

MAGNETOCALORIC EFFECT ON $Tb_{1-x}Y_xCo_2$ COMPOUNDS

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Abstract. The structural, magnetic and magnetocaloric properties of several $Tb_{1-x}Y_xCo_2$ compounds were investigated. The investigated compounds are ferrimagnetically ordered. The decrease of the transition temperatures and cobalt moments, when increasing Y content, were attributed to diminution of the exchange interactions. A second-order magnetic phase transition at T_C was evidenced. The magnetocaloric effect was also studied. The obtained maximum entropy change values were found to decrease from 5.3 J/kgK for $x = 1$ to 1.9 J/kgK for $x = 6$ for a magnetic field change from 0 to 4 T. It was found that $RCP(\Delta S)/\Delta B$ values are quite independent of Y concentration.

Key words: Intermetallic compounds; Magnetic properties; Magnetic entropy change; Refrigerant capacity.

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1. INTRODUCTION

Materials showing a large magnetocaloric effect (MCE) have attracted attention for their potential application in magnetic refrigeration technology [1–3]. The compounds which undergo temperature driven paramagnetic to ferromagnetic first order transitions show relatively large “negative” MCE, in which the isothermal magnetic entropy change, $\Delta Sm = S(H,T) - S(0,T)$ is negative [4]. The heavy rare earths elements and their ferromagnetic compounds are considered as best candidate materials for finding a large MCE due to their high magnetic moments [5]. Several Laves phase compounds RM_2 (R = rare earth metal and $M = 3d$ transition metal) have been investigated for magnetocaloric effect because of simply crystal structure [6–8]. The RCO_2 intermetallic compounds were intensively studied due to the metamagnetic character of its cobalt sublattice [9,10]. It was reported that in the compounds with Dy, Ho or Er the ferrimagnetic state is coupled to a structural transition, leading to a first order transition at the critical

temperature [11–13]. Large entropy changes at the transition temperature were reported [14,15].

The RCo_2 compounds crystallize in a cubic Laves phase structure in which the R and Co atoms occupy each one type of site only [16]. Useful information on the magnetic behavior of the constituent atoms can be found due to the high symmetry [10,11]. For nonmagnetic rare earths spin fluctuations type behavior was evidenced. First-order metamagnetic transition under external field above a critical value was observed in ErCo_2 ($T_C = 32 \text{ K}$) [17], whereas a second-order transition was found in TbCo_2 ($T_C = 227 \text{ K}$) [18]. Some phenomenological models have been proposed to discuss the order of the magnetic phase transition [19,20]. It has been found that in the system $(\text{Er}_{1-x}\text{Tb}_x\text{Co}_2)$, the magnetic transition changes from first to second order around $x = 0.60$ [17]. The collapse of cobalt magnetization was reported in ErCo_2 under pressure [21]

Voiron *et al.* [18] have measured the specific heat in TbCo_2 at zero applied field, and no anomalous behavior was found above T_C . It was reported that the substitution of magnetic R-atom by yttrium reveals a decrease of the magnetic order and finally leads to an exchange-enhanced Pauli paramagnetism in YCo_2 . The composition dependence of Co-magnetic moment in the $\text{R}_{1-x}\text{Y}_x\text{Co}_2$ systems shows a sharp fall approaching a critical yttrium concentration x_c . Previously, studies of the behavior of heavy rare earth and Co magnetic subsystems with Y-substitution were performed [22–30]. In the vicinity of x_c , where the long-range magnetic order disappears and the Co moments are unstable, anomalies in the transport properties, the specific heat and neutron diffraction have been reported. Neutron diffraction measurements have showed that in the narrow concentration range near critical concentration $\text{Er}_{1-x}\text{Y}_x\text{Co}_2$ and $\text{Ho}_{1-x}\text{Y}_x\text{Co}_2$ —exhibit both Bragg magnetic reflections and diffuse maximums which indicate a coexistence of long-range and short-range magnetic orders [28]. The $\text{Tb}_{1-x}\text{Y}_x\text{Co}_2$ compounds show ferrimagnetic order in the concentration range $0 < x < 0.8$ while in the concentration range $0.8 < x < 1.0$ the compounds show spin glass behavior [26]. It was reported that an inhomogeneous phase appears with increasing the yttrium concentration. This phase was associated with a spin-glass state of non-typical kind. Kuentzler and Tari have shown that the critical concentration for the onset of cobalt magnetism is around $x_c = 0.9$ [26].

Previously, we have studied the magnetic properties of cobalt in pseudobinary RCO_3 and RCO_2 compounds [31–35]. The cobalt magnetic moment was found to be sensitive to the local environment. In order to obtain additional information on cobalt magnetic behavior in rare-earths based intermetallic compounds we study the magnetic properties and magnetocaloric effect in $\text{Tb}_{1-x}\text{Y}_x\text{Co}_2$ system. In all cases the magnetic entropy changes around transition temperatures were evaluated.

2. EXPERIMENTAL

The $Tb_{1-x}Y_xCo_2$ compounds were prepared by arc melting the high purity Co (99.9%), Y (99.9%) and Tb (99.95%) ingots (Alfa Aesar, Jonson & Matthey, Karlsruhe, Germany) in a purified argon atmosphere. A small excess of rare earth (yttrium) elements were used in order to compensate for losses during melting. The ingots were remelted several times in order to ensure a good homogeneity. All the samples were heat treated in vacuum at 1000°C for 5 days. The crystal structure was checked by X-ray Diffraction using a Bruker 8 XD diffractometer. The intensities were measured from 20° to 100° with a step size of 0.02° and a counting rate of 3 s per scanning step. Structure refinement was performed according to the Rietveld technique, supported by the FULLPROF computer code [36].

The magnetic measurements were performed in the temperature range 4.2–650 K and external fields up to 12T using a close cycle 12 T Vibrating Sample Magnetometer (VSM) from Cryogenics. The spontaneous magnetizations, M_s , were determined from magnetization isotherms according to approach to saturation law, $M = M_s(1 - b/H) + \chi_o H$. We denoted by b the coefficient of magnetic hardness and χ_o is a Pauli-type contribution. The entropy changes were determined from magnetization isotherms, between zero field and a maximum field (H_0) using the thermodynamic relation:

$$\Delta S_m(T, H_0) = S_m(T, H_0) - S_m(T, 0) = \frac{1}{\Delta T} \int_0^{H_0} [M(T + \Delta T, H) - M(T, H)] dH \quad (1)$$

where ΔT is the temperature increment between measured magnetization isotherms ($\Delta T = 5K$ for our data). The magnetic cooling efficiency was evaluated by considering the maximum magnitude of the magnetic entropy change, ΔS_M , and the full-width at half-maximum value of the $\Delta S_M(T)$ curve [15]:

$$RCP(S) = -\Delta S_M \delta_{FWHM} \quad (2)$$

This is the so-called relative cooling power (RCP) based on the magnetic entropy change.

3. RESULTS AND DISCUSSIONS

The X-ray diffraction patterns of the studied $Tb_{1-x}Y_xCo_2$ compounds are shown in Fig. 1. The X-ray analysis shows, in the limit of experimental errors, the presence of one phase only, for $x \leq 0.75$, with the cubic $MgCu_2$ structure, with the rare-earth or yttrium and Co atoms occupying only on type of site each. The lattice parameters are quite independent on yttrium concentration, having values around 7.21 Å.

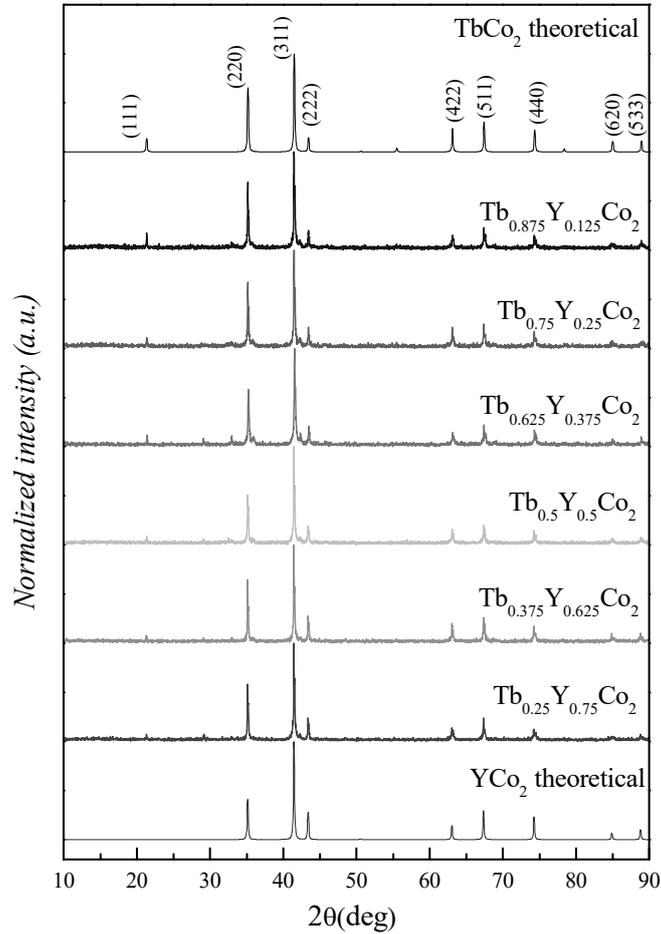


Fig. 1 – The X-ray diffraction patterns of $Tb_{1-x}Y_xCo_2$ compounds measured at room temperature.

The almost constant value of the lattice parameters could be explained by the small difference between Y^{3+} ionic radius and respectively Tb^{3+} ionic radius which is around 2%. The transition temperatures, T_C , (defined as the temperatures at which the dM/dT versus temperature curves measured during heating present a minimum) were determined from the temperature dependences of the magnetization measured in a low magnetic field of 0.2 T. The T_C values were found to decrease approximately linearly with increasing Y content in the composition region $0 \leq x \leq 0.375$ – see Fig. 2. This decrease becomes more rapid for $x > 0.375$. The decrease in transition temperature, T_C , can be attributed to the diminution of the exchange field as the terbium content decrease. This assumption is sustained by the magnetic moments of Co which decrease with increasing yttrium content. The exchange interactions in RCO_2 are interdependent within the spatial extension of the unit cell. The induced

cobalt moment by $4f-5d-3d$ exchange path is stabilized by the Co $3d-3d$ direct exchange interactions. Concomitantly, with the appearance of a cobalt magnetic moment, an additional polarization $M_{5d}(d)$ is induced on $R5d$ band by a reverse path [37]. The cobalt moments parallelly with $R5d$ band polarization are strongly influenced by the magnetic dilution effects, both at R and Co sites, as for example in $Gd(Co_{1-x}Ni_x)_2$ [38] or $Gd_xY_{1-x}Co_2$ [39] pseudo-binary compounds. Similar behavior was reported in the past in $(ErY)Co_2$ [40], $(YGd)Co_2$ [41], respectively $(GdTb)Co_2$ compounds [42].

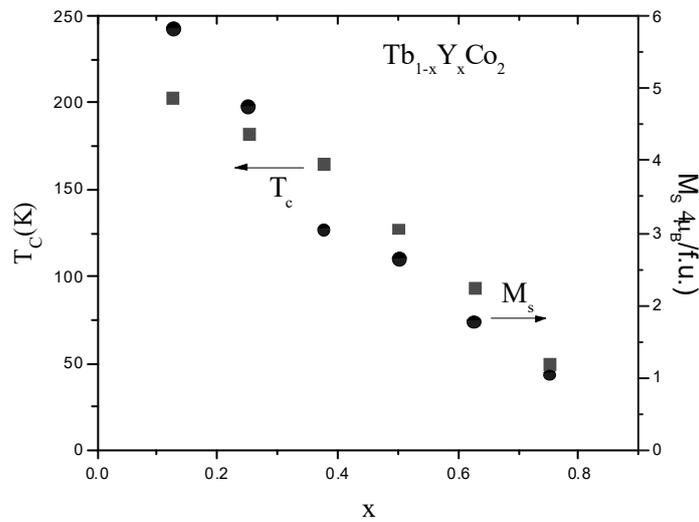


Fig. 2 – The composition dependences of the Curie temperatures and saturation magnetizations for the $Tb_{1-x}Y_xCo_2$ compounds.

The magnetization isotherms, measured in external magnetic fields up to 12 T, are presented in Fig. 3. All the investigated compounds are ferrimagnetically ordered. The saturation moments at 5 K were found to decrease from $5.83 \mu_B/f.u.$ for $x = 0.125$ to $1.04 \mu_B/f.u.$ for $x = 0.75$ – see Fig. 2. This behavior is consistent with an antiparallel coupling between $3d$ transition metals and heavy rare earths [43]. In a first approximation we can consider the Tb magnetic moment equal to that determined by neutron diffraction studies in $TbCo_2$ compounds [11], *i.e.* $8.80 \mu_B/atom$. Based on this supposition the cobalt magnetic moments were determined. The cobalt magnetic moments at 4.2 K are quite constant for the compounds with $x < 0.375$ and decrease for higher Y content from $1.08 \mu_B/atom$ ($x = 0.375$) to $0.57 \mu_B/atom$ ($x = 0.75$). The decreasing of the Co magnetic moment at 4.2 K, at high yttrium concentration, is the result of diminishing the exchange field acting on cobalt. It was shown previously that the cobalt magnetic moments are very sensitive to the local environment [31–35, 38]. The exchange interactions in the present system are described by the $4f-5d-3d$ model [44]. In the intermetallic heavy rare-earths- $3d$ transition metal compounds

the $4f$ - $3d$ interactions are antiferromagnetic [45,46]. The band structure calculations and magnetic measurements performed on RM_2 compounds, [35,47], suggested that there is an interplay between induced $R5d$ band polarizations and $M3d$ magnetic moments.

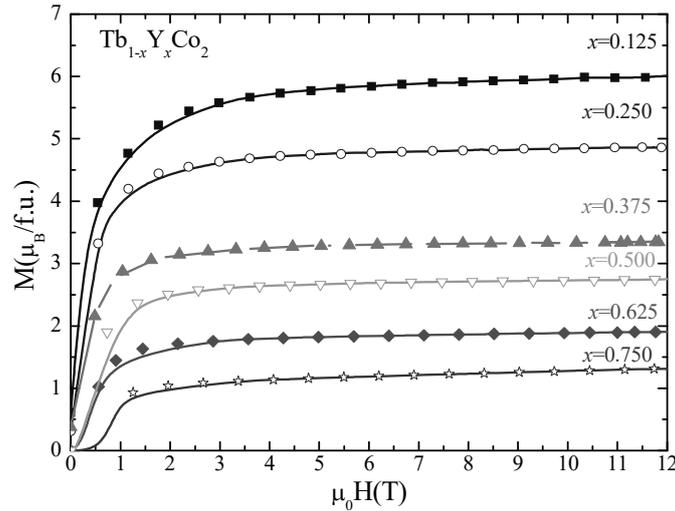


Fig. 3 – The external magnetic field dependences of the magnetization isotherms.

It was shown that the $R5d$ band polarization can be described, in a first approximation, as being due to $4f$ - $5d$ local exchange as well as to $5d$ - $3d$ short range exchange interactions. The $M3d$ magnetic moments are influenced by the $R5d$ band polarizations. This will contribute additionally to $M3d$ polarization. The $R5d$ band polarizations, induced by short range exchange interactions, are dependent, in a first approximation, on the number of magnetic M atoms situated in the first coordination shell and their moments. It was shown that the transition metal contribution to $R5d$ band polarization is related to the exchange splitting of cobalt band, proportional to the exchange field ($M_{Co} = 0$ if $H_{exch} < 75T$ in $ErCo_2$) [21]. A contribution associated with $R5d$ - $M3d$ hybridization was identified and it was shown that this contribution is dependent on R 's partner [48]. By the exchange interactions among the $3d$ electrons the density of states in the up and down spin subbands split and shift towards lower and higher energy sides respectively and a magnetic moment will be developed on the transition metal site. The $3d$ - $4d$ hybridization is reduced for the spin up states lowering the occupation of $4d$ spin up states while for the opposite spins the effect is contrary. As a consequence, a magnetic polarization (about $0.23 \mu_B/\text{atom}$) on $R5d$ ($Y4d$) band appears [49]. Due to the changes in the neighborhood of the Co atoms when Y ions substitute the Tb ions, the contribution associated with $R5d$ - $M3d$ hybridization and finally the cobalt magnetic moment will be modified.

The magnetization isotherms for the sample with $x = 0.25$ measured in a wide temperature range around the transition temperature with a step of 5 K are shown in Fig. 4. Similar behaviors were observed for all investigated compounds.

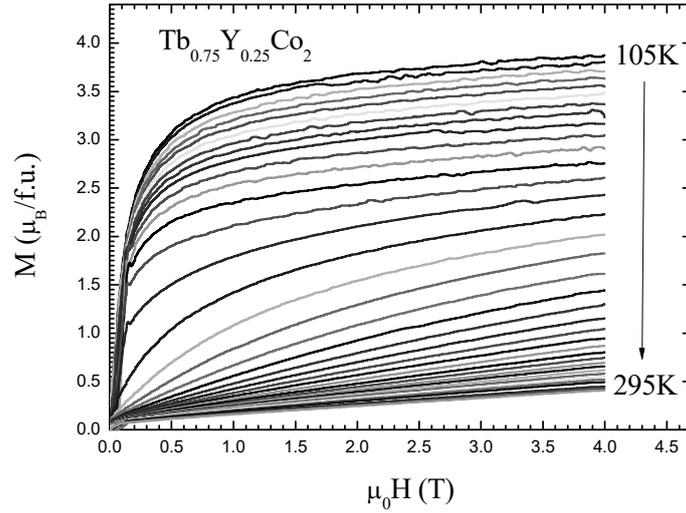


Fig. 4 – Magnetization isotherms for the $\text{Tb}_{0.75}\text{Y}_{0.25}\text{Co}_2$ compounds measured around the transition temperature with a step of 5K.

From the magnetization isotherms we have calculated and represented in Fig. 5 the Arrott plots [50]. The order of the magnetic transition can be derived from the shape of the M^2 versus H/M dependences. The negative slope or inflexion point on Arrott plots are usually indicative of a first-order transition, while the linear shape of these dependencies above T_C implies that a second-order magnetic transition occurs. From the Arrott plots, we can see that the compounds undergo essentially a second-order magnetic phase transition at the Curie temperature. Similar behaviors were found for all of the investigated compounds. The Curie temperatures estimated from Arrott plots are close to that determined from the magnetization derivative against temperature.

The magnetocaloric effect in external magnetic fields between 0 and 4 T was also studied. The magnetic entropy change *versus* temperature plots in applied field changes of 0–2 T and 0–4 T for all of the investigated compounds are presented in Fig. 6. The ΔS_M (T) peaks are broad and have a symmetrical shape around the transition temperature for the samples with high terbium content, a behavior which is characteristic for materials exhibiting a second-order magnetic phase transition [51]. In the case of compounds with high yttrium content the shape of the ΔS_M (T) peaks show a slight asymmetry suggesting inhomogeneities in ion distribution. The obtained maximum entropy change values were found to decrease from 5.3 J/kgK

for $x = 0.125$ to 1.9 J/kgK for $x = 0.75$ for a magnetic field change from 0 to 4 T. In an external magnetic field change from 0 to 2 T, the magnetic entropy change values were found to decrease to 3.25 J/kgK for $x = 0.125$ and 1.2 J/kgK for $x = 0.75$ respectively.

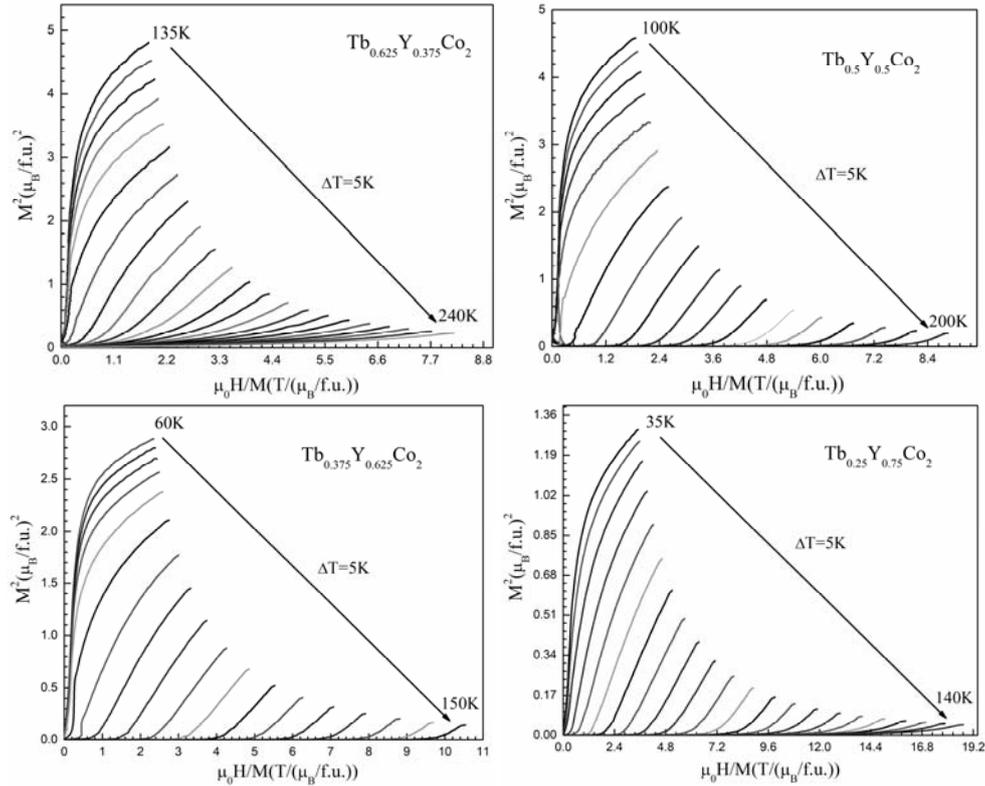


Fig. 5 – Arrott plots for the $\text{Tb}_{1-x}\text{Y}_x\text{Co}_2$ compounds with $x=0.375, 0.50, 0.625$ and 0.75 .

The decrease of magnetic entropy change with increasing yttrium content may be caused by the decrease in the concentration of Tb^{3+} ions. Similar behavior was reported in $(\text{ErY})\text{Co}_2$ compounds [52]. In an earlier paper Wada *et al.* [53], have reported the same tendency when Y substitute Er in $(\text{ErY})\text{Co}_2$ compounds. The decrease of the magnetic entropy change was explained by Oliveira *et al.* through the model in which the localized spins of the rare-earth ions are under the effect of the crystalline electric field and are coupled to an effective subsystem of itinerant electrons [54]. According to this model, the introduction of Y instead of Er ions in ErCo_2 results only in the decrease in the effective Er–Er interaction. An opposite behavior was observed for the $\text{Dy}_{1-x}\text{Y}_x\text{Co}_2$ compounds [55]. It was reported that the increase in the yttrium concentration in $\text{Dy}_{1-x}\text{Y}_x\text{Co}_2$ system up to $x = 0.3$ does

not have as result a decrease of the ΔS_m value as expected but, contrary, is accompanied by the growth of the magnetic entropy change. This behavior of the magnetocaloric effect in $\text{Dy}_{1-x}\text{Y}_x\text{Co}_2$ compounds could not be explained by the Oliveira model because it neglects the contribution to the magnetic entropy change from the itinerant d electrons.

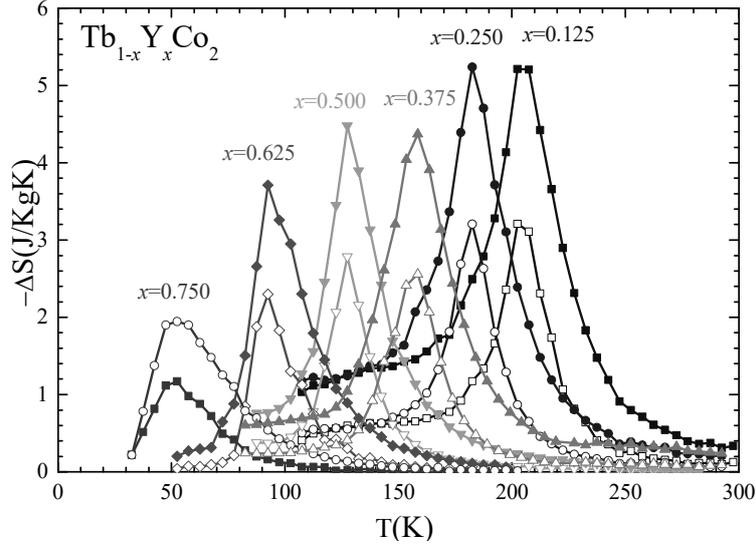


Fig. 6 – The magnetic entropy changes as function of temperature in applied field changes of 0–4 T and 0–2 T for all of the investigated samples belonging to the $\text{Tb}_{1-x}\text{Y}_x\text{Co}_2$ system.

A characteristic parameter for magnetocaloric materials is the relative cooling power (RCP). A large $\text{RCP}(\Delta S)$ corresponds to a better magnetocaloric material. It was also suggested that for characterizing magnetocaloric materials, it is more convenient to use the specific renormalized cooling power, defined as $\text{RCP}(\Delta S)/\Delta B$, relative to the external field variation ΔB [56]. In the present system, high $\text{RCP}(\Delta S)$ values were found, due to the large δT_{FWHM} values. For example, an $\text{RCP}(\Delta S)/\Delta B$ value of 53.25 J/kgT was obtained for the sample with $x = 0.125$, while for the sample with $x = 0.75$ a value of 37.8 J/kgT was obtained – see Table 1. Also, it is worthwhile to note that the $\text{RCP}(\Delta S)/\Delta B$ values do not vary significantly for applied field changes of 0–4 T and 0–2 T respectively, a fact which is important for magnetic refrigeration applications in the intermediate temperature range. We note that the determined $|\Delta S_M|$ values are only approximate. These are influenced by the rate of increasing magnetic field during the measurements, as well as by the approximation used in determining $|\Delta S_M|$ values from discrete sets of magnetization data [57]. The entropy changes are also sensitive to the magnetic hardness of the material [58].

Table 1

Curie temperatures, RCP(ΔS) and RCP(ΔS)/ ΔB values in external magnetic fields of 0–4 T respectively 0–2 T , for the investigated $Tb_{1-x}Y_xCo_2$ compounds.

x	T_C (K)	δT_{FWHM} (0–4T) K	RCP(ΔS) (0–4T) J/kg	RCP(ΔS)/ ΔB (0–4T) J/kgT	δT_{FWHM} (0–2T) K	RCP(ΔS) (0–2T) J/kg	RCP(ΔS)/ ΔB (0–2T) J/kgT
0.125	203	41.04	213	53.25	27.56	86	43
0.250	183	34.95	192.4	48.1	24.2	77.28	38.64
0.375	165	34.16	116.2	29.05	27.2	52.92	26.46
0.500	129	26.97	121.5	30.37	20.23	56	28
0.625	94	27.9	104.4	26.1	21.14	50.6	25.3
0.750	50	40.21	83.42	20.85	30.99	36.58	18.29

4. CONCLUSIONS

In this work, the structural, magnetic and magnetocaloric properties of $Tb_{1-x}Y_xCo_2$ compounds were presented. The compounds with $x = 0.125, 0.25, 0.375, 0.50, 0.625$ and 0.75 were successfully prepared. X-ray diffraction measurements confirm the formation of the cubic $MgCu_2$ (C15) structure in all of the investigated samples. The lattice parameters were found to be little dependent on yttrium content. All of the investigated compounds were found to be ferrimagnetically ordered. The Curie temperatures and the cobalt magnetic moments at 4.2 K were found to decrease with increasing Y content. Local $4f-5d$ exchange interactions as well as $5d-3d$ short range interactions between neighboring Co and Tb atoms are present. The variations of cobalt moments, when substituting magnetic Tb by nonmagnetic Y, can be attributed to diminution of the exchange interactions.

The magnetocaloric effect was also studied. The obtained maximum entropy change values were found to decrease from 5.3 J/kgK for $x = 0.125$ to 1.9 J/kgK for $x = 0.75$ for a magnetic field change from 0 to 4 T . In an external magnetic field change from 0 to 2 T , the magnetic entropy change values were found to decrease to 3.25 J/kgK for $x = 0.125$ and 1.2 J/kgK for $x = 0.75$ respectively. The decrease of magnetic entropy change with increasing yttrium content may be caused by the decrease in the concentration of Tb^{3+} ions. The large RCP values obtained in these materials were mainly attributed to the large δT_{FWHM} values. It was found that RCP(ΔS)/ ΔB values are quite independent of Y concentration.

Due to their high RCP values these compounds are promising candidates for applications in magnetic refrigeration devices in the intermediate temperature range.

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REFERENCES

1. S.A. Nikitin, A.S. Andreenko, A.M. Tishin, A.M. Arkharov, and A.A. Zherdev, *Fiz. Met. Metalloved.* 56, 327 (1985).
2. K.A. Gschneider Jr. and V.K. Pecharsky, *Annu. Rev. Mater. Sci.* 30, 387 (2000).
3. V.K. Pecharsky, K.A. Gschneider Jr., *Phys. Rev. Lett.* 78, 4494 (1997).
4. H. Wada and Y. Tanabe, *Appl. Phys. Lett.* 79, 3302 (2001).
5. E. Bruck, O. Tegus, X.W. Li, F.R. de Boer, K.H.J. Buschow, *Physica B* 327, 431 (2003).
6. H.D. Liu, D.H. Wang, S.L. Tang, Q.Q. Cao, T. Tang, B.X. Gu, Y.W. Du, *J. Alloy Compd.* 346, 314 (2002).
7. H. Wada, S. Tomekawa, M. Shiga, *J. Magn. Magn. Mater.* 196–197, 689 (1999).
8. D.H. Wang, S.L. Tang, H.D. Liu, W.L. Gao and Y.W. Du, *Intermetallics* 10, 819 (2002).
9. E. Burzo, *Rev. Roum. Phys.*, 23, 689 (1978).
10. E. Burzo, *J. Less. Comm. Met.*, 77, 251 (1981).
11. R. Moon, W.C. Koehler and J. Farrel, *J. Appl. Phys.* 36, 978 (1965).
12. P. Hendy and E.W. Lee, *Phys. Status Solidi a* 50, 101 (1978).
13. W. Ross and J. Crangle, *Phys. Rev.* 133 A509 (1964).
14. A.M. Tishin, in *Handbook of Magnetic Materials*, edited by K.H.J. Buschow, Elsevier Science, New York, Vol. 12 (1999).
15. A.M. Tishin and Y.I. Spichkin, *The Magnetocaloric effect and its Applications*, 1st ed., Institute of Physics, New York (2003).
16. K.H.J. Buschow, *Rep. Progr. Phys.* 40, 1179 (1977).
17. F.Garcia, M.R.Soares, A.Y.Takeuchia, S.F. da Cunha, *J. Alloys Compd.* 279, 117 (1998).
18. J. Voiron, A. Berton, J. Chaussy, *Phys. Lett.* 50A, 17 (1974).
19. D. Bloch, D.M. Edwards, M. Shimizu, J. Voiron, *J. Phys. F: Metal Phys.* 5, 1217 (1975).
20. J. Inoue, M. Shimizu, *J. Phys. F: Metal Phys.* 12, 1811 (1982).
21. D.P. Kozlenko, E. Burzo, P. Vlaic, S.E. Kichanov, A.V. Rutkauskas, B.N. Savenko, *Scientific Reports*, 5, 8620 (2015).
22. W. Steiner, E. Gratz, H. Ortbauer, H.W. Camen, *J. Phys. F* 8, 1525 (1978).
23. E. Gratz, N. Pillmayr, E. Bauer, G. Hilscher, *J. Magn. Magn. Mater.* 70, 159 (1987).
24. N.V. Baranov, A.I. Kozlov, A.N. Pirogov, E.V. Sinitsyn, *Sov. Phys. JETP* 69, 382 (1989).
25. N.V. Baranov, A.N. Pirogov, *J. Alloys Compounds* 217, 31 (1995).
26. R. Kuentzler, A. Tari, *J. Magn. Magn. Mater.* 61 (1986).
27. N. Pillmayr, C. Schmitzer, E. Gratz, G. Hilscher, V. Sechovsky, *J. Magn. Magn. Mater.* 70, 162 (1987).
28. G. Hilscher, N. Pillmayr, C. Schmitzer, E. Gratz, *Phys. Rev. B* 37, 3480 (1988).
29. N.V. Baranov, A.A. Yermakov, A.N. Pirogov, A.E. Teplykh, K. Inoue, Yu. Hosokoshi, *Physica B* 269, 284 (1999).
30. M. Forcker, P. de la Presa, A.F. Pasquevich, *J. Phys: Condens. Matter*, 18, 1 253 (2006).
31. R. Tetean, E. Burzo, I.G. Deac, *J. Alloys and Compd.* 442, 206 (2007).
32. R. Tetean, E. Burzo, I. Chioncel, *J. Alloys and Compd.*, 430, 19 (2007).
33. R. Tetean, E. Burzo, *J. Magn. Magn. Mater* E599, 272 (2004).
34. R. Tetean, E. Burzo, L. Chioncel, T. Crainic, *Phys. Stat Solidi a* 196, 301 (2003).
35. E. Burzo, R. Tetean, Zs. Sarkozi, L. Chioncel, M. Neumann, *J. Alloys and. Comp.* 490, 323, (2001).
36. H.M. Rietveld, *J. Appl. Cryst.* 2, 65 (1969).
37. E. Burzo, L. Chioncel, *Rom. J. Phys.*, 63, 601 (2018).
38. E. Burzo, D.P. Lazar, M. Ciorascu, *Phys. Stat. Solidi (b)*, 65, K145 (1974).
39. E. Burzo, D.P. Lazar, *J. Solid State Chem*, 16 (3–4), 257–263 (1976).
40. R. Hauser, E. Bauer, E. Gratz, H. Müller, M. Rotter, H. Michor, G. Hilscher, A.S. Markosyan, K. Kamishima and T. Goto, *Phys. Rev. B* 61, 1198 (2000).

41. E. Burzo, M. Bălănescu, M. Chipară, J. Solid State Chem. 37 (1), 1–5 (1981).
42. K.W. Zhou, Y.H. Zhuang Solid State Commun 137, 275 (2006).
43. E. Burzo, S.G. Chiuzbaian, L. Chioncel, M. Neumann, J. Phys.: Condens. Matter 12, 27, 5897 (2000).
44. E. Burzo, L. Chioncel, R. Tetean, O. Isnard, J. Phys: Condens. Matter 23, 026001 (2011).
45. I.A. Campbell, J. Phys. F 2, L47 (1972).
46. J.J.M. Franse, R.J. Radwansky in *Ferromagnetic Materials*, K.H.P. Buschow Ed., North-Holland, Amsterdam, vol.7 (1993).
47. S. Mican, D. Benea, S. Mankovsky, S. Polesya, O. Ginsca, R. Tetean, J. Phys: Condens. Matter 25, 466003 (2013).
48. M.A. Laguna-Marco, J. Chaboy and C. Piquer, Phys. Rev. B 77, 125132 (2008).
49. A. Bezerghéanu, *Magnetocaloric effect in rare earth-3d transition metal intermetallic and oxidic compounds*, PhD thesis, Babes-Bolyai University, Cluj Napoca (2012).
50. A. Arrott, Phys. Rev. 108, 1394 (1957).
51. J. Lyubina, O. Gutfleisch, M.D. Kuz'min, M. Richter, J. Magn. Magn. Mater 320, 2252 (2008).
52. N.V. Baranov, A.V. Proshkin, C. Czternasty, M. Meißner, A. Podlesnyak, and S.M. Podgornykh, Phys. Rev. B 79, 184420 (2009).
53. H. Wada, S.Tomekawa, and M.Shiga, Cryogenics 39, 915 (1999).
54. N.A. de Oliveira, P.J. von Ranke, M.V.Tovar Costa and A.Troper, Phys. Rev. B 66, 094402 (2002).
55. N.H. Duc, D.T.K.Anh, and P.E.Brommer, Physica B 319, 1 (2002).
56. C.B. Zimm, P.M. Ratzmann, J.A. Barclay, G.F. Green, and J.N. Chafe, Adv. Cryog. Eng. 36, 763 (1990).
57. R.B. Helmholtz, T.T. Palstra, G.J. Nieuwenhuys, J.A. Mydosh, A.M. van der Kraan, Phys. Rev. B 34, 169 (1986).
58. E. Burzo, I. Balasz, I. Deac, R. Tetean, J. Magn. Magn. Mater 332, 1109 (2010).