

Irreversibility of the magnetic state of $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ revealed by specific heat, electrical resistivity, and neutron diffraction measurements

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The substitution of Tb for Tm in the Laves phase compound TmCo_2 leads to appearance of a magnetic moment on the Co atoms through the metamagnetic transition in the itinerant d -electron subsystem and gives rise to long-range ferrimagnetic order in $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ at $x \geq 0.15$. The magnetic state of the compound $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$, i.e., just below the critical Tb concentration, is characterized by the presence of large regions with short-range magnetic order and localized spin fluctuations (LSFs) induced in the Co $3d$ -electron subsystem by the fluctuating f - d exchange due to the Tm-Tb substitution. The peculiar magnetic state of this compound is strongly influenced by an external magnetic field which produces a first-order magnetic phase transition to a long-range ferrimagnetic state with the magnetic moment on the Co atoms up to $(0.7-0.8)\mu_B$. This field-induced transition in $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ is found to be irreversible. It is accompanied by a giant and irreversible reduction of the electrical resistivity ($\Delta\rho/\rho \sim -45\%$), specific heat (by about 3.7 times at 2 K), and intensity of magnetic neutron scattering. Such behavior is associated with the field-induced metamagnetic transition in the itinerant d -electron subsystem mediated by the f - d exchange. Significantly enhanced values of the residual resistivity and the coefficient γ of the T -linear contribution to the specific heat in the compound with $x=0.1$ as well as their unusual behavior with temperature and under application of the magnetic field is ascribed to the presence of LSF.

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I. INTRODUCTION

Because of the peculiar shape of the density of electronic states curve $N(E)$ in the vicinity of the Fermi energy E_F , the rare earth cubic Laves phases $R\text{Co}_2$ reveal so-called itinerant electron metamagnetism (IEM): the Co magnetic moment M_{Co} increases abruptly from zero up to a value of about $1\mu_B$, when the effective field H_{eff} acting on the d -electron subsystem reaches a critical value H_c of about 70 T.^{1,2} The $R\text{Co}_2$ compounds, where the R ion is nonmagnetic yttrium or lutetium, are exchange-enhanced Pauli paramagnets, while other $R\text{Co}_2$ compounds (except TmCo_2) with R ions having localized magnetic moments M_R show a magnetic order with parallel (in the case of light R elements) or antiparallel (for heavy R elements) alignment of the magnetic moments of R and Co ions. An estimation of the molecular field for TmCo_2 has given a value of about 60 T which is not enough to produce the IEM transition in this compound.³ Therefore, the TmCo_2 compound seems to be unique within the $R\text{Co}_2$ series since it does not exhibit a magnetic moment on the Co atoms despite the presence of a local magnetic moment on Tm. As shown by Goto *et al.*⁴ a metamagnetic transition in the itinerant d -electron subsystem can also be produced in the paramagnetic compounds YCo_2 and LuCo_2 by application of high magnetic fields above 70 T. The value of H_{eff} in $R\text{Co}_2$ may be changed by substitution of one R ion by another one R' , together with the application of an external field H , where $H_{\text{eff}} = H_{\text{mol}} \pm H$. The molecular field H_{mol} originates from the f - d exchange interaction between the localized f electrons of the R ions and the itinerant Co $3d$ electrons

hybridized with the R $5d$ electrons. Application of an external magnetic field reduces H_{eff} in the compounds with heavy R ions but increases the effective field in the case of the ferromagnetic alignment of M_R and M_{Co} . A partial substitution of some elements ($A = \text{Al, Ga, Si}$) for Co in $R(\text{Co}_{1-x}\text{A}_x)_2$ is found to decrease the critical field of the metamagnetic transition, while application of hydrostatic pressure has an opposite influence on the H_c value.^{1,2,5} The change of the magnetic state of the d -electron subsystem caused by substitution in the R or Co sublattice, or by application of hydrostatic pressure, influences significantly the main physical properties of the compounds. In particular, a significant growth of the electronic specific heat coefficient and residual resistivity was observed just below the critical concentration x_c for onset of magnetism in $\text{Y}_{1-x}\text{R}_x\text{Co}_2$ (see Ref. 6 and references therein). Such behavior is attributed to the presence of localized spin fluctuations (LSFs) in the d -electron subsystem caused by fluctuations of the exchange field owing to the substitution. Despite the understanding of the general behavior of $R\text{Co}_2$ compounds (see Refs. 1 and 2 for an overview) some basic properties associated with the appearance of long-range magnetic order remain unclear yet. In particular, there is no clear evidence of the presence of a long-range magnetic order in the R subsystem of $\text{Y}_{1-x}\text{R}_x\text{Co}_2$ compounds when the magnetic moment on the Co atoms is absent at $x < x_c$. In a narrow concentration range near x_c in some $\text{Y}_{1-x}\text{R}_x\text{Co}_2$ ($R = \text{Er, Ho}$) compounds, coexistence of long-range and short-range magnetic orders was evidenced by neutron diffraction measurements.⁷ Some anomalies in the temperature dependencies of the specific heat and elec-

trical resistivity observed in $Y_{1-x}Er_xCo_2$ ($x=0.6$) were suggested to be indicative of separate magnetic ordering of Er and Co subsystems at different Curie temperatures,⁸ while a neutron diffraction study performed on single crystals of $ErCo_2$ and $Y_{0.4}Er_{0.6}Co_2$ revealed that the magnetic order appears simultaneously in both rare earth and Co sublattices with decreasing temperature below T_C .⁹ For $ErCo_2$, field-induced metamagnetic transition and well-defined short-range magnetic correlations were also observed above T_C by neutron diffraction measurements.¹⁰ As shown by measurements on single-crystalline samples of $ErCo_2$ and $HoCo_2$,¹¹ application of a magnetic field just above T_C leads to a step like increase of the magnetization and giant reduction of the electrical resistivity due to the field-induced first-order phase transition. The first-order type of the magnetic phase transition at T_C in RCo_2 ($R=Er, Ho, \text{ and } Dy$) and the second-order type in $TbCo_2$ and $GdCo_2$, having higher Curie temperatures ($T_C > 200$ K), was explained by Bloch *et al.*¹² and Inoue and Shimizu¹³ by the suggestion of identity of the electronic structures of all compounds RCo_2 . However, the Inoue-Shimizu model does not provide an explanation for the second-order type of magnetic phase transition in $PrCo_2$ and $NdCo_2$, which have T_C values much less than 200 K. Another explanation of the transition order changes, which takes into account a possible change of the electronic structure of RCo_2 when going from light to heavy rare earths, was proposed by Khmelevsky and Mohn.¹⁴ Meanwhile, the recent study of magnetic hyperfine interactions in RCo_2 using a ¹¹¹Cd probe¹⁵ has shown that the magnetic phase transitions in RCo_2 with light rare earths ($R=Nd$ and Pr) may be also classified as first-order transitions. This unexpected result requires further investigations of the nature of the magnetic phase transitions in RCo_2 .

In this work we present results of the complex behavior of the $Tm_{1-x}Tb_xCo_2$ compounds in the vicinity of the critical concentration for onset of long-range magnetic order in the itinerant Co $3d$ -electron subsystem. In the earlier works, the compound $TmCo_2$ ranking within the RCo_2 series between the paramagnetic compound $LuCo_2$ and ferrimagnetic $ErCo_2$ was suggested to exhibit also ferrimagnetic order below $T_C = 2-7$ K with the cobalt magnetic moment $MCo = (0.6-0.8)\mu_B$.¹⁶⁻¹⁸ The phase transition at $T=T_C$ was classified as of the first-order type¹⁸ as well as of the second one.¹⁶ According to the above mentioned theories,^{12,13} $TmCo_2$ should have a magnetic phase transition of first order like other RCo_2 with heavy R ions. However, neutron diffraction studies^{3,19} have revealed the absence of a magnetic moment on Co atoms in $TmCo_2$ down to 1.4 K. Moreover, the arrangement of Tm magnetic moments below the ordering temperature $T_C \sim 3.9$ K is found to differ in different samples (collinear, noncollinear, or “not fully ordered”) depending on small variations in the stoichiometry. The fact that the Co atoms in $TmCo_2$ do not have a magnetic moment was attributed to the lower value of H_{mol} in this compound in comparison with $H_c = 70$ T.⁴ Therefore, one could expect that a magnetic moment on Co atoms will appear if some part of the Tm ions are replaced by other rare earths having a higher spin value of the $4f$ -electron shell. Such behavior was observed for $Tm_{1-x}R_xCo_2$ systems with $R=Er$ (Ref. 20), and Gd ,²¹ indeed. In the present work we have chosen Tb as a

substitutional element because of its higher spin value ($S=3$) in comparison with Tm ($S=1$) and its lower absorption cross section for neutrons with respect to Gd.²² Our work focused on the low-Tb-concentration part of the $Tm_{1-x}Tb_xCo_2$ system in order to study hysteresis effects in the vicinity of the onset of long-range magnetic order in the Co sublattice, assuming the first-order type of this phase transition. Moreover, since the partial substitution of Tb for Tm ions should lead to fluctuations of the exchange field owing to the substantial difference in spin values of their $4f$ shells, the localized spin fluctuations that can be induced by such nonuniform exchange field in the itinerant d -electron subsystem are expected to be extremely important for physical properties of these compounds. Therefore, we used magnetic susceptibility, specific heat, and electrical resistivity measurements together with neutron diffraction experiments in order to examine the behavior of $Tm_{1-x}Tb_xCo_2$ compounds.

II. EXPERIMENTAL DETAILS

The polycrystalline $Tm_{1-x}Tb_xCo_2$ compounds were obtained by induction melting followed by homogenization at 850 °C in evacuated quartz tubes for a period of one week. The 6 wt % excess of the rare earth element was taken in order to prevent the formation of Co-rich phases. The phase purity of the samples was checked by a metallographic method and by powder x-ray diffraction. All the samples were confirmed by x-ray diffraction to have the $MgCu_2$ cubic Laves phase structure at room temperature. The content of foreign phases was estimated to be less than 3%. The magnetic ac susceptibility was measured by a superconducting quantum interference device magnetometer (2–300 K). The measurements of dc electrical resistivity were performed on parallelepiped samples of $1 \times 1 \times 5$ mm³ using a conventional four-contact method in the temperature interval from 2 up to 300 K in magnetic fields up to 7 T. Specific heat was measured using a Quantum Design PPMS-6000 on 5–15 mg pieces of polycrystalline samples in applied magnetic fields up to 7 T. The neutron powder diffraction experiments at zero magnetic fields were performed at the DMC diffractometer at the spallation source SINQ, Switzerland. The evolution of the magnetic state of the $Tm_{1-x}Tb_xCo_2$ compound under application of a magnetic field was studied by means of the three-axis spectrometer TASP, located at the SINQ source. The spectrometer was operated in the elastic mode with the neutron wave vector $k_i = 2.57 \text{ \AA}^{-1}$ and was used as a regular diffractometer. The (002) reflection of pyrolytic graphite (PG) was used to monochromate and analyze the incident and scattered neutron beams. A PG filter placed in the incoming neutron beam was used to suppress contamination from higher-order neutron wavelengths. The horizontal collimation was guide-80°-80°-80°. For measurements in magnetic fields up to 6 T, a cylindrical sample with a height of about 50 mm and diameter of 5 mm was composed of tablets, which were compacted from the powdered compound. The magnetic field was applied along the cylinder axis.

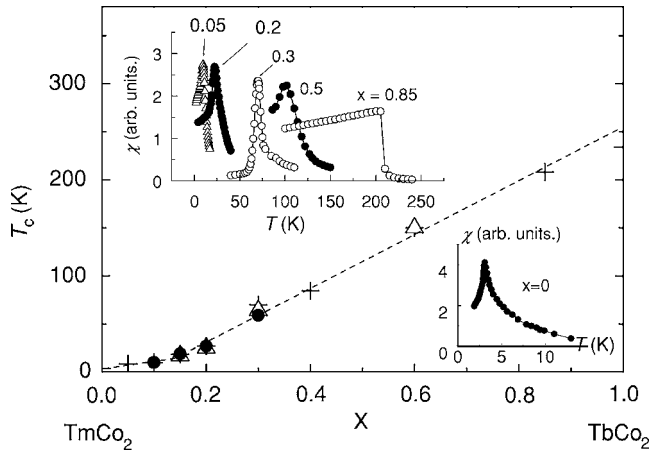


FIG. 1. Concentration dependence of the magnetic ordering temperature for the $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ system. Crosses, triangles, and full circles correspond to T_{ord} values obtained by ac susceptibility, electrical resistivity, and specific heat measurements, respectively. Insets show temperature dependencies of the magnetic ac susceptibility for compounds with various Tb content.

III. RESULTS

A. Magnetic susceptibility and electrical resistivity measurements

Figure 1 shows the concentration dependencies of the magnetic ordering temperature T_{ord} for the $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ system. The values of T_{ord} were defined from the position of an anomaly in the temperature dependencies of the ac susceptibility measured for the compounds with various Tb content (see insets in Fig. 1). Moreover, for some compounds with low Tb content the magnetic ordering temperatures were obtained from the measurements of the temperature dependencies of the specific heat and electrical resistivity (see below). In the last case the value of T_{ord} was obtained by using a singularity in $d\rho/dT$. As one can see, the different methods give nearly the same values of T_{ord} . The concentration dependence $T_{ord}(x)$ shows a change in slope around $x \sim 0.15$ which may be indicative of a change in the magnetic state. It should be noted that an analogous behavior of the ordering temperature was observed in Ref. 7 for the $\text{Y}_{1-x}\text{Gd}_x\text{Co}_2$ system in which a change of the magnetic state from a cluster-glass type at $0.05 \leq x < 0.15$ to a long-range ferrimagnetic order of Gd and Co magnetic moments in the compounds at higher Gd content was suggested from analysis of the magnetic and magnetoresistance data.

The assumption about the change of the magnetic state in $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ with increasing x above $x = 0.15$ is supported by the measurements of the temperature dependencies of the electrical resistivity. As follows from Fig. 2, the substitution of Tb for Tm modifies significantly the low-temperature behavior of the resistivity. The $\rho(T)$ dependence for compounds with x up to $x = 0.1$ shows a substantially enhanced residual resistivity and a pronounced minimum around 30 K. With decreasing temperature below 30 K the resistivity of $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ shows nonmonotonic behavior with a maximum around 8–10 K. Further increase of the Tb content reduces the residual resistivity and leads to the appearance of

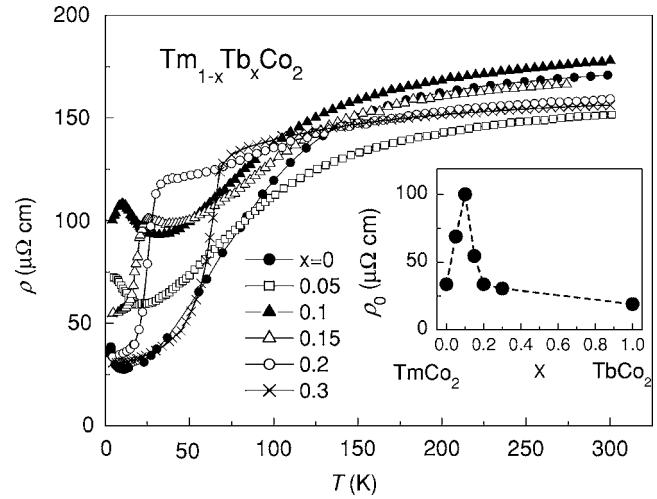


FIG. 2. Temperature dependencies of the electrical resistivity of $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ at various Tb content. Inset displays the concentration dependence of the residual resistivity.

a steplike change of ρ when the temperature approaches a critical value T_{ord} for the appropriate compound. Such $\rho(T)$ dependencies are quite typical for $R\text{Co}_2$ and $R_{1-x}R'_x\text{Co}_2$ compounds exhibiting a magnetic phase transition of first order. However, in our case the temperature interval in which the abrupt resistivity change is observed seems to be rather wide (~ 10 K for $x = 0.2$) in comparison with ErCo_2 , where this transition occurs within ~ 0.9 K.⁹ The broadening of the magnetic transition in $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ with $x = 0.15, 0.2,$ and 0.3 may result from a statistical distribution of Tb atoms in the rare earth sublattice. Considering the electrical resistivity as a sum of the residual, phonon, and magnetic contributions, $\rho(T) = \rho_0 + \rho_{ph}(T) + \rho_m(T)$, a drastic change of ρ in the vicinity of the first-order phase transition in $R\text{Co}_2$ is attributed to a change of the magnetic contribution associated mainly with the conduction electron scattering from spin fluctuations in the d -electron subsystem.²³ Nevertheless, measurements of the temperature dependencies of the susceptibility and electrical resistivity do not allow us to answer the question of the order of the magnetic phase transition in $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ compounds at $0.1 \leq x \leq 0.3$. Bearing in mind that the 10% substitution of Tb for Tm brings the $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ system very close to the onset of long-range magnetic order and appearance of magnetic moments on the Co atoms, one may expect that the first-order nature of IEM will be clearly evidenced in the compound $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ by experiments under application of a magnetic field.

Figure 3 shows the field dependencies of the longitudinal magnetoresistance for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ measured at different temperatures. Application of a relatively low magnetic field (~ 1 T) at $T = 4.2$ K significantly reduces the electrical resistivity ($|\Delta\rho/\rho| \approx 45\%$). Moreover, this reduction is found to be irreversible, since on further variation of the magnetic field within the range $-7 < \mu_0 H < 7$ T the sample does not regain its initial value of resistivity, while the field dependencies of the magnetoresistance measured above 8 K do not show a noticeable hysteresis. These observations suggest an irreversible change of the magnetic state of $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$

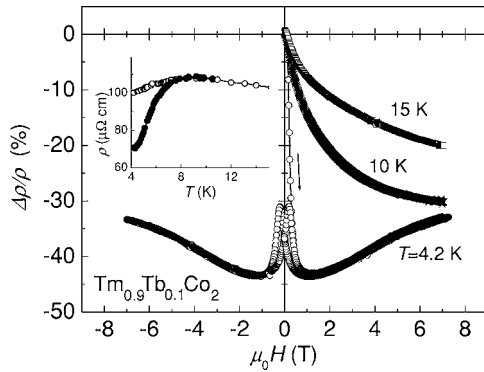


FIG. 3. Field dependencies of the longitudinal magnetoresistance for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ measured at various temperatures. Inset: Low-temperature parts of the $\rho(T)$ dependence measured at zero magnetic field on zero-field-cooled (ZFC) sample (open circles) and after application of the field $\mu_0H=2$ T at $T=4.2$ K (full circles).

under application of a magnetic field at low temperature. As it turned out, the sample may be reinstated into the initial state by heating above 8 K and by subsequent cooling down at zero field. This is supported by the inset in Fig. 3 which displays the low-temperature part of the $\rho(T)$ curve measured at $\mu_0H=0$ on the zero-field-cooled (ZFC) sample (open circles) and on the sample measured at zero field after application of the field 2 T (full circles). An increase of the Tb content up to $x=0.15$ significantly modifies the magnetoresistance behavior (see Fig. 4). The $\Delta\rho/\rho$ versus H dependence measured for $\text{Tm}_{0.85}\text{Tb}_{0.15}\text{Co}_2$ at 4.2 K shows a decrease down to $\sim -15\%$ in the low-field region (up to 1 T), while further increase of the field leads to gradual growth of the resistivity. After switching off the field the electrical resistivity of $\text{Tm}_{0.85}\text{Tb}_{0.15}\text{Co}_2$ is found to revert to its initial value, which was not the case for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$. In the paramagnetic region the field dependencies of the magnetoresistance reveal a gradual decrease for both compounds with $x=0.1$ and 0.15.

B. Specific heat

Figure 5(a) displays the temperature dependencies of the specific heat for $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ compounds within the concentration range $0.1 \leq x \leq 0.3$. As to the specific heat behav-

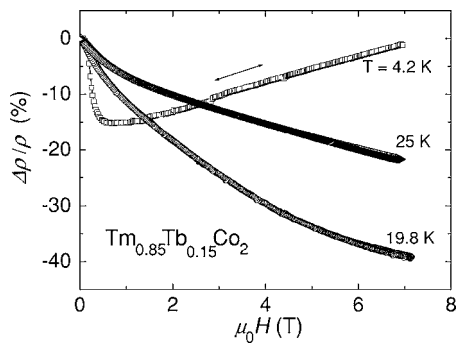


FIG. 4. Field dependencies of the longitudinal magnetoresistance for $\text{Tm}_{0.85}\text{Tb}_{0.15}\text{Co}_2$ measured at various temperatures.

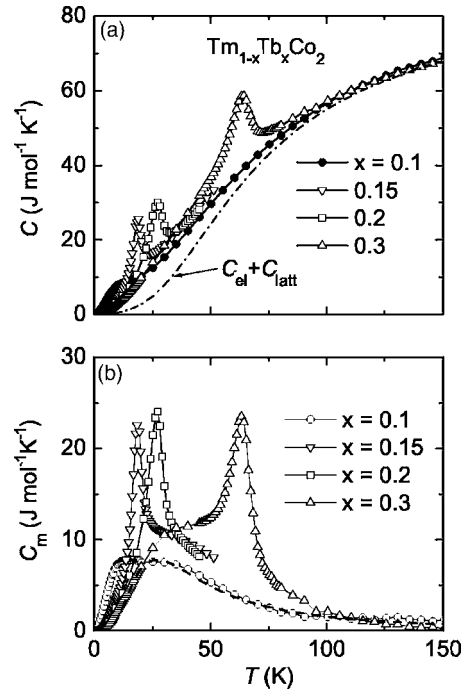


FIG. 5. (a) Experimental specific heat for $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ compounds together with the nonmagnetic contribution (chain curve). (b) Magnetic part of the specific heat together with a Schottky contribution (dashed line) calculated for $\Delta=150$ K (see text).

ior of the pure TmCo_2 compound, it was discussed in Ref. 21. As can be seen in Fig. 5 the $C_p(T)$ dependencies for the compounds with $x=0.15, 0.2,$ and 0.3 exhibit a pronounced maximum associated with the magnetic phase transition from the long-range ferromagnetic order to the paramagnetic state in these compounds. The positions of the maxima indicate the magnetic ordering temperatures T_{ord} , which are in agreement with magnetic susceptibility and electrical resistivity data (see Fig. 1). Instead of the maximum only a smeared anomaly of the specific heat around 8–10 K is observed for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$. The chain line in Fig. 5(a) presents the nonmagnetic part of the total specific heat, which was calculated by using the values of the electronic specific heat coefficient $\gamma=29$ mJ mol⁻¹ K⁻² and Debye temperature $T_D=280$ K for the paramagnetic compound LuCo_2 .²⁴ After subtraction of the sum of the electronic and lattice contributions ($C_{el} + C_{latt}$) from the experimental $C_p(T)$ curves we have obtained the magnetic contribution C_m , which is shown in Fig. 5(b). As can be seen, a significant part of C_m extends over a wide temperature range well above the magnetic ordering temperatures of compounds, which may be associated with the presence of the short-range magnetic correlations and Schottky contribution. The last results from the crystal-field effects, since the cubic crystal field splits the 13 degenerate levels of both the 3H_6 ground-state multiplet of Tm^{3+} and the 7F_6 multiplet of Tb^{3+} into three triplets, one doublet, and two singlets. The best fitting of the Schottky contribution for $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ with $x=0.1$ and 0.15 [shown by the dashed line in Fig. 5(b)] was obtained for the total splitting $\Delta=150$ K by using a standard expression.²⁵ It is worthy of mention that the value of $\Delta=150$ K is close to that derived for TbCo_2

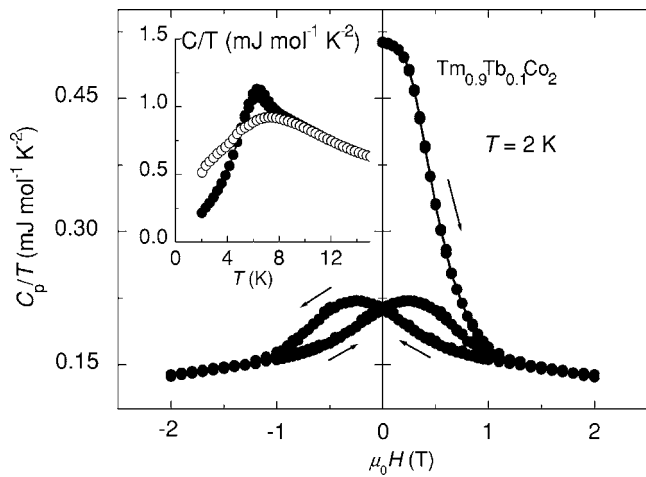


FIG. 6. C_p/T versus H dependence for $Tm_{0.9}Tb_{0.1}Co_2$ measured at $T=2$ K. Inset shows temperature dependencies of the specific heat measured at $H=0$ T on the ZFC sample (open circles) and after application of the field $\mu_0H=2$ T at $T=2$ K (full circles).

from analysis of the magnetization along the principal crystallographic directions and lattice distortion measurements ($\Delta=139.2$ K).²⁶

Since PPMS employs a thermal relaxation method, it may be used not only for measuring the thermal variation of the specific heat but also for determining the field dependencies of the specific heat at given temperature. The specific heat of the $Tm_{0.9}Tb_{0.1}Co_2$ compound measured at $T=2$ K as a function of an applied field is found to reveal a sharp fall in the low-field region (see Fig. 6). The C_p/T value decreases by ~ 3.7 times under application of the field 2 T and, surprisingly, the C_p/T versus H dependence shows a hysteresis loop at further variation of the field within 2 T. As a result, after

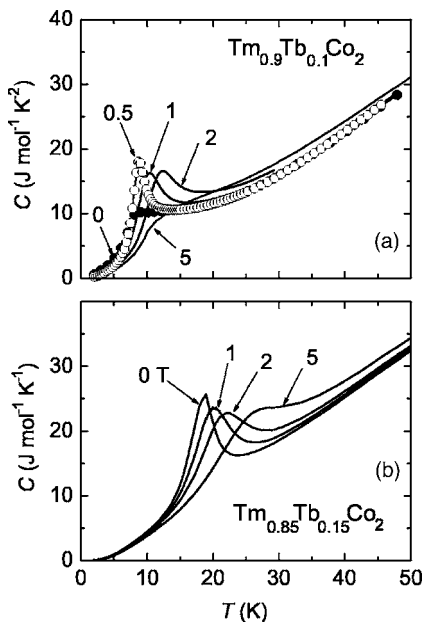


FIG. 7. Temperature dependencies of the specific heat of $Tm_{1-x}Tb_xCo_2$ compounds with $x=0.1$ (a) and 0.15 (b) measured at various magnetic fields as labeled.

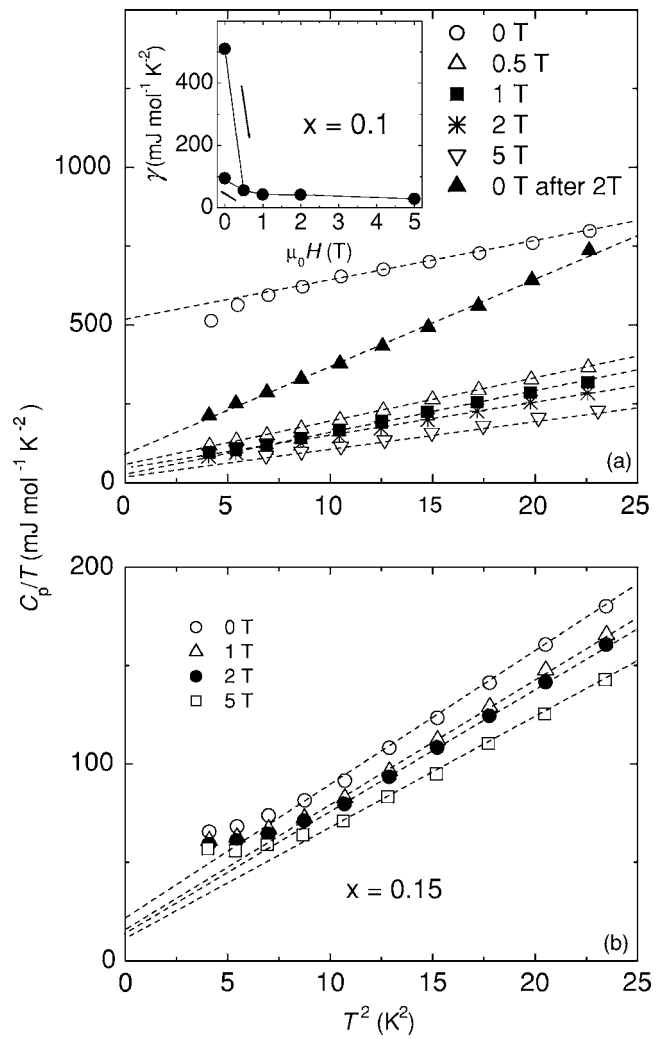


FIG. 8. C_p/T versus T^2 dependencies for $Tm_{1-x}Tb_xCo_2$ with $x=0.1$ (a) and 0.15 (b) measured at various magnetic fields. Inset shows the field dependence of the coefficient γ of the T -linear specific heat for $Tm_{0.9}Tb_{0.1}Co_2$.

switching off the field the $Tm_{0.9}Tb_{0.1}Co_2$ sample exhibits a substantially reduced value (by 2.4 times) of the specific heat. It should be noted that substantial irreversibility ($\sim 27\%$) in the field dependence of the specific heat was observed at the metamagnetic transition for the $Pr_{0.63}Ca_{0.37}MnO_3$ compound.²⁷ The influence of the magnetic prehistory on the specific heat behavior is also evidenced by the measurements of $C_p(T)$ dependencies (shown in the inset in Fig. 6). Together with the reduction of the C_p/T value below 5 K the application and subsequent removal of the 2 T field leads to the growth of C_p/T around 7 K, while above 10 K the $C_p(T)$ curve seems to be unchanged. A substantial difference between $Tm_{0.9}Tb_{0.1}Co_2$ and compounds with higher Tb content was revealed by the measurements of the specific heat at different magnetic fields (see Fig. 7). As it follows from Fig. 7(a), instead of the smeared anomaly observed for $x=0.1$ at zero field around 8 K a pronounced peak develops on the $C_p(T)$ curve at $T\sim 8.7$ K under application of the field 0.5 T. Further increases in field for $x=0.1$ lead to reduction of the peak height and shift its position toward

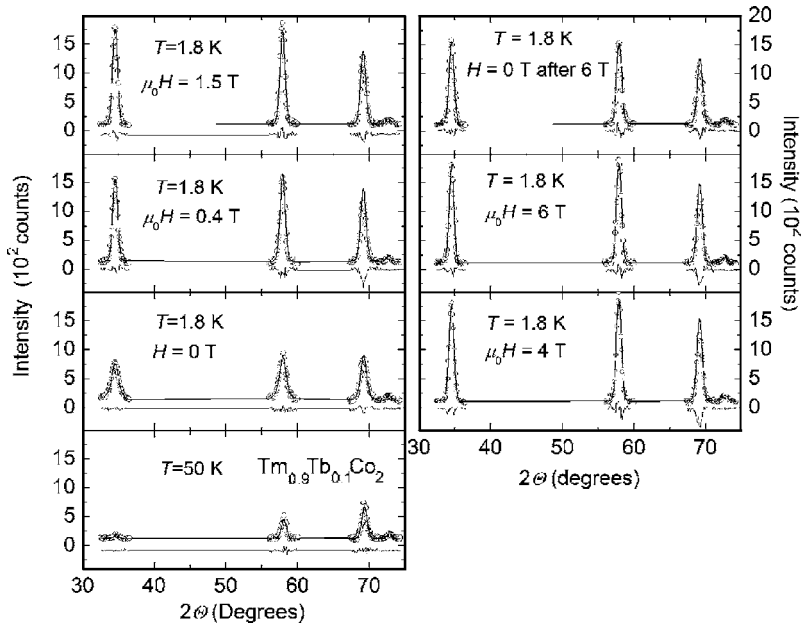


FIG. 9. The intensity of neutron scattering in the vicinity of [111], [220], [222], and [311] reflections for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ at various magnetic fields. The neutron diffraction pattern obtained in the paramagnetic state ($T=50$ K) is presented for comparison. The open circles correspond to the observed intensities, the solid lines are the calculated profiles. The difference between the experimental and calculated intensities is shown at the bottom.

higher temperatures. The $C_p(T)$ dependence for $\text{Tm}_{0.85}\text{Tb}_{0.15}\text{Co}_2$ shows a well developed maximum at $T_c \sim 19$ K even at zero applied field [see Fig. 7(b)]. Unlike the $x=0.1$ case, application of a magnetic field does not enhance the C_p value around T_c for $x=0.15$. The C_p peak height for $\text{Tm}_{0.85}\text{Tb}_{0.15}\text{Co}_2$ reduces monotonically with increasing field as is usually observed for ordinary ferro- or ferrimagnets.

Using the specific heat data obtained for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ at different magnetic fields we plotted C_p/T as a function of T^2 in the low-temperature range in Fig. 8(a). The C_p/T versus T^2 dependencies seem to be linear in the temperature range from 2 up to 5 K. The coefficient γ of the T -linear specific heat decreases dramatically from ~ 510 $\text{mJ mol}^{-1} \text{K}^{-2}$ down to 29 $\text{mJ mol}^{-1} \text{K}^{-2}$ with increasing external field. Note that an increase of the T -linear specific heat together with maximal value of the residual resistivity in the vicinity of the critical concentration is a quite common feature.²⁸ However, such large values of γ as observed for $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ are hardly attained in the usual metallic systems. They are rather typical for heavy fermion compounds. The value of $\gamma = 29$ $\text{mJ mol}^{-1} \text{K}^{-2}$ obtained at $\mu_0 H = 5$ T is found to be close to that observed for YCo_2 [$\gamma = 34\text{--}36.5$ $\text{mJ mol}^{-1} \text{K}^{-2}$ (Refs. 29 and 30)] and LuCo_2 [$\gamma = 26.7\text{--}29.1$ $\text{mJ mol}^{-1} \text{K}^{-2}$ (Refs. 24 and 31)]. From the measurements performed at zero external field for the sample influenced by the application of the field 2 T at $T=2$ K we have obtained the γ value about 95 $\text{mJ mol}^{-1} \text{K}^{-2}$ which is significantly lower than that obtained for the noninfluenced sample. This remanent value of γ is indicative of the formation of a different metastable magnetic state in $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ under application of a magnetic field. Unlike the compound with $x=0.1$, in the case of $x=0.15$ the T -linear heat capacity does not show such a strong field dependence [see Fig. 8(b)]. The γ value for $\text{Tm}_{0.85}\text{Tb}_{0.15}\text{Co}_2$ is estimated to be within the range between 21 $\text{mJ mol}^{-1} \text{K}^{-2}$ at zero field and 11 $\text{mJ mol}^{-1} \text{K}^{-2}$ at $\mu_0 H = 5$ T.

C. Neutron diffraction

In order to check our suggestion about the irreversible change of the magnetic state of $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ under application of a magnetic field and to clarify the magnetic ground state of this compound we have performed powder neutron diffraction measurements for this compound as well as for other $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ compounds with higher Tb content. The neutron diffraction patterns taken at $T=4.2$ K (i.e., below T_c) for the compounds with $0.15 < x \leq 1.0$ were found to be typical for $R\text{Co}_2$ compounds with ferrimagnetic alignment of the magnetic moments of rare earth and Co sublattices. As to the compound with $x=0.1$, we have measured the intensity of neutron scattering around [111], [220], [222], and [311] reflections as a function of the temperature (2–50 K) and magnetic field (0–6 T) using the TASP spectrometer.

The results of these measurements are displayed in Figs. 9–11. The comparison of zero-field data obtained at $T=1.8$ K with those obtained at 50 K, i.e., in the paramagnetic state, shows that the low-temperature neutron diffraction pattern exhibits broad reflections with an enhanced intensity (see Fig. 9). The change of the neutron scattering intensity with temperature, which is presented in Fig. 10 for the [111] reflection as an instance, may be associated with the evolution of the magnetic state of the compound. A diffuse magnetic scattering appears and the integrated intensity of the [111] reflection starts to grow substantially when the temperature decreases below ~ 30 K. The presence of the magnetic diffuse scattering in the $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ compound at low temperatures is indicative of the absence of long-range magnetic order and the presence of magnetic inhomogeneity caused by the partial substitution of Tb for Tm. The magnetic state of $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ below $T_{ord} \sim 8$ K may be characterized as of cluster-glass type as in $\text{Y}_{1-x}\text{Gd}_x\text{Co}_2$ compounds below $x < 0.15$ (see Ref. 6 and references therein). Application of a magnetic field at $T=1.8$ K leads to substantial growth of the intensity of the neutron magnetic scattering

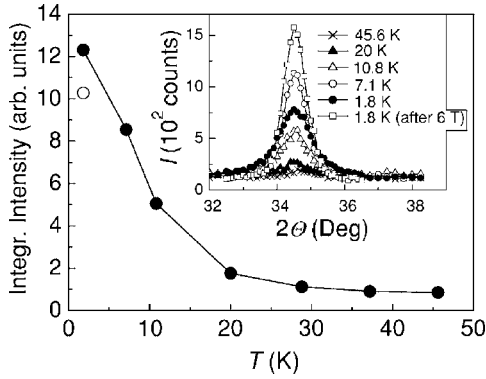


FIG. 10. Temperature dependence of the integrated intensity of the [111] reflection for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ at zero external field. The full circles correspond to the data obtained with increasing temperature after application and removal of the 6 T field at $T=1.8$ K. Open circle corresponds to the value of the integrated intensity for the ZFC sample. The inset shows the evolution of the [111] reflection with temperature and under application and switching off the magnetic field at $T=1.8$ K.

and to a change of the reflection shape from the dominating Lorenz type at $\mu_0 H=0$ to that described by a Gaussian function at $\mu_0 H=0.6$ T (Fig. 9). Such a transformation of the neutron diffraction pattern indicates the transition from the peculiar magnetic state in which short-range magnetic order dominates to long-range ferrimagnetic order under influence of an external magnetic field. Moreover, this field-induced change of the magnetic state in $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ is found to be irreversible. The reflections are not restored to their initial shape and intensity after switching off the field. The irreversibility is evidenced also by the field dependence of the integrated intensity of the [111] reflection displayed in Fig. 11(a).

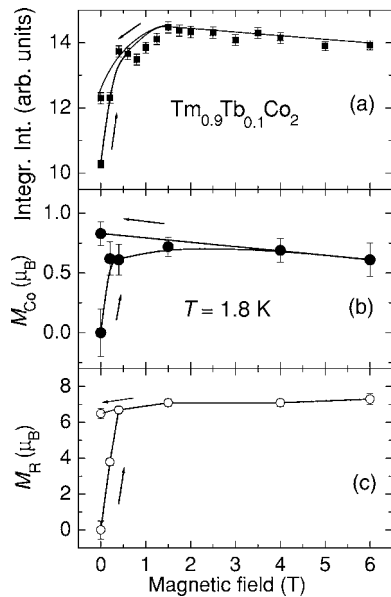


FIG. 11. The integrated intensity of the neutron scattering around the [111] reflection (a) and the average magnetization of the Co (b) and rare earth (c) sublattices calculated per Co and R atoms from neutron diffraction data for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ at $T=1.8$ K.

IV. DISCUSSION

The neutron diffraction experiments together with electrical resistivity and specific heat data obtained for the $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ compound allow us to conclude that this compound does not exhibit a phase transition to long-range magnetic order with decreasing temperature down to 2 K. The magnetic state of this compound may be classified as of cluster-glass type. Using the angle width of the magnetic diffuse maxima we have estimated the mean size of magnetic inhomogeneities which exist in this compound at $T=2$ K. This estimation has given a value of about 10 nm which exceeds significantly the dimensions of short-range magnetic clusters ($\sim 2-3$ nm) observed in $\text{Y}_{1-x}\text{R}_x\text{Co}_2$ compounds ($R=\text{Er}, \text{Ho}$) just below the critical concentrations.^{7,32} Such a difference in magnetic correlation lengths in $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ and $\text{Y}_{1-x}\text{R}_x\text{Co}_2$ near the critical concentration is, we think, caused by the presence of the local $4f$ magnetic moment on Tm ions, unlike Y ions. As was mentioned above, the exchange field acting on the Co atoms from the Tm sublattice in TmCo_2 is not sufficient for the spin polarization of Co $3d$ electrons. The insertion of Tb ions having a larger spin value instead of Tm is suggested to result in the appearance of a magnetic moment on Co atoms located in the nearest neighborhood. The mechanism responsible for this kind of localized spin density fluctuations in the Co $3d$ -electron subsystem involves the intra-atomic $4f-5d$ exchange, that polarizes $5d$ electrons of the Tb ion in the same directions as $4f$ electrons, and $5d-3d$ exchange interaction which results in the alignment of $3d$ electron spins in opposite directions.³³ This Co $3d$ -electron polarization around the Tb ion may support the alignment of the Tm $4f$ moments together with the $f-f$ indirect exchange of the RKKY type leading to a wider extent of spin correlations. As a result, in the vicinity of Tb ions a large region may appear (up to 10 nm) with antiparallel ordering of R ($4f$) and Co ($3d$) spins.

Using the neutron diffraction data for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ at $T=1.8$ K we have determined the magnetization of both the rare earth and Co sublattices at different magnetic fields. The calculations were made by using the FULLPROF program.³⁴ The calculated profiles of reflections are shown in Fig. 9 by the solid line. The evolution of average magnetic moment per Co atom, M_{Co} , is found to increase under application of a magnetic field from nearly zero up to $(0.72 \pm 0.1)\mu_B$ at $\mu_0 H=1.5$ T. After switching off the field 6 T the Co subsystem remains magnetized up to $M_{\text{Co}}=(0.83 \pm 0.1)\mu_B$. The maximal value of M_{Co} observed in the field-induced ferrimagnetic state of $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ is close to that observed for other RCO_2 compounds with heavy rare earth elements ($M_{\text{Co}} \approx 1.0\mu_B$).^{1,2} It should be noted that the field-induced growth of the Co magnetic moment at the IEM transition was also observed by neutron diffraction above the Curie temperature of $\text{Y}_{1-x}\text{Er}_x\text{Co}_2$ ($x=1, 0.4$) single crystals.⁹ However, in the case of $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ such a transition being induced at low temperature is found to be strongly irreversible. The irreversibility of this transition, which is supported also by electrical resistivity and specific heat measurements (see Figs. 3 and 5), results apparently from the first-order type of the IEM transition in the Co $3d$ -electron subsystem and the hysteresis

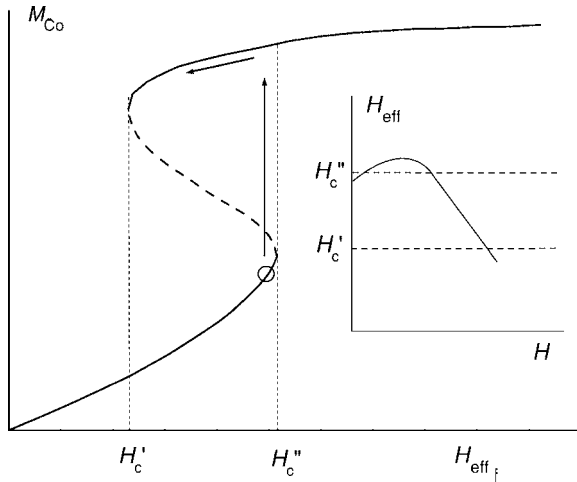


FIG. 12. Schematic dependence of the cobalt magnetic moment on the effective field for the $Tm_{1-x}Tb_xCo_2$ system. Open circle corresponds to the magnetic state of the Co subsystem at $x=0.1$. The arrow indicates the change of M_{Co} with increasing external magnetic field. Inset displays the schematic dependence of H_{eff} on the external field for $Tm_{0.9}Tb_{0.1}Co_2$.

of the $M_{Co}(H_{eff})$ dependence in the vicinity of the critical value H_{eff}^{crit} . The S shape of the $M_{Co}(H_{eff})$ curve was derived by Shimizu³⁵ from the magnetic equation of state for $M = M_{Co}$ and H_{eff} :

$$H_{eff} = aM + bM^3 + cM^5 \quad (1)$$

at the following conditions: $a > 0$, $b < 0$, $c > 0$, and $9/20 > ac/b^2 > 3/16$, where a , b , and c are the Landau expansion coefficients, which are dependent on the density of states $N(E)$ and its derivatives near the Fermi level for the itinerant electron system. Accounting for spin fluctuations in the IEM theory led to the limitation of the temperature interval in which the first-order phase transition may be realized.³⁶ The critical fields at which the metamagnetic transitions occur, when the field increases (H'_c) and decreases (H''_c), are found to depend on the Landau expansion coefficient in Eq. (1).³⁵ This means that the hysteresis value $\Delta H = H''_c - H'_c$ at $T=0$ is determined by the peculiarities of the $N(E)$ shape near the Fermi level. In particular for YCo_2 , the value of $\Delta\mu_0H$ was calculated to be ~ 26 T,³⁵ which is by about one order higher than that observed experimentally for this compound⁴ ($\Delta\mu_0H \approx 2.5$ T at $T=8$ K). This is apparently because the theoretical consideration³⁵ did not take into account the kinetics of the metamagnetic transition occurring usually through the nucleation of a new magnetic phase followed by motion of interphase boundaries. The extremely low critical field of the metamagnetic transition (~ 0.5 T) revealed by magnetoresistance, specific heat, and neutron diffraction in $Tm_{0.9}Tb_{0.1}Co_2$ implies that the ground magnetic state of the d -electron subsystem of this compound corresponds to that marked by the open circle on the $M(H_{eff})$ dependence shown in Fig. 12, i.e., within the hysteresis loop very close to the upper critical field H''_c . Here we take into account that the 10 at. % substitution of Tb for Tm should increase the average value of H_{mol} from the initial 60 T for pure³ $TmCo_2$ up

to a value almost equal to 70 T which is needed for the IEM transition in RCo_2 compounds with heavy rare earth elements. Bearing in mind our neutron diffraction data for $Tm_{0.9}Tb_{0.1}Co_2$ one can suggest that the dependence of H_{eff} on the external magnetic field H has a nonmonotonic character as is schematically shown in the inset in Fig. 12. At first, application of an external field produces an ordering effect on the magnetic moments of R ions, which results in the growth of the magnetization of the R sublattice up to $(7.1 \pm 0.2)\mu_B$ per R ion at $\mu_0H = 1.5$ T [see Fig. 11(c)]. This increase of M_R leads to the growth of H_{eff} through the f - d exchange up to the critical value and to the sharp increase of magnetic moments on Co atoms. In this case the exchange interaction between $4f$ electrons of R ions and Co $3d$ electrons may be considered as a peculiar amplifier of the external field since the magnetic fields which were used in our experiments are significantly lower than the H_m value arising from the f - d exchange. The IEM transition and appearance of long-range ferromagnetic order induced by an applied field are accompanied by the giant reduction of the electrical resistivity and specific heat owing to the suppression of LSFs. Increase of an external field hereafter does not increase M_R further [see Fig. 11(c)], while it may cause an inverse effect on the Co subsystem and may lead to the disappearance of the Co magnetic moment, i.e., to inverse IEM. Because of the antiparallel alignment of magnetizations of R and Co sublattices, the increase of the external magnetic field directed parallel to the R moments will reduce the effective field acting on Co atoms approaching the lower critical field H'_c . Unfortunately, we could not observe a collapse of the magnetic moment on Co atoms in our neutron experiments because of limited magnetic fields; however, the inverse IEM was observed by measurements of the volume magnetostriction in higher magnetic fields (~ 12 – 17 T) in $Tm(Co_{0.95}Al_{0.05})_2$ (Ref. 37) as well in other RCo_2 -based compounds.³⁸ Nevertheless, there is a set of peculiarities observed with increasing field: (i) a tendency to the reduction of the integrated intensity of neutron scattering around the [111] reflection [see Fig. 11(a)]; (ii) the decrease of M_{Co} above 1.5 T [see Fig. 11(b)]; (iii) the growth of the resistivity observed at $T=4.2$ K after its initial reduction in the low-field region (see Figs. 3 and 4), which may be indicative of the movement of the Co $3d$ -electron subsystem on the $M(H_{eff})$ curve in the direction of H'_c . This direction is shown by the arrow in Fig. 12.

Initially there may seem to be some contradiction with the current opinion that an applied field should suppress spin fluctuations and, as a consequence, should reduce the electrical resistivity of this compound. However, the growth of ρ with increasing field in this case seems to be quite reasonable, since the itinerant d -electron subsystem destabilizes when H_{eff} decreases approaching the critical value H'_c for the collapse of the magnetic moment on Co atoms, which results in the development of spin fluctuations and positive change of the electrical resistivity.

The presence of magnetic clusters in $Tm_{1-x}Tb_xCo_2$ with the Tb content just below the critical concentration $x_c \sim 0.15$ is, we think, a main reason for the significant enhancement of the residual resistivity (see inset in Fig. 2). The

additional contribution to the ρ_0 value for the compounds with $x \sim 0.1$ may be associated with conduction electron scattering from a disordered array of large cluster moments, which are formed by the $4f$ spins of Tm and Tb ions, and from localized spin fluctuations induced on Co ions located within these clusters. The last contribution plays apparently a predominant role in the enhancement of the ρ_0 value as well as the coefficient γ of the T -linear specific heat around $x = 0.1$. The unusually high γ value observed for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ originates from the complicated magnetic state of this compound as well as from the proximity of the measuring temperature interval to T_{ord} . Measurements of the specific heat and electrical properties under application of a magnetic field at lower temperatures (below 2 K) seem to be very desirable for this compound.

It should be noted that this kind of enhancement of the residual resistivity in the vicinity of the critical concentration as observed in $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ as well as in the binary $\text{Y}_{1-x}\text{R}_x\text{Co}_2$ systems was not revealed in the Ni-based compounds $\text{Y}_{1-x}\text{R}_x\text{Ni}_2$,^{7,39} in which the Ni $3d$ -electron subsystem does not reveal any instabilities and IEM transitions. The steplike increase of the Co magnetic moment, when the effective field approaches the critical value with increasing Tb content in $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$, causes the development of LSF just before the critical concentration for the onset of long-range ferrimagnetic order. The appearance of LSFs and their evolution with decreasing temperature in $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ compounds with low Tb content are suggested to be also responsible for the presence of the pronounced minimum and nonmonotonic change of $\rho(T)$ for $x < 0.2$ at low temperatures. It is interesting to note that there is an evident correlation in the behavior of $\rho(T)$ (see Fig. 2 and the inset in Fig. 3) and the change of the intensity of the magnetic diffuse scattering (see Fig. 10) with decreasing temperature for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ in the low-temperature region. Both these characteristics start to grow with decreasing temperature from 30 K down to 8–5 K. An appreciable reduction of ρ with further decrease of temperature down to 2 K is apparently associated with increasing size of the regions with a magnetic short-range order. This is because the conduction electron scattering in metallic systems with magnetic clusters strongly depends on the interrelation between the electron mean free path and magnetic cluster dimension.⁴⁰

The giant change of the specific heat observed at low temperatures in $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ under an applied magnetic field suggests an unusual behavior of the entropy of this compound. From the experimental heat capacity measured at $H=0$ on the ZFC sample and after application and removal of the field 2 T we have calculated the total entropy as

$$S(T, H) = \int_2^T \frac{C(T, H)}{T} dT, \quad (2)$$

where the lower limit of integration (2 K) was the common lowest temperature for $C_p(T)$ dependencies in our experiments. As it seen from Fig. 13(a), in the whole temperature range the entropy of this compound in the field-induced state, S_i , is lower than that obtained for the zero-field state, S_0 . The temperature dependence of the isothermal difference

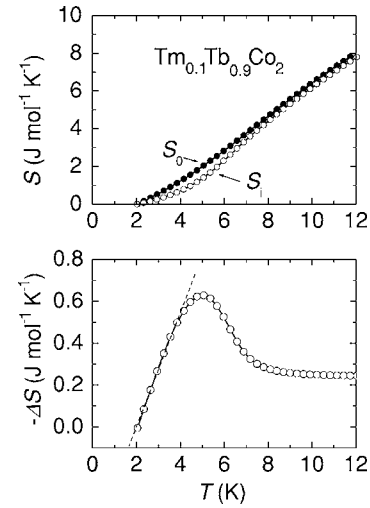


FIG. 13. (a) Temperature dependencies of the total entropy of the $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ compound at $H=0$ calculated for ZFC sample (full circles) and after application and switching off the field 2 T (open circles). (b) The temperature dependence of the isothermal difference $-\Delta S = S_i - S_0$.

$-\Delta S = S_i - S_0$ presented in Fig. 13(b) shows the maximal value around ~ 5 K, i.e., at lower temperature than the ordering temperature (~ 8 – 9 K) for $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$, while in binary RCo_2 compounds with heavy rare earth elements the maximal difference between zero-field- and field-measured entropy is observed in the vicinity of or just above the magnetic ordering temperature.⁴¹ This is because the $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ compound does not exhibit a long-range magnetic order down to 2 K and, therefore, it is strongly influenced by an external magnetic field even at low temperatures, while in RCo_2 , having long-range ferrimagnetic order, such an influence below T_C is insignificant if the applied field is appreciably lower than H_{eff} . It should be noted that in the calculation of ΔS we did not take into account the difference between S_0 and S_i that arises from the temperature interval below 2 K. The total entropy change at the field-induced phase transition in $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ may include electronic, magnetoelastic, and magnetic contributions:

$$\Delta S = \Delta S_{el} + \Delta S_{me} + \Delta S_m. \quad (3)$$

The magnetoelastic interactions are observed to significantly affect the IEM transition in RCo_2 compounds.^{1,2} As one can see from Fig. 13(b) in the temperature interval below ~ 4 K the temperature dependence of ΔS is nearly linear and can therefore be ascribed mainly to the change of the T -linear (electronic) contribution,

$$\Delta S \approx \int_2^T \gamma_i dT - \int_2^T \gamma_0 dT = S_i - S_0 = \Delta \gamma T \quad (4)$$

(where $\Delta \gamma = \gamma_i - \gamma_0$; γ_i and γ_0 are the values of the coefficient of T -linear specific heat for the field-induced and zero-field states, respectively). Therefore, the linearity of the $\Delta S(T)$ dependence below 4 K may be indicative of the prevailing electronic contribution to the total entropy change at the

field-induced first-order phase transition under application of the magnetic field in $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$.

V. CONCLUSION

The investigation of the complex behavior of $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ compounds by means of magnetic susceptibility, electrical resistivity, specific heat, and powder neutron diffraction measurements has revealed that the substitution of Tb ions for Tm above the critical concentration $x_c \sim 0.15$ causes the appearance of a magnetic moment on Co atoms and long-range ferrimagnetic order with antiparallel alignment of the magnetizations of the rare earth and Co sublattices. Such an evolution of the magnetic state is caused by increasing molecular field with the substitution because the Tb ion has a larger spin value ($S=3$) than the Tm ion ($S=1$). When the molecular field reaches a critical value (~ 70 T) it produces the IEM transition in the Co $3d$ -electron subsystem. The magnetic state of the compounds with $0.1 < x < 0.15$ is nonhomogeneous. It may be classified as of the cluster-glass type, which consists of large regions (up to ~ 10 nm) around Tb ions with short-range magnetic order of the ferrimagnetic nature. The $4f$ electrons of Tb ions located in these clusters polarize the $3d$ electrons of the neighbor cobalt ions forming localized spin density fluctuations. These localized spin fluctuations differ from the usual thermally activated spin fluctuations in nearly magnetic materials since in our case the LSFs are produced by fluctuations of the f - d exchange interaction due to the Tb-Tm substitution and, therefore, LSFs are localized in real space, unlike thermally activated spin fluctuations in a homogeneous medium which

are localized in reciprocal space.⁴² The appearance of LSFs at low temperatures in $\text{Tm}_{1-x}\text{Tb}_x\text{Co}_2$ with Tb content just below the critical concentration is responsible for the unusual behavior of different physical properties of these compounds, in particular, the substantially enhanced values of the residual resistivity and the coefficient γ of the T -linear specific heat as well as the presence of the pronounced minimum in the temperature dependence of the resistivity. Because of the closeness of the molecular field acting on the Co subsystem in $\text{Tm}_{0.9}\text{Tb}_{0.1}\text{Co}_2$ to the critical field of the IEM transition, the magnetic state of this compound is found to be very sensitive to the external magnetic field. An applied magnetic field (~ 1 – 2 T) being amplified by the f - d exchange interaction produces a phase transition from short-range to long-range ferromagnetic order, which is accompanied by the growth of the Co magnetic moment from nearly zero up to $(0.7$ – $0.8)\mu_B$ and suppression of LSFs. Such a transition results in irreversible decrease of the electrical resistivity, specific heat, and total entropy of the compound, which is indicative of the first-order nature of this transition in agreement with the theory of IEM transitions in the d -electron subsystem.

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