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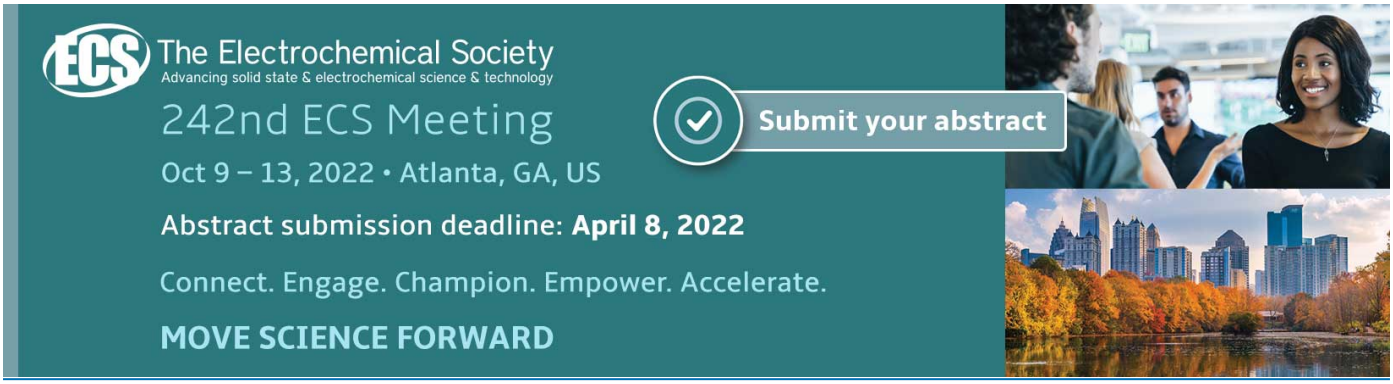

Magnetocaloric properties of multicomponent Laves phase compounds and their composites

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Abstract. Heat capacity measurements have been performed for multicomponent $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds with x = 0.05, 0.1, and 0.15. The isothermal magnetic entropy change, ΔS_{mag}, allowing the estimation of the magnetocaloric effect, was determined based on the heat capacity measurements in magnetic fields up to 2 T. A numerical method, with the magnetic entropy change of individual $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds, was used to calculate the optimal molar composition of the constituents and the resulting change of the isothermal magnetic entropy of composite, ΔS_{comp}. The results show that proposed composite can be considered as a refrigerant material in magnetic refrigerators performing an Ericsson cycle in a temperature range of 90-130 K.

1. Introduction

The magnetocaloric effect (MCE) consists in the magnetic materials' thermal response when they are subjected to magnetic field variations. It can be quantified as the reversible change in temperature, ΔT_{ad}, during adiabatic process, or the reversible change of the magnetic entropy, ΔS_{mag}, if the change in field takes place in near isothermal process. Both ΔT_{ad} and ΔS_{mag} are characteristic values of the MCE, according to the initial temperature and the value of change in the magnetic field. This effect is particularly pronounced at temperatures and fields corresponding to magnetic phase transitions.

It has been found that in the case of RCo_2 with heavy rare earth elements (R = Ho, Dy and Er) the magnetic phase transitions are of the first order and these compounds exhibit large magnetic entropy changes [1,2]. Numerous investigations of the MCE of RCo_2 compounds with substitutions either in rare - earth sublattice $(RR')Co_2$ or in Co - sublattice $RCo_{2-x}M_x$ (where M = Si, Ga, Ge, Al, Fe, Ni, Mn) have been performed [3,4], while the multicomponent $(RR'R'')Co_2$ alloys lack systematic investigations of their thermal properties [5,6]. In one of our previous works, the magnetic and magnetocaloric properties of such compositions were studied [7]. In the present work, $Ho_{0.9}Er_{0.1}Co_2$ compound was selected as a potential candidate for refrigerant in magnetic refrigerators. This compound is characterized by the first-order magnetic phase transitions with T_C = 72 K, and ΔS_{mag} = 14.2 J/kgK at a magnetic field change of 0 to 3 T [7]. In order to expand the range of applications, the $GdCo_2$ compound was used for the partial substitution for $Ho_{0.9}Er_{0.1}Co_2$ to form $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ since the T_C temperature of $GdCo_2$ is about 400 K [8].

The purpose of this paper is, using heat capacity measurements, to present the magnetocaloric properties of the composite material based on $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds,.

2. Materials and experiment

Polycrystalline samples of $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds, with x = 0.05, 0.1 and 0.15 were prepared by arc-melting using a water-cooled copper crucible and a high purity argon atmosphere. The 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 of buttons. 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 850°C for four weeks.

The heat capacity was measured in a temperature range of 2-300 K in zero, 1 and 2 T magnetic fields using a PPMS 14 Heat Capacity System (Quantum Design). X-ray powder diffraction analysis showed that the $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ samples are single-phase and have the cubic C15 structure (space group Fd-3m) and the substitution of gadolinium for rare earth leads to the increase in the lattice parameter. At room temperature, we have obtained a = 0.7172 nm, for $(Ho_{0.9}Er_{0.1})_{0.95}Gd_{0.05}Co_2$, a = 0.7175 nm, for $(Ho_{0.9}Er_{0.1})_{0.9}Gd_{0.1}Co_2$ and a = 0.7178 nm, for $(Ho_{0.9}Er_{0.1})_{0.85}Gd_{0.15}Co_2$.

3. Results and discussion

The heat capacity measurements performed as a function of temperature in a given magnetic field provide the most complete characterization of any magnetic materials with respect to their magnetocaloric properties. It is well known that the heat capacity of metals can be considered as the sum of independent electronic, lattice (phonon), and magnetic contributions:

$$C_p(T) = C_{el}(T) + C_{ph}(T) + C_{mag}(T). \quad (1)$$

The electronic and phonon contributions to the heat capacity can be calculated by expression [9]:

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

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 $x = \hbar\omega/k_BT$. The $C_{el+ph}(T)$ dependence for each of the investigated samples was calculated by Eq. 2. The best fitting for the wide temperature range could be obtained by fixing the parameter $\gamma \sim 30$ mJ/molK^2, while the Debye temperature fluctuated around 230 - 235 K, and is very close to that reported by Oliveira et al. [10] for pure $DyCo_2$ (Θ_D = 230 K).

For all $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds, the magnetic contribution $C_{mag}(T)$ was estimated by subtracting the sum of electronic and phonon contributions from the total heat capacity $C_P(T)$. As the examples, the temperature dependences of the heat capacity, $C_P(T)$, the sum of electronic and phonon, $C_{el+ph}(T)$, and magnetic contributions, $C_{mag}(T)$, measured for $(Ho_{0.9}Er_{0.1})_{0.95}Gd_{0.05}Co_2$ in zero magnetic field are shown in Figure 1. In the case of all multicomponent compounds under study, two specific heat peaks are observed in the curves. The first of them is attributed to a spin-reorientation transition and the other well-defined maximum corresponds to the magnetic ordering temperature, T_C. A possible mechanism for the relatively small smooth step-like anomaly in $C_P(T)$ plots at low temperatures might be a spin reorientation in the R 4*f*-electron subsystem, which is similar to that observed for $HoCo_2$ (T_{SR} = 15 K) and $NdCo_2$ (T_{SR} = 43 K) [11]. The inset in Fig. 1 shows temperature dependences of the heat capacity of $(Ho_{0.9}Er_{0.1})_{0.95}Gd_{0.05}Co_2$ measured, additionally, in magnetic fields. It is seen that the maximum of peaks in the $C_P(T)$ dependences measured in zero, 1 and 2 T magnetic fields shifts to the high-temperature range and gradually decreases with increasing magnetic field.

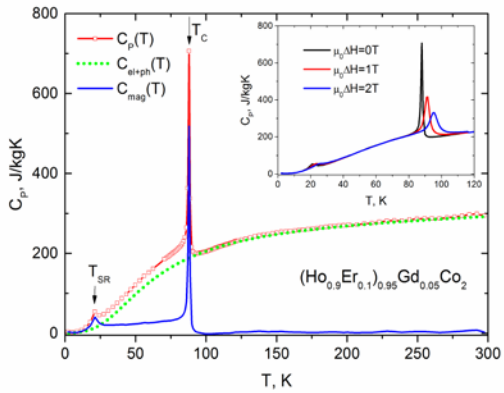

Figure 1. Temperature dependences of heat capacity $C_P(T)$ of $(Ho_{0.9}Er_{0.1})_{0.95}Gd_{0.05}Co_2$ measured in zero magnetic field; the calculated sum of electronic and phonon contribution, $C_{el+ph}(T)$, as well as estimated magnetic contribution, $C_{mag}(T)$ are shown. Inset shows $C_P(T)$ dependences measured in zero, 1 and 2 T magnetic fields.

Figures 2 (a-c) show the temperature dependences of C_{mag} for $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds in zero, 1 and 2 T magnetic fields. The observed maximum in the $C_{mag}(T)$ appears in the vicinity of T_C and then seems to be the result of the magnetic phase transitions. The introduction of Gd in $Ho_{0.9}Er_{0.1}Co_2$ leads to the increase in the magnetic ordering temperature. The T_C temperature increases from 89.2 K for $(Ho_{0.9}Er_{0.1})_{0.95}Gd_{0.05}Co_2$ to 127 K for $(Ho_{0.9}Er_{0.1})_{0.85}Gd_{0.15}Co_2$. For all compositions, the observed maximum decreases in height, broadens and moves toward the high-temperature range in applying the magnetic field (see Figs. 2b and 2c).

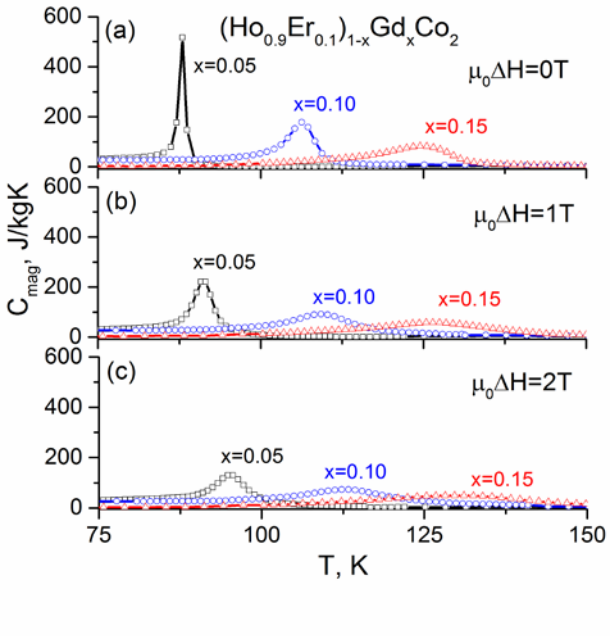

Figure 2. Temperature dependences of C_{mag} for $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds in zero (a), 1 T (b) and 2 T (c) magnetic fields.

The value of magnetic entropy, $S_{mag}(T)$, was calculated from the experimental heat capacity data using $C_{mag}(T)$ curves by standard formula :

$$S_{mag}(T) = \int_0^T \frac{C_{mag}(T)}{T} dT \quad (3)$$

and, from the calculated curves $S_{mag}(T, \mu_0 H = 0)$ and $S_{mag}(T, \mu_0 H \neq 0)$, we obtaine the magnetic entropy change $\Delta S_{mag} = S_{mag}(T, \mu_0 H) - S_{mag}(T, 0)$. Temperature dependences of the magnetic entropy change, $\Delta S_{mag}(T)$, for investigated compounds, caused by the magnetic field changes $\mu_0 \Delta H = 1$ T and $\mu_0 \Delta H = 2$ T are shown in Fig. 3 and Fig. 4, respectively. At 1 T magnetic field change, the maximum magnetic entropy change reaches values : $\Delta S_{mag} = 5.1$ J/kgK, for $(Ho_{0.9}Er_{0.1})_{0.95}Gd_{0.05}Co_2$, 3.3 J/kgK for $(Ho_{0.9}Er_{0.1})_{0.9}Gd_{0.1}Co_2$, and 2.6 J/kgK for $(Ho_{0.9}Er_{0.1})_{0.85}Gd_{0.15}Co_2$. At 2 T magnetic field change, $\Delta S_{mag} = 9.1$ J/kgK, for $(Ho_{0.9}Er_{0.1})_{0.95}Gd_{0.05}Co_2$, 6.0 J/kgK for $(Ho_{0.9}Er_{0.1})_{0.9}Gd_{0.1}Co_2$, and 4.6 J/kgK for $(Ho_{0.9}Er_{0.1})_{0.85}Gd_{0.15}Co_2$. It should be noted that the maximum values of ΔS_{mag} obtained from the heat capacity data are similar to those reported based on magnetization measurements [7].

According to literature data, the Ericsson cycle is the appropriate one to be used in magnetic refrigerator [12]. This cycle employs a constant value for the ΔS_{mag} in the temperature range of refrigeration, which is necessary for the improvement of the regenerative processes [13].

Unfortunately, as can be seen from Figures 3 and 4, $\Delta S_{mag}(T)$ for single multicomponent compounds is not constant in the temperature range. To overcome this difficulty, the numerical simulations, according to the procedure proposed in Refs. [14-16] to construct a composite material formed by $[(Ho_{0.9}Er_{0.1})_{0.95}Gd_{0.05}Co_2]y_1$; $[(Ho_{0.9}Er_{0.1})_{0.9}Gd_{0.1}Co_2]y_2$ and $[(Ho_{0.9}Er_{0.1})_{0.85}Gd_{0.15}Co_2]y_3$ was done. The factors y_i represent the mass ratio of each multicomponent compounds under the condition $y_1+y_2+y_3=1$. The effective isothermal magnetic entropy change upon magnetic field variation of the composite material is given by [15];

$$\left|\Delta S_{comp}\right| = \sum_{i=1}^{3} y_i \left|(\Delta S_{mag})_i\right|, \tag{4}$$

where $(\Delta S_{mag})_i$ represent the isothermal magnetic entropy change of the single materials $(Ho_{0.9}Er_{0.1})_{0.95}Gd_{0.05}Co_2$; $(Ho_{0.9}Er_{0.1})_{0.9}Gd_{0.1}Co_2$ and $(Ho_{0.9}Er_{0.1})_{0.85}Gd_{0.15}Co_2$, respectively.

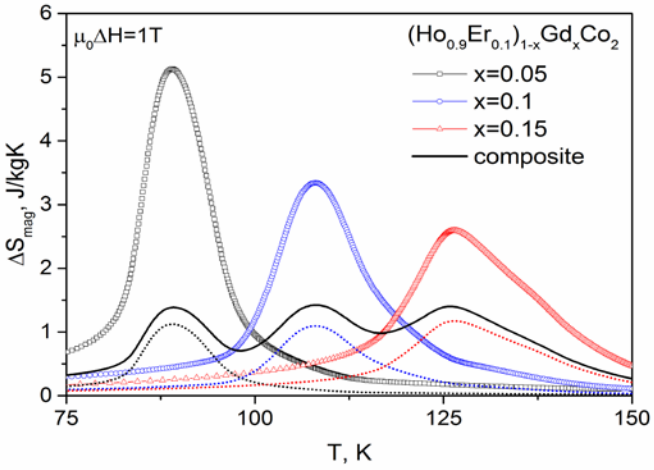

Figure 3. Temperature dependences of the magnetic entropy change, $\Delta S_{mag}(T)$, for investigated compounds and composite (solid line) based on them, for magnetic field change 0 to 1 T. The dotted lines represent ΔS_{mag} vs. temperature for $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds after the numerical simulations using $y_1 = 0.219$, $y_2 = 0.328$ and $y_3 = 0.453$, for x = 0.05, 0.1 and 0.15, respectively.

The solids lines in Figures 3 and 4 show the calculated isothermal entropy change for these composite materials using $y_1 = 0.219$, $y_2 = 0.328$ and $y_3 = 0.453$ for a magnetic field variation from 0 to 1 T and $y_1 = 0.222$, $y_2 = 0.290$ and $y_3 = 0.487$ for a magnetic field variation from 0 to 2 T, respectively. From those figures, one can notice that the peaks corresponding to the magnetic transition temperature of the three multicomponent compounds and the magnitude of the peak values decreases and the shape of the peaks gets broadened. The maximum magnetic entropy change fluctuates around 1.4 J/kgK, at $\mu_0 \Delta H = 1$ T, and 2.7 J/kgK for $\mu_0 \Delta H = 2$ T in a temperature range from 90 to 127 K.

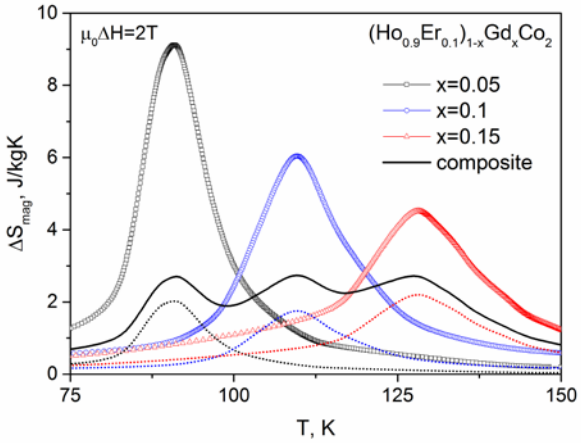

Figure 4. Temperature dependences of the magnetic entropy change, $\Delta S_{mag}(T)$, for investigated compounds and composite (solid line) based on them, for magnetic field change from 0 to 2 T. The dotted lines represent ΔS_{mag} vs. temperature for $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds after the numerical simulations using $y_1 = 0.222$, $y_2 = 0.290$ and $y_3 = 0.487$, for x = 0.05, 0.1 and 0.15, respectively.

4. Conclusions

On the basis of the experimental heat capacity measurements, the isothermal magnetic entropy changes for multicomponent $(Ho_{0.9}Er_{0.1})_{1-x}Gd_xCo_2$ compounds (x = 0.05, 0.1 and 0.15) were calculated. Also, it was determined theoretically the optimum molar fraction of these three compounds in order to form a composite to be considered as an optimal refrigerant material working in an Ericsson cycle in the temperature range 90-130 K. Moreover, the obtained molar concentrations of the composite showed the slight dependence on $\mu_0\Delta H$ in the magnetic field range under study.

Acknowledgments

The work was supported by the National Science Center, Poland through the OPUS Program under Grant No. 2019/33/B/ST5/01853.

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