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$LaMg_2PdH_7$, a new complex metal hydride containing tetrahedral $[PdH_4]^{4-}$ anions

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Abstract

Hydrogenation of the intermetallic compound $LaMg_2Pd$ at 200 °C and 10 bar leads to a complex metal hydride of composition $LaMg_2PdH_7$. Its structure has orthorhombic symmetry and displays tetrahedral $[PdH_4]^{4-}$ anions. The Pd–H bond distances as measured on the deuteride range from 1.71 to 1.78 Å and the H–Pd–H bond angles from 95° to 122°. Three additional hydride anions H^- occupy La_2Mg_2-type interstices having tetrahedral metal configurations. Band structure calculations suggest the hydride to be non-metallic and to have a band gap of ∼1.0 eV. The compound desorbs hydrogen at 125 °C yielding a pressure of more than 1 bar absolute.

Keywords: Metal hydrides; Crystal structure

1. Introduction

Recently, we have reported on a hydrogen induced insulating state in the nickel based metal–hydrogen system $LaMg_2Ni$-H [1]. The intermetallic compound $LaMg_2Ni$ was found to absorb hydrogen below 200 °C and 8 bar hydrogen pressure hereby forming a non-metallic hydride of composition $LaMg_2NiH_7$ which has monoclinic symmetry and a nearly unchanged metal host structure (atom shifts < 0.7 Å). The metal-insulator transition was interpreted as the result of charge transfer of conduction electrons into tetrahedral 18-electron $[NiH_4]^{4-}$ complex anions and hydride anions H^- surrounded by La^{3+} and Mg^{2+} cations only. The hydrogenation reaction, however, was not reversible under practical conditions. Here, we report on a similar transition in the analogous palladium system $LaMg_2Pd$-H. It will be shown that the intermetallic compound $LaMg_2Pd$ absorbs hydrogen under relatively mild conditions (100 °C, 10 bar) hereby forming a non-metallic hydride of composition $LaMg_2PdH_7$. The reaction leads to the formation of tetrahedral $[PdH_4]^{4-}$ complexes and leaves the metal host structure nearly unchanged (metal atom shifts ∼0.7 Å). In contrast to the nickel system, the reaction is at least partially reversible under practical conditions and thus of greater interest for applications.

2. Experimental

The intermetallic compound $LaMg_2Pd$ was prepared by a two-step procedure. First La rods (Johnson Mattey, 99.99%) and Pd foil (Strem Chemicals, 99.9%) were arc-melted in a 1/1 mixture. No weight loss was observed. The LaPd pellets were then crushed and ground in a glove box and mixed with Mg powder (Strem Chemicals 99.8%) in the molar ratio LaPd/Mg = 1/2. The mixtures were pressed to pellets, wrapped into Ta foil and put into an iron tube which was sealed under argon. The tube was put into a resistance furnace, heated up to 923 K for 1 h and then annealed at 873 K for 48 h. After opening the tube in a glove box the sintered sample was crushed and ground under an argon atmosphere. It had a grey colour and metallic luster. Two alloy batches were prepared, one weighting 6 g and the other 5 g. Both were tested by X-ray powder diffraction (XPD) and found to be single phase. The first batch was used to prepare 0.5 g of hydride powder for a synchrotron diffraction experiment, and 5.0 g of a deuteride powder for neutron scattering experiments. The second batch was used for all other experiments, in particular for measuring physico-chemical properties. The hydride (deuteride) samples were prepared in high-temperature high-pressure autoclaves as follows. Alloy powders of the first batch were evacuated to about 10^{-2} mbar for 8 h and then exposed to hydrogen (deuterium) gas (Polygaz, Geneva, Switzerland, 99.9999% for H_2; AGA, 99.8% for D_2) at an initial pressure ∼8 bar at room temperature. The autoclave was then heated up to 373 K yielding a hydrogen (deuterium) pressure of 10 bar, and left at this temperature for 2 days. After cooling down in air the autoclave was opened in a glove box and the hydride (deuteride) powder was retrieved. It had a dark-grey colour, was pyrophoric in air and lost hydrogen slowly under ambient pressure.

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Table 1
Crystal data and refinement results for $LaMg_2Pd$ from X-ray powder diffraction; e.s.d.s in parentheses

Atoms	Site	x	y	z	B (Å^2)
La	4c	0	0.4395(1)	0.25	0.78(4)
Mg	8f	0	0.1497(5)	0.0603(6)	2.4(1)
Pd	4c	0	0.7248(1)	0.25	0.50(5)

Space group *Cmcm* (No. 63); $a = 4.3228(1)$ Å, $b = 10.5289(2)$, $c = 8.3095(1)$ Å, $V = 378.20(2)$ Å^3, all sites fully occupied, $R_{\text{Bragg}} = 9.9\%$, $R_{\text{wp}} = 16.2\%$, $\chi^2 = 3.94$.

Gravimetric measurements suggested the composition to be close to the formula $LaMg_2PdH(D)_7$.

All samples were examined by XPD (Bruker D8, $\lambda = 1.50456$ Å, $8° < 2\theta < 120°$, step size $\Delta\theta = 0.0144°$). The hydride sample was also measured on the Swiss–Norwegian beamlines (BM1) at ESRF (Grenoble, France) in Debye–Scherrer geometry ($\lambda = 0.51979$ Å, six Si(1 1 1) analysers in the diffracted beam, angular range $1° < 2\theta < 45°$, step size $\Delta\theta = 0.004°$, room temperature). Prior to the experiment the sample was ground to a fine powder (grain size = 1–10 μm) and introduced into a sealed Lindeman tube (Ø = 0.5 mm). The deuteride sample was investigated by neutron powder diffraction on the instrument D2B at ILL (Grenoble, France) ($\lambda = 1.594$ Å, angular range $0° < 2\theta < 160°$, step size $\Delta\theta = 0.05°$, cylindrical vanadium container of 9 mm inner diameter, room temperature).

The hydrogen (deuterium) free samples were single phase and contained the intermetallic compound $LaMg_2Pd$. Its diffraction patterns indicated an ordered ternary derivative of the orthorhombic Re_3B-type structure (space group *Cmcm*). Given that no structure data have been reported for this compound yet, it was decided to refine the structure by using the atomic coordinates as reported for the nickel analogue $LaMg_2Ni$ [1]. Results are summarized in Table 1. For the hydride (deuteride) samples a study of the systematically absent reflections on the synchrotron pattern led to the non-centrosymetric orthorhombic space group $P2_12_12_1$ which differs from the centrosymmetric monoclinic space group $P2_1/c$ as reported for the Ni analogue $LaMg_2NiH_7$. The structure was solved ab initio from both the synchrotron and neutron data by the programme Fox [2]. It revealed one La site, two Mg sites, one Pd site, and seven D sites. Altogether 51 parameters were refined: 1 scale, 5 profile, 3 cell, 38 atomic parameters (33 positional and 5 displacement) and 4 background. Refinement results based on neutron data are summarized in Table 2, and selected bond distances and bond angles are given in Table 3. All structure refinements were done by the programme Fullprof 2000 [3].

Pressure composition isotherms (PCT) were measured at $T = 398$ and 373 K during desorption on a commercial Sieverts' apparatus (PCTPro-2000) by using ~0.94 g of the $LaMg_2Pd$ sample from the second batch. Measurements of the electric resistance were performed on both the intermetallic compound and pressed hydride powders in the temperature range between 300 and 10 K in steps of 0.5 K by using a standard four-wire technique.

Table 2
Crystal data and refinement results for $LaMg_2PdD_7$ from neutron powder diffraction at room temperature; e.s.d.s in parentheses

Atoms	Site	x	y	z	B (Å^2)
La	4a	0.2494(3)	0.0308(2)	0.1994(3)	1.19(4)
Mg1	4a	0.233(1)	0.3507(3)	0.0918(4)	1.36(4)
Mg2	4a	0.250(1)	0.3525(3)	0.4764(4)	B_{Mg1}
Pd	4a	0.7225(9)	0.2555(2)	0.2209(4)	2.54(6)
D11	4a	0.785(1)	0.1206(3)	0.1506(4)	2.98(4)
D12	4a	0.3630(6)	0.2322(4)	0.2655(6)	B_{D11}
D13	4a	0.8457(8)	0.3021(3)	0.4085(5)	B_{D11}
D14	4a	0.780(1)	0.3583(3)	0.0750(5)	B_{D11}
D1	4a	0.5242(9)	0.4622(3)	0.5356(5)	1.94(4)
D2	4a	0.227(1)	0.4477(2)	0.2816(4)	B_{D1}
D3	4a	0.0045(9)	0.4828(3)	0.5453(5)	B_{D1}

Space group $P2_12_12_1$ (No. 19) $a = 4.7745(1)$, $b = 11.7160(3)$ and $c = 8.1036(2)$ Å, $V = 453.30(2)$ Å^3 $Z = 4$, all sites fully occupied, $R_{\text{Bragg}} = 4.3\%$ $R_{\text{wp}} = 7.9\%$ $\chi^2 = 5.04$, e.s.d.s in parentheses. Cell parameters of hydride $LaMg_2PdH_7$: $a = 4.7845(1)$, $b = 11.7435(3)$, $c = 8.1174(2)$ Å.

Table 3
Shortest metal-deuterium distances (Å), and D–Pd–D bond angles in $LaMg_2PdD_7$ (e.s.d.s in parentheses)

	Complex D atoms			
	D11	D12	D13	D14
La	2.486(5)	2.480(5)	2.855(4)	2.729(4)
Mg1	2.008(5)	2.072(6)	3.214(6)	2.169(7)
Mg2	3.044(5)	2.280(6)	2.088(5) 2.092(6)	3.952(6)
Pd	1.706(5)	1.775(5)	1.719(5)	1.710(5)

	Angle (°)
D11–Pd–D12	95.4(5)
D11–Pd–D13	122.0(4)
D11–Pd–D14	113.2(4)
D12–Pd–D13	101.5(4)
D12–Pd–D14	113.9(4)
D13–Pd–D14	109.4(4)

	Interstitial D atoms		
	D1	D2	D3
La	2.403(5)	2.479(5)	2.391(5)
La	2.333(5)	2.687(5)	2.406(5)
Mg1	2.554(5)	1.913(4)	2.349(5)
Mg2	1.896(6)	1.936(4)	2.004(6)

3. Results and discussion

3.1. Crystal structure

Hydrogen-free $LaMg_2Pd$ is isostructural with its nickel analogue $LaMg_2Ni$. Both compounds are centrosymmetric and crystallize with orthorhombic symmetry. Interestingly, their hydrides structures, although being very similar, differ in detail. While the nickel compound $LaMg_2NiH_7$ crystallizes with a centrosymmetric structure having monoclinic symmetry and contains 2 (symmetry independent) Ni and 14 H sites, $LaMg_2PdH_7$ crystallizes with a non-centrosymmetric structure having orthorhombic symmetry and contains only one Pd site and seven H sites. Among the latter, four are bonded to palladium in a tetrahedral configuration (see D11–D14 in Fig. 1), and three (D1–D3) occupy La_2Mg_2-type interstices (not shown) having tetrahedral metal configurations. The shortest D–D distances are 2.1 Å. As shown in Table 3, the Pd–D bond distances (1.71–1.78 Å) are consistent with those in Sr_2PdD_4 and Ba_2PdD_4 that also contain tetrahedral coordinated Pd atoms (Pd–D = 1.76–1.81 Å [4]), and the D–Pd–D bond angles ($LaMg_2PdD_7$: 95–122°) are similar to the D–Ni–D angles in the Ni analogue $LaMg_2NiD_7$ (93–124°). The shortest La–D and Mg–D distances are 2.33 and 1.89 Å, respectively, i.e. slightly inferior to those in the corresponding saline binary hydrides (LaD_3: 2.43 Å, MgD_2: 1.95 Å). Thus, the metal–hydrogen bonds in $LaMg_2PdH_7$ are expected to have covalent (i.e.

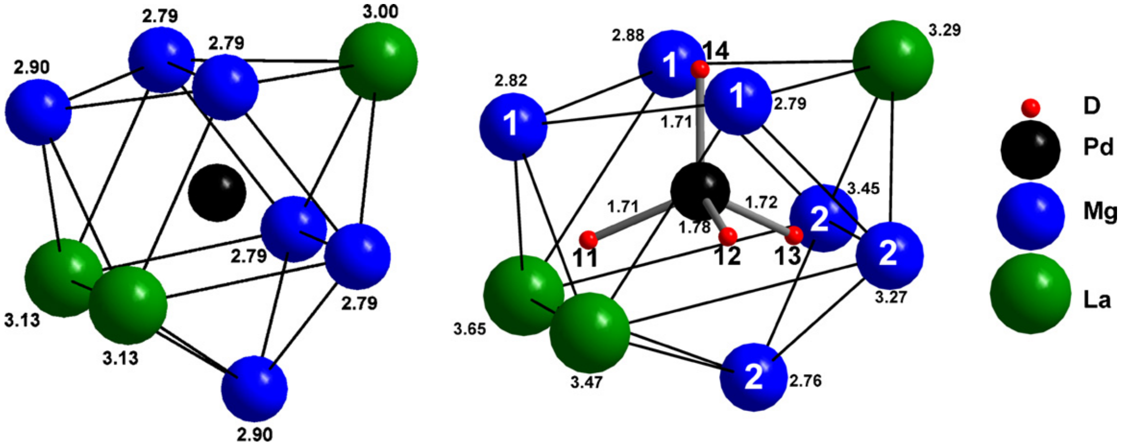

Fig. 1. Palladium atom environment in $LaMg_2Pd$ (left) and $LaMg_2PdD_7$ (right); Pd-metal and Pd–D bond distances (Å) indicated; atom numbering as in Table 2.

directional) character for palladium (presumably of sp^3-type) and ionic (i.e. non-directional) character for lanthanum and magnesium.

Thus, from a bonding point of view the hydride structure can be rationalized in terms of a palladium centered tetrahedral $[PdH_4]^{4-}$ "complex" having terminal hydrogen ligands (called "complex" hydrogen hereon), and hydrogen anions H^- surrounded by Mg^{2+} and La^{3+} cations only (called "interstitial" hydrogen hereon), corresponding to the limiting ionic formula $LaMg_2PdH_7 = La^{3+} 2\,Mg^{2+} [PdH_4]^{4-} \cdot 3H^-$. The $[PdH_4]^{4-}$ complex conforms to the 18-electron rule, i.e. Pd is formally zero-valent and has an electronic d^{10} configuration. This bonding description implies a charge transfer from La and Mg to both complex and interstitial hydrogen such that the Pd d-bands are nearly filled and all valence electrons are localized in metal–hydrogen bonds. In other words, the hydride is expected to be non-metallic (see Sections 3.2 and 3.3). Except for the tetrahedral $[PdH_4]^{4-}$ complexes in $LaMg_2PdH_7$ and Sr_2PdD_4 (or Ba_2PdH_4), all other solid state palladium hydride complexes known are either linear such as $[PdH_2]^{2-}$ in Li_2PdH_2 and Na_2PdH_2 [5], triangular such as $[PdH_3]^{3-}$ in $NaBaPdH_3$ [6], or square planar such as $[PdH_4]^{2-}$ in Na_2PdH_4 [7] (for a recent review, see ref. [8]).

Apart from the hydrogen induced decrease in symmetry (from centrosymmetric to non-centrosymmetric) and the increase in cell volume ($\Delta V/V \sim 20\%$) the metal substructure of the $LaMg_2Pd$-H system remains essentially unchanged during hydrogenation (atom shifts ∼0.7 Å). As expected, the largest shifts occur in the vicinity of the tetrahedral $[PdH_4]^{4-}$ complex. As shown in Fig. 1, the metal atom environment around Pd consists of a tricapped trigonal prism composed of three La and six Mg atoms. While the palladium-metal distances in the intermetallic compound $LaMg_2Pd$ cover the ranges Pd–La = 3.00–3.13 Å and Pd–Mg = 2.79–2.90 Å, those in the deuteride increase to Pd–La = 3.29–3.65 Å and Pd–Mg = 2.76–3.45 Å. The biggest increase (∼0.7 Å) occurs for one of the magnesium atoms (Mg_2) and is presumably due to steric hindrance by the three surrounding relatively rigid $[PdH_4]^{4-}$ complexes.

3.2. PCT and electric resistance

PCT data as collected during desorption at $T = 398$ and 373 K down to 10^{-2} mbar are shown in Fig. 2. Clearly, the hydrogen loss observed (∼1.4 wt.%, i.e. ∼4H/formula unit.) is lower than expected for full desorption of $LaMg_2PdH_7$ (2.38 wt.%) and suggests the formation of an intermediate hydride. The equilibrium plateaus at these temperatures are situated at ∼0.5 (373 K) and ∼1 bar (398 K), i.e. the hydride can be considered to be partly reversible under technically useful conditions. The desorption enthalpy as estimated from these data by using Van't Hoff's equation is $(\Delta H)_{des} \sim 50$ kJ/(mol H_2).

The resistivity measurements (not shown here) confirmed the hydride to be non-metallic, similar to the nickel analogue. A reliable value for the band gap, however, could not be obtained.

3.3. Electronic structure

Theoretical calculations were carried out using the Vienna ab initio simulation package (VASP) based on density functional

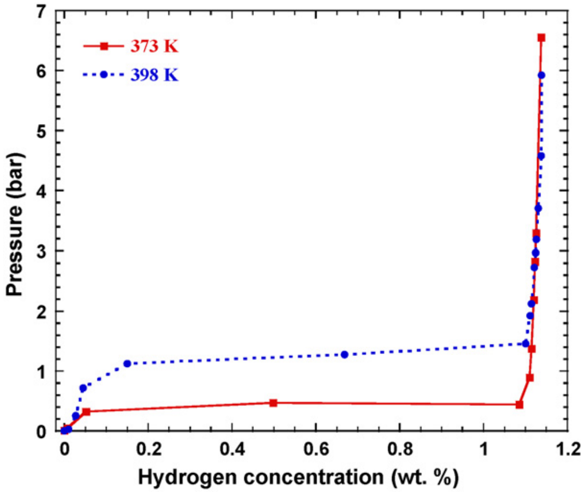

Fig. 2. PCT curves of $LaMg_2PdH_7$ as measured during desorption at $T = 373$ K (solid line) and 398 K (dotted line).

Table 4
Hydrogenation induced structural and electronic changes in intermetallic compounds forming transition metal–hydrogen complexes[a]

Compound (symmetry)	Hydride (symmetry)	$\Delta V/V$ (%)	Maximun shift (Å)	Complexes and H^- anions	Hydride properties	Reference
Mg_2Ni (hexagonal)	Mg_2NiH_4 (monoclinic)	32	~2.0	$[NiH_4]^{4-}$	Non-metallic, brownish	[10,11]
Mg_3Ir (hexagonal)	$Mg_6Ir_2H_{11}$ (monoclinic)	40	~1.9	$3[IrH_4]^{4-}$, $[IrH_5]^{4-}5H^-$	Non-metallic, red	[12]
$LaMg_2Ni$ (orthorhombic)	$LaMg_2NiH_7$ (monoclinic)	18	~0.7	$[NiH_4]^{4-}$, $3H^-$	Non-metallic, dark grey	[1]
$LaMg_2Pd$ (orthorhombic)	$LaMg_2PdH_7$ (orthorhombic)	20	~0.7	$[PdH_4]^{4-}$, $3H^-$	Non-metallic, dark grey	This work

[a] Adapted and completed from ref. [1].

theory and the projector augmented wave method (PAW) with plane waves [9]. The generalized gradient approximation (GGA) was used. The energy cutoff is 600 eV and the k-point set used was 8 × 14 × 6 for $LaMg_2PdH_7$. The outer core shells (5s and 5p) of La were included as valence states. A gap appears upon hydrogenation and an examination of the band structure (not shown) reveals a fundamental direct gap of 0.7 eV at Γ, which is smaller than the Ni analogue (0.9 eV [1]). This is the GGA value, while the real gap is estimated to be more than 1.0 eV. The projected density of states (PDOS) plot for the hydride $LaMg_2PdH_7$ is shown in Fig. 3(a and b), with the energy zero set at the top of the valence band. The projection radii used were 1.5 Å for La, 1.1 Å for Mg, 0.9 Å for Pd, and 0.8 Å for H. With the small H value, not all the charge was captured, but the energy-distribution trend is visible in these plots. These PDOS plots represent a sum over the various atoms sites for a single element. As one can see from Fig. 3a, almost all the Pd d states are below the gap, indicating an approximately closed d shell, while the peak around +2 eV is associated with the (unoccupied) La f bands. One can identify three broad peaks in the PDOS associated with hydrogen. They can be associated with states (in the order of rising energy) from H-s in the complex, H-s interstitial, and (a small peak from) H-s in the complex, respectively. An examination of the charge density (not shown) concludes that magnesium behaves like an electron donor with very little valence charge in its vicinity, while both types of hydrogen attract charge as expected from its relatively large electronegativity.

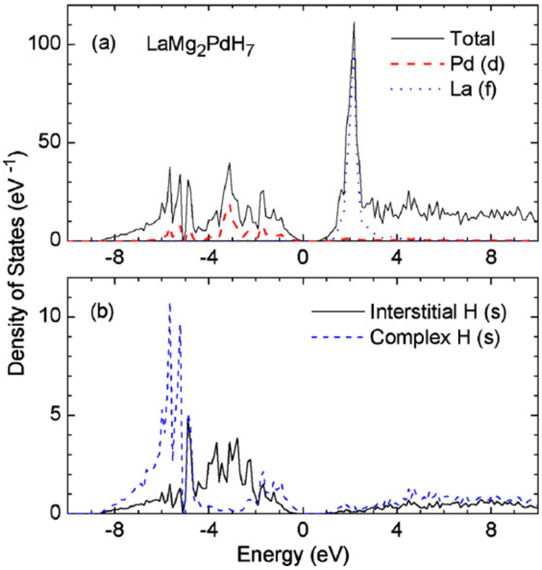

Fig. 3. Total density of states and projected density of states of $LaMg_2PdH_7$ for Pd d and La f (a). Projected density of states for interstitial and complex hydrogen (b).

4. Conclusions and outlook

The interest in the $LaMg_2Pd$-H system is at least twofold. Firstly, in contrast to the nickel analogue, the palladium system is partially reversible under practical conditions and thus of greater interest for applications. Secondly, it provides another example for a hydrogen induced metal–insulator transition. Such transitions are relatively rare for transition metal-hydrogen systems and of both practical and fundamental interest. Those involving transition elements are summarized in Table 4. A particularly well-documented example is the ternary nickel system Mg_2Ni-H in which metallic Mg_2Ni transforms into non-metallic Mg_2NiH_4 that shows optical mirror properties [11]. The nature of the electron correlations leading to this transition is poorly understood. One reason is due to the fact that the transition in this system is accompanied by atomic shifts of up to 2 Å that lead to a breaking of metal–metal bonds. Such a bond breaking does not occur in the quaternary $LaMg_2Ni$-H and $LaMg_2Pd$-H systems for which the atomic shifts during hydrogenation are ~0.7 Å and thus provide a better ground for studies of the electron correlations. A full account of this work will appear elsewhere.

Acknowledgments

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