Chemistry of Metals and Alloys

Chem. Met. Alloys 16 (2023) 52-58
Ivan Franko National University of Lviv
http://publications.lnu.edu.ua/chemetal

A new representative of the structure type $Sc_{0.6}Fe_2Si_{4.9}$ in the Tm–Pd–Al–Ga system

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Received October 24, 2023; accepted December 19, 2023
https://doi.org/10.30970/cma16.0437

The crystal structure of the new quaternary phase $Tm_{0.67}Pd_2(Al_{0.79(7)}Ga_{0.21(7)})_5$ was refined from X-ray powder diffraction data (structure type $Sc_{0.6}Fe_2Si_{4.9}$, Pearson symbol *hP*20, space group $P6_3/mmc$, $a = 4.28311(9)$, $c = 16.3748(4)$ Å). The crystal structure belongs to a homologous series of structures with the general formula $(R_{0.67})_mT_nM_{2n+m}$, and consists of monoatomic layers of the compositions $Tm_{0.67}M$ ($m = 1$) and PdM_2 ($n = 2$), where *M* is a statistical mixture of aluminum and gallium atoms. The $Tm_{0.67}$(Al,Ga) layers are built from Tm atoms (Wyckoff position 2*c*) and triangles, formed by Al and Ga atoms (position 6*h*), in the ratio 2:1.

Tm–Pd–Al–Ga system, X-ray diffraction, crystal structure, $Sc_{0.6}Fe_2Si_{4.9}$ structure type

Introduction

Preliminary studies of the Dy–Ni–Al–Ga system indicated the formation of a new quaternary phase, $Dy_{0.67}Ni_2(Al,Ga)_5$, with the structure type $Sc_{0.6}Fe_2Si_{4.9}$ (Pearson symbol *hP*20, space group $P6_3/mmc$) [1]. Thirty compounds with the structure type $Sc_{0.6}Fe_2Si_{4.9}$ [2] have so far been reported in systems with rare-earth metals [3]: {Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}–Fe–Si [4], Sm–{Pd,Pt}–Al [5], Ce-Pt-Al [3], {Y, Gd, Tb, Dy, Ho, Er, Tm}–Pt–Al [6], {La, Lu}–Pt–Al [7], {La, Ce, Pr}–Pt–Ga [3], {Y, Sm, Ho}–Ni–Ga–Ge [8], Tb–Ni–Ga–Si [8], Ce–La–Pt–Ga [3] and Gd–Pt–Al–Si [9].

Being one of the best-known catalysts, palladium was chosen as transition metal in our investigation. Intermetallic compounds with palladium are expected to provide selectivity, efficiency, and economy in many chemical processes. This work is part of a project to search for new phases in the Tm–Pd–Al–Ga system and determine their crystal structures.

Experimental

A sample of nominal composition $Tm_{10}Pd_{25}Al_{50}Ga_{15}$ was prepared by arc-melting of pure elements (Tm ≥ 99.89 wt.%, Pd ≥ 99.95 wt.%, Al ≥ 99.985 wt.%, and Ga ≥ 99.99 wt.%) under a purified argon atmosphere. The mass of the alloy was 1 g and the loss during the preparation was less than 1 % of the total mass. The alloy was annealed at 600°C for 70 days in an evacuated quartz ampoule and quenched in cold water. The crystal structure was refined from X-ray powder diffraction data recorded with a STOE Stadi P diffractometer (Cu $K\alpha_1$ radiation, angular range 4.000-110.545°, step 0.015), using the program package FullProf Suite [10]. The elemental composition was independently determined by energy-dispersive X-ray spectroscopy, performed on a scanning electron microscope TESCAN Vega3 LMU equipped with an energy-dispersive X-ray analyzer Oxford Instruments Aztec ONE with an X-Max^{N}20 detector. The program STRUCTURE TIDY [11] was used to standardize the structural parameters.

3. Results and discussion

The results of the analysis by energy-dispersive X-ray spectroscopy of the $Tm_{10}Pd_{25}Al_{50}Ga_{15}$ sample are given in Table 1, and a photo of the polished surface of the sample is shown in Fig. 1. The sample was found to be multiphase with the main phase having the composition $Tm_{8.4(1)}Pd_{26.5(1)}Al_{51.7(4)}Ga_{13.4(6)}$. The gray part is another quaternary phase, $Tm_{10.4(8)}Pd_{24.6(9)}Al_{59(3)}Ga_{6(1)}$, and the dark (black) part has a composition close to Pd_2Al_3 ($Tm_{0.3(1)}Pd_{40.8(7)}Al_{56.6(1)}Ga_{2.3(4)}$). The known binary compound Pd_2Al_3 with Ni_2Al_3-type structure type was thus found to contain very small amounts of Ga (~2 at.%) and no significant amounts of Tm.

Table 1 Results of the EDX analysis of the sample of nominal composition $Tm_{10}Pd_{25}Al_{50}Ga_{15}$.

Spectrum	Phase composition	Average phase composition	Ideal phase composition
1	$Tm_{9.82}Pd_{24.42}Al_{61.08}Ga_{4.68}$		$Tm_{10.8}Pd_{24.3}(Al,Ga)_{64.9}$
2	$Tm_{9.62}Pd_{24.11}Al_{59.17}Ga_{6.10}$	$Tm_{10.4(8)}Pd_{24.6(9)}Al_{59(3)}Ga_{6(1)}$	(structure type $Gd_{1.33}Pt_3Al_8$)
3	$Tm_{11.40}Pd_{25.92}Al_{55.78}Ga_{6.90}$		
4	$Tm_{0.40}Pd_{43.91}Al_{53.21}Ga_{2.48}$		$Pd_{40}(Al,Ga)_{60}$
5	$Tm_{0.10}Pd_{39.69}Al_{57.66}Ga_{2.55}$	$Tm_{0.3(1)}Pd_{40.8(7)}Al_{56.6(1)}Ga_{2.3(4)}$	(structure type Ni_2Al_3)
6	$Tm_{0.29}Pd_{38.87}Al_{58.96}Ga_{1.88}$		
7	$Tm_{8.35}Pd_{26.45}Al_{51.76}Ga_{13.44}$		$Tm_{8.7}Pd_{26.1}Al_{51.5}Ga_{13.7}$ [a]
8	$Tm_{8.49}Pd_{25.42}Al_{52.10}Ga_{13.99}$	$Tm_{8.4(1)}Pd_{26.5(1)}Al_{51.7(4)}Ga_{13.4(6)}$	(structure type $Sc_{0.6}Fe_2Si_{4.9}$)
9	$Tm_{8.42}Pd_{27.47}Al_{51.24}Ga_{12.87}$		

[a] from Rietveld refinement

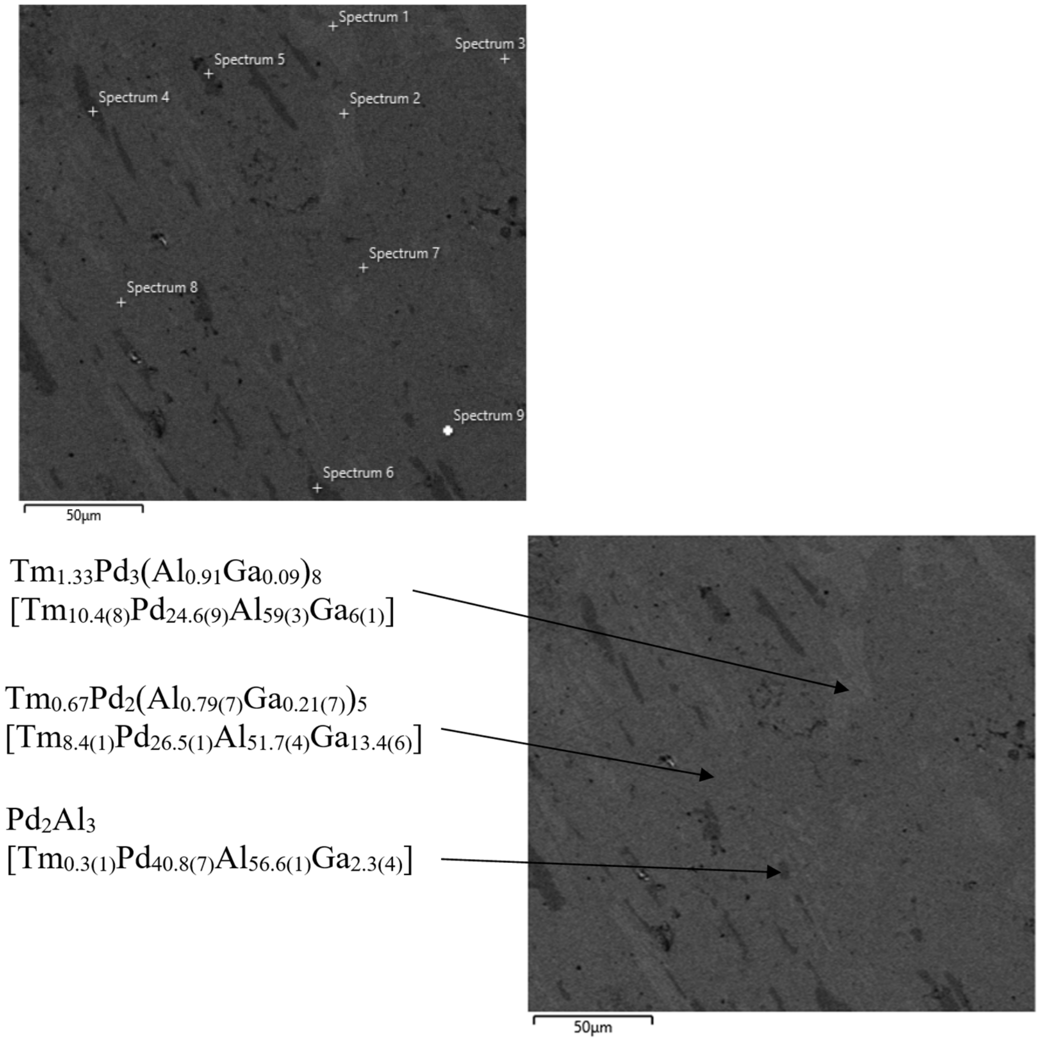


Fig. 1 Photo of the surface of the $Tm_{10}Pd_{25}Al_{50}Ga_{15}$ sample (scanning electron microscope TESCAN Vega3 LMU).

The results of overall EDX analyses of the $Tm_{10}Pd_{25}Al_{50}Ga_{15}$ sample showed good agreement with the nominal composition: $Tm_{8.23}Pd_{26.63}Al_{51.7}Ga_{13.44}$.

The X-ray phase analysis confirmed that the sample contained two new quaternary phases, which were found to adopt the structure types $Sc_{0.6}Fe_2Si_{4.9}$ and $Gd_{1.33}Pt_3Al_8$, respectively. The phase with $Sc_{0.6}Fe_2Si_{4.9}$-type structure (Pearson symbol *hP*20, space group *P*6$_3$*/mmc*) was predominant with a content of 90.3(5) wt.%. In addition to the quaternary phases, minor amounts of the binary compound Pd_2Al_3 (Ni_2Al_3 structure type, *hP*5, *P*-3*m*1) were also confirmed (2.9(1) wt.%).

X-ray diffraction patterns of the polycrystalline sample $Tm_{10}Pd_{25}Al_{50}Ga_{15}$ are shown in Fig. 2. Details of the structural refinements on X-ray powder diffraction data from the sample annealed at 600°C are given in Table 2.

A complete structure refinement using the Rietveld method was performed on X-ray powder diffraction data obtained for the $Tm_{10}Pd_{25}Al_{50}Ga_{15}$ sample (STOE Stadi P diffractometer, Cu $K\alpha_1$ radiation). The atomic coordinates of the initial model for the refinement of the structure of the majority phase were taken from the structure of $Dy_{0.67}Ni_2(Al,Ga)_5$ [1]. The occupancy of the Tm site (Wyckoff position 2*c*) was fixed to 0.67 and the 6*h* position, occupied by a statistical mixture of Al and Ga atoms, was refined fixing the sum of the occupancies by Al and Ga atoms to 0.33 (Table 3). The low content (6.8 wt.%) of the second quaternary phase, $Tm_{1.33}Pd_3(Al_{0.91}Ga_{0.09})_8$, did not allow carrying out a complete structure refinement, but this will be the subject of a future investigation. The atom coordinates refined for $Gd_{1.33}Pt_3Al_8$ were used here and the Al/Ga ratio was taken from the EDX analysis ($Tm_{1.33}Pd_3(Al_{0.91}Ga_{0.09})_8$). Pd_2Al_3 was assumed to be purely binary.

The new quaternary compound $Tm_{0.67}Pd_2(Al_{0.79}Ga_{0.21})_5$ belongs to the structure type $Sc_{0.6}Fe_2Si_{4.9}$ (Pearson symbol *hP*20, space group *P*6$_3$*/mmc*), while the other new quaternary phase, $Tm_{1.33}Pd_3(Al_{0.91}Ga_{0.09})_8$, belongs to the structure type $Gd_{1.33}Pt_3Al_8$ (*hR*51, *R*-3*m*). The crystal structures of both compounds belong to a homologous series of compounds with the general formula $(R_{0.67})_mT_nM_{2n+m}$, consisting of layers of the compositions $R_{0.67}M$ (*m*) and TM_2 (*n*). The monoatomic $Tm_{0.67}$(Al,Ga) layers are built from Tm atoms (Wyckoff position 2*c*) and triangles, formed by a statistical mixture of Al and Ga atoms (position 6*h*), in the ratio 2:1. It appears from this model that the ideal composition of the structure type refined as $Sc_{0.6}Fe_2Si_{4.9}$ is $Sc_{0.67}Fe_2Si_5$.

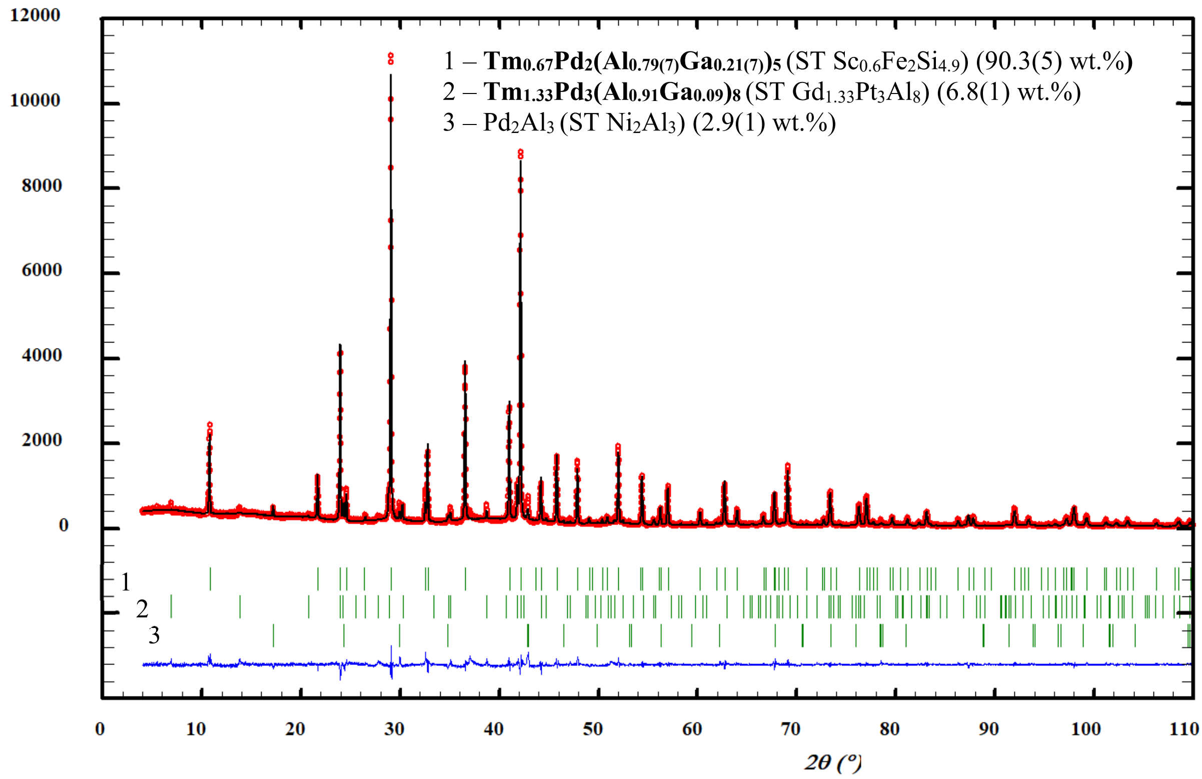


Fig. 2 Observed, calculated and difference (bottom) X-ray powder diffraction patterns for the $Tm_{10}Pd_{25}Al_{50}Ga_{15}$ sample; Cu $K\alpha_1$ radiation.

Table 2 Experimental details of the Rietveld refinement of the $Tm_{10}Pd_{25}Al_{50}Ga_{15}$ sample (diffractometer STOE Stadi P, Cu $K\alpha_1$ radiation).

Sample	$Tm_{10}Pd_{25}Al_{50}Ga_{15}$		
Phase	$Tm_{0.67}Pd_2(Al_{0.79(7)}Ga_{0.21(7)})_5$	$Tm_{1.33}Pd_3(Al_{0.91}Ga_{0.09})_8$	Pd_2Al_3
EDX results	$Tm_{8.4(1)}Pd_{26.5(1)}\times$ $\times Al_{51.7(4)}Ga_{13.4(6)}$	$Tm_{10.4(8)}Pd_{24.6(9)}\times$ $\times Al_{59(3)}Ga_{6(1)}$	$Tm_{0.3(1)}Pd_{40.8(7)}\times$ $\times Al_{56.6(1)}Ga_{2.3(4)}$
Content, wt.%	90.3(5)	6.8(1)	2.9(1)
Structure type	$Sc_{0.6}Fe_2Si_{4.9}$	$Gd_{1.33}Pt_3Al_8$	Ni_2Al_3
Pearson symbol	*hP*20	*hR*51	*hP*5
Space group	$P6_3/mmc$	*R*-3*m*	*P*-3*m*1
Cell parameters:			
a, Å	4.28311(9)	4.3146(2)	4.2199(3)
c, Å	16.3748(4)	38.529(3)	5.1544(6)
Cell volume *V*, Å^3	260.16(1)	621.18(7)	79.50(1)
Formula units per unit cell *Z*	2	3	1
Density D_X, g/cm^3	9.674	9.146	3.068
Preferred orientation [direction]	0.960(3) [110]	–	–
2θ range, ° (step, °)	4.000-110.545 (0.015)		
Number of measured reflections	7104		
Number of refined parameters	27		
FWHM parameters *U*, *V*, *W*	0.053(2), -0.014(2), 0.0133(5)		
Mixing parameter η	0.458(7)		
Asymmetry parameters	0.089(3) 0.020(1)	–	–
Reliability factors:			
R_B	0.0366	–	–
R_p, R_{wp}, R_{exp}, χ^2	0.0808, 0.111, 0.0656, 2.85		

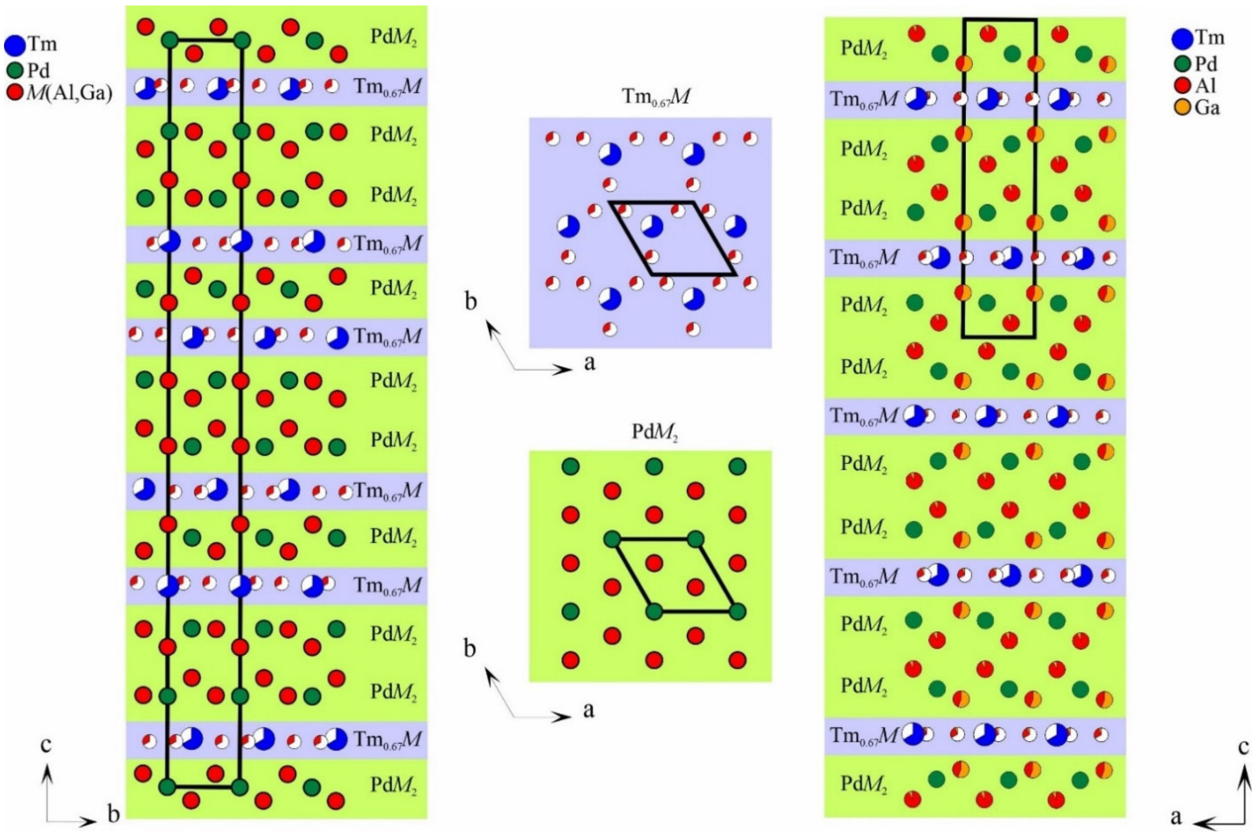
The two structures are shown in Fig. 3. The monoatomic layers containing the rare-earth metal atoms ($Tm_{0.67}M$) are separated by either double or single puckered layers PdM_2. For $Tm_{1.33}Pd_3(Al_{0.91}Ga_{0.09})_8$, the sequence includes one $Tm_{0.67}M$ layer, followed by two PdM_2 layers, then another $Tm_{0.67}M$ layer, and one more PdM_2 layer, and so on ($m = 2$, $n = 3$). For the structure type $Sc_{0.6}Fe_2Si_{4.9}$, the sequence includes one $Tm_{0.67}M$ layer, followed by two PdM_2 layers, then another $Tm_{0.67}M$ layer, and two more PdM_2 layers, and so on ($m = 1$, $n = 2$). The projection of the layers along the [001] direction is shown in the middle of the figure.

The phase analysis of the $Tm_{10}Pd_{25}Al_{50}Ga_{15}$ sample allowed us to draw tentative phase equilibria in the Pd–Al rich region of the quaternary system Tm–Pd–Al–Ga (Fig. 4).

Table 3 Atomic coordinates and displacement parameters for $Tm_{0.67}Pd_2(Al_{0.79(7)}Ga_{0.21(7)})_5$ (structure type $Sc_{0.6}Fe_2Si_{4.9}$, Pearson symbol *hP*20, space group *P*6₃/*mmc*, *a* = 4.28311(9), *c* = 16.3748(4) Å).

Atom	Wyckoff position	Atomic coordinates			Occupancy	B_{iso}, Å^2
		x	*y*	*z*		
Tm	2*c*	⅓	⅔	1/4	0.67 [a]	0.99(4)
Pd	4*f*	⅓	⅔	0.60847(6)	1	0.98(3)
Ga1 Al1	6*h*	0.5421(7)	0.0840(13)	1/4	0.16(1) 0.17(1) [b]	0.56(14)
Ga2 Al2	4*f*	⅓	⅔	0.0479(2)	0.04(1) 0.96(1) [c]	0.63(8)
Ga3 Al3	4*e*	0	0	0.1395(2)	0.23(1) 0.77(1) [c]	0.63(7)

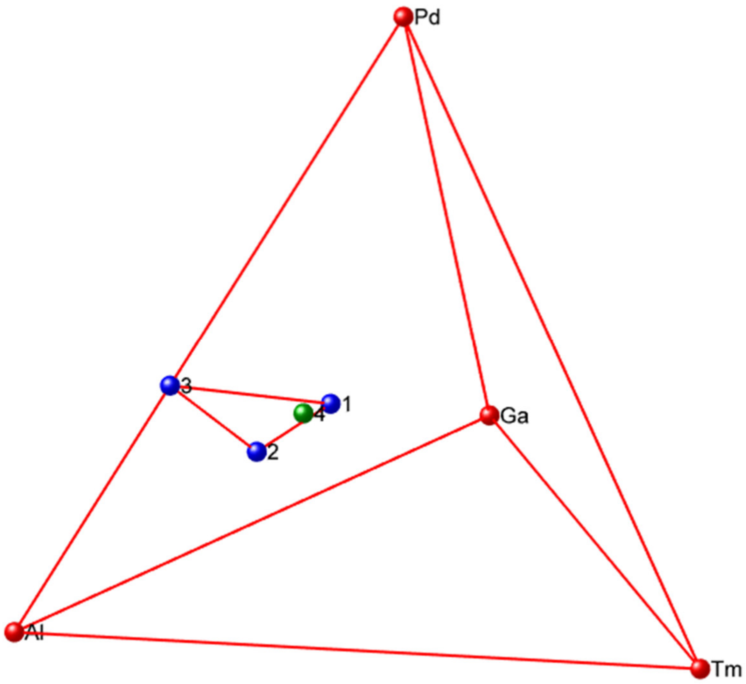
[a] fixed, [b] sum fixed to 0.33, [c] sum fixed to 1



$Tm_{1.33}Pd_3(Al_{0.91}Ga_{0.09})_8$
a = 4.322(1), *c* = 38.54(2) Å

$Tm_{0.67}Pd_2(Al_{0.79}Ga_{0.21})_5$
a = 4.28311(9), *c* = 16.3748(4) Å

Fig. 3 Arrangement of atomic layers in the structures of $Tm_{1.33}Pd_3(Al_{0.91}Ga_{0.09})_8$ and $Tm_{0.67}Pd_2(Al_{0.79}Ga_{0.21})_5$ and projections of the two kinds of layer along [001].



1 – $Tm_{0.67}Pd_2(Al_{0.79}Ga_{0.21})_5$ (ST $Sc_{0.6}Fe_2Si_{4.9}$) (90.3(5) wt.%)
2 – $Tm_{1.33}Pd_3(Al_{0.91}Ga_{0.09})_8$ (ST $Gd_{1.33}Pt_3Al_8$) (6.8(1) wt.%)
3 – Pd_2Al_3 (ST Ni_2Al_3) (2.9(1) wt.%)
4 – $Tm_{10}Pd_{30}Al_{50}Ga_{10}$ (nominal composition of the sample)

Fig. 4 Phase equilibria in the Tm–Pd–Al–Ga system at 600°C involved in the sample $Tm_{10}Pd_{30}Al_{50}Ga_{10}$.

Conclusions

The existence of two new quaternary phases, $Tm_{0.67}Pd_2(Al_{0.79(7)}Ga_{0.21(7)})_5$ and $Tm_{1.33}Pd_3(Al_{0.91}Ga_{0.09})_8$ was established based on X-ray powder diffraction and energy-dispersive X-ray spectroscopy. A complete structure refinement using the Rietveld method was performed for the $Tm_{0.67}Pd_2(Al_{0.79(7)}Ga_{0.21(7)})_5$ phase. Its structure belongs to the type $Sc_{0.6}Fe_2Si_{4.9}$ (Pearson symbol *hP*20, space group $P6_3/mmc$, $a = 4.28311(9)$, $c = 16.3748(4)$ Å). The crystal structures of both new compounds belong to a homologous series of structures with the general formula $(R_{0.67})_mT_nM_{2n+m}$, consisting of monoatomic layers of the composition $R_{0.67}M$ and puckered layers TM_2.

Acknowledgement

This work was supported by the Ministry of Education and Science of Ukraine under the grant No. 0121U109766.

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