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Butterflylike specific heat, magnetocaloric effect, and itinerant metamagnetism in (Er, Y)Co_2 compounds

N. V. Baranov,[1,2,*] A. V. Proshkin,[1,2] C. Czternasty,[3] M. Meißner,[3] A. Podlesnyak,[4] and S. M. Podgornykh[2]
[1]*Institute of Metal Physics, Russian Academy of Science, 620219 Ekaterinburg, Russia*
[2]*Institute of Physics and Applied Mathematics, Ural State University, 620083 Ekaterinburg, Russia*
[3]*Helmholtz-Zentrum Berlin, SF-1, Glienicker Straße 100, D-14109 Berlin, Germany*
[4]*Spallation Neutron Source, Oak Ridge National Laboratory, P.O. Box 2008, MS6473, Oak Ridge, Tennessee 37831, USA*
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The field-induced first-order phase transition in $(Er_{1-x}Y_x)Co_2$ with the yttrium concentration $x=0.45$ is observed to be accompanied by a butterflylike behavior and significant irreversibility of the specific heat. The coefficient γ of the T-linear specific heat decreases by ~48% under application and removal of a magnetic field up to 20 kOe. This behavior is attributed to the itinerant electron metamagnetism of Co 3*d* electrons. The isothermal magnetic entropy change ΔS_m in $Er_{0.55}Y_{0.45}Co_2$ includes a large contribution associated with spin fluctuations induced by the *f*-*d* exchange interaction in the hybridized 3*d*-5*d*-electron subsystem. These spin fluctuations are suggested to contribute substantially to the magnetocaloric effect of the RCo_2 type compounds. The maximal ΔS_m value observed for $ErCo_2$ just above the Curie temperature is ascribed to the closeness of the T_C value to the spin-fluctuation temperature T_{sf} of itinerant Co 3*d* electrons. The nonmonotonous change in ΔS_m with the Curie temperature of $R_{1-x}R'_xCo_2$ compounds is explained by the temperature variation in the spin-fluctuation contribution to the magnetocaloric effect.

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I. INTRODUCTION

The attention on specific heat and magnetocaloric effect (MCE) studies has recently substantially increased because of potential applications for magnetic cooling. The cubic Laves phases compounds RT_2 (R=rare-earth elements, T=Co, Ni) are considered as good candidates for using as active materials in a magnetic refrigerator.[1–6] Within the RT_2 families, the RCo_2 compounds are of particular interest, since these compounds display interesting magnetic properties which arise from the coexistence and interaction of the well localized rare-earth 4*f* electrons and of the itinerant 3*d* electrons of Co. In RCo_2, the Co 3*d* electrons hybridize with 5*d* (4*d* in the case of Y) electrons of R ions revealing so-called itinerant electron metamagnetism (IEM).[7,8] The Co magnetic moment (M_{Co}) in RCo_2 with heavy rare earths has an induced nature and its value increases abruptly via a first-order phase transition from zero up to a value of about $0.7-1.0\mu_B$ when the effective field H_{eff} acting on the *d*-electron subsystem exceeds a critical value of about 700 kOe. The RCo_2 compounds, where the R ion is nonmagnetic yttrium or lutetium, are exchange-enhanced Pauli paramagnets, while other RCo_2 compounds (except $TmCo_2$) with R ions having localized magnetic moments M_R show a long-range magnetic order below their Curie temperatures. The magnetic phase transition at $T=T_C$ is found to be of the first-order type in RCo_2 with R=Dy, Ho, Er.[7,8] These compounds exhibiting the first-order type transitions below 150 K reveal the highest isothermal magnetic entropy change (ΔS_m) values with the variation in a magnetic field. The maximal magnetic entropy change (ΔS_m^{max}) in RCo_2 compounds in the vicinity of T_C is found to exceed values obtained in the same magnetic fields for RAl_2 compounds (Ref. 3 and references therein). The difference between ΔS_m^{max} (RCo_2) and $\Delta S_m^{max}(RR')Al_2$ becomes more favorable at low temperatures and increases from ~5 J kg^{-1} K^{-1} up to ~20 J kg^{-1} K^{-1} with decreasing Curie temperature from ~250 K down to ~35 K.[3] Several possible origins responsible for the large ΔS_m^{max} values in RCo_2 are currently discussed in literature: (i) the first-order magnetic phase transition within the system of R localized magnetic moments coupled with itinerant 3*d* electrons of Co (Ref. 4); (ii) the structural and lattice volume changes at the first-order transition;[9] (iii) a contribution from spin fluctuations in the itinerant 3*d*-electron subsystem of Co.[3,6] According to the Ref. 4, the main contribution to the magnetic entropy of RCo_2 (R=Er, Ho, Dy) originates from the subsystem of 4*f* localized moments of R ions, while the contribution from the itinerant 3*d*-electron subsystem was assumed to be negligible. The coupling between 3*d* itinerant electrons and the 4*f* localized spins results in the first-order phase transition which is accompanied with the jump of the magnetic entropy just above T_C. However, the large MCE was observed also in 3*d* metal based compounds which do not contain magnetic rare-earth ions. In particular, the isothermal magnetic entropy change ~20–35 J kg^{-1} K^{-1} was observed in MnAs,[10] MnFe(P,As),[11] and $La(Fe,Si)_{13}H_y$ (Ref. 12) compounds in the vicinity of room temperature. The magnetocaloric effect in these compounds is associated with magnetism of itinerant 3*d* electrons.[12] Bearing in mind that the first-order nature of magnetic phase transitions in RCo_2 compounds (R=Dy, Ho, Er) is associated with the itinerant 3*d* electrons as in above-mentioned compounds one can suggest that despite the difference in their magnetic properties the Co 3*d*-electron subsystem in RCo_2 may influence the MCE together with the rare-earth magnetic sublattice. It is well known that some properties of RCo_2 are strongly affected by spin fluctuations in the itinerant *d*-electron subsystem. The substitution of nonmagnetic Y ions for Dy, Ho, or Er in $R_{1-x}Y_xCo_2$ reduces T_C values and the order of the phase transition changes from first to second. The further increase in the Y concentration up to a critical value x_c suppresses a long-range magnetic order and drastically decreases Co magnetic moment.[7,8] Anomalous behavior of different physical properties at $x \sim x_c$ is also observed, which is associated with the localized spin-density fluctuations induced in the Co 3*d*-electron subsystem by the fluctuating *f*-*d* exchange.[13–17]

In the present work we focus on the behavior of the heat capacity of the $Er_{0.55}Y_{0.45}Co_2$ compound. At $x=0.45$ an average value of the nonhomogeneous exchange field acting from the rare-earth sublattice on the itinerant 3*d*-electron subsystem is slightly lower than the critical value H_c for the IEM transition.[13,17] According to neutron-diffraction measurements the long-range (LR) and short-range (SR) magnetic orders coexist in this compound.[14,18] Under application of a relatively small magnetic field the sample undergoes a first-order phase transition to a LR ferrimagnetic structure. This transition is accompanied by a drastic increase in the average magnetic moment on Co atoms and by significant decrease in the electrical resistivity.[13,18] The magnetic state of $Er_{0.55}Y_{0.45}Co_2$ and the behavior of this compound in magnetic fields at low temperatures are similar to those observed in the nondiluted compound $ErCo_2$ at temperatures just above the Curie temperature $T_C \approx 32$ K. The presence of short-range correlations (magnetic clusters) with antiparallel alignment of Er and Co magnetic moments is clearly evidenced in $ErCo_2$ above T_C by neutron scattering and x-ray magnetic circular dichroism (MCD) experiments.[19,20] In $ErCo_2$, application of the external field above T_C produces the metamagnetic transition accompanied by a sudden volume expansion[19] and by a giant magnetoresistance effect[21] as in $Er_{0.55}Y_{0.45}Co_2$ at low temperatures. The detailed study of the magnetothermal properties of $Er_{0.55}Y_{0.45}Co_2$ in a low-temperature region will give us a good insight into the physical mechanism that governs the magnetocaloric effect in the RCo_2-type compounds for temperatures around T_C.

II. EXPERIMENTAL DETAILS

The $Er_{0.55}Y_{0.45}Co_2$ polycrystalline sample was prepared by arc 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. Because of the drastic change in the magnetic state which is observed in the $Er_{1-x}Y_xCo_2$ at yttrium concentrations from $x=0.4$ up to $x=0.5$ the variations in the Er:Y ratio around $x=0.45$ are found to strongly influence the behavior of the compounds at low temperatures. The phase purity of the $Er_{0.55}Y_{0.45}Co_2$ sample was checked by a metallographic method and by powder x-ray diffraction. No evidence of foreign phases was found in the limit of x-ray detection. The sample has $MgCu_2$ cubic Laves crystal structure at room temperature. The specific-heat measurements were carried out in the laboratory for magnetic measurements at BENSC (HZB, Berlin). A relaxation type microcalorimeter MagLab^{HC} (Oxford Instruments) has been used which operates in a temperature range 0.35–40 K and in magnetic field up to 20 kOe. Details on the thermal relaxation method and the subsequent evaluation of specific-heat data have been described in Ref. 22. The sample mass was ~27 mg corresponding to a sample dimension of about $2 \times 2 \times 1$ mm^3. The magnetization and ac susceptibility were measured by using a superconducting quantum interference device magnetometer (Quantum Design).

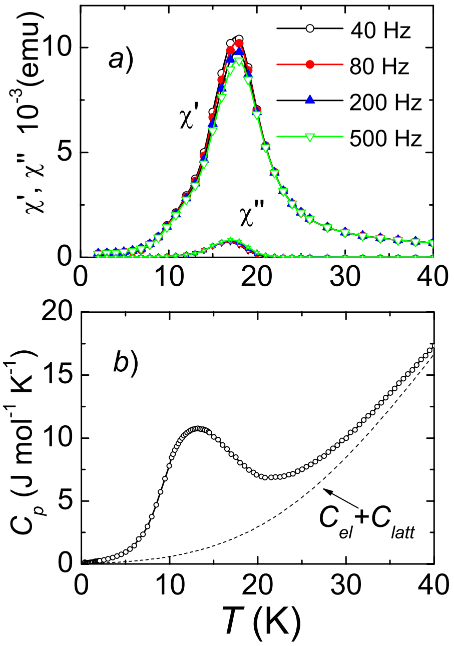

FIG. 1. (Color online) (a) Temperature dependencies of the ac susceptibility of $Er_{0.55}Y_{0.45}Co_2$ measured at various frequencies. (b) Temperature dependence of the specific heat for $Er_{0.55}Y_{0.45}Co_2$ at $H=0$. Dashed line indicates the nonmagnetic contribution to the total specific heat.

III. RESULTS

Figure 1 shows the temperature dependencies of the ac susceptibility and specific heat for $Er_{0.55}Y_{0.45}Co_2$. As can be seen, this compound shows an unusual behavior of both these characteristics: (i) the maximum on the $\chi'(T)$ dependence is observed at substantially higher temperature ~17.5 K than the maximum of the specific heat ~12 K; (ii) the ac susceptibility reveals a frequency dependence around 17.5 K; (iii) the specific heat shows a smeared hump instead of a sharp peak observed on $C(T)$ dependence at $T_C \approx 32$ K for the nondiluted $ErCo_2$ exhibiting a first-order phase transition.[23] Besides the maximum at $T_{crit} \approx 17.5$ K we did not observe any other anomalies on the temperature dependence of the ac susceptibility up to 60 K. Note that the difference between the peak positions of ac susceptibility and C_p was also observed for $Er_{0.6}Y_{0.4}Co_2$.[23]

As for other RCo_2-type compounds (see Ref. 24, for instance) the total specific heat of $Er_{0.55}Y_{0.45}Co_2$ can be presented with the nuclear, lattice, electronic, and magnetic contributions: $C=C_n+C_{el}+C_{latt}+C_m$. The sum of the electronic and lattice contributions $\gamma T+C_{latt}$ one can estimate using the data for paramagnetic isostructural compounds $LuCo_2$ and YCo_2. It should be noted that there is some scatter of data

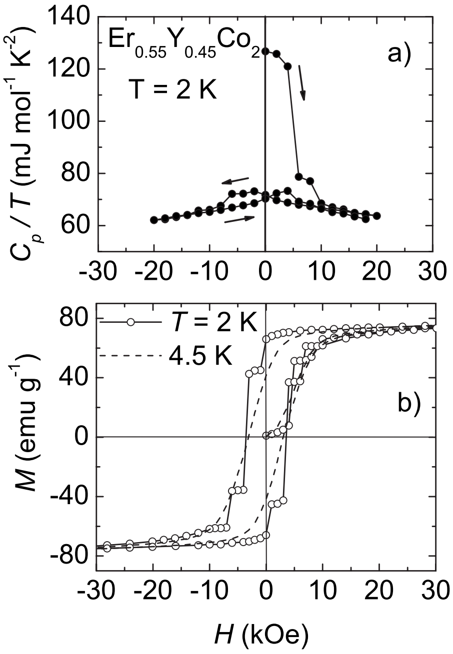

FIG. 2. (a) C/T versus H dependence for $Er_{0.55}Y_{0.45}Co_2$ at $T = 2$ K. The arrows show the magnetic-field change. (b) Field dependence of the magnetization measured at 2 and 4.5 K.

presented in literature on the electronic specific coefficient γ for YCo_2 ($\gamma=34-36.5$ mJ mol^{-1} K^{-2}) (Refs. 24–26) and $LuCo_2$ ($\gamma=26.7-29.1$ mJ mol^{-1} K^{-2}).[26,27] The same relates to the estimations of the Debye temperature in these compounds. The values $\Theta_D=226-305$ K (Refs. 26 and 28) have been reported for YCo_2 and $\Theta_D=238-280$ K (Refs. 26 and 29) for $LuCo_2$. We calculated the temperature dependence of a nonmagnetic contribution $\gamma_0 T+C_{latt}$ with $\gamma_0=30$ mJ mol^{-1} K^{-2} and $\Theta_D=270$ K [shown by dashed line in Fig. 1(b)]. The value $\Theta_D=270$ K was derived in Ref. 23 from specific heat data obtained in the paramagnetic state for the compound $Er_{1-x}Y_xCo_2$ with a close composition $x=0.4$.

Another distinctive feature of the specific-heat behavior of $Er_{0.55}Y_{0.45}Co_2$ is the strong dependence on the magnetic prehistory, which was revealed by the measurements in magnetic fields. Since a thermal relaxation method can be used not only for measuring the thermal variation in the specific heat but also for determining the field dependencies of the specific heat at given temperature we have measured C_p versus H dependence at $T=2$ K. As follows from Fig. 2(a), the increase in a magnetic field at $T=2$ K above ~4 kOe leads to the drastic decrease in the specific heat. Further variation in the field within ±20 kOe leads to a butterflylike hysteresis loop in which the C_p/T value varies between 62 mJ mol^{-1} K^{-2} and 73 mJ mol^{-1} K^{-2}. Switching off the field does not restore the initial value of C_p/T. The sample may be reinstated into the initial state by heating above 20 K and subsequent zero-field cooling. An analogous behavior of the specific heat was recently observed in the $Tm_{1-x}Tb_xCo_2$ system at $x=0.1$.[30] In $Er_{0.55}Y_{0.45}Co_2$, the steplike decrease in the specific heat occurs at the same field at which the magnetization of the sample starts to increase. As one can see in Fig. 2(b), the $M(H)$ dependence at $T=2$ K exhibits a pronounced stepwise behavior in the vicinity of the coercive field. Some steps can be also seen on the hysteresis loop of the specific heat. The increase in the temperature up to 4.5 K is observed to smooth the $M(H)$ dependence in $Er_{0.55}Y_{0.45}Co_2$ [shown by dashed line in Fig. 2(b)]. It should be noted that several and very different compounds are reported to exhibit a staircase behavior of the magnetization at low temperatures ($T<5$ K), associated either with the avalanchelike magnetization jumps in disordered magnets[31–33] or resonant quantum tunneling of high-spin molecules.[34]

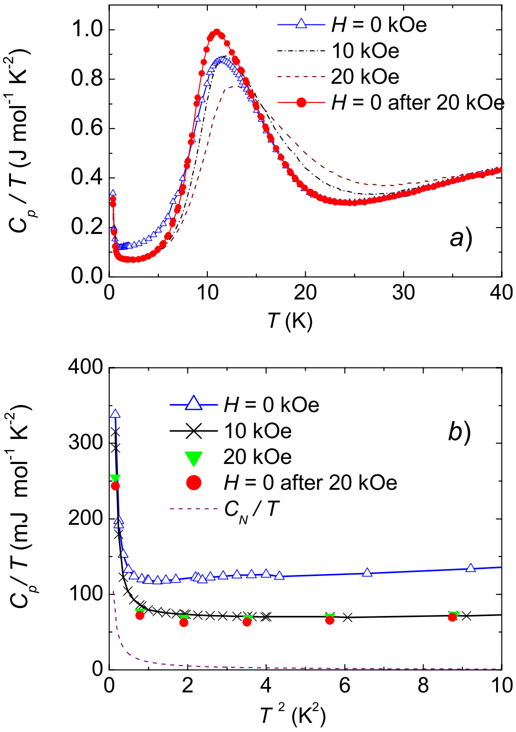

FIG. 3. (Color online) (a) C/T versus T dependencies for $Er_{0.55}Y_{0.45}Co_2$ at various magnetic fields. (b) C/T versus T^2 dependencies for $Er_{0.55}Y_{0.45}Co_2$ in a low-temperature region. Dashed curve corresponds to the nuclear contribution of Er.

The influence of the magnetic prehistory on the specific-heat behavior is also evidenced by the measurements of temperature dependencies of the specific heat at various magnetic fields. As follows from Fig. 3(a), together with the reduction in the C_p/T value below 8 K, the application and subsequent removal of the 20 kOe field leads to the growth of Cp/T at 9 K$<T<$12 K. The low-temperature upturn of Cp/T is associated with the nuclear contribution to the specific heat. In Fig. 3(b) we plotted the C_p/T dependencies as a function of T^2 in the low-temperature region. At $T<3$ K, the data can be well fitted to $C=AT^{-2}+\gamma T+\beta T^3$. The first term AT^{-2} describes the high-temperature part of the nuclear specific heat which is associated mainly with Er since the effective hyperfine field for Er ($H_{eff}=7.2\times10^6$ Oe) (Ref. 35) exceeds substantially that obtained for Co ($H_{eff}=2.23\times10^5$ Oe).[36] As it is clearly seen from Fig. 3(b), the application of a magnetic field $H>20$ kOe is accompanied by a significant decrease in the T-linear contribution to the total specific heat of $Er_{0.55}Y_{0.45}Co_2$. The coefficient γ reduces from the initial value 115 mJ mol^{-1} K^{-2} down to 60 mJ mol^{-1} K^{-2} after an application and removal of the

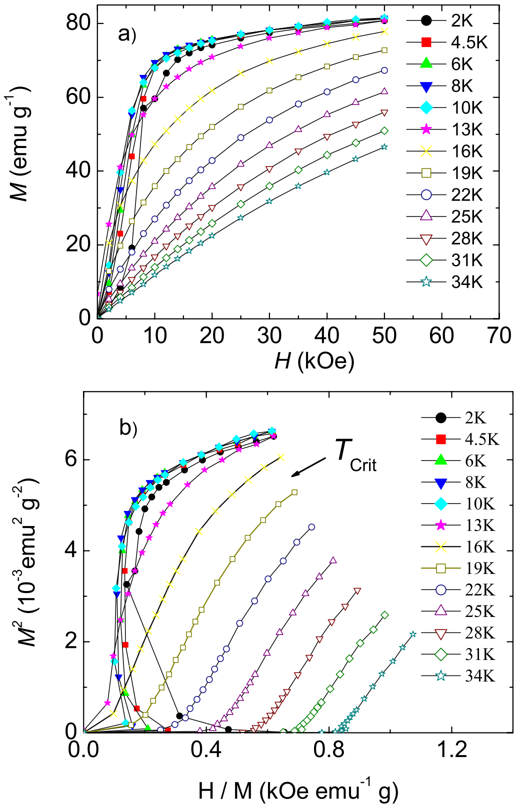

FIG. 4. (Color online) Magnetization isotherms (a) and Belov-Arrot plots (b) for $Er_{0.55}Y_{0.45}Co_2$.

field 20 kOe at 0.4 K. Zero-field coefficient $\gamma(0)$ observed for $Er_{0.55}Y_{0.45}Co_2$ exceeds significantly γ values for YCo_2 (see above) as well as for $ErCo_2$ ($\gamma=38$ mJ mol^{-1} K^{-2}) (Ref. 23). A nonmonotonous change in γ (with a maximum in the vicinity on appearance/disappearance of a magnetic moment on Co atoms) was observed in other $R_{1-x}Y_xCo_2$.[15,16]

Figure 4(a) shows field dependencies of the magnetization measured on $Er_{0.55}Y_{0.45}Co_2$ at various temperatures. At $T > 10$ K, the magnetization curves do not show any critical points which can be attributed to the field-induced first-order phase transition as it was observed just above T_C in $Er_{1-x}Y_xCo_2$ with low yttrium concentrations $x<0.4$. It is known (see Refs. 7 and 8, for instance), that the conclusion about the order of magnetic phase transitions in RCo_2 can be derived from the shape of the M^2 versus H/M dependencies (Belov-Arrot plots). The negative slope or inflection point on Belov-Arrot curves are often indicative of a first-order transition, while the linear shape of these dependencies above T_c implies that a second-order magnetic transition occurs. As follows from Fig. 4(b), the M^2 versus H/M plots do not exhibit a linear behavior around the critical temperature $T_{crit} \sim 17.5$ K as expected in the case of the second-order type transition.

IV. DISCUSSION

Our specific heat, ac-susceptibility, and magnetization data for $Er_{0.55}Y_{0.45}Co_2$ confirm the complicated magnetic state of compounds with the yttrium concentration near the critical value at which the itinerant 3*d*-electron subsystem of Co reveals instability even at low temperatures. According to the neutron-diffraction studies the $Er_{1-x}Y_xCo_2$ compounds exhibit a long-range ferromagnetic order with antiparallel alignment of Er and Co magnetic moments when the yttrium concentration does not exceed $x=0.4$,[13,18] while the compound with $x=0.5$ is found to reveal the presence of a short-range magnetic order only. The magnetic moment on Co atoms M_{Co} shows a sharp decrease with increasing Y content from $\sim 0.6\mu_B$ at $x=0.4$ down to nearly zero at $x=0.5$.[13] The neutron-diffraction measurements performed for the $Er_{1-x}Y_xCo_2$ compounds with the yttrium content $x=0.43$ (Ref. 37) and $x=0.45$ (Refs. 13, 14, and 18) have shown that within a narrow concentration range, where the M_{Co} value shows a sharp reduction with increasing *x*, the LR and SR magnetic orders coexist. The magnetic state of $Er_{0.55}Y_{0.45}Co_2$ is characterized by the nonhomogeneous distribution of the spin density within Co 3*d* subsystem, i.e., by the presence of localized spin-density fluctuations caused by fluctuations of the exchange field acting from rare-earth sublattice due to the substitution of nonmagnetic yttrium for Er ions.

The average magnetic moment per Co ion in $Er_{0.55}Y_{0.45}Co_2$ is estimated to be $\sim 0.2 \pm 0.05\mu_B$.[18] The presence of a nonhomogeneous magnetic state in $Er_{0.55}Y_{0.45}Co_2$ is, we think, responsible for the frequency dependence of the peak height of the ac susceptibility (Fig. 1), which is inherent for spin-glass or cluster-glass type materials.[38] Since the appearance of a magnetic moment on Co ions in $Er_{1-x}Y_xCo_2$ is accompanied by the lattice expansion[7,8] the nonhomogeneous distribution of the spin density in the Co subsystem of $Er_{0.55}Y_{0.45}Co_2$ leads apparently to the elastic stresses which should be nonhomogeneously distributed in the sample volume.

The coexistence of the SR magnetic order regions with zero Co magnetic moment and LR ferromagnetic regions with high Co moment in the initial zero-field cooled state of $Er_{0.55}Y_{0.45}Co_2$ (Ref. 18) implies that the phase transition to a LR ferrimagnetic state under application of a magnetic field occurs through increase in the volume of LR regions. Since the initial mixed magnetic state and final field-induced ferrimagnetic state exhibit substantially different specific-heat values mainly due to the difference in the *T*-linear term, the reduction in the specific heat [Fig. 2(a)] results apparently from the growth of the LR volume with the lower specific heat. The specific heat and magnetization jumps [Fig. 2(b)] at the initial magnetization process at $T=2$ K may be associated with the avalanchelike propagation of the interphase SR-LR boundaries. The butterflylike behavior of the specific heat and the presence of the hysteresis on the C_p/T versus *H* dependence indicate that the field-induced ferrimagnetic state in $Er_{0.55}Y_{0.45}Co_2$ is nonhomogeneous as well and LR magnetic order do not occupy whole volume of the sample probably because of the nonhomogeneous distribution of yttrium atoms in the rare-earth sublattice. This magnetic nonhomogeneity may lead to some jumps which are observed on the field dependencies of the specific heat in the field-induced state [Fig. 2(b)].

The peculiar magnetic state of $Er_{0.55}Y_{0.45}Co_2$ affects also the magnetization behavior around the magnetic ordering temperature. Unlike nondiluted $ErCo_2$ exhibiting *S* shape of

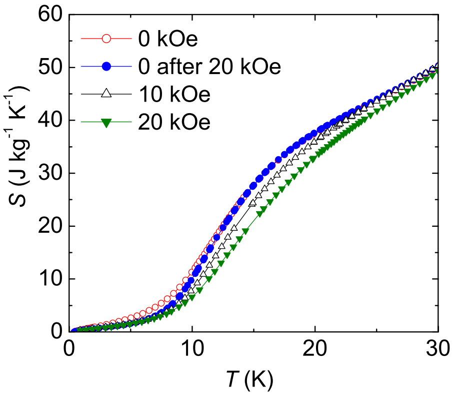

FIG. 5. (Color online) Temperature dependencies of the entropy calculated from specific-heat data for $Er_{0.55}Y_{0.45}Co_2$.

the M^2 versus H/M dependencies in the vicinity of T_C, the nonlinearity of Belov-Arrot plots observed for $Er_{0.55}Y_{0.45}Co_2$ at $T \sim T_C$ may be considered as an evidence of a smeared first-order type magnetic phase transition. In both $ErCo_2$ and $Er_{0.55}Y_{0.45}Co_2$ compounds, the change in the magnetic state is accompanied by the lattice volume changes.[8,17]

Bearing in mind such a complicated magnetic state of $Er_{0.55}Y_{0.45}Co_2$ one can suggest that the electronic S_{el} and lattice S_{lat} contributions to the total entropy and primarily the magnetic contribution associated with the local 4*f* moments S_{4f} should be field dependent in this compound: $S(T,H) = S_{el}(T,H) + S_{lat}(T,H) + S_{4f}(T,H)$. Here we suppose that the nuclear contribution to the entropy is not significant at temperatures above 2 K. Note that it is difficult to separate these contributions owing to the strong coupling of electronic, lattice, and magnetic subsystems in RCo$_2$-type compounds. By integration of $C_p(T)/T$ versus T dependencies we obtained the $S(T,H)$ dependencies for our sample. As can be seen from Fig. 5, at temperatures below 12 K, the $S(T)$ curve measured at $H=0$ after application of the field 20 kOe lies below than that obtained for the initial noninfluenced state. Such a behavior evidences the first-order nature of the field-induced phase transition in this compound. The enhanced γ value implies that the T-linear entropy may contribute substantially to the total entropy of $Er_{0.55}Y_{0.45}Co_2$. Figure 6(a) displays the temperature dependencies of the isothermal magnetic entropy change $\Delta S_m = S(T,H) - S(T,0)$ calculated from specific-heat data and magnetization measurements for $Er_{0.55}Y_{0.45}Co_2$. The last results were obtained by using Maxwell equation.[39] As can be seen, the ΔS_m values evaluated from $M(H)_T$ measurements for 20 kOe in the temperature interval 12–30 K [Fig. 6(a)] are in a good agreement with that calculated from the specific-heat data. The highest value of ΔS_m for $Er_{0.55}Y_{0.45}Co_2$ under a field change of 50 kOe is estimated from the magnetization data to be about 13.8 J kg^{-1} K^{-1} at $T \approx 17$ K which is by a factor of about 3 lower in comparison with that observed for $ErCo_2$ (36–38 J kg^{-1} K^{-1} at $T \approx 33$ K).[2,3] A reduction in ΔS_m may be caused by the decrease in the concentration of Er ions having a magnetic moment, by smearing the first-order magnetic phase transition as well as by the reduction in the spin-fluctuation contribution. The decrease in ΔS_m due to the substitution of 20% Y for Er in $ErCo_2$ was also observed earlier by Wada *et al.*[2] It was explained by the model in which the localized spins of the rare-earth ions are under the effect of the crystalline electric field and are coupled to an effective subsystem of itinerant electrons.[4] According to this model, the introduction of Y instead of Er ions in $ErCo_2$ results only in the decrease in the effective Er-Er interaction. However, an opposite behavior was observed for the $Dy_{1-x}Y_xCo_2$ system.[3] According to Ref. 3, the increase in the yttrium concentration in $Dy_{1-x}Y_xCo_2$ up to $x=0.3$ does not decrease the ΔS_m value as expected but is accompanied by the growth of ΔS_m. Such a behavior of the magnetocaloric effect in $Dy_{1-x}Y_xCo_2$ could not be explained by the model[4] which neglects the contribution to ΔS_m from the itinerant *d* electrons.

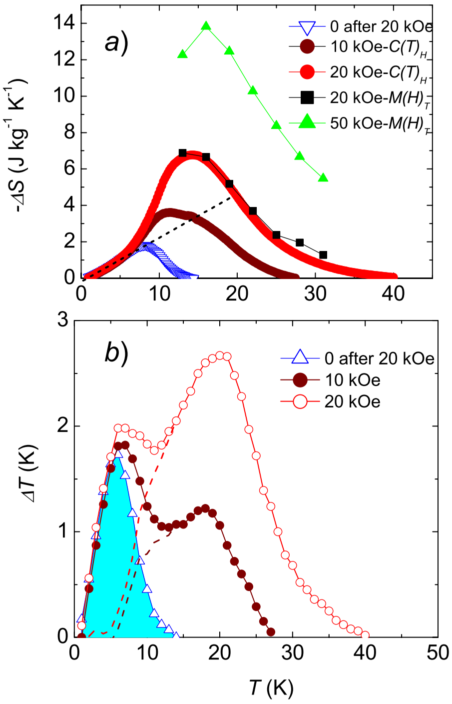

FIG. 6. (Color online) (a) Temperature dependencies of the isothermal magnetic entropy change ΔS_m calculated from specific heat $C(T)_H$ and magnetization $M(H)_T$ data for $Er_{0.55}Y_{0.45}Co_2$ at different magnetic-field changes. (b) Adiabatic temperature changes calculated from specific-heat data as a function of temperature for magnetic-field changes up to 20 kOe. The filled areas correspond to the irreversible reduction in the entropy and irreversible heating of the sample under application of magnetic fields up to 20 kOe.

The filled area in Fig. 6(a) indicates the irreversible entropy change. This irreversibility is associated with the presence of a substantial hysteresis at the field-induced IEM transition in the 3*d*-electron subsystem of Co.[7,8] It is evident that the thermal hysteresis is decreasing with increasing T_C. It turns out to be about 12 K in $Er_{0.55}Y_{0.45}Co_2$. In $ErCo_2$ ($T_C \sim 32$ K) the thermal hysteresis is about 1–1.5 K only,[23] while the $DyCo_2$ compound does not exhibit a visible thermal hysteresis apparently because of a high value of the Curie temperature [$T_C \sim 135-142$ K (Refs. 7 and 8)]. The reduction in the hysteresis with increasing T_C implies the decrease in the irreversibility in the entropy change in RCo$_2$ compounds with increasing Curie temperature. The giant re-

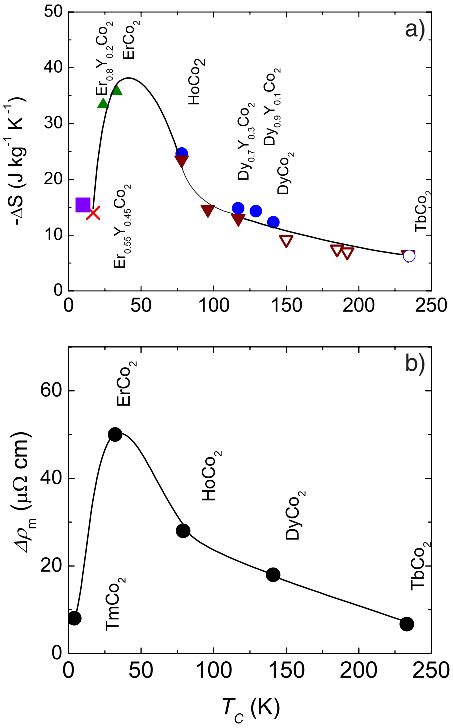

FIG. 7. (Color online) (a) The ΔS_m as a function of the Curie temperature of $R_{1-x}Y_xCo_2$ compounds for a field change 50 kOe (×—present work, ▲—Ref. 2, ●—Ref. 3, ■—Ref. 30, ▼—Ref. 47). Full symbols correspond to the first-order transition at $T=T_C$ and open symbols to the second one. The solid line is a guide to the eye. (b) The extra magnetic contribution $\Delta\rho_m$ to the electrical resistivity of RCo_2 according to Ref. 8. The $\Delta\rho_m$ value for $TmCo_2$ is taken from Ref. 48.

duction in the γ value (~48%) observed in the present work for $Er_{0.55}Y_{0.45}Co_2$ under application of a magnetic field suggests a significant change in the T-linear contribution to the total entropy change, $\Delta S_{el}=\Delta\gamma\cdot T$. Using the data presented in Fig. 3 one can estimate the ΔS_{el}. Suggesting the temperature independence of $\Delta\gamma$, the estimation gives a value ~0.8 J mol^{-1} K^{-1} (2.8 J kg^{-1} K^{-1}) for $T=15$ K which is about one half of the maximal value $|\Delta S_m|$ of the isothermal entropy change for a field change of 20 kOe [see Fig. 6(a)].

In Fig. 6(b) we plot the adiabatic temperature changes ΔT obtained from specific-heat data for magnetic-field changes up to 20 kOe. A maximum of $\Delta T=1.8-2$ K at $T\sim 6-7$ K is associated with irreversible heating of the sample due to the first-order nature of the IEM transition. After subtraction of the irreversible part from ΔT versus T curves we received the reversible adiabatic temperature changes in $Er_{0.55}Y_{0.45}Co_2$ [shown by dashed lines in Fig. 6(b)]. Figure 7(a) shows the variation in the maximal ΔS_m value for a field change 50 kOe as a function of the Curie temperature for RCo_2 with heavy rare earths as well as for some pseudobinary $R_{1-x}R'_xCo_2$ compounds: for $R_{1-x}Y_xCo_2$, $Ho_{1-x}Tb_xCo_2$, and $Tm_{0.1}Tb_{0.9}Co_2$. In the last case, the substitution of Tb for Tm in the compound $TmCo_2$ leads to appearance of a magnetic moment on the Co atoms while the magnetic moment on Co is absent in pure $TmCo_2$.[8] Bearing in mind the results obtained in Ref. 30, the magnetic state of our $Er_{0.55}Y_{0.45}Co_2$ sample seems to be analogous with that observed in $Tm_{0.1}Tb_{0.9}Co_2$. The value of $\Delta S_m=15.4$ J kg^{-1} K^{-1} for $Tm_{0.1}Tb_{0.9}Co_2$ was obtained by using the specific data presented in Ref. 30. We did not include in Fig. 7 the ΔS_m data existing in the literature for the substituted $R(Co_{1-x}M_x)_2$ compounds with M=Ni, Al, Ga, Si since the partial substitution of M atoms for Co affects substantially the electronic structure, the order of a magnetic phase transition at $T=T_C$, and spin-fluctuations behavior.[7,8] There are some features of the ΔS_m versus T_C dependence, which should be mentioned: (i) the $\Delta S_m(T_C)$ dependence for $R_{1-x}R'_xCo_2$ compounds exhibits a nonmonotonous behavior with a maximum around 40–50 K; (ii) the ΔS_m values for the compounds revealing the second-order (open symbols) and first-order phase transition (full symbols) lie on the same curve; (iii) the substitution of Y for Er in $ErCo_2$ leads to decrease in ΔS_m (Ref. 2) while the increase in the yttrium concentration in $Dy_{1-x}Y_xCo_2$ up to $x=0.3$ does not decrease the ΔS_m value, as it could be expected, but is accompanied by the growth of ΔS_m.[3] The enhancement of ΔS_m is also observed in $Ho_{1-x}Y_xCo_2$ at the dilution of the Ho sublattice by nonmagnetic yttrium up to $x=0.2$.

As was mentioned above, several mechanisms were proposed for the explanation of the enhanced ΔS_m values in RCo_2 in comparison with that observed in the RAl_2 and RNi_2-type compounds and the substantial growth of ΔS_m when going from $TbCo_2$ to $ErCo_2$, i.e., with decreasing T_C. The first-order nature of the phase magnetic transition and structural deformations at $T=T_C$ are considered as main origins of such behavior.[4,9] The fact that the change of the order of the ferrimagnetic to paramagnetic phase transition in $R_{1-x}R'_xCo_2$ compounds around 150 K is not accompanied by drastic changes in ΔS_m [Fig. 7(a)] may be explained by a gradual conversion of the second-order type transition to the first-order type owing to the substitution. The substituted compounds with Curie temperatures within a crossover region exhibit apparently the smeared first-order transitions.

As to the lattice contribution, our estimation shows that the changes in the lattice parameters at the first-order phase transition in $ErCo_2$ as well as in $Er_{0.55}Y_{0.45}Co_2$ are accompanied by about 2 K change in the Debye temperature (Θ_D). We have made this estimation using the expression $\Theta_D=\Theta_D^0(1-\Gamma\cdot\omega)$, where Γ is the Grüneisen parameter, $\omega=\Delta V/V$ is the change in the lattice volume, and Θ_D^0 is the Debye temperature of a paramagnetic compound. The values of ω were taken from Refs. 23 and 17 and Γ—from Ref. 23. The maximal entropy change associated with the lattice expansion under application of a magnetic field in $Er_{0.55}Y_{0.45}Co_2$ and $ErCo_2$ is found to be about 3×10^{-3} J kg^{-1} K^{-1} and 1.4×10^{-1} J kg^{-1} K^{-1}, respectively. These values are significantly lower than the magnetic and electronic contributions. The analysis of the magnetoelastic and magnetothermal properties of RCo_2 shows that the isothermal magnetic entropy change within the RCo_2 series does not follow the ω change. Thus, the ΔS_m value increases from ~12 J kg^{-1} K^{-1} up to ~36 J kg^{-1} K^{-1} when going from $DyCo_2$ to $ErCo_2$ [see Fig. 7(a)] while the magnetovolume anomaly ω decreases from $\omega\approx 5.5\times 10^{-3}$ for $DyCo_2$ down to $\omega\approx 4.7\times 10^{-3}$ for $ErCo_2$.[40]

It should be noted that the theoretical values of the maximal magnetic contribution to the entropy associated with rare-earth sublattice in $R\mathrm{Co}_2$ (R=Tm,Er,Ho,Dy,Tb) $S_m^{\mathrm{theor}} = R\ln(2J+1)$ lie within in a quite narrow interval 21.3–23.6 J mol^{-1} K^{-1} (74.7–83.3 J kg^{-1} K^{-1}). Bearing in mind the estimations of the total energy level splitting of R ions by crystalline electric field[2,30] such values may be reached at zero field above ~150 K. The saturation magnetizations of these compounds are close as well. These data do not imply the presence of a large difference in ΔS_m for $R\mathrm{Co}_2$ with different R ions and nonmonotonous shape of the ΔS_m versus T_C dependence. Zero-field entropy changes at the first-order magnetic phase transition in $R\mathrm{Co}_2$ are observed to be substantially lower than S_m^{theor} values. Thus, for ErCo_2, the zero-field magnetic entropy jump at the Curie temperature is found to be about 31.5 J kg^{-1} K^{-1} only,[2] i.e., ~40% of S_m^{theor}. The entropy change at the field-induced first-order phase transition above T_C may be also obtained from the magnetization data by using the Clausius-Clapeyron equation

$$\Delta S = -\Delta M \frac{dH_c}{dT}, \tag{1}$$

where ΔM is the magnetization jump at the critical field H_C. The critical transition fields obtained along principal crystallographic directions of ErCo_2 increase quadratically with temperature.[21,41] The T^2 behavior of H_C is derived from the theory of spin fluctuations[42] and is typical for the first-order magnetic phase transitions in itinerant electron systems the behavior of which is strongly affected by spin fluctuations, in particular for $\mathrm{Co(S,Se)}_2$, YCo_2, and $\mathrm{Lu(Co},M)_2$ (M=Ga,Al) (see Refs. 7, 8, and 43 and references therein). Unlike the ErCo_2 case, the critical transition fields of the first-order magnetic phase transitions above T_C along the main axes of a HoCo_2 single crystal show a linear growth with increasing temperature,[21] which may be indicative of a lesser influence of spin fluctuations in this compound. The positive shift of H_C in ErCo_2 caused by spin fluctuations results in a higher average value of dH_c/dT at $T \to T_C$ in this compound (~4.7 kOe/K) in comparison with that observed for HoCo_2 (~2.8 kOe/K).[21] Bearing in mind the closeness of magnetization jumps above T_C in ErCo_2 and HoCo_2 (Ref. 8) one can suggest that the large difference in dH_c/dT values for these compounds is responsible for the observed difference in the isothermal magnetic entropy changes in these compounds.

The large ΔS_{el} contribution observed in $\mathrm{Er}_{0.55}\mathrm{Y}_{0.45}\mathrm{Co}_2$ seems to be not surprising since there are several 3d-metal based compounds [$\mathrm{La(Fe,Si)}_{13}$,[12] $\mathrm{Co(S,Se)}_2$,[44] for instance] which exhibit an itinerant electron metamagnetism and show the enhanced magnetocaloric properties. Yamada and Goto[45] have shown that the magnetocaloric effect in such compounds can be described in the frame of the spin-fluctuation theory of IEM. Bearing in mind the above-mentioned similarity of the magnetic state of $\mathrm{Er}_{0.55}\mathrm{Y}_{0.45}\mathrm{Co}_2$ at low temperatures and the magnetic state of ErCo_2 just above T_C one can suggest that the isothermal magnetic entropy change in ErCo_2 includes also a substantial contribution from spin fluctuations. This additional contribution to ΔS_m from spin fluctuations is apparently highest for ErCo_2 because the Curie temperature of this compound (T_C~32 K) is close to the so-called spin-fluctuation temperature T_{sf}~35 K (Ref. 46) which characterizes the excitation energy of spin fluctuations in the itinerant 3d-electron subsystem of YCo_2. It means that the inducement of spin fluctuations in the itinerant Co 3d-electron subsystem by the exchange field arising from Er 4f electrons in ErCo_2 above T_C should be very effective.

It is worth to mention that the additional spin-fluctuation contribution (~14–19%) to the magnetic entropy was observed recently in the compound GdNi_2.[49] Such a contribution in GdNi_2 was explained by the enhanced γ value in GdNi_2 (γ=22 mJ mol^{-1} K^{-2}) in comparison with that obtained for paramagnetic YNi_2 and LuNi_2 compounds (γ=5.2–5.4 mJ mol^{-1} K^{-2}). The increased γ value in the Gd-containing compound is attributed to spin fluctuations induced by the f-d exchange interaction in the hybridized 3d-5d-electron subsystem. The YNi_2 and LuNi_2 compounds can hardly be considered as systems which are strongly influenced by spin fluctuations, because their γ values are substantially lower than those of usual systems exhibiting a spin-fluctuation behavior. The fact that the spin-fluctuating paramagnetic compound YCo_2 shows the γ value increased by about six times in comparison with YNi_2 implies that the influence of the f-d exchange induced spin fluctuations may be more substantial in $R\mathrm{Co}_2$ especially in the vicinity of the magnetic-ordering temperature.

An additional argument to support our suggestion about the influence of spin fluctuations on the magnetocaloric effect in $R\mathrm{Co}_2$ is an extra magnetic contribution to the electrical resistivity ($\Delta\rho_m = \rho_{R\mathrm{Co}_2} - \rho_{\mathrm{YCo}_2}$) which appears just above T_C [Fig. 7(b)]. The $\Delta\rho_m$ data for TmCo_2 are taken from Ref. 48 while for other $R\mathrm{Co}_2$ (R=Er,Ho,Dy,Tb) from Ref. 8. The observed spin-density fluctuations in $R\mathrm{Co}_2$ above T_C are also responsible for the additional magnetic contribution to the electrical resistivity in the magnetically ordered compounds[7,8] in comparison with paramagnetic YCo_2: $\Delta\rho(T,H) = \rho_{R\mathrm{Co}_2} - \rho_{\mathrm{YCo}_2}$.[50,51] This excess of the resistivity at $T > T_C$ may be suppressed by application of a magnetic field which leads to a giant magnetoresistance effect.[21] It should be emphasized here that for many different compounds, a clear correlation between the behaviors of the isothermal magnetic entropy and resistivity changes [$\Delta S_m(T) \propto \Delta\rho_m(T)$] has been established.[52] As follows from Fig. 7(b), an extra magnetic contribution to the electrical resistivity $\Delta\rho_{\max}$ exhibits a nonmonotonous behavior as a function of temperature with a maximum around $T \sim T_{\mathrm{sf}}$,[50,51] i.e., analogous to that observed for the ΔS_m versus T_C dependence. The nonmonotonous dependence of the $\Delta\rho$ versus T_C for $R\mathrm{Co}_2$ was recently confirmed by Burkov *et al.*[53] The presence of spin fluctuations as a main origin of a large $\Delta\rho$ value and significant magnetoresistance in $R\mathrm{Co}_2$ is generally accepted in the literature (see Ref. 50, for instance). In our opinion, the correlation between $\Delta S_m(T_C)$ and $\Delta\rho_m(T_C)$ is an additional argument in favor of the significant role of spin fluctuations on the magnetocaloric effect in $R\mathrm{Co}_2$ compounds.

The suggestion about nonmonotonous change in the spin-fluctuation contribution to ΔS_m allows us to answer the question why the substitution of Y for Dy in $\mathrm{Dy}_{1-x}\mathrm{Y}_x\mathrm{Co}_2$ increases ΔS_m (Ref. 3) while the increase in the yttrium content in $\mathrm{Er}_{1-x}\mathrm{Y}_x\mathrm{Co}_2$ leads to reduction in ΔS_m (Ref. 2) (Fig. 7), although both these systems exhibit a first-order type magnetic transition at $x \sim 0.3$. In our opinion, the opposite behavior of ΔS_m in these systems results from the fact that the increase in the yttrium concentration shifts T_C toward the T_{sf} in case of $Dy_{1-x}Y_xCo_2$ while sets the magnetic-ordering temperature apart from T_{sf} in the $Er_{1-x}Y_xCo_2$ case.

V. CONCLUSION

Instability of the itinerant 3*d*-electron subsystem and nonhomogeneous magnetic state of $Er_{0.55}Y_{0.45}Co_2$ at temperatures below ~17 K result in unusual magnetothermal properties of this compound. The specific heat of $Er_{0.55}Y_{0.45}Co_2$ being measured at $T=2$ K as a function of an applied magnetic field demonstrates a butterflylike behavior and pronounced irreversibility. The coefficient γ of the *T*-linear specific heat is found to decrease by about 48% after application and removal of the field 20 kOe. The large zero-field γ value (~ 115 mJ mol^{-1} K^{-2}) is associated with the presence of spin-density fluctuations induced in the hybridized 3*d*-5*d*-electron subsystem by the fluctuating *f*-*d* exchange interaction due to the Er-Y substitution. An irreversible reduction of the specific heat of $Er_{0.55}Y_{0.45}Co_2$ below 8 K under application of a magnetic field is explained by the first-order phase transition in the 3*d*-electron subsystem, i.e., by the itinerant electron metamagnetism. The isothermal magnetic entropy change in $Er_{0.55}Y_{0.45}Co_2$ includes a large part associated with contribution from spin-density fluctuations. Bearing in mind a similarity of the low-temperature magnetic state of $Er_{0.55}Y_{0.45}Co_2$ and the magnetic state of $ErCo_2$ just above T_C, the magnetocaloric effect in $ErCo_2$ and in other RCo$_2$ compounds is suggested to be strongly influenced by these fluctuations as well. The additional spin-fluctuation contribution to the isothermal entropy change is substantially temperature dependent with a maximum value in case of $T_C \sim T_{sf}$. This suggestion allows us to explain a nonmonotonous dependence of ΔS_m on the magnetic ordering temperature in $R_{1-x}Y_xCo_2$ compounds. The dependence of the isothermal magnetic entropy change on the magnetic ordering temperature for RCo_2 is observed to correlate with behavior of the extra magnetic contribution to the electrical resistivity above T_C, which supports further our assumption about the influence of spin fluctuations on magnetothermal properties of these compounds.

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[*] Corresponding author; nikolai.baranov@usu.ru

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