Synthesis and Crystal Structure of Pd_5InSe

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Pd_5InSe has been prepared from the elements. The use of iodine as a mineralizing agent enables the synthesis of single-phase powder samples as well as of single crystals. Pd_5InSe is stable in cold air, but reacts to give Pd, In_2O_3 and Pd_4Se at 400 °C. The crystal structure of Pd_5InSe was determined from single-crystal X-ray diffraction data (space group $P4/mmm$, $a = 4.0255(7)$, $c = 6.972(1)$ Å, $z(Pd2) = 0.28111(8)$) and belongs to the Pd_5TlAs-type structure with full occupation of all atomic sites. EDX analysis on the single crystal ($Pd_{5.0(1)}In_{0.99(3)}Se_{1.0(1)}$) confirms the stoichiometric composition. The relationship to the cubic close packing (Cu-type structure), which may be visualized by the crystal chemical formula $Pd_4PdTlAs\square$, is proven by a Bärnighausen symmetry tree.

Key words: Palladium, Cubic Close Packing, Single-crystal X-Ray Diffraction, Bärnighausen Symmetry Tree, Pd_5TlAs Type

Introduction

Palladium-rich intermetallic compounds with main group elements often crystallize in one of many possible superstructures of the cubic close packing (ccp) instead of ccp-based solid solutions [1]. Which of these will be obtained for a certain combination of elements is difficult to predict, because the different ordered ccp variants vary only slightly in energy. This is also one of the reasons why it is often difficult to synthesize single-phase samples. It has been shown, however, that in this respect the use of iodine as a mineralizing agent may be helpful in two ways. First, the activation barrier for the reaction of palladium with other metals is lowered considerably, thereby paving the way for the synthesis of metastable compounds and for observing better phase purity [2, 3]. Second, the chemical transport with iodine may be used to grow single crystals [4, 5].

The Pd_5TlAs-type structure can be described as a twofold ccp superstructure with an ordered vacancy according to a crystal chemical formula $Pd_4PdTlAs\square$. 40 representatives are known for Pd_5MX with M being a main group or transition metal and X being P, As, Se, Si, or Sb; however, most of them were only obtained as phase mixtures, and no single crystals could be grown [6]. Only for one of these compounds refined crystal structure parameters are known so far, *i. e.* Pd_5HgSe, whose crystal structure was refined from powder X-ray diffraction data [7].

In the system Pd-In-Se, two compounds Pd_5InSe and Pd_8In_2Se were reported, however, they could only be prepared as mixtures of both. The first one was assigned to the Pd_5TlAs-type structure, but no refined atomic parameters were given [8]. In this contribution we report on an improved synthesis of Pd_5InSe, leading to single-phase samples, its reaction at elevated temperatures in air and its single-crystal structure. Furthermore, the structural relationship of the Pd_5TlAs-type structure to ccp and ccp superstructures is analyzed by means of a Bärnighausen symmetry tree.

Results and Discussion

Synthesis and sample characterization

The synthesis yields a grey powder with a metallic luster and plate-like crystals in the size of

several hundred micrometers; for example, the size of the single crystal fragment measured by single-crystal X-ray diffraction (see below) amounts to $0.18 \times 0.15 \times 0.02$ mm^3. Based on the chemical analysis of the crystal the empirical formula $Pd_{5.0(1)}In_{0.99(3)}Se_{1.0(1)}$ was determined, averaged from fourteen EDX spectra measured on the edge and plane of the crystal. In order to obtain single-phase materials and single crystals, iodine was used as a transport agent. Without the use of iodine the reaction resulted in the formation of a mixture of Pd_5InSe with Pd_8In_2Se [8] as the minor phase. Pd_5InSe is air stable over months and reacts in air at temperatures above $400\,^{\circ}C$ to In_2O_3, Pd and Pd_4Se.

Crystal structure

Pd_5InSe was reported [8] to crystallize in the Pd_5TlAs-type [6] structure. However, no refined atomic positions are known as yet. We refined the crystal structure of Pd_5InSe from single-crystal X-ray data and confirmed its structure type (Fig. 1). The structure of Pd_5InSe differs from one in a hypothetical $HoCoGa_5$ type [9] only by exchanging the palladium atom on the $1a$ site with the indium atom on the $1c$ site (*vide infra*). Because both atoms ($Z = 46$ and 49, respectively) have similar atomic form factors for X-rays, the $HoCoGa_5$-type arrangement was tested as a possible alternative structure description. Interchange of atoms in this way yielded an increase in residual values (R_1 rises from 0.026 to 0.041, wR_2
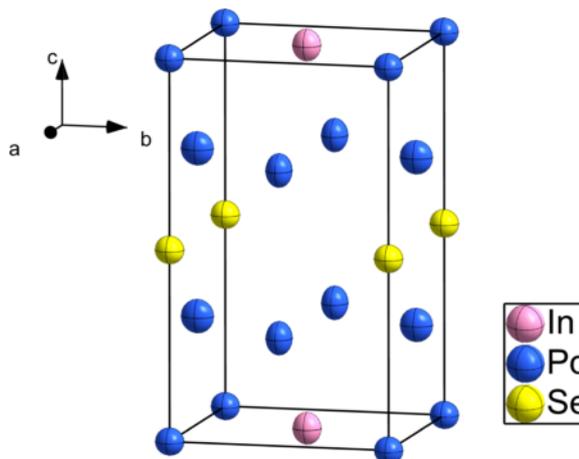

Fig. 1 (color online). View of the crystal structure of Pd_5InSe. Displacement ellipsoids are shown at the 99% probability level.

from 0.067 to 0.150 and the goodness of fit from 1.21 to 2.94). Thus we conclude that the $HoCoGa_5$-type structure can be ruled out for Pd_5InSe, and that the Pd_5TlAs type is the most suitable model (Tables 1 and 2).

Powder diffraction data have shown that the samples were (almost) single-phase. Rietveld refinement on the powder X-ray diffraction data show a good correspondence with the single crystal data except for $z(Pd2) = 0.2881(4)$, owing to the correlation of this coordinate with the preferred orientation parameters (Rietveld-Toraya model, see Fig. 2).

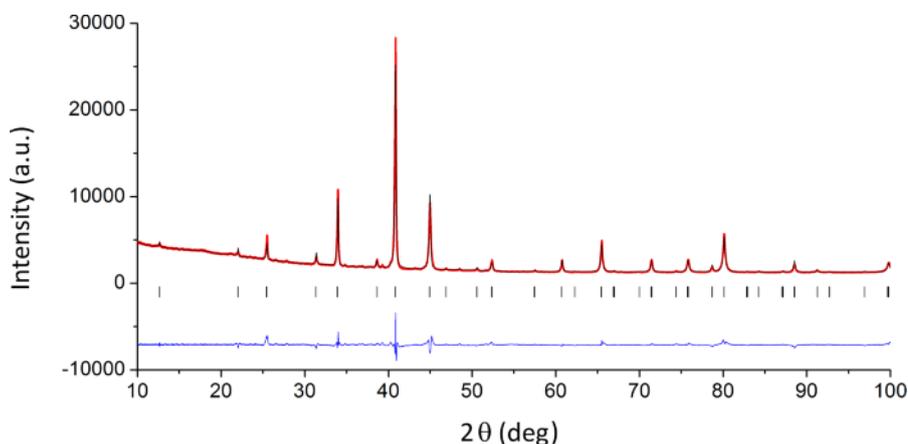Fig. 2 (color online). Rietveld refinement of the crystal structure of Pd_5InSe. Observed (red line), calculated (black line), and difference (observed–calculated; bottom) powder X-ray diffraction patterns ($\lambda = 1.54056$ Å). Markers indicate Bragg peak positions of Pd_5InSe. $R_p = 0.0327$; $R_{wp} = 0.0472$; $R_{exp} = 0.0219$; $R_{Bragg}(Pd_5InSe) = 0.163$; $a = 4.0269(4)$, $c = 6.9829(8)$ Å.

Table 1. Crystallographic data and structure refinement of Pd_5InSe.

Empirical formula	Pd_5InSe
Formula mass, g mol⁻¹	725.78
Crystal system	tetragonal
Space group	$P4/mmm$
Cell parameters	
a, Å	4.0255(7)
c, Å	6.9722(14)
Cell volume, Å³	112.94(4)
X-Ray density, g cm⁻³	10.67
Absorption coefficient, mm⁻¹	17.1
$F(000)$, e	313
Diffractometer	Stoe IPDS I
Radiation; wavelength λ, Å	AgK_α; 0.56086
2θ range, deg	11.3 – 55.72
Absorption correction	numerical [20, 21]
Measured/independent reflections	2134/195
Data with $I > 2\,\sigma(I)$	191
Refined parameters	12
Weighting scheme	$w = 1/[\sigma^2 F_o^2 + (0.0428P)^2]$ with $P = [F_c^2 + \mathrm{Max}(F_o^2,0)]/3$
Extinction coefficient	$x = 0.027(5)$
Extinction expression	$F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$ with the overall scale factor k
Refinement	full-matrix least-squares on F^2
R_{int}/R_σ	0.0475/0.0273
$R1\,[I > 2\,\sigma(I)]/$ $wR2\,[I > 2\,\sigma(I)]$	0.0260/0.0669
$R1$ (all data)/$wR2$ (all data)	0.0272/0.0674
GooF (all data)	1.209
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å⁻³	−2.967/2.025

The palladium atom (Pd1) at the origin is surrounded by four indium atoms and eight Pd2 atoms in a distorted cuboctahedron. The indium atom has also $[4+8]$ coordination to the Pd1 and Pd2 atoms and is therefore also located in the center of a cuboctahedron. The Pd2 atom with the free positional parameter (Wyckoff position $4i$ 0, 1/2, z, see Table 2) is surrounded by two Pd1, indium and selenium atoms each
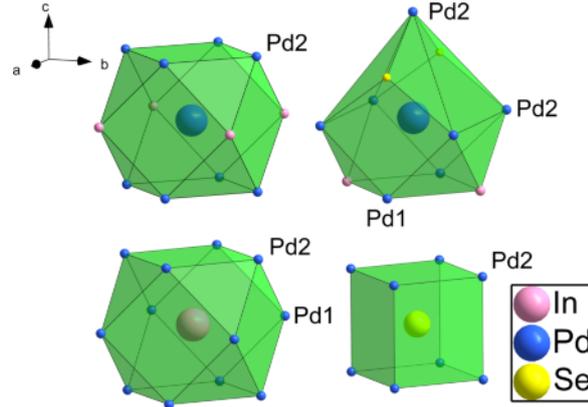
Fig. 3 (color online). Coordination polyhedra in the Pd_5InSe crystal structure of Pd1 (top, left), Pd2 (top, right), In (bottom, left), and Se (bottom, right).

and four Pd2 atoms, which are arranged in the middle plane of the coordination polyhedron. Another Pd2 atom is located at a larger distance normal to that plane near to the selenium atoms. The selenium atom can be found in the center of a tetragonal prism of equidistant Pd2 atoms. All coordination polyhedra are shown in Fig. 3. The crystal structure can be viewed as alternating layers of indium-centered cuboctahedra and two-dimensional selenium layers along [001] (Fig. 4). In contrast to this structural motif, channels of selenium atoms along the c axis were recently found in the new metallic compound $Pd_{17}In_4Se_4$ [10]. Table 3 shows the bond lengths in Pd_5InSe obtained from single-crystal X-ray diffraction data. The interatomic distances between the palladium atoms are greater than in elemental palladium (2.75 Å) [11]. However, the observed values are comparable to those of well-known phases like $InPd_3$ in the $TiAl_3$ type (2.744 – 2.899 Å) [12]. Furthermore, the Pd–In bond length agrees also with the one found in the mentioned $InPd_3$ modification. The Pd–Se distance is consistent with the one observed in $Pd_{17}Se_{15}$ (2.433 – 2.586 Å) [13].

Table 2. Coordinates, anisotropic and equivalent isotropic displacement parameters of Pd_5InSe ($U_{eq} = 1/3\,[U_{11} + U_{22} + U_{33}]$. $U_{12} = U_{23} = U_{13} = 0$).

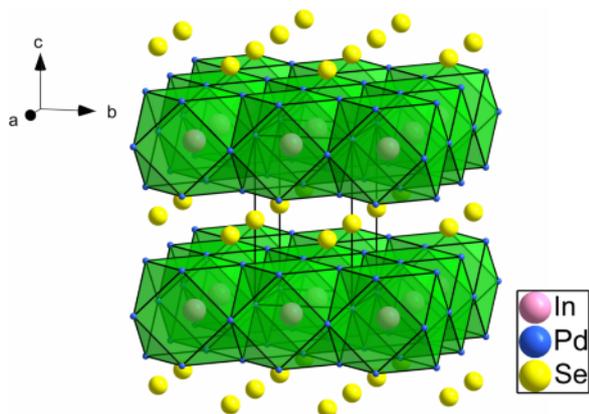| Atom	Wyckoff position	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}
In1	$1c$	1/2	1/2	0	0.0071(2)	0.0061(3)	$= U_{11}$	0.0091(4)
Pd2	$1a$	0	0	0	0.0068(2)	0.0066(3)	$= U_{11}$	0.0073(4)
Pd3	$4i$	0	1/2	0.28111(8)	0.0080(2)	0.0085(3)	0.0054(2)	0.0100(3)
Se4	$1b$	0	0	1/2	0.0072(3)	0.0066(3)	$= U_{11}$	0.0084(5)

Fig. 4 (color online). View of the two-dimensional selenium layers between the indium-centered cuboctahedra. Unit cell edges are shown.

Table 3. Selected bond lengths (Å) for Pd_5InSe with estimated standard uncertainties in parentheses.

Pd1	$8 \times$ Pd2	2.8094(5)	Pd2	$2 \times$ Se	2.5259(5)
	$4 \times$ In	2.8465(5)		$2 \times$ In	2.8094(5)
In	$8 \times$ Pd2	2.8094(5)		$2 \times$ Pd1	2.8094(5)
	$4 \times$ Pd1	2.8465(5)		$4 \times$ Pd2	2.8465(5)
Se	$8 \times$ Pd2	2.5259(5)		$1 \times$ Pd2	3.0523(12)

Structural relationship to the cubic close packing

The relationship of the crystal structure of Pd_5InSe to that of a cubic close packing (ccp) is obvious from Fig. 1. The unit cell is doubled in one direction leading to a symmetry reduction from cubic to tetragonal. One position remains unoccupied, *i. e.* the eight positions of the structure are occupied by 5 Pd, 1 In, 1 Se, 1 □. The

structure types of $TiAl_3$ and $HoCoGa_5$ are closely related as well (Fig. 5). While in Pd_5InSe the majority element occupies $1a$ and $4i$ positions, in the latter structure type it is $1c$ and $4i$. A simple shift of the origin cannot transform one into the other, however, interchanging the atoms on positions $1a$ and $1c$ (Table 2, Fig. 5), as well as a shift of the layer of atoms (Pd1 and In) with $z = 0$ by a vector of 1/2, 1/2, 0, lead to this transformation (Fig. 5). The structure type of $HoCoGa_5$ is thus a partial inverse derivative of the Pd_5TlAs type. The former is very well known for hosting heavy-fermion intermetallic compounds such as $CeIrIn_5$ and $CeRhIn_5$ [14, 15]. The same relation holds for Pd_3In in the $TiAl_3$ structure [12, 16]. By shifting all atoms with $z = 0$ by a vector of 1/2, 1/2, 0 and leaving the position 1/2, 1/2, 1/2 unoccupied, the structure of Pd_5InSe is formed. Thus, both $HoCoGa_5$ and Pd_5InSe may be described as ordered substitution vacancy derivatives of the $TiAl_3$-type structure. The relationship to the Cu_2Sb type, yet another ccp vacancy derivative, was shown earlier [17].

The classification of the crystal structure of Pd_5InSe as an ordered ccp superstructure can also be proven by crystallographic group-subgroup relationships [18]. Loss of the three-fold axis in the first step of a *translationengleiche* transition of index 3 renders the indium-type structure, a tetragonally distorted cubic close packing (Fig. 6). Losing the body centering in a *klassengleiche* transition yields two crystallographically independent atoms in the AuCu type [12], which further split up into three in the next step of doubling of the c axis ($ZnCdPt_2$ type). The last isomorphic transition to the Pd_5TlAs type results in the final splitting into one fourfold and four onefold positions. This
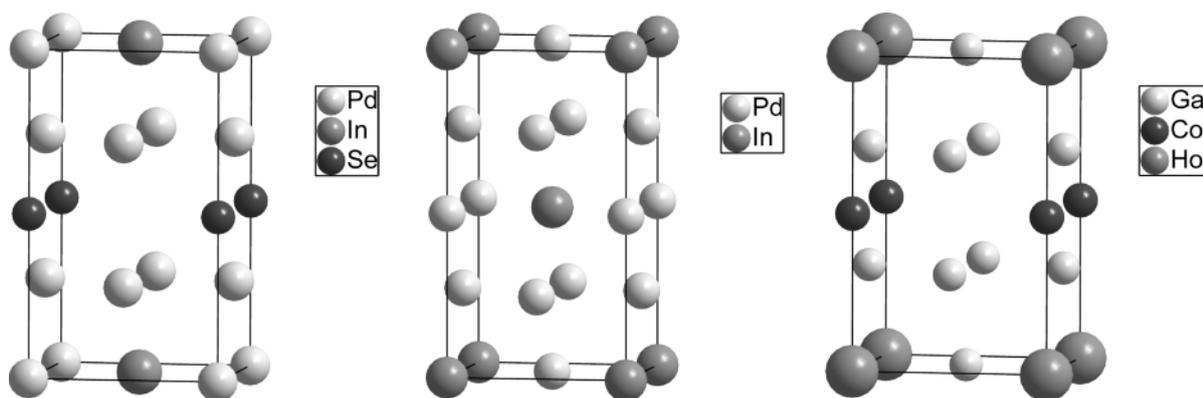

Fig. 5. Comparison of the crystal structures of Pd_5InSe (left, Pd_5TlAs-type structure), Pd_3In (middle, $TiAl_3$-type structure) and $HoCoGa_5$ (right). Crystallographic c axis is pointing vertical.
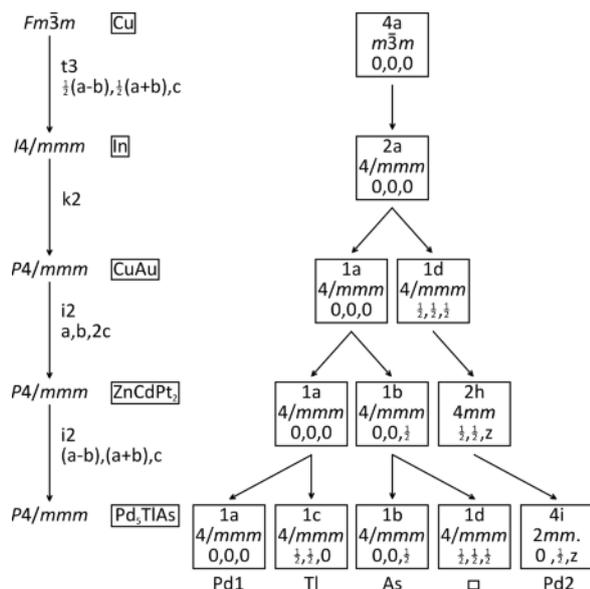
Fig. 6. Bärnighausen symmetry tree of the Pd$_5$TlAs structure type.

now gives enough freedom to distribute three different kinds of atoms in the fashion M$_4$MM′M″□. The Pd$_5$TlAs type and the HoCoGa$_5$ type are two possible configurations for such a formula under the given symmetry restrictions. One of the palladium atoms also gains a positional degree of freedom in z direction. The refined z parameter (Table 2) is somewhat larger than the ideal one of 0.25 resulting from the Bärnighausen tree (Fig. 6). This reflects a move towards the vacancy in 1/2 1/2 1/2 with respect to the ZnCdPt$_2$ type. Hence, both the Pd$_5$TlAs type and the HoCoGa$_5$ type are ordered ccp superstructures in a strict crystallographic group theoretical sense. *Bärnighausen* trees describing further relationships between differently ordered ccp superstructures have been reported earlier [12, 19].

Experimental Section

Synthesis and EDX analysis of Pd$_5$InSe

The ternary compound was synthesized by chemical vapor transport from the elements. Stoichiometric amounts of palladium powder (Ventron Alpha Produkte), indium (tear drops, 99.99 %, Alfa Aesar) and selenium (drops, pure, VEB Laborchemie, Apolda) were placed in a silica glass tube. A crystal of iodine (resublimed, Merck) was added to enhance the reactivity by means of chemical vapor transport.

The silica glass ampoule was sealed in vacuum and heated to 950 °C within four hours and held at this temperature for three hours. After cooling to 750 °C within two hours, this temperature was maintained for one week, before cooling to room temperature within three hours. The product was ground under ethanol using agate mortar and pestle. Chemical analysis was performed by an EDX INCA SYSTEM from Oxford Instruments mounted on a Zeiss LEO 1530 scanning electron microscope with an acceleration voltage of 20 kV and a working distance of 15 mm. Pd$_5$InSe is stable in cold air, but reacts at 400 °C to give Pd, In$_2$O$_3$ and Pd$_4$Se (12 h reaction time in an open alumina crucible).

Single-crystal X-ray diffraction

Single-crystal data were measured on an IPDS-I diffractometer (Stoe & Cie GmbH, Darmstadt, Germany) equipped with an image plate detector using AgK_α radiation ($\lambda =$ 0.56086 Å, graphite monochromator). A numerical absorption correction was performed with X-RED [20]. Crystal faces were optimized with the program X-SHAPE [21]. The structure was solved with Direct Methods. Structure refinement was performed with SHELX-97 [22].

Powder X-ray diffraction

Powder X-ray diffraction data were collected using flat transmission samples on an image plate Guinier powder diffractometer (Huber Guinier camera G670 at $T = 296$ K with Cu$K_{\alpha 1}$ radiation, $\lambda = 1.54056$ Å, Ge(111) monochromator). Rietveld refinements were carried out with the program FULL-PROF [23, 24], and the Pearson VII function was used to generate the shape of the diffraction peaks in the refinement.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-427161.

Note added in proof

During preparation of this manuscript a refinement of the crystal structure of Pd$_5$InSe based on powder X-ray diffraction data was published [25], which is in accordance with our results.

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