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Letter

$LiSr_2PdH_5$, the first mixed alkali–alkaline earth transition metal hydride

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1. Introduction

Recently, we have reported on several quaternary transition metal hydrides based on two alkaline earth elements, such as $CaMgNiH_4$ [1], $SrMg_2FeH_8$ [2] and $Ca_4Mg_4Fe_3H_{22}$ [3]. Here we report on the first quaternary transition metal hydride which is based on alkali and alkaline earth elements.

2. Experimental details

Ternary metal alloys of nominal composition $Li_{1.5}Sr_2Pd$ were prepared from the elements (lithium (Johnson Matthey, rod 99.8%); strontium (Alfa Products, rod 99%); palladium (Johnson Matthey, sponge 99.9%)) by arc melting. The ingots were powdered under an argon atmosphere, wrapped in molybdenum foil and placed in a high temperature, high pressure autoclave. After evacuating to about 10^{-2} mbar and flushing the autoclave with argon it was charged with hydrogen (deuterium) gas (H_2, Polygaz, 99.9999%; D_2, AGA 99.8%) to an initial pressure of about 75 bar at room temperature. The temperature was increased to 520–530 °C, yielding a hydrogen (deuterium) pressure of 155 bar, this temperature was maintained for 10–14 days and then decreased to ambient conditions. The samples were transferred to an argon-filled glove box and ground, yielding a powder of dark green colour which was sensitive to air.

Results and discussion

The samples were characterized by X-ray powder diffraction (Guinier camera, Cu Kα radiation; internal standard was silicon powder with $a = 5.4308$ Å). The patterns showed a new hydride phase which was indexed on a tetragonal lattice with refined cell parameters $a = 3.9294(3)$ Å and $c = 7.4214(9)$ Å (hydride) and $a = 3.9263(3)$ Å and $c = 7.4175(7)$ Å (deuteride) at room temperature. No impurity phase was detected. The reflection intensities were consistent with a $CdPt_2Zn$-type metal atom arrangement (space group *P4/mmm*; No. 123), *i.e.* an ordered CsCl derivative structure in which palladium and lithium alternate at the centres of strontium cubes along the fourfold axis. Measurements at low temperature showed no evidence for a structural phase transition down to 10 K. The lithium and hydrogen positions were determined from neutron powder diffraction on the deuteride using the DMC diffractometer [4] at the SAPHIR reactor at PSI, Villigen (Ge(511) monochromator; $\lambda = 1.0862$ Å; angular 2θ range, 3.0°–135.0°; 2θ step, 0.1°; sample weight, 5 g; cylindrical vanadium container of inner diameter 8 mm). The sample was cooled to 14 K and measured in the high resolution mode.

The data showed no evidence for a structural phase transition. Traces of the impurity phase LiD were found. The lithium site in the structure was confirmed and three deuterium sites were found. Two sites were fully occupied and one site was partially occupied. The occupancy of this latter site was nearly 50% during preliminary refinements and was fixed at the value during final refinements, thus corresponding to the composition $LiSr_2PdD_5$. The program DBWS-9006 [5] and nuclear scattering lengths (lithium, −0.190; strontium, 0.702; palladium, 0.591; deuterium, 0.6671×10^{-12} cm), as tabulated in ref. 6, were used. The following 20 parameters were allowed to vary: two scale factors, three peak width parameters, one zero correction parameter, three cell parameters (two for $LiSr_2PdD_5$ and one for LiD), nine atomic and two asymmetry parameters. The results are summarized in Table 1.

As shown in Fig. 1, the structure of $LiSr_2PdD_5$ can be described in terms of $SrLiD_3$-type slabs having an ordered perovskite-type structure, and $SrPdD_{3-x}$-type slabs having a disordered defect perovskite-like structure. The slabs are stacked along [001] and are intergrown via common strontium and deuterium atoms. In the ordered perovskite-type slabs, lithium is coordinated

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TABLE 1. Refinement results of neutron powder diffraction for $LiSr_2PdD_5$(T = 14 K)

Atom	Position	x	y	z	$U_{iso}\times 100$ (Å)
Li	1(b)	0	0	1/2	0.31(2)
Sr	2(h)	1/2	1/2	0.2547(3)	U_{iso}(Li)
Pd	1(a)	0	0	0	0.57(5)
D1	2(g)	0	0	0.2287(5)	3.81(7)
D2	2(e)	0	1/2	1/2	1.75(4)
D3[a]	2(f)	0	1/2	0	4.1(2)

Space group: $P4/mmm$ (No. 123).
Cell parameters: a = 3.9016(2) Å; c = 7.3929(4) Å.
Agreement indexes: $R_p = 2.99\%$; $R_{wp} = 3.88\%$; $R_B = 7.73\%$.
Form of temperature factor: $T = \exp[-8\pi^2 U_{iso}(\sin\theta/\lambda)^2]$.
Estimated standard deviations in parentheses.
[a]Population parameter, 0.5.

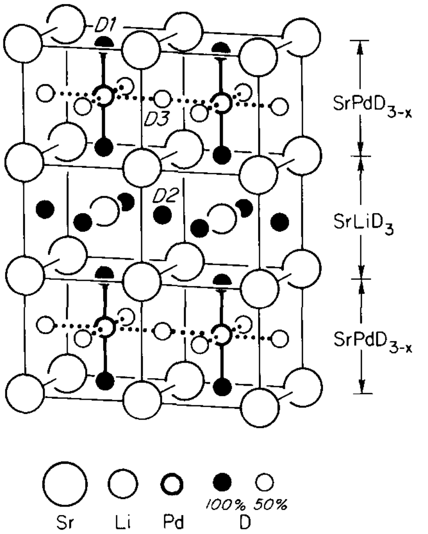

Fig. 1. Structure of tetragonal $LiSr_2PdD_5$ viewed approximately perpendicular to the fourfold axis. The D1 and D2 sites are fully occupied and the D3 site is half occupied. The D1 and D3 sites have large displacement amplitudes.

by six deuterium atoms (D1, D2) in a nearly ordered octahedral configuration.

The bond distances [Li–2D1] = 2.006(4) Å and [Li–4D2] = 1.9508(1) Å) are slightly longer than those in $SrLiH_3$, *i.e.* [Li–6D] = 1.917(1) Å [7], which has the inverse perovskite structure. The relatively large displacement amplitudes of the two D1 atoms which are bonded to palladium indicate some positional disorder. In the defect perovskite-like slabs, palladium is coordinated by three deuterium atoms on average in a partially disordered configuration. Two deuterium atoms (D1) are ordered on opposite vertices of an octahedron and form a linear (or nearly linear) configuration. Their bond distances are relatively short ([Pd–D1] = 1.691(4) Å) and consistent with those in $SrPdH_2$ [8], which also has a defect perovskite-like structure. The third deuterium atom (D3) is disordered on the four remaining octahedral vertices. Its average bond distance is relatively long ([Pd–D3] ≈ 1.95 Å) but its local bond distance is presumably shorter than 1.95 Å, because the D3 sites represent only average deuterium positions with relatively large displacement amplitudes (see Table 1).

Thus, the local deuterium environment around palladium is unknown. Possible configurations are T-shaped PdD_3 groups in which the two colinear deuterium ligands (D1) occupy positions on (or near) the tetragonal axis, while the third ligand (D3) is disordered over four positions away from that axis. Alternatively, there is a mixture between linear PdD_2 and saddle-like PdD_4 groups in which the colinear ligands occupy the former two positions and the remaining ligands are disordered over the latter (four) positions. Linear $[PdD_2]^{2-}$ complexes are common in deuterides with palladium in the formal oxidation state zero, as in the present compound. The observed bond distances in these complexes ([Pd–D] = 1.68–1.84 Å [9]) are consistent with those in $LiSr_2PdD_5$ ([Pd–D] = 1.69 Å). T-shaped PdD_3 and saddle-like PdD_4 groups are not yet known among palladium deuterides but such groups exist for ruthenium in Mg_3RuD_3 [10] and Mg_2RuD_4 [11] respectively.

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