



Hydrogenation of palladium rich compounds of aluminium, gallium and indium

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ARTICLE INFO

Article history:

Received 2 September 2009

Received in revised form

23 November 2009

Accepted 29 November 2009

Available online 5 December 2009

Keywords:

In situ techniques

Thermal analysis

Metal hydrides

Palladium

Hydrogenation

ABSTRACT

Palladium rich intermetallic compounds of aluminium, gallium and indium have been studied before and after hydrogenation by powder X-ray diffraction and during hydrogenation by *in situ* thermal analysis (DSC) at hydrogen gas pressures up to 39 MPa and temperatures up to 700 K. Very weak DSC signals and small unit cell increases of below 1% for AlPd_2 , AlPd_3 , GaPd_2 , $\text{Ga}_5\text{Pd}_{13}$, In_3Pd_5 , and InPd_2 suggest negligible hydrogen uptake. In contrast, for both tetragonal modifications of InPd_3 (ZrAl_3 and TiAl_3 type), heating to 523 K at 2 MPa hydrogen pressure leads to a rearrangement of the intermetallic structure to a cubic AuCu_3 type with an increase in unit cell volume per formula unit by 3.6–3.9%. Gravimetric analysis suggests a composition $\text{InPd}_3\text{H}_{\approx 0.8}$ for the hydrogenation product. Very similar behaviour is found for the deuteration of InPd_3 .

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1. Introduction

Ever since Graham's observation in 1866 of a considerable uptake of gaseous hydrogen by palladium [1,2], the metal and its intermetallic compounds have been extensively studied with respect to hydrogen sorption properties, hydrogen embrittlement, electronic and magnetic properties of the hydrides, etc. [3–5]. Ternary hydrides of palladium exhibit a large variety of structures and bonding properties, ranging from typical interstitial metallic hydrides [5] to semiconducting complex hydrides with 18-electron anionic hydrido metallate complexes [6,7].

Some palladium rich compounds exhibit a considerable reactivity towards hydrogen, such as MPd_3 phases ($M=\text{Mg}$ [8,9], Ca [10], Y [11], Mn [12], Ce [13]), which form binary hydrides $\text{MPd}_3\text{H}_{\leq 1}$. The crystal structures of palladium rich intermetallics can often be derived from a cubic closest packing (ccp, Cu type) of atoms by an ordered substitution [14]. Recently, it was found that their order is very susceptible to the presence of hydrogen, even more than to synthesis conditions, such as temperature, cooling rates and annealing time. Hydrogen induced rearrangement of the atoms in palladium rich intermetallics was observed for MnPd_3 [15] and MgPd_3 [8,9]. In order to shed more light on this phenomenon we aim at a systematic investigation of the hydrogenation behaviour of this class of compounds, and as a part of this study present here the case of palladium rich compounds of aluminium, gallium and indium.

2. Experimental details

2.1. Synthesis of intermetallic compounds

Intermetallic compounds were synthesized in evacuated sealed silica ampoules. Stoichiometric amounts of the elements (aluminium pieces cut from a rod, 99.999%, ChemPur; gallium pieces, 99.999%, ChemPur; indium pieces, 99.99%, Schuchard; palladium powder, $< 60 \mu\text{m}$, 99.9%, ChemPur) were placed inside the silica ampoules and iodine (Merck, purified by sublimation, $\approx 1 \text{ mol}\%$ with respect to the group III metal) was added to enhance the reactivity by means of chemical vapour transport. In the case of GaPd_2 an additional corundum crucible inside the silica tube had been used, in order to avoid reaction of the products with the silica from the ampoule at higher temperatures (see below). The ampoules were sealed in vacuum while cooling the starting materials with liquid nitrogen in order to avoid sublimation of iodine. The silica ampoules were heated at 50 K/min to 1100 K (GaPd_2), 850 K (AlPd_2 , AlPd_3 , $\text{Ga}_5\text{Pd}_{13}$, In_3Pd_5 , InPd_2 , InPd_3 in ZrAl_3 type) and 750 K (InPd_3 in TiAl_3 type), respectively, kept at this temperature for 55 h and quenched in air. Iodine was sublimed off the products by gently heating one end of the ampoule. The syntheses produced the intermetallic compounds as grey powders, which were not sensitive to air. In some cases regrinding of the products, addition of fresh iodine and repetition of the heat treatment in evacuated silica ampoules were necessary in order to yield single phase products. For InPd_3 only the ZrAl_3 type structure could be prepared in single phase, whereas the modification in the TiAl_3 type did always contain

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Table 1
Hydrogenation (deuteration) of palladium rich intermetallics of aluminium, gallium and indium in an autoclave (see Section 2.2) or during an *in situ* thermal analysis, DSC (entries in italics, see Section 2.3) under various hydrogen (deuterium) gas pressures p , temperatures T and reaction times t .

Compound	$p(\text{H}_2/\text{D}_2)$ (MPa)	T (K)	t (h)	Space group	Z	Lattice parameters (pm)	Unit cell volume (10^6pm^3)	ΔV (%)
AlPd ₂				<i>Pnma</i>	4	<i>a</i> =542.91(2) <i>b</i> =405.58(2) <i>c</i> =777.11(3)	171.11(1)	
	39.0 (H)	500	22.5	<i>Pnma</i>	4	<i>a</i> =542.95(2) <i>b</i> =406.05(1) <i>c</i> =777.57(3)	171.43(1)	0.2
	2.8 (H)	700	1	<i>Pnma</i>	4	<i>a</i> =542.45(3) <i>b</i> =405.36(2) <i>c</i> =776.79(4)	170.81(1)	−0.2
AlPd ₃				<i>Pmc2</i> ₁	6	<i>a</i> =402.81(3) <i>b</i> =1580.4(1) <i>c</i> =540.48(4)	344.06(4)	
	8.0 (H)	293	597	<i>Pmc2</i> ₁	6	<i>a</i> =402.87(4) <i>b</i> =1585.2(1) <i>c</i> =541.74(5)	345.98(6)	0.6
	36.5 (H)	523	163	<i>Pmc2</i> ₁	6	<i>a</i> =402.78(1) <i>b</i> =1580.74(3) <i>c</i> =540.60(1)	344.19(1)	0.0
	2.5 (H)	700	1	<i>Pmc2</i> ₁	6	<i>a</i> =402.94(2) <i>b</i> =1582.33(6) <i>c</i> =540.60(1)	344.68(2)	0.2
GaPd ₂				<i>Pnma</i>	4	<i>a</i> =549.12(7) <i>b</i> =406.21(4) <i>c</i> =779.4(1)	173.85(4)	
	37.5(H)	523	60	<i>Pnma</i>	4	<i>a</i> =549.14(6) <i>b</i> =406.27(4) <i>c</i> =780.31(9)	174.09(3)	0.1
Ga ₅ Pd ₁₃				<i>C2/m</i>	2	<i>a</i> =2420.5(2) <i>b</i> =404.86(3) <i>c</i> =543.54(4) β =102.645(5)	519.71(7)	
	8.0 (H)	293	597	<i>C2/m</i>	2	<i>a</i> =2428.59(6) <i>b</i> =404.78(1) <i>c</i> =545.13(1) β =102.594(3)	522.99(2)	0.6
	5.3 (D)	523	23.5	<i>C2/m</i>	2	<i>a</i> =2425.14(6) <i>b</i> =404.91(1) <i>c</i> =544.62(1) β =102.634(3)	521.85(2)	0.4
	0.2 (H)	700	1	<i>C2/m</i>	2	<i>a</i> =2424.26(9)	521.27(3)	0.3

In ₃ Pd ₅						<i>Pbam</i>	2	<i>b</i> =404.88(1) <i>c</i> =544.36(2) <i>β</i> =102.645		
	14.0 (H)	293	50			<i>Pbam</i>	2	<i>a</i> =1104.19(2) <i>b</i> =561.345(7) <i>c</i> =424.261(6)	262.971(6)	
	14.0 (H)	523	50			<i>Pbam</i>	2	<i>a</i> =1104.33(3) <i>b</i> =561.42(1) <i>c</i> =424.25(1)	263.03(1)	0.0
InPd ₂								<i>a</i> =1104.24(2) <i>b</i> =561.385(8) <i>c</i> =424.273(6)	263.008(6)	0.0
						<i>Pnma</i>	4	<i>a</i> =561.674(6) <i>b</i> =421.709(4) <i>c</i> =822.776(8)	194.885(3)	
	14.0 (H)	293	50					<i>a</i> =561.675(6) <i>b</i> =421.685(4) <i>c</i> =822.80(8)	194.881(3)	0.0
InPd ₃ (TiAl ₃ type)	14.0 (H)	523	50					<i>a</i> =561.736(6) <i>b</i> =421.685(4) <i>c</i> =822.913(8)	194.928(3)	0.0
						<i>I4/mmm</i>	4	<i>a</i> =410.03(3) <i>c</i> =747.84(8)	125.73(2)	
	1.7 (H)	293	24.5			<i>I4/mmm</i>	4	<i>a</i> =410.20(1) <i>c</i> =748.27(4)	125.91(1)	0.1
InPd ₃ (ZrAl ₃ type)	2.3 (H)	523	17.5			<i>Pm3m</i>	1	<i>a</i> =402.680(5)	65.295(1)	3.9
	18.9 (H)	523	120.5			<i>Pm3m</i>	1	<i>a</i> =402.671(5)	65.291(1)	3.9
	2.0 (H)	523	1			<i>Pm3m</i>	1	<i>a</i> =402.669(7)	65.290(2)	3.9
						<i>I4/mmm</i>	2	<i>a</i> =406.675(7) <i>c</i> =1520.90(4)	251.534(5)	
	1.7 (H)	293	24.5			<i>I4/mmm</i>	2	<i>a</i> =406.815(6) <i>c</i> =1522.76(4)	252.014(5)	0.2
InPd ₃ (ZrAl ₃ type)	2.3 (H)	523	17.5			<i>Pm3m</i>	1	<i>a</i> =402.658(5)	65.284(1)	3.8
	18.9 (H)	523	120.5			<i>Pm3m</i>	1	<i>a</i> =402.671(5)	65.291(1)	3.8
	5.3 (D)	523	23.5			<i>Pm3m</i>	1	<i>a</i> =402.48(1)	65.196(3)	3.7
	1.3 (H)	523	1			<i>Pm3m</i>	1	<i>a</i> =402.369(4)	65.144(1)	3.6

ΔV gives the relative increase of the unit cell volumes per formula unit upon hydrogenation (deuteration). Note that in the case of InPd₃ the unit cell is halved (TiAl₃ type) or quartered (ZrAl₃ type) upon hydrogenation to the cubic hydride (deuteride), which is taken into account for the calculation of ΔV .

considerable amounts (typically 30–40%) of the former modification.

2.2. Hydrogenation of intermetallic compounds in an autoclave

Finely ground intermetallics were put in crucibles machined from hydrogen-resistant Nicrofer® 5219 Nb-alloy 718 and charged with hydrogen (99.999%, Praxair) or deuterium gas (isotopic purity 99.8%, chemical purity 99.999%, Praxair) in an autoclave made from the same alloy. The autoclave was heated within two hours to the temperatures given in Table 1 and held at those temperatures for periods of time given in Table 1. After cooling back to room temperature, the gas pressure was released and the samples were prepared for XRPD (see chapter 2.4). None of the hydrogenated samples was found to be sensitive to air. The results were fully reproducible and did not depend on the amount of starting material, which varied between 0.2 and 2.0 g.

2.3. In situ thermal analysis (DSC)

Differential scanning calorimetry was performed *in situ* under hydrogen pressures of up to 2.8 MPa on a Q1000 DSC (TA Instruments) equipped with a gas pressure chamber. 20–30 mg of the powdered intermetallics were put in aluminium crucibles, which were closed with aluminium lids. These were placed inside the pressure chamber, which was then purged several times with hydrogen gas before filling it to the desired hydrogen gas pressure. The samples were heated at a rate of 10 K/min, held at the final temperature for 1 h and cooled back to 300 K at 10 K/min. Usually, two or three such runs were performed, before the hydrogen pressure was released, the sample taken out and structural characterization undertaken.

2.4. X-ray powder diffraction (XRPD)

XRPD 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 $\text{CuK}\alpha 1$ radiation, $\lambda=154.056$ pm). Rietveld refinements were carried out with the programme FULLPROF [16] and pseudo-Voigt as profile function.

3. Results and discussion

In this work we study the hydrogenation behaviour of palladium rich intermetallics of aluminium, gallium and indium by X-ray powder diffraction (XRPD) and *in situ* differential scanning calorimetry (DSC). An uptake of hydrogen by the intermetallic compound and the subsequent formation of a metal hydride can be monitored by the thermal signal from the reaction enthalpy in DSC and by the increase in the unit cell volume as seen by XRPD caused by the expansion due to interstitial hydrogen in the intermetallic matrix. By the combination of both methods useful information on the hydrogen absorption properties of intermetallic compounds can be collected conveniently.

XRPD of the intermetallics AlPd_2 , AlPd_3 , GaPd_2 , $\text{Ga}_5\text{Pd}_{13}$, In_3Pd_5 , and InPd_2 before and after hydrogenation shows very similar patterns, i.e. the structure types of the respective compounds are retained. For the before mentioned aluminium and gallium compounds, a weak DSC signal (Fig. 1) and a slight increase in unit cell volume could be detected (Table 1), indicating a moderate hydrogen uptake by incorporating hydrogen atoms in interstitial sites. The latter effect is most notable at room temperature and decreases with increasing temperature, most

probably reflecting an increased desorption pressure. However, even for the largest value amongst the before mentioned compounds, 0.6% unit cell volume increase at room temperature and 8.0 MPa hydrogen pressure in AlPd_3 and $\text{Ga}_5\text{Pd}_{13}$, it has to be noted that this increase is rather small when compared to other typical relative volume enhancements, e.g. 12% from elemental palladium to its hydride, $\text{PdH}_{0.7}$. The slight unit cell volume decrease (negative ΔV) observed in AlPd_2 (Table 1) is probably due to an increased ordering within the intermetallic compound upon heat treatment in hydrogen atmosphere. This is concluded from the fact that XRPD reflections become more narrower upon hydrogenation, indicating improved crystallinity and an increased order.

In contrast to the above mentioned compounds InPd_3 (ZrAl_3 type [17]) shows a large exothermic signal in the *in situ* DSC measurement by heating in the first run, but no signals upon cooling and in the subsequent runs, indicating an irreversible reaction (Fig. 2). XRPD of the product after the DSC runs shows a

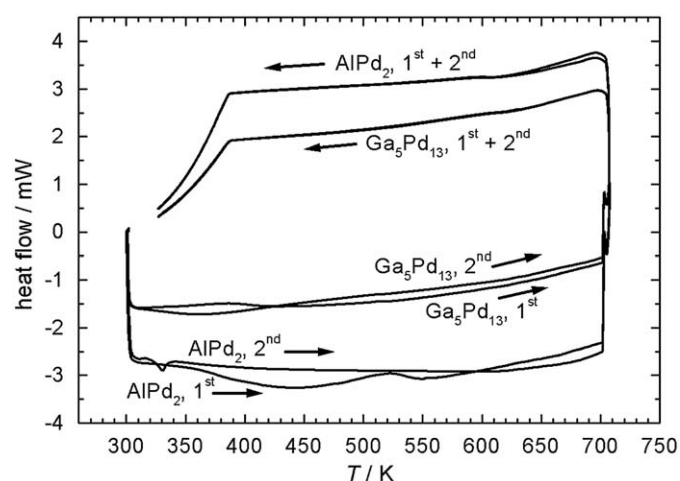


Fig. 1. *In situ* DSC of the hydrogenation of AlPd_2 and $\text{Ga}_5\text{Pd}_{13}$ at 2.8 and 0.2 MPa hydrogen pressure, respectively, showing only very weak thermal signals (compare to Fig. 2). Heating and cooling rates 10 K/min. 1st and 2nd denote first and second cycles of the measurement on the same sample.

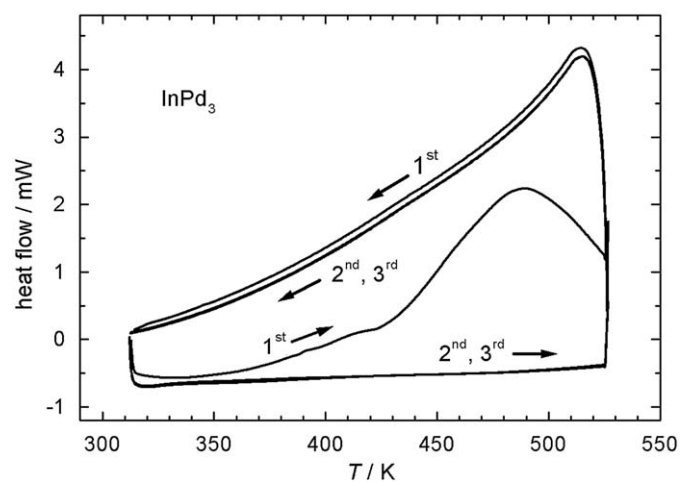


Fig. 2. *In situ* DSC of the hydrogenation of tetragonal InPd_3 (ZrAl_3 type) at 1.3 MPa hydrogen pressure. Heating and cooling rates 10 K/min. 1st: first cycle showing exothermic hydrogen uptake and formation of $\text{InPd}_3\text{H}_{\approx 0.8}$; 2nd, 3rd: second and third cycles of the measurement on the same sample without further thermal effects.

new diffraction pattern, which could be indexed to a cubic primitive lattice with a lattice parameter of 402.4 pm. Intensities are in agreement with a AuCu_3 type structure and the refinement resulted in a good match of observed and calculated powder data with $a=402.369(4)$ pm (Figs. 3 and 4). Hydrogen positions cannot be derived from XRPD data, but the analogy to other MPd_3 hydrides (see above) suggests an anti-perovskite type with statistical distribution of hydrogen atoms in $[\text{Pd}_6]$ voids. Because of the spatial separation of these sites, well above the so-called ‘blocking radius’ [18], ordering of the statistically distributed hydrogen atoms like in some Laves phase hydrides [19–21] is unlikely. The unit cell volume per formula unit increases by 3.6–3.8% as compared to the parent intermetallic, indicating a considerable hydrogen uptake. Gravimetric analysis of a larger sample suggests a hydrogen content of $\text{InPd}_3\text{H}_{\approx 0.8}$. The corresponding reaction of InPd_3 with

deuterium results in a deuteride with the same AuCu_3 type for the metallic substructure and very similar lattice parameters and deuterium content.

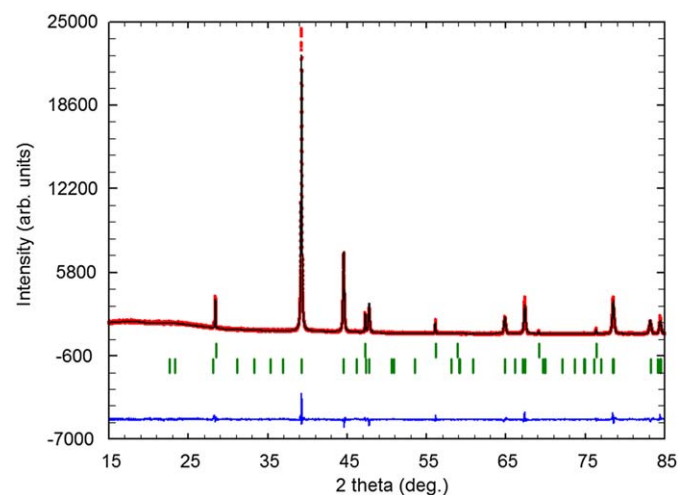


Fig. 3. Rietveld refinement of the crystal structure of tetragonal InPd_3 (ZrAl_3 type) on X-ray powder diffraction data ($\text{CuK}\alpha_1$ radiation). Observed (circles), calculated (solid line) and difference (observed–calculated; bottom) X-ray powder diffraction patterns. Markers indicate Bragg peak positions of the internal silicon standard (top) and InPd_3 (bottom). Intensity in arbitrary units.

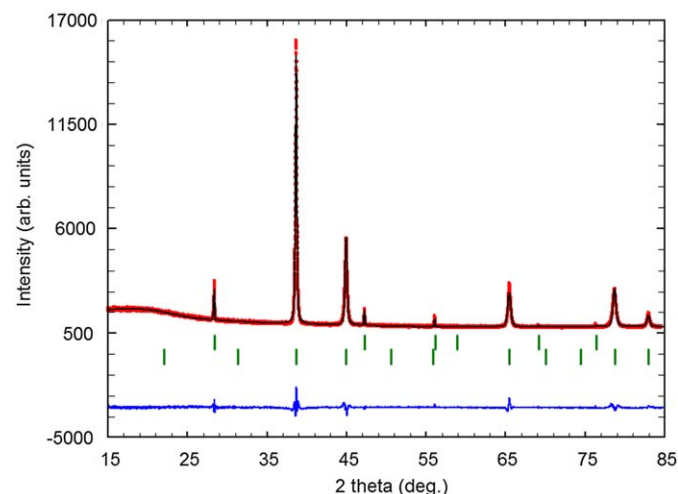


Fig. 4. Rietveld refinement of the crystal structure of cubic $\text{InPd}_3\text{H}_{\approx 0.8}$ (metal substructure in AuCu_3 type, $a=402.369(4)$ pm) on X-ray powder diffraction data ($\text{CuK}\alpha_1$ radiation). Observed (circles), calculated (solid line) and difference (observed–calculated; bottom) X-ray powder diffraction patterns. Markers indicate Bragg peak positions of the internal silicon standard (top) and $\text{InPd}_3\text{H}_{\approx 0.8}$ (bottom). Intensity in arbitrary units.

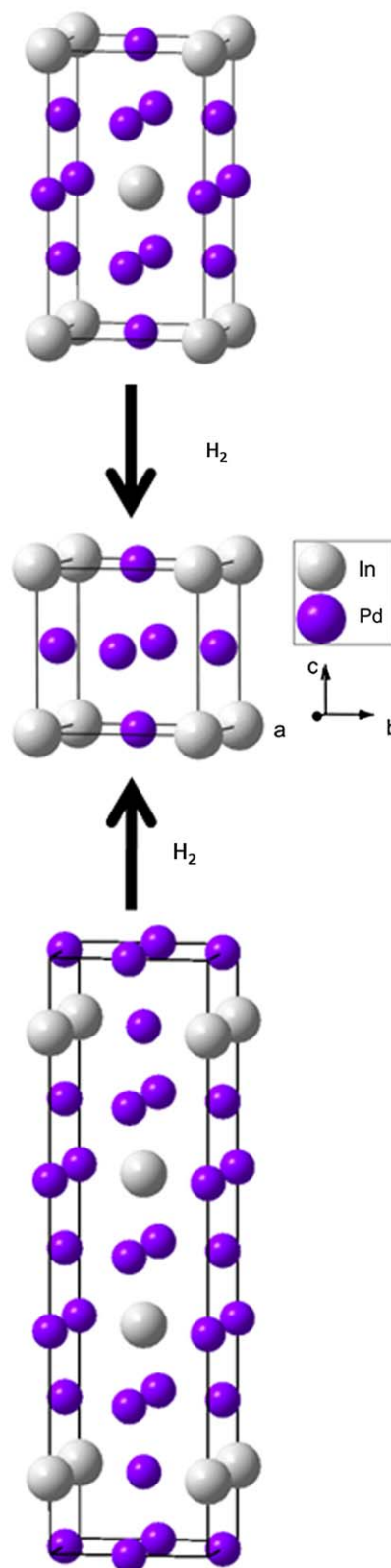


Fig. 5. Rearrangement of the intermetallic crystal structures of InPd_3 before (top: TiAl_3 type, bottom: ZrAl_3 type) to the AuCu_3 type (middle) after hydrogenation. Note that all shown structures are ordered, two of them distorted, variants of a cubic closest packing.

The same behaviour upon hydrogenation and deuteration was found for the InPd_3 modification in the TiAl_3 type [17]. The latter is the first TiAl_3 type compound, for which a hydrogen induced rearrangement to the AuCu_3 type structure has been observed. The structural relationship of the starting materials, InPd_3 in the TiAl_3 and in the ZrAl_3 type, to the product in a AuCu_3 type structure is shown in Fig. 5. All the three structures represent ordered, two of them also tetragonally distorted, variants of a cubic closest packing. Furthermore, the TiAl_3 and the ZrAl_3 type can be derived from the AuCu_3 type by introducing anti-phase boundaries $1/2$ [110]. The enhanced reactivity of compounds with AuCu_3 type related structures towards hydrogen was explained by a possible hydrogen assisted gliding along $1/2$ [110] (direction with respect to AuCu_3 type lattice) within these structures. The findings discussed in this paper support this idea, since the only good hydrogen absorber in the series of palladium rich compounds of aluminium, gallium and indium, was found to be the two modifications of InPd_3 , both of which belong to the above mentioned AuCu_3 type related structures. Even the structurally closely related AlPd_3 and $\text{Ga}_5\text{Pd}_{13}$, which also are ordered ccp variants [14], but cannot be derived from the AuCu_3 type by introducing anti-phase boundaries $1/2$ [110], show considerably less activity towards hydrogen and do not exhibit any hydrogen induced structural changes. Furthermore, the *in situ* DSC data (Fig. 2) suggest that the hydrogenation of InPd_3 is already complete at temperatures below 500K, i.e. only a small activation energy is necessary for the hydrogen induced structural rearrangement to the AuCu_3 type.

4. Conclusion

The hydrogenation of palladium rich intermetallic compounds of aluminium, gallium and indium has been studied by *in situ* DSC and *ex situ* XRPD. Negligible hydrogen absorption was found for AlPd_2 , AlPd_3 , GaPd_2 , $\text{Ga}_5\text{Pd}_{13}$, In_3Pd_5 , and InPd_2 . Both the modifications of InPd_3 form a hydride $\text{InPd}_3\text{H}_{\approx 0.8}$ in an exother-

mic reaction. The hydride crystallizes in a cubic AuCu_3 type arrangement ($a=402.369(4)$ pm) for the metal atoms. The hydrogenation of InPd_3 is a further example for the hydrogen induced removal of anti-phase boundaries $1/2$ [110] in AuCu_3 type related structures and the first one with a TiAl_3 type structure for an intermetallic before hydrogenation. *In situ* DSC has proven to be an effective tool for screening the hydrogen absorption by intermetallic compounds.

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