

# MAGNETIC AND MAGNETOCALORIC PROPERTIES OF $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$ COMPOUNDS WITH $x \leq 0.3$

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The magnetic properties of  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds with  $x \leq 0.3$  were studied in a large temperature range and fields up to 12 T. Band structure calculations were also performed. The complex and interdependent exchange interactions, at the level of unit cell, are discussed. The cobalt magnetic behaviour above the Curie temperature, has been analysed in the spin fluctuations model. High entropy changes were shown when the compounds show first order magnetic transitions. The specific renormalized cooling powers decrease as the erbium is gradually replaced by yttrium.

*Key words:* rare-earth compounds, magnetic properties, magnetocaloric effects.

## 1. INTRODUCTION

The  $\text{ErCo}_2$  compound, above the Curie point,  $T_c$ , has a cubic  $\text{Fd}\bar{3}\text{m}$  type structure [1]. Below  $T_c$ , the structure is rhombohedrally distorted, the space group being  $\text{R}\bar{3}\text{m}$ . In this lattice, the cobalt atoms are located at 3b and 9e sites. The difference between their magnetic moments is of the order of experimental errors and thus, from magnetically point of view, the presence of only one cobalt site can be considered. The cobalt magnetic moment is of  $1 \mu_B$  and that of erbium of  $9 \mu_B$ , as expected from  $g_J J$  value [2, 3]. The magnetic transition is of first order. A sequential collapse of cobalt magnetization was shown, as pressure increases [3–5]. Above the Curie point, the reciprocal susceptibilities follow a non-linear temperature dependence, as expected for a ferrimagnetic-type ordering [5, 6].

The  $\text{YCo}_2$ , at low temperatures, is an exchange enhanced paramagnet. Above  $T^* = 550 \text{ K}$ , the magnetic susceptibility follows a Curie-Weiss type dependence, as predicted by the spin-fluctuations model. The effective cobalt moment is close to that of free  $\text{Co}^{2+}$  ion [7].

The magnetic properties of  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  were studied, particularly below the magnetic ordering temperature. As function of yttrium content, the cobalt moments decrease and the magnetic transitions change from first order, to second order, at  $x = 0.3$  [8]. Two separate transitions of Er and Co magnetic sublattices were evidenced for a sample with  $x = 0.4$  [9]. The same magnetic ordering temperatures, for the two sublattices, have been shown for  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds with  $x \leq 0.6$  [10, 11].

In this paper, the magnetic properties of  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds with  $x \leq 0.3$ , are analysed in a large temperature range, including paramagnetic region. Band structure calculations were also made. The Er5d and Y4d band polarizations are analysed in correlation with cobalt moments. The entropy changes decrease as the erbium is substituted by yttrium, particularly for alloys which show a second order type magnetic transition.

## 2. EXPERIMENTAL AND COMPUTING METHOD

The  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds with  $x \leq 0.3$  were prepared by melting the high-purity elements in an induction furnace under high purity argon atmosphere. In order to avoid the formation of other phases richer in cobalt, as result of Er(Y) loss during melting, an initial atomic ratio  $\text{Er(Y)}/\text{Co} = 1/1.95$  has been used. The samples were thermally treated at  $T = 900$  °C, in vacuum, for one week. The X-ray diffraction patterns evidenced the presence of only one phase. The lattice parameters, determined at room temperature, show a Vegard-type dependence – Fig. 1.

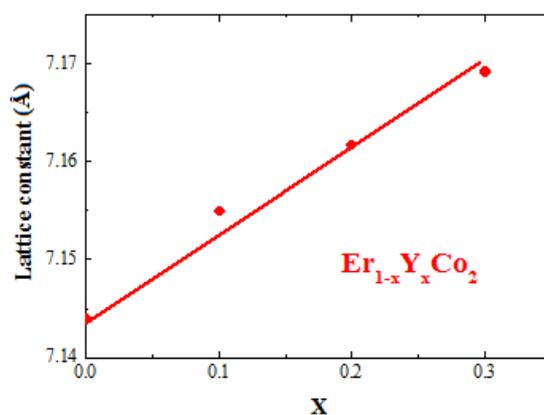


Fig. 1 – Composition dependence of lattice parameters.

The magnetic measurements were generally performed in the temperature range 4 K–800 K, in fields up to 12 T. The end series compounds were studied in a larger temperature range ( $T < 1150$  K). The spontaneous magnetizations,  $M_s$ , were

determined from magnetization isotherms, according to approach to saturation law,  $M = M_s(1 - a/H) + \chi_0 H$ . By  $a$  is denoted the coefficient of magnetic hardness and  $\chi_0$  a field independent susceptibility. Above the Curie points, the susceptibilities were determined from their field dependences [12, 13]. No magnetic ordered phases, above  $T_c$ , were evidenced.

The entropy changes have been determined from magnetization isotherms, by using Maxwell relation.

The ground state electronic structures were analysed by using tight binding linear muffin tin orbital method (TB-LMTO) in the atomic sphere approximation (ASA). In the framework of the local density approximation (LDA), the total electronic potential is the sum of the external, Coulomb and exchange correlation potentials [14]. The functional form of the exchange correlation energy, used in the present work, was the free electron-gas parametrization of von Barth and Hedin [15]. Relativistic correlations are included without spin-orbit coupling. We note that the addition of Hubbard term to 4f- and 3d-electrons in computing the band structure, shifts the 4f-sates in the right energy positions, however does not change significantly the cobalt magnetic moments.

### 3. MAGNETIC PROPERTIES

The temperature dependences of magnetizations of zero field cooled (ZFC) and field cooled (FC)  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds with  $x = 0$  and 0.3 are given Fig. 2. The differences observed in their temperature evolution can be attributed to the anisotropies and/or domain structures. The anisotropy field decreases when increasing yttrium content. The easy direction of magnetizations is the [111] axis.

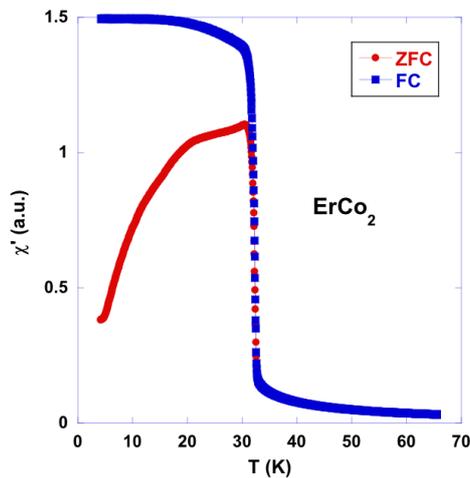


Fig. 2

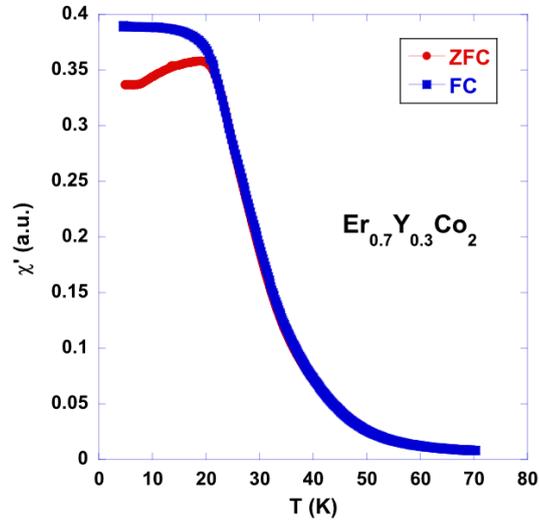


Fig. 2 (continued) – Temperature dependences of magnetizations in a field of 0.5 T, for samples with  $x = 0$  and  $x = 0.3$  field cooled (FC) and zero field cooled (ZFC).

The magnetization isotherms of  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  samples, with  $x = 0$  and 0.2, are plotted in Fig. 3. The compounds are ferrimagnetically ordered. The magnetizations decrease when erbium is substituted by yttrium. Assuming a two sublattices ferrimagnet and  $M_{\text{Er}} = 9 \mu_{\text{B}}$ , as obtained by neutron diffraction studies, the cobalt moments were determined. These values decrease gradually, as result of magnetic dilution, from  $1.0 \mu_{\text{B}}$  ( $x = 0$ ) up to  $0.75 \mu_{\text{B}}$  ( $x = 0.3$ ) – Fig. 4. The above determined  $M_{\text{Co}}$  values are in agreement with those previously reported [8].

The thermal variations of reciprocal susceptibilities,  $\chi^{-1}$ , show a non-linear behaviour characteristic for ferrimagnetic systems – Fig. 5. Above  $T^* \cong 550$  K, in the asymptotic region, linear dependences are shown. Assuming that the effective erbium moment is given by its free ion value [16], the contributions of cobalt atoms to the Curie constants were determined. The effective cobalt moments,  $M_{\text{eff}}(\text{Co})$ , decrease little in the investigated composition range – Fig. 6. Previously [17], a cobalt magnetic moment  $M_{\text{Co}} = 0.2 \mu_{\text{B}}$  has been determined at  $T > T_c$  ( $T \cong \cong 60$  K) in  $\text{ErCo}_2$ . The corresponding effective moment  $M_{\text{eff}}(\text{Co}) = g\sqrt{S(S+1)}$ , taking into account the above spin value,  $S = 0.1$ , is of  $\cong 0.7 \mu_{\text{B}}$ . According to experimental data [7] and spin fluctuations model [18] the effective cobalt moments increase with temperature up to a value  $M_{\text{eff}}(\text{Co}) = 3.65 \mu_{\text{B}}$ , as determined from charge neutrality condition, at  $T > 550$  K. Similar behaviour can be shown also for pseudobinary  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds with  $0.1 \leq x \leq 0.3$ .

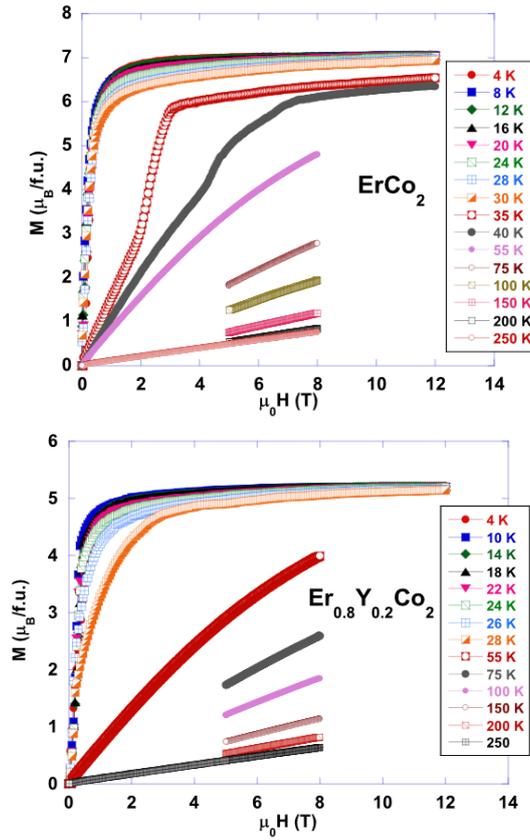


Fig. 3 – Magnetizations isotherms for  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds with  $x = 0$  and  $0.2$ .

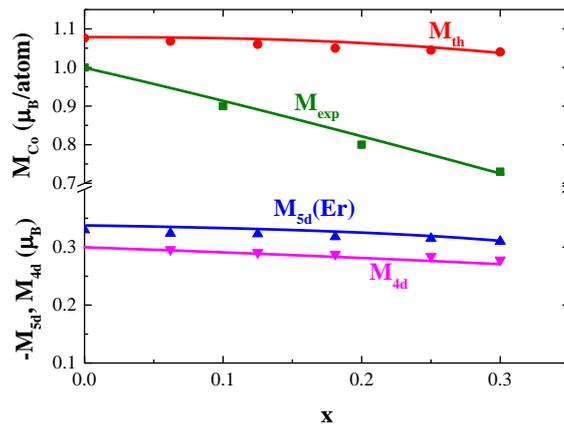


Fig. 4 – Composition dependences of cobalt moments determined at  $T = 4$  K and the values obtained from band structure calculations. The computed Er5d and Y4d bands polarizations are also given.

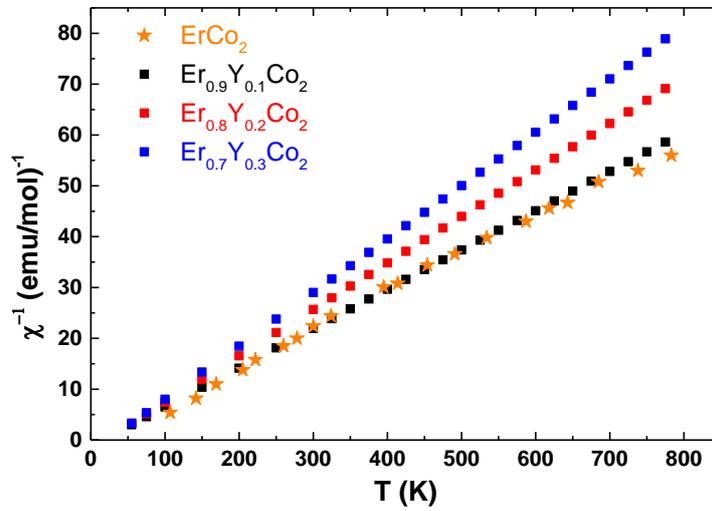


Fig. 5 – Thermal variations of reciprocal susceptibilities.

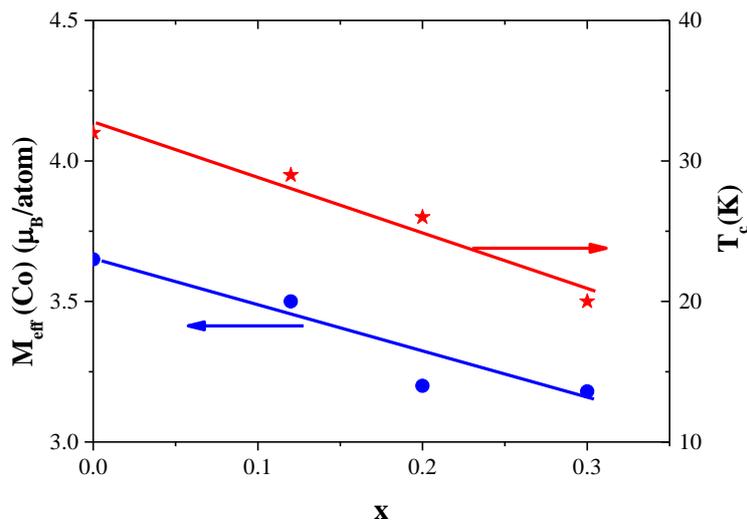


Fig. 6 – Composition dependences of the effective cobalt moments and of Curie temperatures.

Starting from the determined saturation,  $M_{Co} = gS_0$ , and effective cobalt moments,  $M_{\text{eff}}(\text{Co}) = g\sqrt{S_p(S_p+1)}$ , in  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds, the ratios  $r = S_p/S_0$  have been determined. The  $r$  values thus obtained, as well as those determined in  $\text{RCo}_2$  ( $R = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ ) [18] compounds, are plotted in Fig. 7. Their dependence, on the Curie temperatures, seems to be rather well described by a  $T_c^{-2/3}$  law, as predicted by the spin fluctuations model [19, 20].

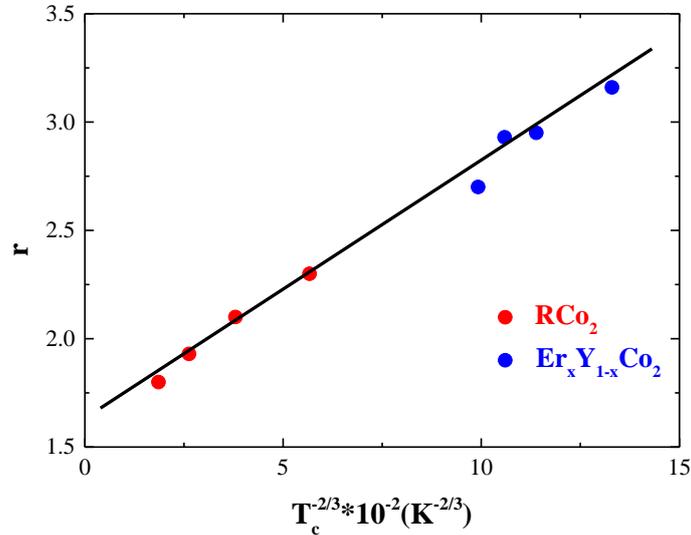


Fig. 7 – The dependence of the ratios  $r = S_p/S_0$  on the Curie temperatures. The  $r$  values determined in  $\text{RCo}_2$  ( $\text{R} = \text{Gd, Tb, Dy, Ho}$ ) [18] are also given.

#### 4. BAND STRUCTURE CALCULATIONS

The cobalt moments, determined from band structure calculations, show a smaller decrease when increasing yttrium content than the experimentally determined values and are little higher – Fig. 4. The experimental data were obtained from saturation magnetizations, assuming  $M_{\text{Er}} = 9 \mu_B$ . Band structure calculations evidence an induced polarization on R5d band, parallelly oriented to the rare-earth moments. If the above polarization is taken into account the cobalt moments can be by  $0.13\text{--}0.16 \mu_B$  higher, and more close to those calculated.

The Er5d band polarizations,  $M_{5d}$ , are higher by  $0.04 \mu_B$  than the polarization induced on Y4d band,  $M_{4d}$ . The difference can be attributed to the contribution of the local 4f–5d exchange, which amounts at  $0.05 \mu_B$  in  $\text{ErCo}_2$  [21]. The above value,  $M_{5d}(f)$ , was shown to be not influenced for a given structure type, in  $\text{RM}_x$  compounds, by the transition metal partner, M, or magnetic dilutions at R or M sites. The ratios  $(M_{5d}(d) \text{ or } M_{4d}) / \sum_i z_i M_{\text{Co}_i}$  where  $z_i$  is the number of magnetic atoms situated in a first coordination shell to an R one and  $M_{\text{Co}_i}$  their magnetic moments is of  $(2.15 \pm 0.10) \cdot 10^{-2}$ . This value is nearly the same as that already evidenced in  $\text{RM}_2$  ( $\text{M} = \text{Fe, Co, Ni}$ ) – based compounds [21, 22] and seems to be a constant parameter for the cubic Laves phase type structure [23, 24].

The exchange interactions in  $\text{RCO}_2$  compounds are rather complex and interdependent. The exchange interactions between R and Co atoms are of 4f–5d–3d type while those between cobalt atoms are of short range. Since the high extension of R5d orbitals, short range interactions between rare-earths are also present [25], in addition to those by means of conduction electrons. The induced cobalt moment by 4f–5d–3d exchange path is stabilized by Co3d–Co3d short range exchange interactions. Concomitantly, an additional polarization,  $M_{5d}(d)$ , to that resulting from 4f–5d local interaction  $M_{5d}(f)$ , is induced on R5d band. The changes of  $M_{5d} = M_{5d}(f) + M_{5d}(d)$  total band polarizations and of cobalt moments, respectively take place both when replacing a magnetic rare-earth by a nonmagnetic element or of cobalt by small magnetic/non-magnetic atoms. In the first case, the  $M_{5d}(f)$  contribution to  $M_{5d}$  band polarization is not affected by substitution but implies, for a magnetic R atom, a higher number of cobalt atoms connected by 5d–3d interactions. In the second case, as the cobalt sublattice magnetization is diminished, as for example in  $\text{Gd}(\text{Co}_x\text{Ni}_{1-x})_2$  compounds [22, 26], the cobalt moment is stabilized by Co3d–Co3d interactions to a smaller value than that of the end series compound ( $x = 1$ ). These can be correlated also with the diminution of  $M_{5d}(d)$  contribution to R5d band polarization. In this way the exchange field acting on cobalt is also altered. The values of cobalt magnetic moments and the R5d band polarizations are strongly interconnected. Thus, the cobalt moment is the result of a type of “equilibrium”, at the level of unit cell, between R5d band polarizations and transition metal sublattice moment, as resulting from the complex and interdependent magnetic interactions.

## 5. MAGNETOCALORIC EFFECTS

The entropy changes,  $\Delta S$ , in  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds, were computed from magnetization isotherms and successive values of the external field. In this case, the Maxwell equation can be approximated by the relation [27, 28]:

$$\Delta S = \sum_i (M_{i+1} - M_i) \Delta H_i / (T_{i+1} - T_i). \quad (1)$$

By  $M_{i+1}$  and  $M_i$  are denoted the magnetizations measured in the field  $H$ , at temperatures  $T_{i+1}$  and  $T_i$ , respectively.

The computed entropy changes,  $\Delta S$ , for the  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds with  $x = 0.1$  and  $0.3$  are plotted in Fig. 8. The maxima of  $\Delta S$  are shifted to higher temperatures by  $\Delta T$ , as the external field increases. The  $\Delta T/\Delta H$  values decrease from 2.4 K/T ( $x = 0$ ) to 0.4 K/T ( $x = 0.1$ ) and 0.1 K/T ( $x = 0.3$ ) as the yttrium content increases.

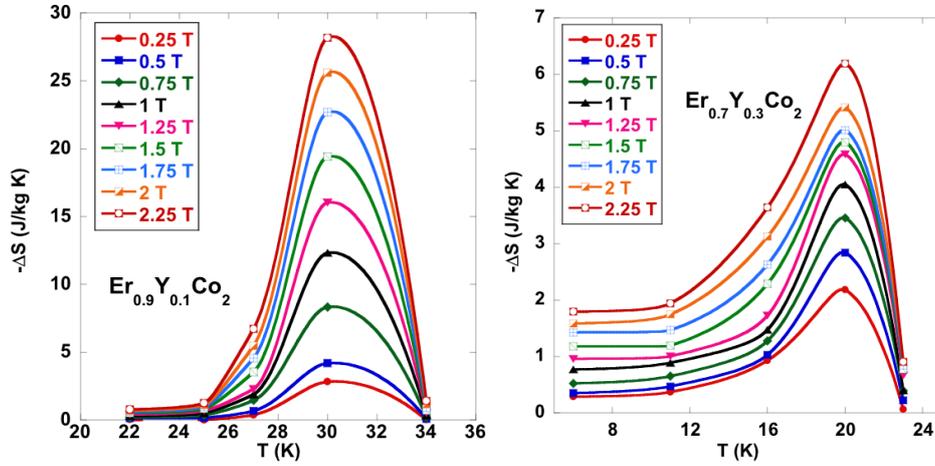


Fig. 8 – Field and temperature dependences of the entropy changes in compounds with  $x = 0.1$  and  $0.3$ .

The maxima of the entropy changes,  $\Delta S_{\text{max}}$ , decrease parallelly when increasing yttrium content, from 32 J/kgK in  $\text{ErCo}_2$  up to  $\cong 7$  J/kgK in  $\text{Er}_{0.7}\text{Y}_{0.3}\text{Co}_2$  compound. Higher  $\Delta S_{\text{max}}$  values are evidenced in samples which show first order magnetic transitions. The maxima in entropy changes, at  $H > 1$  T, follow a  $H^{2/3}$  field dependence, in agreement with the prediction of mean-field model [29, 30] – Fig. 9.

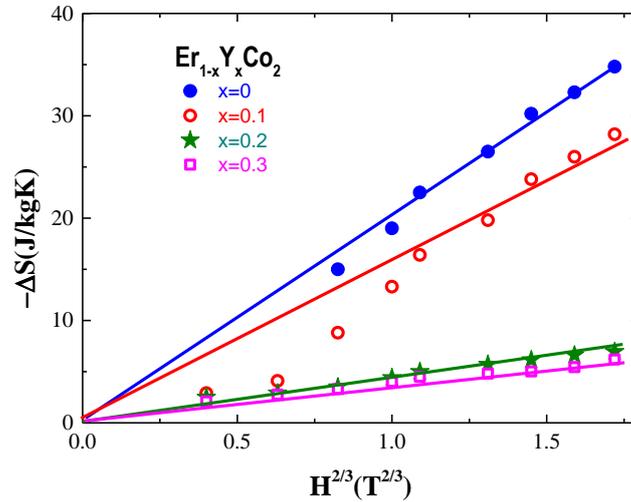


Fig. 9 – Field dependences of  $\Delta S_{\text{max}}$ , the maxima of the entropy changes, in  $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$  compounds with  $x \leq 0.3$ .

The relative cooling power  $RCP(\Delta S) = |\Delta S_{\max}| \delta T_m$ , defined as the product of the maximum value of the entropy change  $|\Delta S_{\max}|$  and the full-width at half maximum,  $\delta T_m$ , measures the amount of heat transfer between the cold and hot reservoirs in an ideal refrigerant cycle [31]. Values of  $\cong 130$  J/kg were evidenced in  $Er_{0.9}Y_{0.1}Co_2$ , these decreasing up 42 J/kg for the sample with  $x = 0.3$ , in a field of 2.25 T. The  $RCP(\Delta S)$  are smaller than those reported in gadolinium metal [32] or in  $Gd_5Ge_2Si_2$  compound [33]. More convenient is to characterize the magnetocaloric material when using the specific renormalized cooling power, defined as  $RCP(\Delta S)/\Delta H$ , relative to the external field variations. For a given composition,  $x$  in  $Er_{1-x}Y_xCo_2$ , these values are rather constant, decreasing when increasing yttrium content. As example, the  $RCP(\Delta S)/\Delta H$  values are of  $\cong 61$  J/kgT for  $x = 0.1$  and 20 J/kgT for the sample with  $x = 0.3$ .

## 6. CONCLUSIONS

The  $Er_{1-x}Y_xCo_2$  compounds with  $x \leq 0.3$  are ferrimagnetically ordered. The cobalt moments decrease when Er is replaced by Y, behaviour connected with the complex and interdependent magnetic interactions at the level of unit cell. The induced cobalt moment by 4f–5d–3d exchange path is stabilized by Co3d–Co3d short range exchange interactions, the induced  $M_{5d}(M_{4d})$  band polarizations, respectively.

Above the Curie temperatures cobalt shows a spin fluctuations type behaviour. As function of temperature, the effective cobalt moment in  $ErCo_2$  increases from  $\cong 0.70 \mu_B$  ( $T \cong 60$  K) up to  $3.65 \mu_B$  at  $T > 550$  K. Similar behaviour is evidenced also in pseudobinary  $Er_{1-x}Y_xCo_2$  compounds with  $0.1 \leq x \leq 0.3$ . The evolution with temperature of the ratios  $r = S_p/S_o$  between the number of spins determined from effective cobalt moment and the saturation one follows a relation  $r \propto T_c^{-2/3}$ , as predicted by spin fluctuations model.

The entropy changes in  $Er_{1-x}Y_xCo_2$  series are considerable higher for compounds which show first order magnetic transition. The  $\Delta S_{\max}$  values follow a  $H^{2/3}$  dependence, for  $H > 1$  T, in agreement with the prediction of mean field model.

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