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MAGNETOCALORIC EFFECT AND PHASE TRANSFORMATION IN $Ho_{1-x}Gd_xCo_2$ AND $Ho_{1-x}Tb_xCo_2$ COMPOUNDS

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ABSTRACT

The rare - earth transition metal intermetallics RCo_2 have attracted much attention due to their interesting magnetic properties related to the magnetic instability of the cobalt 3d electrons. This instability induces a first order magnetic transition (FOMT) leading to large magnetic entropy changes in some RCo_2 compounds such as $ErCo_2$, $HoCo_2$ and $DyCo_2$. Here, we present recent results obtained with $Ho_{1-x}Tb_xCo_2$ and $Ho_{1-x}Gd_xCo_2$ solid solutions. Structural, magnetic phase transition and magnetocaloric properties of these materials ($0 \leq x \leq 1$) were investigated by X – ray diffraction and magnetic measurements and then analyzed in terms of Landau theory. The $Ho_{1-x}Gd_xCo_2$ and $Ho_{1-x}Tb_xCo_2$ alloys present the C15 cubic $MgCu_2$ – type structure. The cell parameter a and the Curie temperature T_C both increase, increasing the Tb and Gd concentrations. T_C shifts from 81 to 233 K (x = 0 to 1) for $Ho_{1-x}Tb_xCo_2$ and from 81 to 300 K (x = 0 to 0.6) in the case of $Ho_{1-x}Gd_xCo_2$. The change of isothermal entropy ΔS was calculated according to magnetic measurements, using the thermodynamic Maxwell's relation. Besides, the increase of T_C is accompanied by a decrease of the entropy change. The reduction of the magnetocaloric effect (MCE) for $Ho_{1-x}(Gd, Tb)_xCo_2$ compounds could be explained by the fact that substitution of Tb and Gd to Ho weakens and supersedes the field–induced magnetic transition existing close to T_C and accordingly transforms the transition from first to second order type.

INTRODUCTION

The magnetocaloric effect (MCE) is defined as an intrinsic property of many magnetic materials to heat up or cool down when they are submitted to variations of external field in adiabatic conditions. This effect is measured both by the adiabatic temperature change and by the isothermal entropy change. Based on the MCE, magnetic refrigeration is becoming a promising technology enabling replace the conventional gas–compression / expansion technique according to environment friendly and energy efficient considerations. Nowadays, a large number of materials are under detailed investigation to define the optimum magnetocaloric material(s) to be installed in magnetic cooling systems. The MCE was discovered by Warburg [1] in 1881, and has been used for cryogenic refrigeration since 1930's. Using metal gadolinium as the magnetic refrigeration substance, Brown was the first applying magnetic cooling near room temperature in 1976 at Lewis Research Center of American NASA [2]. Late the 1990's, two major developments occur successively. The first one, based on a demonstration refrigerator, proves that at temperature ranging to 300 K the principle of magnetic refrigeration is a viable and competitive technology [3] with potential energy savings of up to 30%. The second fact was the evidence of a giant magnetocaloric effect in $Gd_5Ge_2Si_2$ [4]. Calculation of the isothermal entropy change in $Gd_5Ge_2Si_2$ yielded a value twice higher than for gadolinium. At T = 276 K and for a

magnetic field variation from 0 to 5 T, the entropy change being ~ 18.5 J/kg K. Such a large value result both from the 1st magnetic phase transition combined with a crystal structure transformation. Besides, after discovering the giant MCE in $Gd_5Ge_2Si_2$, research interests to MCE materials were considerably enhanced. A wide range of prototype materials, e.g. intermetallic compounds, were systematically checked for in order to achieve large MCE signals at selected temperatures. Most part of this effort was concentrated on materials that exhibit interestingly high magnetocaloric properties close room temperature such as $MnAs_{1-x}Sb_x$ [5], $MnFeP_{1-x}As_x$ [6] and $La(Fe_{1-x}Si_x)_{13}$ [7]. Parallel, the binaries RCo_2 (R rare earth) have attracted much attention in recent years because of a 1st order metamagnetic transition existing in some of these compounds, which could lead to large MCE. The RCo_2 compounds crystallize in the C15 Laves-phase structure, and are representatives of systems with unstable 3d magnetic moments due to the itinerant character of the cobalt sublattice. In these compounds, the cobalt moment is induced by the localized one of the R atoms, acting as exchange field. This interaction supports the metamagnetic character of the cobalt sublattice from paramagnetic to ferromagnetic (or ferrimagnetic) state [8, 9]. Unstability of the cobalt moment is the origin of the 1st order (meta) magnetic transition in several of the RCo_2 compounds. For example, $HoCo_2$ exhibits a 1st order transition from ferro- to paramagnetic states at T_C = 81 K; correspondingly the maximum value of entropy change is for ~ 23.2 J/Kg K under a field change of 5 T. Obviously $HoCo_2$ presents a large MCE, but the low T_C value restricts application. Since the T_C values of $TbCo_2$ and $GdCo_2$ are close to 233 and 400 K respectively, we expect that T_C can be increased interestingly in the respective solid solutions. Thus in the present paper, we report on the impact of Tb and Gd substitution in the $HoCo_2$ compound in terms of phase transitions and MCE.

1 EXPERIMENTAL

The $Ho_{1-x}(Tb,Gd)_xCo_2$ compounds were prepared by arc-melting mixtures of pure elements (purity of the metals ≥ 3N) in an pure argon atmosphere (purity ≥ 5N). After being melted several times to insure homogeneity, the samples were annealed at 800°C for a week in evacuated quartz ampoules and then water-quenched. X-ray diffraction analysis shows that all the samples are single phase with the C15 $MgCu_2$- type structure. Magnetic measurements were performed using dedicated magnetometers developed at Louis Nèel Laboratory, Grenoble. The isothermal entropy change was evaluated from the magnetic field dependence of magnetization at various temperatures by using the thermodynamic Maxwell relation.

2 RESULTS

The x (Gd, Tb) composition dependence of the Curie temperature is shown in Fig. 1 for the $Ho_{1-x}Gd_xCo_2$ and $Ho_{1-x}Tb_xCo_2$ compounds. The Curie temperature was estimated from the temperature dependence of magnetization measured in a magnetic field of 0.1 T, so T_C is determined when (dM/dT) forms an inflexion point. As shown in Fig. 1, we observe that T_C increases from 81 to 402 K with increasing Gd content from x = 0 to x = 1 and that T_C is close to 300 K when x = 0.6 in the case of the $Ho_{1-x}Gd_xCo_2$ solid solution. Besides, for the $Ho_{1-x}Tb_xCo_2$ system, T_C shifts from 81 to 233 K for x varying from 0 to 1. Inoue and Shimizu [10] have described the evolution of Curie temperature for the materials with R = Gd, Tb and Dy by using the same value for the R – R and R – Co exchange interactions as those used for RCo_2. The increase of T_C induced for $Ho_{1-x}(Tb, Gd)_xCo_2$ is very advantageous for magnetic refrigeration since its requires magnetic materials with noticeable magnetocaloric properties on a relatively large range of temperature. However, a magnetic refrigerator will work well close to T_C where the magnetocaloric effect is maximum. So, optimized materials with different T_C can be obtained

easily by changing the Tb / Gd concentration. Moreover, where the physical and the chemical properties are similar, a series of these patent materials can be combined in order to form a composite refrigerant working in the temperature range covering all the different Curie temperatures.

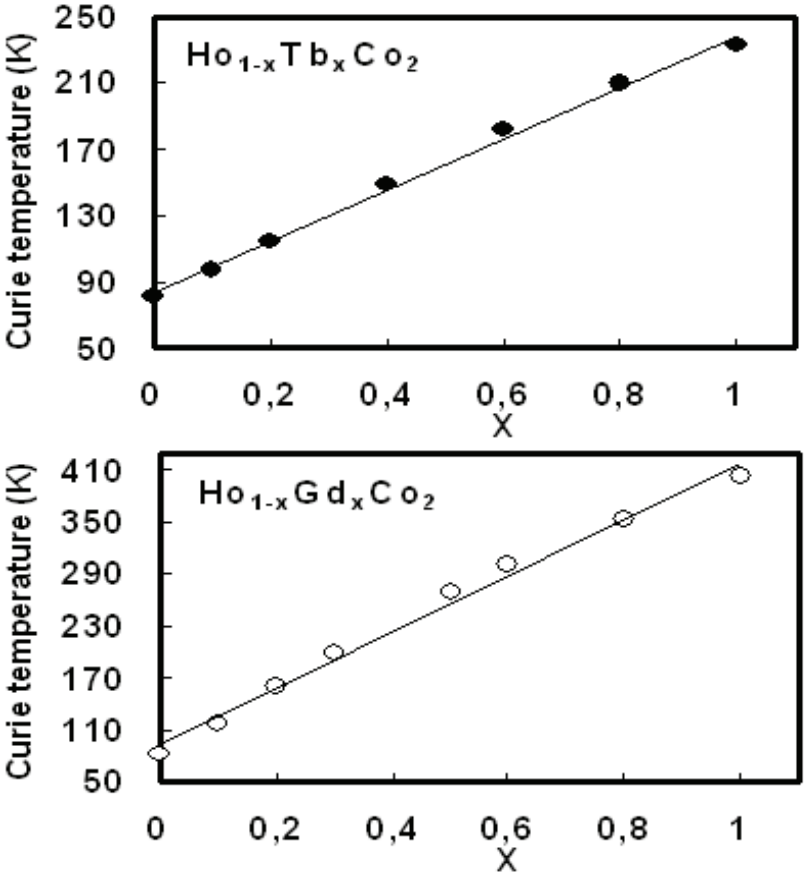

Figure 1: Curie temperature T_C of the $Ho_{1-x}Gd_xCo_2$ and $Ho_{1-x}Gd_xCo_2$ compounds.

The magnetocaloric effect is intrinsic to all magnetic materials and is induced via the coupling of the magnetic sublattice with the magnetic field, which alters the magnetic part of the total entropy due to change in external magnetic field. The MCE represented by the isothermal entropy change can be determined according to magnetic measurements based on the Maxwell relation:

$$\Delta S(T,0 \rightarrow H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_{H'} dH' \qquad (1)$$

For magnetization measurements M made at constant temperature for successive values of field H, the Maxwell relation can be approximated by the following expression

$$\Delta S = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i \qquad (2)$$

where M_{i+1} and M_i are the magnetization values measured in a field H, at temperatures T_{i+1} and T_i, respectively. The accuracy of ΔS calculated using this technique is about 3 – 10 % [11].

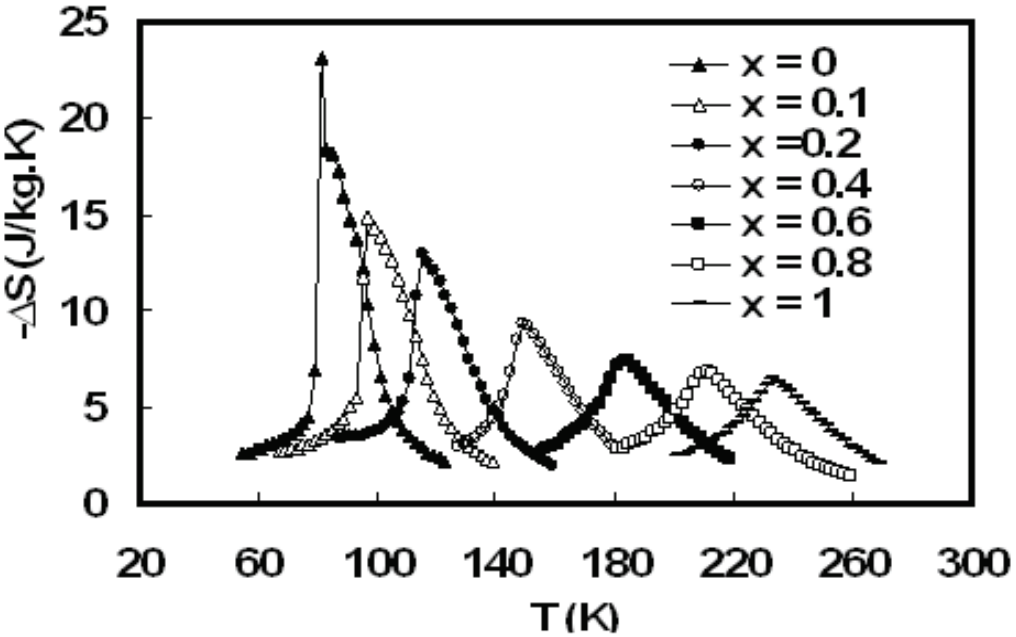

Figure 2: Temperature dependence of the entropy change for $Ho_{1-x}Tb_xCo_2$ upon an external field change of 5 T for x = 0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1

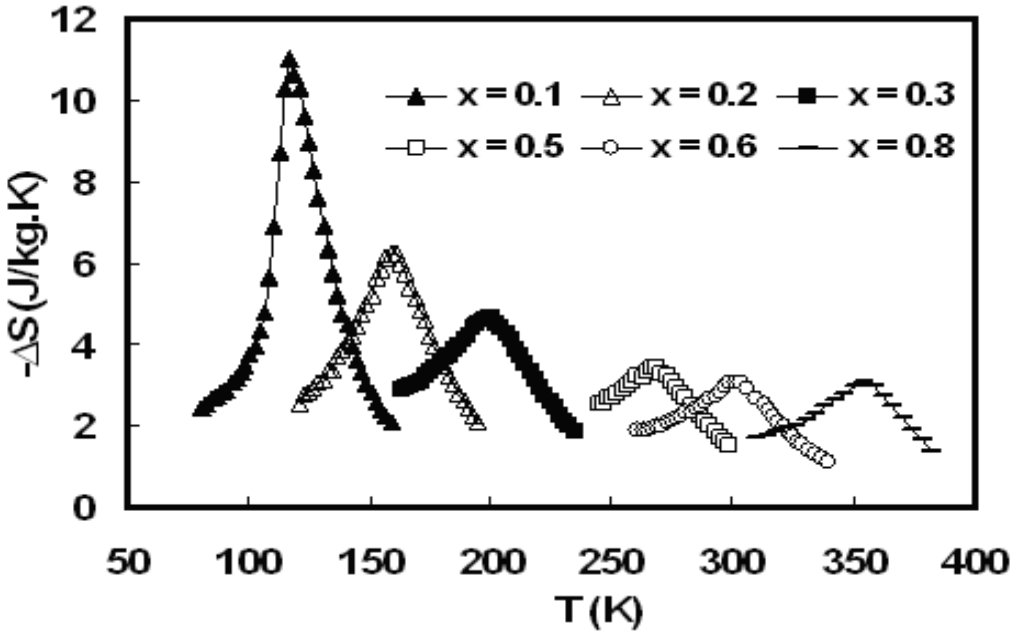

Figure 3: Temperature dependence of the entropy change of $Ho_{1-x}Gd_xCo_2$ upon an external field change of 5 T for x = 0.1, 0.2, 0.3, 0.5, 0.6 and 0.8

The entropy change ΔS as a function of temperature, was calculated from the isothermal magnetization curves using relation (2) for both the $Ho_{1-x}Tb_xCo_2$ and $Ho_{1-x}Gd_xCo_2$ alloys upon a change of magnetic field of 5 T are given respectively in Figs. 2 and 3. The entropy changes

reach their maximum close to the corresponding Curie temperatures. Indeed, since T_C increases with increasing the Tb and Gd content, the peak of ΔS shifts notably to higher temperatures. Under 5 T, the entropy change in $HoCo_2$ is about 23.2 J/kg K at T_C = 81 K. The giant magnetocaloric effect observed in $HoCo_2$ should be attributed to the important change of magnetization occurring close to T_C because of the itinerant - electron - metamagnetic transition (IEMT) induced by magnetic field causes a 1st transition from para- to ferromagnetic state. In addition, equation (1) shows that isothermal entropy change is large when the magnetization changes more abruptly in the vicinity of a phase transition, which leads to a large ΔS. However, for x varying from 0 to 0.8 the maximum entropy change for $Ho_{1-x}Gd_xCo_2$ passes from 23.2 to 3 J/kg K, while that for $Ho_{1-x}Tb_xCo_2$, it decreases down to 6.5 J/kg K for x varying from x = 0 to 1. This reduction of magnetocaloric properties is due essentially to a change of the magnetic transition character from a first to second order type. When and why the transition changes from a first-order to second-order upon the Tb and Gd substitution?

Arrott plots as built from magnetization isotherms are usually used to identify the order of transition for a magnetic material. If negative slopes or inflection point are found in the Arrott plots close to T_C, the magnetic transition is of 1st order type. Oppositely, if the Arrott plots present an almost linear trend, the transition is of 2nd order type. Fig. 4 and 5 show the Arrott plots for the $Ho_{1-x}Tb_xCo_2$ and $Ho_{1-x}Gd_xCo_2$ series respectively. Concerning the $Ho_{1-x}Tb_xCo_2$ compounds, for x = 0, 0.1 and 0.2 the inflection point in the Arrott plots indicates the occurrence of a 1st order field induced magnetic transition. Besides, for the x = 0.4, 0.6, 0.8 and 1 compositions, the Arrott plots above T_C exhibit an almost linear variation, which is typical of a 2nd order magnetic transition. This result is in fair agreement with that obtained by Duc et al [12] in $Ho_{1-x}Tb_xCo_2$ series from magnetic, resistivity measurements and Landau theory. They found that the transition is of first order for x = 0, 0.1, 0.15 and 0.3, while for x = 0.7, 0.9 and 1 the transition is of second order. For $Ho_{1-x}Gd_xCo_2$ compounds, Fig. 5 indicates that the transition is of 1st order for x = 0 and 0.1, while for x > 0.1 a 2nd order magnetic transition occurs.

Another method to determine the transition type is based on the Inoue – Shimizu model, which has been successfully used to describe the phase transition in RCo_2 compounds [13, 14]. According to this model, the Landau expansion of the magnetic free energy up to sixth power of the total magnetization M applies:

$$F = (1/2)\, a(T).M^2 + (1/4)\, b(T).M^4 + (1/6)\, c(T).M^6 - \mu_0 MH \qquad (3)$$

From the equilibrium condition $(\partial F/\partial M) = 0$, one obtains the following equation to describe the magnetization behaviour near the Curie temperature;

$$a(T).M + b(T).M^3 + c(T).M^5 = \mu_0 H \qquad (4)$$

where the Landau coefficients a (T), b (T) and c (T) can be calculated by fitting the magnetization isothermal traces using the here above equation. The susceptibility presents a maximum value at T_C, so, a minimum in a (T) occurs correspondly. However, the Landau coefficient b (T) at T_C may be positive, zero or negative, where zero and positive values correspond to a 2nd order transition and negative value corresponds to a 1st order transition. Calculated values of T_C from the M (T) measurements and that obtained from Landau coefficient a (T) as well as the nature of the magnetic transition deduced from b (T) for $Ho_{1-x}(Tb, Gd)_xCo_2$ are listed in Table 1 and 2. One notice that the derived Curie temperature obtained via a (T) is within standard deviation similar to that obtained from magnetic measurements. Besides, the

order of the phase transition determined from *b* (*T*) parameter is compatible with the Arrott plots results.

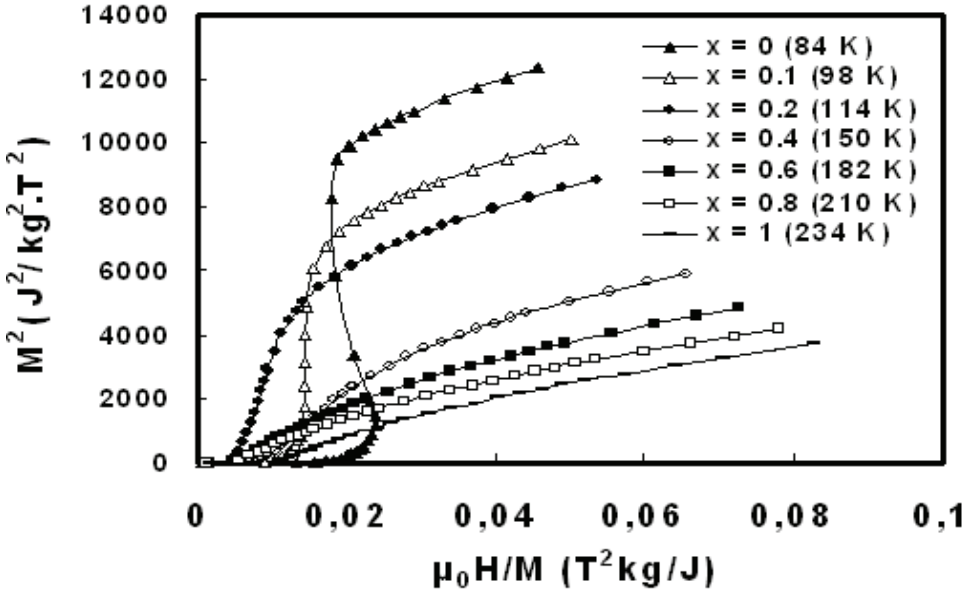

Figure 4: Arrott plots close to the transition temperature for $Ho_{1-x}Tb_xCo_2$ with x = 0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1

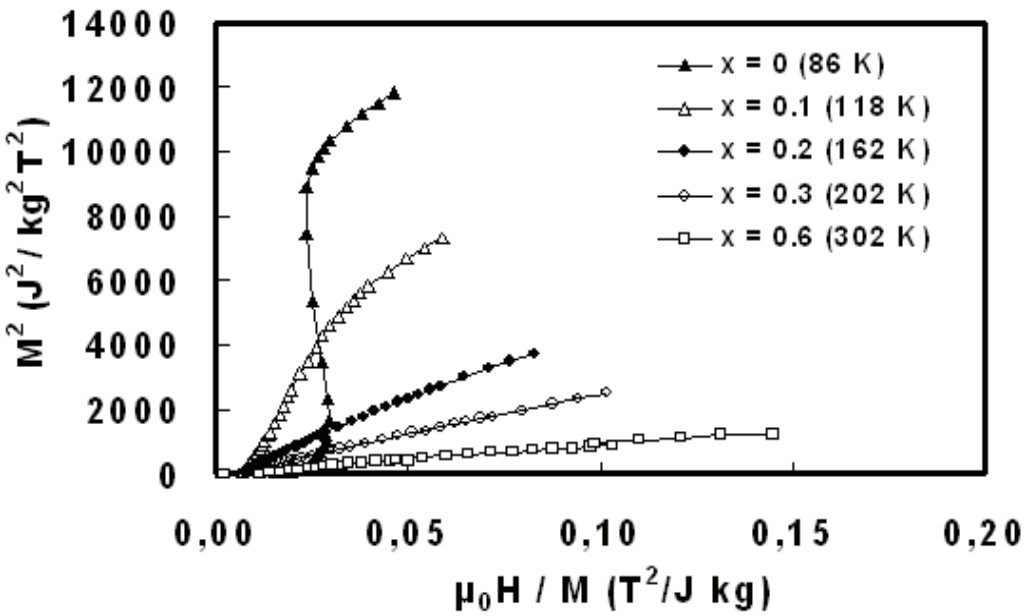

Figure 5: Arrott plots close to the transition temperature for $Ho_{1-x}Gd_xCo_2$ with x = 0, 0.1, 0.2, 0.3 and 0.6

Table 1: Lattice parameter, Curie temperature and order of the magnetic phase transition for the $Ho_{1-x}Tb_xCo_2$ samples. T_{C1} and T_{C2} correspond to the Curie temperatures deduced respectively from magnetic measurements and from the Landau theory.

x	a (Å)	$T_{C1} \pm 2$ (K)	$T_{C2} \pm 2$ (K)	type of transition
0	7.1512	81	81	**first-order**
0.1	7.1731	97	100	**first-order**
0.2	7.1767	115	118	**first-order**
0.4	7.1823	149	150	**second-order**
0.6	7.1889	182	178	**second-order**
0.8	7.1956	210	210	**second-order**
1	7.1991	233	226	**second-order**

Table 2: Lattice parameter, Curie temperature and order of the magnetic phase transition for the $Ho_{1-x}Gd_xCo_2$ samples. T_{C1} and T_{C2} correspond to the Curie temperatures deduced respectively from magnetic measurements and from the Landau theory.

x	a (Å)	$T_{C1} \pm 1$ (K)	$T_{C2} \pm 1$ (K)	Type of transition
0	7.1512	81	81	**first-order**
0.1	7.1721	117	118	**first-order**
0.2	7.1897	160	160	**second-order**
0.3	7.1877	200	202	**second-order**
0.5	7.2068	268	268	**second-order**
0.6	7.2194	300	300	**second-order**
0.8	7.2341	352	352	**second-order**
1	7.2599	402	402	**second-order**

CONCLUSION

In the work here reported, different samples of the $Ho_{1-x}Gd_xCo_2$ and $Ho_{1-x}Tb_xCo_2$ series of compounds were prepared. The impact of Gd and Tb substitutions for Ho in $HoCo_2$ on the magnetic, the magnetocaloric effect and the change of the magnetic transition type from1st order to 2nd order were investigated. The R metal atoms substitutions allow to form single phase compounds with the cubic Laves phase structure up to x = 1, leading to increase the Curie temperature from 81 to 233 K for $Ho_{1-x}Tb_xCo_2$ and from 81 to 402 K for $Ho_{1-x}Gd_xCo_2$. These increases of T_C are accompanied by a reduction of the magnetocaloric effect. For both series, a large entropy change was observed for low Tb and Gd contents to be related to the existence of FOMT. Under an applied field of 5 T and when increasing x from 0 to 0.8, the maximum isothermal entropy variation decreases quickly from 23.2 to 3 J/kg K in the case of $Ho_{1-x}Gd_xCo_2$, while that for $Ho_{1-x}Tb_xCo_2$ decreases down to 6.5 J/kg K for x varying from 0 to 1. This reduction of the MCE contribution should be attributed essentially to the change in the order of the magnetic transition. Arrott plots and the temperature dependence of Landau coefficients indicate that increasing the Gd and Tb concentration eliminates the field induced magnetic transition and as a consequence it drives the transition from 1st to 2nd order. Besides, in addition to the interesting magnetocaloric properties, the $Ho_{1-x}(Gd,Tb)_xCo_2$ are chemically stable and can

be prepared easily, which is an important point when considering practical materials for magnetic refrigeration.

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