, Tereshina E, Nikitin S, Burkhanov G, Chistyakov O, Karpenkov A 2010 *J. Phys.: Conf. Series* **200** 092012
- [20] Koon N C, Williams C M, Das B N 1991 *J. Magn. Magn. Matter.* **100** 173
- [21] Yamada H, Goto T 2003 *Phys. Rev. B* **68** 184417
- [22] Nikitin S A 1984 *Sov. Phys. JETP* **59(5)** 1010
- [23] Spichkin Y I and Tishin A M 2005 *J. Magn. Magn. Matter.* **290-291** 700