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Single crystal investigation of $CePd_2In_4$ and $CePt_2In_4$ compounds

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Abstract

The new ternary indides $CePd_2In_4$ and $CePt_2In_4$ were synthesized by arc-melting of the elements and subsequent annealing at 770 K for 1 month. The crystal structure of both the compounds was refined from the single crystal X-ray data. $CePd_2In_4$ and $CePt_2In_4$ crystallize in the orthorhombic $NdRh_2Sn_4$-type structure (space group *Pnma*), $a = 18.449(3)$ Å, $b = 4.5647(6)$ Å, $c = 7.4145(15)$ Å, $V = 624.4(2)$ Å^3, $R_F = 5.96\%$ for $CePd_2In_4$, $a = 18.460(4)$ Å, $b = 4.5299(13)$ Å, $c = 7.2670(16)$ Å, $V = 607.7(3)$ Å^3, $R_F = 7.47\%$ for $CePt_2In_4$.

Keywords: Crystal structure; Rare earth compounds; Indides; X-ray diffraction

1. Introduction

Cerium containing intermetallic compounds exhibit variety of interesting electrical and magnetic properties. However, until now there are only fragmentary data concerning the interaction of the components and structures of compounds in the ternary systems including the rare earth metals, noble metals and indium. During the investigation of the phase equilibria in the Ce–Pd–In [1] and Ce–Pt–In systems several compounds with unknown crystal structure were found. Herein, we report the crystal structure of the new compounds $CePd_2In_4$ and $CePt_2In_4$.

2. Experimental

The specimens with a total weight of 1 g were synthesized by arc-melting of stoichiometric amounts of high purity metals on a water-cooled copper hearth under a pure argon atmosphere with Zr getter. All specimens were remelted several times to ensure homogeneity. The mass losses after arc-melting were less than 1%. The alloys were wrapped into niobium foil and annealed at 770 K in sealed quartz ampoules for 750 h following by the quenching in water. Both as-cast and annealed alloys were investigated. Suitable single crystals of 0.08 mm sizes were picked from the as-cast ingots. The single crystals were first checked by Laue and rotation methods (camera RKOP, Cu Kα radiation) to establish the symmetry and suitability for X-ray intensity data collection. The intensity data were collected at room temperature with a four-circle CAD-4 Enraf-Nonius diffractometer with graphite monochromatized Mo Kα radiation. The starting atomic parameters were deduced by direct methods using SHELXS-97 [2] and both structures were refined using SHELXL-97 [3] (full-matrix least-squares on F^2) with anisotropic displacement parameters for all atoms. The experimental details are listed in Table 1. The refined atomic and displacement parameters as well as interatomic distances are listed in Tables 2 and 3.

3. Results and discussion

The $CePd_2In_4$ and $CePt_2In_4$ compounds are the earlier unknown representatives of the $NdRh_2Sn_4$ structure type [4]. Every crystallographic position is fully occupied by atoms of one sort only, namely the positions of the Nd atoms are occupied by Ce, the positions of the Rh atoms by Pd (Pt) and the positions of the Sn atoms by In. A projection of the $CePd_2In_4$ ($CePt_2In_4$) unit cell on the *xz* plane and coordination polyhedra of atoms are shown in Fig. 1. A coordination number of (CN) = 16 is characteristic for Ce atoms (Fig. 1a), of which the coordination polyhedra $[Pd_6In_{10}]$ can be considered as irregular pentagonal prisms with four additional atoms, situated opposite to the lateral faces and edges. Trigonal-prismatic coordination $[Ce_2In_7]$ is appropriate for palladium and platinum (Fig. 1b and c).

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Table 1
Parameters for the single crystal X-ray data collection and refinement for $CePd_2In_4$ and $CePt_2In_4$

Parameter	$CePd_2In_4$	$CePt_2In_4$
Space group	*Pnma* (No 62)	*Pnma* (No 62)
Unit cell dimensions (Å)	$a = 18.449(3)$, $b = 4.5647(6)$, $c = 7.4145(15)$, $Z = 4$	$a = 18.460(4)$, $b = 4.5299(13)$, $c = 7.2670(16)$, $Z = 4$
Unit cell volume ($Å^3$)	624.4(2)	607.7(3)
Formula weight ($g\,mol^{-1}$)	812.2	989.58
Calculated density ($g\,cm^{-3}$)	8.640	10.816
Absorbtion coefficient (cm^{-1})	27.12	67.94
Radiation	Mo Kα; 0.71073 Å	Mo Kα; 0.71073 Å
Θ range	3.53–36.95°	2.21–36.95°
Index range	$0 \le h \le 30$, $0 \le k \le 7$, $0 \le l \le 12$	$0 \le h \le 31$, $0 \le k \le 7$, $0 \le l \le 12$
Number of measured reflections	1466	1419
Number of reflections in the refinement with $F_0 > 4\sigma(F_0)$	1072	942
Number of refined parameters	43	43
Goodness-of-fit on F^2	0.962	1.057
R_F, R_W	0.0596, 0.1584	0.0747, 0.1784
Computer programs	SHELXL 97, SHELXS 97	

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $CePd_2In_4$ and $CePt_2In_4$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq} ($Å^2 \times 10^3$)
Pd1	0.54315(9)	0.25	0.2642(2)	18.1(3)
Pd2	0.77681(8)	0.25	0.4510(2)	13.8(3)
Ce3	0.35768(6)	0.25	0.54043(16)	14.6(2)
In4	0.68644(7)	0.25	0.15433(18)	13.1(3)
In5	0.69151(7)	0.25	0.75473(18)	12.1(3)
In6	0.53317(7)	0.25	0.6444(2)	15.8(3)
In7	0.42939(7)	0.25	1.01377(18)	12.5(3)
Pt1	0.54105(7)	0.25	0.2586(2)	15.7(3)
Pt2	0.77992(7)	0.25	0.46268(17)	11.9(3)
Ce3	0.35835(9)	0.25	0.5286(3)	12.7(3)
In4	0.68578(11)	0.25	0.1684(3)	12.0(4)
In5	0.69101(11)	0.25	0.7631(3)	10.0(4)
In6	0.53389(11)	0.25	0.6486(3)	13.2(4)
In7	0.42986(11)	0.25	0.0016(3)	12.7(4)

The side faces of the trigonal prisms for the Pd1, Pd2, and Pt1, Pt2 atoms are capped with additional atoms. Polyhedra of In4 [$Ce_3Pd_4In_5$] in the case of palladium, and of In5 and In6 [$Ce_3Pt_3In_6$] in the case of platinum are deformed cubes [$Ce_3Pd_3In_6$] and [$Ce_3Pt_3In_6$] (Fig. 1d–f), with four additional atoms opposite to side faces. Those for In7 atoms are pentagonal prisms with four additional atoms: [$CePd_4In_9$] and [$CePt_4In_9$] (Fig. 1g). The shortest interatomic distances in the structure of both compounds are the Pd–In (2.747–2.827 Å) and Pt–In (2.732–2.999 Å) contacts. However, the largest reductions run up to 11 and 11.5%, for $CePd_2In_4$ and $CePt_2In_4$, respectively, in the case of In4–In5 distances as compared with average In–In distance of 3.337 Å in the tetragonal body-centered indium [5].

The 1:2:4 phases were not found in the other systems of rare-earth metals with indium and palladium or platinum. Moreover, as far as we know the investigated compounds are the only representatives of this composition among the ternary indides.

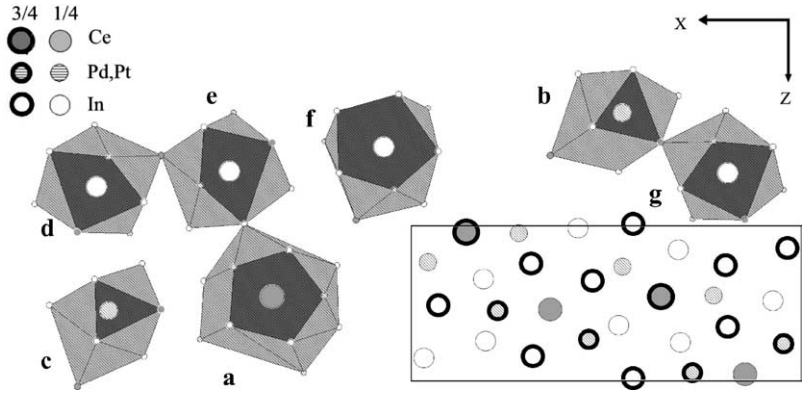

Fig. 1. Projection of the unit cell of $CePd_2In_4$ ($CePt_2In_4$) on the *xz* plane and coordination polyhedra of the atoms Ce (a), Pd(Pt) (b and c), In (d–g).

Table 3
Selected interatomic distances for the $CePd_2In_4$ and $CePt_2In_4$ compounds

$CePd_2In_4$			$CePt_2In_4$		
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Pd1	2In6	2.7659(12)	Pt1	2In6	2.7384(15)
	1In4	2.766(2)		1In4	2.751(2)
	1In7	2.802(2)		1In7	2.778(3)
	1In6	2.825(2)		1In6	2.837(3)
	2In7	3.1168(15)		2In7	2.9996(18)
	2Ce3	3.2641(15)		2Ce3	3.3119(18)
Pd2	In5	2.747(2)	Pt2	1In5	2.732(2)
	In4	2.760(2)		1In4	2.755(3)
	2In5	2.7694(12)		2In5	2.7424(15)
	2In4	2.8179(13)		2In4	2.7869(16)
	In7	2.827(2)		1In7	2.777(2)
	2Ce3	3.3718(15)		2Ce3	3.4130(17)
Ce3	2Pd1	3.2641(15)	Ce3	2In5	3.234(2)
	2In5	3.2897(13)		2In4	3.262(2)
	2In4	3.3157(14)		2In6	3.278(2)
	3In6	3.3282(18)		2Pt1	3.3119(18)
	2Pd2	3.3718(15)		1In6	3.356(3)
	1In5	3.4213(18)		2Pt2	3.4130(17)
				1In5	3.440(3)
In4	2Pd2	2.8179(13)	In4	2Pt2	2.7869(16)
	In5	2.964(2)		1In5	2.947(3)
	2In5	3.2915(14)		2In5	3.283(2)
	2Ce3	3.3157(14)		2Ce3	3.262(2)
	Ce3	3.4736(18)		2In7	3.346(2)
	2In7	3.3658(15)		1Ce3	3.493(3)
In5	2Pd2	2.7694(12)	In5	2Pt2	2.7424(15)
	1In4	2.964(2)		1In4	2.947(3)
	1In6	3.0334(19)		1In6	3.018(3)
	2Ce3	3.2897(13)		2Ce3	3.234(2)
	2In4	3.2915(14)		2In4	3.283(2)
	Ce3	3.4213(18)		1Ce3	3.440(3)
In6	2Pd1	2.7659(12)	In6	2Pt1	2.7384(15)
	2Ce1	3.3382(14)		2Ce3	3.278(2)
	1In7	3.341(2)		1In7	3.207(3)
	2In6	3.361(2)		2In6	3.370(4)
In7	1Pd1	2.802(2)	In7	1Pt2	2.777(2)
	1Pd2	2.827(2)		2Pt1	2.9996(18)
	2Pd1	3.1168(15)		1In6	3.207(3)
	2In4	3.3658(15)		2In4	3.346(2)

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