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# Observation of praseodymium polyhydrides synthesized at high temperatures and pressures

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Rare earth element polyhydrides have been predicted to exhibit high- $T_c$  superconductivity at extreme compressions. Through a series of *in-situ* high-pressure high-temperature x-ray powder diffraction experiments combined with density functional theory (DFT) calculations, we report the emergence of polyhydride species in the praseodymium-hydrogen system. We initially observe the formation of PrH<sub>3</sub>, which continuously increases in hydrogen content on compression towards PrH<sub>4</sub>. Laser heating PrH<sub>4</sub> in a hydrogen medium at pressures of 85 GPa leads to the synthesis of both PrH<sub>9</sub> and PrH<sub>7</sub>. Both structures are characterized by hexagonal arrays of praseodymium atoms surrounded by hydrogen clathrate cages.

It has been postulated that the presence of heavy elements within a hydrogen lattice may provide ‘chemical precompression’, resulting in the dissociation of H<sub>2</sub> molecules at considerably lower pressure than expected for elemental H<sub>2</sub> [1]. These materials are generally referred as hydrides or polyhydrides. They have captivated scientific experimental and theoretical attention in the last decade as they are predicted to show exotic properties such as metallicity and high- $T_c$  superconductivity at conditions accessible with current experimental capabilities [2–5]. The most promising structural candidates are characterised by high-symmetry lattices of metal atoms surrounded by clathrate cages of hydrogen, allowing very high H-content without forming H<sub>2</sub> molecules [6].

Rare earth metals (RE) react with hydrogen to form cubic, non-stoichiometric hydrides [7–9]. When exposed to a hydrogen atmosphere and high-temperatures, most of these hydrides can absorb additional hydrogen up to a composition limit of approximately REH<sub>3</sub> [10, 11]. Through the combined application of pressure and temperature (above 100 GPa and 1000 K), new phases are expected to emerge with significantly higher hydrogen content. In particular, rare earth hydrides (REH) have emerged as the most promising candidates to form clathrate cages of H which may present many attractive and novel properties [12, 13]. For example, the combined high pressure and high temperature (laser heating) synthetic route has recently been used to form a ‘superhydride’, LaH<sub>10</sub> [5]. It was later reported that this compound exhibits superconductivity at 260 K at pressures between 180-200 GPa [14, 15]. ~~Given the remarkable possibilities of rare earth hydrides it is imperative to investigate other possible candidates and explore their synthetic routes, stability ranges and properties.~~

Due to the identical structure of their outermost electron shells, rare earth metals exhibit physical properties that depend only weakly on the occupancy of the 4*f* shell. Therefore, it should be expected that similar high pressure and temperature routes would induce the formation

of superhydrides in other rare earth metals [11]. In particular, praseodymium polyhydrides have been predicted to show high-temperature superconductivity ( $T_c$  above 50 K) when the ratio H to Pr is above 9 [13]. Theoretical studies of the Pr-H system suggest that PrH<sub>4</sub> (space group  $I4/mmm$ ) should be the most stable stoichiometry up to 50 GPa. Polyhydride species with H-rich cages are predicted to stabilize at higher pressure: PrH<sub>8</sub> ( $P63mc$ ) at 100 GPa, PrH<sub>9</sub> ( $F\bar{4}3m$ ) at 200 GPa, and only at around 400 GPa does the analogous PrH<sub>10</sub> phase become energetically favoured [13]. A recent study reported the synthesis of PrH<sub>9</sub> at 115 GPa and 1650 K [16]. Two polymorphs, hexagonal  $P6_3/mmc$  and cubic  $F\bar{4}3m$ , were produced in the pressure range between 115 and 125 GPa, however the pressure stability ranges of such compounds were not fully explored.

Here, through a combination of high-pressure high-temperature experiments using x-ray diffraction as diagnostic, combined with density functional theory (DFT) calculations, we report the synthesis and pressure-dependent behaviour of previously unobserved praseodymium polyhydrides. We document the expected reaction of Pr and H<sub>2</sub> forming PrH<sub>3</sub> adopting  $Fm\bar{3}m$  structure below 5 GPa. On compression, the H-content of the PrH<sub>3</sub> species increases, exhibiting a continuous phase transition towards PrH<sub>4</sub> by 40 GPa. Laser heating this phase between 85-95 GPa leads to a radical transformation of the sample producing two new Pr-H compounds: PrH<sub>9</sub> and PrH<sub>7</sub>. Both phases crystallise in hexagonal structures, distinguished by their different volumes and stabilities. PrH<sub>9</sub> contains PrH<sub>29</sub> clusters and is stable from 76 GPa to at least 96 GPa. The secondary reaction product, PrH<sub>7</sub>, contains PrH<sub>21</sub> clusters and has a wider stability range from 96 GPa down to 60 GPa. The hexagonal structure of PrH<sub>9</sub> is unexpected, as former predictions suggested that a cubic structure should be observed instead [13]. These results demonstrate that the pressure-temperature-composition phase space of praseodymium hydrides is more complex than

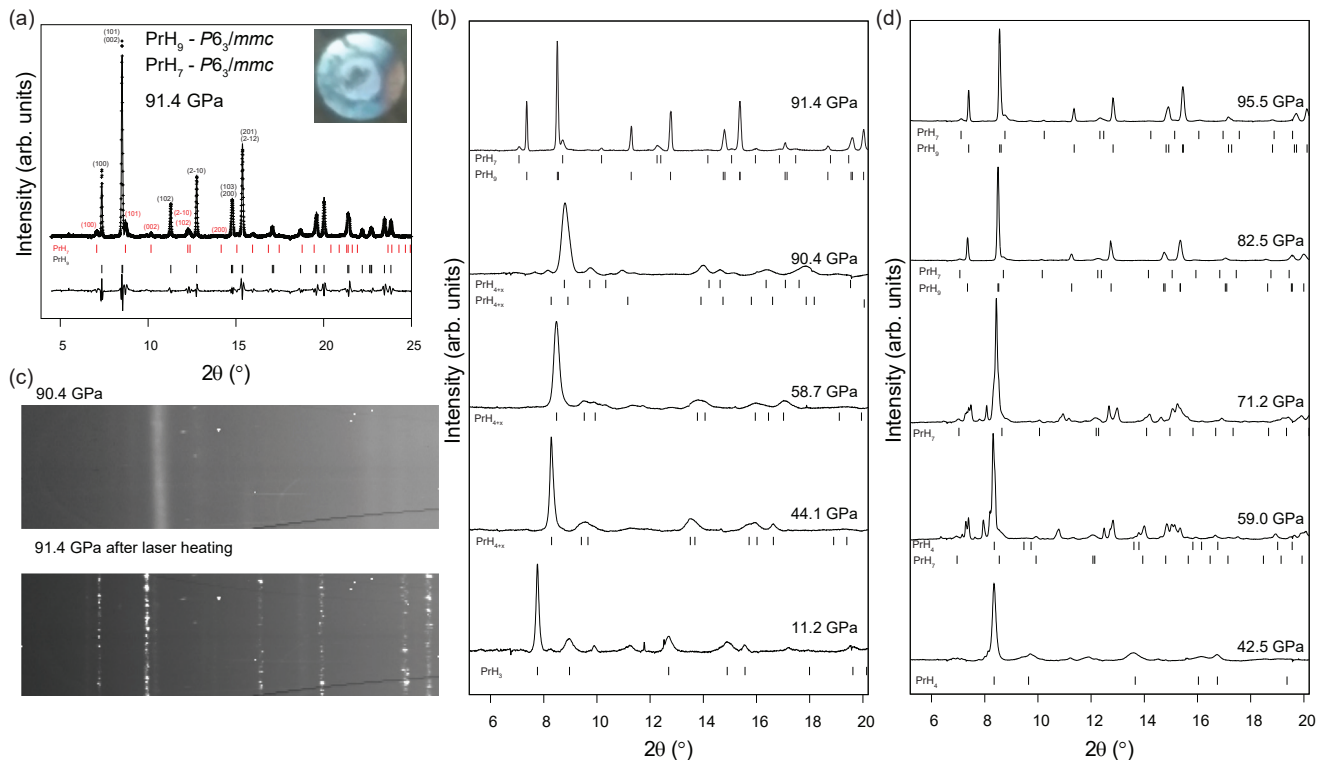


FIG. 1. (a) Representative Le Bail refinement of high-pressure x-ray diffraction data of  $\text{PrH}_7/\text{PrH}_9$  mixture at 91.4 GPa. Tick marks indicate the calculated peak positions, the difference between observed and calculated profiles is shown below,  $wR_p = 0.82\%$ . Inset shows an image of the sample chamber at 20 GPa. Culet size is  $50 \mu\text{m}$ ; (b) High pressure x-ray diffraction patterns ( $\lambda = 0.4115 \text{ \AA}$ ) taken on compression showing the continuous transition from cubic ( $Fm\bar{3}m$ )  $\text{PrH}_3$  to tetragonal ( $I4/mmm$ )  $\text{PrH}_4$ . Subsequent laser heating above 90 GPa leads to the synthesis of new praseodymium hydrides  $\text{PrH}_9$  ( $P6_3/mmc$ ) and with  $\text{PrH}_7$  ( $P6_3/mmc$ ) as a minor phase; (c) X-ray diffraction patterns before and after laser heating; (d) Diffraction patterns taken on decompression showing the transition of  $\text{PrH}_9$  from a hexagonal to a complex unknown structure below 82.5 GPa followed by its decomposition to  $\text{PrH}_4$  below 59 GPa.  $\text{PrH}_7$  remains stable down to 54 GPa. Both polyhydrides eventually decompose to  $\text{PrH}_4$  with further decompression.

previously thought.

High-purity Pr powder (99.5%, sim 40 mesh, Alfa-Aesar) was initially compressed into foils of approx.  $8 \times 8$  micron and loaded into diamond anvil cells (DAC) together with a gold pressure marker [20]. The sample preparation was conducted in an inert environment glove box and the Pr foils were hermetically sealed within the Re gasket chamber. Research grade hydrogen (99.9999%) was subsequently gas loaded at a pressure of 0.17 GPa. Loading of hydrogen was confirmed by the observation of the hydrogen vibrational mode using a custom-built micro-focused Raman system [21].  $\text{NH}_3\text{BH}_3$  has become a widely accepted method for in situ hydrogen generation to facilitate the synthesis of high pressure polyhydrides.[14–16, 22] However, using pure  $\text{H}_2$  instead of  $\text{NH}_3\text{BH}_3$  guarantees a higher density of hydrogen atoms available to synthesize high stoichiometry hydrides. Rhenium gaskets, indented to 9–18  $\mu\text{m}$  thickness, were used to form the sample chamber in all experimental runs. The diamond anvil culets ranged from 50 to 100  $\mu\text{m}$ , with sample sizes ranging between 20 to 60

$\mu\text{m}$  once hydrogen was in the solid state. Once loaded, pressure was increased to above the hydrogen solidification point, and the Pr foil was hydrogenated over a period of 7–14 days before x-ray diffraction measurements were conducted. Angle-dispersive x-ray diffraction patterns were recorded on a MAR-555 detector with synchrotron radiation ( $\lambda = 0.4115 \text{ \AA}$ , 30 keV) at the ID15B beamline (ESRF, France). Two-dimensional image-plate data were integrated with *DIOPTAS* to yield intensity vs.  $2\theta$  plots [23]. Diffraction patterns were indexed with *CONOGRAPH*, Le Bail refinement was carried out in *Jana2006* [24–26].

Total energy calculations were carried out within the framework of density functional theory (DFT) in conjunction with the projector-augmented wave (PAW) method and a plane wave basis, as implemented in the VASP code [27, 28]. We used the PBE exchange-correlation functional [29] and “hard” PAW data sets (cutoff radii:  $r_{\text{Pr}} = 2.8 a_B$ ,  $r_{\text{H}} = 0.8 a_B$ ) that included the Pr  $5s^2 5p^6 6s^2 4f^3$  electrons in the valence space. Pure hydrogen phases I and III were modelled in a eight-

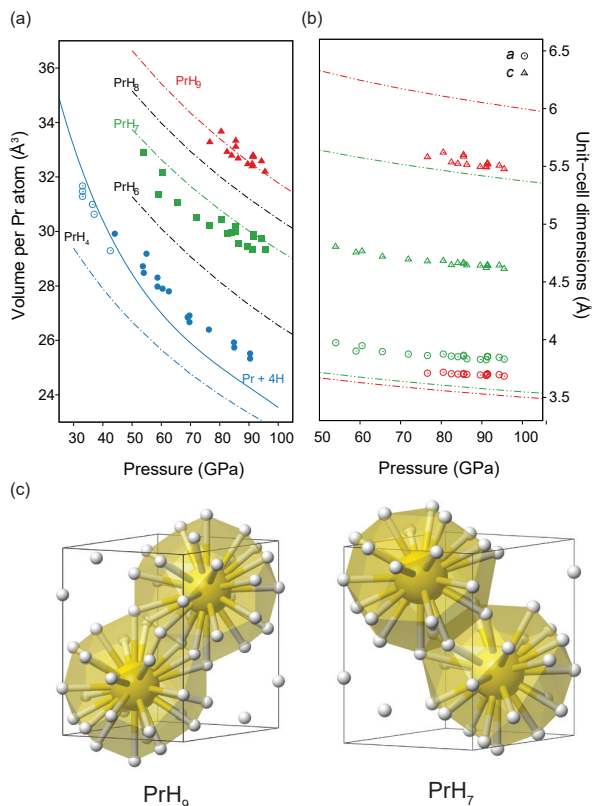


FIG. 2. (a) Volume per Pr atom for praseodymium hydrides. Empty circles correspond to the cubic phase of PrH<sub>4</sub>, filled circles, the tetragonal (*I4/mmm*) phase. Dark blue points correspond to high-pressure PrH<sub>4+x</sub> polymorph. Solid line indicates volume derived from the atomic volumes of the elements [17–19], while dashed lines refer to volumes derived from our DFT calculations. (b) Unit cell parameters for PrH<sub>7</sub> (green) and PrH<sub>9</sub> (red). Dashed lines correspond to the DFT predicted values. (c) Crystal structures of Pr polyhydrides, PrH<sub>7</sub> (*P6<sub>3</sub>/mmc*) and PrH<sub>9</sub> (*P6<sub>3</sub>/mmc*); Pr atoms are yellow, H are white.

molecule cell of *P6<sub>3</sub>/m* symmetry and a *C2/c* phase, respectively. The plane wave cutoff energy was 800 eV and Brillouin zone sampling was done on regular *k*-point grids with separations of 0.033 Å<sup>-1</sup>. Zero-point energy (ZPE) contributions were initially included to test the stability of the cubic vs hexagonal PrH<sub>9</sub> structures, however, it was found to make no difference. As such, ZPE effects were not included for the calculated stability ranges of other phases. Spin-orbit coupling was included in the calculations, and found to have minor effects on relative stabilities and electronic properties.

At pressures above 5 GPa, x-ray diffraction patterns show only the presence of the known hydride PrH<sub>3</sub> with a *fcc* (*Fm3m*) structure ( $a = 5.2719(3)$  Å at 11.2 GPa). The synthesis of PrH<sub>3</sub> under pressure from its constituents, appears to produce poorly crystalline samples, characterized by broad diffraction peaks and a rapid drop-off in diffracted intensity with  $2\theta$  (Fig. 1). This

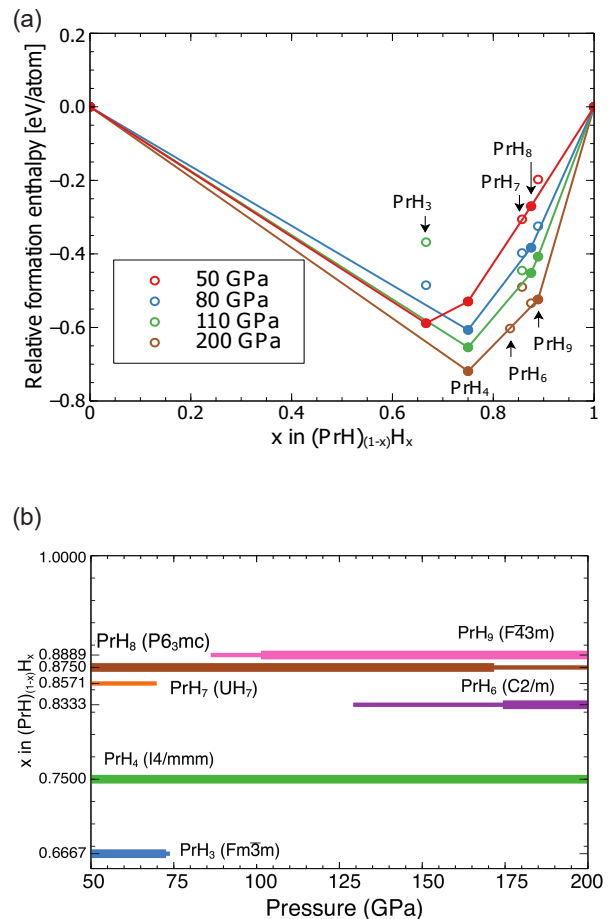


FIG. 3. (a) Convex hull construction for PrH<sub>n</sub> phases relative to PrH and 1/2 H<sub>2</sub>, at a sequence of pressures. Empty (filled) symbols denote metastable (stable) phases, the latter form the convex hull at each pressure. The stoichiometries considered are indicated. (b) Stability ranges of Pr-hydrides from spin-orbit coupling DFT calculations. Compositions and space groups/prototypes are indicated. Thin lines denote pressure ranges where the phases are metastable, defined as up to 10 meV/atom above the convex hull.

PrH<sub>3</sub> phase, remains stable up to at least 30 GPa. However, on further compression, the associated changes in volume per Pr atom with pressure suggest a continuous increase in hydrogen content. The PrH<sub>3</sub> *fcc* (002) and (202) reflections split indicating a transition to a body-centred tetragonal structure ( $a = 3.4547(4)$ ,  $c = 5.0130(10)$  Å at 44.1 GPa). Comparison with the volume calculated from the equations of state of the elements [17, 18] suggests a hydrogen-content approaching PrH<sub>4</sub> by 40 GPa (Fig. 2). Increasing pressure sees the volume per Pr atoms rising above that of Pr+4H, indicating the formation of a solid solution approximating PrH<sub>4+x</sub> (Fig. 2). The formation of PrH<sub>4+x</sub> is in agreement with computational studies predicting PrH<sub>4</sub> (*I4/mmm*) as the most stable low-pressure Pr hydride [13]. This PrH<sub>4+x</sub> phase is also poorly crystalline, again

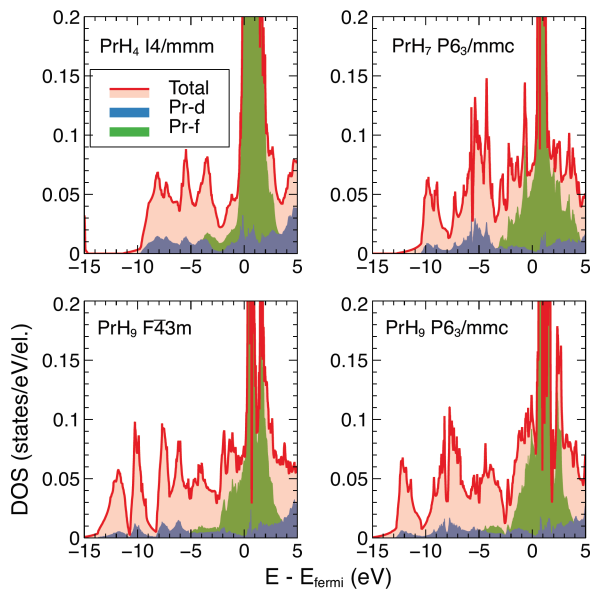


FIG. 4. Electronic densities of state (DOS) for  $\text{PrH}_4$ ,  $\text{PrH}_7$ ,  $\text{PrH}_9$  ( $F\bar{4}3m$ ), and  $\text{PrH}_9$  ( $P6_3/mmc$ ) from spin-orbit coupling calculations, all at 80 GPa.

characterised by broad diffraction peaks. Above 75 GPa we observe the emergence of additional broad weak peaks which we tentatively index to a body-centered tetragonal cell ( $a = 2.9926(7)$   $c = 5.6998(32)$  Å at 90.4 GPa) with a volume similar to that of  $\text{PrH}_{4+x}$  at the same pressure (25.330 and 25.523 Å<sup>3</sup>, respectively) suggesting a sluggish transition to a new polymorph.

Laser heating of metals in a high-pressure hydrogen environment has been a successful synthetic tool to overcome kinetic barriers and promote the formation of metal hydrides with unexpected stoichiometries.[4, 5, 30–35]. In this work,  $\text{PrH}_{4+x}$  in a  $\text{H}_2$  medium was laser heated using a 1064 nm Nd:YAG laser at pressures above 85 GPa. Temperatures were held between 1000 K-1400 K for a period of 10 s. Diffraction patterns indicated no changes during heating beyond the thermal lattice expansion of  $\text{PrH}_{4+x}$ . However, on quenching, the sample showed radical transformations in the obtained diffraction patterns with no shift in pressure. As seen in Fig. 1 upon quenching, the low-intensity broad diffraction peaks of  $\text{PrH}_{4+x}$  were replaced by well-defined rings. Comparison of the ring textures indicated the presence of two new phases, and all the observed peaks could be indexed with two hexagonal unit cells:  $a = 3.7022(1)$ ,  $c = 5.5215(3)$  Å and a minor phase with unit cell:  $a = 3.8535(4)$ ,  $c = 4.6442(7)$  Å at 91.4 GPa (Fig. 1).

Examination of the unit-cell volumes with pressure provides the best available probe to estimate the stoichiometry of these compounds. The unit-cell volume of the major phase is clearly greater than that of the predicted stable phase at this pressure,  $\text{PrH}_8$  (Fig. 2(a)), suggesting instead a stoichiometry of  $\text{PrH}_9$ . We have

TABLE I. Crystal structure parameters for praseodymium polyhydrides optimised by DFT calculations including spin-orbit coupling at 80 GPa.

PrH <sub>7</sub> at 80 GPa $a = 3.6070$ Å $c = 5.4688$ Å ( $P6_3/mmc$ )			
Atom	$x$	$y$	$z$
Pr1 ( $2d$ )	1/3	2/3	3/4
H1 ( $2b$ )	0	0	1/4
H2 ( $12k$ )	0.17499	0.34997	0.07268
PrH <sub>9</sub> at 80 GPa $a = 3.5652$ Å $c = 6.0943$ Å ( $P6_3/mmc$ )			
Pr1 ( $2d$ )	1/3	2/3	3/4
H1 ( $2c$ )	1/3	2/3	1/4
H2 ( $4e$ )	0	0	0.16591
H3 ( $12k$ )	0.17694	0.35389	0.05950

performed our own DFT geometry optimisation calculations for our determined  $\text{PrH}_9$  structure and find excellent agreement between the experimentally observed volumes and those theoretically derived (see Fig. 2(a)). Interestingly, previous predictions report that  $\text{PrH}_9$  should only adopt a cubic crystal structure ( $F\bar{4}3m$ ) [13]. Instead, in agreement with Ref. [16], we find that  $\text{PrH}_9$  also adopts a  $P6_3/mmc$  structure, found experimentally in  $\text{NdH}_9$ [36],  $\text{ThH}_9$ [37] and for  $\text{CeH}_9$  [22, 38]. However, Ref. [16] find coexistence between both  $P6_3/mmc$  and  $F\bar{4}3m$  hydride phases through high temperature synthesis at the higher pressure of 105 GPa, whilst we only observe the former structure at 85 GPa. As such, the  $F\bar{4}3m$   $\text{PrH}_9$  must emerge only at pressures greater than 85 GPa.

The minor  $\text{PrH}_7$  phase also displays a hexagonal structure, in agreement with a number of predicted stoichiometries in the range  $\text{REH}_{6-9}$  [13, 39]. On the basis of our DFT geometry optimization and stability searches within the pressure range 50-100 GPa we find the closest agreement in volume with  $\text{PrH}_7$  (see Figs. 2 and 3), isostructural to  $\text{UH}_7$  [39]. The degree of mismatch between the predicted and experimentally observed  $\text{PrH}_7$  volumes may suggest  $\text{PrH}_7$  is a non-stoichiometric solid solution. However, confirmation of this would require neutron diffraction to determine hydrogen atomic positions, which is currently outwith experimental capabilities due to the pressures required for synthesis.

Fig. 3 (a) shows the full convex hulls of the Pr-H binary system at representative pressures. The relative formation enthalpies  $\Delta H_f$  are with respect to decomposition into PrH and  $\text{H}_2$ , in the appropriate ratios. At 50 GPa, we find  $\text{PrH}_3$ ,  $\text{PrH}_4$ , and  $\text{PrH}_8$  stable, while  $\text{PrH}_7$  (in the  $\text{UH}_7$  structure type) is very close to stability. The latter, as well as  $\text{PrH}_3$ , becomes unstable at higher pressures.  $\text{PrH}_4$  persists throughout the entire pressure range, while  $\text{PrH}_8$  is predicted to be replaced by  $\text{PrH}_9$  ( $P6_3/mmc$  structure). It is interesting that high-temperature synthesis leads to the coexistence of both

PrH<sub>7</sub> and PrH<sub>9</sub>. In our calculations, both these phases are metastable at 85 GPa with respect to PrH<sub>8</sub> (Fig. 3). But, both being not far off stability region. Results at scalar-relativistic level (not shown) are very similar and agree very well with previous calculations [13], with the biggest difference being that PrH<sub>7</sub> is found to be stable up to 65 GPa. The hexagonal phase of PrH<sub>9</sub> is 0.35-0.45 eV/f.u. higher in enthalpy than the cubic phase in the pressure range 50-200 GPa; this is independent of whether spin-orbit coupling is considered or not.

Structure solution suggested Pr atoms to lie on special positions ( $2/3$ ,  $1/3$ ,  $1/4$ ), resulting in *hcp* lattices. Data were not of sufficient quality for full Rietveld refinement and therefore utilized DFT geometry optimisation calculations to confirm the formulae and structure of these phases (Table I). Both the PrH<sub>7</sub> and PrH<sub>9</sub>  $P6_3/mmc$  structures consist of hexagonal close-packed lattices of face-sharing Pr-H clusters. As seen in Fig. 2(b), in PrH<sub>9</sub> each Pr atom is surrounded by 29 H atoms, in PrH<sub>7</sub> the clusters consist of 21 H atoms. The electronic density of states (DOS) of these compounds are shown in Fig. 4, and compared both to PrH<sub>4</sub> and the cubic phase PrH<sub>9</sub>- $F43m$ . As seen, all the hydrides are very good metals. Nevertheless, hydrogen-richer hydrides have wider valence bands but the DOS at the Fermi level, which is dominated by Pr-*f* states, are not affected in a systematic way. Common structural features (atomic hydrogen clathrate cages encapsulating individual Pr atoms) and electronic properties (large DOS of similar character at the Fermi energy) suggest that electron-phonon coupling and therefore superconducting properties could be very similar across all of these superhydrides.

Samples of PrH<sub>9</sub> and PrH<sub>7</sub> were subsequently decompressed to establish the stability ranges of these new compounds. Diffraction peaks due to PrH<sub>9</sub> remain observable down to 80.5 GPa, below this pressure peaks due to PrH<sub>9</sub> clearly split indicating a phase transition to yet another lower symmetry structure (Fig. 1(d)). This low-symmetry phase is stable for a relatively narrow pressure range from 71.2 to 59 GPa. The diffraction peaks from this phase could not be indexed by any predicted RE-H structure, nor by any distorted subgroups of  $P6_3/mmc$ . Exhaustive searches with a number of indexing routines also failed to produce a convincing index, and the structure of this phase remains unknown. By contrast, PrH<sub>7</sub> retains its hexagonal symmetry until it too decomposes below 54 GPa, to the previously observed PrH<sub>4</sub> (Fig. 1(d)). Former reports on PrH<sub>*x*</sub> did not discuss the existence of PrH<sub>7</sub>[16] because as DFT calculations show, it is not favoured above 75 GPa pressures, while experimentally we see it up to 95 GPa. However, these results demonstrate that measurements within the whole experimental pressure range are required for a full thermodynamic understanding of the reaction path. **The use of NH<sub>3</sub>BH<sub>3</sub> as hydrogen source is opening an avenue to many aspects of hydrogen related high pressure science**

as it avoids the requirement of H<sub>2</sub> gas loading. However, it is still a relatively new technique in the field, and it is not yet clear how side products such as BNH<sub>*x*</sub> or BN [40] could interfere in the desired hydrogen-metal reaction or in the interpretation of the XRD patterns. Zhou et al. [16] and this present report use NH<sub>3</sub>BH<sub>3</sub> and H<sub>2</sub> gas loading, respectively. Both works find hexagonal PrH<sub>9</sub> at pressures around 100 GPa, therefore these results represent an important example where the same reaction product can be obtained using different hydrogen precursors.

In conclusion, through laser heating a Pr foil within a pure H<sub>2</sub> atmosphere we have explored the Pr-H system up to pressures of 95 GPa with combined x-ray diffraction experiments and first-principles DFT calculations, unveiling the formation of polyhydride species. This work demonstrates that the formation of hydrogen-rich phases at extreme pressure-temperature conditions could potentially be realised in other REH compounds. ~~which are promising systems to exhibit high-temperature superconductivity.~~

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