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Ternary compounds with $Sc_{0.6}Fe_2Si_{4.9}$-type structure in the systems Sm–{Pd, Pt}–Al

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Two new ternary samarium aluminides, $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$, were synthesized. Their crystal structures were refined from X-ray powder diffraction data: structure type $Sc_{0.6}Fe_2Si_{4.9}$, Pearson symbol *hP*20-4.67, space group $P6_3/mmc$, $a = 4.3314(3)$, $c = 16.423(2)$ Å for the Pd-containing compound and $a = 4.2909(3)$, $c = 16.447(1)$ Å for the Pt-containing compound. The structures are disordered with respect to the distribution of *R* atoms and Al_3 triangles.

Aluminum / Samarium / Palladium / Platinum / X-ray powder diffraction / Crystal structure

Introduction

23 representatives of the hexagonal structure type $Sc_{0.6}Fe_2Si_{4.9}$ (idealized formula $Sc_{0.67}Fe_2Si_5$, Pearson symbol *hP*20-4.67, space group $P6_3/mmc$, $a = 3.897$, $c = 15.160$ Å [1]) are known so far according to Pearson's Crystal Data [2]. They are ternary aluminides, gallides, or silicides of zirconium, rare-earth elements, or uranium and transition metals of group VIII (Table 1) and one quaternary alumosilicide of gadolinium and platinum. The ternary silicides were reported with the approximate composition $R_{0.6}Fe_2Si_{4.9}$, whereas the ternary gallide and aluminides have composition $R_{0.67}T_2M_5$. The structure of the quaternary phase $Gd_{0.67}Pt_2Al_4Si$ belongs to the ternary type $Sc_{0.6}Fe_2Si_{4.9}$. Three more quaternary compounds, gallidogermanides of rare-earth elements and nickel with the approximate composition $R_{0.67}Ni_2Ga_{4.33}Ge_{0.67}$, have been reported with the quaternary type $Y_{0.67}Ni_2Ga_3(Ga_{0.67}Ge_{0.33})_2$ (Pearson symbol *hP*20-4.67, space group $P6_3/mmc$, $a = 4.179$, $c = 15.993$ Å [13]), which is a partly ordered derivative (with respect to the distribution of Ga and Ge atoms) of $Sc_{0.6}Fe_2Si_{4.9}$. One more compound, $Yb_2Pt_6Al_{15}$, was reported with a closely related structure of own type

Table 1 Ternary compounds with $Sc_{0.6}Fe_2Si_{4.9}$-type structure (Pearson symbol *hP*20-4.67, space group $P6_3/mmc$).

R *T*	Sc	Y	Zr	Ce	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	U
Aluminides														
Pd					[a]									[3]
Pt		[4]	[4]	[5]	[a]	[6]	[4]	[4]	[4]	[4]		[7][b]		[8]
Gallides														
Pt				[9]										
Silicides														
Fe	[1]	[10]				[10]	[10]	[10]	[10]	[11]	[10]	[10]	[10]	[12]
Alumosilicides														
Pt						[6]								
Gallidogermanides														
Ni		[13][c]			[13][c]				[13][c]					

[a] this work; [b] $Yb_2Pt_6Al_{15}$-type structure; [c] $Y_{0.67}Ni_2Ga_3(Ga_{0.67}Ge_{0.33})_2$-type structure.

(Pearson symbol *oS*92, space group *Cmcm*, $a = 12.7966$, $b = 7.38813$, $c = 16.3604$ Å [7]). The structure was predicted in [14] and is an ordered variant of $Sc_{0.6}Fe_2Si_{4.9}$.

We present here the results of a structural investigation of two new ternary samarium aluminides, $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$. In the corresponding systems the existence of three compounds has been reported so far: $SmPd_2Al_3$, SmPdAl, and SmPtAl. The structure of the former aluminide belongs to the type $PrNi_2Al_3$ (Pearson symbol *hP*6, space group *P*6/*mmm*, $a = 5.41310$, $c = 4.19971$ Å [15]) and the structures of the aluminides with equiatomic composition belong to the type TiNiSi (Pearson symbol *oP*12, space group *Pnma*, $a = 7.013$, $b = 4.493$, $c = 7.766$ Å for SmPdAl and $a = 7.026$, $b = 4.432$, $c = 7.746$ Å for SmPtAl [16]).

Experimental

Alloys of nominal composition $Sm_{7.7}Pd_{23.1}Al_{69.2}$ and $Sm_{8.7}Pt_{26.1}Al_{65.2}$ were synthesized from high-purity metals (Sm ≥ 99.996 wt.%, Pd ≥ 99.9 wt.%, Pt ≥ 99.9 wt.%, Al ≥ 99.998 wt.%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. To achieve high efficiency of the interaction between the components the samples were melted twice. The ingots were annealed at 600°C in evacuated quartz ampoules for one month and subsequently quenched in cold water. The loss during the preparation of the samples was less than 0.5 % of the total mass, which was approximately 1 g for each alloy.

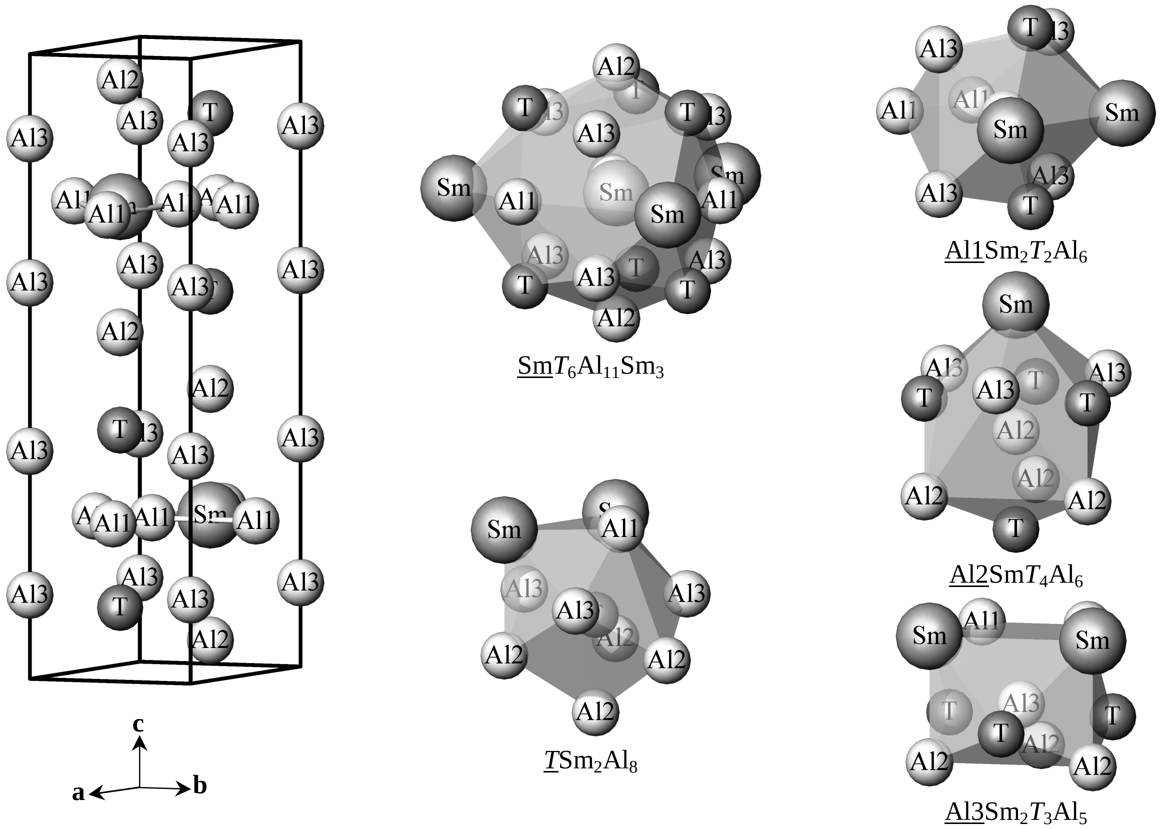
X-ray powder diffraction patterns of the compounds $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$ were obtained at room temperature on a DRON-4.07 diffractometer. The structures were refined by the Rietveld method, starting from the coordinates of the parent structure type $Sc_{0.6}Fe_2Al_{4.9}$ [1], using the DBWS-9807 program [17]. No superstructure reflections, corresponding to any of the ordered derivatives, were observed. In the final cycle of each refinement 16 parameters were allowed to vary: zero shift, scale factor, two cell parameters, four profile parameters (pseudo-Voigt function), four positional and three atomic displacement parameters, and one texture parameter. The isotropic displacement parameters for the same chemical element were constrained to be equal. The background was defined by linear extrapolation of 25 points. The main feature of the refined structures is the statistical distribution of Sm atoms (Wyckoff position 2*c*) and Al_3 triangles (Wyckoff position 6*h*) within atomic layers of composition $Sm_{0.67}Al$. The occupancy of the site in Wyckoff position 6*h* cannot exceed 1/3 because higher occupancy would lead to the appearance of impossibly short Al-Al distances (~1.6 Å) in the structure. During the final cycles of the refinements, the occupancies were fixed at occ. = 0.67 for Sm in 2*c* and occ. = 0.33 for Al in 6*h*. Experimental details and crystallographic data are listed in Table 2, atomic coordinates and isotropic displacement parameters are given in Table 3. The content of the unit cell for $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$ is shown in Fig. 1 (drawn with the program ATOMS-5.0.7 [18]).

Table 2 Experimental details and crystallographic data for the compounds $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$.

Compound	$Sm_{0.67}Pd_2Al_5$	$Sm_{0.67}Pt_2Al_5$
Formula weight M_r	448.44	625.82
Structure type	$Sc_{0.6}Fe_2Si_{4.9}$	
Pearson symbol	*hP*20-4.67	
Space group	$P6_3/mmc$	
Formula units per cell *Z*	2	
Unit-cell parameters *a*, *c*, Å	4.3314(3), 16.423(2)	4.2909(3), 16.447(1)
Cell volume *V*, Å^3	266.83(4)	262.24(3)
Density D_X, g cm^{-3}	5.581	7.923
Preferred orientation parameter [direction]	0.955(4) [0 0 1]	0.884(4) [0 0 1]
Radiation type, wavelength λ, Å	Fe *K*α, 1.93735	
Scanning mode	$\theta/2\theta$	
Range 2θ, °	20-110	
Step size, °	0.05	
Profile parameters *U*, *V*, *W*	0.089(8), 0, 0.102(3)	0.068(7), 0, 0.090(3)
Mixing parameter	0.56(2)	0.57(2)
Asymmetry parameter	-0.06(3)	-0.02(2)
# of reflections	54	52
# of refined parameters	16	16
Reliability factors R_B, R_p, R_{wp}	0.0868, 0.0436, 0.0555	0.1094, 0.0479, 0.0650
Goodness of fit *S*	0.42	0.66

Table 3 Atomic coordinates and isotropic displacement parameters for the compounds $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$ (space group $P6_3/mmc$).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2	Occ.
			$Sm_{0.67}Pd_2Al_5$			
Sm	2*c*	⅓	⅔	¼	0.57(10)	0.67
Pd	4*f*	⅓	⅔	0.6077(1)	0.79(7)	1
Al1	6*h*	0.549(6)	0.098(6)	¼	0.8(2)	0.33
Al2	4*f*	⅓	⅔	0.0488(4)	0.8(2)	1
Al3	4*e*	0	0	0.1346(6)	0.8(2)	1
			$Sm_{0.67}Pt_2Al_5$			
Sm	2*c*	⅓	⅔	¼	0.61(16)	0.67
Pt	4*f*	⅓	⅔	0.6079(1)	0.62(6)	1
Al1	6*h*	0.535(7)	0.070(7)	¼	0.7(3)	0.33
Al2	4*f*	⅓	⅔	0.0456(6)	0.7(3)	1
Al3	4*e*	0	0	0.1313(8)	0.7(3)	1



$\underline{Sm}T_6Al_{11}Sm_3$

$\underline{T}Sm_2Al_8$

$\underline{Al1}Sm_2T_2Al_6$

$\underline{Al2}SmT_4Al_6$

$\underline{Al3}Sm_2T_3Al_5$

Fig. 1 Unit cell and coordination polyhedra in the structures of $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$ (either a Sm atom or an Al_3 triangle (site Al1) is present).

Results and discussion

Interatomic distances and coordination numbers for the compounds $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$ are listed in Table 4; the corresponding coordination polyhedra are shown in Fig. 1. The Sm atoms centre hexagonal prisms (composition T_6Al_6) with additional atoms (5Al + 3Sm) above all the faces. The Pd/Pt atoms are situated inside defect (two missing vertices) icosahedra of composition Sm_2Al_8, which can be reduced to cubes if only the Al atoms are considered. The Al atoms from the three crystallographically independent sites also centre defect icosahedra. The compositions are $Sm_2T_2Al_6$ for Al1, SmT_4Al_6 for Al2, and $Sm_2T_3Al_5$ for Al3.

As can be seen from Fig. 1, the structures of $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$ are built up from two kinds of slab, stacked along the crystallographic

Table 4 Interatomic distances and coordination numbers for the compounds $Sm_{0.67}Pd_2Al_5$ and $Sm_{0.67}Pt_2Al_5$.

Atoms		δ ± 0.020, Å		Coordination number
		$Sm_{0.67}Pd_2Al_5$	$Sm_{0.67}Pt_2Al_5$	
Sm	– 3 Al1	3.040	3.085	20
	– 6 Al3	3.138	3.154	
	– 2 Al2	3.304	3.362	
	– 6 *T*	3.423	3.406	
	– 3 Sm	4.331	4.291	
T	– 1 Al1	2.498	2.534	10
	– 3 Al3	2.540	2.507	
	– 1 Al2	2.570	2.525	
	– 3 Al2	2.681	2.681	
	– 2 Sm	3.423	3.406	
Al1	– 2 *T*	2.498	2.534	10
	– 2 Al1	2.802	2.596	
	– 4 Al3	2.901	2.912	
	– 2 Sm	3.040	3.085	
Al2	– 1 *T*	2.570	2.525	11
	– 3 *T*	2.681	2.681	
	– 3 Al3	2.870	2.850	
	– 3 Al2	2.970	2.896	
	– 1 Sm	3.304	3.362	
Al3	– 3 *T*	2.540	2.507	10
	– 3 Al2	2.870	2.850	
	– 2 Al1	2.901	2.912	
	– 2 Sm	3.138	3.154	

direction [0 0 1]: flat layers of composition $Sm_{0.67}Al$ (a Sm atom or an Al_3 triangle with probability 2/3 and 1/3, respectively) and puckered layers of composition TAl_2 (Al-*T*-Al). Both kinds of slab possess the motif of a close-packed layers. The translation period contains two $Sm_{0.67}Al$ and four TAl_2 layers in the sequence TAl_2-$Sm_{0.67}Al$-TAl_2-TAl_2-$Sm_{0.67}Al$-TAl_2.

The prototype $Sc_{0.6}Fe_2Si_{4.9}$ is a member of the homologous series $R_{0.67}T_nM_{2n+1}$ [19] with $n = 2$. Other members are the following structure types: $Tb_{0.67}PdAl_3$ [19], $Ho_2Rh_3Al_9$ [20], and $Y_2Co_3Ga_9$ [21] with $n = 1$, $Yb_2Pt_6Al_{15}$ [7] with $n = 2$, and $Gd_{1.33}Pt_3Al_8$ [6], $Er_{1.33}Pt_3Al_8$ [22], $Y_4Pt_9Al_{24}$ [22], $Dy_4Ni_9Al_{24}$ [23], and $Er_4Pt_9Al_{24}$ [22] with $n = 1.5$. Hexagonal $Tb_{0.67}PdAl_3$ and trigonal (rhombohedral) $Gd_{1.33}Pt_3Al_8$ (like hexagonal $Sc_{0.6}Fe_2Si_{4.9}$) are “fully” disordered types with respect to the distribution of the *R* atoms and Al_3 (Si_3) triangles in the $R_{0.67}Al$ ($R_{0.67}Si$) layers. Fully ordered types are orthorhombic $Y_2Co_3Ga_9$ and $Yb_2Pt_6Al_{15}$ and triclinic $Er_4Pt_9Al_{24}$. The other types are partly disordered variants of these. The unit-cell volume of the $Yb_2Pt_6Al_{15}$-type structure is six times larger than the volume of the $Sc_{0.6}Fe_2Si_{4.9}$-type structure ($\mathbf{a}' = 3\mathbf{a} + 3\mathbf{b}$, $\mathbf{b}' = -\mathbf{a} + \mathbf{b}$, $\mathbf{c}' = \mathbf{c}$) [14]. The ternary type $Sc_{0.6}Fe_2Si_{4.9}$ has also a quaternary partly-ordered derivative $Y_{0.67}Ni_2Ga_3(Ga_{0.67}Ge_{0.33})_2$ [13]. It is characterized by complete disorder with respect to the distribution of the Y atoms and Ga_3 triangles, but the Ge atoms prefer one of two Ga sites in the puckered $Ni(Ga,Ge)_2$ layers.

The cell volume of $Sm_{0.67}Pd_2Al_5$ is larger than the cell volume of $Sm_{0.67}Pt_2Al_5$ (266.83(4) and 262.24(3) $Å^3$, respectively). Larger cell volume for the Pd-containing compound than for the Pt-containing compound was also reported for another couple of isotypic compounds, $U_{0.67}Pd_2Al_5$ and $U_{0.67}Pt_2Al_5$ (264.18 and 259.76 $Å^3$, respectively) [3,8]. Similarities between the Sm–*T*–Al and U–*T*–Al systems are also observed for the *c*/*a* ratio when passing from the Pd- to the Pt-containing compound ($c/a = 3.792$ and 3.763 for $Sm_{0.67}Pd_2Al_5$ and $U_{0.67}Pd_2Al_5$, and $c/a = 3.833$ and 3.791 for $Sm_{0.67}Pt_2Al_5$ and $U_{0.67}Pt_2Al_5$).

Conclusions

The new samarium aluminide $Sm_{0.67}Pt_2Al_5$ continues a long row of isotypic Pt-containing compounds $R_{0.67}Pt_2Al_5$ (R = Y, Zr, Ce, Gd-Er, Yb, U) with $Sc_{0.6}Fe_2Si_{4.9}$-type structure, whereas the new samarium aluminide $Sm_{0.67}Pd_2Al_5$ is only the second representative of this structure type among Pd-containing compounds (the first representative being $U_{0.67}Pd_2Al_5$). The structures are disordered with respect to the distribution of *R* atoms and Al_3 triangles. They can be decomposed into two kinds of slab and are members of the homologous series $R_{0.67}T_nM_{2n+1}$.

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