Hydrogen absorption in transition metal silicides.

La$_3$Pd$_5$Si-hydrogen system

Yaroslav O. Tokaychuk[*,†,‡], Yaroslav E. Filinchuk[†,§], Denis V. Sheptyakov[¶], Klaus Yvon[†]

[†] *Laboratory of Crystallography, University of Geneva,*
24 quai Ernest Ansermet, CH-1211 Geneva, Switzerland

[§] *Swiss-Norwegian Beam Lines, European Synchrotron Radiation Facility,*
6 rue Jules Horowitz, 38043 Grenoble, France

[¶] *Laboratory for Neutron Scattering, ETH Zurich & Paul Scherrer Institute, CH-5232 Villigen PSI,*
Switzerland

SUPPORTING INFORMATION

[*] To whom correspondence should be addressed. E-mail: tokaychuk@mail.lviv.ua.

[‡] Present address: *Chimie Métallurgique des Terres Rares, Institut de Chimie et des Matériaux Paris-Est CNRS UMR 7182, 2-8 rue Henri Dunant 94320 Thiais, France*

Experimental details

Synthesis. Five 2-5 g alloys of nominal composition La_3Pd_5Si were synthesized by arc-melting of elemental La (Aldrich, 99.9%), Pd (bulk, 99.9+%) and Si (Aldrich, m6N) on a water-cooled copper base under a purified argon atmosphere. To ensure homogeneity each sample was remelted three times with nearly no mass losses.

The powdered alloy **1** was placed into an autoclave and evacuated for 2 hours at 473 K. 100 bar of hydrogen pressure was after applied. Temperature was decreased to 373 K after a day and to 293 K after the next 12 hours. After the rapid X-ray check, which show the anisotropic expansion of the unit cell by 11.3 %, sample was filled into thin-walled glass capillary for the synchrotron experiments. The 5 g sample **2** was deuterided under 150 bar D_2 (temperature changed slowly from 473 to 293 K). The sample was transported to PSI in an autoclave under 100 bar D_2. There sample was refilled into V-cylinder for the measurements on HRPT.

Alloy **3** was deuterided in situ on DMC and α-deuteride was obtained and measured on HRPT.

To obtain the γ-deuteride $La_3Pd_5SiD_{\sim5}$, that forms only at very high hydrogen (deuterium) pressures, the La_3Pd_5Si alloy **4** was deuterided at 150 bar, cooling slowly an autoclave from 473 K down to room temperature and transported to the PSI in the autoclave. Then, it was slowly cooled at PSI to 90 K during two weeks. Then, the autoclave was quickly opened and the sample was refilled into a V-cylinder, immediately frozen in Orange cryostat to 125 K and measured on HRPT for 9 hours. The small portion of the same sample was recharged with D_2 at 75 bar pressure and temperature 473 K and *in-situ* desorption experiment was carried out at SLS at room temperature.

Alloy **5** was synthesized by the same way as **1** and was used for PCT experiments.

Structure characterization by synchrotron and neutron powder diffraction. For the synchrotron experiments, hydride **1** was filled in the thin-walled glass capillary few days before measurements, whereas the hydride **2** was transported in the autoclave under hydrogen pressure which was released just before the data collection. Room temperature synchrotron powder diffraction experiments were carried out at a Swiss-Norwegian Beam Lines (SNBL) at ESRF (Grenoble, France) by using the wavelengths $\lambda = 0.59954(1)$ Å (hydride **1**) or 0.52014(1) Å (hydride **2;** just above the Pd K-absorption edge at 0.50915 Å), Debye-Scherrer geometry, 2θ range 4.5-50.5° with the step size 0.07° (sample **1**) or 3-42.8° with the step size 0.04° (sample **2**). The wavelengths and zero-shifts were refined from a standard Si sample. High-resolution neutron powder diffraction data of deuterides **2**, **3** and **4** were collected on the diffractometer HRPT at SINQ (PSI, Villigen, Switzerland) by using the wavelengths $\lambda = 1.493814(1)$ Å (deuteride **2**, room temperature), 1.372060(1) Å (deuteride **3**, room temperature) or 1.372000(1) Å (deuteride **4**, 125 K), 2θ range 4.5-164.5°

with the step size 0.1°, data collection time ~7-9 h per pattern. The wavelengths and zero-shifts were refined from a standard $Na_2Ca_3Al_2F_{14}$ (NAC) sample.

All diffraction profile and structure refinements were performed by using the FULLPROF SUITE software. As a starting model of the metal substructures in both, α and β phases the atomic parameters of La_3Pd_5Si in the space group *Imma* were used. The structure of α-$La_3Pd_5SiD_{1.44(3)}$ (solid solution of deuterium in the parent intermetallic structure) was refined from the neutron powder data (room temperature) of the deuteride **3**, containing two phases: α-$La_3Pd_5SiD_{1.44(3)}$ (60.7(5) wt.%, $a = 13.3342(11)$, $b = 7.5479(5)$, $c = 7.6995(7)$ Å, $V = 774.92(11)$ Å^3) and β-$La_3Pd_5SiD_x$ (39.3(4) wt.%, $a = 12.8886(14)$, $b = 7.6530(8)$, $c = 8.3075(8)$ Å, $V = 819.42(15)$ Å^3). In the first step the metal atom positions were fixed as in the La_3Pd_5Si and one deuterium atom site was located by using the program FOX. At the second step, 25 parameters were refined for the main α-phase by using Rietveld algorithm: one scale factor, three cell parameters, 6 profile parameters (Pseudo-Voigt peak shape function), 8 atomic coordinates, 6 isotropic displacements parameters and one occupancy factor for D-atom. The background was defined by using a Fourier filtering technique with a window of 50°. The observed, calculated and difference patterns are shown on Figure S1.
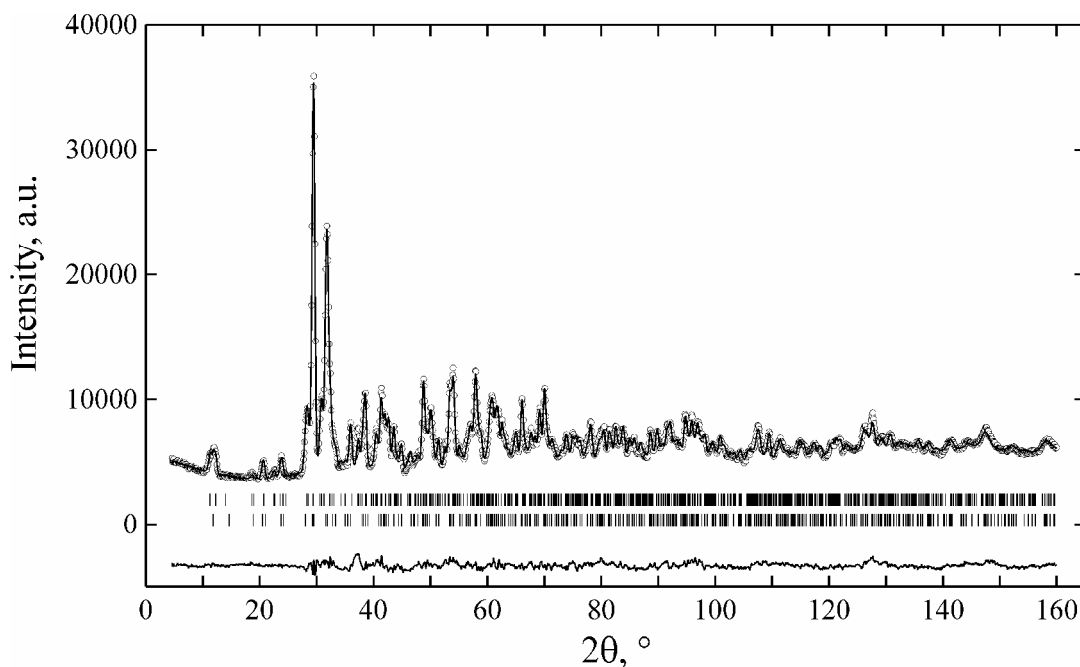
Figure S1. Observed (circles), calculated (line) and difference (bottom line) neutron powder diffraction pattern for $La_3Pd_5SiD_x$ sample (deuteride **3**). Vertical bars indicate the Bragg positions of contributing phases: α-$La_3Pd_5SiD_{1.44(3)}$, 61 wt.% and β-$La_3Pd_5SiD_{3.47(4)}$, 39 wt.%.

High resolution synchrotron data did not show any distortion of the orthorhombic cell for β-phase, but revealed an anisotropic peak broadening typical for hydrides with anisotropically expanded unit cell. The metal atoms positions in the β-$La_3Pd_5SiH_x$ were refined using two synchrotron powder patterns collected at room temperature for its H-poor and H-rich limits (hydrides **2** and **3**). The hydride sample **2** contain three phases: β-$La_3Pd_5SiH_x$ (H-poor limit, 74 wt.%), α-$La_3Pd_5SiH_x$ (H-rich limit, 14 wt.%) and La_3Pd_5Si (13 wt.%). Hydride **3** contains two phases: β-$La_3Pd_5SiH_x$ (H-rich limit, 91 wt.%) and new high-pressure γ-$La_3Pd_5SiH_x$ phase (8 wt.%). The peaks from the second phase disappeared rapidly due to fast desorption of hydrogen from the sample. In the final cycles of the refinements 19(26) parameters (for the patterns of the hydrides **2** and **3** respectively) were allowed to vary for the main phase (β-$La_3Pd_5SiH_x$): 1(1) scale factor, 3(3) cell parameters, 6(7) profile parameters (Pseudo-Voigt peak shape function), 0(3) strain parameters, 7(7) atomic coordinates and 2(5) isotropic displacement parameters. The isotropic displacement parameters of the two La atoms and two Pd and one Si for the β-phase in the hydride **2** were refined by one parameter. Noticeable anisotropic peak broadening in the pattern of the hydride **3** was modeled by three parameters. The background was defined by using a Fourier filtering technique with a window of 21° (hydride **2**) or polynomial function with 5 refined coefficients (hydride **3**). Two deuterium atoms in the β-phase (D-poor limit) were located from the neutron data (deuteride **2;** room temperature) using program FOX. 25 parameters were refined for the main phase (β-$La_3Pd_5SiD_{3.47}$, 88 wt.%): 1 scale factor, three cell parameters, 5 profile parameters (Pseudo-Voigt peak shape function), 2 strain parameters, 9 atomic coordinates, 6 isotropic displacement parameters and 2 occupancy parameters for D-atoms. The secondary α-$La_3Pd_5SiD_{1.44(3)}$ phase was also included into the refinement. The background was defined by using a Fourier filtering technique with a window of 80°. The observed, calculated and difference synchrotron and neutron powder diffraction patterns of the samples containing β-phase are shown on Figure S2. Rietveld refinement results for α and β phases are summarized in Table S1. Selected interatomic distances in La_3Pd_5Si, α-$La_3Pd_5SiD_{1.44(3)}$ and β-$La_3Pd_5SiD_{3.47(2)}$ are listed in Table S2.
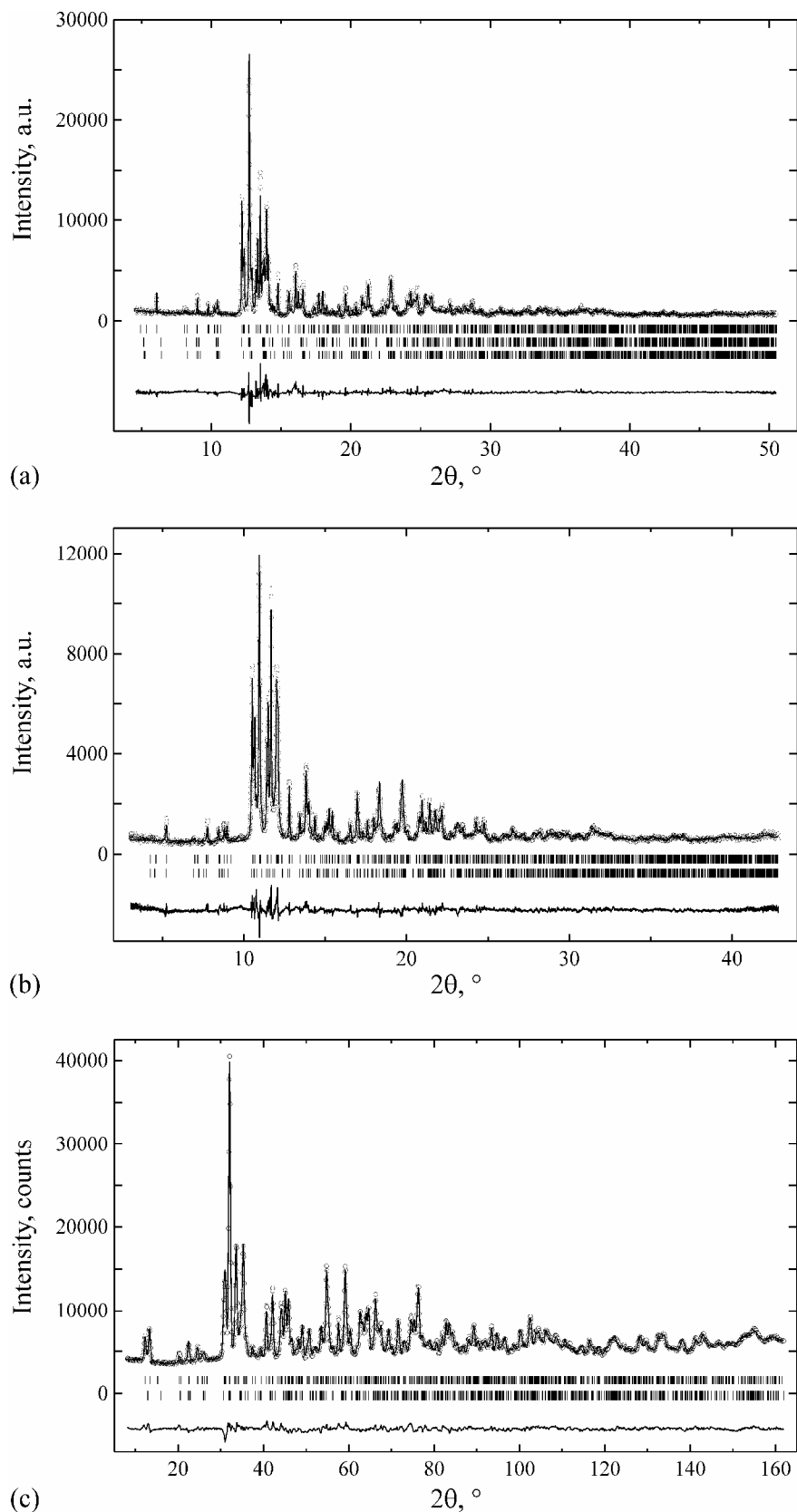
Figure S2. Observed (circles), calculated (line) and difference (bottom line) synchrotron powder diffraction patterns (a) and (b) for $La_3Pd_5SiH_x$ samples (hydrides **1** and **2**) and neutron powder diffraction pattern (c) for $La_3Pd_5SiD_x$ sample (deuteride **2**). Vertical bars indicate the Bragg positions of contributing phases: β-$La_3Pd_5SiH_x$, 74 wt.%, α-$La_3Pd_5SiH_x$, 14 wt.% and La_3Pd_5Si, 13 wt.% in (a); β-$La_3Pd_5SiH_x$, 91 wt.% and α-$La_3Pd_5SiH_x$, 8 wt.% in (b); β-$La_3Pd_5SiD_{3.47(2)}$, 88 wt.% and α-$La_3Pd_5SiD_{1.25(12)}$, 12 wt.% in (c).

Table S1. Atomic coordinates, occupancies and displacement parameters in α- and β-La$_3$Pd$_5$SiH(D)$_x$

Atom	Wyckoff site	Occ.	x	y	z	$B_{iso} \times 10^2$, Å^2
α-La$_3$Pd$_5$SiD$_{1.44(3)}$ (deuteride **3**), neutron powder diffraction, 25 °C: space group *Imma*, $a = 13.3342(11)$, $b = 7.5479(5)$, $c = 7.6995(7)$ Å, $V = 774.92(11)$ Å^3, $R_B = 0.044$, $R_F = 0.030$, $\chi^2 = 5.29$, $R_p = 0.022$, $R_{wp} = 0.028$.						
La1	4e	1	0	¼	0.3784(7)	1.26(7)
La2	8i	1	0.2012(3)	¼	0.0166(4)	0.94(4)
Pd1	4a	1	0	0	0	1.32(9)
Pd2	16j	1	0.1352(2)	0.0522(5)	0.6869(6)	1.46(4)
Si	4e	1	0	¼	0.7989(15)	1.24(10)
D1	8g	0.720(15)	1/4	0.0326(12)	1/4	3.21(11)
β-La$_3$Pd$_5$SiH$_x$ (lower end, hydride **1**), synchrotron powder diffraction, 25 °C: space group *Imma*, $a = 12.8966(4)$, $b = 7.6744(2)$, $c = 8.3229(2)$ Å, $V = 823.75(4)$ Å^3, $R_B = 0.071$, $R_F = 0.032$, $\chi^2 = 10.7$, $R_p = 0.073$, $R_{wp} = 0.099$.						
La1	4e	1	0	1/4	0.4106(4)	0.53(4)
La2	8i	1	0.20146(16)	1/4	0.0173(3)	0.53(4)
Pd1	4a	1	0	0	0	0.32(4)
Pd2	16j	1	0.13391(16)	0.0548(2)	0.7057(3)	0.32(4)
Si	4e	1	0	1/4	0.8054(18)	0.32(4)
β-La$_3$Pd$_5$SiD$_{3.47(2)}$ (lower end, deuteride **2**), neutron powder diffraction, 25 °C: space group *Imma*, $a = 12.8919(7)$, $b = 7.6741(4)$, $c = 8.3116(3)$ Å, $V = 822.30(7)$ Å^3, $R_B = 0.048$, $R_F = 0.026$, $\chi^2 = 5.66$, $R_p = 0.023$, $R_{wp} = 0.030$.						
La1	4e	1	0	1/4	0.4095(4)	0.88(5)
La2	8i	1	0.20193(18)	1/4	0.0168(3)	1.08(4)
Pd1	4a	1	0	0	0	1.51(9)
Pd2	16j	1	0.13470(17)	0.0565(3)	0.7075(3)	0.95(3)
Si	4e	1	0	1/4	0.8054(7)	0.90(10)
D1	8g	0.816(9)	1/4	0.0590(7)	1/4	2.93(7)
D2	8f	0.916(8)	0.1429(3)	0	1/2	2.93(7)
β-La$_3$Pd$_5$SiH$_x$ (upper end, hydride **2**), synchrotron powder diffraction, 25 °C: space group *Imma*, $a = 12.9562(3)$, $b = 7.74426(17)$, $c = 8.32015(18)$ Å, $V = 834.81(3)$ Å^3, $R_B = 0.062$, $R_F = 0.044$, $\chi^2 = 4.58$, $R_p = 0.064$, $R_{wp} = 0.076$.						
La1	4e	1	0	1/4	0.4118(3)	0.24(5)
La2	8i	1	0.20457(11)	1/4	0.02069(19)	0.01(5)
Pd1	4a	1	0	0	0	1.60(8)
Pd2	16j	1	0.13383(14)	0.05832(17)	0.70860(17)	0.82(5)
Si	4e	1	0	1/4	0.8187(12)	0.9(3)

Table S2. Selected distances (Å) in La_3Pd_5Si, α-$La_3Pd_5SiD_{1.44(3)}$ and β-$La_3Pd_5SiD_{3.47(2)}$

Atoms		La_3Pd_5Si	α-$La_3Pd_5SiD_{1.44(3)}$	β-$La_3Pd_5SiD_{3.47(2)}$
La1	– 4D2			2.764(3)
	– 4Pd2	2.972(2)	2.951(2)	3.081(3)
	– Si	3.10(2)	3.238(13)	3.291(7)
La2	– 2D1		2.519(6)	2.508(4)
	– 2D2			2.776(3)
	– 2Pd2	2.993(3)	3.073(4)	3.092(3)
	– 2Pd2	3.076(3)	3.074(5)	3.181(3)
	– Si	3.188(13)	3.163(7)	3.141(4)
	– 2Pd1	3.249(2)	3.282(3)	3.237(2)
Pd1	– 2Si	2.444(15)	2.441(7)	2.510(4)
	– 4Pd2	3.067(3)	3.036(4)	3.019(2)
	– 4La2	3.249(2)	3.282(3)	3.237(2)
	– 4D1		3.857(2)	3.861(2)
Pd2	– D1		1.729(4)	1.766(3)
	– D2			1.782(2)
	– Si	2.522(8)	2.495(5)	2.425(3)
	– Pd2	2.953(4)	2.984(6)	2.970(3)
	– Pd2	2.964(3)	2.986(2)	3.056(3)
	– La1	2.972(2)	2.951(2)	3.081(3)
	– La2	2.993(3)	3.073(4)	3.092(3)
	– Pd2	2.998(3)	3.212(4)	3.473(3)
	– Pd1	3.067(3)	3.036(4)	3.019(2)
	– La2	3.076(3)	3.074(5)	3.181(3)
Si	– 2Pd1	2.444(15)	2.441(7)	2.510(4)
	– 4Pd2	2.522(8)	2.495(5)	2.425(3)
	– La1	3.10(2)	3.238(13)	3.291(7)
	– 2La2	3.188(13)	3.163(7)	3.141(4)
	– 4D2			3.677(4)
	– 2D1		3.975(5)	4.028(3)
D1	– 2Pd2		1.729(4)	1.766(3)
	– 2La2		2.519(6)	2.508(4)
	– 2D2			2.536(3)
	– D1		3.282(13)	2.932(7)
	– Si		3.975(5)	4.028(3)
D2	– 2Pd2			1.782(2)
	– 2D1			2.536(3)
	– 2La1			2.764(3)
	– 2La2			2.776(3)
	– Si			3.677(4)

The crystal structure determination of the H(D)-rich γ-phase was done in two steps. In the first one, metal atom substructure has been determined from high-resolution synchrotron powder data on the deuteride **4**, collected during the *in-situ* desorption experiment at Materials Science Beam Line at SLS (Villigen, Switzerland). The experiment was performed on the sample freshly loaded with deuterium (75 bar) using a fast strip detector. One complete powder pattern has been collected in 10 seconds, using the wavelength of 0.70832(1) Å, Debye-Scherrer geometry, resulting in the data in 2θ range 4.5-50.5° with step size 0.0037°. The pattern has been modelled with a structure of the intermetallic compound having a larger unit cell volume, but some small peaks indicated a possible superstructure. These peaks have been indexed by tripling the *b* parameter. Thus, the relations between the unit cell parameters for the γ- and β-hydrides are as following: $a_\gamma \sim a_\beta$, $b_\gamma \sim 3b_\beta$ and $c_\gamma \sim c_\beta$, $V_\gamma \sim 3V_\beta$. Such 3-fold superstructure along *b* of an *Imma* structure corresponds to an isomorphic subgroup *Imma*. On the next stage, only direct subgroups of *Imma* (tripled cell) were considered: four orthorhombic *I*-centered and eight orthorhombic *P*-centered space groups. Superstructure lines are very weak compared to the main peaks. However, their existence violates the *I*-centering and the *a* glide plane perpendicular to the *c*-axis. Among the four remaining direct subgroups of *Imma* (*Pnnb*, *Pnmb*, *Pmnb* and *Pmmb*), the most stable refinements for metal atom substructures, using synchrotron data only, were obtained in *Pnmb* and *Pmnb*. The solution of D-atoms' positions from neutron data was successful only in the space group *Pnmb*. The reliable full-matrix full profile Rietveld refinement of all structural and profile parameters in the space group *Pnmb* confirms the validity of our choice. The metal atom substructure was successfully refined in space group *Pmnb* (non-standard setting of *Pnma*). Positional parameter for all metal atoms were transformed from space group *Imma* to *Pmnb* by using the POWDER CELL program and refined with FULLPROF. The cell contains 18 metal atoms.

To obtain the neutron powder pattern of γ-deuteride, deuteride **4** was transported to the PSI in the autoclave under 150 bar of D_2 and high-resolution neutron powder pattern was collected at 125 K on HRPT. Eight deuterium atoms were located using the program FOX and fixing the coordinates of the metal atoms. The result was verified by analyzing the difference nuclear Fourier maps. Due to very high complexity of the neutron pattern, the refinement of profile parameters and solution of the deuterium atoms substructure were done iteratively. 87 profile and structural parameters were included to the final cycles of the Rietveld refinement: 1 scale factor, 3 cell parameters, 4 profile parameters (Pseudo-Voigt peak shape function), 69 atomic coordinates, 1 overall isotropic displacement parameter and 8 occupancy parameters for D-atoms. Soft restraints were applied to some Pd-Si and Pd-D distances: $d_{Pd1-Si2}$, $d_{Pd1-Si3}$, $d_{Pd2-Si1}$, $d_{Pd2-Si3}$, $d_{Pd3-Si1}$, $d_{Pd3-Si2}$, $d_{Pd5-Si2}$, $d_{Pd6-Si1}$ and $d_{Pd9-Si3}$ were restrained to 2.45(2) Å, and d_{Pd5-D4}, d_{Pd6-D5} and d_{Pd8-D6} were restrained to 1.70(2) Å. The background was defined by a Fourier filtering technique with a window of 50°. The observed, calculated and difference neutron powder diffraction patterns of γ-phase sample (deuteride **4)** are

shown on Figure S3. Rietveld refinement results for γ-phase are presented in Table S3. The shortest D-La, D-Pd, D-Si, Si-Pd and Si-La distances in γ-La$_3$Pd$_5$SiD$_{4.67(7)}$ are listed in Tables S4 and S5.
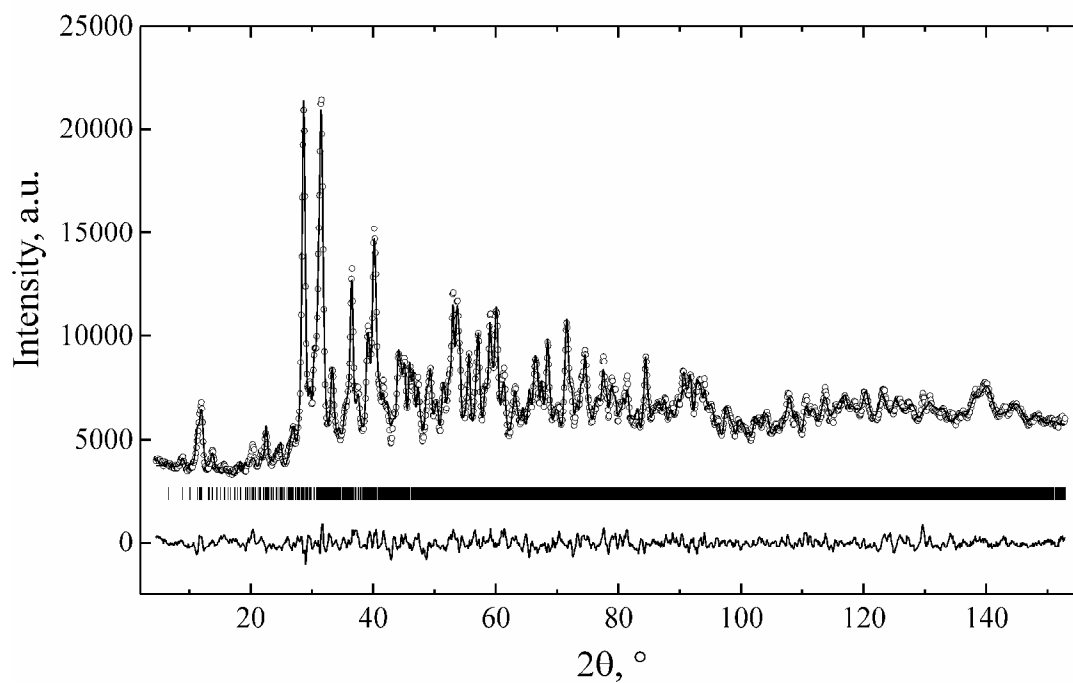
Figure S3. Observed (circles), calculated (line) and difference (bottom line) neutron powder diffraction pattern for La$_3$Pd$_5$SiD$_x$ sample (deuteride **4**). Vertical bars indicate the Bragg positions of the γ-La$_3$Pd$_5$SiD$_{4.67(7)}$ phase.

Table S3. Atomic coordinates, occupancies and displacement parameters in γ-La$_3$Pd$_5$SiH$_x$[a] (upper lines in italic) refined from synchrotron powder diffraction data (deuteride **4,** SLS, room temperature) and γ-La$_3$Pd$_5$SiD$_{4.67(7)}$[b] (lower lines in bold) refined from neutron powder diffraction data (deuteride **4,** HRPT, 125 K).

Atom	Wyckoff site	Occ.	x	y	z	B_{iso}[c] $\times 10^2$, Å^2
La1	4*c*	1	1/4	*0.0068(5)*	*0.6590(11)*	*0.62(3)*
				0.0083(10)	**0.632(3)**	**1.052(13)**
La2	4*c*	1	1/4	*0.6698(5)*	*0.6486(11)*	*0.62(3)*
				0.6636(9)	**0.658(3)**	**1.052(13)**
La3	4*c*	1	1/4	*0.3474(4)*	*0.6312(10)*	*0.62(3*
				0.3432(11)	**0.640(3)**	**1.052(13)**
La4	8*d*	1	*0.0484(5)*	*0.5024(4)*	*0.2242(8)*	*0.62(3)*
			0.0503(10)	**0.5047(7)**	**0.2084(15)**	**1.052(13)**
La5	8*d*	1	*0.9585(6)*	*0.3290(3)*	*0.7222(8)*	*0.62(3)*
			0.9633(12)	**0.3319(7)**	**0.739(2)**	**1.052(13)**
La6	8*d*	1	*0.5423(6)*	*0.6666(3)*	*0.7578(6)*	*0.62(3)*
			0.5444(12)	**0.6683(7)**	**0.751(2)**	**1.052(13)**
Pd1	4*c*	1	1/4	*0.7490(6)*	*0.2686(14)*	*0.62(3)*
				0.7478(8)	**0.268(3)**	**1.052(13)**
Pd2	4*c*	1	1/4	*0.4145(6)*	*0.2690(14)*	*0.62(3)*
				0.4325(8)	**0.248(3)**	**1.052(13)**
Pd3	4*c*	1	1/4	*0.5970(4)*	*0.2680(14)*	*0.62(3)*
				0.5904(9)	**0.232(3)**	**1.052(13)**
Pd4	8*d*	1	*0.3647(7)*	*0.2814(4)*	*0.9246(9)*	*0.62(3)*
			0.3648(16)	**0.2814(9)**	**0.945(3)**	**1.052(13)**
Pd5	8*d*	1	*0.1296(7)*	*0.7376(4)*	*0.9620(11)*	*0.62(3)*
			0.1309(15)	**0.7428(6)**	**0.944(2)**	**1.052(13)**
Pd6	8*d*	1	*0.3752(6)*	*0.9515(4)*	*0.9552(11)*	*0.62(3)*
			0.3748(15)	**0.9516(7)**	**0.9568(19)**	**1.052(13)**
Pd7	8*d*	1	*0.1012(6)*	*0.0710(4)*	*0.9632(10)*	*0.62(3)*
			0.1003(14)	**0.0773(9)**	**0.955(3)**	**1.052(13)**
Pd8	8*d*	1	*0.3690(7)*	*0.6087(3)*	*0.9568(11)*	*0.62(3)*
			0.3745(18)	**0.6080(8)**	**0.947(2)**	**1.052(13)**
Pd9	8*d*	1	*0.1159(7)*	*0.4065(4)*	*0.9453(12)*	*0.62(3)*
			0.1198(15)	**0.4004(8)**	**0.953(3)**	**1.052(13)**
Si1	4*c*	1	1/4	*0.0158(19)*	*0.071(6)*	*0.62(3)*
				0.0158(6)	**0.067(2)**	**1.052(13)**
Si2	4*c*	1	1/4	*0.6907(17)*	*0.081(5)*	*0.62(3)*
				0.6748(6)	**0.056(2)**	**1.052(13)**
Si3	4*c*	1	1/4	*0.3335(16)*	*0.067(5)*	*0.62(3)*
				0.3428(6)	**0.099(3)**	**1.052(13)**
D1	8*d*	**0.93(4)**	**0.9254(13)**	**0.8451(9)**	**0.050(3**	**1.052(13)**
D2	8*d*	**0.71(4)**	**0.587(2)**	**0.5214(11)**	**0.049(4)**	**1.052(13)**
D3	8*d*	**0.94(4)**	**0.0969(14)**	**0.9121(9)**	**0.769(3)**	**1.052(13)**
D4	8*d*	**0.94(4)**	**0.5915(16)**	**0.6905(6)**	**0.487(2)**	**1.052(13)**
D5	8*d*	**1.03(3)**	**0.6073(12)**	**0.0802(8)**	**0.8711(17)**	**1.052(13)**
D6	8*d*	**0.86(4)**	**0.1157(15)**	**0.5820(9)**	**0.753(2)**	**1.052(13)**
D7	8*d*	**0.86(3)**	**0.4891(16)**	**0.2706(7)**	**0.022(2)**	**1.052(13)**
D8	8*d*	**0.74(4)**	**0.0892(19)**	**0.7361(10)**	**0.747(4)**	**1.052(13)**

[a] space group *Pmnb*, $a = 13.1793(3)$, $b = 23.8018(5)$, $c = 8.20820(16)$ Å, $V = 2574.84(9)$ Å^3, $R_B = 0.086$, $R_F = 0.053$, $\chi^2 = 11.4$, $R_p = 0.092$, $R_{wp} = 0.116$.

[b] space group *Pmnb*, $a = 13.1228(15)$, $b = 23.830(3)$, $c = 8.2091(9)$ Å, $V = 2567.1(5)$ Å^3, $R_B = 0.063$, $R_F = 0.033$, $\chi^2 = 12.8$, $R_p = 0.033$, $R_{wp} = 0.042$.

[c] overall isotropic displacement parameters for all atoms were refined in both cases.

**Table S4.** Shortest D-La, D-Pd and D-Si distances in γ-La$_3$Pd$_5$SiD$_{4.67(7)}$

Atoms		distance, Å	Atoms		distance, Å
D1	– Pd7	1.88(3)	D5	– Pd6^a	1.62(2)
	– La6	2.29(3)		– Pd2	2.149(19)
	– La5	2.44(3)		– La6	2.47(2)
	– La2	2.48(2)		– La4	2.54(2)
	– Si1	4.15(2)		– Si1	3.00(2)
D2	– Pd9	1.91(3)	D6	– Pd8^a	1.71(2)
	– La4	2.26(3)		– Pd7	1.72(3)
	– La4	2.27(3)		– La1	2.66(3)
	– La1	2.34(3)		– Si1	3.53(2)
	– Si3	4.06(3)	D7	– Pd4	1.77(3)
D3	– Pd6	1.84(3)		– Pd5	1.91(3)
	– Pd9	1.87(3)		– La6	2.41(3)
	– La5	2.59(3)		– Si3	3.63(2)
	– La3	2.70(3)	D8	– Pd5	1.71(4)
	– Si3	3.99(3)		– Pd4	2.00(4)
D4	– Pd5^a	1.71(2)		– La6	2.39(3)
	– La6	2.31(3)		– La2	2.82(3)
	– La3	2.46(2)		– La5	2.82(3)
	– La5	2.56(3)		– Si2	3.61(3)
	– Si2	3.87(2)			

^{a} D-Pd distances were refined using soft distances restrains (see at the experimental section)

Table S5. Shortest Si-Pd and Si-La distances in γ-La$_3$Pd$_5$SiD$_{4.67(7)}$

Atoms		distance, Å
Si1	– 2Pd6^a	2.42(2)
	– Pd3^a	2.43(3)
	– Pd2^a	2.50(3)
	– 2Pd7	2.62(2)
	– 2La4	3.215(17)
	– La1	3.58(3)
Si2	– 2Pd5^a	2.43(2)
	–2Pd8	2.45(2)
	– Pd1^a	2.46(3)
	– Pd3^a	2.48(3)
	– 2La5	3.270(18)
	– La2	3.28(3)
Si3	–2Pd4	2.45(3)
	– Pd2^a	2.46(3)
	–2Pd9^a	2.50(3)
	– Pd1^a	2.51(3)
	– 2La6	2.987(19)
	– La3	3.77(3)

^{a} Si-Pd distances were refined using soft distances restrains
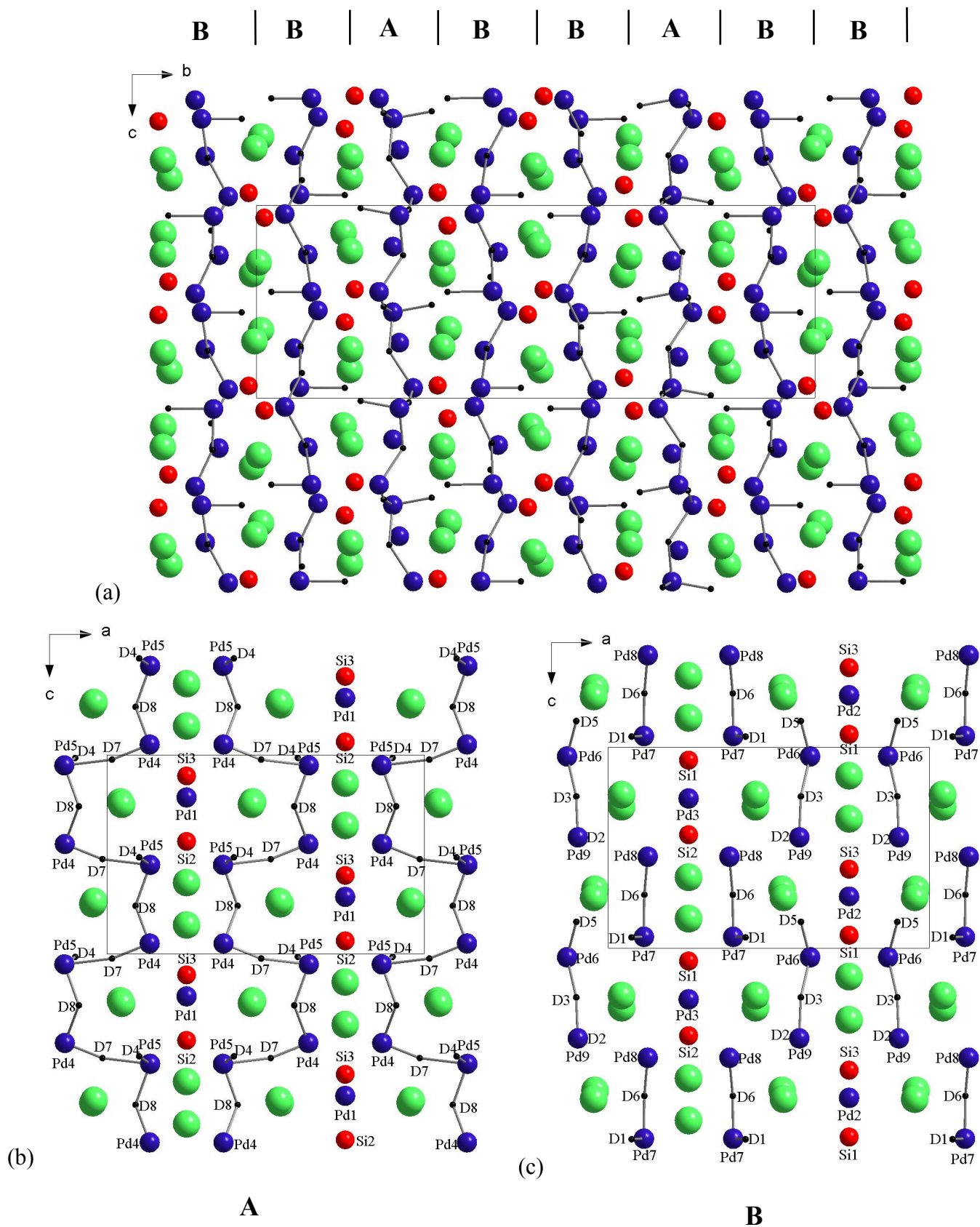
Figure S4. Unit cell projection of the γ-La$_3$Pd$_5$SiD$_{4.67(7)}$ structure on *bc* plane (a). Two types of "layers" containing Pd-D anions are selected: (b) **A** (containing infinite -Pd-D- *zig-zag* chains) and (c) **B** (containing quasi isolated 5-membered [D5-Pd6-D3-Pd9-D2] and 4-membered [D1-Pd7-D6-Pd8] fragments).
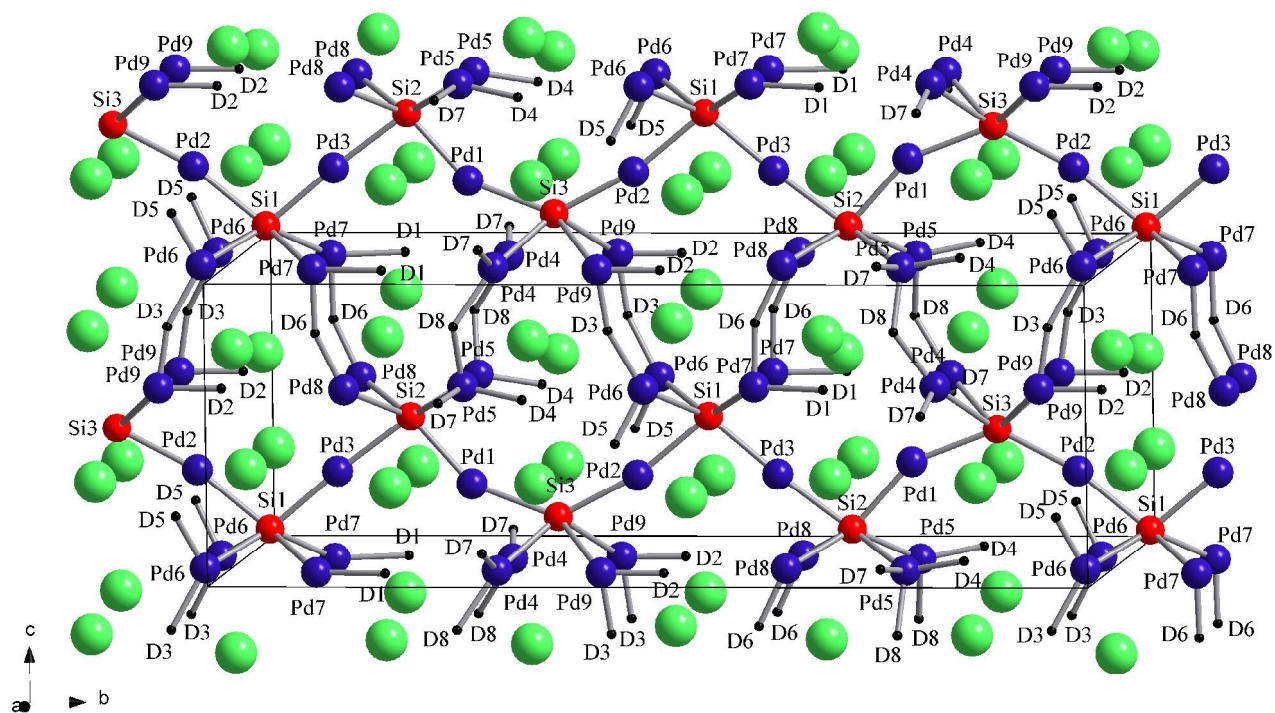
Figure S5. Part of the γ-La$_3$Pd$_5$SiD$_{4.67(7)}$ unit cell viewed perpendicularly to *a* axis (*a* ~ 1/4).