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

Alexander Inishev*, Evgeny Gerasimov, Nikolay Mushnikov, Pavel Terentev, and Vasily Gaviko

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

Abstract. The magnetic and magnetothermal properties of the non-stoichiometric TbCo$_2$Ni$_x$ (0 ≤ $x$ ≤ 0.2) alloys were studied. It was found that the concentration dependence of the Curie temperature and magnetic moment of the 3d-sublattice have a maximum at $x$ = 0.025. The obtained experimental magnetic properties of the TbCo$_2$Ni$_{1-x}$ alloys were discussed under assumption that the Co magnetic moment in the compounds changes with increasing $x$. The magnetic entropy change was determined using the temperature dependences of the magnetization and Maxwell’s thermodynamic relation. The obtained results for TbCo$_2$Ni$_{1-x}$ were compared with those for the ErCo$_2$Mn$_x$ alloys.

1 Introduction

It was found recently that ternary $RM_2$Mn ($R$ – rare-earth metal, $M$ – 3d transition metal Ni, Co) compounds crystallize in the Laves-phase MgCu$_2$-type cubic structure in spite of the ratio of the $R$ and $M$ components is 1 to 3. The Mn atoms in Laves-phase structure of the $RM_2$Mn compounds partially occupy both the $M$ (16d) and rare earth (8a) sites [1-3]. The Curie temperatures $T_C$ are considerably higher for the $RNi_2Mn$ alloys in comparison with $T_C$ for corresponding binary $RNi_2$ and $RMn$. Later, the structure and magnetic properties of the non-stoichiometric $RM_2Mn_x$ (0 ≤ $x$ ≤ 1.5) compounds with $R$ = Tb, Dy, Gd were studied [4-7]. It was established that the MgCu$_2$-type structure exists up to the manganese content $x = 0.8$ for ErCo$_2$Mn$_{1-x}$, and up to $x = 1.5$ for ErNi$_2$Mn$_{1-x}$. It was established that $T_C$ is a non-monotonous function of Mn concentration, which has a maximum at $x < 1$. It was found also that the maximum isothermal entropy change and the adiabatic temperature change remain weakly changed in a wide temperature range in ErCo$_2$Mn$_{1-x}$. Thus, there is new opportunity to modify magnetic properties of the Laves phase compounds by adding Mn and forming non-stoichiometric $RM_2Mn_x$ compounds.

Up to now the properties of $RM_2M'_x$ – type compounds with $M'$=Mn were studied only. However, we expect that non-stoichiometric $RM_2M'_x$ compounds with another 3d transition metals can exist. In particularly, such type compounds can forms in case $M'$=Ni.

In the present paper, we report the results of studies of the structure, magnetic and magnetothermal properties of the non-stoichiometric TbCo$_2$Ni$_{1-x}$. The obtained results are compared with those for ErCo$_2$Mn$_{1-x}$ which we previously studied.

2 Experimental details

The ingots of the TbCo$_2$Ni$_{1-x}$ 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 a DRON-type diffractometer with Cr Kα radiation. The x-ray diffraction patterns were analysed with the PowderCell 2.4 program. To determine the Curie temperature of the compounds, we measured temperature dependences of ac magnetic susceptibility $\chi$'s and used the position of minimum in the temperature dependences of derivative $d\chi/(dT)/dT$, which corresponds to the more abrupt decrease in the susceptibility with increasing temperature. The spontaneous magnetization $\mu_s$ of compounds was determined from the demagnetization curves as magnetization extrapolated to zero internal field.

3 Results and discussion

Fig. 1 shows the room temperature X-ray diffraction patterns of TbCo$_2$Ni$_{1-x}$ alloys. All main reflections in the X-ray diffraction patterns are adequately described in terms of the MgCu$_2$-type structure ($Fd\bar{3}m$); the volume fraction of impurity phases with the PuNi$_3$-type structure ($R3m$) does not exceed 8 vol. %. According to X-ray diffraction studies, the single phase non-stoichiometric TbCo$_2$Ni$_{1-x}$ compounds with the cubic Laves-phase structure exist up to critical nickel concentration $x = 0.1$ [8]. This value is much lower than $x = 0.8$-1.5 which

* Corresponding author: inishev@imp.uran.ru

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were observed early for non-stoichiometric \( RM_2Mn_x \) compounds. It is known that the stability of the Laves phases is determined by factors such as the relationship of atomic radii of \( R \) and \( M \) elements and the average number of valence electrons per atom. The chemical bonds in Laves phases are assumed to be mixed metallic–covalence–ionic. Because of this, to analyse the stability of the phases, atomic radii of elements are sometimes used. It is likely that the same factors must affect the concentration boundaries of the existence of the nonstoichiometric \( RM_2Ni_x \) compounds. This may be due to that the atomic and ionic radii of \( Ni \) are less than those of \( Mn \). And, correspondingly, large difference between \( Ni \) and \( R \) does not allows to occupy enough amount of \( R \) (8a) sites by \( Ni \) atoms. Thus, the non-stoichiometric \( RCo_2Ni_x \) alloys with cubic \( MgCu_2 \)-type Laves phase structure can be obtained in more narrow concentration range than in case of alloying with \( Mn \).

The lattice parameter of the \( Ni \)-containing compounds are virtually independent of \( x \) (Fig. 2). Such behavior caused by two opposite factors. It is known that the atoms of the alloying element (\( Ni \) or \( Mn \)) occupy both the \( R \) (8a) and the \( M \) (16d) sites. The partial substitution of the \( R \) atoms by \( Ni \) or \( Mn \) at the 8a sites leads to decrease the lattice parameter. On the other hand, the substitution of the \( Co \) atoms at the 16d sites by a 3d element with a larger ionic or metallic radius leads to increasing of the lattice parameter. Two opposite tendencies lead to a weak concentration change of the lattice parameter for \( RM_2M'_x \).

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**Fig. 1.** X-ray diffraction patterns of \( TbCo_2Ni_x \) alloys with different \( x \). Bragg peak positions are indicated by the markers for \( MgCu_2 \)-type structure (open circles). \( PuNi_3 \)-type structures (line bars).

**Fig. 2.** Concentration dependences of the lattice parameter for \( TbCo_2Ni_x \) compounds.

**Fig. 3.** Concentration dependences of the Curie temperature for \( ErCo_2Mn_x \) and \( TbCo_2Ni_x \) compounds in range of concentration from \( x = 0 \) up to maximal concentration for which exist single phase non-stoichiometric \( TbCo_2Ni_x \) compounds with \( MgCu_2 \)-type structure.

As can be seen in Fig. 3, concentration dependence of the Curie temperature increases sharply at small \( Ni \) concentrations and has maximum at \( T = 233 \text{ K} \). With further increasing the \( Ni \) content, the concentration dependence of the \( T_C \) decreases. The Curie temperature of \( ErCo_2Mn_x \) compounds monotonically increases and reaches maximum value 212 K at manganese concentration \( x = 0.6 \) [6].

**Fig. 4.** Concentration dependences of the magnetic moment of 3d-sublattice of \( ErCo_2Mn_x \) and \( TbCo_2Ni_x \) compounds. We calculated magnetic moment of 3d-sublattice \( \mu_{3d} \) in assumption that the \( R \) and 3d magnetic moments have collinear antiparallel alignment:
\[ \mu_{3d} = (\mu_R - \mu_s)/(2 + x), \]  

(1)

where \( \mu_s \) - spontaneous magnetic moment of the compounds, \( \mu_R \) - magnetic moment of the rare-earth ion. The maximum \( \mu_{3d} \) value is 1.38 \( \mu_B \) for \( \text{TbCo}_2\text{Ni}_{0.025} \) compound and 1.5 \( \mu_B \) for \( \text{ErCo}_2\text{Mn}_{0.6} \) compound. It is seen that character of the \( \mu_{3d}(x) \) concentration dependencies both for \( \text{ErCo}_2\text{Mn}_x \) and for \( \text{TbCo}_2\text{Ni}_x \) is very similar to those for Curie temperatures.

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\[ \Delta S_m = -\left( \frac{\partial M}{\partial T} \right)_H |_{H=H_1} \Delta H \approx \frac{\partial M}{\partial T} |_{H=H_1} \Delta H_1. \]  

(2)

Fig. 4 shows the temperature dependences of entropy change for \( \text{ErCo}_2\text{Mn}_x \) and \( \text{TbCo}_2\text{Ni}_x \) compounds. Maximum isothermal entropy change is -1.1 J kg\(^{-1}\)K\(^{-1}\) for \( \text{TbCo}_2\text{Ni}_{0.025} \) and -1.15 J kg\(^{-1}\)K\(^{-1}\) for \( \text{ErCo}_2\text{Mn}_{0.2} \) for the magnetic field change 1 T. These values are close to those observed, for the binary \( \text{TbCo}_2 \)-based compounds.

**4 Conclusion**

We studied the effect of Ni alloying on the structure, magnetic and magnetothermal properties of \( \text{TbCo}_2\text{Ni}_x \) alloys. It was established that single-phase non-stoichiometric compounds with the cubic MgCu\(_2\)-type structure are formed at the Ni content \( x \leq 0.1 \). We found that concentration dependences of the Curie temperature and magnetic moment of 3d-sublattice have maximum at Ni content \( x = 0.025 \). Our analysis shows that all these changes are associated with changes in the Co magnetic moment which can arise from changes of compounds electron band structure.

Using magnetization measurements, we estimated the magnetocaloric effect in the \( \text{ErCo}_2\text{Mn}_x \) and \( \text{TbCo}_2\text{Ni}_x \) compounds. The maximum values of the \( \Delta S_m \) of \( \text{TbCo}_2\text{Ni}_x \) compounds are sufficiently close for all nickel concentrations.

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