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Journal of Alloys and Compounds 319 (2001) 145–147

Journal of ALLOYS AND COMPOUNDS

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Crystal structure of the new compound $Ce_4Pd_{29}Si_{14}$

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Received 11 July 2000; accepted 11 October 2000

Abstract

The crystal structure of the new intermetallic compound $Ce_4Pd_{29}Si_{14}$, was determined by X-ray single-crystal diffraction method revealing space group *Fm3m* with $a = 1.8010(2)$ nm and $Z = 4$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cerium palladium silicide; Crystal structure; $Ce_4Pd_{29}Si_{14}$

1. Introduction

This research was performed in the framework of a systematic study of intermetallic compounds from RE–T–X systems (RE, rare earth; T, transition metal; X, element from the III or IV group).

Many of these intermetallic compounds have been the subject of a number of investigations for they exibit a variety of interesting physical properties, including magnetism, superconductivity, heavy-electron behaviour and valence fluctuations.

Recently we have published X-ray data of a new intermetallic compound in the Ce–Pd–Si system [1].

In the present study we report the results of an X-ray single-crystal study of a new ternary compound found in the Ce–Pd–Si system.

2. Experimental details

An ingot of 1 g was prepared by melting the starting mixture of the $Ce_8Pd_{62}Si_{30}$ composition in an arc furnace in an argon atmosphere. The purity of the starting metals was better than 99%.

The obtained sample was examined by differential thermal analysis (DTA) and X-ray single-crystal analysis.

DTA was carried out on a VDTA-8M_2 device in Al_2O_3 crucible with w/w (20% Re) thermocouples with heating and cooling rates of 2.5°/min.

A single crystal of about $0.06 \times 0.09 \times 0.12$ mm was used for diffraction studies. X-ray data collection was performed using an Enraf-Nonius CAD-4 autodiffractometer (Mo K_α-radiation, flat graphite monochromator, ω-scanning) 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 indicates two thermal effects at $T_1 = 1110 \pm 5$°C, and $T_2 = 1160 \pm 5$°C. The T_2 effect corresponds to the final melting.

The projection of the unit cell of the $Ce_4Pd_{29}Si_{14}$ structure onto the *XY*-plane is given in Fig. 1.

The Ce1 atoms have a typical cubo-octahedral polyhedron, the coordination of the Ce2 atom is a rather irregular polyhedron with nine apexes. The geometry of the palladium coordination polyhedron can be described as tetragonal antiprism with one additional atom (Pd4), as a polyhedron with eight apexes (Pd1 and Pd2) and with 10 apexes (Pd3). The Si1 and Si2 atoms have polyhedra typical for Si-trigonal prisms. Si3 forms monocapped trigonal prisms and Si4 forms distorted trigonal prisms.

The Pd5, Si4 and Si3 atoms occupy 32*f* positions (see Table 2) with $x = 0.0543$ (P1), 0.0879 (P2) and 0.1253 (P3), respectively. We assume that the partial occupancies (0.5) of the Pd5, Si4 and Si3 positions are interrelated. For example, when the Pd5 atom occupies the position P1, the position P3 of the Si3 atom is also occupied and the P2 position of Si4 is empty. And vice versa, if the P2 position of the atom Si4 is filled, the P1 and P3 positions are

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0925-8388/01/$ – see front matter
PII: S0925-8388(00)01271-8

Table 1
Crystallographic data and experimental conditions for the structure refinement of $Ce_4Pd_{29}Si_{14}$

Space group	$Fm3m$
a (nm)	1.8010(2)
Cell volume (nm^3)	5.8417(11)
Z	4
$D_{calc.}$($g*cm^{-3}$)	9.186(1)
Radiation	Monochromatized Mo Kα, λ=0.071073 nm
Diffractometer	CAD-4
F(000)	14 096
Absorption coefficient (μ, mm^{-1})	23.990
Two-theta max. (°)	69.90
Scan technique	ω
Data collection h,k,l	$-29\le h\le 0$, $0\le k\le 22$, $0\le l\le 18$
Number of measured reflections	2626
Independent reflections	708
Reflections used in refinement $\|F_0\|\ge 4\sigma\|F_0\|$	686
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	39
$R(F)$	0.0562
Goodness of fit	0.902
Computer programs	SHELXS97 [2], SHELXL97 [3]

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters ($nm^2\times10^5$) for $Ce_4Pd_{29}Si_{14}$

Site	Number of atoms	X	Y	Z	$U_{eq.}$	Occupancy
8c	8 Ce1	1/4	1/4	1/4	11(1)	1.0
24e	24 Ce2	0.2230(1)	0	0	9(1)	1.0
48i	48 Pd1	0.1600(1)	0	$1/2-x$	12(1)	1.0
48h	48 Pd2	0.1623(1)	0	x	8(1)	1.0
96k	96 Pd3	0.1295(1)	x	0.2545(1)	14(1)	1.0
24e	24 Pd4	0.1158(2)	0	1/2	12(1)	1.0
32f	16 Pd5	0.0543(2)	$-x$	x	13(1)	0.5
48g	48 Si1	0.0675(4)	1/4	1/4	9(1)	1.0
32f	32 Si2	0.1018(3)	x	$1/2-x$	11(2)	1.0
32f	16 Si3	0.1253(6)	x	x	12(4)	0.5
32f	16 Si4	0.0879(6)	x	x	6(3)	0.5

Table 4
Interatomic distances in the structure of $Ce_4Pd_{29}Si_{14}$

Atom 1	Atom 2	Distance (nm)	Atom 1	Atom 2	Distance (nm)
Ce1	12 Pd3	0.3070(2)	Pd4	4 Si2	0.2604(8)
Ce2	1 Pd4	0.2903(4)	Pd4	1 Ce2	0.2903(4)
Ce2	4 Pd2	0.3121(2)	Pd4	4 Pd4	0.2949(5)
Ce2	4 Si4	0.3306(3)	Pd4	3 Pd1	0.2990(2)
Ce2	3 Pd5	0.3339(2)	Pd5	3 Pd5	0.1954(7)
Pd1	2 Si2	0.2358(2)	Pd5	1 Si3	0.222(2)
Pd1	2 Si1	0.2594(4)	Pd5	3 Si4	0.270(2)
Pd1	4 Pd3	0.2849(2)	Pd5	3 Pd5	0.2764(9)
Pd1	2 Pd4	0.2990(2)	Si1	1 Si1	0.243(2)
Pd1	2 Pd2	0.3201(2)	Si1	4 Pd3	0.2442(4)
Pd2	2 Si3	0.2445(4)	Si1	2 Pd2	0.2543(4)
Pd2	2 Si4	0.2469(5)	Si1	2 Pd1	0.2594(4)
Pd2	2 Si1	0.2544(4)	Si2	3 Pd1	0.2358(2)
Pd2	2 Pd5	0.2920(4)	Si2	3 Pd4	0.2604(7)
Pd2	4 Pd3	0.2923(2)	Si2	3 Pd3	0.2684(8)
Pd3	1 Si3	0.233(1)	Si3	1 Pd5	0.222(2)
Pd3	2 Si1	0.2442(4)	Si3	3 Pd3	0.2328(1)
Pd3	1 Si2	0.2684(8)	Si3	3 Pd2	0.2445(4)
Pd3	2 Pd1	0.2849(2)	Si4	3 Pd2	0.2469(5)
Pd3	2 Pd2	0.2923(2)	Si4	3 Pd5	0.270(2)
Pd3	2 Pd3	0.2956(3)			

Table 3
Anisotropic displacement parameters U_{ij} ($nm^2\times10^5$) for $Ce_4Pd_{29}Si_{14}$

Name	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(2,3)$	$U(1,3)$	$B(1,2)$
Ce1	11(1)	11(1)	11(1)	0	0	0
Ce2	9(1)	9(1)	9(1)	0	0	0
Pd1	14(1)	7(1)	14(1)	0	6(1)	0
Pd2	8(1)	8(1)	8(1)	0	0(1)	0(1)
Pd3	10(1)	10(1)	22(1)	2(1)	2(1)	2(1)
Pd4	10(1)	13(1)	13(1)	0	0	0
Pd5	13(1)	13(1)	13(1)	1(1)	−1(1)	1(1)
Si1	6(3)	11(2)	11(2)	9(3)	0	0
Si2	11(2)	11(2)	11(2)	2(2)	2(2)	−2(2)
Si3	12(4)	12(4)	12(4)	−5(4)	−5(4)	−5(4)
Si4	6(3)	6(3)	6(3)	4(4)	4(4)	4(4)

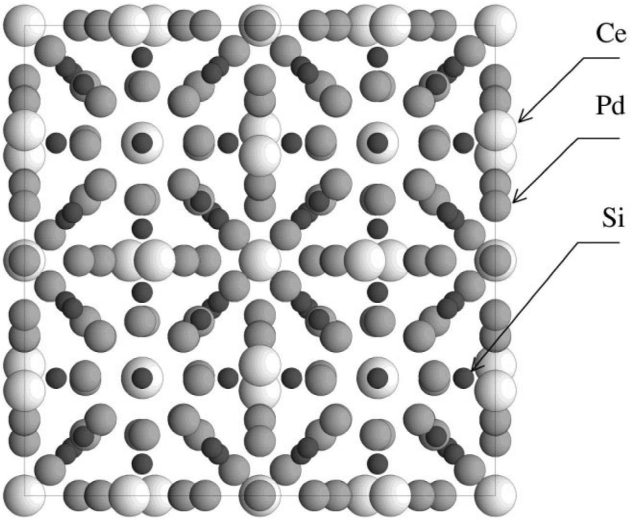

Fig. 1. Projection of the unit cell of the $Ce_4Pd_{29}Si_{14}$ structure onto *XY*-plane.

empty. This disorder possibly indicates the presence of the superstructure. However, we have not found such a superstructure by using the experimental methods described in this paper.

Acknowledgements

This work is supported by the Russian Foundation of Basic Research (grant number 00-03-32651a).

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