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Effect of hydrogenation on the crystal structure of La_2Pd_2In

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ABSTRACT

The paper is focusing on the modification of the crystal lattice upon the hydrogenation of La_2Pd_2In and hydrogen desorption from La_2Pd_2In hydrides. The synthesis at 1 bar of hydrogen produces a crystalline hydride with 1.5 H atoms per formula unit and the volume expansion of $\Delta V/V = 6.0\%$. The synthesis at 10 and 100 bar H_2 pressures leads to an amorphous state and with $4+\delta$ H atoms/f.u. The uptake of hydrogen leads to the decrease of the Debye temperature of La_2Pd_2In and modification of the optical phonon spectrum.

1. Introduction

The hydrogenation is long since established as the powerful tool for tuning the electronic structure of rare earth compounds. Usually it is considered as the instrument for tuning magnetic interactions both due to the negative chemical pressure and electron doping [1]. Consequently, primary objects of the hydrogenation studies are intermetallics with existing or incipient magnetic order. Yet the modification of the electronic density of the parent compound due to incorporated hydrogen atoms leads not only to weaker or stronger magnetic exchange interaction but it also affects the atomic bonding.

It has been shown that the “2:2:1” compounds on the basis of U or rare earths exhibit a significant tunability by the H absorption [2–8]. The uranium intermetallics absorb up to 2 H atoms/f.u. Their crystal lattice is expanded by the H uptake, which sometimes requires H pressure as high as 100 bar. The volume increase in U compounds can be substantial, reaching almost 8% in some cases [2], yet the tetragonal symmetry is often preserved [4]. The strengthening of magnetism, common in U compounds, is generally attributed to the 5f band narrowing due to enhanced atomic spacing in the hydrides. It is usual for hydrogen atoms to occupy the interstitials in the U3-Ni tetrahedra [4].

The “2:2:1” intermetallics containing rare-earth atoms, e.g. RE_2Ni_2X (RE = rare-earth metal; X = Mg, In) absorb H more willingly than their U-containing counterparts even at low pressures. The hydrogen content can reach 8 H atoms/f.u. in some cases (producing a monoclinic distortion) [9], although the hydrides with 4–5 H atoms/f.u. are more usual. The tendency to accommodate more H compared to the uranium “2:2:1” leads to an orthorhombic distortion (space group *Pbma*) and expansion by almost 22% [6,10]. It was suggested that for some compounds, e.g. RE_2Ni_2In, there exists the sequence of distinct hydrides with 2, 4, and 6 H atoms per formula unit [10]. So far the main attention was focused on Ni-containing intermetallics with only one recent exception [7], whereas the question concerning the physical properties of the “2:2:1” intermetallic hydrides with other transition metals remains open. Therefore, we have decided to synthesize and study the same series of the RE-compounds with Pd instead of Ni. The intermetallics with lanthanum are always the important reference systems because La, as the largest of the lanthanides, typically provides the largest possible H absorbing interstitials. Moreover, as non-magnetic material they can serve as reference compounds for subsequently investigated magnetic rare earths or Ce, the valence of which gets stabilized to Ce^{3+} by hydrogenation [7,8]. For the reasons stated above we have chosen the non-magnetic ternary La_2Pd_2In as the subject for the present study.

2. Experimental details

Polycrystalline ingots of La_2Pd_2In were obtained by arc melting in the Ar atmosphere of the constituent elemental metals in the stoichiometric proportion. The ingots were remelted several times in order to assure the sample homogeneity. The structure and composition of the synthesized intermetallic were verified by X-ray powder diffraction (XRD). The commercial Brucker D8 Advance diffractometer

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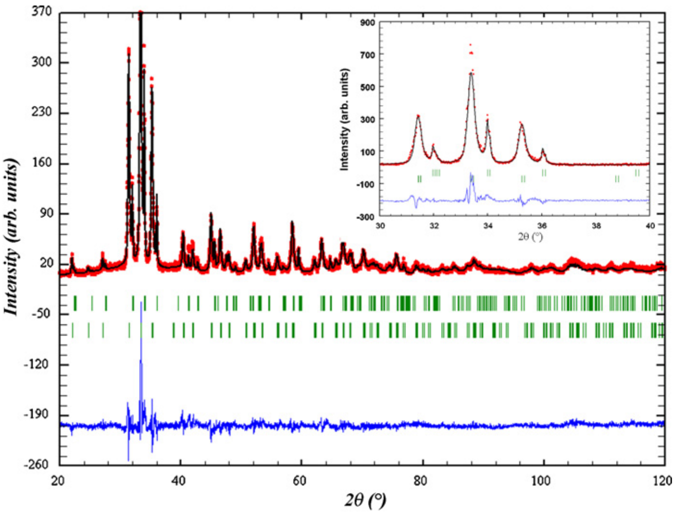

Fig. 1. Rietveld refinement of the powder X-ray pattern of $La_2Pd_2InH_{1.5}$. The highest (2 1 1) peak is truncated by the figure frame. The inset shows the low-angle detail of the XRD pattern with the peaks due to $La_2Pd_2InH_{1.5}$ and La_2Pd_2In. The upper row of the markers indicates the diffraction peaks from the parent compound and the lower one – from the hydride.

with the Cu K_α radiation was used for the data collection and the FullProf software package – for the Rietveld refinement.

The synthesized ingots were used for the hydrogenation, which was carried out at room temperature and the H_2 pressures of 1 bar, 10 bar, and 100 bar. Prior to the hydrogenation the ingots were crushed into sub-millimeter particles and activated in a dynamic vacuum (5×10^{-6} mbar) by heating to 250 °C for 2 h. After cooling to the room temperature the crushed polycrystal was exposed to the H_2 gas at a given pressure for at least 24 h. Hydrogen content was determined by measuring the pressure drop in the reaction chamber (error bar approx. 1%) during absorption as well as from the weight change during the hydrogenation (error bar approx. 10%). The difference between the number of the H atoms per formula unit (H at./f.u.) given by the two methods was within 10%. The samples synthesized at 1 bar were subsequently cycled in the H_2 atmosphere by heating up to 200 °C at the rate of 3 °C/min, holding at the elevated temperature and then cooling back at the same temperature rate.

Parts of the $La_2Pd_2InH_x$ samples were dehydrogenated by heating them in an evacuated reactor at the rate of 3 °C/min up to 750 °C. The dehydrogenation experiments were performed in 2 runs. At each run the sample was heated up to 750 °C in vacuum, then the reactor was disconnected from the rest of the hydrogenation apparatus and cooled down. The pressure of the released hydrogen was used to determine the composition of the sample, after which the released gas was pumped out and the whole procedure was repeated. The H content was also verified by measuring the weight change of the dehydrogenated material.

Crystal structure of the hydrides and the dehydrogenated samples was examined by the powder XRD. Specific heat measurements were performed at the commercial Physical Property Measurement System by Quantum Design. The hydride powder was compacted into thin pellets for this measurement.

3. Results

La_2Pd_2In absorbs hydrogen already at the pressure of 1 bar and the hydrogen content achieved at this pressure is $x_{H2} = 1.5 \pm 0.2$ H atoms per formula unit. The Rietveld refinement of the X-ray pattern of $La_2Pd_2InH_x$ has revealed that despite the cycling in the H_2 atmosphere up to 200 °C, a non-negligible amount of the parent intermetallic was still present (16%). The hydrogen content $x_{H2} = 1.5 \pm 0.2$ H atoms/f.u. was calculated from the pressure drop and the weight change during hydrogenation taking into account the presence of the residual La_2Pd_2In phase. The diffraction lines from both La_2Pd_2In and $La_2Pd_2InH_{1.5}$ can be clearly distinguished indicating that the material consists of the two distinct phases (Fig. 1).

It was determined that the crystal lattice formed by the metal atoms in the hydride has the same Mo_2FeBe_2-type structure (space group $P4/mbm$) as that of the parent compound. The atomic positions of hydrogen atoms cannot be determined by X-ray diffraction.

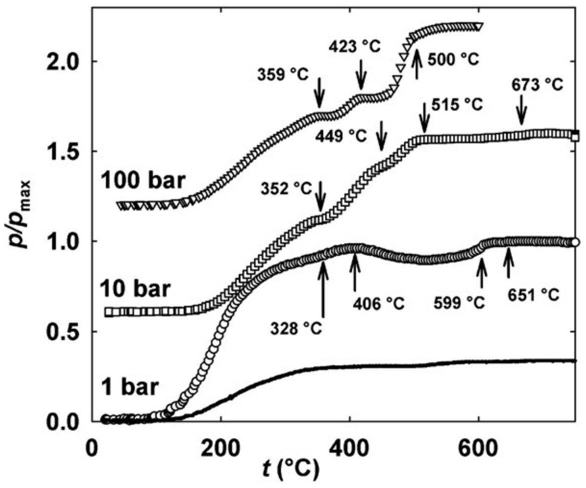

Fig. 2. Normalized decomposition curves for the La_2Pd_2In hydrides obtained at p_{H2} = 1 bar, 10 bar, and 100 bar. The solid line corresponds to the second decomposition run for the 1 bar hydride. The $p/p_{max}(t)$ curves are shifted by 0.6 with respect to each other for clarity. The arrows indicate the positions of the decomposition plateaus.

The alternative synthesis routes, namely the hydrogenation at room temperature and the higher pressures of 10 bar and 100 bar, have produced an amorphous material with no traces of a crystalline phase. The estimated hydrogen content in the high-pressure phases was 4 and 4.7 H atoms per formula unit for the synthesis pressures of 10 bar and 100 bar, respectively. The amorphisation of the $La_2Pd_2InH_{4+\delta}$ hydrides is similar to the behavior of $Ce_2Pd_2InH_{4.0}$ reported in [7].

All three hydrides synthesized at 1 bar, 10 bar, and 100 bar were dehydrogenated by heating up to 750 °C in the two-run procedure described above. Their normalized decomposition curves $p/p_{max}(t)$ typically have a step-wise form with 4 anomalies (Fig. 2). The temperatures, at which the decomposition plateaus are observed, are different for the crystalline $La_2Pd_2InH_{1.5}$ and the amorphous $La_2Pd_2InH_{4+\delta}$ compounds.

One can assume that the pressure decrease above $T = 406$ °C for $La_2Pd_2InH_{1.5}$ is associated with the decomposition of this hydride. Usually a simpler than a quaternary hydride can accommodate more hydrogen at the given pressure (30 mbar H_2 in this case), and the higher temperature stimulates the transformation. However, after additional temperature increase even the simpler hydride loses hydrogen and the compound can recombine again. Such scenario is supported by the comparison of the decomposition curves obtained during the first and the second runs, namely the re-absorption (and hence the decomposition) does not occur during the second run when the actual H_2 pressure is slightly below 10 mbar. The decomposition–recombination scenario is also supported by the presence of a substantial amount (20%) of impurity phases (mainly "1:1:1" – LaPdIn) in La_2Pd_2In obtained by dehydrogenating both the amorphous $La_2Pd_2InH_{4+\delta}$ and the crystalline $La_2Pd_2InH_{1.5}$ phase.

All desorption curves become similar above 600 °C, which most likely indicates that La_2Pd_2In is recovered by that temperature. Also the $p/p_{max}(t)$ curves for both amorphous hydrides are very similar and even their respective decomposition plateaus are located close to each other.

According to the X-ray data, the original La_2Pd_2In phase has been indeed recovered from both amorphous $La_2Pd_2InH_{4+\delta}$ compounds by the heating them up to 750 °C. The product of the dehydrogenation consisted of approximately 80% of the parent La_2Pd_2In phase and 20% of LaPdIn, while the amount of LaPdIn in the starting material was on the verge of detection by X-rays,

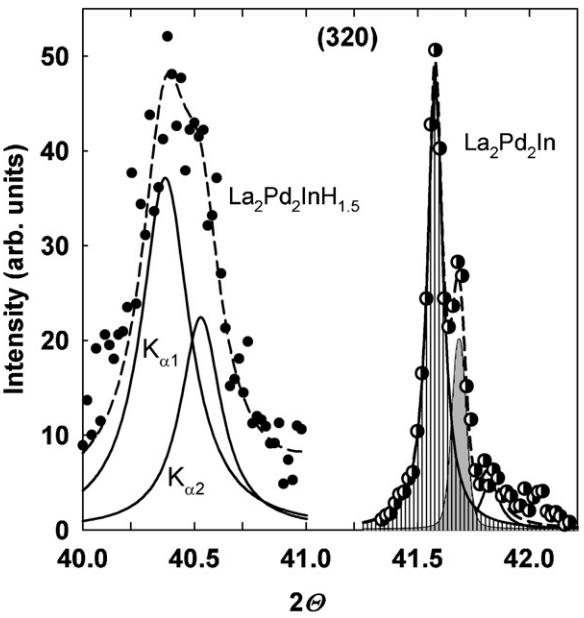

Fig. 3. XRD peak broadening due to the hydrogenation of La_2Pd_2In. On the left – the (3 2 0) peak of $La_2Pd_2InH_{1.5}$ and on the right – the (3 2 0) peak of the parent La_2Pd_2In. Solid and half-open circles represent the experimental data for the two compounds, the solid lines – the fits of the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines to the Voigt functions, and the dashed lines – the sum of the $K_{\alpha 1}$ and $K_{\alpha 2}$ contributions. In the La_2Pd_2In dataset the $K_{\alpha 1}$ line is hatched, and the $K_{\alpha 2}$ line is shaded for better visibility.

e.g. 3–5%. The XRD patterns of both dehydrogenated $La_2Pd_2InH_{4+\delta}$ compounds samples have in addition several weak impurity peaks, which could not be indexed. Also their patterns did not show any broad features at low 2Θ angles, which are typically associated with the short-range order regions. This we interpret as the indication of the complete transformation of the amorphous hydride phase.

The X-ray diffraction lines of $La_2Pd_2InH_{1.5}$ were substantially broader compared to those of the parent La_2Pd_2In: for example the integral breadth of the (3 2 0) line shown in Fig. 3 has increased by the factor of 3 after the hydrogenation. It is reasonable to assume that the broadening is due to the combined effect of the reduction of the crystallite size and the increase of the microstrain following the volume expansion cause by the hydrogen uptake. The XRD peaks remained broadened even after the removal of hydrogen from $La_2Pd_2InH_{1.5}$ as well as $La_2Pd_2InH_{4+\delta}$. This may point to the reduced crystallite size because the conditions, at which La_2Pd_2In is formed during the recombination, can be considered as the thermodynamic equilibrium.

According to the powder diffraction data the uptake of 1.5 H atoms per formula unit of La_2Pd_2In at $p_{H2} = 1$ bar has led to 6.0% relative increase of volume or +4.9 Å^3/H atom. The unit cell expansion along the *a*-axis is 1.5 times larger than the one along the *c*-axis (Table 1). The relative atomic positions are weakly affected by the hydrogenation (Table 1), yet the ratios between the interatomic distances are changed as the result of the anisotropic volume expansion (Table 2). Since La_2Pd_2In is the nonmagnetic reference for the RE_2Pd_2In series it is worth examining the La–La distances before and after the hydrogenation in more detail.

Table 1
Lattice parameters and atomic positions of La_2Pd_2In and $La_2Pd_2InH_{1.5\pm0.2}$. Both compounds crystallize in the Mo_2FeBe_2-type structure (space group *P4/mbm*).

	a (Å)	*c* (Å)	*V* (Å^3)		*x*	*y*	*z*
La_2Pd_2In	7.8645(1)	3.9698(1)	245.5				
La				4h	0.1761(2)	0.6761(2)	1/2
Pd				4g	0.3738(3)	0.8738(3)	0
In				2a	0	0	0
$La_2Pd_2InH_{1.5}$	8.0411(6) +2.2%	4.0246(4) +1.4%	260.2 +6.0%				
La				4h	0.1776(3)	0.6776(3)	1/2
Pd				4g	0.3738(4)	0.8738(4)	0
In				2a	0	0	0

Table 2
The influence of hydrogenation on the interatomic distances in La_2Pd_2In. All distances are in Angstrom.

	La_2Pd_2In (Å)	$La_2Pd_2InH_{1.5}$ (Å)	$\Delta d/d$
$d_{La-La\,1}$	3.9185	4.0723	+3.9%
$d_{La-La\,2}$	4.1002	4.1793	+1.9%
$d_{La-La\,3}$	3.9698	4.0246	+1.4%
d_{La-Pd}	2.9624	2.9940	+1.1%
d_{La-In}	3.5136	3.5753	+1.8%

The shortest La–La distance in La_2Pd_2In is $d_{La-La\,1} = 3.9185$ Å located in the basal plane between the lanthanum atoms from the adjacent unit cells. The next nearest La–La neighbors are located along the *c*-axis with $d_{La-La\,3} = 3.9698$ Å. After the hydrogenation the distances were switched: $d_{La-La\,3}$ became shorter than $d_{La-La\,1}$ due to the more pronounced expansion in the basal plane. Hence, the nearest La neighbors in the hydride are along the *c*-axis. It is worth mentioning that the distances between the La atoms within the basal plane and along the *c*-axis are rather similar and the difference between them is less than 4%. So in both La_2Pd_2In and $La_2Pd_2InH_{1.5}$ each La atom is coordinated by 7 La atoms (5 in the basal plane and 2 along the *c*-axis) at approximately 4 Å distance.

At the present stage it is impossible to determine the crystallographic positions of the hydrogen atoms in $La_2Pd_2InH_{1.5}$ because the H atoms have very little scattering cross-section for X-rays. A certain idea about possible hydrogen position can be drawn from the analogy with the isostructural $U_2Ni_2SnD_{1.8}$ deuteride [4]. This uranium compound has the same structure type as $La_2Pd_2InH_{1.5}$ and similarly to La_2Pd_2In-H its expansion upon the hydrogen uptake is anisotropic: $\Delta a/a > \Delta c/c$, hence one may expect that hydrogen atoms would occupy the same positions in U_2Ni_2Sn and La_2Pd_2In hydrides.

The suggested hydrogen position is the 8*k* (x, $x+1/2$, z) inside the La3–Pd tetrahedra (Fig. 4). Such coordination of the H atoms is often found in rare-earth and uranium intermetallics: e.g. RNiIn [11], UPdIn [12] or UNiAl [13]. The La3–Pd tetrahedra in La_2Pd_2In share the common face laying in the (0 0 1) plane. This feature imposes certain limitations on the occupation of the H sites. For example, if the hydrogen atoms occupy the same positions as in $U_2Ni_2SnD_{1.8}$ with $z = 0.53$ then the shortest H–H distance would be well below 2.1 Å, which, according to the Switendick rule [14], is the shortest allowed H–H separation in metal hydrides. In order to fulfill the Switendick rule, the 8*k* site should have the occupancy not larger than 50%. Such occupancy of the 8*k* site would

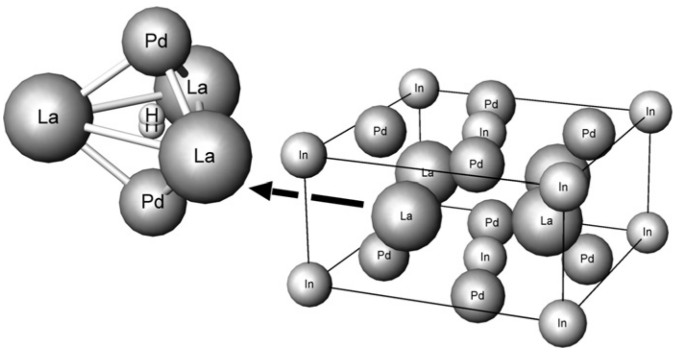

Fig. 4. Crystal structure of $La_2Pd_2InH_{1.5}$. The proposed hydrogen positions within the two adjacent La3-Pd tetrahedra are shown.

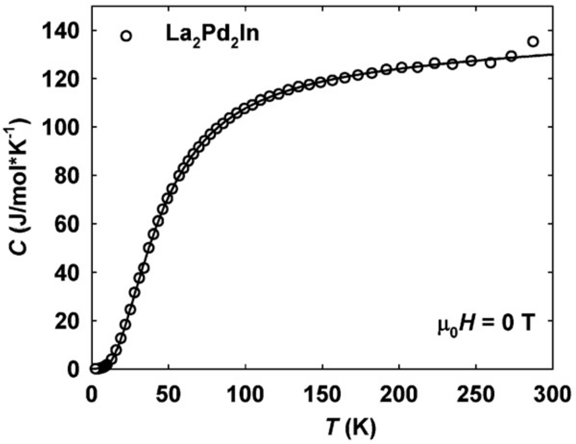

Fig. 5. Temperature dependence of the specific heat of La_2Pd_2In in zero magnetic field. Open circles are the experimental data points and the solid line is the fit to Eq. (2).

account for compositions with up to 2 H atoms per formula unit of La_2Pd_2In. In order to achieve higher hydrogen content at least one more hydrogen site should be occupied. There are several possible interstitials, which can be filled by hydrogen, e.g. La3–In and La2–Pd–In tetrahedra or La4–In pyramid, but without the neutron diffraction studies it is impossible to establish the hydrogen positions unambiguously. Also it is possible to reach the composition of more than 2 H atoms/f.u. in La_2Pd_2In by having $z \approx 0.75$ in the $8k$ position. In such case the shortest H–H distance would be 2.0 Å or just on the verge of the Switendick rule.

Specific heat measurements were performed both for the parent compound La_2Pd_2In and for the $La_2Pd_2InH_{1.5}$ hydride synthesized at 1 bar. Due to fast decomposition the hydride sample used for the measurements contained the mixture of La_2Pd_2In and $La_2Pd_2InH_{1.5}$, and ratio between the two phases could be established only approximately. This did not allow to perform thorough analysis of its $C(T)$ curves of the hydride.

The data for La_2Pd_2In were fitted to the following expression (Fig. 5):

$$C = C_{\mathrm{el}} + C_{\mathrm{Debye}} + C_{\mathrm{Einstein}} \tag{1}$$

where C_{el}, C_{Debye} and C_{Einstein} are electron, Debye and Einstein terms, respectively. Their analytic forms are:

$$C = \gamma_0 T + n_D R \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx + R \sum_i n_{\mathrm{E}i} \left(\frac{\Theta_{\mathrm{E}i}}{T}\right)^2 \frac{e^{\Theta_{\mathrm{E}i}/T}}{(e^{\Theta_{\mathrm{E}i}/T}-1)^2} \tag{2}$$

where γ_0 – Sommerfeld coefficient, Θ_D – Debye temperature, n_D – the total degeneracy of the Debye energy, $\Theta_{\mathrm{E}i}$ – Einstein temperature of the ith optical phonon branch, $n_{\mathrm{E}i}$ – the degeneracy of the ith optical phonon branch, and R – the universal gas constant. In order to simplify the fitting expression and reduce the number of the adjustable parameters it was assumed that there is only one Debye temperature. Also the number of the Einstein terms was kept at the absolute minimum. It was further assumed that the Debye term corresponds to the acoustic branches of the phonon spectrum, and the Einstein terms – to the optical ones. For this reason the sum $(n_D + n_{E1} + n_{E2} + \ldots)$ was always kept equal to $3n$, where n is the number of the atoms in the unit cell. The numbers n_D and $n_{\mathrm{E}i}$ were not restricted to the integers because the samples might have been inhomogeneous, which would result in the distribution of Θ_D and $\Theta_{\mathrm{E}i}$ values across their volume, and besides the modeling by Eq. (1) is relatively rough approximation by itself so keeping n_D and $n_{\mathrm{E}i}$ integer would not improve the precision of the model.

The contribution to the specific heat due to the free electrons γ_0 was estimated from the fits of $C/T(T^2)$ in the range of 2.5–7 K. The choice of this rather limited temperature range was due to a notable non-linearity of the $C/T(T^2)$ dependences already above 7 K. The values of the Debye and Einstein temperatures were obtained from the $C(T)$ fits across at least 2 decades in temperature. The data used for fitting were weighted as $1/C$ in order to insure that the low-temperature features of the specific heat curves were reproduced properly and by that the Debye temperature was not overestimated. The obtained values of the Debye and Einstein temperatures were verified by fitting the $C/T(T^2)$ data assuring that the difference between two methods was below ±5 K. The latter verification was done because $C(T)$ and $C/T(T^2)$ curves have different derivatives and data point densities in the temperature range of interest, and both of these factors influence the sensitivity of the least square approximation.

According to the fits (Fig. 5), the electronic contribution to the specific heat of La_2Pd_2In is $\gamma_0 = 8$ mJ/mol K^2 where the "mole" refers to the formula unit of the compound. The lattice contribution to the specific heat ($C_{\mathrm{Debye}} + C_{\mathrm{Eisnstein}}$) consists of 1 Debye branch with $\Theta_D = 192$ K and the degeneracy $n_{\mathrm{D}} = 13.2$, and of 1 Einstein branch with $\Theta_{\mathrm{E}} = 78$ K and $n_{\mathrm{E}} = 1.8$. The Θ_D values for the parent compound reported in literature are 130 K [15] and 172 K [16]. We tend to assign the difference between the present findings and Θ_D reported in [15] primarily to the difference in the fitting procedure itself.

Since the $La_2Pd_2InH_x$ sample consisted of the mixture of the La_2Pd_2In and $La_2Pd_2InH_{1.5}$ phases it was possible to estimate only the general features of the specific heat of the hydride. But even from that we can conclude that the hydrogenation of La_2Pd_2In leads to the decrease of its Debye temperature down to at least $\Theta_D = 150$ K and the increase of the Einstein temperature till at least $\Theta_{\mathrm{E}} = 280$ K. It is also likely that an additional optical branch appears in the phonon spectrum with $\Theta_{\mathrm{E}} > 500$ K. The Sommerfeld coefficient could not be evaluated reliably.

4. Discussion and conclusions

Hydrogenation of La_2Pd_2In at $p_{H2} = 1$ bar produces the compound with approximately 1.5 H atoms per formula unit accompanied by +6.0% relative volume increase. The expansion does not affect the lattice symmetry and $La_2Pd_2InH_{1.5\pm0.2}$ remains tetragonal (space group $P4/mbm$) unlike RE_2Ni_2In [6,8], which absorbs more than 6 H atoms/f.u. for the price of the orthorhombic distortion, but similarly to Ce_2Pd_2In with the comparable hydrogen content below 2 H/f.u. [7]. The increase of the synthesis pressure and hence the H content leads to amorphisation. The amorphisation itself is not unusual in the hydrides of intermetallic compounds. It occurs in case when the requirement for the minimization of energy upon H bonding leads to a local structure arrangement, which is not compatible with a long-range 3D periodicity. After the dehydrogenation of both the crystalline ($La_2Pd_2InH_{1.5}$) and the amorphous ($La_2Pd_2InH_{4+\delta}$) hydrides the parent La_2Pd_2In is recovered.

The volume expansion due to hydrogenation is anisotropic, which leads to the switchover of the shortest La–La distance. In La_2Pd_2In the nearest La neighbors lie in the basal plane whereas in $La_2Pd_2InH_{1.5}$ they are already along the c-axis.

The analysis of the specific heat indicates that hydrogenation results in "softening" of the crystal lattice, which is envisaged by the decrease of the Debye temperature. The increase of the Einstein temperature and possibly the appearance of the additional Einstein term could be associated with the oscillations of heavy metal atoms in a new environment containing much lighter hydrogen atoms and oscillations of the hydrogen atoms themselves.

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