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Magnetic properties and spin state of Co^{3+} ions of layered cobaltite $DyBaCo_2O_{5.49}$

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In cobaltites $DyBaCo_2O_{5.49}$, the spin state of Co^{3+} ions near the metal–insulator transition was determined for the first time. In the non-conducting phase, as in other rare earth (R) cobaltites $RBaCo_2O_{5.50}$, Co^{3+} ions are in low (LS, $S = 0$) and intermediate (IS, $S = 1$) spin states. In the metal phase, Co^{3+} ions are in an intermediate (IS, $S = 1$) spin state. The metal–insulator transition occurs when the spin state of Co^{3+} ions from IS/LS in octahedra changes, without changing the IS state in pyramids. Temperature hysteresis of magnetization shows that the metal–insulator transition in $DyBaCo_2O_{5.50}$ is a first-order phase transition. It is assumed that the metamagnetic behavior of rare earth cobaltites $RBaCo_2O_{5.50}$ is due to their layered structure and is determined by the size of the rare earth ion.

Keywords: metalI–insulator transition, rare earth ion, metamagnetic behavior.

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1. Introduction

Layered cobaltites $RBaCo_2O_{5.50}$, where R is a rare-earth ion, are of interest because of their unusual electronic, structural and magnetic transitions [1–9]. A number of sequential transitions were found in them: metal–insulator (MI), paramagnetic (PM) → ferromagnetic (FM) → antiferromagnetic (AFM) junction. It is assumed that these phenomena occur as a result of strongly correlated interactions between electronic, orbital and spin degrees of freedom [2]. Unlike manganites, the transition in cobaltites is not associated with magnetic ordering, which is a consequence of the magnetically active (antiferromagnetic) nature of the $RMnO_3$ matrix in the case of manganites and the weakly magnetic (paramagnetic) behavior of $RCoO_3$ in the case of cobaltites [7]. $RBaCo_2O_{5.50}$ oxides have a layered perovskite crystal structure consisting of layers arranged along the c-axis, in which $RO_{0.5}$ and BaO layers are interspersed with CoO_2 layers. They are strongly anisotropic due to their layering [2]. Only Co^{3+} ions are present in $RBaCo_2O_{5.50}$, which are located in a crystal lattice of an equal number of CoO_6 octahedra and CoO_5 square pyramids.

The origin and elucidation of the driving forces of the metal–insulator transition is the main issue for these materials. It was recognized that the key to understanding these phenomena is the change of the spin state of Co^{3+} ions depending on the temperature. It is concluded from structural and magnetic data [3] that the transition from a nonconducting phase to a metallic phase in $GdBaCo_2O_{5.50}$ is attributable to the excitation of LS-state electrons in the e_g-band of HS-state Co^{3+} in octahedra without changes of the IS-state Co^{3+} in the pyramids. Although this model contradicts the structural data, it is widely accepted and is considered valid for all rare-earth ions. The spin state of Co^{3+} ions is determined by magnetic measurements, taking into account the PM-contribution of rare-earth ions. Clarification of the paramagnetic contribution of R^{3+} ions shows [10] that the transition to a non-metallic state occurs due to a change of the high-spin (HS, $S = 2$) state to a low-spin (LS, $S = 0$) state in octahedra, and the transformation of the low-spin LS state of Co^{3+} ions into an intermediate (IS, $S = 1$) spin state in pyramids.

The size of the rare-earth ion slightly affects the transition temperature of the metal–insulator, and the Curie temperature [11]. Layered cobaltites exhibit metamagnetic behavior, the transition temperature (T_m) from the FM state to AFM depends on the magnetic field [2,5,6]. The metamagnetic behavior of $NdBaCo_2O_{5+\delta}$, $\delta \approx 0.50$, in large magnetic fields at low temperatures is explained [6] by the large size of rare-earth ions based on the L. Landau metamagnetic model [12].

The size of the rare-earth element affects the magnetic state of $RBaCo_2O_{5.50}$. FM correlations occur in the AFM state with an increase of the size of rare-earth ions $R = \mathrm{Eu} \rightarrow \mathrm{Nd} \rightarrow \mathrm{Pr}$. FM interactions are present in $RBaCo_2O_{5.50}$, where $R =$ Eu, Nd, Pr, at all temperatures below Néel temperature T_N even in the antiferromagnetically ordered phase [6,13–15]. The nature of the metamagnetic behavior and FM state in the AFM phase is not clear.

Of all the synthesized $RBaCo_2O_{5.50}$ compounds, where R can be Pr, Nd, Sm, Eu, Gd, Tb or Dy, the compounds with the smallest ions, $R =$ Dy and Ho, are currently the least studied. Only three papers are known, one [16] is devoted to the study of magnetic and electrical properties, the other two cover structural data DyBaCo$_2$O$_{5.50}$ [17,18]. A distinctive feature of these compounds is that the transition of the metal–insulator takes place at $\delta \approx 0.50$.

Powder neutron diffraction demonstrated that DyBaCo$_2$O$_{5.50}$ has an antiferromagnetic structure below 230 K with Co^{3+} ions in the intermediate (IS, $S = 1$) spin state in the octahedral and pyramidal environment. The magnetic moments of Co^3 ions have a beveled magnetic structure at low temperatures [17]. X-ray and neutronographic studies of the DyBaCo$_2$O$_{5.50}$ single crystal revealed a structural transition and electrical resistance anomalies below $T_{\mathrm{MI}} \approx 325$ K. A series of very weak superstructural X-ray reflections from an DyBaCo$_2$O$_{5.50}$ single crystal is explained under the assumption that a structural transition of the 2nd kind occurs at T_{MI} from the phase c of the Pmmm space group to the Pmma phase [18]. We show below that the transition of the metal–insulator to DyBaCo$_2$O$_{5.49}$ at $T = 325$ K occurs due to a phase transition of the 1st kind.

The study is aimed at determining the spin state of Co^{3+} ions near the metal–insulator junction and elucidating the nature of metamagnetic behavior in layered cobalt DyBaCo$_2$O$_{5.50}$.

2. Samples and techniques

DyBaCo$_2$O$_{5.49(2)}$ polycrystals were synthesized by the solid-phase method from the initial components Dy$_2$O$_3$, BaCO$_3$ and Co$_3$O$_4$ by stepped annealing in air at $T = 900-1100^\circ$C [1,10]. Samples with an oxygen content of $\delta \approx 0,50$ were prepared using the method proposed in Ref. [16]. DyBaCo$_2$O$_{5.49}$ polycrystals are described by an orthorhombic structure at room temperature (space group Pmmm, #47) with lattice cell parameters $a = 3.871(0)$ Å, $b = 7.827(9)$ Å, $c = 7.527(8)$ Å. The values of the structural parameters of the samples are consistent with the literature data [16,17]. The electrical resistance was measured using a four-contact method. The work was performed using the equipment of the Center for Collective Use „Testing Center for Nanotechnology and Advanced Materials“ of Metal Physics, Ural Branch, Russian Academy of Sciences.

3. Magnetic properties

Figure 1 shows the temperature dependences of DyBaCo$_2$O$_{5.49}$ in the range of 10–350 K for three values of the magnetic field: $H = 1$, 10 and 50 kOe (Figure 1). The magnetization $M_{\mathrm{exp}}(T)$, measured in a magnetic field of 1 kOe after cooling in a zero field (solid curve *1*), sharply increases at the Curie temperature $T_{\mathrm{C}} \approx 290$ K. It exists in a small (~ 50 K) temperature range, reaching a maximum at $T_{\max} \approx 267$ K, below which it sharply decreases, characterizing the transition from the FM (or beveled AFM) to the AFM state at $T_{\mathrm{N}}(\mathrm{Co}^{3+}) \leq 200$ K. The Curie temperature $T_{\mathrm{C}} = 290 \pm 1$ K, estimated based on the magnetization derivative $\mathrm{d}M/\mathrm{d}T$, agrees with the known data [1,16]. The cooling curves in the zero magnetic field and the cooling curves in the field (solid and dotted curves *1*, respectively) are close and almost coincide, which indicates the absence of the FM component. These results indicate the perfection of the crystal and the oxygen content of δ in it, close to $\delta \approx 0.50$. It can be seen that the PM contribution of Dy^{3+} ions, determined with the parameters of the free ion Dy, exceeds the experimental values of the magnetization M_{exp} below $T \approx 150$ K (curve *2* Figure 1). (PM-behavior of the magnetization of the sample below 200 K at 10 and 50 kOe is not shown for clarity of images.)

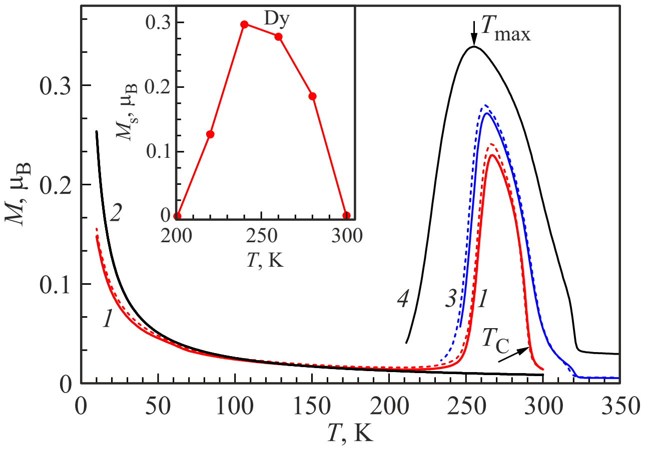

Figure 1. Temperature dependences of the magnetization DyBaCo$_2$O$_{5.49}$ at $H = 1$, 10 and 50 kOe (curves *1*, *3* and *4*, respectively; curve *2* — paramagnetic contribution of the free ion Dy). Insert: temperature dependence of spontaneous magnetization DyBaCo$_2$O$_{5.49}$.

When the magnetic field increases to 50 kOe the temperature of the maximum magnetization $T_{\max}$ shifts towards low temperatures by about 12–14 K, i. e. the magnetic field inhibits the AFM and strengthens the FM state, i. e. the DyBaCo$_2$O$_{5.49}$ compound shows signs of metamagnetic behavior.

Figure 1 shows the temperature dependence of the spontaneous magnetization M_{s}, obtained from extrapolation of the magnetization $M(H)$ in a magnetic field up to 90 kOe. It can be seen that M_{s} occurs at $T_{\mathrm{C}} \approx 290$ K and disappears at $200\,\mathrm{K} \leq T \leq 220\,\mathrm{K}$ in accordance with the results of neutron studies [17]. The magnetic moments of Co ions are in the state (IS, $S = 1$) and are beveled in the plane (a, b) in an octahedral and pyramidal environment at low temperatures [17]. The value of spontaneous magnetization in the FM state is small — $M_{\mathrm{s}} < 0.3\,\mu_{\mathrm{B}}$, and less than the expected value of $M_{\mathrm{s}} \approx 0.5\,\mu_{\mathrm{B}}$ for the state (IS, $S = 1$) of Co^{3+} ions for the twinning structure of samples [2]. The results are explained by the beveled magnetic structure of Co^{3+} ions.

A temperature hysteresis of magnetization was found from studies of magnetization at 10 kOe (curve *3* Figure 1)

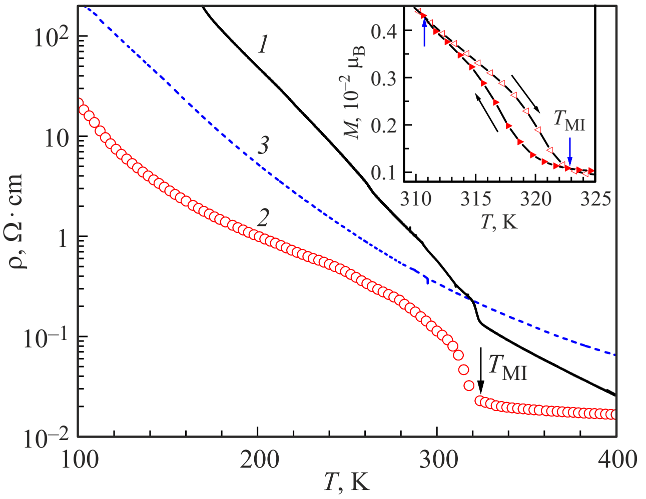

Figure 2. Temperature dependences of electrical resistance of three samples $DyBaCo_2O_{5+\delta}$. (see text). Insert: temperature hysteresis of magnetization $DyBaCo_2O_{5.49}$.

(insert Figure 2). In case of heating above $T = 323$ K, the sample cools down to $T = 310$ K at lower magnetization. The temperature hysteresis is a typical property of a phase transition of the 1st kind. Usually, such a transition is a consequence of a structural phase transition. The energy differences between different spin states of Co ions are small in layered cobaltites. As a result, transitions of Co ions from one spin state to another [2] can easily occur in cobaltites in case of change of the ambient parameters (temperature, magnetic fields, etc.). These transitions are accompanied by a structural phase transition, the disappearance of the energy gap, a change of transport properties and a transition to a quasi-metallic state.

4. Electrical properties

Figure 2 shows the temperature dependences of electrical resistance for three samples $DyBaCo_2O_{5+\delta}$, where δ is the oxygen content. $DyBaCo_2O_{5+\delta}$ powders synthesized at 1150°C by the solid-phase method from the initial components Dy_2O_3, $BaCO_3$ and Co_3O_4 were tested for single-phase condition by X-ray methods, pressed into tablets and annealed at 900°C in an atmosphere of pure argon for 4–5 h to $\delta \approx 0$. Further, the tablets were subjected to various heat treatments, and the oxygen content δ was determined based on the weight change [2]. The sample № 1 with $\delta = 0.50(2)$ was annealed in the oxygen stream at 250°C for 10 h and cooled to room temperature together with an oven. The sample № 2 with $\delta = 0.49(2)$ was annealed in the oxygen stream at 250°C for 10 h and tempered. The sample № 3 with $\delta = 0.58(2)$ was annealed at the oxygen pressure of 4 atm at 400 K and cooled at 250 K to room temperature together with an oven. The MI transition is more sharp in the hardened sample № 2. No MI transition was found in the sample with $\delta = 0.58(2)$.

The phase transition temperature $T = 323$ K (see insert Figure 2) matches the transition temperature MI with an accuracy of several degrees. The metal–insulator transition in $DyBaCo_2O_{5.49}$ occurs due to a phase transition of the 1st kind at $T = 323$ K.

5. Spin state of Co^{3+} ions of layered cobaltite $DyBaCo_2O_{5.49}$

Currently, when determining the spin state of Co ions it is believed that rare-earth ions in layered cobaltites act as a non-interacting free ion. However, the magnetic moments R^{3+}, determined at low temperatures from $RBaCo_2O_{5.50}$ magnetic data, where R = Gd, Tb, Pr, Nd [5,6,10,19], are less than the expected values of the moments for R^{3+} free ions. Magnetization of Tb^{3+} ions in $TbBaCo_2O_{5.50}$ single crystal at 2 K is approximately 2 times less than the moment of Tb^{3+} free ions [5]. At the same time, the magnetization of $TbBaCo_2O_{5.50}$ at high temperatures is well described by the susceptibility of Tb^{3+} fee ion [5]. A similar behavior of the magnetic properties is shown below in $DyBaCo_2O_{5.49}$.

The field dependences of the magnetization of $DyBaCo_2O_{5.49}$ was studied in a wide temperature range of $T = 5$–400 K in a magnetic field up to 90 kOe to clarify the nature of the PM-contribution of Dy ions. The magnetization M of non-interacting rare-earth ions is described by the Brillouin function $B_S(x)$ at low temperatures and large magnetic fields [20]:

$$M = N_A \cdot g \cdot \mu_B \cdot J \cdot B_S(x), \qquad (1)$$

where N_A — Avogadro number, g — Lande factor, μ_B — Bohr magneton, J — total magnetic moment, $x = gJ \cdot \mu_B \cdot H/(k_B T)$, k_B — Boltzmann constant.

The results of experiments are shown by empty symbols in Figure 3, *a* and *b*, and dotted lines *1* show the results of calculations of the magnetization M of $DyBaCo_2O_{5.49}$ polycrystal using expression (1) with the following parameters for Dy^{3+} free ions: $J = 15/2\mu_B$, $g = 4/3$. The transition of $DyBaCo_2O_{5.50}$ compound into the AFM state occurs below $T_N \approx 230$ K according to the neutron studies. There is no spontaneous moment $DyBaCo_2O_{5.49}$ below 200 K, $M_s = 0$ (insert Figure 1). Therefore, the magnetization of $DyBaCo_2O_{5.49}$ below $T \approx 200$ K is determined solely by the contribution of Dy^{3+} ions.

The experimental values of magnetization M_{exp} (symbols *2* Figure 3, *a*) are less than expected values at 5 K (dotted curve *1* Figure 3, *a*) almost by 2 times. It can be seen (Figure 3, *b*) that the difference between the experimental and calculated values of magnetization decreases with an increase of temperature at $T = 50$–160 K, and the experimental values of magnetization slightly exceed the calculated ones only at $T \approx 160$ K, characterizing the occurrence of the contribution of Co ions. The data for $T > 160$ K are not given for clarity of the images. These results show that Dy ions are interacting at low temperatures and non-interacting at high temperatures.

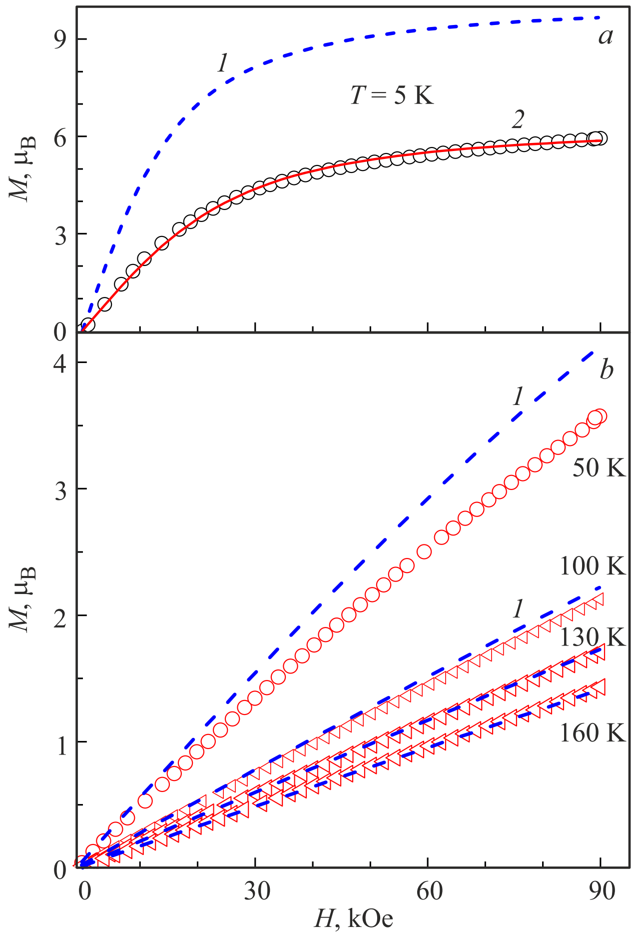

Figure 3. Magnetization of $DyBaCo_2O_{5.49}$ polycrystal as a function of the magnetic field strength at *a*) 5 K and *b*) 50–160 K. Empty symbols — experiment, dotted line *1* — calculation using expression (1).

The results are explained by the temperature-dependent non-collinear (beveled) magnetic structure of Dy^{3+} rare-earth ions. It is assumed that at low temperatures, Dy ions are ordered into a non-collinear magnetic structure. The magnetic field acts not on the total magnetic moment J of the rare-earth ion due to the beveling of the Dy ions, but only on its component J_z, and the ions show reduced values of the magnetic moment at low temperatures. It can be seen (solid line *2* Figure 3, *a*) that the experimental values of the magnetization of $DyBaCo_2O_{5.49}$ at 5 K are well described by the expression (1) at $J = 4.65\,\mu_B$, which corresponds to the bevel angle of about 53°. The transformation of the non-collinear structure of $DyBaCo_2O_{5.49}$ to collinear with the increase of the temperature is explained by the competition of the antiferromagnetic dipole-dipole interaction of rare-earth ions and their exchange interaction with Co ions. It is important for determination of the spin state of Co^{3+} ions that Dy ions above $T \approx 160$ K can be considered as non-interacting, and the PM contribution can be determined from the expression (1).

Preliminary experiments showed that the contribution of Co^{3+} ions to $DyBaCo_2O_{5.49}$ is significantly less (no more than 5–6% of the total magnetization) compared with the contributions of other RBaCo$_2$O$_{5.49}$ compounds, where R = Gd, Tb, Nd or Pr [6,10,19,21]. For obtaining reliable values of the spin state of Co^{3+} ions the magnetization $M(T)$To was measured at 50 kOe, and it was measured at $H = 10$ kOe in the temperature stabilization mode by averaging the magnetization from 3 measurements.

Figure 4 (right axis) shows the temperature dependence of the experimental values of the inverse PM-susceptibility $\chi_{\mathrm{exp}}^{-1}(T)$ of the sample of $DyBaCo_2O_{5.49}$ measured in the magnetic field $H = 10$ and 50 kOe. A linear dependence $\chi_{\mathrm{exp}}^{-1}(T)$ is observed in the interval of 400–340 K, a small jump below $T_{\mathrm{MI}} \approx 330$ K, followed by a clearly nonlinear dependence $\chi_{\mathrm{exp}}^{-1}(T)$. The value $\mu_{\mathrm{eff}} \approx 11.1\,\mu_B$ estimated using the to Curie–Weiss law is too high to be attributed to the spin state Co^{3+}. The value $\mu_{\mathrm{eff}} = 11.1\,\mu_B$ corresponds to the effective magnetic moment $\mu_{\mathrm{eff}} = 10.65\,\mu_B$ of Dy^{3+} ion in the ground state $^6H_{15/2}$. The contribution of Dy^{3+} ions was subtracted according to the expression (1) to extract the contribution of Co^{3+} ions from the total magnetization of the sample and $\chi_{\mathrm{Co}}^{-1}(T)$ was recalculated for cobalt ions (left axis Figure 4). Taking into account the contribution of Dy^{3+} ions increases the values of $\chi_{\mathrm{Co}}^{-1}(T)$ in the metal phase by 12–15 times.

The inverse PM-susceptibility $\chi_{\mathrm{Co}}^{-1}(T)$ has an approximately linear dependence on temperature in the temperature range of 390–340 K. The nonlinear part of $\chi_{\mathrm{Co}}^{-1}(T)$ begins below $T \approx 340$ K: a sharp jump of$\chi_{\mathrm{Co}}^{-1}(T)$ occurs below $T_{\mathrm{MI}} \approx 335$ K, followed by a monotonous nonlinear decrease of $\chi^{-1}(T)$ with a decrease of the temperature. The PM-susceptibility is described by Curie–Weiss law in the temperature range of 390–340 K, with PM-temperature $\theta_{\mathrm{PM}} = -150$ K and with $\mu_{\mathrm{eff}}/\mathrm{Co} = 2.57 \pm 0.10\,\mu_B$ and $\theta_{\mathrm{PM}} = -200 \pm 5$ K and with $\mu_{\mathrm{eff}}/\mathrm{Co} = 2.43 \pm 0.10\,\mu_B$ in the magnetic field of 10 and 50 kOe.

It is practically impossible to define a linear section on the dependence $\chi_{\mathrm{Co}}^{-1}(T)$ in the temperature range of $T \approx 340$–300 K: the values sharply decrease. $\mu_{\mathrm{eff}}/\mathrm{Co} \approx 1.3\,\mu_B$ and $\theta_{\mathrm{PM}} = +298\,\mathrm{K} \approx T_C$ can describe paramagnetic susceptibility in the small temperature range of 300–315 K. In fact, this means that the transition is accompanied by a change of $\mu_{\mathrm{eff}}(T)$ with temperature. Linear sections $\chi_{\mathrm{Co}}^{-1}(T)$ were defined in the temperature range of 300–330 K to confirm this assumption, and differential values of μ_{eff} were determined for each section according to the Curie–Weiss law. It can be seen (symbols *1* Figure 4, *b*) that the values of $\mu_{\mathrm{eff}}T$ reach a minimum and then monotonously increase. Negative and positive values of θ_{PM} characterize the competition of FM and AFM-interactions.

The mixture of IS-states ($t_{2g}^5e_g^1$, $S = 1$) in octahedra and pyramids with $\mu_{\mathrm{eff}}/\mathrm{Co} = 2.82\,\mu_B$ with the equal ratio 1 : 1 is the closest of all possible states of Co^{3+} ions (Figure 4, *b*) to the average value of $\mu_{\mathrm{eff}}/\mathrm{Co} \approx 2.50 \pm 0.10\,\mu_B$

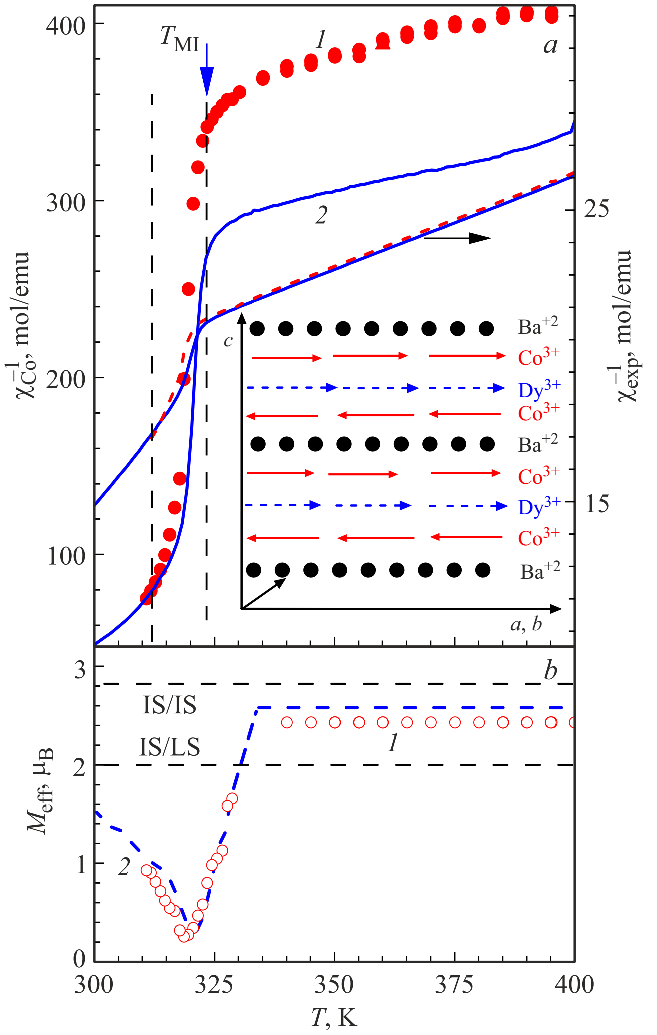

Figure 4. *a*) Temperature dependence of the experimental (right axis) values of the inverse paramagnetic susceptibility $\chi_{\mathrm{Co}}^{-1}(T)$ of $\mathrm{DyBaCo_2O_{5.49}}$ polycrystal and values minus the PM contribution of Dy ions (left axis). *b*) Temperature dependences of the effective magnetic moment $\mu_{\mathrm{eff}}/\mathrm{Co}$ for $H = 10$ and 50 kOe — curves *1* and *2*, respectively. Insert: diagram of the magnetic structure of the layered compound $R\mathrm{BaCo_2O_{5.50}}$.

and $\theta_{\mathrm{PM}} \approx -175\,\mathrm{K}$ in the metallic state ($T \approx 330{-}390\,\mathrm{K}$). The value of $\mu_{\mathrm{eff}}/\mathrm{Co} = 1.40 \pm 0.05\,\mu_{\mathrm{B}}$ below T_{MI}, near T_{C} ($T = 300{-}320\,\mathrm{K}$) means that no more than one quarter of Co^{3+} ions are in the IS-state ($t_{2g}^5 e_g^1$, $S = 1$), the remaining ions are in the LS-state. The prevalence of the LS-state fraction near T_{MI} $\mathrm{TbBaCo_2O_{5.50}}$ was also found in Ref. [5].

Thus, the spin states of Co^{3+} ions near the metal–insulator transition in $\mathrm{DyBaCo_2O_{5.49}}$ differ from cobaltites with larger sizes of rare-earth ions. Metal–insulator transition in $\mathrm{DyBaCo_2O_{5.49}}$ takes place in case of the conversion of the spin state of Co^{3+} ions from the IS-state to the LS-state in octahedra without change of the IS-state in the pyramids. The metal–insulator transition takes place in $R\mathrm{BaCo_2O_{5.50}}$, ($R =$ Tb, Gd, Nd, Pr) in case of the conversion of the spin state of Co^{3+} ions from the HS-state to the LS-state in octahedra and from the LS-state to the IS-state in pyramids [6,10,19,22].

Vertical lines in Figure 4 show the lower and upper temperatures of the phase transition of the 1st kind. It can be seen that the metal–insulator transition in $\mathrm{DyBaCo_2O_{5.49}}$ occurs below the temperature of the phase transition of the 1st kind and it is accompanied by a sharp decrease of the reverse PM-susceptibility and the spin state of Co^{3+} ions.

6. Metamagnetic behavior

It can be seen from Figure 1 that the application of the magnetic field $\mathrm{DyBaCo_2O_{5.49}}$ contributes to the transition to the FM-state from the AFM-state at lower temperatures. Compounds that exhibit magnetic field-induced transitions from the AFM-state to FM-state at low temperatures are called metamagnets.

A sharp transition from the AFM-state to the FM-state was found in $\mathrm{GdBaCo_2O_{5.50}}$ single crystals below the metamagnetic transition temperature $T_{\mathrm{m}} = 260\,\mathrm{K}$, in case of application of a magnetic field above the critical value. The critical field grows approximately linearly with cooling and reaches a value of the order of 200 kOe at $T = 0$. It is assumed that a reorientation of weakly coupled magnetic sublattices occurs in the magnetic field. The results are explained as a metamagnetic transition [2].

The metamagnetic behavior of magnetization was observed in $\mathrm{EuBaCo_2O_{5.50}}$ single crystals [15]. It was suggested in Ref. [6] that the metamagnetic behavior in $\mathrm{NdBaCo_2O_{5.47}}$ at low temperatures is caused by the large size of Nd ions. The results are explained in the Landau metamagnetic model [12] for layered AFM-compounds, in which it is assumed that the FM-layers are antiferromagnetically ordered, the interaction in the FM-layers is stronger than the AFM-interaction between the layers.

We conducted some additional studies, analyzed the known results and concluded that the metamagnetic behavior in layered cobaltites may be determined by the size of rare-earth ions. A diagram of the structure of the layered compound $R\mathrm{BaCo_2O_{5.50}}$ along the *c*-axis is shown in Figure 4 to substantiate the above. $R\mathrm{BaCo_2O_{5.50}}$ compounds have a layered perovskite structure consisting of layers arranged along the *c*-axis, in which ordered layers of $R\mathrm{O_{0.5}}$ and BaO are interspersed with layers of $\mathrm{CoO_2}$ [1,2]. FM-layers of Co^{3+} ions separated by rare-earth ions are ordered antiferromagnetically. The substitution of half of the R^{3+} ions in $R\mathrm{CoO_3}$ with larger non-magnetic Ba^{+2} ions shields the magnetic layers of $\mathrm{Co}^{3+}{-}R^{3+}{-}\mathrm{Co}^{3+}$ in $R\mathrm{BaCo_2O_{5.50}}$ from the impact of adjacent layers of Co^{3+} ions. The exchange AFM-interaction between FM-layers decreases with the increase of the distance between them. As a result, the AFM-interaction between FM-layers depends on the size of the rare-earth ion. This model is supported by the fact that the AFM state does not exist at all in $\mathrm{LaBaCo_2O_{5.50}}$ with a large size of La ions [22].

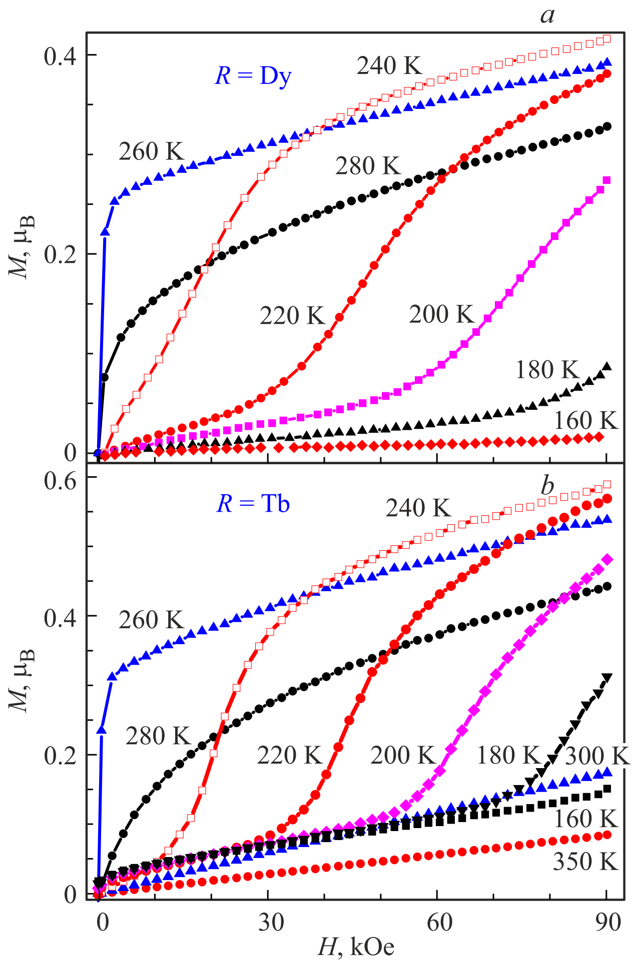

Figure 5. Magnetization *a*) $DyBaCo_2O_{5.49}$ and *b*) $TbBaCo_2O_{5.47}$ depending on the magnetic field strength at different temperatures.

Critical fields for $DyBaCo_2O_{5.49}$ and $TbBaCo_2O_{5.48}$ compounds were determined to study the effect of the size of the R-ion on the metamagnetic behavior (Figure 5). Tb and Dy ions are known to have smaller sizes than Gd ions [11]. It can be seen that the transition from AFM to FM-state occurs in the magnetic field and the critical field increases with a decrease of the temperature. The analysis shows that the critical field of the H_{cr} junction increases linearly with the decrease of the temperature and is described by approximately the same numerical expressions for both compounds: $H_{cr}[\text{kOe}] = 250 - 0.98T[\text{K}]$.

It can be seen that the critical fields increase with a decrease of the size of R-ions to several hundreds of kOe in $RBaCo_2O_{5.50}$ compounds, where $R = \text{Dy}$, Tb, Gd. The critical fields H_{cr} decrease from 50 to 30 kOe at 5 K depending on the size of the rare-earth ion in case of the reduction of the size of R-ions in $RBaCo_2O_{5.50}$, where $R = \text{Eu}$ [15], Nd [6] and Pr (not published). The results show the effect of ion size on metamagnetic behavior and are consistent with the proposed model.

On the other hand, the sizes of Eu and Gd ions differ by only 1%. Surprisingly, the magnetic field-induced metamagnetic transition occurs in $EuBaCo_2O_{5.50}$ single crystal in the AF-phase in the magnetic field $H_{cr} \approx 50$ kOe at 5 K which is significantly smaller than $H_{cr} \approx 200$ kOe in the compound with Gd. It should be noted that the magnetic moment of rare-earth ions decreases with the increase of the size. Eu^{3+} ions have no magnetic moment, $J = 0$. The values of the magnetic moments $J \approx 3\mu_B$ of of Nd and Pr ions are small compared to $J \approx 10\mu_B$ for Gd–Dy ions [23]. It can be assumed that the small values of H_{cr} are attributable to the weakening of dipole-dipole AFM interactions against the background of strengthening of FM-interactions with an increase of the size of rare-earth ions.

7. Conclusion

1. It was shown that the Dy ion at high temperatures can be considered as a free paramagnetic ion.

2. It was shown that the spin states of Co^{3+} ions near the transition to $DyBaCo_2O_{5.49}$ differ from the spin states of cobaltites with larger sizes of rare-earth ions. Metal–insulator transition takes place in case of the conversion of spin state of Co^{3+} ions from the IS-state to the LS-state in octahedra, without change of the IS-state in pyramids. At the same time, the spin state of Co^{3+} ions changes from the HS-state to the LS-state in octahedra and from the LS-state to the IS-state in pyramids in other rare-earth cobaltites.

3. Metal–insulator transition in $DyBaCo_2O_{5.49}$ and a decrease of the spin state of Co^{3+} ions is accompanied by a phase transition of the 1st kind.

4. It is assumed that the metamagnetic behavior of rare-earth cobaltites $RBaCo_2O_{5.50}$ is attributable to their layered structure and is determined by the size of the rare-earth ion.

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Conflict of interest

The authors declare that they have no conflict of interest.

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