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Metamagnetism, giant magnetoresistance and magnetocaloric effects in RCo_2-based compounds in the vicinity of the Curie temperature

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Abstract

Magnetisation and magnetoresistance isotherms were measured for a number of $(R,R')Co_2$, $(R,Y)Co_2$ and $R(Co,Si)_2$ (R,R' = rare earth) compounds. A metamagnetic transition is observed just above the Curie temperature (T_C) of compounds having a first order phase transition, i.e. $ErCo_2$-, $HoCo_2$-, and $DyCo_2$-based ones. Both 4f- and 3d-sublattice magnetic moments contribute to a sharp change of the magnetisation at this transition. The concurring suppression of the magnetoresistance can be considered to be due to quenching of spin fluctuations. In addition, the magnetic entropy change ΔS_m is estimated from the magnetisation data by using a Maxwell equation. The resulting giant magnetocaloric effects are discussed in terms of the 4f(R)-localised spin and the 3d(Co)-spin fluctuations as well as the nature of the phase transition.

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Keywords: Rare-earth-transition metal compounds; Metamagnetic transition; Giant magnetoresistance; Giant magnetocaloric effects

1. Introduction

The RCo_2 (R = rare earth) compounds crystallise in the cubic Laves phase structure. No stable 3d-magnetic moment is detectable down to the lowest temperatures in case the R ions do not have a local moment, i.e. have a filled or an empty 4f-shell, e.g. YCo_2, $LuCo_2$ or $ScCo_2$ [1,2 and refs therein]. These compounds, however, undergo a metamagnetic transition (MMT) from the paramagnetic state to a ferromagnetic state at a critical magnetic field of about 70 T and show large effects of spin fluctuations. Suppression of spin fluctuations in magnetic fields has been found in low-temperature specific-heat measurements, in applied fields up to 10 T [3]. Also for some strongly Pauli paramagnetic $Y(Co_{1-x}Al_x)_2$ compounds, metamagnetism and quenching of spin fluctuations were observed in magnetoresistance measurements [4,5].

Magnetic investigations revealed that, in case the R ions do have a local moment, an induced Co moment arises in the magnetically ordered state due to the 4f–3d exchange interactions [1,2]. The

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metamagnetic properties of the Co subsystem play a decisive role in determining the order of the magnetic transition e.g. first order (FOT) for $ErCo_2$ ($T_C = 33.6$ K), $HoCo_2$ ($T_C = 75$ K), and $DyCo_2$ ($T_C = 140$ K), but second order (SOT) for $TbCo_2$ ($T_C = 227$ K). Above T_C, in zero field, there is no Co moment. Nevertheless, as expected by comparing with the paramagnetic $Y(Lu)Co_2$ compounds, the magnetic properties of the Co subsystem still play an important role, in some cases leading to metamagnetic behaviour and quenching of spin fluctuations in the complete, interacting, 4f–3d system (see below).

In addition, it was indicated [6] that the size of the magnetocaloric effect (MCE), which is an important parameter for magnetic-refrigeration applications, depends not only on the number of (localised) 4f-spins and the nature of the transition, but also on the contribution of the 3d-itinerant electrons. In this context, taking into account the modelling possibilities by manipulating the metamagnetic properties as well as the Curie temperatures, one may consider the RCo_2 intermetallics as promising candidates for application.

The aim of this paper is to investigate the formation of the 3d-magnetic moments and the quenching of spin fluctuations, as well as the MCE in the vicinity of T_C for a large number of RCo_2-based compounds. The results allow to determine some general trends. We shall show that quenching of spin fluctuations is responsible for the field suppression of resistivity above T_C. The MCE, however, is closely related to the type of the magnetic phase transition.

2. Experimental

The investigated samples were fabricated by melting stoichiometric mixtures of Gd, Tb, Dy, Ho, Er and Y (4N8), Co and Si (5N) in an induction furnace under argon atmosphere. The resulting buttons were wrapped in Ta foil, sealed under argon in silica tubes and annealed at 950°C. X-ray analysis shows the presence of a single phase (C15) only. Magnetisation was measured using the induction method in fields up to 10 T at the Laboratoire Louis Néel (Grenoble). The magnetoresistance measurements were carried out by means of a four-terminal measuring technique on bar-shaped samples (size about $1 \times 1 \times 7\,mm^3$).

3. Results and discussion

3.1. Magnetisation

Figs. 1(a–c) illustrate magnetisation isotherms for $HoCo_2$, $DyCo_2$ and $TbCo_2$ in the vicinity of T_C. Clearly, metamagnetism is observed in $HoCo_2$ (Fig. 1(a), see also Ref. [2]) with characteristics (i) a large hysteresis of magnetisation and (ii) an increase of the critical field (B_C) and a decrease of the magnetisation jump at the MMT with increasing temperature. In addition, the MMT exists only in a small range of temperatures, with $\Delta T \approx 20$ K above the FOT. A similar, even more intense metamagnetic behaviour is found for $ErCo_2$ (see Fig. 71 in Ref. [2]). For $DyCo_2$, the MMT is weakly evidenced by only the hysteresis of the magnetisation curves above T_C (Fig. 1(b), see also Ref. [2]) The absence of an MMT in $TbCo_2$ is characterised by the disappearance of not only the magnetisation jump but also of the hysteresis (Fig. 1(c)). Arrott plots of the investigated compounds are presented in Figs. 2(a–c). In case an MMT occurs, i.e. for $HoCo_2$ and $DyCo_2$, they show an S-shape. Such an S-shaped curve is expected when there is a negative contribution of some higher order term in the Landau free energy expansion (a negative M^4-term, for instance, i.e. a negative coefficient c_3 as defined in e.g. Ref. [2], leads to a negative initial slope of the Arrott plot). For $TbCo_2$, the upper parts of the Arrott plots exhibit the linear dependence expected for a SOT. Deviations at low fields may partly be caused by inhomogeneities, whereas spin fluctuations and the remnants of the Co 3d-metamagnetism may be responsible for the curvatures, observed in particular near T_C (≈ 230 K). Similar S-shaped Arrott plots were also found for $(Dy_xY_{1-x})Co_2$ ($x = 0.9$ and 0.7), $Ho(Co_{1-x}Si_x)_2$ ($x \leqslant 0.075$), and $Er(Co_{1-x}Si_x)_2$ ($x \leqslant 0.075$), compounds that show a FOT as well as metamagnetic behaviour for $T > T_C$. A more standard type of Arrott plots was

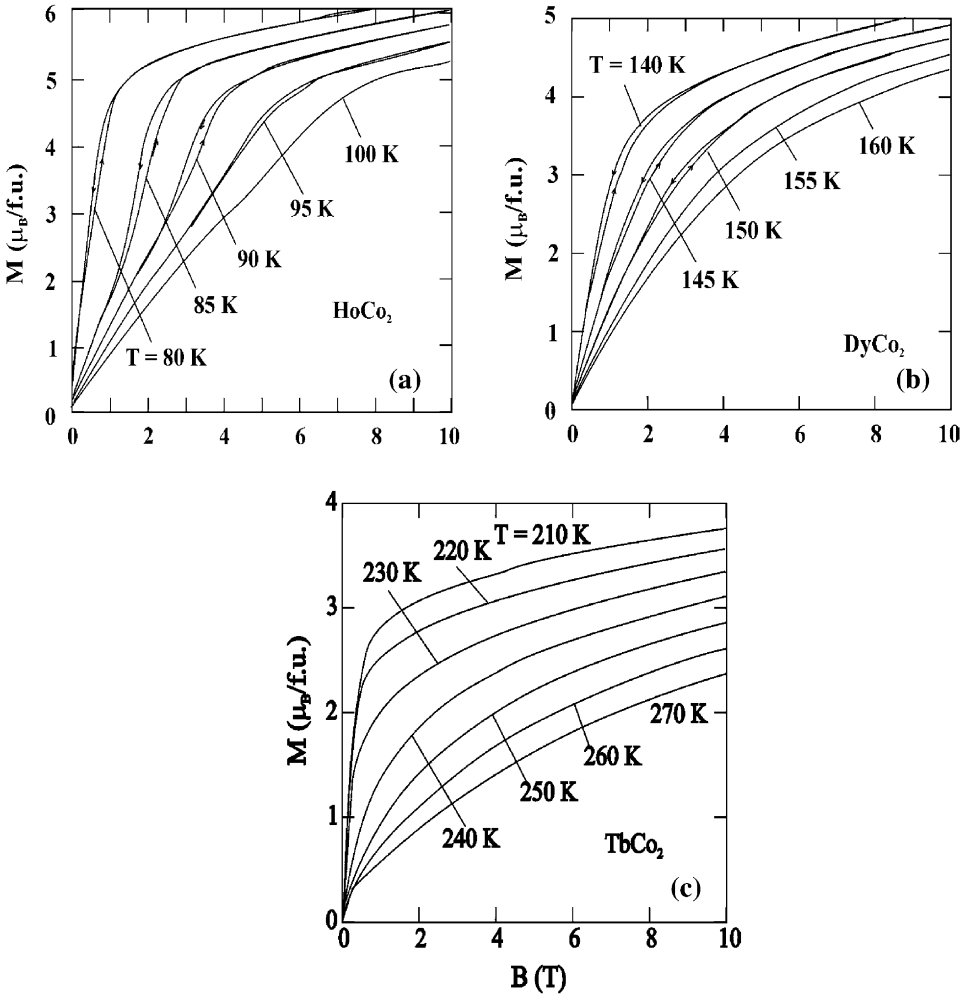

Fig. 1. Magnetisation isotherms for (a) $HoCo_2$ ($T_C = 75$ K), (b) $DyCo_2$ ($T_C = 140$ K), and (c) $TbCo_2$ ($T_C = 227$ K).

observed for $Gd_{0.4}Tb_{0.6}Co_2$, $Gd_{0.65}Lu_{0.35}Co_2$, $Gd_{0.65}Y_{0.35}Co_2$ and $Er(Co_{1-x}Si_x)_2$ ($x > 0.075$), compounds with a SOT (and not showing an MMT).

3.2. Magnetoresistance

Magnetoresistance data of $HoCo_2$, $DyCo_2$ and $TbCo_2$ are presented in Figs. 3(a–c) in a plot of $\Delta R/R(0) = [R(B) - R(0)]/R(0)$ vs. B, where $R(0)$ and $R(B)$ are the resistance in zero field and in applied field, respectively. For $HoCo_2$ (Fig. 3(a), see also Ref. [2]), at $T > T_C$ a rise in B to B_C initially causes an insignificant change in $\Delta R/R(0)$ even though the magnetisation of the compounds, which is mainly determined by the R-subsystem in these fields, reaches a rather large value (approximately more than one-half of maximum value at several temperatures). This behaviour may point to a minor role of spin disorder scattering by the 4f-moments (although they probably are involved in the spin fluctuation scattering, see below). The metamagnetic nature of the magnetisation process at $T > T_C$, however, is clearly manifested in the sharp drop of the electrical resistance, amounting to more than 60%, at $B \sim B_C$ where there is a jump

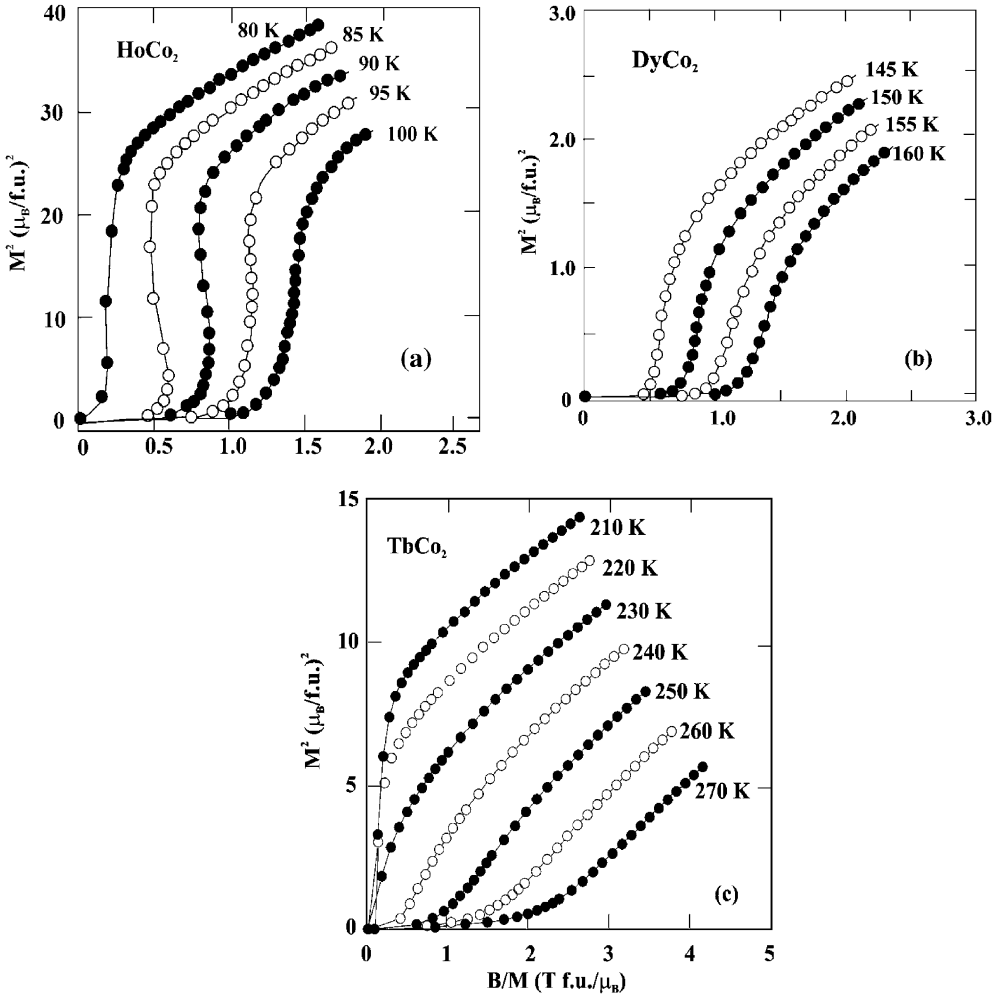

Fig. 2. Arrott plots corresponding to magnetisation isotherms like shown in Fig. 1 (decreasing field only).

in the magnetisation. For $DyCo_2$ (Fig. 3(b), see also Ref. [2]), the MMT is less abrupt in the magnetoresistance data (with a maximum resistance change of about 30% only), in accordance with the observed magnetisation data discussed above. For $TbCo_2$ (Fig. 3(c)), $\Delta R/R(0)$ is still lower (about 17% only), also in line with the absence of abrupt variations in the observed magnetisation data.

For the RCo_2 compounds, the suppression of resistivity at T_C is thought to be due to ordering of the 4f-moments, ordering of the 3d-moments or itinerant-band effects of the 3d-subsystem, and quenching of spin fluctuations at the Co-sites. Then, under the assumption that these contributions are additive, the magnetoresistance can be written as

$$\Delta R(B,T) = \Delta R_{3d}(B,T) + \Delta R_{4f}(B,T) + \Delta R_{sf}(B,T). \quad (1)$$

Here, $\Delta R_{3d}(B,T)$ is a positive contribution, ascribed to the formation of 3d-magnetic moment. Such a contribution was found in ferromagnetic $Y(Co,Al)_2$ compounds [2,5]. There, the observed quadratic dependence on the magnetisation was taken as evidence that $\Delta R_{3d}(B,T)$ is a pure volume

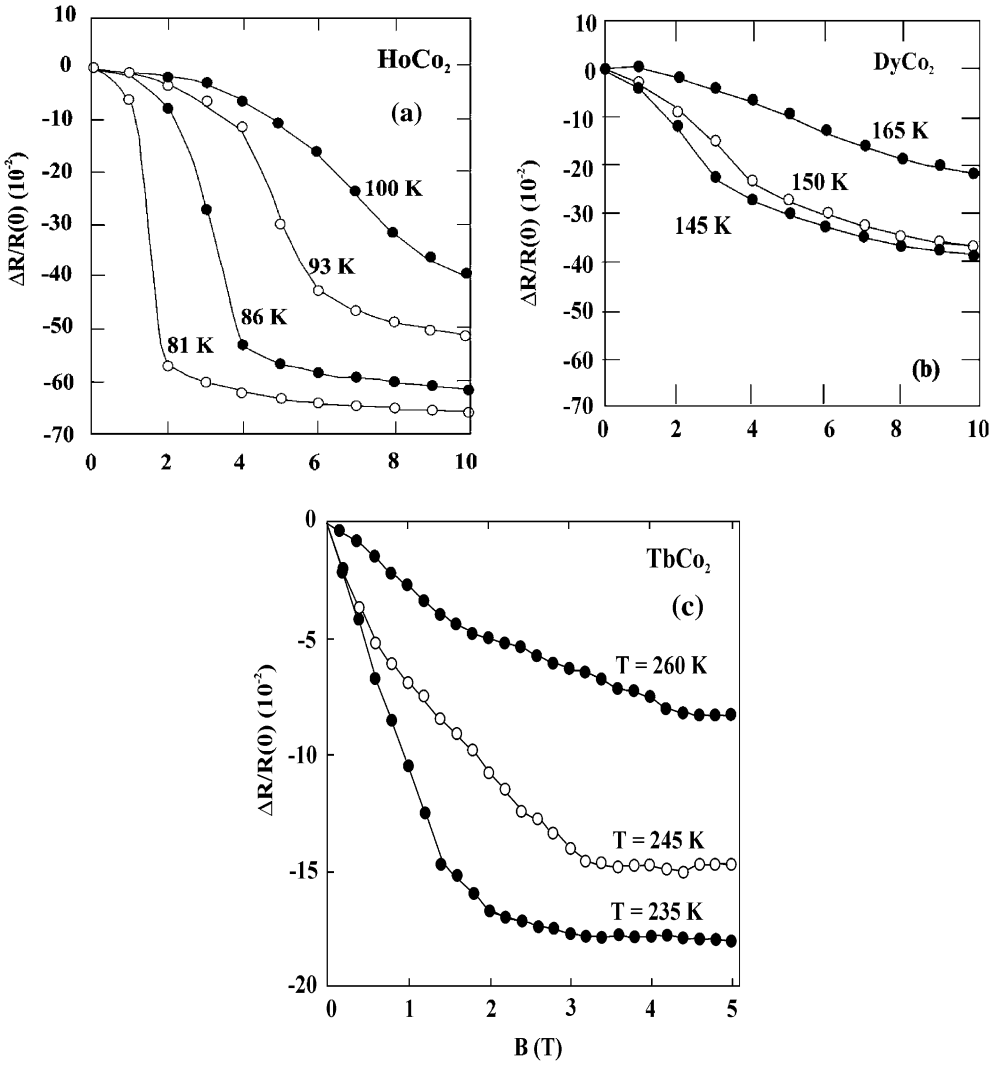

Fig. 3. Magnetoresistance at $T > T_C$ for RCo_2, for R = Ho (a), Dy (b) and Tb (c).

effect. $\Delta R_{4f}(B,T)$ is a negative 4f-spin disorder scattering contribution. $\Delta R_{sf}(B,T)$ is a negative contribution due to the quenching of spin fluctuations.

In view of the remark above that the 4f-spin disorder scattering contribution, $\Delta R_{4f}(B,T)$, probably plays a minor role, and in view of the observed positive sign of $\Delta R_{3d}(B,T)$, we may conclude that the drop in resistance, $\Delta R(B,T)$, in applied magnetic fields is due to the suppression of the spin fluctuations. The temperature dependence, i.e. the decrease and smoothing of the resistance drop, can be understood by recalling that in RCo_2 compounds with a magnetic 4f-ion, such as $ErCo_2$, $HoCo_2$ and $DyCo_2$, for T approaching T_C from above, the spin fluctuation contribution is clearly enhanced with respect to that in ferromagnetic $Y(Co_{1-x}Al_x)_2$ compounds [2,7].

3.3. Magnetocaloric effects

The magnetic entropy change (ΔS_m) was derived from magnetic isotherms $M(T_i,B)$ observed at a

sequence of temperatures T_i. ΔS_m was calculated with Eq. (2), which can be derived by making use of the Maxwell relation $\partial M/\partial T = \partial S/\partial B$ [8,9]:

$$\Delta S_m(T_{av,i}B_2) = \int_{B_1=0}^{B_2}\left(\frac{\partial M(T,B)}{\partial T}\right)T_{av,i}\,dB \approx \frac{1}{T_{i+1}-T_i}\int_0^{B_2}[M(T_{i+1},B) - M(T_i,B)]\,dB, \quad (2)$$

Here, $T_{av,i} = (T_{i+1} + T_i)/2$. ΔS_m can be regarded as a measure for the difference in area under two magnetisation curves as e.g. shown in Fig. 1.

In Figs. 4(a–c), the obtained ΔS_m values are shown for $HoCo_2$, $DyCo_2$ and $TbCo_2$, respectively. Note that, ΔS_m always shows its maximum (ΔS_m^{max}) at or near T_C. For $TbCo_2$, $\Delta S_m^{max} = 6.5\,J/kgK$ for a field change of 5 T ($B_2 = 5\,T$). In addition, ΔS_m is almost symmetric with respect to T_C. This is a general behaviour for materials with a SOT. For $HoCo_2$, that exhibits a FOT, ΔS_m^{max} reaches a huge value of 22.5 J/kgK for $B_2 = 4\,T$. In this compound, ΔS_m falls abruptly just below T_C, but it still has a rather large value in a small temperature range above T_C, where the MMT occurs.

In order to see whether these materials can be used in room temperature MCE applications, samples were prepared of $Gd_{0.4}Tb_{0.6}Co_2$, $Gd_{0.65}Lu_{0.35}Co_2$, and $Gd_{0.65}Y_{0.35}Co_2$ which have Curie temperatures (SOT) of 306, 301 and 301 K, respectively. The results are shown in Fig. 5. These intermetallic compounds show a value of $\Delta S_m^{max} \approx 6\,J/kgK$ for $B_2 = 6\,T$. These entropy changes are comparable to that of Gd metal, which is used as a working material nowadays [4,10].

We also determined ΔS_m for some $R(Co,Si)_2$ compounds (R: Ho, Er; magnetization data were partly published [11,12]; see also Ref. [2]). Fig. 6 illustrates the results obtained for $Er(Co_{1-x}Si_x)_2$ ($x = 0, 0.05$ and 0.15). For $B_2 = 5\,T$, we find $\Delta S_m^{max} = 38\,J/kgK$ for $ErCo_2$ ($T_C = 34.6\,K$). As, for $Er(Co_{0.95}Si_{0.05})_2$, the ordering temperature

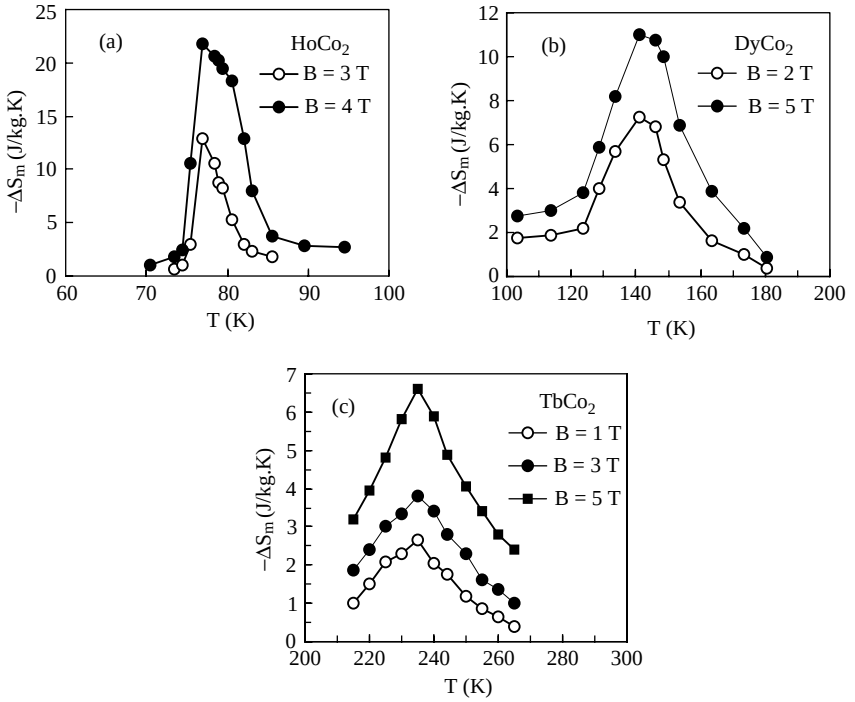

Fig. 4. $\Delta S_m(T,B)$ vs. T for $HoCo_2$ (a) $DyCo_2$, (b) and $TbCo_2$, (c) for various field changes B.

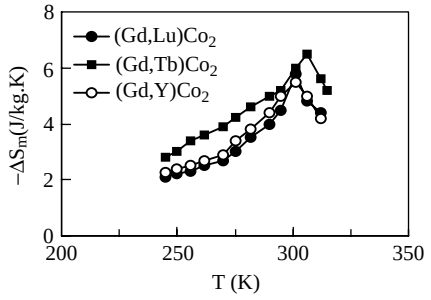

Fig. 5. $\Delta S_m(T,B)$ vs. T for $Gd_{0.4}Tb_{0.6}Co_2$, $Gd_{0.65}Lu_{0.35}Co_2$, $Gd_{0.65}Y_{0.35}Co_2$ for a field change $B = 6\,T$.

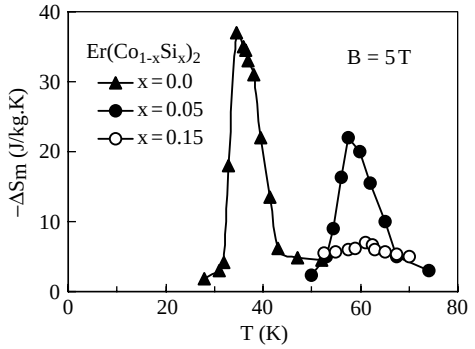

Fig. 6. $\Delta S_m(T,B)$ vs. T for $Er(Co_{1-x}Si_x)_2$ for a field change $B = 5\,T$.

increases to 60 K, ΔS_m^{max} decreases to 22 J/kgK. A dramatic reduction is observed for $Er(Co_{0.85}Si_{0.15})_2$ ($\Delta S_m^{max} = 8\,J/kgK$), although the ordering temperature is only slightly higher. Since the latter compound exhibits a SOT, and the other ones a FOT, we tried to clarify whether this reduction is related to the nature of the magnetic phase transitions. Therefore we estimated and collected ΔS_m^{max} for a large number of RCo_2, $(R,R')Co_2$, $(R,Y)Co_2$ and $R(Co,Si)_2$ compounds (Fig. 7). Moreover, we included some literature data [7] for $(R,R')Al_2$ (with a SOT). Apparently, for these intermetallic systems, ΔS_m^{max} exhibits quite generally the tendency to increase with decreasing temperature. For temperatures below 200 K, ΔS_m^{max} ($RR'Al_2$) is much smaller than the corresponding $\Delta S_m^{max}(RCo_2)$, e.g. at $T_C = 35\,K$, $[\Delta S_m^{max}(RCo_2) - \Delta S_m^{max}(RR'Al_2)] \approx 20\,J/kgK$. This large difference may be imagined to be related to

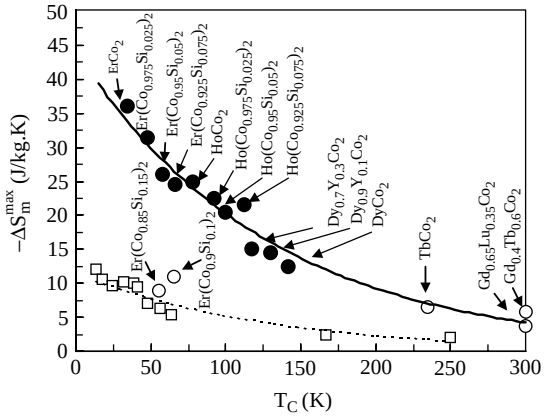

Fig. 7. ΔS_m^{max} vs. T_C of RCo_2-based compounds (filled circles—FOT, open circles—SOT) and $(R,R')Al_2$-based compounds (open squares—SOT; [7]) for a field change of 5 T.

either the nature of the transition (FOT or SOT) or to quenching of spin fluctuations (typically enhanced in RCo_2). It was indicated that the quenching of spin fluctuations reduced the electronic entropy $\Delta S_e = \Delta\gamma T$, where γ is the electronic specific heat constant. From the change of the electronic specific heat $\Delta\gamma$ at the MMT, for which data were collected in Refs. [2,3] for several $Y(Lu)Co_2$ related compounds, it turns out that the electronic contribution to the entropy change is less than 3 J/kgK. Such a contribution is rather small with respect to the above mentioned entropy difference between RCo_2 and other rare earth intermetallics. Therefore, the giant MCE observed in RCo_2 with low ordering temperature can be related to the occurrence of a FOT. The dramatic reduction of ΔS_m^{max} for the $Er(Co,Si)_2$ compounds with a SOT, does support this argument: experimental data of these compounds seem to fit well in the variation of ΔS_m of the $(R,R')Al_2$ compounds (see Fig. 7).

4. Final remarks

In conclusion, we have observed the formation of 3d-magnetic moments under an MMT and the quenching of spin fluctuations above the FOT not only by magnetisation measurements, but also by magnetoresistance measurements for a number of

RCo_2 compounds. The resistance in the RCo_2 is influenced by several parameters. According to our analysis, however, the suppression of the magnetoresistance is mainly due to quenching of spin fluctuations. The magnetoresistance at the MMT, thus, can be considered as an useful way to measure the effects of spin fluctuations in the investigated compounds.

The MCE in RCo_2 is mainly governed by the nature of the magnetic phase transition, or, more generally, by the occurrence of a sharp transition. For the RCo_2 compounds, the occurrence of a FOT is caused by the metamagnetic behaviour of the Co subsystem. In case there is a FOT indeed, the MMT is still a sharp transition in a certain temperature range above T_C. Hence, an appreciable MCE can be observed there too. In the Inoue–Shimizu like models (as disscussed in Ref. [2]), the negative c_3 value (necessary for an MMT as mentioned above) results from the competition between a negative contribution of the metamagnetic Co subsystem and a positive contribution of the local moment system. This inherently positive contribution increases with increasing temperature. So, it can be understood that at high temperatures a FOT is difficult to achieve.

The size of the MCE observed in $(R,R')Co_2$ compounds with a SOT at room temperature is comparable to that of pure Gd metal. The intermetallics, however, are of lower cost. Moreover, the transition temperature can be modeled by adapting the constitution of the compound. Thus, these compounds are very promising for magnetic refrigeration applications.

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References

[1] N.H. Duc, T. Goto, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 28, North-Holland, Amsterdam, 1999, p. 177 (Chapter 171).
[2] N.H. Duc, P.E. Brommer, in: K.H.J. Buschow (Ed.), Handbook on Magnetic Materials, Vol. 12, North-Holland, Amsterdam, 1999, p. 259 (Chapter 3).
[3] T. Goto, H. Aruga, T. Sakakibara, H. Mitamura, K. Fukamichi, K. Murata, J. Appl. Phys. 76 (1994) 6682.
[4] N.H. Duc, J. Magn. Magn. Mater. 131 (1994) 224.
[5] N.H. Duc, P.E. Brommer, X. Li, F.R. de Boer, J.M.M. Franse, Physica B 212 (1995) 83.
[6] M. Foldeaki, A. Giguere, R. Chahine, T.K. Bose, Adv. Cryogenic Eng. 43 (1998) 1533.
[7] N.H. Duc, T.D. Hien, P.P. Mai, P.E. Brommer, Physica B 172 (1991) 339.
[8] M.A. Tishin, in: K.H.J. Buschow (Ed.), Handbook on Magnetic Materials, Vol. 12, North-Holland, Amsterdam, 1999, p. 395 (Chapter 4).
[9] V.K. Pecharsky, K.A. Gschneidner Jr., J. Appl. Phys. 86 (1999) 565.
[10] B. Tegus, E. Brück, K.H.J. Buschow, F.R. de Boer, Nature 415 (2002) 150.
[11] N.H. Duc, T.K. Oanh, J. Phys.: Condens. Matter 151 (1997) 1585.
[12] T.D. Cuong, N.H. Duc, P.E. Brommer, Z. Arnold, J. Kamarad, V. Sechovski, J. Magn. Magn. Mater. 182 (1998) 143.