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The Tb–Ag–Al system

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Abstract

The interaction between the components in the Tb–Ag–Al system at 870 K has been studied using X-ray analysis. The phase diagram in the region up to 50 at.% of terbium has been constructed. The limiting composition of the solid solution ranges of the binary compounds and the homogeneity ranges of the ternary ones have been determined. The crystal structures of the ternary aluminides $Tb_3Ag_{2.5}Al_{8.5}$ (La_3Al_{11}-type structure, $a=0.43026(1)$, $b=1.25972(4)$, $c=1.00160(3)$ nm), $TbAg_{0.9}Al_{2.1}$ ($PuNi_3$-type structure, $a=0.55461(4)$, $c=2.6286(2)$ nm) and $TbAg_{1.1}Al_{0.9}$ (KHg_2-type structure, $a=0.45866(3)$, $b=0.71666(4)$, $c=0.78652(5)$ nm) have been studied for the first time. The atomic coordinates, thermal parameters and the Ag and Al atom distribution in the $Tb_{1.8}Ag_{8.6}Al_{8.4}$ (Th_2Ni_{17}-type structure), $Tb_8Ag_{21.1}Al_{44.9}$ ($Yb_8Cu_{17}Al_{49}$-type structure) and $TbAg_{2.7}Al_{2.5}$ ($DyAg_{2.4}Al_{2.6}$-type structure) have been refined.

Keywords: Rare earth compounds; Crystal structure; Phase diagram; X-ray diffraction

1. Introduction

The interaction in the Tb–Ag–Al system has not been studied systematically. Earlier, the formation of some ternary aluminides has been reported [1–5]. The crystallographic data for the known ternary compounds are listed in Table 1.

The binary systems Ag–Al and Tb–Ag [6,7] were studied exhaustively. The Tb–Ag system was studied in the region up to 50 at.% of aluminium [8]. The existence of three intermediate phases in the Ag–Al system has been reported in [6]. The intermediate δ-phase (Mg-type structure) is peritectically formed at 1000 K, extending from 22.9 to 41.9 at.% of Al. The high-temperature intermediate β-phase (W-type) exists in the temperature region of 876–1051 K and it extends from 21.0 to 24.0 at.% Al. The low-temperature μ-phase (β-Mn-type structure) decomposes peritectoidally into Ag and the δ-phase above 723 K. It extends from 21.2 to 23.4 at.% Al at 573 K. According to Ref. [7] in the Tb–Ag system the compounds TbAg, $TbAg_2$ and $Tb_{14}Ag_{51}$ are formed from the melt at 1415, 1185 and 1235, respectively (the crystallographic data for them are listed in Table 2). The binary compounds Tb_2Al ($PbCl_2$-type structure), Tb_3Al_2 (Zr_3Al_2-type structure), TbAl (Table 2) are peritectically formed at 1230, 1257 and 1339 K, respectively [8]. The $TbAl_2$ compound (Table 2) is formed from the melt at 1784 K. The compound $TbAl_3$ (Table 2) has two polymorphous modifications with a transformation temperature of 912 K, the $BaPb_3$-type structure and $HoAl_3$-type structure (low-temperature modification) are adopted by them.

2. Experimental

Forty-nine ternary samples were synthesized to investigate the interaction between the components in the Tb–Ag–Al system. Samples were prepared by arc melting under purified argon atmosphere of the elemental components with certified purities of 99.5 wt.% Tb, 99.95 wt.% Ag and 99.95 wt.% Al. We weighted all alloys after melting and, if losses were larger than 3% of the starting components mass, the samples were prepared again. All alloys prepared were heat treated at 870 K in evacuated quartz ampoules during ~1000 h. The annealed alloys were quenched in cold water without breaking the ampoules.

Phase analysis was carried out using X-ray powder diffraction patterns obtained by the Debye–Scherrer techniques with nonfiltered Cr-K radiation. The lattice parameters were refined by full-matrix least-squares using powder

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Table 1
Crystallographic data of limit composition of the solid solutions of the binary and ternary compounds in the Tb–Ag–Al system

No	Phase	Structure type	Space group	Lattice parameters (nm)			Ref.
				a	*b*	*c*	
[a]	$TbAg_{0.24}Al_{1.76}$	$MgCu_2$	*Fd3m*	0.78676(4)			[b]
[a]	$TbAg_{0.5}Al_{0.5}$	CsCl	*Pm3m*	0.3607(4)			[b]
1	$TbAg_{5.5}Al_{6.5}$	$ThMn_{12}$	*I4/mmm*	0.91442(4)		0.54461(3)	[1]
	$TbAg_{5.2-5.8}Al_{6.8-6.2}$			0.9142(4)[d]		0.5444(3)	[b]
2	$Tb_{1.75}Ag_8Al_9$	Th_2Ni_{17}	$P6_3/mmc$	0.9287(4)		0.9078(3)	[2]
	$Tb_{1.8}Ag_{8.0-8.6}Al_{9.0-8.4}$			0.92815(3)[d]		0.90715(4)	[b]
3	$Tb_8Ag_{17}Al_{49}$	$Yb_8Cu_{17}Al_{49}$	*I4/mmm*	0.8804(2)		1.6799(6)	[3]
	$Tb_8Ag_{21.1}Al_{44.9}$			0.88099(4)[d]		1.6771(1)	[b]
4	$TbAg_{2.5}Al_{2.5}$	$DyAg_{2.4}Al_{2.6}$	$P6_3/mmc$	0.9173(3)		0.9415(5)	[4]
	$TbAg_{2.4-3.0}Al_{2.8-2.2}$			0.91739(4)[d]		0.94151(6)	[b]
5	$\sim Tb_{18}Ag_{57}Al_{25}$	Unknown	–	–	–	–	[b]
[c]	$TbAgAl_3$	*o*-$CeNi_{2+x}Sb_{2-x}$	*Immm*	0.4304(2)	0.4189(2)	1.0003(5)	[5]
6	$Tb_3Ag_{2.5}Al_{8.5}$	La_3Al_{11}	*Immm*	0.43026(1)	1.25972(4)	1.00160(3)	[b]
7	$Tb_3Ag_{0.9}Al_{2.1}$	$PuNi_3$	$R\bar{3}m$	0.55461(4)		2.6286(2)	[b]
8	$TbAg_{1.1}Al_{0.9}$	KHg_2	*Imma*	0.45866(3)	0.71666(4)	0.78652(5)	[b]

[a] Limit composition of solid solution.
[b] Results of present work.
[c] $TbAgAl_3$ compound is not found at 870 K.
[d] Lattice parameters presented here are given for compositions listed in Table 3.

diffraction patterns recorded on a powder DRON-3 M diffractometer in the continuous mode (Cu-Kα radiation). For the crystal structure determination of the compounds, diffraction data were collected using θ–2θ scan technique with steps of 0.05° 2θ ($2\theta_{max}$=140°) and exposition time of 25 s at every point.

Silver and aluminium have nearly the same atomic radii (r_{Ag}=0.1455 and r_{Al}=0.1432 nm [9]), so their mutual substitution in crystal structures does not lead to considerable changes in lattice parameters within the homogeneity ranges of the binary and ternary compounds. Therefore, we have determined the limits of the homogeneity ranges of the compounds using the results of phase analysis. All calculations were performed using CSD software [10].

3. Results

3.1. Phase diagram

The phase diagram of the Tb–Ag–Al system at 870 K is shown in Fig. 1. We confirmed the existence of the binary compounds, that are shown in Fig. 1. The lattice parameters calculated for them are in good agreement with literature data (Table 2).

The formation of solid solution ranges for the binary compounds TbAg and $TbAl_2$ has been observed. The limiting composition of the $TbAl_2$ solid solution range has been determined by refinement of the distribution of Ag and Al in the crystallographic positions for two-phase

Table 2
Crystallographic characteristics of the binary compounds in the Ag–Al, Tb–Ag and Tb–Al systems

Compound	Structure type	Space group	Lattice parameters (nm)			Ref.
			a	*b*	*c*	
δ-phase	Mg	$P6_3/mmc$	0.2871(2)		0.4665(3)	[6]
			0.2869(2)		0.4668(3)	[a]
$Tb_{14}Ag_{51}$	$Gd_{14}Ag_{51}$	*P6/m*	1.2650		0.9280	[7]
			1.2647(3)		0.9280(3)	[a]
$TbAg_2$	$MoSi_2$	*I4/mmm*	0.371		0.925	[7]
			0.3697(5)		0.9248(3)	[a]
TbAg	CsCl	*Pm3m*	0.3625			[7]
			0.3607(4)			[a]
$TbAl_3$	$HoAl_3$	$R\bar{3}m$	0.6095		3.596	[8]
			0.6093(2)		3.592(6)	[a]
$TbAl_2$	$MgCu_2$	*Fd3m*	0.7867			[8]
			0.78676(4)			[b]
TbAl	DyAl	*Pbcm*	0.5834	1.1370	0.5621	[8]
			0.5831(3)	1.1368(2)	0.5624(3)	[a]

[a] Data obtained by the indexing of diffractograms of two- and three-phase samples.
[b] The constants are obtained during the refinement of the atomic distribution in binary sample containing $TbAl_2$ as a main phase.

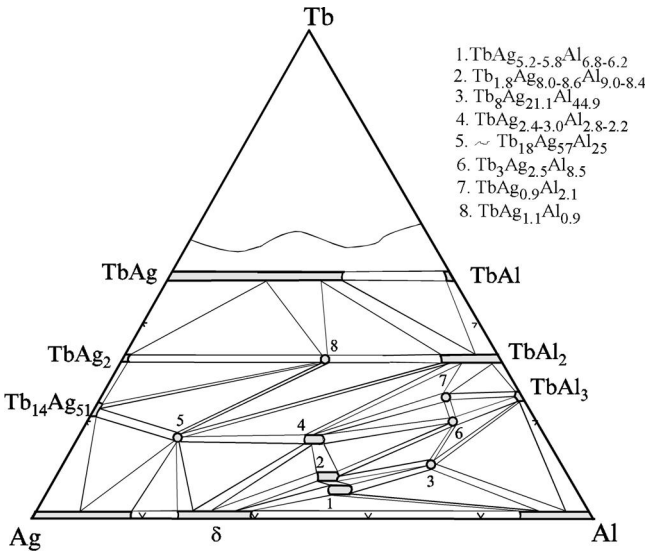

Fig. 1. The isothermal section of the Tb–Ag–Al system at 870 K.

samples, containing the solid solution as the main phase and the KHg_2-type phase. The compound $TbAl_2$ dissolves up to 7.9 at.% Ag (R_I=0.061, for 28 unique reflections). The solubility of Al in the TbAg compound is about ~28 at.%. It was determined using the results of phase analysis.

The existence of four earlier known aluminides: $TbAg_{5.5}Al_{6.5}$ ($ThMn_{12}$-type structure) [1], $Tb_{1.75}Ag_8Al_9$ (Th_2Ni_{17}-type structure) [2], $TbAg_{2.5}Al_{2.5}$ ($DyAg_{2.4}Al_{2.6}$-type structure) [4] and $Tb_8Ag_{17}Al_{49}$ ($Yb_8Cu_{17}Al_{49}$-type structure) [3] in Tb–Ag–Al system was confirmed. As one can see from Fig. 1, the first three of them have homogeneity ranges, and earlier reported compositions are in the limits of the respective compositions of solid solutions (Table 1). The compound with *o*-$CeNi_{2+x}Sb_{2-x}$-type structure has not been found at 870 K. However, we have obtained the compound of the approximate composition $Tb_3Ag_{2.5}Al_{8.5}$ (La_3Al_{11}-type structure). The crystallographic characteristics and the results of refinement for the compounds in the Tb–Ag–Al system are listed in Table 3.

3.2. Ternary compounds and their crystal structure

The crystal structure of the $Tb_{1.8}Ag_{8.6}Al_{8.4}$ (Th_2Ni_{17}-type structure) is characterized by a partial occupation (90%) of the 2(*b*) position by the Tb atoms (Table 4) like that found for the earlier reported $Dy_{1.75}Ag_{8.2}Al_{9.2}$ [11] and $Y_{1.8}Ag_{8.3}Al_{8.7}$ [12] structures. In the $Dy_{1.75}Ag_{8.2}Al_{9.2}$ compound the Ag atoms also partially occupy the 4(*e*) position (11%). In contrast, in the crystal structure of the $Tb_{1.8}Ag_{8.6}Al_{8.4}$ compound this position is non-occupied. The statistical mixtures of Ag and Al occupy the crystallographic positions of the smallest atoms with the coordination number 12 and 14, which makes the mentioned compound more closely related with the $Y_{1.8}Ag_{8.3}Al_{8.7}$.

The existence of the compound $Tb_8Ag_{17}Al_{49}$ ($Yb_8Cu_{17}Al_{49}$-type structure) is reported in Ref. [3], but the atomic coordinates, mode of atomic distribution and thermal parameters were not refined. As one can see from Table 4, the crystallographic positions of the smallest atoms are occupied by a statistical mixture of Ag and Al. $Tb_8Ag_{21.1}Al_{44.9}$ is a unique compound in the Tb–Ag–Al system with hexahedric coordination of the smallest atoms (the coordination sphere of the Al1 contains eight T4 atoms (Table 5)).

The crystal structure of the compound $TbAg_{2.7}Al_{2.5}$ ($DyAg_{2.4}Al_{2.6}$-type structure) is characterized by the presence of the defective 2(*b*) and 4(*e*) positions, which are occupied by Ag atoms. In the earlier reported compounds $YAg_{2.5}Al_{2.7}$ [12] and $DyAg_{2.4}Al_{2.5}$ [13] the position 2(*a*) is partially occupied by Al 70% and 59% respectively, while in the crystal structure of the $TbAg_{2.7}Al_{2.5}$ compound this position is completely occupied. So, the $TbAg_{2.7}Al_{2.5}$ compound somewhat differs from similar isotypic compounds.

The existence of the compound $Tb_3Ag_{2.5}Al_{8.5}$ (La_3Al_{11}-type structure) in the Tb–Ag–Al system has been established for the first time. This compound has approximately the same composition as $TbAgAl_3$ (*o*-$CeNi_{2+x}Sb_{2-x}$-type structure) [5]. The compounds of La_3Al_{11}-type structure have been revealed in the ternary Ln–Ag–Al system, where Ln–Y [12], Dy, Ho [14], in which the compounds with the *o*-$CeNi_{2+x}Sb_{2-x}$-type structure were known before [5]. Both La_3Al_{11} and *o*-$CeNi_{2+x}Sb_{2-x}$-type structures are derivatives from the $BaAl_4$-type structure and can be obtained by an orthorhombic distortion of tetragonal $BaAl_4$ cell. Besides, in La_3Al_{11}, one of the smaller unit cell constants is three times larger. Because of that, some difficulties in differentiation of these types may arise. The

Table 3
Crystallographic data and results of the refinement of the structure of the ternary compounds

	Compound					
	$Tb_{1.8}Ag_{8.6}Al_{8.4}$	$Tb_8Ag_{21.1}Al_{44.9}$	$TbAg_{2.7}Al_{2.5}$	$Tb_3Ag_{2.5}Al_{8.5}$[a]	$TbAg_{0.9}Al^a_{2.1}$	$TbAg_{1.1}Al^a_{0.9}$
Structure type	Th_2Ni_{17}	$Yb_8Cu_{17}Al_{49}$	$DyAg_{2.4}Al_{2.6}$	La_3Al_{11}	$PuNi_3$	KHg_2
Cell volume (nm^3)	0.6768(4)	1.3016(7)	0.6862(3)	0.5429(3)	0.7003(2)	0.2585(5)
Number of atoms in cell	37.8	74	37.3	28	36	12
Calculated density (g/cm^3)	7.110	6.065	7.576	6.101	6.687	7.649
Number of free parameters	17	21	21	17	12	7
R-factors	R_I=0.077	R_I=0.070	R_I=0.082	R_I=0.085	R_I=0.087	R_I=0.089
	R_p=0.141	R_p=0.156	R_p=0.165	R_p=0.118	R_p=0.161	R_p=0.169

[a] Ternary aluminides which are found for the first time.

Table 4
Atomic coordinates, isotropic thermal parameters and coordination numbers (CN) of the atoms in the structures of the Tb–Ag–Al compounds

Compounds: composition and distribution of atoms 1	Space group and position 2	CN 3	Coordinates			$B_{iso}\times10^2$ (nm^2) 7
			x 4	*y* 5	*z* 6	
$Tb_{1.8}Ag_{8.6}Al_{8.4}$	$P6_3/mmc$					
1.8(1)Tb1	2(*b*)	18	0	0	1/4	0.5(1)
2Tb2	2(*d*)	20	1/3	2/3	3/4	0.7(1)
T1(2.8(1)Ag+1.2(1)Al)	4(*f*)	14	1/3	2/3	0.0956(5)	0.4(1)
T2(1.2(1)Ag+4.8(1)Al)	6(*g*)	12	1/2	0	0	2.0(3)
T3(7.8(1)Ag+4.2(1)Al)	12(*j*)	12	0.3307(4)	0.9685(3)	1/4	1.0(1)
T4(5.3(1)Ag+6.7(1)Al)	12(*k*)	12	0.1613(2)	2*x*	0.9780(3)	0.3(1)
$Tb_8Ag_{21.1}Al_{44.9}$	$I4/mmm$					
4Tb1	4(*c*)	20	1/2	0	1/2	1.3(1)
4Tb2	4(*e*)	16	0	0	0.7225(3)	1.4(1)
2Al1	2(*b*)	8	0	0	1/2	1.3(1)
8Al2	8(*f*)	12	1/4	1/4	1/4	1.3(1)
T1(4.4(1)Ag+3.6 (1)Al)	8(*h*)	10	0.1537(6)	*x*	0	1.2(1)
T2(0.8(1)Ag+15.2(1)Al)	16(*n*)	13	0.2274(2)	0	0.1388(8)	1.7(2)
T3(13.0(1)Ag+3.0(1)Al)	16(*n*)	12	0.3471(5)	0	0.3239(2)	1.6(1)
T4(2.9(1)Ag+14.1(1)Al)	16(*m*)	13	0.1674(8)	*x*	0.4195(5)	1.9(2)
$TbAg_{2.7}Al_{2.5}$	$P6_3/mmc$					
6Tb(1)	6(*h*)	16	0.1955(2)	2*x*	1/4	0.4(1)
2Al1	2(*a*)	12	0	0	0	2.5(1)
T1(0.8(1)Ag+3.2(1)Al)	4(*f*)	12	2/3	1/3	0.5218(1)	1.4(3)
T2(3.7(1)Ag+2.3(1)Al)	6(*g*)	12	1/2	0	1/2	0.7(2)
T3(1.3(1)Ag+4.7(1)Al)	6(*h*)	12	0.5687(5)	2*x*−1	1/4	0.8(1)
T4(9.5(1)Ag+2.5(1)Al)	12(*k*)	11	0.1586(2)	2*x*	0.5916(4)	0.8(1)
0.4(1)Ag1	2(*b*)	6+3	0	0	1/4	1.6(1)
0.2(1)Ag2	4(*e*)	6+3	0	0	0.337(4)	1.9(1)
$Tb_3Ag_{2.5}Al_{8.5}$	$Immm$					
2Tb1	2(*a*)	20	0	0	0	0.3(1)
4Tb2	4(*g*)	19	0	0.3139(2)	0	0.7(1)
T1(0.2(1)Ag+1.8(1)Al)	2(*c*)	12	1/2	1/2	0	2.0(1)
T2(1.4(1)Ag+2.6(1)Al)	4(*j*)	12	1/2	0	0.7096(9)	1.3(1)
T3(0.6(1)Ag+7.4(1)Al)	8(*l*)	12	0	0.144(1)	0.2766(9)	2.0(1)
T4(3.0(1)Ag+5.0(1)Al)	8(*l*)	12	0	0.3394(6)	0.0.3681(5)	1.4(1)
$TbAg_{0.9}Al_{2.1}$	$R\bar{3}m$					
3Tb1	3(*a*)	20	0	0	0	0.7(1)
6Tb2	6(*c*)	16	0	0	0.1421(1)	0.4(1)
6Ag1	6(*c*)	12	0	0	0.3362(2)	0.6(1)
T1(0.2(1)Ag+2.8(1)Al)	3(*b*)	12	0	0	1/2	1.5(1)
T2(2.0(1)Ag+16.0(1)Al)	18(*h*)	12	0.173(1)	−*x*	0.4169(3)	1.6(1)
$TbAg_{1.1}Al_{0.9}$	$Imma$					
4Tb1	4(*l*)	16	1/4	1/2	0.7839(5)	2.0(1)
T1(4.4(1)Ag+3.6(1)Al)	8(*h*)	9	1/4	0.2974(8)	0.4194(9)	2.6(1)

diffractogram of the sample with $Tb_{21}Ag_{19}Al_{58}$ composition was the best indexed with the following cell parameters $a=0.43026(1)$, $b=1.25972(4)$, $c=1.00160(3)$ nm. The refinement of the atomic coordinates and the mode of the atomic distribution in the crystallographic positions (Tables 3 and 4) gives reasons to propose for $Tb_3Ag_{2.5}Al_{8.5}$ the La_3Al_{11}-type structure, with $R_I=0.070$. X-ray phase analysis did not confirm the existence of the $TbAgAl_3$ compound with *o*-$CeNi_{2+x}Sb_{2-x}$-type structure.

In the Y–Ag–Al system a compound with $Ca_3Cu_2Al_7$-type structure (superstructure to $PuNi_3$) is known. This compound is characterized by a completely ordered distribution of the smaller atoms in all crystallographic positions [15]. In the Tb–Ag–Al system we have found the $TbAg_{0.9}Al_{2.1}$ compound ($PuNi_3$-type structure) for the first time. Refinement of the atomic parameters in the structure of $TbAg_{0.9}Al_{2.1}$ showed a partially ordered distribution of the Al and Ag atoms: the position 6(*c*) is occupied exclusively by Ag atoms, the other positions of smaller atoms (3(*b*) and 18(*h*)) being occupied by a statistical mixture of Ag and Al with a predominating content of the first one.

Table 5
The shortest interatomic distances (δ, nm) in the structures of the Tb–Ag–Al compounds

	Atom	δ, nm
$Tb_{1.8}Ag_{8.6}Al_{8.4}$	Tb1–6T4	0.3317(3)
	Tb2–2T1	0.3135(4)
	T1–1T1	0.2801(6)
	T2–4T3	0.2691(2)
	T4–2T4	0.2624(3)
$Tb_8Ag_{21.1}Al_{44.9}$	Tb1–4T3	0.3246(4)
	Tb2–4T2	0.3071(1)
	Al1–8T4	0.2484(8)
	Al2–4T3	0.2668(2)
	T1–2T4	0.2606(9)
	T2–2T1	0.2771(1)
$TbAg_{2.7}Al_{2.5}$	Tb1–2Tb1	0.3793(2)
	Tb1–2T1	0.3068(8)
	Tb1–1Ag1	0.3107(1)[a]
	T4–1Ag2	0.2618(1)[a]
	T4–1Al1	0.2664(2)[a]
	T1–3T2	0.2656(1)
	T2–2T3	0.2594(2)
	T4–2T2	0.2848(2)
$Tb_3Ag_{2.5}Al_{8.5}$	Tb1–2Tb2	0.3955(3)
	Tb1–8T4	0.3236(5)
	Tb2–2T1	0.3147(7)
	T1–4T3	0.288(1)
	T2–2T4	0.2572(9)
	T3–2T4	0.2602(6)
$TbAg_{0.9}Al_{2.1}$	Tb1–2Tb2	0.3739(4)
	Tb1–6Ag1	0.3200(1)
	Tb2–6T2	0.3172(2)
	Ag1–6T2	0.2676(5)
	T1–12T2	0.2764(1)
$TbAg_{1.1}Al_{0.9}$	Tb1–2Tb1	0.3622(1)
	Tb1–12T1	0.3150(5)
	T1–2T1	0.2621(5)

[a] Atoms which partially occupy the crystallographic positions.

The new ternary compound with KHg_2-type structure has been identified in the sample of ~$Tb_{33}Ag_{33}Al_{34}$ composition. Indexing of the diffractogram, refinement of the atomic coordinates and the mode of occupation of the crystallographic positions and also of the thermal parameters of atoms (Table 4) resulted in the composition $TbAg_{1.1}Al_{0.9}$ and the reliability factor R_I=0.089 (Table 3). Isotypic compounds are also known in the Y–Ag–Al [15] and Dy–Ag–Al [16] systems.

The minimum interatomic distances (δ) in the structures of the investigated compounds are listed in Table 5. As a rule, they are close to the sum of the atomic radii of the components [9]. The greatest shortening of distances is observed between the Al1–8T4 atoms (0.2484(8) nm) in the structure of the $Tb_8Ag_{21.1}Al_{44.9}$ compound. In this case Al1 atoms have hexahedric coordination which is not typical for structures of ternary aluminides.

A new compound ~$Tb_{18}Ag_{57}Al_{25}$ with unknown structure has been found in the Tb–Ag–Al system. Its crystal structure may be isotypic with ~$YAg_{3.8}Al_{1.2}$ [15].

4. Discussion

Among the systems Ln–Ag–Al (where Ln is a rare earth element of the yttrium group) the Tb–Ag–Al system is the third one that was studied systematically. The formation of solid solution ranges for the binary compounds $LnAl_2$ ($MgCu_2$-type structure) and LnAg (CsCl-type structure) has been observed like that for the Y–Ag–Al and Dy–Ag–Al systems. All ternary compounds in the mentioned three systems crystallize with the same structures. An exception is the $TbAg_{0.9}Al_{2.1}$ compound with $PuNi_3$ type which was not found in the Dy–Ag–Al system. This may prove the relation of the Tb–Ag–Al system (and Y–Ag–Al) with Ln–Ag–Al systems containing rare earth elements of the cerium group, which are characterized by the formation of the ternary aluminides with $PuNi_3$-type structure. In the Ln–Ag–Al systems (where Ln=Pr [17], Nd [18], Sm [19] and Dy [16]), which were studied in the whole concentration region, no compounds were found over 50 at.% of rare earth metal and, therefore, the absence of those compounds in the investigating system may be expected.

In the Tb–Ag–Al system we have established the existence of eight ternary aluminides. The compounds $TbAg_{5.5}Al_{6.5}$ ($ThMn_{12}$-type structure), $Tb_{1.75}Ag_8Al_9$ (Th_2Ni_{17}-type structure), $TbAg_{2.5}Al_{2.5}$ ($DyAg_{2.4}Al_{2.6}$-type structure) and $TbAg_{0.9}Al_{2.1}$ ($PuNi_3$-type structure) are characterized by icosahedric coordination of the smaller atoms. In compound $Tb_8Ag_{17}Al_{49}$ ($Yb_8Cu_{17}Al_{49}$-type structure) one finds hexahedric coordination of the smaller atoms. The compound $Tb_3Ag_{2.5}Al_{8.5}$ (La_3Al_{11}-type structure) is characterized by an Archemedian-cubic environment of the smaller atoms and in the $TbAg_{1.1}Al_{0.9}$ compound (KHg_2-type structure) the smaller atoms possess trigonal-prismatic coordination. It should be noticed that in the earlier investigated systems Ln–{Ag,Cu}–Al the structures of the compounds with rare earth contents up to 20 at.% and an Ag content higher than that of Al (for example, $NaZn_{13}$, $BaCd_{11}$, Th_2Zn_{17}, $CaCu_5$) are also characterized by icosahedric coordination of the smaller atoms. As a result of close values of the atomic radii of Ag and Al, the crystallographic positions of the smaller atoms in the structures, as a rule, are occupied by a statistical mixture of the above mentioned elements.

Ternary aluminides with La_3Al_{11}-type structure were revealed in the Ln–Ag–Al systems (where Ln–Y, Tb, Dy, Ho). Therefore, we expect the existence of isotypic compounds in the analogous Gd and Er systems. Also we can suppose the presence of isotypic compounds of KHg_2-type structure in the Ln–Ag–Al systems (where Ln–Gd, Ho, Er), since such compounds were already found in the systems with Sm, Y, Tb and Dy.

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