Experimental Study of the Magnetocaloric Effect in the Pseudo Binary Laves-Phase Compounds

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Abstract Polycrystalline samples of DyCo_2 , HoCo_2 , ErCo_2 and their solid solutions $\text{Dy}_{1-x}\text{Ho}_x\text{Co}_2$, $\text{Dy}_{1-x}\text{Er}_x\text{Co}_2$, $\text{Ho}_{1-x}\text{Er}_x\text{Co}_2$ have been studied using X-ray diffraction analysis, heat capacity and magnetic measurements. The X-ray diffraction performed at room temperature allowed to reveal that all solid solutions solidify with the formation of the C15 cubic Laves-phase structure corresponding to the $Fd\bar{3}m$ space group. All binary compounds and their solid solutions are typical ferrimagnets and are magnetically ordered at temperature below 140 K. In all doped solid solutions an decrease of the magnetic ordering temperature is observed. At high temperatures, all samples are Curie-Weiss paramagnets. The magnetization behaviour and the magnetic transition are analyzed in terms of Landau theory. The magnetocaloric effect has been estimated using the heat capacity data. Comparison of the influence of doping effect in pseudo-binary compounds on their magnetic and magnetocaloric properties for all solid solutions is presented.

Keywords Intermetallic compounds · Magnetocaloric effect · Magnetic susceptibility · Magnetization · Heat capacity

1 Introduction

In recent years, intermetallic compounds RCo_2 (R = rare-earth) having the C15 cubic Laves-phase crystal structure are the subject of extensive investigations owing interesting intrinsic magnetic properties of the materials. A large

magnetocaloric effect (MCE) observed in some of these compounds makes them suitable candidates for magnetic refrigeration technology [1, 2]. Materials showing promise for magnetic refrigeration applications must exhibit a first-order magnetic phase transition [3]. In this context, RCo_2 intermetallic compounds are among the attractive candidates. According to [4, 5], the ferrimagnetic-paramagnetic phase transformations in RCo_2 compounds with heavy rare-earth elements are first-order transitions, and, thus, these compounds exhibit a large magnetic entropy change. The magnetic moment at Co atoms in RCo_2 compounds is induced by exchange interaction with rare-earth moments [6, 7]. The Co-atom moments in the light rare-earth compounds range from 0.5 to 0.8 μ_B , while the moments are almost unchanged ($\sim 1.0 \mu_B$) for the compounds with the heavy rare-earth elements. The induced moments are aligned in parallel to the 4f moments in the light rare-earth compounds and are antiparallel in the heavy rare-earth compounds [8]. DyCo_2 , HoCo_2 and ErCo_2 were selected from a great number of intermetallic compounds; their Curie temperatures are 140, 76 and 35 K, respectively [9]. According to data of Tishin et al. [10] for the parent compounds, the maximum magnitude ΔT_{ad} at a field change $\mu_0 H$ of 10 T for DyCo_2 at 141 K, HoCo_2 at 84 K and ErCo_2 at 36 K reaches 9.6, 10 and 10.8 K, respectively. The theoretical calculations performed by Oliveira suggest that composite materials made up of several samples of the doped compounds $\text{R}_{1-x}\text{R}'_x\text{Co}_2$ (where R, R' = rare earth elements) can be very useful to work as magnetic refrigerant in the intermediate range of temperature, for example 100–200 K [11]. The authors have shown that the nature of the magnetic phase transformation retains the first-order transition for all the pseudobinary compounds. In the present work I want to respond to above suggestion and perform the comparative analysis of their magnetic and magnetocaloric properties.

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2 Experimental Details

Polycrystalline samples of $R_{1-x}R^{\prime}_xCo_2$ ($0.1 \leq x \leq 0.5$) solid solutions were prepared by arc-melting using a water-cooled copper crucible and a high purity argon atmosphere. The high-purity starting materials (Co 99.99 % purity and rare-earth metals 99.9 % purity) were taken in stoichiometric proportions. The alloys were melted repeatedly (four times) to ensure the adequate homogeneity. The mass losses after the melting were less than 1 wt %. The buttons obtained were wrapped in a tantalum foil, sealed in evacuated quartz ampoules, and annealed at 700°C for four weeks.

The crystal structure and the phase purity of the samples were determined using the X-ray diffraction (XRD) analysis. Temperature dependences of the DC magnetic susceptibility were measured at 4.2–290 K in a static magnetic field of 0.03 T using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). Magnetization measurements were carried out using a vibration sample magnetometer with a step motor in an applied field up to maximum 14 T using a Bitter-type magnet. The heat capacity was measured using Quantum Design PPMS 14 Heat Capacity System in a temperature range of 2–295 K without the magnetic field and in a magnetic field of 0.5, 1, 1.5 and 2 T.

Isothermal magnetic entropy change ΔS_H and adiabatic temperature change ΔT_{ad} has been estimated using the heat capacity data.

3 Results and Discussion

The principal magnetic parameters and crystallographic data of investigated samples are collected in Table 1. As it seen, all the solid solutions under study are found to have the cubic C15 Laves phase, $MgCu_2$ – type structure. The lattice parameters for all $R_{1-x}R^{\prime}_xCo_2$ compounds decreases with increasing $R^{\prime}$ content. For $Dy_{1-x}Ho_xCo_2$ and $Dy_{1-x}Er_xCo_2$ when a part of Dy atoms is substituted by Ho and Er, accordingly, the T_C values decreases. Similarly situation is observed for $Ho_{1-x}Er_xCo_2$ the added Er atoms decreases T_C of $Ho_{1-x}Er_xCo_2$ solid solutions. Magnetization isotherms of all the $R_{1-x}R^{\prime}_xCo_2$ ($0.1 \leq x \leq 0.5$) solid solutions were measured at selected temperatures in the vicinity of their ordering temperatures in a maximum applied magnetic field of 5 T. As an example, the magnetization isotherms measured for $Dy_{0.6}Ho_{0.4}Co_2$ at temperatures of from 104 to 152 K are illustrated in Fig. 1. It was found that, above $T_C = 113$ K, the metamagnetic behavior characterized by hysteretic transitions in magnetization curves is observed. The decrease in the critical field of metamagnetic transitions and magnetization jumps occur with increasing temperature. The presence of a metamagnetic transition in

the compounds studied is seen not only in the magnetization isotherms but also in the corresponding Belov-Arrott plots which are usually used to determine the transition order of magnetic materials [12, 13]. On the one hand, if negative slopes or inflection points are found in Belov-Arrott plot curves, they often indicate a first-order transition. On the other hand, if the Belov-Arrott plot above T_C displays an almost linear behavior, it implies that a second-order magnetic transition occurs. As an example, the Belov-Arrott plots for $Ho_{0.6}Er_{0.4}Co_2$ are shown in Fig. 2. The inflection point above T_C (56 K) suggests the occurrence of a metamagnetic transition from paramagnetic to ferrimagnetic order. The S-shape curves in Fig. 2 indicate a first-order type transition in this sample. The same trend is observed for all $R_{1-x}R^{\prime}_xCo_2$ solid solutions with $0.1 \leq x \leq 0.5$.

According to the metamagnetic behaviour plays a critical role in determining the order of a magnetic transition which influences directly the magnitude of magnetocaloric effect. In order to confirm that present series showed first-order transitions, it has used the Inoue–Shimizu s-d model [14], which has been widely used to discuss behavior of several types of magnetocaloric materials. In this model, a Landau expansion of magnetic free energy up to the sixth power of total magnetization M is used :

$$F = \frac{1}{2}a(T)M^2 + \frac{1}{4}b(T)M^4 + \frac{1}{6}c(T)M^6 + \dots - \mu_0MH \quad (1)$$

The Landau coefficients are accessible through the equation of state linking M and the magnetic field :

$$\mu_0H = a(T)M + b(T)M^3 + c(T)M^5 \quad (2)$$

The coefficients $a(T)$, $b(T)$ and $c(T)$ depend on the temperature with respect to a thermal variation of spin fluctuations amplitude and can be determined by fitting the magnetization isothermal data using the above equation. Examination of the free energy demonstrates that the parameter $a(T)$ is always positive and would get a minimum value at the Curie temperature corresponding to a maximum of susceptibility. On other hand, the order of magnetic transition is governed by the sign of $b(T)$: the 1st order transition takes place if $b(T_C) < 0$, while the 2nd order transition occurs when $b(T_C) \geq 0$. Besides, $c(T)$ is positive at T_C and, in the other temperature regions, can be negative or positive. The values of Landau's coefficients are determined by fitting the magnetization traces to (2).

Accordingly, $b(T)$ is found to be negative for all $R_{1-x}R^{\prime}_xCo_2$ studied indicating the 1st order of magnetic transition for entire series. As example, Fig. 3 shows the temperature dependence of Landau coefficients $a(T)$, $b(T)$ and $c(T)$ for $Dy_{0.5}Ho_{0.5}Co_2$ compound. As explained, $a(T)$ is positive with a minimum at T_C , corresponding to a maximum in the susceptibility curve. The $b(T)$ value at T_C is

Table 1 Physical properties of $R_{1-x}R'_x\text{Co}_2$ solid solutions obtained from structural, magnetic and heat capacity measurements: a is the lattice parameter, V is the volume of elementary cell, T_{SR} is the temperature of spin-reorientation, T_{C} is the Curie temperature, Θ_{D} is Debye temperature, γ is the Sommerfeld coefficient

Compound	a , nm	V , nm ³	T_{SR} , K	T_{C} , K	Θ_{D} , K	γ , mJ/molK ²
Dy _{0.9} Ho _{0.1} Co ₂	0.7186	0.37107	68	130	235	40
Dy _{0.8} Ho _{0.2} Co ₂	0.7184	0.37077	69	127	235	
Dy _{0.7} Ho _{0.3} Co ₂	0.7183	0.37061	70	120	238	
Dy _{0.6} Ho _{0.4} Co ₂	0.7181	0.3703	71	113	242	
Dy _{0.5} Ho _{0.5} Co ₂	0.7179	0.36999	72	109	245	
Dy _{0.9} Er _{0.1} Co ₂	0.7187	0.37123	-	128	230	42
Dy _{0.8} Er _{0.2} Co ₂	0.7183	0.37061	-	119	235	
Dy _{0.7} Er _{0.3} Co ₂	0.7181	0.3703	7	106	245	
Dy _{0.6} Er _{0.4} Co ₂	0.7178	0.36984	12	97	245	
Dy _{0.5} Er _{0.5} Co ₂	0.7174	0.36922	16	86	240	
Ho _{0.9} Er _{0.1} Co ₂	0.7171	0.36876	24	72	240	30
Ho _{0.8} Er _{0.2} Co ₂	0.7169	0.36845	32	66	250	
Ho _{0.7} Er _{0.3} Co ₂	0.7168	0.36829	38	64	264	
Ho _{0.6} Er _{0.4} Co ₂	0.7166	0.36799	44	56	270	
Ho _{0.5} Er _{0.5} Co ₂	0.7164	0.36768	-	50	280	

negative showing a first-order magnetic transition in this compound.

Figure 4 shows the temperature dependences of the specific heat of $\text{Dy}_{1-x}\text{Er}_x\text{Co}_2$ measured in zero magnetic field. It can be seen that sharp peaks associated with the first-order magnetic phase transitions take place. The Curie temperatures decrease from 140 K for DyCo_2 down to 86 K

for $\text{Dy}_{0.5}\text{Er}_{0.5}\text{Co}_2$. Moreover, for $x = 0.3$ and 0.5 in the low temperature region (see inset of Fig. 4) additional peak is observed. A possible mechanism for the relatively small smooth step-like anomaly in $C_{\text{P}}(T)$ plots at low temperatures might be a spin reorientation in the R-electron subsystem, which is similar than that observed for HoCo_2 ($T_{\text{SR}} = 15$ K) and NdCo_2 ($T_{\text{SR}} = 43$ K) [15]. It is assumed

Fig. 1 Magnetization isotherms of $\text{Dy}_{0.6}\text{Ho}_{0.4}\text{Co}_2$ measured at several selected temperatures near T_{C}

Fig. 2 Belov-Arrott plots for $\text{Ho}_{0.6}\text{Er}_{0.4}\text{Co}_2$

that the spin reorientation in those two compounds is driven by an interplay of molecular and crystal fields, thus, giving rise to the change of easy magnetization direction from $[1\ 0\ 0]$ to $[1\ 1\ 0]$ with decreasing temperature. The spin reorientation transition was observed in all $\text{R}_{1-x}\text{R}'_x\text{Co}_2$ solid solutions and can be understood as an effect of competition between the magnetocrystalline anisotropies of the Co and R sublattices.

It is well known that the heat capacity of metals can be considered as the sum of independent electronic, lattice (phonon), and magnetic contributions :

$$C_p(T) = C_{el}(T) + C_{ph}(T) + C_{mag}(T) \quad (3)$$

The electronic and phonon contributions to the specific heat can be calculated by expression

$$C_{el+ph}(T) = \gamma T + 9NR \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (4)$$

where the first term represents the electronic heat capacity and the second term corresponds to the phonon Debye contribution; γ is the Sommerfeld coefficient, Θ_D is the Debye temperature, $N = 3$ is the number of atoms per formula unit; R is the universal gas constant; and $x \equiv \hbar\omega/k_B T$.

Fig. 3 Temperature dependences of a and b Landau coefficients $a(T)$, $b(T)$ and $c(T)$ for $\text{Dy}_{0.5}\text{Ho}_{0.5}\text{Co}_2$

Fig. 4 Temperature dependences of the specific heat $C_p(T)$ of $\text{Dy}_{1-x}\text{Er}_x\text{Co}_2$ ($0.0 \leq x \leq 0.5$) measured in zero magnetic field. The inset shows low temperature range near spin reorientation temperature

The $C_{\text{el+ph}}(T)$ dependence for each of the investigated $\text{R}_{1-x}\text{R}'_x\text{Co}_2$ compounds was calculated by (4) and as example, the temperature dependences of the heat capacity $C_p(T)$, the sum of electronic and phonon $C_{\text{el+ph}}(T)$ and magnetic contributions $C_{\text{mag}}(T)$ for the $\text{Dy}_{0.7}\text{Er}_{0.3}\text{Co}_2$ compound measured in zero magnetic field is shown in Fig. 5. For $\text{Dy}_{0.7}\text{Er}_{0.3}\text{Co}_2$, the best fitting for the wide temperature range could be obtained by fixing the parameter $\gamma \sim 42 \text{ mJ/molK}^2$, while the Debye temperature fluctuates around 245 K. The values of γ and Debye temperature of all $\text{R}_{1-x}\text{R}'_x\text{Co}_2$ with changing composition are presented in Table 1. The inset in Fig. 5 shows temperature dependences

of the specific heat of $\text{Dy}_{0.7}\text{Er}_{0.3}\text{Co}_2$ measured in magnetic fields. It is seen that the maximum of peaks in the $C_p(T)$ dependences measured in magnetic fields shifts to the high-temperature range and gradually decreases with increasing magnetic field.

The adiabatic temperature change ΔT_{ad} caused by the magnetic field change, ie. magnetocaloric effect, can be obtained as :

$$\Delta T_{\text{ad}} = -\frac{T}{C_H} \Delta S_H \quad (5)$$

Fig. 5 Total specific heat capacity $C_{\text{tot}}(T)$ of $\text{Dy}_{0.7}\text{Er}_{0.3}\text{Co}_2$ measured in zero magnetic field. The calculated sum of electronic and phonon contributions $C_{\text{el+ph}}$ as well as estimated magnetic contribution C_{mag} . The inset shows $C_p(T)$ curve measured in zero and 0.5-, 1- and 1.5-T magnetic fields for $\text{Dy}_{0.7}\text{Er}_{0.3}\text{Co}_2$

Fig. 6 The maximum value of ΔT_{ad} vs. T for $R_{1-x}R'_xCo_2$ compounds

where C_H is the experimental dependence of heat capacity measured in magnetic field, and

$$\Delta S_H = \int_0^T \frac{\Delta C_H}{T} dT \quad (6)$$

is isothermal entropy change calculated from heat capacity data [10].

Figure 6 summarizes the experimental temperature dependences of maximum ΔT_{ad} values for all solid solutions under study in applying magnetic field of 2 T for $Ho_{1-x}Er_xCo_2$ and $Dy_{1-x}Ho_xCo_2$, and 1.5 T for $Dy_{1-x}Er_xCo_2$. As can be seen, the maximum peak value increases with increasing R' content. In the case of $Ho_{1-x}Er_xCo_2$, the increase is more pronounced and ranges from 4 K ($x=0.1$) to 7 K ($x=0.5$). For $Dy_{1-x}Ho_xCo_2$, the maximum peak value fluctuates within 3–4 K, while for $Dy_{1-x}Er_xCo_2 \sim 3$ K.

4 Conclusion

Comparison of the influence of doping effect in pseudobinary $R_{1-x}R'_xCo_2$ (R, R' -rare earth) solid solutions on the structure and some physical properties has been studied experimentally. It was confirmed that the main phase in all solid solutions has the cubic C15 structure. The substitution of Ho and Er for Dy in $Dy_{1-x}Ho_xCo_2$ and $Dy_{1-x}Er_xCo_2$ results in the decrease of the ordering temperature. The same trend is observed for $Ho_{1-x}Er_xCo_2$ when Ho is substituted by Er. Analysis of magnetic ordering transition

using the Landau theory and Belov-Arrot plots reveals the occurrence of the first-order phase transition in all sample, which confirms the theoretical considerations performed by Oliveira [11].

Results of the heat capacity measurements agree well with those of magnetic studies and confirm the fact that the substitution of R' for $RR'Co_2$ decreases the magnetic ordering temperature. In addition to changes associated with the magnetic transition, the anomalies caused by the magnetic spin reorientation are observed in the curves $C(T)$ and $\chi_g(T)$.

It should be noted that the decrease in T_C is accompanied by increase in magnetocaloric properties in all measured solid solutions. Among the presented sample, the best MCE was observed for $Ho_{1-x}Er_xCo_2$ solid solutions.

Summarizing, the presented compounds display the higher MCE values, which make them candidates for magnetic refrigeration applications in intermediate (50–140 K) temperature regions.

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