

# Magnetocaloric effects on $\text{TbCo}_{3-x}\text{Al}_x$ compounds

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The  $\text{TbCo}_{3-x}\text{Al}_x$  compounds with  $x < 1$  crystallize in a rhombohedral structure having  $R\bar{3}m$  space group. The saturation magnetizations, at 4.2 K, increase as cobalt is replaced by aluminium from  $3.8 \mu_B/\text{f.u.}$  ( $x=0$ ) to  $6.14 \mu_B/\text{f.u.}$  ( $x=1$ ) in agreement with antiparallel ordering of Tb and Co sublattices. The magnetic behaviour of cobalt was analyzed in the spin fluctuation model. The adiabatic magnetic entropy changes,  $|\Delta S|$ , were determined from magnetization data. The largest magnetic entropy change,  $|\Delta S|_{\text{max}}$ , was obtained for the sample with  $x=0.99$  which have the Curie temperature around 300 K.

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## 1. Introduction

Magnetic materials showing a large magnetocaloric effect (MCE) have attracted considerable attention for their potential application in magnetic refrigeration technology [1-3]. The compounds which undergo temperature driven paramagnetic to ferromagnetic transitions show relatively large “negative” MCE, in which the isothermal magnetic entropy change,  $\Delta S_m = S(H, T) - S(0, T)$  is negative [4]. Refrigeration in the temperature range 250-300 K is of particular interest because of potential impact on energy savings and environmental concerns. The materials to be applied in magnetic refrigeration must present a series of properties: (i) a first order field induced transition near the working temperature, in order to use the entropy changes associated with this transition; (ii) a high refrigerant capacity:

$$q = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S(T)_{\Delta H} dT ; \text{ (iii) a low magnetic hysteresis in}$$

order to avoid the losses due to domains rotations in a magnetic refrigeration cycle; (iv) a low heat capacity; (v) low costs and harmless. The best magnetic refrigerants in the whole temperature range are rare earths based compounds.

The physical properties of  $\text{RM}_3$  intermetallic compounds, where R is a rare-earth or yttrium and M a transition metal were extensively investigated. As a function of alloying partner and composition the transition metals can cover a wide range of behavior from nonmagnetic state to well defined magnetism [4].  $\text{TbCo}_3$  compound crystallizes in a rhombohedral  $\text{PuNi}_3$ -type structure, having  $R\bar{3}m$  space group. In this structure the Tb atoms occupy two non-equivalent sites while Co atoms three types of sites. The  $\text{TbCo}_3$  compound is ferrimagnetically ordered, the Tb magnetization being antiparallely oriented to that of cobalt. The magnetic moments of Co atoms are dependent on lattice sites. By

magnetic measurements only their mean value can be determined.

Previously, we have analyzed the magnetic properties of  $\text{GdCo}_{3-x}\text{Al}_x$  compounds [5]. It was shown that the cobalt moments decrease when increasing Al content. The above behaviour was correlated with p-d hybridisation effects. In order to obtain additional information on pseudobinary compounds with Al substitutions we analysed the magnetocaloric effect in  $\text{TbCo}_{3-x}\text{Al}_x$  system in the composition range where rhombohedral solid solutions are formed.

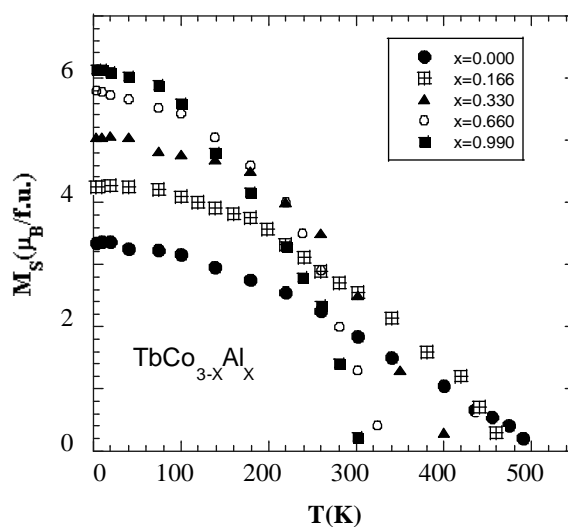


Fig. 1. Thermal variations of spontaneous magnetizations for  $\text{TbCo}_{3-x}\text{Al}_x$  compounds.

## 2. Experimental

The  $\text{TbCo}_{3-x}\text{Al}_x$  compounds were prepared by arc melting the constituent elements in a purified argon atmosphere. A small excess of rare earth element was used in order to compensate for losses during melting. The ingots were remelted several times in order to ensure a good homogeneity. The samples were heat treated in vacuum, at 1000 °C, for 5 days. The X-ray analysis shows, in the limit of experimental errors, the presence of one phase only, for  $x < 1$ , having  $R\bar{3}m$  space group. The lattice parameters decrease slightly when Al content increases, fact attributed to smaller radius of Al ion compared with Co one (see Table 1).

Table 1. Composition dependences of lattice parameters, Curie temperatures and ratio  $r = S_p/S_0$  for  $\text{TbCo}_{3-x}\text{Al}_x$  compounds.

x	0.000	0.166	0.330	0.660	0.990
a (Å)	5.010	5.008	5.006	5.004	5.001
c (Å)	24.390	24.383	24.380	24.360	24.350
T <sub>C</sub> (K)	506	472	409	361	304
r=S <sub>p</sub> /S <sub>0</sub>	1.14	1.24	1.37	1.47	1.56

Magnetic measurements were performed in the temperature range 4.2-950 K and external fields up to 9T. The spontaneous magnetizations,  $M_s$ , were determined from magnetization isotherms according to approach to saturation law,  $M = M_s(1 - a/H) + \chi_o H$ . We denoted by  $a$  the coefficient of magnetic hardness and  $\chi_o$  is a Pauli-type contribution. Above the Curie points, the susceptibilities were determined by using a Faraday type balance, the samples being sealed in vacuum.

The entropy changes were determined from magnetization isotherms, between zero field and a maximum field ( $H_0$ ) using the thermodynamic relation:

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

where  $\Delta T$  is the temperature increment between measured magnetization isotherms ( $\Delta T = 5$  K for our data).

## 3. Results and discussion

The thermal variations of spontaneous magnetizations are plotted in Fig. 1. The saturation magnetizations, at 4.2 K, increase from 3.8  $\mu_B$ /f.u. at  $x=0$  to 6.14  $\mu_B$ /f.u. at  $x=0.99$ . The above behaviour is in agreement with the presence of a ferrimagnetic type ordering. Assuming that the terbium mean magnetic moment, at 4.2 K, is the same like that determined on  $\text{TbCo}_3$  compound by neutron diffraction study [7] the cobalt contributions to magnetizations were determined. The mean cobalt moments decrease gradually when cobalt atoms are

replaced by aluminium ones – Fig. 2. The ordered-paramagnetic transitions are of second order.

The temperature dependences of reciprocal susceptibilities,  $\chi^{-1}$ , follow a hyperbolic law of Néel-type, characteristic for ferrimagnetic ordering. At high temperatures, the  $\chi^{-1}$  vs. T plots shows linear dependences. The Curie constants, determined in the above temperature ranges, are higher than the characteristic values for  $\text{Tb}^{3+}$  ion suggesting the presence of contributions from the cobalt atoms. According to addition law of susceptibilities and supposing that the Curie constant of terbium is the same as that of  $\text{Tb}^{3+}$  ion, we determined the contributions of Co, to the Curie constants and the effective cobalt moments,  $M_{\text{eff}}(\text{Co})$ , respectively-Fig. 2.

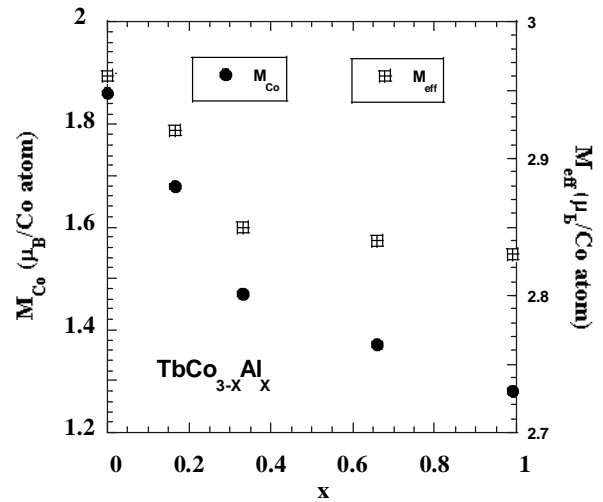


Fig. 2. Composition dependences of the mean cobalt magnetic moment at 4.2 K and mean effective moments.

The  $M_{\text{eff}}(\text{Co})$  values are only slightly composition dependent. The Curie temperatures  $T_C$ , decrease when  $x$  increase, varying from 506 K for  $x=0$  to 311 K for  $x=0.99$ . We note that there is a linear dependence of mean cobalt moments on the Curie temperatures. The ratio  $r=S_p/S_0$  between the number of spins obtained from effective cobalt moments,  $S_p$ , and saturation moments,  $S_0$ , increase with Al content - Table 1. In the local moment limit we have  $r=1.0$ . For a weak ferromagnet the  $r$  values increase considerably. In case of  $\text{TbCo}_3$  compound the  $r=1.14$  value suggest that cobalt has mainly a localized moment. The gradual substitution of Co by Al increase the  $r$  values, the itinerancy degree, respectively. The above behaviour can be analyzed in spin fluctuation model [8]. When the amplitude of local spin fluctuations (LSF) is large and fixed, there is a local moment limit, where only the transverse components of LSF are important. As the amplitude of LSF is small, there is the weakly ferromagnet

limit, where the longitudinal components of LSF or temperature variation of amplitude of LSF play an important role. From the variation of  $r$  values in  $\text{TbCo}_{3-x}\text{Al}_x$  system we conclude that there are some contributions from longitudinal components of LSF which increase when Al content is greater, although the transverse components dominate.

The temperature dependence of magnetic entropy change in 5, 7 and 9T external applied field for the compound with  $x=0.99$  are plotted in Fig. 3. The maximum values of entropy change occur almost at the Curie temperature for all the compounds. The maximum value is around 8.5 J/kg K in a 9T magnetic field for the compound with sharper transition ( $x=0.99$ ) around 300 K.

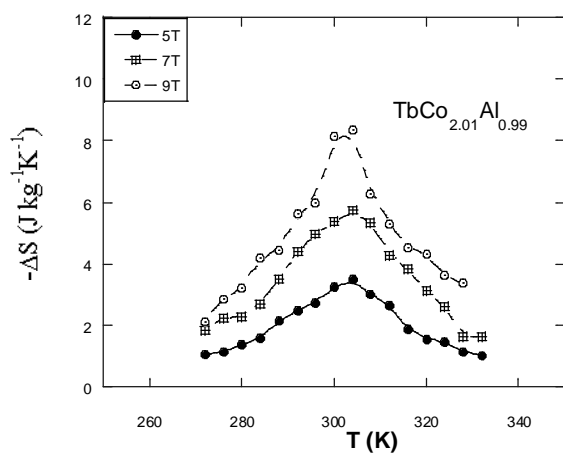


Fig. 3. Magnetic entropy change of the compound with  $x=0.99$  as function of temperature in different applied magnetic fields.

The magnetic entropy change decreases at 6 J/kg K in field of 7T and at 4 J/kg K in field of 5T. These values are somewhat smaller than those evidenced in  $\text{La}(\text{Fe}_{0.88}\text{Al}_{0.12})_{13}\text{C}_x$  interstitial compounds where as function of  $x$  values changes from 9.6 to 8.3 J/kg K were evidenced in field of 5T [9]. The determined  $\Delta S$  values in  $\text{TbCo}_{3-x}\text{Al}_x$  are rather high for compounds showing a second order type transition. In case of the compound with  $x=0.99$  around 65% of the heat is absorbed in a temperature range  $\pm 10$  K, centered at the Curie point.

The origin of the large magnetic entropy change in the compound with  $x=0.99$  could be attributed to the considerable variation of the magnetization near the transition temperature.

#### 4. Conclusions

We have studied the magnetocaloric effect in  $\text{TbCo}_{3-x}\text{Al}_x$  compounds in the region where a rhombohedral structure having  $R\bar{3}m$  space group is formed. Large magnetic entropy change has been observed for all concentrations with a maximum at  $x=0.99$ . The transition temperature can be tuned via Al concentration. These suggest that  $\text{TbCo}_{3-x}\text{Al}_x$  has a potential application as a working substance of magnetic refrigeration.

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