

Crystal structure of the new compound $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$

A.I. Tursina^{a,*}, A.V. Gribanov^a, Y.D. Seropegin^a, K.V. Kuyukov^a, O.I. Bodak^b

^aChemistry Department of the Moscow State University, Leninskie Gory, GSP-2, 119992 Moscow, Russia

^bIvan Franko National University of L'viv, Kyryla and Mefodiya Street 6, 79005 L'viv, Ukraine

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Abstract

The crystal structure of the new ternary compound, $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$, was determined by X-ray analysis of a single crystal (Enraf-Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, 585 independent reflections, $R=0.0487$). The Ce atoms have only one crystallographic position with a very rare tetragonal prism coordination polyhedron.

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1. Introduction

In the search for new heavy fermion compounds ternary Ce intermetallics with Pt offer a good promise as Pt is a constituent element of many heavy fermion systems [1,2]. The investigation of the ternary Ce–Pt–Si phase diagram showed the existence of a new $\text{Ce}_2\text{Pt}_{15}\text{Si}_7$ compound [1], crystallizing in a new cubic face centered structure with a lattice parameter of 16.8 Å. However, the results of X-ray studies on single crystal were not published.

The research on the Ce–Pt–Si system allowed us to establish the accurate composition of a new compound, described by Geibel et al. [1] and to determine the crystal structure using single-crystal X-ray analysis.

2. Experimental

An ingot of 1 g was prepared from the pure elements (Ce 0.98, Pt 0.999, Si 0.9999) by melting a starting mixture of composition $\text{Ce}_8\text{Pt}_{62}\text{Si}_{30}$ in an arc furnace under an argon atmosphere. The sample was annealed in double quartz ampoules at 600 K for 720 h and quenched in cold water. A single crystal used for X-ray analysis was selected from the resultant alloy.

The obtained sample was examined by differential thermal analysis (DTA) on a VDTA-8M₂ device in an

Al_2O_3 crucible with W/(W80%–Re20%) thermocouples with heating and cooling rates of 2.5 °C/min and characterized by X-ray powder diffraction using a DRON-3.0 diffractometer (Cu $K\alpha$ radiation, $20^\circ \leq 2\theta \leq 80^\circ$).

X-Ray data collection on the single crystal was performed using an Enraf-Nonius CAD-4 autodiffractometer (Mo $K\alpha$ radiation, graphite monochromator, ω -scanning, $2\theta_{\text{max}}=69.86^\circ$) at room temperature. The details of the experiment and the results of the refinement are summarized in Tables 1–4.

3. Results and discussion

DTA indicated only one thermal effect at $T=1290^\circ\text{C}$, which corresponds to the final melting.

X-Ray powder diffraction data clearly showed that the sample contained the $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$ compound as the main phase and a small amount (5% or less) of a compound of unrecognized composition.

The projection of the unit cell of the $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$ structure onto the XY -plane is given in Fig. 1.

The cerium atoms are coordinated by tetragonal prisms of eight Pt atoms $\text{Ce}5[\text{Pt}_8]$. This is likely to be the second example of cerium coordination polyhedra with eight apices revealed earlier in the $\text{Ce}_3\text{Pt}_{23}\text{Ge}_{11}$ structure [4]. The coordination polyhedra of the Pt1 and Pt2 atoms are octahedra with four additional atoms $[\text{Pt}_6\text{Si}_4]$, that for the Pt1 atoms being slightly distorted and that for the Pt2 atoms being rather irregular. The Pt3 atoms are coordi-

*Corresponding author.

E-mail address: grav@general.chem.msu.ru (A.I. Tursina).

Table 1

Crystallographic data and experimental conditions for the structure refinement of $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$

Space group	$Fm\bar{3}m$
Lattice constant ($\text{\AA}$)	16.837(6)
Cell volume ($\text{\AA}^3$)	4773(3)
Crystal size (mm^3)	0.3*0.15*0.12
Z	8
D_{calc} (g cm^{-3})	14.518
Absorption coefficient (μ , mm^{-1})	140.307
Scan technique	ω
Data collection h,k,l	$-27 \leq h \leq 0, 0 \leq k \leq 27, -27 \leq l \leq 0$
Number of measured reflections	2835
Independent reflections	585
Reflections used in refinement $I > 2\sigma(I)$	450
Number of refined parameters	29
$R(F)$	0.0487
Extinction coefficient	0.000020(4)
Computer programs	SHELXS97, SHELXL97 [3]

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$

Site	Number of atoms	X	Y	Z	U_i
32f	32 Pt1	0.08305(4)	0.08305(4)	0.08305(4)	0.0068(3)
32f	32 Pt2	0.30841(4)	0.30841(4)	0.30841(4)	0.0074(3)
24l	24 Pt3	1/2	0.12579(9)	0	0.0085(3)
96k	96 Pt4	0.41567(3)	0.08433(3)	0.24816(4)	0.0079(3)
24d	24 Ce5	1/4	1/4	0	0.0091(4)
24l	24 Si6	1/2	0.3296(7)	0	0.006(2)
32f	32 Si7	0.1656(4)	0.1656(4)	0.1656(4)	0.010(2)
32f	32 Si8	0.3939(3)	0.3939(3)	0.3939(3)	0.009(2)

Table 3

Anisotropic displacement parameters U_{ij} ($\text{\AA}^2$) for $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	0.0068(3)	0.0068(3)	0.0068(3)	0.0001(2)	0.0001(2)	−0.0001(2)
Pt2	0.0074(3)	0.0074(3)	0.0074(3)	−0.0003(2)	0.0003(2)	0.0003(2)
Pt3	0.0094(4)	0.0066(6)	0.0094(4)	0.0	0.0	0.0
Pt4	0.0078(3)	0.0079(3)	0.0078(3)	0.00021(14)	0.0011(2)	−0.00021(14)
Ce5	0.0082(6)	0.0082(6)	0.0109(9)	0.0	0.0	−0.0014(6)
Si6	0.006(2)	0.007(4)	0.006(2)	0.0	0.0	0.0
Si7	0.010(2)	0.010(2)	0.010(2)	0.000(2)	0.000(2)	0.000(2)
Si8	0.009(2)	0.009(2)	0.009(2)	0.000(2)	0.000(2)	0.000(2)

Table 4

Interatomic distances in the structure of $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$

Atom 1	Atom 2	Distance ($\text{\AA}$)	Atom 1	Atom 2	Distance ($\text{\AA}$)
Pt1	1Si7	2.408(11)	Pt4	1Pt2	2.726(1)
Pt1	3Si6	2.465(7)	Pt4	2Pt4	2.840(1)
Pt1	3Pt1	2.797(2)	Pt4	1Pt1	2.842(1)
Pt1	3Pt4	2.842(1)	Pt4	1Pt3	2.877(2)
Pt2	3Si7	2.482(8)	Ce5	8Pt4	3.130(1)
Pt2	1Si8	2.492(10)	Si6	4Pt4	2.431(7)
Pt2	3Pt4	2.726(1)	Si6	4Pt1	2.465(7)
Pt2	3Pt2	2.782(2)	Si7	1Pt1	2.408(11)
Pt3	4Si8	2.549(8)	Si7	3Pt4	2.419(3)
Pt3	4Pt4	2.877(2)	Si7	3Pt2	2.482(8)
Pt3	4Pt3	2.995(2)	Si8	3Pt4	2.447(4)
Pt4	1Si7	2.419(3)	Si8	1Pt2	2.492(10)
Pt4	1Si6	2.431(7)	Si8	3Pt3	2.549(8)
Pt4	1Si8	2.447(4)			

nated by four Si and eight Pt atoms. The coordination of the Pt4 atoms can be described as a distorted hexagonal bipyramide [Pt_5Si_3]. The coordination polyhedra of the Si6 atoms are fairly distorted cubes [Pt_8]. The Si7 and Si8 atoms have polyhedra consisting of trigonal prisms with one additional atom [Pt_7], typical for Si atoms.

The structure of $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$ is assigned by us to the structure type of $\text{Ce}_3\text{Pt}_{23}\text{Ge}_{11}$ [4]. However, the space groups of these two structures are different. This disagreement may arise from the low quality of the single crystal of $\text{Ce}_3\text{Pt}_{23}\text{Ge}_{11}$. The poor quality of the single crystal may also account for the relatively high values of the R -factor (0.0735) and the high experimental error reported for the interatomic distances. It is inconceivable that the real space group for the $\text{Ce}_3\text{Pt}_{23}\text{Ge}_{11}$ structure is also $Fm\bar{3}m$.

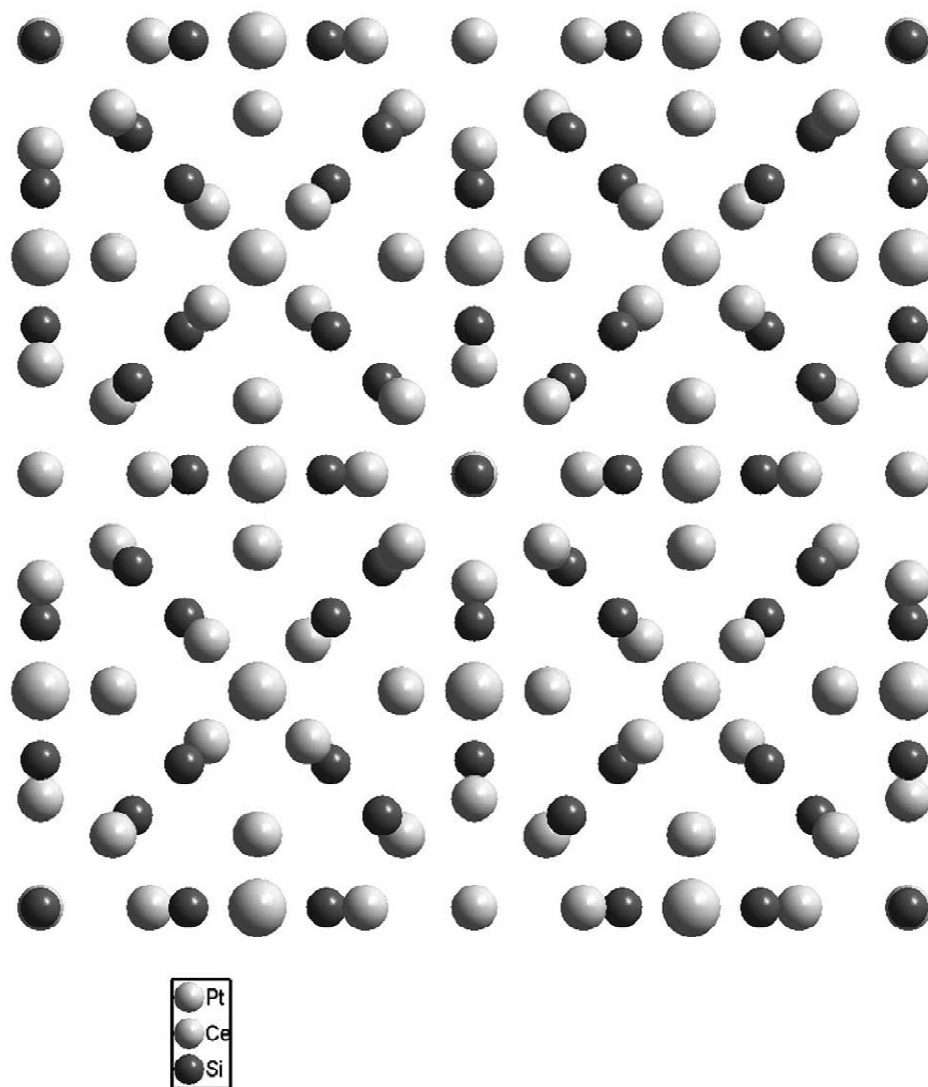


Fig. 1. Projection of the unit cell of the $\text{Ce}_3\text{Pt}_{23}\text{Si}_{11}$ structure onto the XY-plane.

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