Magnetic properties of the non-stoichiometric TbCo$_2$Mn$_x$ and TbCo$_2$Ni$_x$ alloys

To cite this article: A A Inishev et al 2019 J. Phys.: Conf. Ser. 1389 012092
Magnetic properties of the non-stoichiometric TbCo$_2$Mn$_x$ and TbCo$_2$Ni$_x$ alloys

A A Inishev$^{1,2}$, E G Gerasimov$^{1,2}$, N V Mushnikov$^{1,2}$, P B Terentev$^{1,2}$ and V S Gaviko$^{1,2}$

$^1$M.N. Miheev Institute of Metal Physics of UB RAS, Ekaterinburg, Russia
$^2$Institute of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia

E-mail: inishev@imp.uran.ru

Abstract. The crystal structure, magnetic and magnetothermal properties of non-stoichiometric TbCo$_2$Mn$_x$ and TbCo$_2$Ni$_x$ alloys were studied. It was shown that single-phase compounds with the MgCu$_2$-type structure exist up to a certain content of $x$ ($x < 0.4$ for compounds with Mn and $x \leq 0.1$ for compounds with Ni). The concentration changes of the lattice parameter, Curie temperature, magnetic moment of the 3d sublattice in TbCo$_2$Mn$_x$ and TbCo$_2$Ni$_x$ alloys were compared. The magnetocaloric effect in alloys were estimated using data of magnetic and heat capacity measurements.

1. Introduction

Recently, new non-stoichiometric RM$_2$M$_x$ compounds (R - rare-earth metal, M - 3d transition metal Ni, Co) are revealed and their physical properties are actively investigated [1-7]. These compounds crystallize in the MgCu$_2$-type structure (cubic Laves phase C15, space group Fd$\overline{3}$m) same as the binary RM$_2$ compounds. Part of the Mn atoms occupy the 3d metal positions (16d), the remaining part occupies the rare-earth element positions (8a). It is noteworthy that the Curie temperature ($T_C$) of the RM$_2$M$_x$ compounds may be significantly higher than $T_C$ of the RCo$_2$ and RNi$_2$ parent compounds.

The practical interest in studying the magnetic properties of nonstoichiometric RM$_2$M$_x$ compounds is partially related with the intensive search for materials with large magnetocaloric effect. For example, it was shown, that the maximum of the magnetocaloric effect is persisting in very wide temperature range for GdNi$_2$Mn$_x$ and ErCo$_2$Mn$_x$ [4, 5]. This allows considering non-stoichiometric compounds as possible candidates for magnetothermal applications.

On the other hand, rare-earth intermetallic compounds with cobalt, which have the MgCu$_2$-type structure, are simple model objects for the study of band metamagnetism. The magnetic state of the cobalt sublattice can be changed either due to the influence of the molecular field of the rare earth sublattice in compounds with magnetic R, or due to a change in the electronic band structure in compounds in which cobalt is partially replaced by various elements (Al, Ga, Mn, Si, Cr, Ni and etc.) [8-10].

In this paper, we study the influence of manganese and nickel on the formation of non-stoichiometric TbCo$_2$M$_x$-type compounds ($M = \text{Mn, Ni}$) with the MgCu$_2$ type structure and the formation of their physical properties. The changes in the crystal lattice parameter, Curie temperature, magnetic moment of the 3d sublattice, and magnetocaloric effect on the concentration of Mn and Ni in TbCo$_2$M$_x$ are compared.
2. Experimental details
The ingots of the TbCo$_2$Mn$_x$ and TbCo$_2$Ni$_x$ alloys were prepared by induction melting of the constituents in alumina crucibles in argon atmosphere. In order to obtain the equilibrium phase state, the ingots were annealed at 800°C for 7 days. Structural and magnetic studies were performed at the Centre of Collective Use of the Institute of Metal Physics UB RAS. Room temperature X-ray diffraction patterns were measured for powdered samples with the average particle size 30–50 µm using an Empyrean (PANalytical) diffractometer with Cu Kα radiation. The x-ray diffraction patterns were analysed with the High-Score v.4.x software.

Magnetic measurements were carried out using spherical samples. The magnetization in high magnetic fields of up to 10 T was measured in a temperature range of 4.2–320 K by pulsed technique using a pulse magnetometer and a magnetic field pulse duration of 8 ms. The heat capacity was measured using the low-temperature adiabatic calorimeter.

3. Results and discussion
The non-stoichiometric TbCo$_2$Mn$_x$ and TbCo$_2$Ni$_x$ compounds crystallize into the cubic MgCu$_2$ type structure at a certain concentration $x$ ($x < 0.4$ for compounds with Mn and $x \leq 0.1$ for compounds with Ni) [11, 12]. The formation of non-stoichiometric TbCo$_2M_x$ compounds with the MgCu$_2$-type structure apparently occurs as in the case of the previously studied non-stoichiometric compounds, due to the fact that the $M$ atoms occupy the positions of both the rare-earth element (8a) and cobalt (16d).

For compounds with nickel, the concentration interval for the formation of compounds with the MgCu$_2$ structure is less than with manganese. This may be due to the fact that for the formation of non-stoichiometric TbCo$_2M_x$, the atomic radius of the $M$ metal should be closer to the atomic radius of terbium ($r_{\text{Tb}} = 0.1773$ nm). Consequently, Mn is most appropriate metal for formation of such type compounds because its has the largest atomic radius among 3d transition metals Co ($r_{\text{Co}} = 0.125$ nm),

![Figure 1](image1.png)  ![Figure 2](image2.png)

**Figure 1.** Concentration dependences of the lattice parameter for non-stoichiometric TbCo$_2$Mn$_x$ ($\bullet$) and TbCo$_2$Ni$_x$ ($\circ$) alloys.

**Figure 2.** Concentration dependences of the Curie temperature for non-stoichiometric TbCo$_2$Mn$_x$ ($\bullet$) and TbCo$_2$Ni$_x$ ($\circ$) alloys.

Ni ($r_{\text{Ni}} = 0.125$ nm), and Mn ($r_{\text{Mn}} = 0.137$ nm).

Figure 1 shows the concentration dependences of the lattice parameter of non-stoichiometric TbCo$_2M_x$ alloys. It can be seen that for compounds with manganese, the lattice parameter monotonically increases with increasing manganese content. At the same time, for compounds with nickel, a nonmonotonic change in the lattice parameter is observed.

With the addition of Mn, the Curie temperature of TbCo$_2$Mn$_x$ sharply increases and reaches a maximum value of 350 K at a manganese concentration of $x = 0.4$ (figure 2). Qualitatively, the concentration dependence of $T_C$ for TbCo$_2$Mn$_x$ is similar to that observed in substitutional
In particular, in R(Co$_{1-x}$Mn$_x$)$_2$, the dependence $T_C(x)$ sharply increases with increasing $x$ and decreases with a further increase in $x$.

For TbCo$_2$Ni$_x$, when Ni is added $T_C$ increases at small $x$, and then decreases (figure 2). The shape of $T_C(x)$ dependence is similar to the concentration dependence of $T_C$ in substitutional R(Co$_{1-x}$Al$_x$)$_2$ solid solutions with nonmagnetic Al [10].

Figure 3 shows concentration dependences of the total spontaneous magnetic moment $\mu_s$ at 4 K for non-stoichiometric TbCo$_2$Mn$_x$ (■) and TbCo$_2$Ni$_x$ (○) alloys.

Figure 4 shows the concentration dependence of the magnetic moment of the 3d sublattice $\mu_{3d}$ for non-stoichiometric TbCo$_2$Mn$_x$ (■) and TbCo$_2$Ni$_x$ (○) alloys.

Here we assume terbium magnetic moment to be equal to its free-ion value $\mu_{\text{Tb}} = 9 \, \mu_B$, which was confirmed for TbCo$_2$ by neutron diffraction experiments [13].

The concentration dependences of the magnetic moment of the 3d sublattice $\mu_{3d}(x)$ for compounds with manganese and nickel are qualitatively similar to the concentration dependences of the Curie temperature. In both cases, an increase in its values is observed at low concentrations $x$ (figures. 2, 4), and the maximum Curie temperature and magnetic moment of the 3d sublattice is reached at a manganese concentration $x = 0.4$, and at a nickel concentration $x = 0.1$.

To describe the Curie temperature in RCo$_2$ compounds, it is acceptable to use the following expression [14]:

$$T_C = C_R (n_{R,R} + n_{R,3d}^2 \chi_d) = N g^2 \mu_B^2/3k_B \left( n_{R,R} + n_{R,3d}^2 \chi_d \right),$$

were: $C_R$ is the Curie constant of rare earth atoms; $n_{R,R}$ and $n_{R,3d}$ are the molecular field constants of the intrasublattice $R$ -- $R$ and intersublattice $R$ -- Co exchange interactions, respectively; $\chi_d$ is the exchange- enhanced susceptibility of cobalt sublattice; $N$ is the number of $R$ atoms; $J_R$ is the quantum
number of total angular momentum of rare earth ion; \( g \) is the Lande factor; \( \mu_B \) is the Bohr magneton; \( k_B \) is the Boltzmann constant.

Take in account that the spontaneous magnetization of rare earth sublattice is determined by the expression
\[
M_R = N g \mu_B M_R.
\]

The spontaneous magnetization of 3d - sublattice \( M_{3d} \) is induced by the molecular field of rare earth sublattice \( M_R \):
\[
M_{3d} = \chi_{dn} M_R - 3d M_{3d}.
\]

The expression (2) can be rewritten as [5]:
\[
T_C = \frac{g \mu_B (J_g + 1)}{3k_B} \left( n_{R,R} M_R + n_{R,3d} M_{3d} \right).
\] (3)

It is seen from (3) that the Curie temperature of \( RCo_2 \) compounds is proportional to the spontaneous magnetization of both rare-earth and 3d- sublattice. We can assume that the increase in the Curie temperature, which is observed with increasing manganese content, is due to the increase in the magnetic moment of cobalt, which may result from changes in the electron structure of the compounds. It is possible, that alloying with Mn and Ni increase the Co magnetic moment due to the additional splitting of the 3d band. This, in turn, leads to an increase in the Tb-Ni (Mn), Co-Ni (Mn) exchange interaction.

The Curie temperature \( T_C \) sharply increases to 350 K, and the magnetic moment of the 3d sublattice reaches 1.6 \( \mu_B \) for the \( \text{TbCo}_2 \text{Mn}_{0.4} \) compound. For \( \text{TbCo}_2 \text{Ni}_x \) compounds, \( T_C \) increases to 233 K, and the magnetic moment of the 3d sublattice reaches 1.38 \( \mu_B \) at a nickel concentration of \( x = 0.025 \).

From temperature dependences of magnetization \( M(T) \) in magnetic field \( H = 1 \) T [11, 12] using well known Maxwell’s thermodynamic relation:
\[
\Delta S_m(T, \Delta H) = \int_0^{H_1} \left( \frac{\partial M(T, H)}{\partial T} \right)_H \, dH - \frac{\partial M(T, H_2)}{\partial T} \, H_1,
\] (4)

we determined temperature variation of the magnetic entropy change \( \Delta S_m(T) \) in \( \text{TbCo}_2 M_x \) compounds for magnetic field change \( \mu_0 \Delta H = 1 \) T.

Figure 5. Temperature dependences of entropy change of non-stoichiometric \( \text{TbCo}_2 \text{Ni}_x, \text{TbCo}_2 \text{Mn}_x \) alloys for magnetic field change \( \mu_0 \Delta H = 1 \) T.

Figure 6. Temperature dependence of adiabatic temperature change for magnetic field change \( \mu_0 \Delta H = 1 \) T non-stoichiometric \( \text{TbCo}_2 M_x \) alloys.

For compounds with manganese, there is no pronounced maximum at the Curie temperature, which was previously observed for non-stoichiometric \( RM_2 Mn_x \) type compounds [4, 5]. On the other hand, the magnetocaloric effect in \( \text{TbCo}_2 \text{Ni}_x \) is maximal in a narrow temperature range near the Curie temperature. As can be seen from relation (4), the value of the isothermal change in entropy near the Curie temperature is determined by the rate of change of the magnetization with temperature. With a smooth change of \( M(T) \), the \( \Delta S_m(T) \) does not change over a wide temperature range.

Absolute values of \( \Delta S_m \) for \( \text{TbCo}_3 M_x \) decrease with increasing \( M \) content because of decreasing the magnetization of alloys. For compounds with Ni, maximum absolute values of \( \Delta S_m \) is \(-1.1 \text{ J·kg}^{-1}\text{K}^{-1}\) for
\( \mu_0 \Delta H = 1 \, \text{T} \). For compounds with Mn maximum absolute values of \( \Delta S_m \) is \(-0.4 \, \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \) for \( \mu_0 \Delta H = 1 \, \text{T} \).

The data of the temperature dependence of the heat capacity \([11, 12]\) and the entropy change allow us to calculate the temperature change in a magnetic field using the following expression:

\[
\Delta T(T)_{\Delta H} = -\frac{T}{C_p(T,H=0)} \Delta S_m.
\]

(5)

The maximum value of the adiabatic temperature change for the magnetic field changes from 0 to 1 T is \( \Delta T \approx 0.5 \, \text{K} \) (TbCo\(_2\)Mn\(_{0.4}\)) and \( \Delta T \approx 0.9 \, \text{K} \) (TbCo\(_2\)Ni\(_{0.025}\)) (figure 6).

4. Conclusion

Our study showed that single-phase non-stoichiometric TbCo\(_2\)Ni\(_x\) compounds with MgCu\(_2\)-type structure exist at a low nickel concentration \( x \leq 0.1 \). At the same time, single-phase non-stoichiometric TbCo\(_2\)Mn\(_x\) compounds with MgCu\(_2\)-type structure exist up to a manganese concentration \( x < 0.4 \). The concentration range of the existence of the non-stoichiometric TbCo\(_2\)Mn\(_x\) compounds with \( M = \text{Ni} \) is substantially narrower than that for the compounds with \( M = \text{Mn} \). This can be because the atomic and ion radii of Ni and Co are less than those of Mn.

The Curie temperature and magnetic moment of 3d sublattice substantially increase for TbCo\(_2\)Mn\(_x\) and TbCo\(_2\)Ni\(_x\) compounds as the manganese and nickel content increases. In TbCo\(_2\)Mn\(_x\), the maximum values of \( T_C \) (350 K) and magnetic moment of 3d sublattice \( \mu_{3d} \) (1.6 \( \mu_B \)) are reached for TbCo\(_2\)Mn\(_{0.4}\). For TbCo\(_2\)Ni\(_x\), the maximum values of \( T_C \) (223 K) and \( \mu_{3d} \) (1.38 \( \mu_B \)), are reached at a nickel concentration \( x = 0.025 \). The analysis of the obtained results shows that an increase in the Curie temperature with increasing concentrations of nickel and manganese is due to an increase in the magnetic moment of the 3d sublattice, which can occur as a result of changes in the electronic structure of compounds.

The magnetocaloric effect at the magnetic field change from 0 to \( \mu_0 H = 1 \, \text{T} \) was estimated using magnetic and heat-capacity measurements. For the TbCo\(_2\)Ni\(_{0.025}\) compound, the maximum magnetic entropy change is \(-1.1 \, \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \), which corresponds to temperature change of \(~ 0.9 \, \text{K} \). For the TbCo\(_2\)Mn\(_{0.4}\) compound, the maximum magnetic entropy change is \(-0.4 \, \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \) and the temperature change is \(~ 0.5 \, \text{K} \).

Acknowledgments

The research was carried out within the state assignment of Minobrnauki of Russia (theme “Magnet” No. AAAA-A18-118020290129-5), supported in part by RFBR (project No. 18-02-00294).

References

[1] Wang J L, Marquina C, Ibarra M R and Wu G H 2006 Phys. Rev. B 73 094436
[2] Maji B, Suresh K G and Nigam A K 2010 J. Magn.Magn. Mater. 322 2415
[3] Wang J L, Campbell S J, Kennedy S J, Zeng R, Dou S X and Wu G H 2011 J. Phys.: Condens. Matter 23 216002
[4] Gerasimov E G, Mushnikov N V, Terentev P B, Gaviko V S and Inishev A A 2013 J. Alloys Compd. 571 132
[5] Gerasimov E G, Mushnikov N V, Inishev A A, Terentev P B and Gaviko V S 2016 J. Alloys Compd. 680 359
[6] Aryal A, Quetz A, Pandey S, Samanta T, Dubenko I, Mazumdar D, Stadler S and Ali N 2016 J. Appl. Phys. 119 043905
[7] Fang C, Wang J, Hong F, Hutchison W D, Din M F, Studer A J, Kimpton J A, Dou S and Cheng Z 2017 Phys. Rev. B 96 064425
[8] Ballou R and Markosyan A S 1992 J. Magn. Magn. Mater. 110 209
[9] Yokoyama T, Saito H, Fukamichi K, Kamishima K, Goto T and Yamada H 2001 J. Phys.: Condens. Matter 13 9281
[10] Markosyan A S 1982 Fiz. Met. Metallogr. 54 1109
[11] Inishev A A, Gerasimov E G, Mushnikov N V, Terent’ev P B and Gaviko V S 2017 Phys. Met. Metallogr. 118 1059
[12] Inishev A A, Gerasimov E G, Mushnikov N V, Terent’ev P B and Gaviko V S 2018 Phys. Met. Metallogr. 119 1036
[13] Gignoux D and Givord F 1979 J. Phys. F: Met. Phys. 9 1409
[14] Bloch D and Lemaire R 1970 Phys. Rev. B 2 2648