Refinement of the Crystal Structures of Palladium-rich In-Pd Compounds by X-Ray and Neutron Powder Diffraction

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Dedicated to Dr. Bernard Chevalier on the occasion of his 60th birthday

The ternary indium palladium intermetallics In₃Pd₅, InPd₂, and InPd₃ have been synthesized by iodine-catalyzed reactions from the elements. Rietveld refinements on X-ray powder diffraction patterns provide the first accurate crystal structure data for In₃Pd₅ (Pbam, No. 55, a = 1104.20(2), b = 561.346(8), c = 424.263(6) pm, Rh₃Ge₃-type) and InPd₂ (Pnma, No. 62, a = 561.676(6), b = 421.710(4), c = 822.78(8) pm, Co₂Si-type). X-Ray powder diffraction apparently confirms the TiAl₃ structure type proposed in the literature for InPd₃. However, Rietveld refinement on neutron powder diffraction data reveals an In/Pd distributional disorder. Therefore, we describe the crystal structure of InPd₃ in a AuCu-type model instead (P₄/nmm, No. 123, a = 287.224(4), c = 380.079(7) pm), with mixed occupancy of one crystallographic site by 50% In and 50% Pd. In contrast to In₃Pd₅ and InPd₂, which can be considered to be line compounds, InPd₃ shows a non-negligible homogeneity range with unit cell volumes ranging from 0.126132(5) nm³ for the indium-rich to 0.125474(8) nm³ for the palladium-rich In₁₊ₓPd₃₋ₓ phases. Mean In–Pd distances in these indium palladium intermetallics range from 272.3 pm (In₁ in In₃Pd₅) with coordination number 8 for indium to 281.2 pm for 12-coordinated In in InPd₃.

Key words: Intermetallic Compounds, Palladium, Neutron Diffraction, Powder Diffraction, Disorder

Introduction

Various approaches have been used to influence crystal structures and physical properties of intermetallic compounds, as, e.g., high pressure and isotopic substitution [1–3]. A further strategy is the incorporation of hydrogen for tuning the magnetic behaviour of intermetallic compounds of the transition metals [4, 5], and more recently in the group of Chevalier for probing mixed-valent and heavy fermion behaviour of intermetallics with cerium and elements of the groups 8–10 (16–16) and references cited therein). The metal hydrides of intermetallic compounds \( M_nM'_nM''_n'(M' = \text{Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt}) \) reveal a fascinating structural chemistry [17], including unusual coordination geometries [18], high oxidation states [19, 20], and order-disorder transitions [21,22]. Ternary palladium hydrides with divalent metals exhibit a wide variety of chemical bonding, crystal structures and properties, ranging from ionic-covalent complex hydrides to typical interstitial compounds with metallic properties, as, e.g., in the systems Ca-Pd-H [23, 24], Sr-Pd-H [25, 26], and Eu-Pd-H [27]. A particularly interesting example of the subtle influence of hydrogen on the crystal structure of intermetallics is formed upon hydrogenation of MgPd₃. Here, a hydrogen-induced rearrangement of metal atoms from a ZrAl₃ to a AuCu₃ structure has been found [28]. As these structures are closely related, they can easily be mistaken one for the other, especially in the case of incomplete order. Therefore, detailed studies require a precise knowledge of the crystal structures of the intermetallic compounds underlying the metal hydrides. In an extension of our work on palladium-rich intermetallics and hydrides, we report in this paper on the refinement of the crystal structures of the palladium-rich phases In₃Pd₅, InPd₂ and InPd₃, which are interesting candidates for hydrogenation studies.

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In3Pd2: \( \text{Pham (No. 55), } a = 1104.20(2), b = 561.346(8), c = 424.263(6) \text{ pm} \)

\[ R_B = 0.019, R_w = 0.028, R_p = 0.150, R_{wp} = 0.113, R_{wp} = 0.042, S = 1.02 \]

atom site \( x \) \( y \) \( z \) \( B_{iso} (10^4 \text{ pm}^2) \)
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\( \text{In}1 \) 2a 0 0 0 1.4(1)
\( \text{In}2 \) 4h 0.1428(2) 0.3273(4) 1/2 1.59(9)
\( \text{Pd}1 \) 2c 0 1/2 0 0.8(1)
\( \text{Pd}2 \) 4g 0.2443(2) 0.0735(4) 0 0.70(8)
\( \text{Pd}3 \) 4h 0.3915(2) 0.3018(5) 1/2 0.47(8)

**Table 1.** Crystal structure data of In3Pd5 and In3Pd2 as refined from X-ray powder diffraction data \((T = 296(1) K, \lambda = 154.056 \text{ pm})\) and of In3Pd3 as refined from neutron powder diffraction data \((D1A, T = 299(2) K, \lambda = 190.931(3) \text{ pm})\).

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**Experimental Section**

**Synthesis**

Indium palladium intermetallic compounds have been prepared from the elements in evacuated sealed silica tubes in analogy to the iodine-catalyzed synthesis, as applied previously in the systems Al-Pd, Ga-Pd, Be-Pd, and Mg-Pd [29 – 32]. Indium pieces \((99.99 \% \text{, Schuchard, Munich})\) and palladium powder \((< 60 \mu \text{m}, 99.9 \% \text{, ChemPur})\) in stoichiometric ratios, and indium (Merck, purified by sublimation) with molar ratios ranging from 0.5 to 2 \% with respect to indium have been used. The silica ampoules were heated with 50 K h \(^{-1}\) to 850 K, annealed at this temperature for 55 h and quenched in air. Indium was sublimed off the products by gently heating one end of the sealed silica tube. For synthesis temperatures substantially below 850 K incomplete reactions were observed, yielding multiphasic mixtures. In the case of InPd3, reaction at 750 K produced a mixture of two phases of the approximate composition InPd3 with slightly different unit cell volumes.

**Powder diffraction and Rietveld refinement**

X-ray powder diffraction data were collected using flat transmission samples containing an internal silicon standard on an image plate Guinier powder diffractometer (Huber Guinier camera G670 at \(T = 296(1) K\) with CuK\(_{α1}\) radiation, \(\lambda = 154.056 \text{ pm}\)). Rietveld refinements were carried out using the program FULLPROF [33] with a pseudo-Voigt profile function in all cases. For the refinement of In3Pd3 on X-ray powder data the following parameters were allowed to vary: the zero point of the 2\(θ\) scale, one scale parameter, three peak width \((u, v, w)\), one asymmetry, three lattice, six positional and five isotropic displacement parameters for the internal silicon standard, keeping its lattice parameter fixed at 543.0 pm; one scale parameter, three peak width \((u, v, w)\), one asymmetry, three lattice, six positional and five isotropic displacement parameters for the InPd3 phase; one scale and three lattice parameters for the minor phase InPd2 with all profile parameters constrained to those of the main In3Pd5 phase. The background was described by linear interpolation between 28 points. A similar strategy was chosen for the refinement on the InPd2 X-ray powder data. Silicon was treated in exactly the same way as described before, and the main phase InPd2 as well, except for a reduced number of three isotropic displacement parameters. For the minor phase InPd3 one scale parameter, one peak width \(w\) of the Cagliotti formula, one lattice and one overall isotropic displacement parameters were refined, and the background was described by linear interpolation between 24 points.

Neutron powder diffraction data on InPd3 were taken at \(T = 299(2) K\) on the high-resolution powder diffractometer D1A at the Institute Laue-Langevin in Grenoble, France, in the range 6° \(≤ 2\theta \leq 157°\) (step size \(Δ2\theta = 0.05°\)) during a total measurement time of 12 h. Special care was taken of the enhanced neutron absorption of indium by realizing a moderate sample thickness \((3.8 \text{ g InPd3 powder in a vanadium can of 5 mm inner diameter, sealed by indium wire})\). The wavelength used was determined from a measurement on a silicon standard to be \(\lambda = 190.931(3) \text{ pm}\) and kept fixed during refinements. For the refinement on InPd3 neutron powder data the following parameters were allowed to vary: the zero point of the 2\(θ\) scale, five background parameters (polynomial), one scale, three peak width \((u, v, w)\) of the Cagliotti formula, one mixing \(η\), one asymmetry, two lattice, and two isotropic displacement parameters for InPd3. Refined crystal structure data are given in Table 1. Rietveld plots and crystal structure representations in Figs. 1 – 3 and 4 – 6, respectively.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe,
Results and Discussion

\( \text{In}_3\text{Pd}_5 \)

\( \text{In}_3\text{Pd}_5 \) has been reported to crystallize in the orthorhombic \( \text{Rh}_5\text{Ge}_3 \) structure, but the standard uncertainties of positional parameters were rather large [34]. Our diffraction data confirm the structure type of \( \text{Rh}_5\text{Ge}_3 \) [35], which may be described as a stuffed, distorted variety of the \( \text{CoSn} \)-type [36] or a distorted \( \text{Pt}_5\text{Ga}_3 \)-type structure [37]. We provide crystal structure parameters of much better accuracy than reported previously. \( \text{In}_2 \) forms strongly distorted honeycomb nets (6\(^3\) nets) at \( z = 0 \) and 1/2, while \( \text{Pd}_1 \) and \( \text{Pd}_2 \) together form \( \text{Kagomé} \) nets (3.6.3.6 nets) at \( z = 1/4 \) and 3/4 (Fig. 4). This results in trigonal \( \text{In}_2\text{Pd}_6 \) prisms, which are linked by common triangular faces giving infinite columns along the \( c \) axis, and by common edges to a three-dimensional framework. Additional indium (\( \text{In}_1 \)) and palladium (\( \text{Pd}_3 \)) atoms are found within the resulting hexagonal channels, thus completing the coordination sphere of \( \text{In}_2 \) to a total of ten palladium neighbours (\( \text{In}_2\text{–Pd} \) distances ranging from 269.0(4) to 297.4(4) pm with a mean distance of 281.4 pm) by capping two faces of the prisms by one and the third by two \( \text{Pd}_3 \) atoms. The \( \text{In}_1 \) atoms inside the channels have an eightfold coordination by palladium and are located in the middle of a double prism with the shared prism face lying in the \( ab \) plane (Fig. 4) with \( \text{In}–\text{Pd} \) distances ranging from 267.8(2) to 280.67(2) pm. The somewhat shorter average distance \( \text{In}_1\text{–Pd} \) of 272.3 pm reflects the lower coordination number of \( \text{In}_1 \) in comparison to \( \text{In}_2 \).
Crystal Structures of Palladium-rich In-Pd Compounds

InPd$_2$

InPd$_2$ has been reported in the orthorhombic Co$_2$Si-type structure, but the crystal structure was not refined in this early work [34]. Our diffraction data confirm that structure type and for the first time provide refined positional parameters (Table 1). Indium is surrounded by ten palladium atoms as tetracapped trigonal prisms (In–Pd distances ranging from 268.9(2) to 291.8(2) pm with an average distance of 278.1 pm). These prisms are linked via common triangular faces to form infinite columns along the $b$ axis and by common corners to form zigzag chains running along $a$ (Fig. 5). Neighboring chains are shifted by 1/2 $b$, in such a way that prism atoms in one chain are capping atoms in the neighbouring one and vice versa. The lattice parameter ratios $a/c = 0.683$ and $(a+c)/b = 3.28$ (Table 1) place InPd$_2$ into the Co$_2$Si-type [38] branch within the PbCl$_2$-type structure family according to [39], which is to be expected because of the rather low ionicity in such intermetallics.

InPd$_3$

For InPd$_3$ a TiAl$_3$-type structure was proposed on the basis of X-ray powder diffraction data [40]. This structure type represents a superstructure of the cubic closest packing (Cu-type) with identical coordination numbers for all crystallographic sites. Hence, it is lacking a strong crystal chemical differentiation of both elements in contrast to the crystal structures of InPd$_2$ and In$_3$Pd$_5$, making it more prone to a possible occupational In/Pd disorder and compositional variation. The latter can be confirmed from phase diagrams exhibiting a homogeneity range in In$_{1+\delta}$Pd$_{3-\delta}$ from 24.8 to 26, and at temperatures above 1340 K even up to 27 atomic percent indium [41]. In accordance with this, we find different unit cell volumes, depending on the synthesis temperature and on the nominal molar ratios of indium and palladium. Unit cell volumes range from 0.12605(1) nm$^3$ for the indium-rich to 0.125474(8) nm$^3$ for the palladium-rich InPd$_3$ phases prepared by the iodine-catalyzed route at 850 K. For quenched samples synthesized at higher temperatures (1450 K) the indium-rich phase boundary extends even further to 0.126132(5) nm$^3$. The synthesis of InPd$_3$ from stoichiometric amounts of the elements at lower temperatures (750 K) produced a mixture of two phases In$_{1+\delta}$Pd$_{3-\delta}$ with different cell parameters ($a = 406.675(4), c = 760.45(2)$ pm and $a = 410.03(3), c = 747.84(8)$ pm, respectively), one of which is most probably rich in indium ($x > 0$), the other in palladium ($x < 0$).

Unfortunately, indium and palladium are difficult to distinguish by X-rays (49 vs. 46 electrons). Neutrons ($b_t = 4.1$ vs. 5.9 fm [42]) are much better suited for this task and thus we collected neutron powder diffraction data on InPd$_3$ in order to reveal the exact ordering.
of In and Pd, which is of importance in view of the hydrogen-induced atomic rearrangement in palladium-rich intermetallics [28]. The neutron powder diffraction data taken on D1A have shown a considerable intensity mismatch with diagrams calculated on the basis of the proposed ordered TiAl₃-type structure. Refinement of individual Debye-Waller factors or occupation parameters pointed at a mixed In/Pd occupation of the sites 2a (0, 0, 0) and 2b (0, 0, 1/2) in space group P4/mmm, while no such indication was found for the site 4d (0, 1/2, 1/4) occupied by palladium. Refinement of occupation parameters lead to values not significantly different from 0.50 for the 2a and 2d sites. Thus lifting the chemical differentiation between those sites, they become crystallographically equivalent, since the whole structure can now be described in the higher symmetric space group P4/mmm with a′ = \( \frac{1}{2}(a + b) \), b′ = \( \frac{1}{2}(-a + b) \), c′ = \( \frac{1}{2}c \). Such a structural model corresponds to an AuCu-type arrangement with mixed In/Pd occupancy on one of the two crystallographic sites. Rietveld refinement of this model resulted in a good fit (Fig. 3, Table 1), indicating the validity of this structural model. Therefore, we describe the crystal structure of InPd₃ in a partially disordered tetragonal AuCu-type with 50% In and 50% Pd on one crystallographic site (Table 1, Fig. 6). This situation may be expressed by a crystal chemical formula (In₀.₅Pd₀.₅)Pd = InPd₃. Each atom in InPd₃ is surrounded by twelve neighbours in the form of an anticycloboctahedron slightly compressed along the c axis at distances ranging from 278.14(1) to 287.22(1) pm with an average distance of 281.16 pm. Triboluminescent activation did not change the order in InPd₃ in contrast to MgPd₃ [28].

In view of this new structural model, the question arises, whether the X-ray diffraction data in the older literature [41] were mistakenly assigned to the TiAl₃-type, because the disorder was hidden by the almost equal scattering factors of indium and palladium for X-rays. Another possibility, however, is that synthesis conditions such as temperature or the presence of mineralizing agents, as, e.g., iodine as applied in this work, do influence the order in InPd₃, and the structure described here therefore represents a new modification of InPd₃. The existence of a high-temperature modification β-InPd₃ has already been claimed from thermal analysis of the palladium-rich part of the indium-palladium phase diagram, but no structural information has been given [43]. To clarify the question of the number of modifications of InPd₃ and their atomic order, further neutron diffraction experiments on samples prepared under different conditions will be necessary. Unravelling the inherent disorder in InPd₃ is of importance for the planned hydrogenation studies, because hydrogen was found to change just this atomic order in MPd₃ compounds [28].

Conclusion

An iodine-catalyzed synthesis from the elements at moderate temperatures (850 K) gave access to In₃Pd₅, InPd₂ and InPd₃ in the form of well crystallized powders. The crystal structures of In₃Pd₅ and InPd₂ could be confirmed to belong to the proposed Rh₅Ge₃- and Co₅Si-types, respectively. Rietveld refinements on X-ray powder diffraction patterns have provided the first accurate crystal structure data for these compounds. For InPd₃ the proposed TiAl₃-type structure could be not confirmed, because Rietveld refinement on neutron powder diffraction data revealed an In/Pd distributional disorder. We describe the crystal structure of InPd₃ in a partially disordered tetragonal AuCu-type with 50% In and 50% Pd on one crystallographic site. Mean In–Pd distances range from 272.3 pm for coordination number 8 for indium to 281.2 pm for coordination number 12.

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