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Structure, magnetic and magnetothermal properties of the non-stoichiometric $ErCo_2Mn_x$ alloys

E.G. Gerasimov*, N.V. Mushnikov, A.A. Inishev, P.B. Terentev, V.S. Gaviko

Institute of Metal Physics UB RAS, S. Kovalevskaya str. 18, 620990, Ekaterinburg, Russia

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ABSTRACT

The structure, magnetic and magnetothermal properties and heat capacity of the $ErCo_2Mn_x$ ($0 \le x \le 1.4$) non-stoichiometric alloys have been studied. It is shown that the alloys with $x \le 0.8$ are almost single-phase with the $MgCu_2$-type Laves-phase structure, while the alloys for $x \ge 1.0$ contain considerable amount of the cubic Th_6Mn_{23}-type phase. Alloying with manganese leads to a substantial increase in the exchange interactions. For the binary $ErCo_2$ compound, the magnetization shows a first-order magnetic phase transition with the Curie temperature $T_C = 35$ K. For all the Mn-containing alloys studied, the transition is found to be the second-order type; the Curie temperature in $ErCo_2Mn_x$ sharply growths with increasing x and reaches its maximum value 212 K for the $ErCo_2Mn_{0.6}$ alloy. Using the magnetization data and the results of the heat capacity measurements, we estimated the magnetocaloric effect for these compounds. The obtained results are discussed on the assumption of a strong variation of the 3*d*-metal magnetic moments upon alloying with Mn.

1. Introduction

Intermetallic RCo_2 compounds (R is a rare earth metal, Y, or Sc) with the Laves phase structure of the $MgCu_2$-type (space group $Fd\bar{3}m$) are of considerable interest in view of the instability of the Co magnetic moment and itinerant electron metamagnetism of the *d* electrons of cobalt [1]. For binary RCo_2 compounds with non-magnetic R elements (R = Sc, Y, Lu), the Stoner criterion for the 3*d* band ferromagnetism is very close to be fulfilled. Such compounds are exchange-enhanced Pauli paramagnets and show a metamagnetic transition in high magnetic fields [2]. The ground magnetic state of the cobalt sublattice changes to ferromagnetic under the influence of a molecular field produced by the rare earth atoms with a nonzero spin moment. Alternatively, the ferromagnetic state is formed as a result of modification of the *d*-band structure in quasi-binary $R(Co_{1-x}M_x)_2$ compounds in which Co atoms are partially substituted by atoms of other elements M = Al, Ga, Mn, Si, Cr *etc*. [1–6]. An intensive search for materials for magnetothermal applications gives an additional interest to the studies of magnetic properties of the RCo_2 compounds, since the magnetocaloric effect can be rather large in these compounds [7–10].

Recently, Wang et al. [11] discovered a series of novel compounds with a general formula RNi_2Mn (R = Tb, Dy, Ho, Er). These compounds crystallize in the $MgCu_2$-type structure, though the atomic ratio of the rare earth to 3*d*-metal component is 1–3, at which the rhombohedral $PuNi_3$-type structure is usually formed in binary RM_3 alloys. The RNi_2Mn compounds are ferrimagnets and have a much higher temperature of magnetic ordering than the binary compounds RNi_2 and RMn_2. Later, it was reported [12] that the cobalt-containing alloys $HoCo_2Mn$ and $ErCo_2Mn$ with the 1:3 stoichiometry also possess the $MgCu_2$-type structure. X-ray and neutron diffraction studies showed that the Mn atoms in Laves-phase structure of the RNi_2Mn compounds partially occupy both the Ni (16d) and rare earth (8a) sites. Detailed studies of the $TbNi_2Mn$ alloys showed that the structure type depends on the conditions of the alloy preparation. As-cast arc-melted alloys show up the $MgCu_2$ structure [13], while in the samples annealed at 870 °C for several hours, the cubic $AuBe_5$-type structure is formed [14].

Bearing in mind that both RNi_2 and RNi_2Mn have the same structure, we studied magnetic properties and structure of the non-stoichiometric RNi_2Mn_x ($0 \le x \le 1.5$) systems for R = Tb, Dy, Gd [15–17]. We have found that the $MgCu_2$-type structure persists up to the manganese content $x = 0.4$ for R = Gd and up to $x = 1.25$ for R = Tb. The Curie temperature is a non-monotonous function of Mn

* Corresponding author.
E-mail address: gerasimov@imp.uran.ru (E.G. Gerasimov).

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concentration which has a maximum far below the composition $x = 1$. Thus, the RM_2Mn_x (M = Co, Ni) systems give the opportunity to gradually modify magnetic properties of the Laves phase compounds by changing in a wide range the manganese content. In present paper, in order to clarify the effect of alloying with Mn on the structure and magnetic and magnetothermal properties of intermetallic Laves-phase compounds of rare earth elements with cobalt, we studied a series of non-stoichiometric $ErCo_2Mn_x$ alloys for different $x \leq 1.4$.

2. Experimental details

The ingots of the $ErCo_2Mn_x$ alloys for $x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4 were prepared by induction melting of the constituents Er (99.9%), Co (99.99%), and Mn (99.9%) in alumina crucibles in argon atmosphere. To compensate for evaporating of volatile constituents, the excess of 1 wt% of Er and 3 wt% of Mn was added to the working mixture. In order to obtain the equilibrium phase state, the ingots were annealed at 900°C for five days.

Structural and magnetic studies were performed at the Centre of Collective Use of the Institute of Metal Physics UB RAS. X-ray diffraction analysis was carried out on powdered samples with the particle size 30–50 μm using a DRON-type diffractometer with Cr Kα radiation at room temperature. The X-ray diffraction patterns were interpreted with the use of the PowderCell 2.4 program.

For magnetic measurements, we used bulk samples of a spherical form. The magnetization was measured with the Quantum Design PPMS apparatus in magnetic fields up to 9 T in the temperature range 2–320 K. The temperature dependences of the initial ac magnetic susceptibility $\chi_{a\geq}$ were measured with a system of compensated pick-up coils in a sinusoidal alternate magnetic field with the frequency of 80 Hz and amplitude 300 A/m. The heat capacity was measured with the low-temperature adiabatic calorimeter.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the $ErCo_2Mn_x$ alloys. For the compositions with $x \leq 0.4$, the X-ray diffraction patterns can be well described on the assumption of the only cubic Laves phase (space group $Fd\bar{3}m$). In the alloys with the Mn content $x \geq 0.6$, in addition to the Laves phase C15, we observe reflections that belong to a phase with the cubic Th_6Mn_{23}-type structure (space group $Fm\bar{3}m$). The intensities of these reflections are, however, very weak for $x = 0.6$ and 0.8. According to our quantitative analysis, the volume fraction of the Th_6Mn_{23}-type phase does not exceed 10% for these compositions. For the alloys with $x \geq 1.0$, its amount increases and the $ErCo_2Mn_{1.4}$ sample contains 63% of the Th_6Mn_{23}-type phase (see Fig. 2 and Table 1).

The lattice parameter of the parent $ErCo_2$ compound amounts to $a = 0.7160$, which is consistent with the previously reported values. The Mn-containing alloys are characterized by a slightly lower value of the lattice parameter that is virtually independent of the manganese content (Fig. 2). Such a behavior reflects the interplay of two opposite factors. Substitution of Co atoms at the 16*d* sites by Mn atoms with a larger metallic radius tends to increase the lattice volume. On the contrary, partial substitution of Er atoms by Mn at the 8*a* sites tends to decrease the lattice size. For comparison, for the RNi_2Mn_x systems, this competition leads to a non-monotonous concentration dependence of the lattice parameter with a maximum at $x = 0.4$–0.6 [16,17]. The secondary phase formed in RNi_2Mn_x alloys at large x values is the $PuNi_3$-type phase. It was surprising to discover the Th_6Mn_{23}-type phase in the RCo_2Mn_x alloys, since it does not form in the binary R-Co system. The lattice parameter of the Th_6Mn_{23} phase found in our alloy is considerably

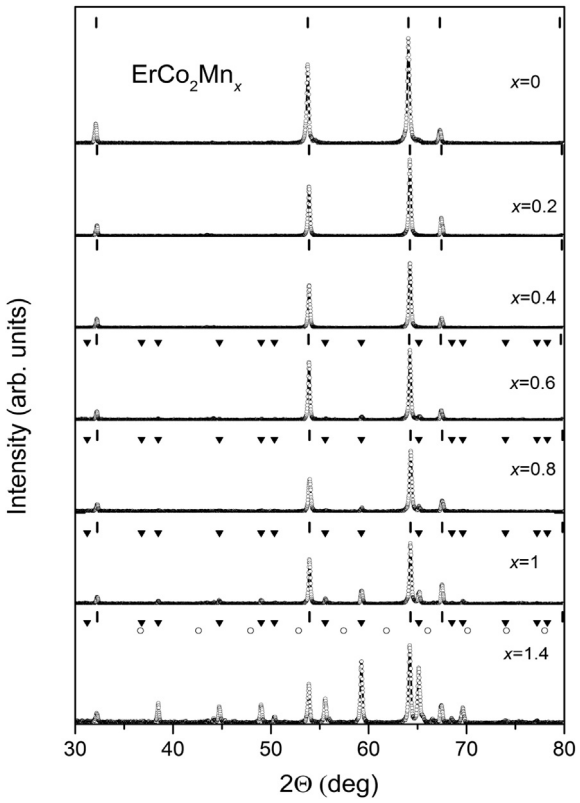

Fig. 1. X-ray diffraction patterns of the $ErCo_2Mn_x$ alloys with different x. Bragg peak positions are indicated by the markers for $MgCu_2$-type structure (line bars), Th_6Mn_{23}-type structure (solid triangles) and Mn (open circles).

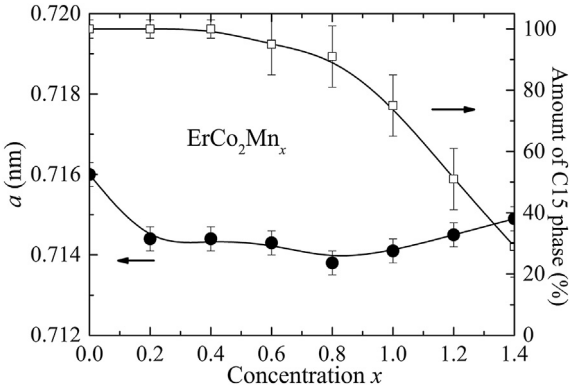

Fig. 2. Concentration dependences of the lattice parameter and the amount of the $MgCu_2$-type phase in $ErCo_2Mn_x$ alloys.

smaller than that of the binary Er_6Mn_{23} compound ($a = 1.2285$ nm). Therefore, the phase is expected to have the composition $Er_6(Mn_{1-x}Co_x)_{23}$ and contain both manganese and cobalt.

Thus, we succeed to obtain the samples with the amount of more than 90% of Laves phase in $ErCo_2Mn_x$ alloys for $x \leq 0.8$ only. It should be noted that in Ref. [12] the authors reported on the $ErCo_2Mn$ compound as a single $MgCu_2$ phase. However, the X-ray diffraction patterns presented in Ref. [12] contain reflections of the Th_6Mn_{23} phase the amount of which has not been estimated. The $ErCo_2Mn$ alloy studied in Ref. [12] was prepared by arc melting with the 6 wt% excess of Mn and annealed at 800 °C for one week. The Mn solubility limit can depend to some extent on the alloying conditions, as well as the temperature and time of the heat