# Magnetic and magnetocaloric properties of some ferrimagnetic compounds

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The magnetocaloric effects in RCo<sub>2</sub>, where R is a heavy rare–earth, GdAl<sub>2</sub>, GdNi<sub>5</sub>, (Gd<sub>x</sub>Y<sub>1-x</sub>)<sub>2</sub>Co<sub>7</sub>B<sub>3</sub> and RFe<sub>2</sub> (R=Y,Er) compounds are analysed in correlation with magnetic properties. In case of ferrimagnetic compounds, when rare-earth and transition metal sublattice magnetizations are strongly coupled, the high values of entropy change can be seen at the Curie temperatures. When the strength of this coupling is relatively, small, there is a high variation of rare-earth sublattices magnetizations and consequently the maxima values of the entropy changes are evidenced at lower temperatures than the Curie points. In these cases there are large linewidth,  $\delta T_m$ , of the  $\Delta S$  vs. T dependences and consequently high values of the specific renormalized cooling power are shown.

(Received April 14, 2010; accepted May 26, 2010)

Keywords: Rare-earth compounds, Magnetic properties, Magnetocaloric effect

### 1. Introduction

The magnetocaloric effect is an intrinsic property of the magnetic materials, induced via the coupling of the magnetic system with an applied magnetic field. The magnetocaloric effect (MCE) is characterized by production or absorption of heat by a magnetic material under the action of a magnetic field. According to the relation

$$dT = -\frac{T}{c_{H,P}} \left(\frac{\partial M}{\partial T}\right)_{H,P}$$

the adiabatic temperature change is directly proportional to the partial derivative of the magnetization, M, versus temperature, where  $c_{H,p}$  is the heat capacity at constant magnetic field, H and pressure, p. The magnetocaloric effect is measured in terms of isothermal magnetic entropy change and/or adiabatic temperature change [1,2].

Materials having large magnetic entropy change,  $\Delta S$ , have attracted attention for their potential applications as magnetic refrigerants. The MCE has been studied in connection with magnetic refrigeration both in paramagnetic salts and magnetic ordered systems. The salts are used commonly to obtain low temperatures (T<15 K), while the magnetic ordered materials can be used for magnetic refrigeration, at higher temperatures (T>25 K).

Large magnetic entropy changes have been observed at the magnetic phase transitions, particularly in materials showing first order transition. An intense studied system is that involving rare–earth (R)–cobalt compounds, RCo<sub>2</sub>, having Laves phase structure [3–16]. From magnetic point of view, this system shows interesting properties [17,18]. The YCo<sub>2</sub> and LuCo<sub>2</sub>, show spin fluctuation behaviour. At low temperatures (T<15 K), the magnetic susceptibilities follow a T<sup>2</sup> dependence. Above a characteristic temperature T\*. a Curie–Weiss behaviour was shown. At a critical field of  $\approx$  70 T, a cobalt ordered moment is induced. Also, by increasing the exchange field, as result of Y or Lu substitution by a magnetic rare-earth, a cobalt moment of  $\cong$ 1  $\mu_{\rm B}$ /Co atom was shown in heavy rare earth compounds [19]. In pseudobinary compounds, of (Y,R)Co<sub>2</sub> type, the determined cobalt moment increases linearly with the internal [20] or external [21] field. The RCo<sub>2</sub> compounds, where R is a heavy rare-earth are ferrimagnetically ordered. A first order magnetic transition was shown when R=Er,Ho,Dy and a second order type for R=Gd,Tb,Tm [17]. In these materials, the temperature width in which large entropy change is shown, is rather narrow and located around the Curie points,  $T_c$ . The working materials which show large magnetic entropy change near T<sub>c</sub>, are not suitable for use in devices using the Ericsson cycle [22]. In these devices, magnetic refrigerants with large MCE, in a relative wide temperature range are of interest. A parameter characteristic for the magnetocaloric materials is the relative cooling power, RCP(S) =  $|\Delta S_m|\delta T_m$ , defined as the product of the maximum value of the entropy change  $|\Delta S_m|$ and the full width at half maximum,  $\delta T_m$ . A large RCP(S) value corresponds to a better magnetocaloric material. It has been also suggested that more convenient for characterizing magnetocaloric materials is to use the value of the specific renormalized cooling power, defined as  $RCP(S)/\Delta H$ , relative to external field variation  $\Delta H$ .

In a previous paper [23], we showed in  $(Gd_xY_{1-x})_3Co_{11}B_4$  compounds, large width,  $\delta T_m$ , in which entropy changes are rather great. In this paper we report the same type behaviour for  $(Gd_xY_{1-x})_2Co_7B_3$  system, as well as in ErFe<sub>2</sub>. In addition, the magnetocaloric effect in GdAl<sub>2</sub> and RCo<sub>2</sub> with R=Gd,Tb,Dy,Ho,Er and Tm compounds are

discussed. In case of  $GdNi_{5}$ , relative large  $\delta T_m$  value has been shown around the Curie temperature.

#### 2. Experimental

The RCo<sub>2</sub> (R=Gd,Tb,Dy,Ho,Er,Tm), RFe<sub>2</sub> (R=Er,Y) GdAl<sub>2</sub>, GdNi<sub>5</sub> and (Gd<sub>x</sub>Y<sub>1-x</sub>)<sub>2</sub>Co<sub>7</sub>B<sub>3</sub> were prepared by levitation method [17,24–28]. After corresponding thermal treatments, the X–ray diffraction studies evidenced the presence of a single phase, having crystal structure in agreement with literature data. The magnetic measurements were performed in large temperature ranges and in fields up to 2.7, 5 and 7 T, respectively. The magnetizations isotherms for RCo<sub>2</sub>, GdAl<sub>2</sub> and GdNi<sub>5</sub> were analysed around the Curie points. Also, has been studied the pressure dependences of the Curie temperatures [24] or their field dependences.

By using the molecular field approximation, the temperature dependences of sublattice magnetizations, in ferrimagnetic compounds, were analysed and correlated with entropy changes.

The entropy changes have been determined from magnetization isotherms, according to Maxwell relation,  $\Delta S(T,0\rightarrow H) = \int_{0}^{H} \left(\frac{\partial M}{\partial T}\right)_{H} dH.$  From magnetization isotherms,

obtained at constant temperature and successive values of the applied field, H, with steps  $\Delta H_i$ , the Maxwell equation, can be approximated by the relation [1,2]:

$$\Delta S = \sum_{i} \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i$$
(1)

The entropy changes were also evaluated from Clapeyron relations:

$$\Delta S = -\frac{\Delta M}{\left(\frac{\partial T_{c}}{\partial T}\right)}$$
(2)

and

$$\Delta S = -\frac{\Delta V}{\left(\frac{\partial T_{\rm C}}{\partial p}\right)} \tag{3}$$

The  $\Delta M$  and  $\Delta V$  are the variation of magnetization and of the volume, respectively, at the Curie temperatures. The our previous data for  $\partial T_C / \partial p$  [24] and those reported for  $\Delta V$  [29,30] have been used in estimating  $\Delta S$  values.

#### 3. Magnetic Properties

The temperature dependences of the magnetization and of reciprocal susceptibility for  $GdAl_2$  are plotted in Fig. 1. The temperature dependence of the magnetization is rather well approximated by a Brillouin function with S=7/2. The effective magnetic moment per formula unit is higher than that of Gd ion. This suggests a strong polarization of the electron conduction band.



Fig.1. Temperature dependences of magnetization and of reciprocal susceptibilities in GdAl<sub>2</sub> compound.



Fig.2. Temperature dependences of the resultant and sublattices magnetizations

The temperature dependences of the resultant and sublattices magnetizations in GdCo<sub>2</sub>, DyCo<sub>2</sub> and HoCo<sub>2</sub> compounds are shown in Fig.2. For HoCo2, a typical behaviour for first order magnetic transition is shown. This is not so evident for DyCo2, where also a first order transition is reported. The GdCo2 compound shows a second order magnetic phase transition. The exchange interactions between R and Co sublattices can be described as being of 4f-5d-3d type [31]. The 5d band polarizations decrease linearly as function of De Gennes factor from Gd to Tm [32]. The exchange interactions between R and Co sublattices, in RCo2 system, are relative high. For example in GdCo<sub>2</sub> ( $J_{Gd-Co}/J_{Co-Co}$ )=0.37 and  $J_{GdGd}/J_{Co-Co}$ =0.18. Thus, the temperature dependence of gadolinium sublattice magnetization varies rather smoothly. Similar results are obtained in case of DyCo2 compound.

The field dependences of the Curie temperatures in some RCo<sub>2</sub> compounds are shown in Fig.3. In the relative low field regions, these seems to be nearly linear. The slopes of these dependences are shown in inset. As the Curie temperatures decrease, the  $\Delta T_C/\Delta H$  values are smaller. We note that the values obtained for ErCo<sub>2</sub> and HoCo<sub>2</sub> are somewhat smaller than those previously reported [29].



Fig. 3. Field dependences of the Curie temperatures in some  $RCo_2$  compounds. In inset is shown the  $\Delta T_C/H$  values as a function of Curie temperatures.



Fig. 4. Magnetization isotherms for DyCo<sub>2</sub> (a), ErCo<sub>2</sub> (b), GdNi<sub>5</sub> (c) and ErFe<sub>2</sub> (d) compounds.

Some magnetization isotherms obtained in case of  $DyCo_2$ ,  $ErCo_2$  GdNi<sub>5</sub> and  $ErFe_2$ , particularly around the magnetic phase transition, are given in Fig.4. Typical dependences for first order magnetic transition can be seen in case of  $ErCo_2$ .



Fig. 5.Temperature dependences of the resultant and sublattices magnetizations in GdNi<sub>5</sub> compound.

The thermal variations of of resultant and sublattices magnetizations of GdNi<sub>5</sub> are plotted in Fig.5. A small magnetic moment, of the order of 0.20  $\mu_B$ /atom, is induced on nickel. Since of small value of nickel moment, the resultant magnetization is determined mainly by that of gadolinium [27,33]

In RNi<sub>5</sub> compounds, nickel shows a spin fluctuation behaviour [27,33]. For YNi<sub>5</sub> and LaNi<sub>5</sub> a similar temperature dependence of the magnetic susceptibilities as for YCo<sub>2</sub>, but with a smaller effective nickel moment, was evidenced.

The ErFe<sub>2</sub> compound is ferrimagnetically ordered. The erbium sublattice magnetization, shows a high decrease in the temperature range 100–250 K, while that of iron is only little modified in the above temperature range, as showed from magnetization isotherms and the temperature dependences of the sublattices magnetizations –Fig.6. The temperature dependence of iron sublattice magnetization in ErFe<sub>2</sub> and that of YFe<sub>2</sub>, in reduced coordinates, M(T)/M(0) versus T/T<sub>c</sub>, are close to that described by a Brillouin function with S=1/2. In ErFe<sub>2</sub> system there is a compensation point at T<sub>co</sub>=490 K. The thermal variation of resultant magnetization, up to 300 K is determined mainly by that by erbium one.



Fig. 6. Temperature dependences of the resultant and sublattices magnetizations in ErFe<sub>2</sub> compound.

The temperature dependences of resultant magnetizations in (Gd<sub>x</sub>Y<sub>1-x</sub>)Co<sub>7</sub>B<sub>3</sub> compounds, evidenced different types of variations, characteristic for ferrimagnetic systems. According to Néel classification [34] these are of P-type for x=0.2, of N type for x=0.4 and 0.6 and R-type for x=0.8 and 1.0 [35]. The temperature dependences of the resultant and sublattices magnetizations for compounds with x=0.8 and 1.0 are plotted in Fig.7. The cobalt moment is dependent on the gadolinium content, exchange interactions, respectively [35]. As a characteristic feature of M vs T curves, there is the rather high decrease of gadolinium sublattice magnetizations, in the temperature range 50-200 K. This behaviour can be correlated with the relative small values of exchange interaction constants between magnetic sublattices. The evaluation of exchange coefficients, in the molecular interaction field approximation, evidenced values  $|J_{Gd-Co}\!/J_{Co-Co}\!|\!=\!0.14$  and  $|J_{Gd-Gd}/J_{CoCo}|=0.03$ . The gadolinium and cobalt sublattices are not strongly coupled and also the exchange interactions between gadolinium atoms are rather weak. As in case of GdNi<sub>5</sub> [27] we suppose that the Gd–Gd exchange interactions takes place through 5d-5d band polarizations. The thermal variations of resultant magnetizations, at T<300 K, in  $(Gd_xY_{1-x})Co_7B_3$  compounds, are mainly due to that of gadolinium sublattices.



MGd MCo M0

(Gd<sub>0.8</sub>Y<sub>0.2</sub>)<sub>2</sub>Co<sub>7</sub>B

15

10

-5

(b)

M(μ<sub>B</sub>/f.u.)

Fig. 7. Temperature dependences of the resultant and sublattices magnetizations in  $(Gd_xY_{1\cdot x})_2Co_7B_3$  compounds with x=1.0 (a) and 0.8 (b).

#### 4. Magnetocaloric effect

The entropy changes, obtained from magnetization isotherms, according to relation (1) for GdAl<sub>2</sub>, GdCo<sub>2</sub>, ErCo<sub>2</sub> and TmCo<sub>2</sub> are shown in Fig.8. The entropy change in GdAl<sub>2</sub>, in field of 2T, of  $-\Delta S \cong 4J/kgK$ , was shown around the Curie temperature. The half width of  $\Delta S$  vs T is around 10 K. The  $-\Delta S$  value is close to that evidenced in GdCo<sub>2</sub> and TmCo<sub>2</sub>. The linewidth,  $\delta T_m$  in GdCo<sub>2</sub> is near the same as in GdAl<sub>2</sub>, while in TmCo<sub>2</sub> a value  $\delta T_m \cong 6K$  was shown.





Fig. 8. The entropy changes in GdAl<sub>2</sub>(a), GdCo<sub>2</sub> (b), DyCo<sub>2</sub> (c), ErCo<sub>2</sub>(d) and TmCo<sub>2</sub> (e) compounds around the Curie temperatures.

Higher  $|\Delta S|$  values can be shown in compounds having first order magnetic transition, as DyCo<sub>2</sub>, HoCo<sub>2</sub> and ErCo<sub>2</sub>. The  $\delta T_m$  values in these cases are of the order of 3–4 K. The maxima in entropy change  $\Delta S_m$ , are shifted to higher temperatures, as the external filed increase, as shown for ErCo<sub>2</sub> and TmCo<sub>2</sub>. This behavior is in agreement with the field dependences of the Curie temperatures, obtained by magnetic measurements, as evidenced in Fig.3. Since the temperature steps in determining magnetization isotherms for DyCo<sub>2</sub> were greater than for the above compounds, no clear evidence of  $\Delta S_m$  shift can be shown. The entropy changes,  $|\Delta S_m|$  increase, with different slopes, both for RCo<sub>2</sub> compounds showing first order or second order magnetic transition, as the Curie temperatures decrease-Fig.9.



Fig. 9. The entropy changes in  $RCo_2$  compounds as function of Curie temperature. The data estimated from  $\partial T_c/\partial H$  and  $\partial T_c/\partial p$  are also plotted. Values for GdAl<sub>2</sub> and GdNi<sub>5</sub> are also given.

Starting from relations (2) and (3) we estimated the entropy changes in  $RCo_2$  compounds taking into account the  $dT_c/dH$  and  $dT_c/dp$  values. These data are also plotted in Fig.9. The entropy changes, thus determined, are in

agreement with those obtained from magnetization isotherms only in case of DyCo<sub>2</sub>. As the Curie temperatures of the RCo<sub>2</sub> compounds decrease, there is an increased difference as compared to the values obtained from magnetization isotherms, both in compounds which show first order (HoCo<sub>2</sub>,ErCo<sub>2</sub>) or second order (TmCo<sub>2</sub>) magnetic transitions. These differences can be correlated with possible errors in estimating  $\Delta M$  and  $\Delta V$  values.

The high  $|\Delta S|$  values for RCo<sub>2</sub> compounds which show first order magnetic transition, can be correlated with sudden decrease of the magnetizations at the transition temperatures, as discussed in introduction. As the Curie points are lower, the magnetization change up to T<sub>c</sub> is smaller and thus at T<sub>c</sub>, there are higher changes in  $\Delta M$ .

Other mechanisms contributing to entropy changes can be also involved, as for example the fact that cobalt in RCo<sub>2</sub> compounds shows spin fluctuation type behavior. Previously [18,36,37], we showed that in YCo<sub>2</sub> and LuCo<sub>2</sub> there is a change from  $T^2$  dependence of the magnetic susceptibility to a Curie-Weiss type behavior as the temperature increases. The effective cobalt moment is close to that of  $Co^{3+}$  one. When the Y or Lu is replaced by a magnetic reare-earth, there is a gradual quenching of spin fluctuations, evidenced by a decrease of effective cobalt moment, as the exchange field acting on cobalt is higher. A similar effect was shown in YCo2 or LuCo2, in the presence of relative high external fields [38]. The presence of spin fluctuations and their gradual quenching influence little the cobalt ordered magnetic moments. Band structure calculations on RCo<sub>2</sub> compounds with magnetic heavy rare-earths, showed, along series, only small changes, of the order of 2 %, in cobalt moment [32]. This is in agreement with neutron diffraction studies, which evidenced a nearly constant cobalt magnetic moment of  $\cong 1\mu_{\rm B}/{\rm Co}$  atom [19]. Thus, the cobalt magnetization do not influence sesizable the determined  $\Delta S_m$  as evidenced by the near the same values obtained in GdCo<sub>2</sub> and TmCo<sub>2</sub>,both showing second order phase transition.

The  $|\Delta S_m|$  value evidenced in GdNi<sub>5</sub>, around the Curie temperature, is of  $\cong$  12 J/kgK, in field of 7 T–Fig.10. A

larger linewidth of  $\Delta S$  vs T is shown , as compared to RCo<sub>2</sub> compounds, namely  $\delta T_m$ =18 K. Thus, for example, in field of 2T, the RCP(S) is  $\cong 200$  J/kg. In this case the change in magnetization, as the temperature approaches to T<sub>c</sub> is more smoothly than in RCo<sub>2</sub> compounds.



Fig. 10. Entropy changes in GdNi<sub>5</sub> as function of external field.

The somewhat high entropy change in YFe<sub>2</sub> can be seen only at Curie temperature–Fig.11a. This is due only to changes in iron magnetization. A different behavior has been shown in ErFe<sub>2</sub> compound –Fig.11b. A peak in  $|\Delta S|$ can be seen at T $\cong$ 180 K, temperature much smaller than the Curie point, T<sub>c</sub>=574 K. A value  $|\Delta S_m|$ =14 J/kgK was obtained in field of 2.5 T. The entropy changes keep rather high values in an extended temperature range. Thus, by decreasing or increasing temperature, from the peak value, the entropy change is not very much modified. As a result, in the temperature range 50–300 K, a decrease of 30 % from the peak value can be only shown. Since of high  $\delta T_m$ width, the relative cooling power is of the order of 10<sup>3</sup> J/kg, in field of 2.5 T.

The temperature dependence of the entropy change in  $ErFe_2$  can be correlated with the thermal variation of magnetization. As can be seen from Fig.6, around 150 K, there is a relative high decrease of the erbium sublattice magnetization and consequently that of resultant magnetization. This behavior can be correlated with no so strong exchange coupling between Er and Fe sublattice magnetizations. The entropy change, at the Curie point, is close to the value obtained in YFe<sub>2</sub> compound. This is in agreement with the magnetic data–Fig.6. Very close to T<sub>c</sub>, the erbium sublattice contribution to the resultant magnetization is very low, the later being mainly the result of iron contribution.



ig. 11. The entropy change in  $YFe_2(a)$  and  $ErFe_2(b)$  compounds.

The entropy changes obtained from magnetization isotherms, in case of  $(Gd_xY_{1-x})_2Co_7B_5$  compounds, show different behavior, according to thermal variations of resultant magnetizations. For compositions x=0.6 and 0.4, having compensation points, there is a change of  $\Delta S$  sign at compensation temperature  $T_{\text{co.}}$  In case of composition x=0.2, the resultant magnetization increases up to a temperature located at T≅250 K and then decreases. The entropy changes follow the observed temperature dependences of the magnetizations. As a characteristic feature there are very extended entropy changes, as function of temperature, generally situated below 200 K. As example, the temperature variations of entropy changes in compounds with x=1.0 and x=0.8 are given in Fig.12, at T < 160 K. The maxima  $|\Delta S_m|$  values are situated at T $\cong$ 70 K. For compounds having x=0.6 and 0.4, the  $|\Delta S_m|$  have maxima located at T $\cong$ 30 K. The maxima in  $|\Delta S_m|$  values, as in case of ErFe<sub>2</sub>, can be correlated with the temperature dependences of the magnetizations, as given in Fig.7. The high decrease with temperature of gadolinium sublattices magnetizations and consequently of the resultant magnetizations can be seen in the temperature range where  $|\Delta S|$  values show maxima. The above behavior can be correlated with the exchange interactions inside and between magnetic sublattices. By using the molecular field approximation, the exchange interactions constants have

been determined. The ratios  $|J_{Gd-Co}/J_{CoCo}| \cong 0.14$  and  $J_{GdGd}/J_{CoCo}=0.03$ , show a relative weak coupling between gadolinium and cobalt magnetizations, as compared to those between cobalt atoms. The last ones are due to 3d–3d short range interactions while those of the Gd–Co involved 5d–3d contributions. These data suggest, as experimentally observed, a rather high decrease with temperature of gadolinium magnetizations, in an intermediate temperature range between 4.2 K and Curie temperatures. The regions with higher dM/dT slopes correspond with those where relative high entropy changes can be shown. Since of high linewidth,  $\delta T_m$ , great values of the relative cooling power were evidenced.



Fig. 12. The entropy changes in  $(Gd_xY_{1,x})_2Co_7B_3$ compounds with x=1.0 (a) and 0.8 (b). 4. Conclusions

The comparative analysis of the magnetic behavior and entropy changes in rare–earth transition metal compounds revealed a strong correlation. In case of the systems having a single magnetic component, as  $GdAl_2$  or  $YFe_2$ , the entropy changes can be observed only at Curie temperatures. Similar behavior, at  $T_c$ , can be seen for rare–earth–transition metal compounds, where the rare–earth contribution to the magnetization, at the above temperature, is very week, as for  $ErFe_2$  or  $Y_2Co_7B_3$ .

High values of the entropy changes in ferrimagnetic

rare-earth-cobalt compounds can be shown, at the Curie temperatures, when the R and Co(Ni) sublattice magnetizations are strongly coupled, particularly in RCo2 and RNi5 compounds. In these systems, the cobalt and nickel moments are essentially induced by exchange interactions with rare-earth ions. The entropy changes at T<sub>c</sub> values can be well correlated with dM/dT slopes, being higher for compounds which show first order magnetic transition. We note that  $\Delta S$  values obtained from magnetization isotherms for RCo2 compounds agree generally with previous reported values [3–16]. The  $\Delta S$ values were also estimated according to Clapevron relations. Although these data agree with those obtained from magnetization isotherms for DyCo<sub>2</sub> compounds, higher values are suggested for RCo<sub>2</sub> compounds having smaller Curie temperatures.

The shifts of the Curie temperature by the external field is followed by a similar effect on the entropy changes maxima, as evidence in some RCo<sub>2</sub> compounds.

The ferrimagnetic  $(Gd_xY_{1-x})_2Co_7B_3$  and  $ErFe_2$  compounds, where the magnetic sublattices are not strongly coupled, show rather great variation of rare–earth magnetizations, at temperatures below the Curie points. Since in this temperature range the Co or Fe sublattice magnetizations are little temperature dependent, the thermal variation of resultant magnetization is due mainly to that of the rare–earths. In the temperature range where dM/dT slopes are relative great, high values of the entropy changes can be shown. Also, relative high  $|\Delta S|$  values can be shown in a large temperature ranges. The relative cooling power in these systems are rather great. The specific renormalized cooling power are of the order of  $10^3 J/kgT$ .

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