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Phase Relationships in the Ce–Pd–In System

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Abstract—The interaction of cerium with palladium and indium was studied, and the 773°C isothermal section of the Ce–Pd–In phase diagram was plotted using physicochemical methods: X-ray powder diffraction, single-crystal X-ray diffraction, and electron probe microanalysis. The existence of 12 ternary intermetallic phases in the title system was confirmed, and three new phases were discovered. Crystal structure was determined for seven intermetallic compounds. A single-crystal X-ray diffraction study of CePdIn was carried out for the first time. A high-temperature phase $CePdIn_4$ was found, and its crystal structure was solved.

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Ternary intermetallic compounds $R_xT_yX_z$ (where R is a rare-earth metal, T is a transition metal, and X is a *p* element) have interesting magnetic and electrical parameters [1–3] and attract the attention of researchers. Investigation of ternary phase diagrams is the only way to systematically search for new ternary and more complex compounds and to determine synthesis parameters for single-phase intermetallic compounds.

Great interest in alloys of the Ce–Pd–In system has existed since the discovery of an unusual combination of heavy-fermion properties and magnetic transition at low temperature in the compound CePdIn [4]. This expression of two competing phenomena (magnetic ordering and/Kondo's effect) was later discovered in a $Ce_8Pd_{24}In$ phase [5].

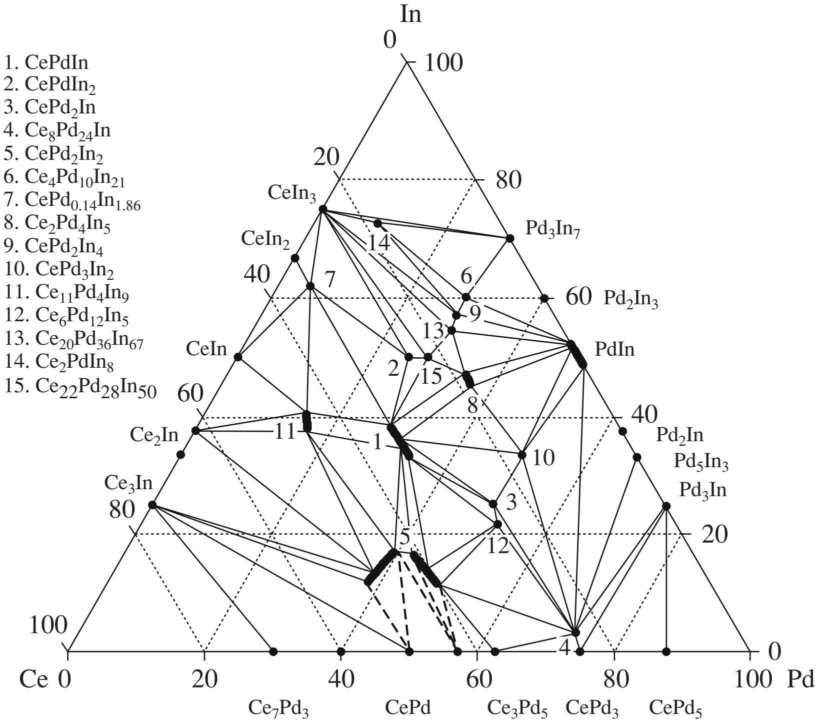
Phase diagrams for cerium–palladium, cerium–indium, and indium–palladium binary systems have been studied sufficiently. Many intermetallic compounds were found to form in these binary systems in equilibrium [6]. There are data on the Ce–Pd–In ternary phase diagram at 1023 K [7]; for some compounds, structure data are reported, but not for most of them. In addition, the experiment temperature chosen in [7] makes it impossible to account for the effect of the intermetallic compound Pd_3In_7, whose formation temperature is 945 K [8]. In this context, in this work we attempted to study the cerium–palladium–indium system at 773 K in order to better study the possibility of formation of new ternary indides, as well as to determine the structure of earlier unknown compounds.

EXPERIMENTAL

Ninety eight ternary and binary alloys were prepared to fulfill this work. Test alloys were prepared in an MAM-1 Buhler laboratory arc furnace with an inconsumable tungsten electrode on a water-cooled copper tray under an argon atmosphere. Titanium served as a getter. The starting metals used were cerium (99.8%), palladium (99.97%), and indium (99.99%). Alloys were melted several times, being turned over after each fusion for better alloying and homogenization. The sample size was 1 g. The alloy composition was monitored by weighing samples before and after fusion and by electron probe microanalysis (EPMA) of alloyed samples. Alloys whose weight loss did not exceed 0.6–0.8% were used in further work. For equilibration, alloys were subject to homogenizing annealing in evacuated quartz ampoules using zirconium chips as a getter. Heat treatment was carried out in tubular furnaces at 773 K for 1000 h followed by quenching to ice-cold water. The microstructure of polished samples was examined on a JEOL JSM 6400 scanning electron microscope. The chemical composition of phases was determined on an Oxford Link-Isis Si/Li energy-dispersive X-ray analysis unit. X-ray powder diffraction analysis was carried on a DRON-4 diffractometer using CuK_α radiation. Crystal structures of intermetallic phases were solved by a single-crystal X-ray diffraction experiment carried out on an Enraf-Nonius CAD-4 single-crystal diffractometer (MoK_α radiation, graphite monochromator) and a Nonius Kappa CCD diffractometer (MoK_α radiation, ω and φ scan modes) using standard procedures at room temperature. The SHELXS-97 and SHELXL-97 program packages [9] were used for structure solution and refinement. Atomic coordinates were standardized using STRUCTURE TIDY program [10].

RESULTS AND DISCUSSION

The results of this study are presented as an isothermal section of the Ce–Pd–In phase diagram (figure) plotted on the basis of X-ray powder diffraction and electron microscopy data. Our study confirmed the existence of the following binary intermetallic compounds stable at 773 K: Ce_3In, Ce_2In, Ce_3In_5, $CeIn_2$, $CeIn_3$, Pd_3In, Pd_3In_5, Pd_2In, PdIn, Pd_2In_3, Pd_3In_7,



Isothermal section of the Ce–Pd–In phase diagram at 773 K.

Ce_7Pd_3, $CePd_2$, Ce_3Pd_4, CePd, $CePd_3$, and $CePd_7$. In the cerium–indium binary system, the near-equiatomic compound CeIn is formed at this temperature.

X-ray diffraction and EPMA show that a previously unknown phase Ce_2PdIn_8 exists near the compound $CeIn_3$ (Table 1); Giovannini et al. [7] did not report the existence of this phase because it likely decomposes at high temperature. We found that the homogeneity range of the compound Ce_3In_5 at 773 K (whose boundary in [7] was determined at ~5 at % Pd on the basis of EPMA data) is actually small and does not exceed 2 at % Pd. Composition $Ce_{33.3}Pd_{4.7}In_{62}$ (at %) corresponds to the ternary intermetallic phase $CePd_{0.14}In_{1.86}$ with a $CaIn_2$-type structure (Table 1). Thus, our ternary phase diagram at 773 K in the region with more than 60 at % In is more complex than the diagram in [7] because it contains more three-phase and two-phase equilibria.

Fifteen ternary intermetallic compounds were found to exist in the Ce–Pd–In system at 773 K. We verified earlier structure data for the following ternary indides at this temperature: $CePdIn_2$ (BRe_3, *Cmcm*) [11], $CePd_2In$ ($InPt_2Y$, *P*63/*mmc*) [12], $Ce_8Pd_{24}In$ ($Ce_8Pd_{24}Sb$, *Pm*-3*m*) [13], Ce_2Pd_2In (Mo_2B_2Fe, *P*4/*mbm*) [14], $Ce_4Pd_{10}In_{21}$ ($Ho_4Ni_{10}Ga_{21}$, *C*2/*m*) [15], and $CePd_{0.14}In_{1.86}$ ($CaIn_2$, $P6_3/mmc$) [16]. We failed to synthesize the compound of composition $Ce_{22}Pd_{28}In_{50}$ in a pure form, likely because of the closeness of the formation temperature of neighboring phases. For the compound CePdIn, a single crystal was isolated, and more precise data were gained compared to powder data in [16]. As a result of structure refining, we obtained the following final values for 195 unique reflections: $R_F = 0.0397$ and $R_w = 0.1122$.

The compound $CePd_3In_2$ crystallizes in an orthorhombic unit cell of a new structure type with $Z = 4$, $V = 468.9(2)$ Å^3, and $\rho = 9.762$ g/cm^3 (Table 1). Its structure was solved in a single-crystal X-ray diffraction experiment and refined to $R_F = 0.046$ and $R_w = 0.1223$ over 952 unique reflections. The $CePd_3In_2$ unit cell parameters correspond to the data by Giovannini et al. [7]. Atomic coordinates and equivalent isotropic thermal factors are listed in Table 2.

The single-crystal experiment shows that $CePd_2In_4$ is a new representative of the $NdRh_2Sn_4$ structure type ($Z = 4$, $V = 624.4(2)$ Å^3, $\rho = 8.64$ g/cm^3 (Table 1), $R_F = 0.0747$, $R_w = 0.1584$, 1072 unique reflections). The results of structure refining are displayed in Table 3.

The ternary compound $Ce_6Pd_{12}In_5$, whose single crystal was separated from the alloy of this composition, crystallizes in a new structure type with hexagonal lattice, $Z = 2$, $V = 955.8(3)$ Å^3, $\rho = 9.411$ g/cm^3 (Table 1). Structure refinement in the anisotropic approximation gave $R_F = 0.0417$ and $R_w = 0.1120$ over 659 unique reflections (Table 4). The unit cell parameters calculated for this structure correlate well with the results reported by Giovannini et al. [7] for a phase with a suggested composition $Ce_4Pd_7In_3$ (τ_7).

A single-crystal X-ray diffraction study of $Ce_2Pd_4In_5$ [17] determined that this compound crystallizes in a monoclinic lattice and is a representative of a

Table 1. Crystallographic data for ternary compounds in the Ce–Pd–In system

Compound	Structure type	Space group	*a*, Å	*b*, Å; β, deg	*c*, Å	Source
CePdIn	Fe_2P	*P*–62*m*	7.704(2)	–	4.019(1)	*
$Ce_{22}Pd_{28}In_{50}$	–	–	–	–	–	7
$CePdIn_2$	BRe_3	*Cmcm*	4.621(3)	10.699(5)	7.455(2)	11
$CePd_2In$	$InPt_2Y$	*P*6$_3$/*mmc*	4.627(4)	–	9.198(7)	12
$Ce_8Pd_{24}In$	$Ce_8Pd_{24}Sb$	*Pm*–3*m*	8.461(8)	–	–	13
Ce_2Pd_2In	Mo_2B_2Fe	*P*4/*mbm*	7.813(4) 7.797(3)	– –	3.908(6) 3.928(3)	14 –
$Ce_4Pd_{10}In_{21}$	$Ho_4Ni_{10}Ga_{21}$	*C*2/*m*	23.082(7)	4.525(2) β = 133.05(8)	19.448(4)	15
$CePd_{0.14}In_{1.86}$	$CaIn_2$	$P6_3/mmc$	4.9100(3)	–	7.6572(2)	16
$Ce_2Pd_4In_5$	–	$P2_1/m$	9.5522(2)	4.6144(1) β = 102.56(1)	10.5815(4)	17
$CePd_2In_4$	–	*Pnma*	18.449(3)	4.565(6)	7.415(5)	*
$CePd_3In_2$	–	*Pnma*	10.265(4) 10.286(1)	4.623(6) 4.625(1)	9.878(2) 9.881(2)	* 7
$Ce_{11}Pd_4In_9$	–	*Cmmm*	14.9270	22.3820	3.8340	*
$Ce_6Pd_{12}In_5$	–	$P6_3/mcm$	8.292(2) 8.291(1)	–	16.051(2) 16.058(7)	18 7
$Ce_{20}Pd_{36}In_{67}$	–	*F*–43*m*	21.8340(2)	–	–	*
Ce_2PdIn_8	Ho_2CoGa_5	*P*4/*mmm*	4.6931(2)	–	12.2048(7)	*
$CePdIn_4^{**}$	$YNiAl_4$	*Cmcm*	4.5351(9)	16.856(5)	7.3080(2)	17

* This study.

** A high-temperature phase.

new structure type ($Z = 2$, $V = 455.3(1)$ Å^3, $\rho = 9.337$ g/cm^3). The final refinement values were $R_F = 0.0302$ and $R_w = 0.0906$; the results of the structure refinement are listed in Table 5. At 773 K, $Ce_2Pd_4In_5$ has a small homogeneity range along a cerium isoconcentration line within 45–47 at % indium. It is noteworthy that previous studies did not discover compounds of this composition.

Table 2. Atomic coordinates in the $CePd_3In_2$ structure

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
In1	0.01549(8)	1/4	0.61695(8)	0.0111(2)
Pd1	0.11901(9)	1/4	0.35491(10)	0.0148(2)
Ce	0.23121(6)	1/4	0.05633(7)	0.0103(2)
Pd2	0.24272(8)	1/4	0.76200(10)	0.0105(2)
In2	0.39564(8)	1/4	0.34127(8)	0.0111(2)
Pd3	0.47450(8)	1/4	0.60669(9)	0.0121(2)

The compound $Ce_{20}Pd_{36}In_{67}$ is the first representative of a new cubic structure type. This structure has a specific occupation of the Pd(1), Pd(2), In(1), and In(2) positions. The Pd(1) and Pd(2) positions are a split position with site occupancies of 0.66 and 0.34, respectively. In the same way, the In(1) and In(2) positions are a single split indium position with their occupancies of 0.68 and 0.32. The final refinement values are as follows: $R_F = 0.034$, $R_w = 0.079$ for 897 reflections. The composition of this intermetallic phase ($Ce_{16.25}Pd_{29.25}In_{54.5}$ (at %)) slightly differs in its higher indium bound from that suggested earlier by Giovannini et al. [7] on the basis of EPMA data ($Ce_{16.676}Pd_{33.33}In_{50}$ (at. 5)).

Proceeding from the first X-ray diffraction experiments on a $Ce_{11}Pd_4In_9$ single crystal, we found this compound to have orthorhombic structure ($Z = 2$, $V = 1280.9(11)$ Å^3, $\rho = 11.767$ g/cm^3) (Table 1) and a small homogeneity range of ~3 at % at 773 K. The atomic coordinates and isotropic thermal factors are listed in Table 6. An earlier study of alloys from the neodymium–palladium–indium system within a similar com-

Table 3. Atomic coordinates in the $CePd_2In_4$ structure

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
Pd1	0.54315(9)	1/4	0.2642(2)	0.0018(3)
Pd2	0.77681(8)	1/4	0.4510(2)	0.0014(3)
Ce3	0.35768(6)	1/4	0.5404(2)	0.0015(2)
In4	0.68644(7)	1/4	0.1543(2)	0.0013(3)
In5	0.69151(7)	1/4	0.7547(2)	0.0012(3)
In6	0.53317(7)	1/4	0.6444(2)	0.0016(3)
In7	0.42939(7)	1/4	1.0138(2)	0.0013(3)

Table 4. Atomic coordinates in the $Ce_6Pd_{12}In_5$ structure

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
Ce	0.27760	0	0.62240(6)	0.0045(3)
In1	0.36940(2)	0	1/4	0.0036(3)
In2	1/3	2/3	0	0.0023(3)
Pd1	0.3851(2)	0	0.07020(8)	0.0071(3)
Pd2	1/3	2/3	0.16710(9)	0.0082(3)
Pd3	0	0	0	0.0151(3)
Pd4	0	0	1/4	0.0053(5)

Table 5. Atomic coordinates in the $Ce_2Pd_4In_5$ structure

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
Ce1	0.6761(1)	1/4	0.7077(1)	0.011(1)
Ce2	0.7776(2)	1/4	0.1067(1)	0.011(1)
Pd1	0.3725(1)	1/4	0.4913(2)	0.013(1)
Pd2	0.4236(1)	1/4	0.8164(1)	0.011(1)
Pd3	0.8785(3)	1/4	0.5032(1)	0.013(1)
Pd4	0.9861(1)	1/4	0.8145(1)	0.011(1)
In1	0.0827(1)	1/4	0.3456(1)	0.010(1)
In2	0.1163(2)	1/4	0.0743(1)	0.015(1)
In3	0.1666(1)	1/4	0.6468(3)	0.011(1)
In4	0.4237(1)	1/4	0.0782(1)	0.011(1)
In5	0.5952(1)	1/4	0.3596(1)	0.010(1)

Table 6. Atomic coordinates in the $Ce_{11}Pd_4In_9$ structure

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
Ce1	0.2396(2)	0.1737(1)	0	0.0117(7)
Ce2	0	0.1616(2)	0	0.0011(1)
Ce3	0	0.3725(2)	0	0.0095(9)
Ce4	0.3084(2)	0	0	0.0092(9)
Ce5	0	0	0	0.0110(8)
Pd	0.3468(2)	0.1013(2)	1/2	0.0151(3)
In1	0.1021(2)	0.2656(2)	1/2	0.0110(8)
In2	0.1485(2)	0.0702(2)	1/2	0.0137(9)
In3	1/2	0	1/2	0.0137(2)

position range revealed the ternary compound $Nd_{11}Pd_4In_9$, of the same structure type [19].

The crystal structure of Ce_2PdIn_8 was solved by the Rietveld analysis of a powder X-ray diffraction pattern of an alloy that also contained a small $CeIn_3$ amount. This phase has an Ho_2CoGa_8-type structure. The final values were as follows: $R_p = 0.057$, $R_{wp} = 0.076$.

A single crystal of ternary indide $CePdIn_4$ was isolated from cast alloy. This intermetallic compound is a new representative of the $YNiAl_4$ structure type ($Z = 4$, $V = 558.5(3)$ Å^3, $\rho = 8.394$ g/cm^3). The final values after the structure refinement (R_F and R_w) were 0.0349 and 0.1075, respectively. X-ray powder diffraction data for alloys containing 60 at % indium or more did not confirm the existence of equilibria involving this phase at 773 K; from this, we infer that this compound is stable only at high temperatures.

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