The anti-perovskite type hydride InPd$_3$H$_{0.89}$

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**Abstract**

Hydrogenation of tetragonal InPd$_3$ in the ZrAl$_3$ type structure (four-fold ccp superstructure) yields a hydride with a cubic AuCu$_3$ type structure (one-fold ccp superstructure). Deuterium can be located by Pd powder diffraction in octahedral voids surrounded exclusively by palladium, [Pd$_6$], which are 88.5(6)% occupied in a statistical manner. The resulting deuteride InPd$_3$D$_{0.89}$ thus crystallizes in a cubic anti-perovskite type structure (space group Pm$ar{3}$m (no. 221), a = 402.25(1) pm at 299(2) K). The Pd–D distance of 201.13(1) pm is typical for interstitial hydrides with palladium. Inelastic neutron scattering on the hydride InPd$_3$H$_{0.89}$, which shows a spectrum similar to that of binary palladium hydride, confirms the cubic site symmetry of hydrogen in [Pd$_6$] interstices. This is also confirmed by the absence of any quadrupole splitting in the $^1$H NMR signal of the deuteride. $^1$H NMR spectra of InPd$_3$H$_{0.89}$ do not show any motional narrowing. Values found for the H jump rate $\tau$ in InPd$_3$H$_{0.89}$ remain below 10$^6$ s$^{-1}$ in the studied temperature range 28–360 K, indicating a small hydrogen mobility in InPd$_3$H$_{0.89}$ as compared with binary palladium hydride, PdH$_{0.6}$, as this can be attributed to the large spatial separation of the [Pd$_6$] sites.

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1. Introduction

It has long been known since the 19th century [1,2] that palladium can take up considerable amounts of gaseous hydrogen. Ever since, palladium and palladium containing intermetallic phases have been used as model systems to ascertain the effect of hydrogen uptake on the structural, magnetic, electronic, optical, and mechanical properties of metallic systems [3–5]. Crystal structures and bonding properties of the ternary palladium hydrides show a huge variation, from the metallic interstitial hydrides, which can possess a variable hydrogen content [5], to the semiconducting complex hydrides with palladium–hydrogen bonding involving 18-electron anionic hydrido metallic complexes with fixed hydrogen content [6,7].

Crystal structures of Pd-rich intermetallics often resemble that of the cubic close packing (ccp, Cu type) of palladium itself. In the case of main-group metals substituting for palladium, ordered superstructures are typically found instead of ccp-based solid solutions. For some of these Pd-rich intermetallic compounds forming ccp superstructures, H-induced rearrangement of the atoms was observed. In MnPd$_3$ [8], MgPd$_3$ [9], and TiPd$_3$ [10], the metal sublattice changes from a tetragonal four-fold ccp superstructure (ZrAl$_3$ type with $a$, $a$, $4a$) to a cubic AuCu$_3$ type with hydrogen (deuterium) incorporated into [Pd$_6$] voids surrounded exclusively by palladium atoms. X-ray powder diffraction and in situ thermal analysis data indicate that the same type of transformation also occurs in InPd$_3$ starting from either its ZrAl$_3$ or TiAl$_3$ type structural arrangement [11]. Hydrogen (deuterium) positions in the hydride (deuteride) formed have thus far not been determined. In this paper, we report on the full crystal structure of the deuteride of InPd$_3$ and the location of deuterium atoms by neutron powder diffraction (NPD), as well as on the dynamics of hydrogen by inelastic neutron scattering (INS) and nuclear magnetic resonance (NMR) spectroscopy.

2. Experimental details

2.1. Synthesis of intermetallic compounds, hydrides, and deuterides

Stoichiometric mixtures of indium pieces (99.99%, Schuchardt$^1$) and palladium powder (99.9%, < 60 μm, ChemPur) were placed in a silica tube and 0.35 mol% (with respect to In) of freshly sublimed iodine added to enhance the reactivity by means of chemical vapor transport. The silica ampoules were heated 50 K/h to 850 K, vapor transport. The silica ampoules were heated 50 K/h to 850 K,

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$^1$ Certain commercial suppliers are identified in this paper to foster understanding. Such identification does not imply our recommendation or endorsement nor does it imply that the materials or equipment identified are necessarily the best for the purpose.

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2.3. Neutron powder diffraction (NPD)

Neutron powder diffraction data on deuterated InPd$_3$ 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 $6 \leq 2\theta \leq 157^\circ$ (step size $\Delta 2\theta=0.05^\circ$) during a total measuring time of 12 h. Special care was taken for the enhanced neutron absorption of indium by using a moderate sample thickness (3.2 g InPd$_3$ 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 $\lambda=190.931(3)$ pm for D1A and kept fixed during refinements.

2.4. Inelastic neutron scattering (INS)

Inelastic neutron scattering measurements of the hydrogen vibrational spectrum at 4 K were performed on the filter-analyzer neutron spectrometer (FANS) [14] at the NIST Center for Neutron Research (Gaithersburg, MD, USA). The measured range of the neutron energy loss was 40–208 meV with an energy resolution varying from 2.4% to 3.3% of the energy transfer.

2.5. Nuclear magnetic resonance spectroscopy (NMR)

NMR measurements were performed on a modernized Bruker SXP pulse spectrometer with quadrature phase detection at the frequencies $\omega/2\pi=23.8$ and 90 MHz (for $^1$H) and 61.4 MHz (for $^2$D). For $^1$H NMR measurements, the magnetic field was provided by a 2.1 T iron-core Bruker magnet, and a home-built multi-nuclear continuous-wave NMR magnetometer working in the range 0.32–2.15 T was used for field stabilization. For $^2$D NMR measurements, the magnetic field was provided by a 9.4 T Oxford superconducting solenoid. For rf pulse generation, we used a home-built computer-controlled pulse programmer, the PTS frequency synthesizer (Programmed Test Sources, Inc.), and a 1 kW Kalmus wideband pulse amplifier. Typical values of the $\pi/2$ pulse length were 2–3 µs. A probehead with the sample was placed into an Oxford Instruments CF1200 continuous-flow cryostat using helium or nitrogen as cooling agents. The sample temperature, monitored by a chromel-(Au–Fe) thermocouple, was stable to $\pm 0.1$ K. The nuclear spin-lattice relaxation rates were measured using the saturation—recovery method. In all cases, the recovery of the nuclear magnetization could be satisfactorily described by a single exponential function. NMR spectra were recorded by Fourier transforming the spin echo signals.

3. Results and discussion

3.1. The crystal structure of InPd$_3$H$_{0.89}$

InPd$_3$ was shown to belong to a group of compounds MPd$_3$, with tetragonal superstructures of the cubic close packing (ccp) which exhibit a considerable reactivity towards hydrogen and form binary hydrides MPd$_3$H$_x$. Upon hydrogenation (deuteration), InPd$_3$ transforms from either a tetragonal TiAl$_3$ (two-fold ccp superstructure) or a tetragonal ZrAl$_3$ type arrangement (four-fold ccp superstructure) to a cubic AuCu$_3$ type (one-fold ccp superstructure), $a=402.702(4)$ pm for the hydride, $a=402.25(1)$ pm for the deuteride at $T=299(2)$ K for the metal sublattice as shown by XRPD [11]. Neutron powder diffraction (NPD) experiments on a deuterated sample of InPd$_3$ now confirm this finding. Fig. 1 shows the NPD data that are in accordance with a single phase of cubic InPd$_3$ (AuCu$_3$ type) with interstitial deuterium atoms.

The location of deuterium positions was found by difference Fourier techniques. Deuterium was found to occupy octahedral interstices surrounded by palladium atoms only, [Pd$_6$], with an occupation of 88.5(6)% in a statistical manner, while other octahedral voids like [In$_2$Pd$_4$] are empty. Full occupation of this site would correspond to a cubic perovskite type AMX$_3$, in which the metal M occupies the position of the non-metal X and vice versa. The resulting AXM$_3$ type is often called cubic antiperovskite, although not all cation and anion positions are interchanged. Thus, the structure of the hydride (deuteride) of InPd$_3$ can be considered as a defect variant of the cubic anti-perovskite type (Table 1, Fig. 2) and the refined deuterium content corresponds to the formula InPd$_3$D$_{0.89}$.

The palladium–deuterium distance of 201.13(1) pm is comparable to the palladium–deuterium distances in the isotypic MnPd$_3$H$_{0.7}$ (196.3 pm [15]) and MgPd$_3$H$_{0.7}$ (199.10(1) pm [9]), but is considerably longer than in typical homoleptic hydrido palladium complexes (160–184 pm [16]), indicating a metallic rather than a covalent metal–deuterium bonding. This agrees well with the dynamic behavior of hydrogen typical for metallic hydrides (see Section 3.2). In contrast to the cubic anti-perovskite type deuteride CeRh$_3$D$_{0.84}$ [17], the deuterium atom in InPd$_3$D$_{0.89}$...
exhibits a rather moderate thermal displacement parameter, which may be explained by the smaller [Pd6] void in the latter as compared to the former. As in other hydrides, e.g. LaNiInD1.63 [18] or Ba9In4H [19], hydrogen (deuterium) does not coordinate indium. In InPd3D0.89, deuterium atoms avoid the neighborhood of indium by occupying only [Pd6] voids.

Hydrides of intermetallics with non-stoichiometric composition with respect to hydrogen often exhibit temperature driven ordering phenomena within the hydrogen substructure, giving rise to structural phase transition and drastic changes in hydrogen diffusion properties [20,21]. However, since the large spatial separation of these deuterium sites in InPd3D0.89 (shortest distance is d = 402.25(1) pm) is well above the so-called 'blocking radius' [20], the D–D repulsion is relatively low, making ordering at low temperatures less likely. Nonetheless, whether or not ordering occurs in such MPd3 hydrides (deuterides) is an open question, regarding which the INS and NMR measurements reported in the next section may shed some light. These were also performed with the aim to learn more about possible diffusion processes. Contrary to many other intermetallic hydrides, the hydrogen positions in MPd3 (M = Mg, In, Tl, Mn) are well separated from each other, i.e., long-range hydrogen diffusion pathways would have to involve [MPd4] voids, which thus far were only found to be occupied in the a modification of the hydride MgPd3H0.79rx0.94 [22]. Despite the structural similarities to PdHx (i.e., the same hydrogen local environment) in which hydrogen exhibits rather fast diffusion processes, there is no direct information on hydrogen diffusion rates in MPd3 hydrides.

3.2. Hydrogen dynamics in InPd3H0.89

For metal-hydrogen systems, inelastic neutron scattering (INS) spectra in the energy transfer range 40–150 meV are usually dominated by the fundamental modes of H optical vibrations. The simplest description of these vibrations is based on the model of a three-dimensional Einstein oscillator [23,24]. For the cubic point symmetry of H sites, this model predicts a single peak in an INS spectrum in the energy transfer range of the fundamental modes. For lower point symmetries of H sites, this peak should be split into either two peaks with the intensity ratio 2:1 (for axial symmetry) or three peaks of nearly equal intensity (for symmetries lower than axial). The measured low-temperature INS spectrum for InPd3H0.89 is shown in Fig. 3. This spectrum is dominated by a single peak...

Table 1

Crystal structure data of InPd3D0.89 as refined from neutron powder diffraction data at room temperature (T = 299(2) K) and interatomic distances (pm) below 350 pm.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Rint/10^6 pm^2</th>
<th>Occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.11(5)</td>
<td>1</td>
</tr>
<tr>
<td>Pd</td>
<td>3c</td>
<td>0</td>
<td>1/2</td>
<td>1/2</td>
<td>0.36(3)</td>
<td>1</td>
</tr>
<tr>
<td>D</td>
<td>1b</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>1.66(7)</td>
<td>0.885(6)</td>
</tr>
</tbody>
</table>

R_p = 0.060 R_w = 0.075 R_w' = 0.281 R_w'' = 0.138 R_w'''' = 0.030 R_p = 0.060 R_w = 0.075 R_w' = 0.281 R_w'' = 0.138 R_w'''' = 0.030

R_p = 0.060 R_w = 0.075 R_w' = 0.281 R_w'' = 0.138 R_w'''' = 0.030

Definition of R factors: R_p = \sum |y/(obs) - y/(calc)|/\sum y/(obs); R_w = \sum w|y/(obs) - y/(calc)|^2/\sum w y/(obs) |25,26| R_w"" and R_w"" are calculated as above but using background corrected counts; R_w'' = \sum |y/(obs) - y/(calc)|/\sum 2y/(obs). Form of the temperature factor: exp[-B_m/2(sin^2 l/l)^2].

Fig. 2. Crystal structure of InPd3D0.89 in the cubic anti-perovskite type (In: large, pink spheres; Pd: middle, blue; D: small, white) (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Fig. 3. The low-temperature INS spectrum for InPd3H0.89. Vertical error bars associated with the data points correspond to one standard deviation.
centered at the energy transfer of 82 meV. This is consistent with the octahedral diﬀraction data showing that H atoms occupy only the octahedral sites with [Pd6] coordination. If a considerable fraction of H atoms were located at the sites with [In2Pd4] coordination, we would expect a splitting of the sharp peak of the INS spectrum. The small high-energy ‘shoulder’ near 100 meV is almost certainly an optoacoustic multiphonon sideband originating from a combination of the fundamental optical mode and the lower-energy acoustic phonon band, as typically seen in other metal-hydride systems [25,26]. The broad band centered at the energy transfer of ~175 meV can be attributed to the second-order (two-phonon) transition, which is expected to appear at nearly double the energy of the fundamental peak.

The shape of the INS spectrum for InPd3H0.89 resembles but is considerably sharper than that for PdH0.7 [24,27,28]. This is not surprising since, in PdH0.7, hydrogen atoms also occupy the octahedral interstitial sites coordinated by six Pd atoms. However, for PdH0.7, the main peak is centered at lower values of the energy transfer (56–69 meV, depending on the H concentration [24]), reﬂecting a somewhat weaker bonding potential. Moreover, PdH0.7 exhibits a much more pronounced high-energy ‘shoulder’ originating from longitudinal optic modes with strong dispersion due to signiﬁcant H–H interactions [29] with the much smaller optoacoustic multiphonon sideband buried underneath. In contrast to PdH0.7, no neighboring octahedral sites are occupied in InPd3H0.89. Hence, its hydrogen atoms are better separated from each other, resulting in largely diminished dispersion eﬀects.

The temperature dependences of the 1H spin-lattice relaxation rates R1 measured at 23.8 and 90 MHz for InPd3H0.89 are shown in Fig. 4. The measured proton spin-lattice relaxation rate does not exhibit any pronounced frequency dependence, and its temperature dependence can be described by a linear function, R1(T) = C1T + R0. Such a behavior is typical of the low-temperature spin-lattice relaxation in metallic hydrides with low concentrations of paramagnetic impurities [30]. The R0 term can be identiﬁed as the low-temperature paramagnetic contribution to R1 resulting from the interaction of proton spins with conduction electrons [30]. The R0 term proportional to the temperature can be identiﬁed as the electronic (Korringa) contribution to R1 resulting from the interaction of proton spins with paramagnetic centers. The dashed line in Fig. 4 shows the linear ﬁt to the experimental R1(T) data at 90 MHz; the corresponding ﬁt parameters are C1 = (2.09 ± 0.04) × 10^{-3} s^{-1}K^{-1} and R0 = 0.02 ± 0.01 s^{-1}. It should be noted that the value of the Korringa constant C1 (which is proportional to the square of the density of electron states at the Fermi level [30]) for InPd3H0.89 is considerably lower than that for PdH0.7 (~1.4 × 10^{-2} s^{-1}K^{-1} for x in the range 0.70–0.80 [31,32]). In the studied temperature range 28–360 K, we cannot discern any contributions to R1 resulting from H jump motion. In metal-hydride systems, such contributions usually become important when the H jump rate τ^{-1} exceeds 10^6 s^{-1}, and leads to a frequency-dependent R1(T) peak when τ^{-1} becomes nearly equal to the resonance frequency ω [30]. Our R1 results indicate that the value of τ^{-1} in InPd3H0.89 remains below 10^6 s^{-1} at 360 K. This conclusion is supported by the absence of motional narrowing of the 1H NMR spectrum in InPd3H0.89. The measured width of the proton NMR spectrum at half-maximum is found to be nearly constant (~17 kHz) over the temperature range 28–300 K. This value of the line width is consistent with the calculated second moment of the 1H NMR line for the ‘rigid’ lattice of InPd3H0.89 <Δω^2> ≈ 1.26 × 10^9 s^{-2}. Comparison of our proton NMR results for InPd3H0.89 with those for Pd hydrides [31,32] shows that H mobility in PdH0.7 is much higher. For example, the measured R1(T) dependence for PdH0.7 at ω/2π = 47 MHz passes through a maximum close to 270 K [32], which indicates that τ^{-1} reaches the value 3 × 10^8 s^{-1} at this temperature. Such a strong diﬀerence between H mobilities in the hydrides with the same type (fcc) of host-metal sublattice can be accounted for in terms of the interse sites for the hydrogen sublattice. In PdH0.7, hydrogen atoms can occupy all octahedral interstitial sites of the fcc host-metal sublattice, and the distance between the nearest-neighbor octahedral sites is about 285 pm. In InPd3H0.89, hydrogen atoms occupy only the octahedral sites with [Pd6] coordination, leaving the [In2Pd4] sites empty; the corresponding distance between the nearest-neighbor sites of the H sublattice is 402 pm. Moreover, the nearest-neighbor H sites in InPd3H0.89 are separated by a Pd atom lying on the line connecting these sites (see Fig. 2). Both the large interse distances and the blocking eﬀect of Pd atoms are expected to inhibit hydrogen diﬀusion in InPd3H0.89.

Fig. 5 shows the temperature dependence of the 2D spin-lattice relaxation rate measured at 61.4 MHz for InPd3D0.89. As can be seen from the comparison of Figs. 4 and 5 for the isotope-substituted hydrides, the measured relaxation rates for 2D are much smaller than those for 1H. This originates mainly from the fact that the gyromagnetic ratio γD for 2D is about 6.5 times
smaller than that for \( ^1\text{H}, \gamma_{\text{H}} \). The low-temperature limit of the data shown in Fig. 5 is determined mainly by difficulties in measuring very small relaxation rates. As in the case of \( ^1\text{H} \) relaxation, the temperature dependence of the \( ^2\text{D} \) spin-lattice relaxation rate can be described by a linear function; this suggests that the \( ^2\text{D} \) relaxation rate is also dominated by electronic (Korringa) contribution. Assuming that the electronic structure of the deuteride is the same as that of the hydride, we expect that the Korringa contribution to the \( ^2\text{D} \) relaxation rate should be a factor of \((\gamma_{\text{H}}/\gamma_{\text{D}})^2 = 42.4 \) smaller than the corresponding contribution to the \( ^1\text{H} \) relaxation rate. The ratio of the experimental \( R_1 \) values for \( ^1\text{H} \) and \( ^2\text{D} \) at 310 K is 47.8. The shape of the \( ^2\text{D} \) NMR spectrum is close to a Gaussian line, and its width at half-maximum (3.3 kHz) remains unchanged over the studied temperature range 210–421 K. Apart from the absence of motional narrowing, these results suggest the cubic point symmetry of D sites. In fact, since deuterium nuclei have a non-zero electric quadrupole moment, the \( ^2\text{D} \) NMR spectrum may exhibit a quadrupole splitting \([33]\) if deuterium nuclei have a non-zero electric quadrupole moment, results suggest the cubic point symmetry of D sites at the centers of the \([\text{Pd}_6]\) octahedra.

4. Conclusion

Hydrogen introduces an atomic rearrangement from a tetragonal \( \text{ZrAl}_3 \) type structure (four-fold ccp superstructure) in \( \text{InPd}_3 \) to a cubic \( \text{AuCu}_3 \) type structure (one-fold ccp superstructure). Deuterium occupies the octahedral voids defined exclusively by palladium, \([\text{Pd}_6]\), to 88.5(6)% in a statistical manner as evidenced by neutron powder diffraction, i.e., \( \text{InPd}_3\text{D}_{0.89} \) crystallizes in a cubic antiperovskite type typical for palladium–deuterium distance of 201.13(1) pm is typical for interstitial hydrides with palladium. Inelastic neutron scattering on the hydride shows a spectrum similar to that of binary palladium hydride but with a sharper and higher-energy peak, which is in accordance with the cubic site symmetry of a \([\text{Pd}_6]\) interstice. This is also confirmed by the absence of any quadrupole splitting in the \( ^2\text{D} \)-NMR signal of the deuteride. The absence of motional narrowing of the \( ^1\text{H} \) NMR spectrum in \( \text{InPd}_3\text{H}_{0.89} \) and the relaxation rate \( R_1 \) indicate that the value of the H jump rate \( \tau_{\text{H}}^{-1} \) in \( \text{InPd}_3\text{H}_{0.89} \) remains below \( 10^6 \) s \(^{-1} \) in the studied temperature range 28–360 K. This small hydrogen mobility in \( \text{InPd}_3\text{H}_{0.89} \) compared to that in the binary palladium hydride, which is orders of magnitude larger, can be attributed to the large spatial separation of \([\text{Pd}_6]\) sites. Neither INS nor NMR measurements give any hint for a phase transition with ordering of the statistically occupied H(D) positions in \( \text{InPd}_3\text{H(D)}_{0.89} \) as in Laves phase hydrides \([34,35]\).

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