Crystal structure of the novel compound Ce$_3$Pt$_4$Al$_6$

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The structure of the novel ternary aluminide Ce$_3$Pt$_4$Al$_6$ was refined from X-ray single crystal data in the orthorhombic space group *Pnma* with a = 13.6589(2), b = 4.3331(1), c = 17.4740(3) Å, Z = 4; R = 0.049. The structure can be described as built up from platinum centered trigonal prisms formed by cerium and aluminum atoms. These prisms form infinite columns in the [010] direction by sharing triangular faces. The columns are condensed into groups by edge sharing of the constituent trigonal prisms.

Cerium platinum aluminide / X-ray crystal structure determination / Ce$_3$Pt$_4$Al$_6$

1. Introduction

In previous papers we have reported on the crystal structures of the new compounds CePt$_3$Al$_5$, which belongs to the site exchange YNi$_5$Si$_3$ structure type [1], Ce$_{0.67}$Pt$_2$Al$_5$ with Gd$_{0.67}$Pt$_2$Al$_5$ type- and Ce$_{1.33}$Pt$_3$Al$_8$ with Gd$_{1.33}$Pt$_3$Al$_8$-type structure [2]. Further studies of the Ce-Pt-Al ternary system revealed the existence of one more new compound, Ce$_3$Pt$_4$Al$_6$.

Up to now, only two structures with the general formula RE$_3$T$_4$M$_6$ (RE – rare earth, T – transition element, M – p-element) are known from the literature: Ce$_3$Pt$_4$Ge$_6$ [3], crystallizing in the space group *Cmcm*, a = 4.419(1), b = 26.222(5), c = 4.422(1) Å and its monoclinically deformed variant Y$_3$Pt$_4$Ge$_6$ [4], crystallizing in the space group $P2_1/m$, a = 8.692(3), b = 4.3062(8), c = 13.162(3) Å, β = 99.45(4)°.

2. Experimental details

A sample with the nominal composition Ce$_{33}$Pt$_{22}$Al$_{45}$ was arc-melted under high-purity argon from the elements (Ce 99.85, Pt 99.99, Al 99.99 wt.%). Mass loss was less than 1 wt.%. The sample was annealed in an evacuated quartz tube at 550ºC for one month, then quenched in cold water. A single crystal with the dimensions 0.05mm×0.05mm×0.045 mm was extracted from the surface of the alloy.

X-ray diffraction was carried out with a Nonius Kappa CCD diffractometer using graphite-monochromatized MoKα radiation. Most of the atoms were located by direct methods employing the program SHELXS-97 [5]. The structure was refined by SHELXL-97 [5]. Crystallographic details are summarized in Table 1. Atomic coordinates and equivalent atomic displacement parameters, with their standard deviations are given in Table 2. Selected interatomic distances are provided in Table 3.

Table 1 Data collection and structure refinement parameters for Ce$_3$Pt$_4$Al$_6$.

Space group	*Pnma*
Lattice parameters	a = 13.6589(2) Å
	b = 4.3331(1) Å
	c = 17.4740(3) Å
Cell volume (Å^3)	1034.21(3)
Formula per unit cell	4
Calculated density (g/cm^3)	8.751
Scan range (degrees)	2.33≤θ≤31.00
Linear absorption coefficient (mm^{-1})	67.249
Range in *hkl*	-19 ≤ h ≤ 19
	-6 ≤ k ≤ 6
	-24 ≤ l ≤ 25
Symmetry-independent reflections	1845
Reflections with I>2σ(I)	1793
Number of refined parameters	80
Goodness of fit	1.114
R	0.049
R$_w$	0.149

Table 2 Atomic coordinates and equivalent isotropic displacement parameters of Ce$_3$Pt$_4$Al$_6$[a].

Atom	Wyckoff site	x	y	z	U_{eq} (Å^2)
Ce1	4c	0.07521(7)	1/4	0.84864(5)	0.0085(2)
Ce2	4c	0.30248(7)	1/4	0.03267(5)	0.0080(2)
Ce3	4c	0.36757(7)	1/4	0.80618(5)	0.0083(2)
Pt1	4c	0.07161(5)	1/4	0.42837(4)	0.0079(2)
Pt2	4c	0.08973(5)	1/4	0.18707(4)	0.0112(2)
Pt3	4c	0.14853(4)	1/4	0.67761(4)	0.0075(2)
Pt4	4c	0.37790(4)	1/4	0.49254(4)	0.0086(2)
Al1	4c	0.0265(4)	1/4	0.5669(3)	0.0082(9)
Al2	4c	0.0562(4)	1/4	0.0437(3)	0.0097(9)
Al3	4c	0.2507(4)	1/4	0.3963(4)	0.0123(10)
Al4	4c	0.2721(4)	1/4	0.2281(3)	0.0082(9)
Al5	4c	0.3277(4)	1/4	0.6306(3)	0.0077(9)
Al6	4c	0.4605(4)	1/4	0.1915(3)	0.0085(9)

[a] The structure was refined with anisotropic displacement parameters for all atoms. The positional parameters were standardized using the program STRUCTURE TIDY [6].

3. Crystal structure description

The structure of Ce$_3$Pt$_4$Al$_6$ shows ordered occupation of all crystallographic sites. It is built of two identical atom layers of six-, five-, four- and three-membered rings at heights $y = 1/4$ and $y = 3/4$ (Fig. 1), related by inversion centers at $y = 0$ and $y = 1/2$. The Ce1 and Ce2 atoms are situated at the centers of hexagonal prisms with three and four additional atoms, respectively (Fig. 2a). The Ce3 atom is at the center of a pentagonal prism with two additional atoms.
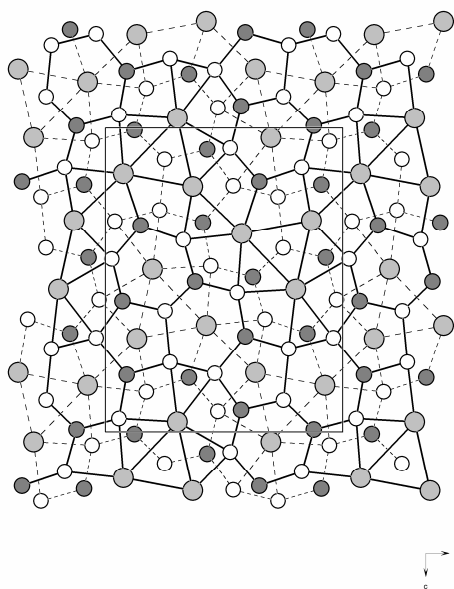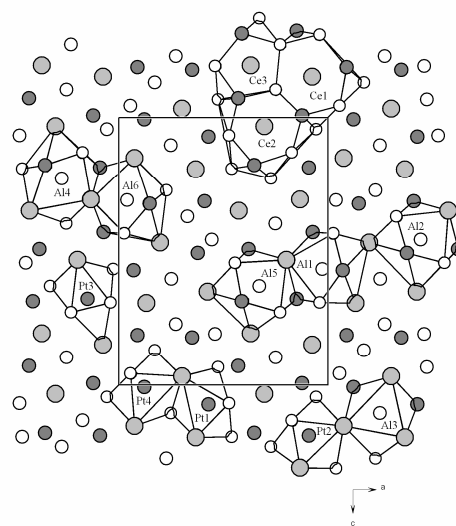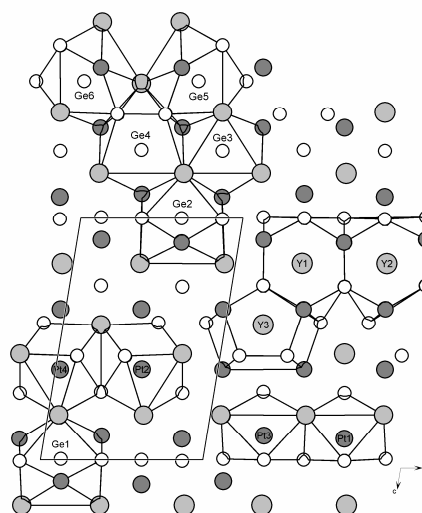

a

Fig. 1 Projection of the structure of Ce$_3$Pt$_4$Al$_6$ on the XZ-plane. Light grey circles correspond to cerium atoms, dark grey circles to platinum atoms, and white circles to aluminum atoms. All atoms lie in the mirror planes at $y = 1/4$ (dashed lines) and $y = 3/4$ (solid lines).


b

Fig. 2 Coordination polyhedra in the structures of Ce$_3$Pt$_4$Al$_6$ (a) and Y$_3$Pt$_4$Ge$_6$ (b).

Table 3 Interatomic distances in Ce$_3$Pt$_4$Al$_6$.

Atom	To atom	d, Å	Atom	To atom	d, Å
Ce1	Pt3	3.1519(11)		2 Ce2	3.3550(8)
	2 Pt2	3.18.72(8)		2 Ce1	3.3804(9)
	2 Al3	3.322(4)			
	2 Pt4	3.3804(9)	Al1	Pt1	2.498(5)
	2 Al2	3.385(4)		2Pt1	2.549(3)
	Al5	3.401(5)		Pt3	2.554(5)
	Al2	3.418(5)		2 Al6	3.077(5)
	2 Al6	3.531(4)		Ce3	3.103(5)
	2 Al4	3.671(4)		2 Ce2	3.242(4)
				2 Al1	3.269(8)
Ce2	2 Al1	3.242(4)		Ce2	3.519(5)
	2 Al5	3.283(4)			
	2 Al3	3.302(5)	Al2	2 Pt4	2.511(3)
	2 Pt1	3.3126(8)		Pt4	2.517(6)
	2 Pt4	3.3550(8)		Pt2	2.547(5)
	Al2	3.369(6)		2 Al2	3.064(8)
	2 Pt3	3.3995(9)		2 Al5	3.084(5)
	Al4	3.441(5)		Ce2	3.369(5)
	Al6	3.516(5)		2 Ce1	3.385(4)
	Al1	3.519(5)		Ce1	3.418(5)
Ce3	2 Pt2	3.0603(8)	Al3	Pt4	2.418(6)
	Al1	3.103(5)		Pt1	2.510(6)
	Al5	3.117(5)		Al4	2.952(8)
	2 Al3	3.128(4)		2 Ce3	3.128(4)
	2 Pt1	3.1532(8)		2 Ce2	3.302(5)
	2 Al4	3.193(4)		2 Ce1	3.322(4)
	2 Al6	3.195(4)			
			Al4	2 Pt3	2.579(3)
Pt1	Al1	2.498(5)		Pt2	2.592(5)
	Al3	2.510(6)		Al6	2.652(7)
	2 Al1	2.549(3)		Al3	2.952(8)
	Al6	2.587(5)		2 Al5	3.075(5)
	2 Ce3	3.1532(8)		2 Ce3	3.193(4)
	2 Ce2	3.3126(8)		Ce2	3.441(5)
				2 Ce1	3.671(4)
Pt2	Al2	2.547(5)			
	Al4	2.592(5)	Al5	Pt4	2.508(5)
	2 Al5	2.635(3)		Pt3	2.581(5)
	Al6	2.760(5)		2 Pt2	2.635(3)
	2 Ce3	3.0603(8)		2 Al4	3.075(5)
	2 Ce1	3.1872(8)		2 Al2	3.084(5)
				Ce3	3.117(5)
Pt3	Al1	2.554(5)		2 Ce2	3.283(4)
	2 Al4	2.579(3)		Ce1	3.401(5)
	Al5	2.581(5)			
	2 Al6	2.640(3)	Al6	Pt1	2.587(5)
	Ce1	3.1519(11)		2 Pt3	2.640(3)
	2 Ce2	3.3995(9)		Al4	2.652(7)
				Pt2	2.760(5)
Pt4	Al3	2.418(6)		2 Al1	3.077(5)
	Al5	2.508(5)		2 Ce3	3.195(4)
	2 Al2	2.511(3)		Ce2	3.516(5)
	Al2	2.517(6)		2 Ce1	3.531(4)

Table 4 Coordination polyhedra in the structures of $Ce_3Pt_4Al_6$ and $Y_3Pt_4Ge_6$ [4].

Atom and its neighbors	CN	Polyhedron	Atom and its neighbors	CN	Polyhedron
$Ce1[Pt_5Al_{10}]$	15	Hexagonal prism with 3 additional atoms	$Y1[Pt_6Ge_9]$	15	Hexagonal prism with 3 additional atoms
$Ce2[Pt_6Al_{10}]$	16	Hexagonal prism with 4 additional atoms	$Y2[Pt_6Ge_9]$	15	Hexagonal prism with 3 additional atoms
$Ce3[Pt_4Al_8]$	12	Pentagonal prism with 2 additional atoms	$Y3[Pt_6Ge_8]$	14	Pentagonal prism with 4 additional atoms
$Pt1[Ce_4Al_5]$	9	Trigonal prism with 3 additional atoms	$Pt1[Y_4Ge_5]$	9	Trigonal prism with 3 additional atoms
$Pt2[Ce_4Al_5]$	9	Trigonal prism with 3 additional atoms	$Pt2[Y_5Ge_5]$	10	Trigonal prism with 4 additional atoms
$Pt3[Ce_3Al_6]$	9	Trigonal prism with 3 additional atoms	$Pt3[Y_4Ge_5]$	9	Trigonal prism with 3 additional atoms
$Pt4[Ce_4Al_5]$	9	Trigonal prism with 3 additional atoms	$Pt4[Y_5Ge_5]$	10	Trigonal prism with 4 additional atoms
$Al1[Ce_4Pt_4Al_4]$	12	Tetragonal prism with 4 additional atoms	$Ge1[Y_4Pt_4Ge_4]$	12	Tetragonal prism with 4 additional atoms
$Al2[Ce_4Pt_4Al_4]$	12	Tetragonal prism with 4 additional atoms	$Ge2[Y_4Pt_4Ge_4]$	12	Tetragonal prism with 4 additional atoms
$Al3[Ce_6Pt_2Al_1]$	9	Trigonal prism with 3 additional atoms	$Ge3[Y_6Pt_3]$	9	Trigonal prism with 3 additional atoms
$Al4[Ce_5Pt_3Al_4]$	12	Tetragonal prism with 4 additional atoms	$Ge4[Y_5Pt_3Ge_4]$	12	Tetragonal prism with 4 additional atoms
$Al5[Ce_4Pt_4Al_4]$	12	Tetragonal prism with 4 additional atoms	$Ge5[Y_4Pt_3Ge_5]$	12	Tetragonal prism with 4 additional atoms
$Al6[Ce_5Pt_4Al_3]$	12	Tetragonal prism with 4 additional atoms	$Ge6[Y_4Pt_3Ge_5]$	12	Tetragonal prism with 4 additional atoms

a   b
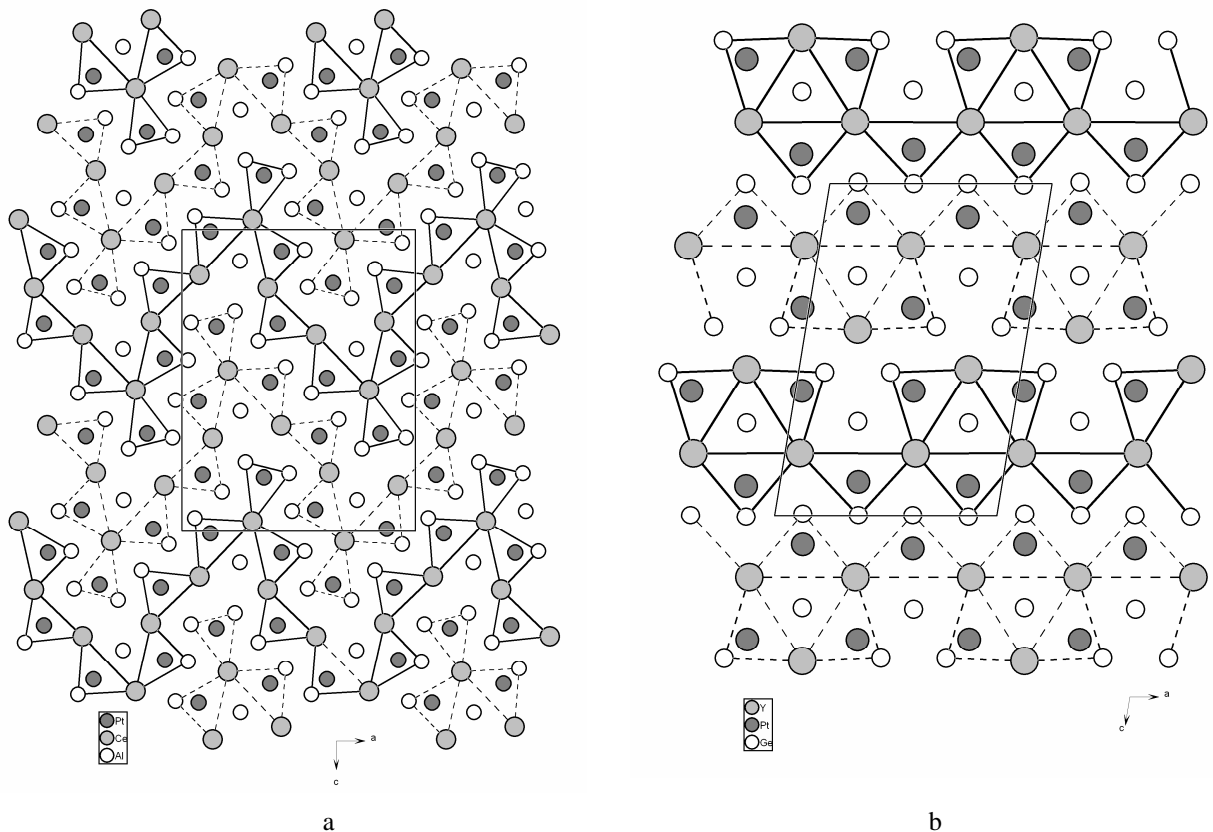
Fig. 3 The arrangement of Pt-centered trigonal prisms in the structures of $Ce_3Pt_4Al_6$ (a) and $Y_3Pt_4Ge_6$ (b).

All platinum atoms, as well as the Al3 atom, are coordinated by distorted trigonal prisms with three additional atoms capping the rectangular faces of the prisms. The remaining five crystallographically different aluminum atoms are located in significantly distorted four-capped tetragonal prisms.

Despite the fact that different sorts of atom form the coordination polyhedra in the structures of $Ce_3Pt_4Al_6$ and $Y_3Pt_4Ge_6$, the basic types of polyhedra of the corresponding elements are similar (Fig. 2), whilst the number of additional atoms is different for the polyhedra of two cerium (yttrium) and two platinum atoms (see Table 4). Though the types of coordination polyhedra in the structures of $Ce_3Pt_4Al_6$ and $Y_3Pt_4Ge_6$ are the same, the arrangement of the polyhedra in the structures is different. This can be demonstrated by representing the two structures as built of platinum centered trigonal prisms formed by cerium (yttrium) and aluminum (germanium) atoms (Fig. 3). These prisms form columns in the [010] direction by sharing triangular faces. The columns are condensed into groups by edge sharing of the constituent trigonal prisms.

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