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Crystal structures of the new intermetallics Ce_3Pt_5Al and $Ce_3Pt_5Al_2$

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The crystal structures of the ternary intermetallics Ce_3Pt_5Al and $Ce_3Pt_5Al_2$ have been determined from single crystal X-ray diffraction data. Ce_3Pt_5Al is a new representative of the Ce_3Pd_5Si-type of structure: space group *Imma*, a = 7.3767(4) Å, b = 13.1733(8) Å, c = 7.5884(4) Å, Pearson symbol *oI*36. $Ce_3Pt_5Al_2$ crystallizes in the triclinic space group *P*-1 with a = 5.689(2) Å, b = 8.432(3) Å, c = 8.7103(13) Å, α = 102.31(2)°, β = 97.89(2)°, γ = 89.10(3)° (Pearson symbol *aP*20) and represents a novel structure type. In both structures, the coordination polyhedra are rather irregular. The structures of Ce_3Pt_5Al and $Ce_3Pt_5Al_2$ can be represented as packings of Ce-centered polyhedra.

Cerium platinum aluminide / X-ray diffraction / Crystal structure / Ce_3Pt_5Al / $Ce_3Pt_5Al_2$

Introduction

A systematic investigation of alloys containing aluminum, platinum and cerium has been in progress in our laboratory for a few years. In addition to the known compounds CePtAl [1], $CePt_4Al$, and $CePt_2Al_3$ [2], $CePtAl_2$, $CePtAl_3$, and $CePt_3Al_2$ [3], five new ternaries from the Al-rich part of the phase diagram were found and structurally characterized: $Ce_{0.67}Pt_2Al_5$ and $Ce_{1.33}Pt_3Al_8$ with $Gd_{0.67}Pt_2Al_5$-type and $Gd_{1.33}Pt_3Al_8$-type structure, respectively [4], $CePt_3Al_5$, which belongs to the YNi_5Si_3 structure type [5] with site exchange, and $Ce_3Pt_4Al_6$ [6] and $Ce_2Pt_9Al_{16}$ [7], crystallizing with their own structure types.

In this paper we report the structures of two new compounds found in the Pt-rich part of the Ce–Pt–Al system.

Experimental

Single crystals of the new compounds were mechanically isolated from annealed samples [8]. For Ce_3Pt_5Al, X-ray single crystal intensity data were collected on a Nonius Kappa CCD diffractometer (Mo *K*α radiation, φ- and ω-scan). An empirical absorption correction was applied using the program SADABS [9]. Single crystal intensity data for $Ce_3Pt_5Al_2$ were collected on a CAD4 Enraf Nonius diffractometer (Mo *K*α radiation, ω-scan). An empirical absorption correction was made on the basis of ψ-scan data [10]. Crystallographic data for $Ce_3Pt_5Al_2$ and Ce_3Pt_5Al and experimental details of the structure determination and refinement are summarized in Table 1.

The structures were solved by direct methods with the SHELXS-97 program, and refined with the SHELXL-97 program [11]. The final atomic coordinates, standardized with the program STRUCTURE TIDY [12], and equivalent isotropic displacement parameters are given in Table 2. The nearest-neighbor interatomic distances are listed in Tables 3,4.

Results and discussion

Crystal structures

a) Ce_3Pt_5Al

Ce_3Pt_5Al is a new representative of the Ce_3Pd_5Si-type of structure [13]: space group *Imma*, a = 7.3767(4) Å, b = 13.1733(8) Å, c = 7.5884(4) Å (Pearson symbol *oI*36). Earlier only silicides were known to crystallize with this structure type: U_3Pt_5Si [14], Ce_3Pt_5Si [15], and La_3Pd_5Si [16].

In the structure of Ce_3Pt_5Al, the two crystallographically independent cerium atoms have 11 nearest neighbors (10Pt+Al) at distances in the range 2.9999(7)-3.241(4) Å for Ce1 and

Table 1 Crystallographic data for Ce_3Pt_5Al and $Ce_3Pt_5Al_2$ and experimental details of the structure determination and refinement.

Compound	Ce_3Pt_5Al	$Ce_3Pt_5Al_2$
Space group	*Imma*	*P*-1
Lattice parameters (Å, º)	a = 7.3767(4), b = 13.1733(8), c = 7.5884(4)	a = 5.689(2), b = 8.432(3), c =8.7103(13) α = 102.31(2), β = 97.89(2), γ = 89.10(3)
Cell volume (Å^3), Z	737.41(7), 4	404.3(2), 2
Calculated density (g/cm^3)	12.816	11.908
Scan range θ (º)	3.85-30.00	2.42-30.98
Linear absorption coefficient	112.572 mm^{-1}	102.769 mm^{-1}
Range in h k l	$-8 \le h \le 10$, $-18 \le k \le 18$, $-10 \le l \le 10$	$-8 \le h \le 8$, $-12 \le k \le 11$, $0 \le l \le 12$
Independent reflections	597	2563
Reflections with $I > 2\sigma(I)$	562	1875
Number of refined parameters	29	92
Goodness of fit	1.127	1.049
R, R_w	0.0288, 0.0677	0.0577, 0.1422

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the structures of Ce_3Pt_5Al and $Ce_3Pt_5Al_2$.

Ce_3Pt_5Al	Atom	x	y	z	U_{eq}
	Ce1	0	0.05036(5)	0.27709(9)	0.00556(19)
	Ce2	0	¼	0.62259(14)	0.0074(2)
	Pt1	0.29498(5)	0.10423(3)	0.56604(4)	0.00786(16)
	Pt2	¼	¼	¼	0.0153(2)
	Al	0	¼	0.0276(8)	0.0075(10)
$Ce_3Pt_5Al_2$	Atom	x	y	z	U_{eq}
	Ce1	0.1459(2)	0.71380(17)	0.06628(13)	0.0065(3)
	Ce2	0.2285(2)	0.42124(17)	0.36681(13)	0.0060(2)
	Ce3	0.3210(2)	0.01060(17)	0.78986(13)	0.0071(3)
	Pt1	0.00269(15)	0.22589(11)	0.57760(9)	0.00550(19)
	Pt2	0.17583(16)	0.08782(12)	0.12280(9)	0.0085(2)
	Pt3	0.39148(15)	0.36000(11)	0.04874(9)	0.0068(2)
	Pt4	0.52558(15)	0.21845(11)	0.57544(9)	0.0058(2)
	Pt5	0.72846(16)	0.33181(12)	0.31981(9)	0.0082(2)
	Al1	0.2163(13)	0.0240(10)	0.3936(7)	0.0078(13)
	Al2	0.3093(12)	0.4096(9)	0.7736(7)	0.0063(13)

Table 3 Interatomic distances in the structure of Ce_3Pt_5Al.

Atom	To atom	d, Å	Atom	To atom	d, Å
Ce1	2 Pt1	2.9999(7)	Pt1	Al	2.5455(17)
	2 Pt1	3.0937(7)		Pt1	2.8697(7)
	2 Pt1	3.1696(6)		Ce2	2.9337(4)
	2 Pt1	3.2092(6)		Pt1	2.9234(8)
	2 Pt2	3.2187(6)		Ce1	2.9999(7)
	Al	3.241(4)		Pt1	3.0247(8)
	Ce1	3.6339(14)		Pt2	3.0902(4)
	2 Ce1	3.7112(2)		Ce1	3.0937(7)
	Ce2	3.7135(10)		Ce1	3.1696(6)
Ce2	4 Pt1	2.9337(4)		Ce1	3.2092(6)
	Al	3.073(6)		Ce2	3.3996(8)
	2 Pt2	3.3757(9)	Pt2	2 Al	2.500(4)
	4 Pt1	3.3996(8)		4 Pt1	3.0902(4)
	2 Ce1	3.7135(10)		4 Ce1	3.2187(6)
				2 Ce2	3.3757(9)
			Al	2 Pt2	2.500(4)
				4 Pt1	2.5455(17)
				Ce2	3.073(6)
				2 Ce1	3.241(4)

2.9337(4)-3.3996(8) Å for Ce2. Ten Pt-atoms build distorted pentagonal prisms around the Ce-atoms and one Al-atom caps one of the side faces of the prisms. The next-nearest neighbors are cerium atoms with a Ce–Ce separation of 3.6339(14) Å for Ce1 and 3.7135(10) Å for Ce2.

The Pt1 atom occupies a general position 16*j* and its coordination polyhedron with 11 apices (Pt1[Ce_6Pt_4Al]) is strongly distorted. The Pt2 atom occupies a 4*c* position and its polyhedron (Pt2[$Ce_6Pt_4Al_2$]) can be described as a slightly distorted cuboctahedron.

The Al atom occupies the center of a fairly distorted trigonal prism formed by six platinum atoms with three additional Ce atoms capping the side faces of the prism Al[Ce_3Pt_6].

b) $Ce_3Pt_5Al_2$

The structure of $Ce_3Pt_5Al_2$ was solved in the triclinic space group *P*-1 with a = 5.689(2) Å, b = 8.432(3) Å, c = 8.7103(13) Å, α = 102.31(2)°, β = 97.89(2)°, γ = 89.10(3)° (Pearson symbol *aP*20) and represents a novel structure type. A space group of higher symmetry could not be evidenced using the program PLATON [17].

In the structure of $Ce_3Pt_5Al_2$, all the Ce-centered polyhedra are strongly distorted with the shortest Ce1–Ce3 and Ce2–Ce2 contacts equal to 3.675(2) Å

Table 4 Interatomic distances in the structure of $Ce_3Pt_5Al_2$.

Atom	To atom	*d*, Å	Atom	To atom	*d*, Å	Atom	To atom	*d*, Å
Ce1	Pt3	2.9538(18)	Pt1	Al1	2.500(8)	Pt5	Al2	2.481(8)
	Pt2	3.0184(17)		Al1	2.539(8)		Ce3	2.847(2)
	Pt2	3.090(2)		Al2	2.549(7)		Pt1	2.8501(13)
	Pt3	3.1126(19)		Pt4	2.7133(15)		Pt3	2.8790(13)
	Pt3	3.257(2)		Pt5	2.8501(13)		Ce2	2.9056(19)
	Pt1	3.2601(15)		Pt4	2.9768(16)		Pt4	2.9751(12)
	Pt4	3.3513(16)		Ce2	3.1205(16)		Ce2	2.9913(19)
	Al2	3.381(7)		Ce2	3.202(2)		Ce2	3.0423(17)
	Al1	3.416(8)		Ce3	3.2251(18)		Ce1	3.4740(15)
	Al2	3.425(7)		Ce1	3.2601(15)	Al1	Pt1	2.500(8)
	Al2	3.459(7)		Ce3	3.6588(18)		Pt2	2.509(6)
	Pt4	3.4740(15)	Pt2	Al1	2.509(6)		Pt4	2.538(8)
Ce2	Pt5	2.9056(19)		Pt3	2.8506(16)		Pt1	2.539(8)
	Pt3	2.9804(14)		Pt2	2.888(2)		Pt4	2.552(8)
	Pt5	2.9913(19)		Ce3	3.0098(19)		Ce3	3.235(7)
	Pt5	3.0423(17)		Ce1	3.0184(17)		Ce3	3.240(7)
	Pt4	3.0780(17)		Ce3	3.0580(14)		Al1	3.353(14)
	Pt1	3.1205(16)		Ce1	3.090(2)		Ce2	3.410(9)
	Pt2	3.1330(19)		Ce2	3.1330(19)		Ce1	3.416(8)
	Pt1	3.202(2)		Ce3	3.1918(19)		Ce3	3.447(6)
	Pt4	3.276(2)	Pt3	Al2	2.500(6)	Al2	Pt5	2.481(8)
	Al1	3.410(9)		Al2	2.677(8)		Pt3	2.500(6)
	Al2	3.491(7)		Pt2	2.8506(16)		Pt4	2.535(7)
	Al2	3.531(7)		Pt5	2.8790(13)		Pt1	2.549(7)
	Al2	3.532(6)		Ce1	2.9538(18)		Pt3	2.677(7)
Ce3	Pt5	2.847(2)		Ce2	2.9804(14)		Ce1	3.381(7)
	Pt2	3.0098(19)		Pt3	3.009(2)		Ce3	3.397(8)
	Pt2	3.0580(14)		Ce1	3.1126(19)		Ce1	3.425(7)
	Pt4	3.1578(17)		Ce1	3.257(2)		Ce1	3.459(7)
	Pt2	3.1918(19)		Ce3	3.2988(19)		Ce2	3.491(7)
	Pt1	3.2251(18)	Pt4	Al2	2.535(7)		Ce2	3.531(7)
	Al1	3.235(7)		Al1	2.538(8)		Ce2	3.532(6)
	Al1	3.240(7)		Al1	2.552(8)			
	Pt3	3.2988(19)		Pt1	2.7133(15)			
	Al2	3.397(8)		Pt5	2.9751(12)			
	Al1	3.447(6)		Pt1	2.9768(16)			
	Pt4	3.5646(16)		Ce2	3.0780(17)			
	Pt1	3.6588(18)		Ce3	3.1578(17)			
				Ce2	3.276(2)			
				Ce1	3.3513(16)			
				Ce3	3.5646(16)			

and 3.680(3) Å, respectively. Though the values of the shortest Ce–Ce contacts in the structures of Ce_3Pt_5Al and $Ce_3Pt_5Al_2$ are comparable, in the structure of $Ce_3Pt_5Al_2$, all three Ce atoms have more non-cerium neighbors (12 or 13) in their environment (see Table 3).

The five crystallographically different Pt sites have different coordination environments: Pt1[$Ce_5Pt_3Al_3$], Pt2[Ce_6Pt_2Al], Pt3[$Ce_5Pt_3Al_2$], Pt4[$Ce_5Pt_3Al_3$], and Pt5[Ce_5Pt_3Al].

The coordination number of the two crystallographically independent aluminum atoms in the structure of $Ce_3Pt_5Al_2$ is equal to 12. However, the Al1 and Al2 atoms have different neighbors. Five Pt atoms, seven Ce atoms and two aluminum atoms are the nearest neighbors of Al1. Al2 is surrounded by five Pt atoms and seven Ce atoms. As a result, the coordination polyhedron of Al2 can be described as a distorted icosahedron, whereas the coordination polyhedron of Al1 can hardly be described in any attractive way.

The structures of Ce_3Pt_5Al and $Ce_3Pt_5Al_2$ can be presented as packings of Ce-centered polyhedra (Fig. 1).

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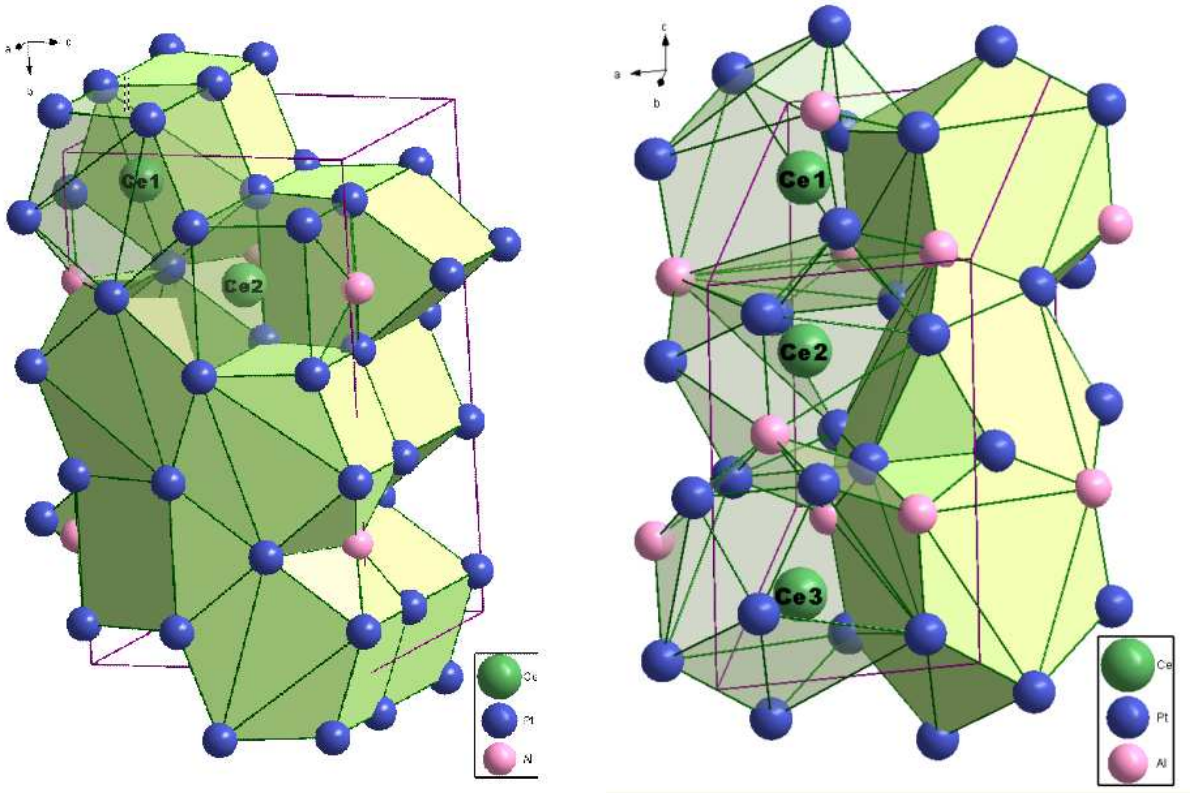

(a) (b)

Fig. 1 Polyhedral representation of the structures of Ce_3Pt_5Al (a) and $Ce_3Pt_5Al_2$ (b).

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