

Contents lists available at ScienceDirect

Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jallcom

Magnetic behaviour and experimental study of the magnetocaloric effect in the pseudobinary Laves phase $Er_{1-x}Dy_xCo_2$

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ARTICLE INFO

Article history: Received 20 September 2010 Received in revised form 19 December 2010 Accepted 21 December 2010 Available online 28 December 2010

PACS: 75.10.Lp 75.30.Sg

Keywords: RCo₂ Laves phases Metamagnetism Magnetocaloric effect Magnetic refrigeration

1. Introduction

Based on the magnetocaloric effect (MCE), magnetic cooling is one of the promising technology, due essentially to its high efficiency, energy saving and environment friendly [1]. MCE as discovered by Warburg in 1881 [2], is defined as the thermal response of a magnetic material upon the application and removal of the external magnetic field. It is induced via the magneto-thermal couplings between the lattice and the magnetic entropy. This effect can be quantified either directly by measuring the adiabatic temperature change ΔT_{ad} or indirectly determining the isothermal entropy change ΔS from magnetization and/or specific heat measurements. From practical point of view, magnetic cooling at room temperature (RT) requires materials with a sufficiently high MCE in a wide enough temperature range. In most magnetic RT-refrigeration prototypes, gadolinium metal (Gd) is taken as the reference material. However, the high cost of Gd with respect to a moderate value of isothermal entropy change limits applications also because of its easy oxidation. After 1997, when Pecharsky and Gschneidner [3]

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ABSTRACT

We have investigated the crystal structure, the bulk magnetization characteristics and the magnetocaloric properties of $\text{Er}_{1-x}\text{Dy}_x\text{Co}_2$ compounds. X-ray diffraction (XRD) analyses confirm that all these Laves phase type compounds crystallize in the cubic MgCu₂-type structure. First, the magnetization behaviour and the magnetic transition are analyzed in terms of Landau theory. Then, a direct correlation was pointed out between the character of the magnetic transition and the behaviour of the cell parameter versus *x*. Substitution of Dy to Er enhances markedly the Curie temperature T_C from 35 to 142 K, while ΔS the corresponding change of isothermal entropy decreases significantly. The refrigerant capacity of the $\text{Er}_{1-x}\text{Dy}_x\text{Co}_2$ compounds is discussed and our experimental data are compared with the corresponding theoretical results reported in the literature [de Oliveira, von Ranke, J. Magn. Magn. Mater. 264 (2003) 55].

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have reported on a giant MCE in $Gd_5(Si_xGe_{1-x})_4$ resulting from a first-order magneto-structural transition, intensive investigations were dedicated to search and develop new MC materials in view of their application in RT-magnetic cooling systems. Successively, several types of compounds with large MCE were pointed out, such as MnAs_{1-x}Sb_x [4], MnFeP_{1-x}As_x [5] and LaFe_{13-x}Si_x [6,7] series. All these compounds exhibit a 1st magnetic phase transition close to room temperature, leading to abrupt variations of magnetization close to the transition temperature, and consequently to a giant MCE.

During last decades, much attention was paid to the RCo₂ (R=rare earth metals) series of Laves phase due to their singular magnetic behaviour attributed to the itinerant character of the cobalt 3d electrons. A markedly large MCE follows the observed metamagnetic behaviour which is attributed to a peculiar shape of the density of states near the Fermi level. Hence in RCo₂, the Co magnetic moment is induced either by a strong enough external field or by the rare earth molecular field. When the considered R-element is non magnetic, which applies for YCo₂ and LuCo₂, an exchange-enhanced Pauli-paramagnetism takes place as revealed by the itinerant-electron metamagnetic (IEM) transition observed under critical fields $H_C \sim 70T$ [8–10]. Conversely for those R elements sharing a localized moment, a correspondingly induced Co moment arises in the magnetically ordered state thanks to the 4f-3d exchange forces. It follows that in RCo₂, the nature of magnetic

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ordering is strongly dependent on intersublattice exchange forces and then on spin–orbit (L – S or L+S) coupling of the considered R element. Then, for the heavy rare earth elements (Gd, Tb, Dy, Ho, Er), the resulting exchange coupling between the moments J_R and M_{Co} is ferrimagnetic, while for the light rare earth elements (Pr, Nd, Sm) the coupling is ferromagnetic.

The metamagnetic properties of the Co subsystem play a decisive role in determining the order of the magnetic transition and as consequence the magnitude of the entropy change in this kind of materials, e.g., first order for ErCo₂, HoCo₂ and DyCo₂, but second order for TbCo₂ [11–14]. Indeed, the origin of large ΔS values at the transition had stimulated many analyses of the RCo₂ peculiarities. In Ref. [15], the large ΔS value was attributed to the 1st order magnetic transition, in Ref. [16] it was related to structural and volume changes at the transition and according to Ref. [11] it was described in terms of spin fluctuation of the 3d (Co) sublattice. Conversely to the latter analysis, in Ref. [15], the entropy change at transition for Er-, Ho- and DyCo₂ was attributed mainly to the sublattice of 4f (R) localized moments. Finally, it was as well estimated [17] that the strength of the MCE arises not only from both the 4f moments and the nature of the transition, but also with a contribution of the 3d-itinerant electron Co sublattice.

As underlined here above, the RCo₂ series of intermetallics reveal high potential candidates for magnetic cooling applications namely ErCo₂, HoCo₂ and DyCo₂ that exhibit a large isothermal entropy change close to their own transition temperature. For example under 5 T, ΔS is for \sim 30, 23 and 11 J/kg K respectively for $ErCo_2$ ($T_C = 32$ K), $HoCo_2$ ($T_C = 80$ K) and $DyCo_2$ ($T_C = 140$ K). However, a low $T_{\rm C}$ restricts applications to a straight temperature span. Aiming to increase the refrigeration range, several works were devoted to substitute elements to the rare earth and (or) the metal transition [11–14,18–21]. There, several models were proposed to better analyse impacts of the order of transition, namely with IEM character, on the strength of MCE in RCo₂ [22]. For instance, Oliveira and von Ranke [22] have calculated theoretically the MCE in the pseudoternary system $Er_{1-x}Dy_xCo_2$. The main assumption of the advanced model was that the localized moments (R) are submitted to some magnetocrystalline electric field effects and then coupled to an effective subsystem of itinerant electrons (Co).

So, in the present paper, we report a detailed experimental study of MCE in the $Er_{1-x}Dy_xCo_2$ series aiming to compare the obtained results to the theoretical derivations as developed in Ref. [22].

2. Experimental

The bulk $Er_{1-x}Dy_xCo_2$ materials were prepared by arc melting technique (elements purity > 3N) in a purified argon atmosphere (4N5). The samples were remelted several times to complete homogeneous compositions. The resulting ingots were annealed at 1073 K for a week in evacuated sealed quartz tube and then water quenched. The crystalline structure of the samples was checked by X-ray diffraction (XRD) using a Siemens D5000 X-ray powder diffractometer with $Co_{K\alpha}$ radiation. Magnetization measurements were carried out versus temperature (4–300 K) and in magnetic field (0–10T) using the BS2 extraction type magnetometer, developed at the Néel Institute, Grenoble, France. The change of magnetic entropy, which is a pre-estimate of the MCE was determined from isothermal magnetization traces versus field using the Maxwell's relation:

$$\Delta S(T, \Delta H) = \int_{0}^{H \max} \left(\frac{\partial M}{\partial T}\right)_{H'} dH'$$
(1)

3. Results and discussion

The X-ray diffraction analyses performed at room temperature confirm that all the samples are single phase with the C15 cubic Laves phase (MgCu₂ type structure), and besides no impurity phase has been detected. The cell parameter a, as shown in Fig. 1a, increases almost linearly with increasing the Dy content, since the Dy atomic radius is correspondingly larger to that of Er.



Fig. 1. Dy content dependence of lattice parameter (a) and Curie temperature (b) of $Er_{1-x}Dy_xCo_2$ compounds.

For an effective magnetic cooling application, the profile of entropy change measured versus temperature and in a given magnetic field, requires specific types of thermodynamic cycle to amplify the MCE. For example, the active magnetic regeneration (AMR) cycle was developed to reach large as possible temperature span between hot and could sources [16]. It requires from the magnetic refrigerant to exhibit a large entropy change on a large temperature range. However, thermodynamic analysis shows that efficiently operating an ideal Ericsson cycles requires maintaining constant ΔS over a large enough operating temperature range. For both AMR as well as Ericsson cycles, when using a single magnetocaloric material only, it is not possible to practically meet this requirement since magnetocaloric properties decrease dramatically apart the transition temperature. However, a composite magnetic material allows fulfil the required conditions. For example, various magnetocaloric compounds with different Curie temperatures can be combined with optimal mass ratio to form a large range composite refrigerant [23,7]. The $Er_{1-x}Dy_xCo_2$ series as well as parent alloys with Er, Tb, Dy, Ho, Gd can satisfy the condition required to ΔS . Fig. 1b, presents the behaviour of Curie temperature versus x for the $Er_{1-x}Dy_xCo_2$ series. It is shown that T_C (temperature where dM/dT is minimum) evolves almost linearly when increasing the Dy content, being at 35, 52, 85, 122 and 142 K for *x* = 0, 0.2, 0.6, 0.8 and 1, respectively. For $ErCo_2$ ($T_C = 35$ K) and $DyCo_2$ ($T_C = 142$ K), the obtained $T_{\rm C}$ fairly agrees those reported by Gschneidner et al. (37 and 142 K) [24]. The continuous increase of ordering temperature should be related to a magneto-volume effect, as shown in Fig. 1, which leads increasing exchange forces. However, the higher value of the Dy de Gennes' factor could as well contribute in boosting up the ordering temperature. As shown in Fig. 1b, it is easy to fix the transition temperature between 30 and 150 K by according Dy to Er substitutions, thus forming magnetic systems working better with Ericsson and AMR thermodynamic cycles.

As explained above, in RCo₂ series the magnetic instability of 3delectrons reveals of interest. There, the metamagnetic behaviour plays a critical role in determining the order of magnetic transition which influences directly the magnitude of the magnetocaloric effect. For the present series, the nature of the magnetic phase



Fig. 2. Temperature dependence of Landau coefficients for $Er_{0.2}Dy_{0.8}Co_2$. The units for a(T), b(T) and c(T) are T^2 kg/J, T^4 kg³/J³, T^6 kg⁵/J⁵, respectively.

transition can be determined using the Inoue–Shimizu s-d model [25,26], which has been widely used to discuss behaviours of several types of magnetocaloric materials.

According to the spin fluctuation model based on the Landau theory [25,26], the magnetic free energy F(M, H) versus magnetization and temperature can be developed as follows:

$$F = \frac{1}{2}a(T)M^2 + \frac{1}{4}b(T)M^4 + \frac{1}{6}c(T)M^6 - \mu_0 MH$$
⁽²⁾

The coefficients a(T), b(T) and c(T) exhibit temperature dependence according to the thermal variation of amplitude of spin fluctuation. In the Inoue–Shimizu model, the magnetic system which consists of localized rare earth moment interacting with itinerant electrons of the Co sub-system, is discussed in terms of s-d model. The parameters of the function *F* are those of Landau expansion corrected by the f-d exchange interaction. In this model, the Landau coefficients express the magnetization dependence of the magnetic free energy. They can be determined through the equation of state linking magnetic field and magnetization. In the thermal equilibrium conditions (dF/dM = 0), the equation of state is derived as:

$$a(T)M + b(T)M^{3} + c(T)M^{5} = \mu_{0}H$$
(3)

Examination of the free energy demonstrates that the parameter a(T) is always positive and would get a minimum value at Curie temperature corresponding to a maximum of the susceptibility. On other hand, the order of magnetic transition is governed by the sign of b(T) at the transition: a 1st transition takes place if $b(T_C) < 0$ while a 2nd order occurs when $b(T_C) \ge 0$. Besides c(T) is positive at T_C but otherwise it is negative or positive. The values of the Landau's coefficients are determined fitting the magnetization traces to Eq. (3). Accordingly, b(T) was found negative for all here studied $\text{Er}_{1-x}\text{Dy}_x\text{Co}_2$ compounds indicating a 1st character to the magnetic transition for all series. For example, Fig. 2



Fig. 3. Arrott plots for $Er_{1-x}Dy_xCo_2$ (*x* = 0, 0.2, 0.6, 0.8 and 1).

shows the temperature dependence of the Landau's parameters for $\text{Er}_{0.2}$ Dy_{0.8}Co₂. As explained above, a(T) was found positive with a minimum close to $T_{\rm C}$ while $b(T_{\rm C})$ was found negative indicating the occurrence of a FOMT. As shown in Fig. 2, the value of Curie temperature $T_{\rm C}$ = 122 K derived from thermomagnetic measurements is exactly that obtained from the a(T) behaviour. These results were confirmed from an analysis of Arrott's plots close to $T_{\rm C}$, as shown in Fig. 3. The inflection point observed in Arrott's plots for all samples confirms occurrence of a field-induced magnetic transition, i.e., FOMT.

In order to better explain the change of order of magnetic transition in RCo₂ occurring within the complete rare-earth series, Khmelevsky and Mohn [27] have proposed a theoretical model based on the behaviour of the RCo₂ cell parameter. In fact, in RCo₂ series, two different situations are observed, depending on the value of the cell parameter a. In a first case, when a is larger than the critical value $a_{\rm C}$ = 7.22 Å, the Co subsystem is spontaneously magnetic even in the absence of external magnetic field and the transition is 2nd order. Conversely, in the second case for $a < a_C$, a metamagnetic transition operates at a critical magnetic field H_C . To induce the IEM transition it needs that a must range 7.05–7.22 Å. Besides, the impact of the cell parameter value on the order of magnetic transition was investigated later by Duc et al. [28]. Effectively, to explain the change of character of the magnetic transition in the (Nd, Dy)Co₂ and (Nd, Pr)Co₂ systems, Duc et al. [28] have estimated $a_{\rm C}$ = 7.275 Å as the critical value for which the Landau's parameter b(T) should change sign. Both analyses by Khmelevsky and Mohn [27] and Duc et al. [28] demonstrate the importance of the cell parameter dependence on the long range magnetic properties. In fact the model proposed by Khmelevsky and Mohn [27] seems to be the valuable description of IEM applying well for both light and heavy rare earth systems [18]. As shown in Fig. 1b, the cell parameters of the presently studied compounds stay in the range 7.05–7.22 Å, values in fair agreement with those of the Khmelevsky and Mohn derivations. However, as reported in Ref. [27] and for the highest ordering temperatures, a simple 2nd order transition takes place even for compounds where the conditions of a FOMT are fulfilled, a phenomenon which was attributed to a spin fluctuations contribution. This should allow justifying, e.g., the nature of magnetic transition observed in $Ho_{1-x}Tb_xCo_2$ and $Ho_{1-x}Gd_xCo_2$ [12,21]. In fact, the magnetic and magnetocaloric properties of the RCo₂ series were discussed owing to such a model as also reported in Ref. [29].

The isothermal entropy change associated with MCE can be evaluated from isothermal magnetization M by integrating Eq. (1) – Maxwell's relation – on an appropriated magnetic field range. From magnetization measurements performed at constant temperature for successive values of the applied field H, the Maxwell's relation



Fig. 4. Temperature dependence of isothermal entropy change of $ErCo_2$ (a) and $DyCo_2$ (b) under different magnetic field variations.

can be numerically approximated as follows:

$$\Delta S = \sum_{i} \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i \tag{4}$$

where M_{i+1} and M_i are magnetization values measured in a field H, at temperatures T_{i+1} and T_i , respectively. In this case, the entropy change is proportional to the area between two successive magnetization isotherms. However, the use of Maxwell's relation to determine the entropy change related to MCE for 1st ordering compounds had led to many controversies [30-33]. For example, Giguère et al. [30] have shown that using of this equation for Gd₅Ge₂Si₂, typically a 1st ordering compound, leads to overestimate the MCE. However, Gschneidner et al. [31] have considered that the Maxwell's relation can be applied even for a 1st order process except for an "ideal" 1st order phase transition occurring infinitely fast at constant temperature, pressure and magnetic field. In fact, both Liu et al. [32] and Balli et al. [33], demonstrated that the thermodynamic Maxwell's relation becomes invalid especially when a magnetic compound maintained close to the transition, mixes paramagnetic and ferromagnetic phases. In such a case, only the part of volume maintained in paramagnetic state contributes to the magnetocaloric effect when transformed to ferromagnetic state by application of a magnetic field. Then, using the Maxwell's relation leads that the total normalised area comprised between two adjacent isotherms is included in the determination of the magnetic entropy variation, which results in spurious values of MCE. However, in the presently studied materials, absence of a mixed phase state close to the transition region because of the low hysteresis effect [12] compared to, e.g., MnAs based compounds, allows determining correctly of the entropy change using Eq. (1).

The results for ErCo_2 and DyCo_2 close to T_{C} and under different magnetic fields are given in Fig. 4. For *H* varying from 0 to 5 T, $-\Delta S$ is found close to 28.1 and 10 J/kg K, respectively for ErCo_2 and DyCo_2 , both values in fair agreement with what was reported in literature



Fig. 5. Temperature dependence of isothermal entropy change of $Er_{1-x}Dy_xCo_2$ compounds in an external field change of 5 and 10 T.

[20,24]. The magnetic entropy change under 5 and 10 T for all samples is shown in Fig. 5. It decreases upon increasing the Dy content and the maximum values for $-\Delta S$ (5 T) are 28.5 J/kgK (T_c = 35 K), 17.4 J/kg K ($T_{\text{C}} = 52 \text{ K}$), 16.4 J/kg K ($T_{\text{C}} = 85 \text{ K}$), 12.5 J/kg K ($T_{\text{C}} = 122 \text{ K}$) and 10 J/kg K ($T_{\text{C}} = 142 \text{ K}$), respectively for x = 0, 0.2, 0.6, 0.8 and 1. This decrease in the magnetic entropy change is attributed essentially to the spin fluctuations, which affects the broadness of the 1st order character of the transition. In addition, the role of enhanced thermal load which reduces the MCE of compounds with higher ordering temperature should be accounted for. Fig. 6 shows the magnetic entropy change plotted versus the Curie temperature for the $Er_{1-x}Dy_xCo_2$ series. Measurements performed on others RCo₂ are also given for comparison [12,21]. As can be seen in Fig. 6, the entropy change of (Er, Ho, Tb, Dy)Co₂ based materials decreases with increasing Curie temperature. The present data illustrates well the difficulty to combine high MCE performances with high critical temperature

In order to assert the $\text{Er}_{1-x}\text{Dy}_x\text{Co}_2$ to work in thermodynamic cycles such as AMR or Ericsson, we have estimated the so-called relative cooling power RCP(*S*) which is defined as:

$$\operatorname{RCP}(S) = -\Delta S(\max) \times \delta T_{\text{FWHM}}$$
(5)

where δT_{FWHM} represents the width at half maximum of ΔS . The results are shown in Fig. 7a for different Dy-content compounds actuated under various magnetic fields. In Fig. 7a, it can be seen that RCP(*S*) of the studied samples is close to 280 J/kg (for 5 T), values of the same magnitude as for Ho_{1-x}Tb_xCo₂ [12] and similar to those of reference materials [5]. Introduced by Gschneidner and Pecharsky in 2000 [34], RCP is of the more accurate estimate refrigeration capacity, better than RC that is deduced from the magnetic entropy change using δT_{FWHM} as integration limit. Moreover, it was



Fig. 6. Evolution of the isothermal entropy change versus Curie temperature in different (Er, Ho, Dy, Tb, Gd)Co₂ based materials. For $Ho_{1-x}Tb_xCo_2$ and $Ho_{1-x}Gd_xCo_2$, data were taken respectively from Refs. [12,21].



Fig. 7. Relative cooling power (a) and refrigerant capacity (b) of $Er_{1-x}Dy_xCo_2$ compounds versus the Dy content and for different magnetic fields.

proposed a rough relationship RCP ~ 4/3 RC when $\Delta S(T)$ exhibits a "caret-like" shape, therefore leading to overestimate the effective RC. Besides, Wood and Potter [35] have defined the cooling capacity for a reversible refrigeration cycle working between T_C (cold source) and T_H (hot source) as the product $\Delta S \times \Delta T$, where ΔS is the magnetic entropy change between hot and cold ends of the cycle and ΔT is the temperature span between T_C and T_H . This approach consists to optimize the thermodynamic cycle ends, maximizing the $\Delta S \times \Delta T$ product. Presently, as widely reported in literature we determined RC = $\int_{FWHM} \Delta S(T) dT$ which results are displayed in Fig. 7b for different magnetic fields. The mean value of RC is close to 200 J/kg for 5 T which is ~3/4 of the calculated RCP(*S*), then confirming the results reported in [34].

Modelling as well as simulation of magnetic and thermomagnetic properties of the magnetocaloric materials is of interest both from fundamental and practical point of views. Typically for compounds with localized magnetic moments thus exhibiting 2nd order transition as, e.g., rare earth compounds, MCE can be calculated using a Weiss molecular mean field theory (MFT) based model. For 1st order transition type compounds in which the exchange interactions strongly depend on the inter-atomic distances, the Bean and Rodbell model developed first to explain the FOMT in MnAs has been used to describe the MCE in pnictides derived from the MnAs and MnFeP_{1-x}As_x series [36,37]. However, for materials with itinerant electron character like RCo2 and $LaFe_{13-x}Si_x$, the development of a more accurate theoretical model is limited by different complex physical phenomenon observed in this kind of materials. In order to explain the MCE in $Er_{1-x}Dy_xCo_2$ Laves phase, de Oliveira and von Ranke [22], have developed a theoretical model in which the localized magnetic spins of the rare earth are under the influence of the crystalline electric field and are coupled with an effective subsystem of itinerant electrons. Aiming to assert the validity of this model, in particular reference to the here studied compounds, comparison between modelled results and the experimental data was made as reported in Fig. 8. As shown, if the experimental Curie temperature scales well with theoretical data (Fig. 8a), a large deviation is observed between experimental and calculated maximum entropy change (Fig. 8b). In fact the calcu-



Fig. 8. Experimental Curie temperature (a) and maximum entropy change (b) compared to the corresponding theoretical data reported in Ref. [22]. Experimental and theoretical ΔS values are compared for 6 T.

lated values of the entropy change overestimate the real values, showing the limit of the model. For example, for high content of Dy, the theoretical entropy change is calculated about twice higher than that determined experimentally. The observed divergence can be attributed to the several successive approximations aiming to simplify the model through the various parameters of those more complex systems.

4. Conclusions

In the present work, we have studied experimentally the crystal structure, magnetic properties and magnetocaloric performances of $Er_{1-x}Dy_xCo_2$ compounds of Laves phase type. When increasing the Dy content, the cubic cell parameter as well as the Curie temperature increase almost linearly. Analysis of the magnetic ordering transition using the Landau theory, Arrott plots and the cell parameter expansion reveals occurrence of a FOMT in the series when x varies from 0 to 1. The isothermal entropy change decreases when increasing the Dy content, essentially due to a weakening of the 1st order character of the magnetic transition. In fact, here it reveals difficult to combine high magnetocaloric performances with high critical temperature. Parallel, the refrigerant capacity of $Er_{1-x}Dy_xCo_2$ decreases with the Dy concentration but it remains relatively comparable even larger than for reference materials. Besides, a large deviation between the experimental entropy change and corresponding theoretical data reported in Ref. [22] is observed, showing the limit of the developed model.

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