

Journal of Alloys and Compounds 398 (2005) 100-105

Journal of ALLOYS AND COMPOUNDS

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# Ternary compounds Ce<sub>0.67</sub>Pt<sub>2</sub>Al<sub>5</sub> and Ce<sub>1.33</sub>Pt<sub>3</sub>Al<sub>8</sub>

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Received 24 January 2005; received in revised form 4 February 2005; accepted 4 February 2005 Available online 13 March 2005

#### Abstract

The ternary intermetallic compounds  $Ce_{0.67}Pt_2Al_5$  (**I**) and  $Ce_{1.33}Pt_3Al_8$  (**II**) were synthesized in the Ce–Pt–Al system by the reaction of elemental Ce, Pt, and Al in an arc furnace under an argon atmosphere. The crystal structures of **I** and **II** were determined from single-crystal X-ray diffraction data. The crystals are characterized by the following unit cell parameters: a = 4.3105(18) Å, c = 16.494(5) Å, space group  $P6_3/mmc$ , Z = 2 (**I**) and a = 4.361(2) Å, c = 39.00(2) Å, space group  $R\bar{3}m$ , Z = 6 (**II**). Both compounds have structures with different packing of layers.

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Keywords: Ternary intermetallides; Crystal structure; X-ray diffraction; Ce<sub>0.67</sub>Pt<sub>2</sub>Al<sub>5</sub>; Ce<sub>1.33</sub>Pt<sub>3</sub>Al<sub>8</sub>

## 1. Introduction

The synthesis and physicochemical properties of the family of intermetallic compounds  $R_{2-x}Pt_4Ga_{8+y}$  (R = La, Ce, Pr, Nd, Sm, Gd, Er, Yb, Y) belonging to a new structure type, were reported in Ref. [1]. The crystal structure was determined for one of the representatives of this family, namely

 $Ce_{2-x}Pt_4Ga_{8+y}(a = 4.313\text{\AA} \text{ and } c = 16.516\text{\AA},$ 

space group  $P\bar{3}1c$ ).

Later [2], 15 compounds of the R<sub>4</sub>Pt<sub>9</sub>Al<sub>24</sub> family (where R = Y, Gd–Lu) were synthesized. These compounds have a pseudohexagonal structure, which has much in common with that of  $R_{2-x}Pt_4Ga_{8+y}$ . Besides, the intermetallic compounds of the Gd<sub>0.67</sub>Pt<sub>2</sub>(Al,Si)<sub>5</sub>, Gd<sub>0.67</sub>Pt<sub>2</sub>Al<sub>5</sub>, Gd<sub>1.33</sub>Pt<sub>3</sub>(Al,Si)<sub>8</sub>, and Gd<sub>1.33</sub>Pt<sub>3</sub>Al<sub>8</sub> compositions were obtained by the reaction of the elemental components in an aluminum flux at 1000 °C [3]. The crystal structures of the former two compounds belong to the Ce<sub>0.67</sub>Pt<sub>2</sub>Ga<sub>5</sub> structural type, and

those of the latter two compounds belong to the R<sub>4</sub>Pt<sub>9</sub>Al<sub>24</sub> structural type. According to Ref. [3], Gd<sub>0.67</sub>Pt<sub>2</sub>(Al,Si)<sub>5</sub> and Gd<sub>0.67</sub>Pt<sub>2</sub>Al<sub>5</sub> crystallize in space group  $P6_3/mmc$ , whereas the symmetry of Ce<sub>0.67</sub>Pt<sub>2</sub>Ga<sub>5</sub> is described in Ref. [1] by the noncentrosymmetric space group  $P\overline{3}1c$ . There is also a difference in opinion as to the crystal system of Gd<sub>1.33</sub>Pt<sub>3</sub>(Al,Si)<sub>8</sub>, and Gd<sub>1.33</sub>Pt<sub>3</sub>Al<sub>8</sub> (trigonal [3]) and R<sub>4</sub>Pt<sub>9</sub>Al<sub>24</sub> (monoclinic for R = Er and triclinic for other elements [2]). Although the symmetry and space group of the structures differ [1–3], in reality there are only two structural models described in Ref. [3]: R<sub>0.67</sub>Pt<sub>2</sub>Al<sub>5</sub> (I) (a = 4.291, c = 16.388,  $P6_3/mmc$ , Z = 2) and R<sub>1.33</sub>Pt<sub>3</sub>Al<sub>8</sub> (II) (a = 4.336, c = 38.702,  $R\overline{3}m$ , Z = 3).

The objectives of this study are two new representatives of these structural models containing cerium, platinum, and aluminum.

#### 2. Experimental

In the course of our studies of the Ce–Pt–Al system, two ternary compounds  $Ce_{0.67}Pt_2Al_5$  (I) and  $Ce_{1.33}Pt_3Al_8$ (II) were obtained in the aluminum-rich region. The synthesis was performed by the reaction of elemental Ce (99.8%), Pt (99.99%) and Al (99.99%) in an arc furnace

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Table 1 Main crystal data and structure-refinement parameters for  $Ce_{0.67}Pt_2Al_5$  and  $Ce_{1.33}Pt_3Al_8$ 

	Ce <sub>0.67</sub> Pt <sub>2</sub> Al <sub>5</sub>	Ce <sub>1.33</sub> Pt <sub>3</sub> Al <sub>8</sub>
Crystal system	Hexagonal	Trigonal
<i>a</i> (Å)	4.3105(18)	4.361(2)
<i>c</i> (Å)	16.494(5)	39.00(2)
$V(Å^3)$	265.41(18)	642.3(5)
Space group	P6 <sub>3</sub> /mmc	R3m
Z	2	6
$d_{\rm calc}$ (g/cm <sup>3</sup> )	7.986	7.611
Radiation	Μο Κα	Μο Κα
$\mu$ (mm <sup>-1</sup> )	61.503	56.285
Total number of reflection	366	416
Number of reflections with $I > 2\sigma(I)$	314	346
Number of the parameters refined	19	27
$R1/wR2 (I > 2\sigma(I))$	0.037/0.098	0.039/0.100
R1/wR2 (all data)	0.042/0.107	0.051/0.111

with a tungsten electrode under an argon atmosphere and a pressure of  $1.1 \times 10^{5}$  Pa. The alloys were homogenized in evacuated quartz ampoules by annealing in electric muffles at 500 °C for 30 days. The compositions of the alloys were checked by the powder X-ray analysis (DRON-3M, Cu Kα radiation) and microprobe analysis (JEOL JSM 6400 scanning electron microscope equipped with a Si/Li energy dispersive analyzer). The greatest amount of I was obtained in the samples with initial Ce:Pt:Al ratios of 10:20:70 and 10:25:65, whereas the 15:15:70 and 15:17:68 ratios afforded the greatest amount of II. Hexagonal-prismatic crystals suitable for X-ray structure analysis were chosen from portions of the annealed samples. The compositions of the intermetallics obtained were determined from single-crystal X-ray diffraction data as Ce<sub>0.67</sub>Pt<sub>2</sub>Al<sub>5</sub> (I) and Ce<sub>1.33</sub>Pt<sub>3</sub>Al<sub>8</sub> (II) (Enraf-Nonius CAD-4 diffractometer). These compositions were confirmed in a series of microprobe analyses. Single-phase samples of Ce<sub>0.67</sub>Pt<sub>2</sub>Al<sub>5</sub> and Ce<sub>1.33</sub>Pt<sub>3</sub>Al<sub>8</sub> were obtained in the alloys with initial Ce:Pt:Al ratios 9:26:65 and 11:24:65, respectively.

The main crystal data and structure-refinement parameters for the intermetallic compounds **I** and **II** are summarized in Table 1. For both compounds, the data sets were corrected for absorption using  $\psi$  scans [4]. The structures of I and II were solved by direct methods (SHELXS97 [5]) and refined by full-matrix least-squares procedures in the anisotropic approximation (SHELXL97 [6]). The atomic coordinates and thermal parameters are listed in Table 2. Selected interatomic distances are given in Table 3.

The test for the second harmonic generation of compound I was performed using a YAG: Nd laser ( $\lambda = 1.064 \,\mu\text{m}$ ) at room temperature. An  $\alpha$ -quartz powder of the same dispersity as the powder studied (3  $\mu$ m) was used as a standard.

### 3. Results and discussion

The intermetallic compounds  $Ce_{0.67}Pt_2Al_5$  (Fig. 1) and  $Ce_{1.33}Pt_3Al_8$  (Fig. 2) crystallize in anisometric hexagonal unit cells: the *c* parameter is longer than the *a* parameter approximately by a factor of four in **I** and nine in **II**. The *a* parameters in **I** and **II** have close values, because the two compounds consist of similar hexagonal nets, which are perpendicular to the *c* axis. The crystal structures of **I** and **II** are analogous to those of  $Gd_{0.67}Pt_2Al_5$  and  $Gd_{1.33}Pt_3Al_8$ , respectively. In these structures, several different layers perpendicular to the [0 0 1] axis are distinguished. The structures of **I** and **II** differ mainly in the pattern of layer alternation and the number of layers per unit cell.

In the structure of **II**, layers of three types can be distinguished: (A)  $Pt_2Al_4$  double layers (Fig. 3a); (B) layers containing disordered aluminum and cerium atoms (Fig. 3b); and (C)  $PtAl_2$  single layers (Fig. 3c). The pattern of their alternation in the unit cell is ... [BABC]BABCBABC....

Structure I consists of A and B layers alternating according to the  $\dots$  [AB]AB... pattern. PtAl<sub>2</sub> single layers (C) are absent in I.

The occupancy values of the Ce- and Al-atoms in the disordered B layers are 2/3 and 1/3, respectively (Fig. 3b). An ordered model of B layers can be described by a supercell ( $\approx$ 7.5 Å) with a close-packing of Ce-atoms, where one third

Table 2

Atomic coordinates and thermal parameters in the structures of Ce <sub>0.67</sub> Pt <sub>2</sub> Al <sub>5</sub> and Ce <sub>1.33</sub> Pt <sub>3</sub> A	18
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Atom	Wyckoff position	x/a	y/b	z/c	$U_{\rm eq}$ (Å <sup>2</sup> )	Occupancy
Ce <sub>0.67</sub> Pt <sub>2</sub> Al	5					
Pt1	4f	2/3	1/3	0.39249(2)	0.0087(2)	1
Ce1	2c	1/3	2/3	1/4	0.0069(5)	0.622(8)
Al1	4e	0	0	0.3682(2)	0.0110(6)	1
A12	4f	2/3	1/3	0.5464(2)	0.0098(6)	1
A13	6h	-0.0729(19)	0.4636(10)	1/4	0.0072(18)	0.330(12)
Ce <sub>1.33</sub> Pt <sub>3</sub> Al	8					
Pt1	6c	0	0	0.121263(17)	0.0065(2)	1
Pt2	3a	0	0	0	0.0063(3)	1
Ce1	6c	0	0	0.26922(4)	0.0053(4)	0.646(6)
Al1	18h	0.5383(12)	0.4617(12)	0.3953(2)	0.007(3)	0.323(17)
A12	6c	0	0	0.18613(19)	0.0110(11)	1
A13	бс	0	0	0.35027(19)	0.0095(10)	1
Al4	бс	0	0	0.44544(16)	0.0079(10)	1

Table 3

Selected interatomic distances  $^a$  (Å) in the structures of  $Ce_{0.67}Pt_2Al_5$  and  $Ce_{1.33}Pt_3Al_8$ 

$\begin{array}{c} Ce_{0.67}Pt_{2}Al_{5} \\ Pt13Al1 \\ Pt1Al2 \\ Pt13Al3 \\ Pt13Al2 \\ Pt12Ce1 \end{array}$	2.5208(12) 2.539(4) 2.543(3) 2.6849(18) 3.4231(9)
Ce1-6Al3	3.092(5)
Ce1-6Al1	3.161(3)
Ce1-2Al2	3.355(5)
Ce1-6Pt1	3.4231(9)
Al1—3Pt1	2.5208(12)
Al1—3Al2	2.860(3)
Al1—6Al3	2.919(3)
Al1—3Ce1	3.161(3)
Al2—Pt1	2.539(4)
Al2—3Pt1	2.6849(18)
Al2—3Al1	2.860(3)
Al2—3Al2	2.919(3)
Al2—Ce1	3.355(5)
A13—2Pt1	2.543(3)
A13—2A13	2.626(13)
A13—4A11	2.919(3)
A13—2Ce1	3.092(5)
Ce <sub>1.33</sub> Pt <sub>3</sub> Al <sub>8</sub> Pt1-3Al1 Pt1-Al2 Pt1-3Al4 Pt1-3Al2 Pt1-3Ce1	2.509(9) 2.530(7) 2.5430(15) 2.714(3) 3.3625(16)
Pt26Al1	2.603(9)
Pt26Al3	2.603(2)
Pt26Ce1	3.5486(16)
Ce1-3Al3	3.118(5)
Ce1-3Al1	3.119(7)
Ce1-3Al4	3.137(4)
Ce1-3Al3	3.161(8)
Ce1-2Al2	3.240(8)
Ce1-3Pt1	3.3624(16)
Ce1-3Pt2	3.5487(16)
Al1—Pt1 Al1—Pt2 Al1—2Al1 Al1—Al3 Al1—Al3 Al1—Al4 Al1—Al4 Al1—Ce1 Al1—Ce1	$\begin{array}{c} 2.517(9)\\ 2.603(9)\\ 2.660(16)\\ 2.80(3)\\ 2.81(3)\\ 2.94(3)\\ 2.95(3)\\ 3.12(3)\\ 3.13(3)\end{array}$
Al2—Pt1	2.530(7)
Al2—3Pt1	2.714(3)
Al2—3Al4	2.866(5)
Al2—3Al2	2.940(8)
Al2—Ce1	3.240(8)
A13-3Pt2	2.603(2)
A13-6A11	2.814(7)
A13-3A13	2.843(7)
A13-3Ce1	3.118(5)
A13-Ce1	3.161(8)

Table 3	(Continued)
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Al4-3Pt1	2.5430(15)
Al4-3Al2	2.866(5)
Al4-6Al1	2.944(8)
Al4-3Ce1	3.137(4)

 $^{a}$  The short distances equal to  $1.516{-}1.550\,\text{\AA}$  (Ce–Al) and equal to  $1.684{-}1.701\,\text{\AA}$  (Al–Al) are omitted.

of the Ce-atoms are exchanged by Al-triangles (Fig. 3d). Such disordered R–Ga-layers were first described for  $Y_2Co_3Ga_9$  [7]. All compounds of the  $R_2Co_3Ga_9$  family crystallize in the orthorhombic C cells, although they are built of pseudo-hexagonal layers similar to those in I and II.

An attempt to explain the disorder of the rare-earth and aluminum atoms in the R–Al-layer of  $R_4Pt_9A_{24}$  was made in Ref. [2]. The authors suggest that these layers are shifted relative to the adjacent layers. As a result, the threefold (sixfold) axis is retained in each separate layer but disappears in the unit cell. This lowers the cell symmetry to the monoclinic system in  $Er_4Pt_9Al_{24}$  and the triclinic system in all other members of the series. In Ref. [3], the disordering of the layer in the structures of  $Gd_{1.33}Pt_3(Al,Si)_8$ ,  $Gd_{0.67}Pt_2(Al,Si)_5$ ,  $Gd_{1.33}Pt_3Al_8$ ,



Fig. 1. View of the Ce<sub>0.67</sub>Pt<sub>2</sub>Al<sub>5</sub> unit cell.



Fig. 2. View of the Ce<sub>1.33</sub>Pt<sub>3</sub>Al<sub>8</sub> unit cell.



Fig. 3. Layers in the structures of  $Ce_{0.67}Pt_2Al_5$  and  $Ce_{1.33}Pt_3Al_8$ : (a)  $Pt_2Al_4$  double layer (A); (b) Ce–Al disordered layer (B) (all the atomic positions are shown); (c)  $PtAl_2$  single layer (C); (d) supercell of possible ordered Ce–Al layer.



Fig. 4. The coordination polyhedra of: (a) Pt1 in **I** and **II**; (b) Pt2 in **II**; (c) Ce1 in **I** and **II**; (d) Al1(Al3) in **II** (**I**); (e) Al2 in **I** and **II**; (f) Al3(Al1) in **II** (**I**); (g) Al4 in **II**. The atom labeling of the coordination environment of atoms corresponds to the **II** structure.



Fig. 4. (Continued).

and Gd  $_{0.67}$ Pt<sub>2</sub>Al<sub>5</sub> is related to the duration of the homogenizing annealing.

It is worth noting that in our study, the annealing of the intermetallics for 30 days did not result in ordering in the layer B.

The crystal structures of **I** and **II** were refined in the centrosymmetric space groups  $P6_3/mmc$  and  $R\bar{3}m$ , respectively. The compound **I** was tested for the second harmonic generation. The value of the signal was only 0.03 units of the quartz standard. This moderate effect can be due to the disordering of the Ce and Al atoms in the structure. The refinement of the structure of **I** in the noncentrosymmetric group  $P\bar{3}1c$  does not improve neither the R-factors nor the errors in the atomic coordinates and interatomic distances. The coordination polyhedra of the Pt atoms in I and II are severely distorted cubes formed of aluminum atoms (CN = 8). In the cubes of the Pt1(I) and Pt1(II) atoms one of the vertices and in the cube of the Pt2(II) atom two vertices are split into three sites, which are equally populated by one third (Fig. 4a and b). The Ce atoms in I and II are identically coordinated by six platinum and eleven aluminum atoms (Fig. 4c). The Ce polyhedron is described as the hexagonal prism, in which half of the lateral edges are centered by disordered aluminum atoms and both basal faces are capped by ordered aluminum atoms. The environments of the aluminum atoms (up to 3.2 Å) include 9–11 atoms, which form severely distorted polyhedra (Fig. 4d–g).

## Acknowledgment

This study was supported by Russian Foundation for Basic Researches (project no. 03-03-20001BNTS\_a).

#### References

- A. Lacerda, P.C. Canfield, W.P. Beyerman, M.F. Hundley, J.D. Thompson, G. Sparn, Z. Fisk, C. Burns, D. Barnhart, A.C. Lawson, G.H. Kwei, J. Goldstone, J. Alloys Comp. 181 (1992) 191.
- [2] V.M.T. Thiede, B. Fehrmann, W. Jeitschko, Z. Anorg. Allg. Chem. 625 (1999) 1417.
- [3] S.E. Latturner, M.G. Kanatzidis, Inorg. Chem. 41 (2002) 5479.
- [4] L.J. Farrugia, WinGX. Version 1.61, third ed., University of Glasgow, Scotland, 1998.
- [5] G.M. Sheldrick, SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, 1997.
- [6] G.M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Gottingen, 1997.
- [7] Y.N. Grin', R.E. Gladyshevskii, O.M. Sichevich, V.E. Zavodnik, Y.P. Yarmolyuk, I.V. Rozhdestvenskaya, Sov. Phys. Crystallogr. 29 (1984) 528.