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Crystal Structure of the New Ternary Th_2Ni_{17}-Type Related Compounds in the R–Mn–Al Systems (R = Gd, Tb, Dy, Ho, Er)

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New hexagonal ternary phases $R_{2-y}Mn_zMn_xAl_{17-x}$ have been obtained in the Mn-rich regions of the R–Mn–Al (R = Gd, Tb, Dy, Ho, Er) systems: $Gd_{2-y}Mn_xAl_{17-x}$ ($0 \le y \le 0.15$, $13.0 \le x \le 15.1$); $Tb_{2-y}Mn_xAl_{17-x}$ ($0 \le y \le 0.23$, $13.2 \le x \le 15.2$); $Dy_{2-y}Mn_xAl_{17-x}$ ($0 \le y <\sim 0.2$, $11.9 \le x \le 14.6$); $Ho_{2-y}Mn_xAl_{17-x}$ ($0 \le y <\sim 0.2$, $11.5 \le x \le 14.2$) and $Er_{2-y}Mn_zMn_xAl_{17-x}$ ($0 \le y \le 0.27$, $0 \le z \le 0.54$, $11.3 \le x \le 14.1$). Th_2Ni_{17}-type of structure occurs in alloys with the content of R = 10.5 at.% (ideal R_2X_{17} stoichiometry). When R < 10.5 at.%, two ways of structure constitution are possible: *i*) formation of the Th_2Ni_{17}- type structure with defective 2(*b*) atomic position (solid solution of subtraction); *ii*) formation of the Th_2Ni_{17}–related type structure with the substitution of part of R atoms by the Mn-Mn pairs (solid solution of multiple substitution).

Key words: crystal structure, ternary compounds, rare earth, manganese, aluminides

Recently R–T–Al (R = rare earth, T = d-transition element) ternary aluminides, which crystallize in the $CaCu_5$ related types of structure ($ThMn_{12}$, Th_2Zn_{17}, Th_2Ni_{17}), are intensively investigated [1,2]. The growing interest is connected with various physical properties of these intermetallics. They exhibit different types of magnetic ordering, which depend on the nature of R and T elements and on site occupations by T and Al atoms in the crystal structure [1,2]. The Mn-containing R–T–Al ternary systems are less investigated in comparison with those containing magnetic d-elements Fe,Co and Ni. The R–Mn–Al (R = Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu) systems have been investigated in the concentration range 0–33.3 at.% R by Rykhal' [3]. He reported the occurrence of RMn_4Al_8 ($ThMn_{12}$ – type of structure) and $R_2Mn_9Al_8$ (Th_2Zn_{17} – type of structure) ternary compounds in each of these systems. These data are in correlation with the previous results [4,5]. However, some contradictions occur in the literature data concerning the stoichiometry of the observed ternaries. This will be discussed in details elsewhere. According to the data of Rykhal' in the Mn-rich regions of these systems, there exist solid solutions of substitution of Mn for Al in the RMn_{12} binary compounds. These solid solutions are in equilibrium with $R_2Mn_9Al_8$ ternary compounds (Th_2Zn_{17} structure type), R_6Mn_{23} binary compounds and with the solid solutions of Al in β-Mn.

During the systematic investigation of the R–Mn–Al (R = Gd, Tb, Dy, Ho, Er) ternary systems we found, besides the $R_2(Mn,Al)_{17}$ ternary compounds of the Th_2Zn_{17}-type structure, a series of new ternary phases $R_{2-y}Mn_zMn_xAl_{17-x}$. These aluminides crystallize in the Th_2Ni_{17} and related structure types and are characterized by wide homogeneity ranges. In this paper we report the crystal structure data of these compounds.

EXPERIMENTAL

The ternary alloys were prepared by arc melting of initial elements with a purity not less than 99.9 wt.% under argon on a water-cooled copper hearth. Ingots were subsequently vacuum annealed in quartz tubes at 600°C for 720 h. Then the ampoules with the alloys were quenched in cold water. The samples were examined by X-ray powder diffraction using DRON-2.0 (FeK_α-radiation) diffractometer. The lattice parameters were obtained by least-squares fits using LATCON program [6]. Ge was used as the internal standard (a = 0.56571 nm). Structure investigations were carried out using X-ray powder diffractometers DRON-3M (CuK_α-radiation) and HZG-4a (FeK_α-radiation). CSD-program [7] was used to examine powder diffractometer data of the alloys and to determine their crystal structure.

RESULTS AND DISCUSSION

During the X-ray investigation of the Mn-rich regions of the R–Mn-Al (R = Gd, Tb, Dy, Ho, Er) ternary systems, the ternary alloys with the content of R ~10 at. % and Mn ~60–80 at.% appear as single phases with the X-ray diffraction data consistent with the hexagonal Th_2Ni_{17} type structure. These ternary phases are characterized by wide homogeneity regions. The crystal structure data are presented in Fig. 1. Dependencies of the lattice parameters along the 10.5 at.% R isoconcentrates, within the homogeneity ranges of the compounds, are presented in Fig. 2. Precise structure refinement was carried out within the homogeneity ranges of these compounds. The

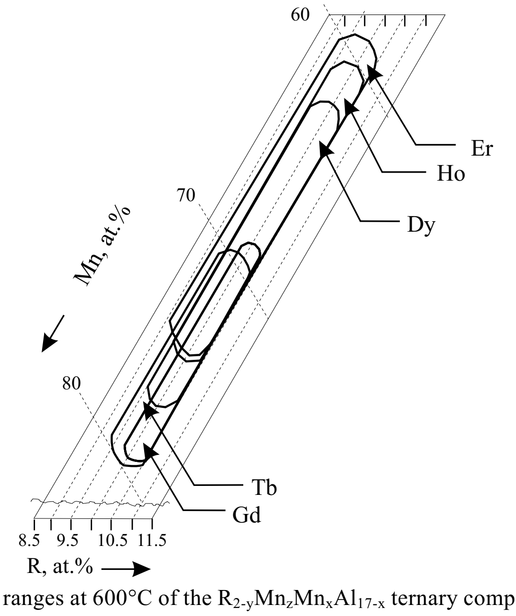

Figure 1. Homogeneity ranges at 600°C of the $R_{2-y}Mn_zMn_xAl_{17-x}$ ternary compounds. Compositions of compounds: for R = Gd – $Gd_{2-y}Mn_xAl_{17-x}$ ($0 \le y \le 0.15$, $13.0 \le x \le 15.1$); R = Tb – $Tb_{2-y}Mn_xAl_{17-x}$ ($0 \le y \le 0.23$, $13.2 \le x \le 15.2$); R = Dy – $Dy_{2-y}Mn_xAl_{17-x}$ ($0 \le y < \sim 0.2$, $11.9 \le x \le 14.6$); R = Ho – $Ho_{2-y}Mn_xAl_{17-x}$ ($0 \le y < \sim 0.2$, $11.5 \le x \le 14.2$); and R = Er – $Er_{2-y}Mn_zMn_xAl_{17-x}$ ($0 \le y \le 0.27$, $0 \le z \le 0.54$, $11.3 \le x \le 14.1$).

alloys with the R_2X_{17} (X = Mn, Al) stoichiometry (R = 10.5 at.%) crystallize in the Th_2Ni_{17}-type of structure (see Table 1). However, for R < 10.5 at.% stoichiometries the 2(*b*) atomic position, occupied by R atoms, becomes defective (see Tables 2, 3). Moreover, in the $Er_{9.0}Mn_{69.2}Al_{21.8}$ alloy the additional position 4(*e*), is partially occupied by Mn atoms as compared to the Th_2Ni_{17} type of structure (see Table 4). Th_2Ni_{17} structure type is one of the structures, like $ThMn_{12}$, Th_2Zn_{17} and others, which are derived from the $CaCu_5$ type by the multiple substitution of part of the large atoms by the pairs of small atoms. Ordered and disordered multiple substitutions are the main features, which connect all these structure types of intermetallics. Hexagonal $CaCu_5$ type of structure is a basic one for deriving a series of other structure types. Among them are hexagonal (Th_2Ni_{17}, $LuFe_{9.5}$, $Dy_{2-x}Ag_y(Ag_{0.44}Al_{0.56})_{17}$ (x = 0.26, y = 0.25) and rhombohedral (Th_2Zn_{17}, $PrFe_7$) types of structures. The relations between the parent $CaCu_5$ and resulting hexagonal and rhombohedral structure types were described earlier [8].

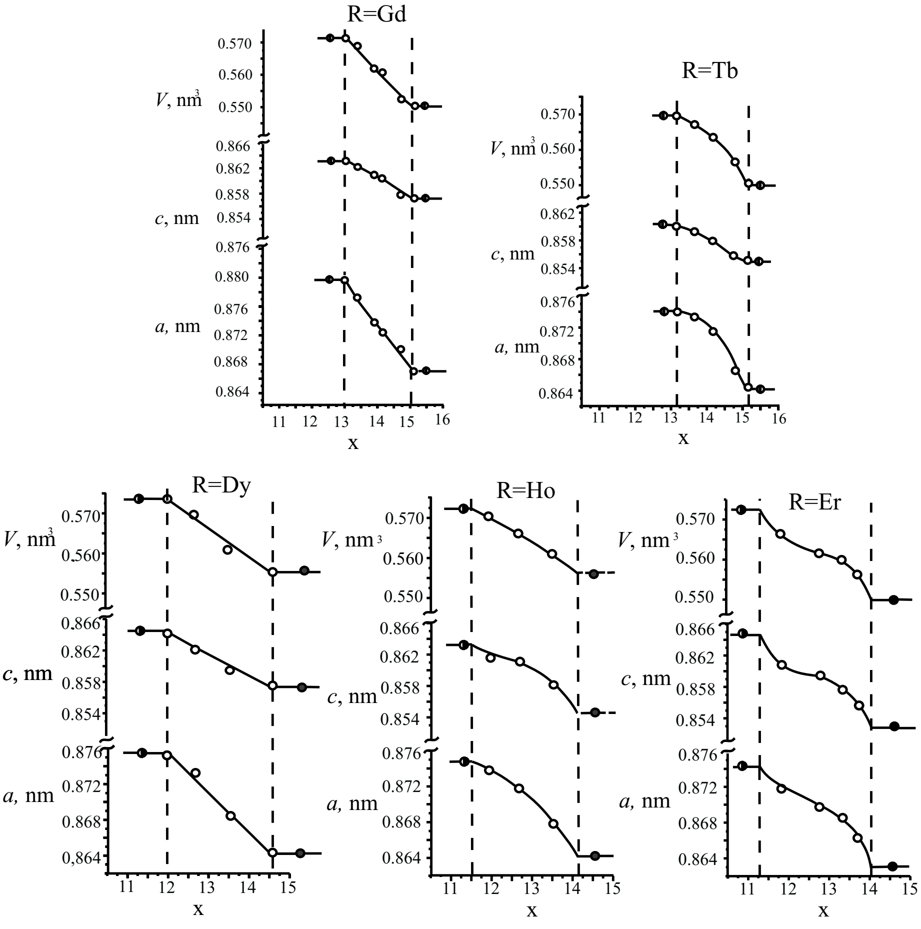

Figure 2. Lattice parameters (*a*, *c*, *V*) *vs*. Mn content (x) for the $R_{2-y}Mn_zMn_xAl_{17-x}$ ternary compounds along the R = 10.5 at.% isoconcentrates.

Table 1. Refined atomic positions, displacement (B_{izo}) parameters and site occupations (*G*) for the alloy $Er_{10.5}Mn_{74.2}Al_{15.3} = Er_{2.0}Mn_{14.1}Al_{2.9}$.

Atom	Site	*x/a*	*y/b*	*z/c*	B_{izo}	*G*
Er1	2*b*	0	0	1/4	1.1(2)	1.00Er
Er2	2*d*	1/3	2/3	3/4	0.5(2)	1.00Er
M1	4*f*	1/3	2/3	0.121(2)	0.3(6)	1.00Mn
M2	6*g*	1/2	0	0	0.4(5)	1.00Mn
M3	12*j*	0.3235(11)	0.3560(9)	1/4	0.4(6)	0.82(4)Mn+0.18(4)Al
M4	12*k*	0.1687(9)	2*x*	0.5104(6)	0.5(2)	0.70(4)Mn+0.30(4)Al

DRON-3M powder diffractometer, CuK_{α}-radiation, 2θ-range: 20°–140°, step width 2θ =0.05°; $R_I = 0.10$; Th_2Ni_{17}-type structure, space group $P6_3/mmc$; lattice parameters: $a = 0.86379(6)$ nm, $c = 0.85408(9)$ nm.

Table 2. Refined atomic positions, displacement (B_{izo}) parameters and site occupations (*G*) for the alloy $Tb_{9.4}Mn_{75.4}Al_{15.2} = Tb_{1.77}Mn_{14.1}Al_{2.9}$.

Atom	Site	*x/a*	*y/b*	*z/c*	B_{izo}	*G*
Tb1	2*b*	0	0	1/4	0.4(2)	0.77(1)Tb
Tb2	2*d*	1/3	2/3	3/4	0.31(11)	1.00Tb
M1	4*f*	1/3	2/3	0.1106(12)	1.4(3)	1.00Mn
M2	6*g*	1/2	0	0	0.0(3)	0.80(6)Mn+0.20(6)Al
M3	12*j*	0.3278(15)	0.3666(13)	1/4	1.7(2)	0.80(3)Mn+0.20(3)Al
M4	12*k*	0.1653(8)	2*x*	0.5197(9)	2.0(2)	0.82(4)Mn+0.18(4)Al

HZG–4a powder diffractometer, FeK_{α}-radiation, 2θ-range: 20°–130°, step width 2θ = 0.05°; $R_I = 0.09$; Th_2Ni_{17}-type structure, space group $P6_3/mmc$; lattice parameters: $a = 0.87146(4)$ nm, $c = 0.85823(6)$ nm.

Table 3. Refined atomic positions, displacement (B_{izo}) parameters and site occupations (*G*) for the alloy $Tb_{9.7}Mn_{70.6}Al_{19.7} = Tb_{1.83}Mn_{13.3}Al_{3.7}$.

Atom	Site	*x/a*	*y/a*	*z/c*	B_{izo}	*G*
Tb1	2*b*	0	0	1/4	0.8(2)	0.83(1)Tb
Tb2	2*d*	1/3	2/3	3/4	0.44(12)	1.00Tb
M1	4*f*	1/3	2/3	0.1084(10)	1.0(3)	0.75(3)Mn+0.25(3)Al
M2	6*g*	1/2	0	0	1.2(3)	0.85(3)Mn+0.15(3)Al
M3	12*j*	0.3222(13)	0.3616(9)	1/4	1.7(2)	0.86(2)Mn+0.14(2)Al
M4	12*k*	0.1698(7)	2*x*	0.5179(6)	2.1(2)	0.66(4)Mn+0.34(4)Al

DRON-3M powder diffractometer, CuK_{α}-radiation, 2θ-range: 20°–140°, step width 2θ = 0.05°; $R_I = 0.08$; Th_2Ni_{17}-type structure, space group $P6_3/mmc$; lattice parameters: $a = 0.87330(5)$ nm, $c = 0.86053(7)$ nm.

Intermetallic phases, which crystallize in the Mn-rich regions of R–Mn–Al ternary systems, can be considered as complex solid solutions. The investigated ternary compounds $R_{2-y}Mn_zMn_xAl_{17-x}$ belong to Th_2Ni_{17} (at $y \to 0$, $z = 0$) or related with it $Dy_{2-x}Ag_y(Ag_{0.44}Al_{0.56})_{17}$ ($x = 0.26$, $y = 0.25$) [9] structure types. One can treat these compounds as solid solutions of substitution (of the ideal R_2X_{17} stoichiometry), as solid solutions with the subtraction of R atoms or/and multiple substitution ($R \to 2X$) (at the $R_{2-y}X_{17}$ stoichiometries).

Table 4. Refined atomic positions, displacement (B_{izo}) parameters and site occupations (G) for the alloy $Er_{9.0}Mn_{69.2}Al_{21.8} = Er_{1.73}Mn_{0.54}Mn_{12.80}Al_{4.20}$.

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	B_{izo}	*G*
Er1	2*b*	0	0	1/4	0.0(2)	0.73(2)Er
Er2	2*d*	1/3	2/3	3/4	0.5(12)	1.00Er
M1	4*f*	1/3	2/3	0.1171(13)	1.4(4)	0.85(4)Mn+0.15(4)Al
M2	6*g*	1/2	0	0	1.9(6)	1.00Mn
M3	12*j*	0.3359(13)	0.3768(10)	1/4	1.5(5)	0.73(3)Mn+0.27(3)Al
M4	12*k*	0.1691(8)	2*x*	0.5180(8)	1.4(4)	0.62(3)Mn+0.38(3)Al
M5	4*e*	0	0	0.411(5)	0.3(4)	0.27(2)Mn

DRON-3M powder diffractometer, CuK_{α}-radiation, 2θ-range: 20°–140°, step width 2θ = 0.05°; $R_I = 0.10$; $Dy_{2-x}Ag_y(Ag_{0.44}Al_{0.56})_{17}$-type structure, space group $P6_3/mmc$; lattice parameters: $a = 0.86843(8)$ nm, $c = 0.8579(1)$ nm.

Th_2Ni_{17} – type structure aluminides crystallize in the R–Mn–Al ternary alloys with the content of R = 10.5 at.% (ideal R_2X_{17} stoichiometry). These are solid solutions, where larger Al atoms are substituted by smaller Mn atoms (or *vice versa*). This substitution causes a decrease of lattice parameters and cell volume with the increase of Mn content (Fig. 2). When R content is less than 10.5 at.%, two ways of structure constitution are possible: *i)* formation of the Th_2Ni_{17}-type structure with the defective 2(*b*) atomic position (*solid solution of subtraction*); *ii*) formation of the Th_2Ni_{17}-related type structure with the substitution of part of R atoms by the Mn-Mn pairs (*solid solution of multiple substitution*).

REFERENCES

1. Suski W. "The $ThMn_{12}$-type compounds of rare earths and actinides: structure, magnetic and related properties", in Handbook on the Physics and Chemistry of Rare Earths, ed. K.A. Gschneidner, Jr, L. Eyring, Elsevier Science B.V., Amsterdam, **22**, 143–294 (1996).
2. Hong-Shuo Li and Coey J.M.D. "Magnetic properties of ternary rare-earth transition-metal compounds", in Handbook of Magnetic Materials, ed. K.H.J. Buschow, Elsevier Science B.V., Amsterdam, **6**, 1–83 (1991).
3. Rykhal' R.M., Nauk.-Pract. Conf. Lvivski Khim. Chytannya, Lviv, 26 May 1995, Abstr., p. 82 (in Ukrainian).
4. Felner I. and Nowik I., *J. Phys. Chem. Solids*., **40**, 1035 (1979).
5. Felner I., *J. Less-Comm. Met*., **72**, 241 (1980).
6. Schwarzenbach D., Program LATCON, University of Lausanne, Switzerland, 1975.
7. Akselrud L.G., Grin Yu.N. and Zavalii P.Yu., XII Europ. Crystallogr. Meeting, Coll. Abstr., August, 1989, Moscow, **3**, 155 (1989).
8. Krypyakevych P.I., Structure Types of Intermetallic Compounds, Nauka, Moscow 1978, p. 66–73 (in Russian).
9. Stel'makhovych B.M., Ph.D Thesis, Ivan Franko Nat. Univ. of Lviv, Lviv 1999 (in Ukrainian).