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High-Pressure Synthesis of Quantum-Stabilised Manganese Superhydride MnH₇

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ABSTRACT

Through high-temperature, high-pressure diamond anvil cell studies combined with in situ synchrotron powder x-ray diffraction, we investigate the reactivity between manganese and hydrogen up to 182 GPa. Laser heating manganese in an H₂ medium at 118 GPa yields body-centred tetragonal MnH₇, which has the highest hydrogen content ever observed in the binary hydrides of group IV–XII transition metals. In addition, we also observe two other new hydrides as minor phases, MnH_{~2} with a tetragonal crystal structure and cubic MnH_{3.67}, formed at the pressures of 105 and 118 GPa, respectively. Upon decompression, MnH_{3.67} and MnH₇ remain stable down to ~30 GPa before decomposing into the monohydride. Our ab initio quantum chemistry computations employing density-functional theory reveal that the key stabilisation factor of MnH_{3.67} and MnH₇ is zero-point energy, however, no isotope effect is observed on the crystal structures of the deuterated samples.

1 | Introduction

The chemical reactivity of molecular H₂ increases dramatically under high pressure. This renders pressure a powerful tool for the synthesis of superhydrides, which are a class of materials with an exceptionally high hydrogen content (typically > 80 at.% H). Binary superhydrides emerge in many of the group I–III elements under pressure, some of which exhibit fascinating properties, such as high-temperature superconductivity [1–28]. Pressures in excess of 100 GPa are required for the synthesis of the vast majority of these materials, and it is important to produce new superhydrides at lower pressures before this class of materials can find any industrial applications.

Despite many binary hydrides forming across the group IV–XII transition metals, there has only been one reported super-

hydride, FeH₅ [29]. This unique compound crystallises in a tetragonal body-centred iron lattice (Pearson symbol *tI4*, space group *I4/mmm*), in which hydrogen forms an extended atomic network consisting of alternating ‘FeH₃’ and ‘FeH₇’ layers [29]. While high pressure generally promotes increased hydrogen uptake, FeH₅ represents the highest hydrogen content achieved so far in a transition-metal hydride. Transition metal hydrides are instead limited to lower stoichiometries, most commonly trihydrides such as FeH₃, IrH₃ and CoH₃ [29–31], all of which contain exclusively atomic hydrogen as opposed to molecular or quasimolecular H₂.

Extended networks of atomic hydrogen are also a defining structural motif of the majority of superconducting superhydrides, and the absence of quasimolecular H₂ units is widely regarded as a key prerequisite for metallicity and superconductivity

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in these materials. In contrast, superhydrides of most other elements predominantly stabilise hydrogen in the form of localised quasimolecular H_2 units, and occasionally H_3^- anions [1–3, 32], which generally leads to insulating behaviour. Within this framework, transition-metal hydrides capable of sustaining dense, fully atomic hydrogen sublattices at high hydrogen content remain exceptionally rare, motivating the exploration of Mn–H compounds as potential candidates for higher-order polyhydrides with metallic electronic structures.

In recent years, extensive quantum chemistry calculations employing density-functional theory (DFT) have been performed for the majority of the binary metal–hydrogen systems under high pressure [33–35]. Manganese superhydride MnH_7 was calculated to have the lowest formation pressure of 40 GPa among all theoretically predicted transition-metal superhydrides [36]. The hexagonal crystal structure of predicted MnH_7 consists of the AA-stacked graphite-like layers of manganese atoms (Pearson symbol $hP2$, space group $P6/mmm$) with quasimolecular H_2 between these layers [35, 36]. In addition, other manganese polyhydrides, MnH_2 ($tI4$, $I4/mmm$), MnH_3 ($tI8$, $I4/m$) [36], and Mn_3H_{11} ($tP3$, $P4/mmm$) [35] have been predicted to form at similar pressures.

Previously, the manganese–hydrogen system has been studied at high pressures up to 8 GPa [37, 38]. Apart from solid solutions, together with non-stoichiometric high-temperature phases, the only manganese hydride known so far is ϵ - $MnH_{\sim 1}$ with a hexagonal close-packed (*hcp*) lattice [38–41]. For simplicity, this phase is called *hcp*- MnH henceforth. This phase possesses an antiferromagnetic order below $T_N = 350$ K [42].

Here, we study the manganese–hydrogen (deuterium) system to pressures of 182 GPa. We discover three new manganese hydrides (deuterides) – $MnH_{\sim 2}$, $MnH(D)_{3.67}$, and $MnH(D)_7$. Surprisingly, the crystal structure of $MnH(D)_7$ is tetragonal body-centred ($tI2$, $I4/mmm$), rather than the previously predicted hexagonal phase ($P6/mmm$) with quasimolecular H_2 [35, 36]. Using our own DFT calculations, we propose a tentative arrangement of hydrogen atoms in MnH_7 , which is analogous to the ‘ FeH_7 ’ layers in FeH_5 [29]. Our DFT calculations demonstrate that the inclusion of the zero-point energy (ZPE) contribution to the formation enthalpy destabilises the hypothetical $P6/mmm$ - MnH_7 with respect to tetragonal $tI2$ - MnH_7 . Similarly, when ZPE is taken into account, the experimentally found cubic $cP3$ - $MnH_{3.67}$ replaces the predicted tetragonal $tI8$ - MnH_3 on the convex hull. We have investigated whether the isotope effect would stabilise different structures in manganese superdeuterides; however, even the reduced ZPE for MnD_7 was still high enough to destabilise the hypothetical $P6/mmm$ phase. Electrical resistance measurements revealed that $cP3$ - $MnD_{3.67}$ and $tI2$ - MnD_7 are not superconducting down to 8.5 K at 147 GPa.

2 | Results and Discussion

2.1 | Synthesis and Structure of MnH_7

Upon exposing manganese to a hydrogen (deuterium) atmosphere at a pressure of 4 GPa (the lowest pressure in this study), *hcp*- $MnH(D)$ forms on the timescale of a few days at room temperature. Upon compression to 138 GPa *hcp*- $MnH(D)$ persists

with no further reaction or phase transition (a typical x-ray diffraction pattern of *hcp*- MnH is shown in Figure 1a). Laser heating at pressures below 101 GPa does not induce any changes in the sample. When *hcp*- MnH is heated in an excess of H_2 at pressures above 118 GPa, the sample expands dramatically (see sample photos in Table S1), indicating the formation of a new hydrogen-rich phase. The effect of the laser heating on the crystal structure of the sample is illustrated by the changes in its x-ray diffraction pattern shown in Figure 1b. This new hydride has a body-centred tetragonal lattice of manganese atoms with Pearson symbol $tI2$ and space group $I4/mmm$, and an axial ratio of $c/a \sim 2.8$ (the relevant crystal structures are summarised in Table 1).

The formation of this new hydride is accompanied by an expansion of the metal lattice by $\Delta V = V(tI2\text{-}MnH_x) - V(hcp\text{-}MnH) = 12.04 \text{ \AA}^3/\text{Mn atom}$ at 118 GPa. Because the overall volume effect for the reaction should be negative according to Le Chatelier’s principle, the H/Mn composition of this new hydride is larger than 6.3, based on the volume of the hydrogen gas at this pressure ($4.52 \text{ \AA}^3/H_2$) [44]. As such, the composition of this new hydride is close to H/Mn = 7.

MnH_7 persists upon subsequent compression and laser heating up to 182 GPa, which was the highest pressure reached in this study. Upon decompression, it remains stable down to 33 GPa and then decomposes into a poorly crystalline product which is presumably MnH . The $V(P)$ dependence of $tI2$ - MnH_7 is shown by the open red diamonds in Figure 1c. This $V(P)$ dependence can be fit well with the Birch–Murnaghan equation of state [45] with the parameters listed in Table 2, as shown by the dashed red curve in Figure 1c, which indicates that the compound remains fully stoichiometric and composition is pressure-independent.

2.2 | The Role of Zero Point Energy in the Stability of MnH_7

Given that the arrangement of the metal atoms in MnH_7 and the ‘ FeH_7 ’ layers in the previously observed FeH_5 [29] is similar, the arrangement of hydrogen atoms should also be similar. In order to elucidate the full crystal structure of MnH_7 , we assumed the arrangement of hydrogen atoms from the ‘ FeH_7 ’ layers and optimised the resulting crystal structure with DFT at 100 GPa. The resulting $Pbcn$ structural model is shown in Figure 2e, and the corresponding crystal structure parameters are listed in Table 1. This structure is based on the $\sqrt{2} \times \sqrt{2} \times 1$ supercell of the experimentally observed body-centred tetragonal unit cell of MnH_7 , with a small orthorhombic distortion ($b/a = 1.027$), which makes this structure dynamically stable (Figure S2). The $V(P)$ dependency and the axial ratios for $Pbcn$ - MnH_7 , shown by the solid black curves in Figure 1c,d are in a reasonable agreement with the experimental data for $tI2$ - MnH_7 (open red diamonds).

The formation enthalpies of $Pbcn$ - MnH_7 and the previously predicted $P6/mmm$ - MnH_7 , calculated with DFT at 100 GPa, are shown by the closed circles and stars, respectively, in Figure 2a. Without ZPE, $P6/mmm$ - MnH_7 is more stable by 9 meV/atom as shown by the grey star.

The hydrogen motif in $Pbcn$ - MnH_7 is purely atomic in contrast to $P6/mmm$ - MnH_7 , where the hydrogen motif contains

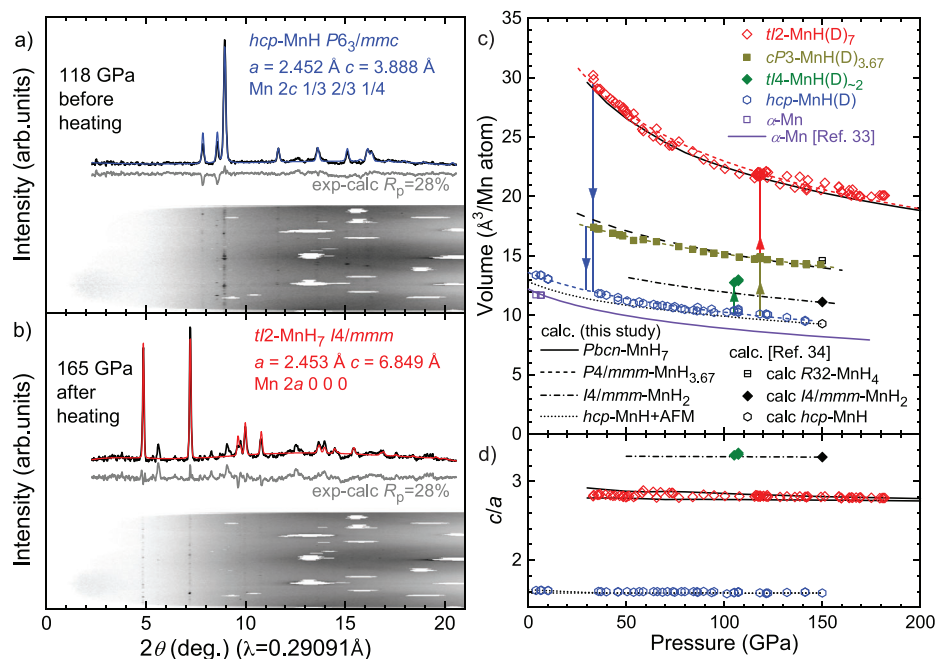


FIGURE 1 | X-ray powder diffraction patterns of a Mn–H sample at 118 GPa (a) and after laser heating at 165 GPa (b), together with the results of the Rietveld refinement of its crystal structure. The bottom panels show the raw detector images in the 2θ -azimuth representation, the black curves are the azimuthally integrated data, the blue and red curves show the calculated contributions from the *hcp*-MnH and *tI2*-MnH₇ phases, respectively, and the grey curves are the refinement residuals. The peaks at 5.6°, 9.1°, and 12.5° in (b) are due to unidentified impurity, MgO, and instrumental background, respectively. Volumes (c) and the axial *c/a* ratios (d) of the studied manganese hydrides (deuterides) as a function of pressure. The literature data for α -Mn is taken from Ref. [43]. The results of the DFT predictions from Ref. [36] at 150 GPa are shown by the black symbols. The black curves show the results of our DFT calculations, and the curves of the other colours show the equation of state fits with the parameters indicated in Table 2. The axial ratios for *Pbcn*-MnH₇, calculated with DFT, are multiplied by $\sqrt{2}$ to enable a comparison with experiment. The vertical arrows indicate the minimal pressures, at which phase transitions were observed upon compression, and the maximal pressures at which they were observed upon decompression.

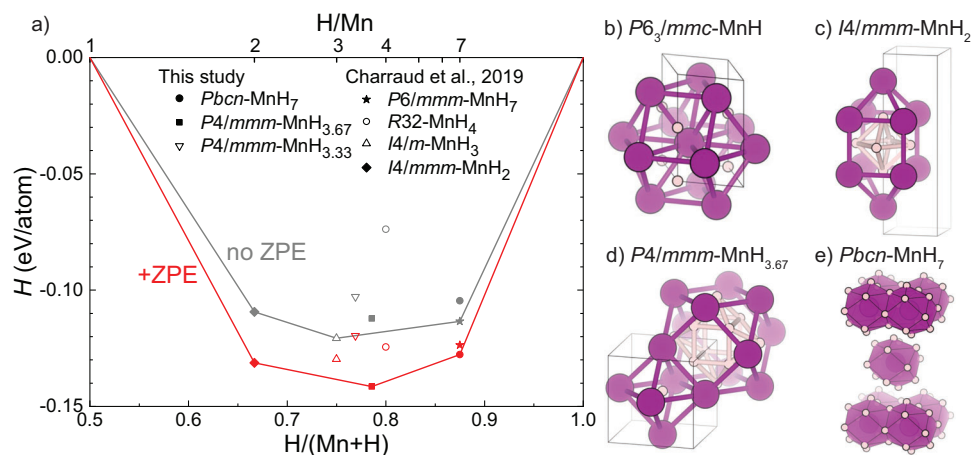


FIGURE 2 | (a) Formation enthalpies of manganese hydrides at $P = 100$ GPa and $T = 0$ K, calculated with DFT with (red) and without (grey) zero-point energy (ZPE) correction. The predicted crystal structures for *I4/mmm*-MnH₂, *I4/m*-MnH₃, *R32*-MnH₄, and *P6/mmm*-MnH₇ are taken from Ref. [36]; the rest of the structures were found in this study. (b–e) Crystal structures of the observed manganese hydrides. Manganese and hydrogen atoms are shown by the purple and pink spheres, respectively. The atomic coordinates for Mn and H atoms, also listed in Table 1, are from the XRD experiments and DFT predictions, respectively.

quasimolecular H₂ units. This is manifested by the calculated phonon density of states of *Pbcn*-MnH₇ (see Figure S3), which, in contrast to that of the hypothetical *P6/mmm*-MnH₇, does not have a high-frequency peak of quasimolecular H₂ vibrations

around 550 meV. As a result, the average phonon energy, $\langle E \rangle$, in *Pbcn*-MnH₇ is smaller than that in *P6/mmm*-MnH₇ by about 8 meV. The ZPE contribution per atom is directly related to the average phonon energy, $ZPE = \frac{3}{2} \langle E \rangle$, so that $ZPE(P6/mmm\text{-}MnH_7)$

TABLE 1 | Crystal structures of the observed manganese hydrides and deuterides with the lattice parameters interpolated to the selected pressures, together with the results of the DFT predictions.

Compound	Pressure (GPa)	Space group and lattice parameters	Atomic coordinates	Source
<i>hcp</i> -MnH(D)	100	<i>P6₃/mmc</i> <i>a</i> = 2.459 Å <i>c</i> = 3.919 Å	Mn 2 <i>c</i> 1/3 2/3 1/4 H 2 <i>a</i> 0 0 0	Exp
<i>tI4</i> – MnH _{~2}	107	<i>I4/mmm</i> <i>a</i> = 2.492 Å <i>c</i> = 8.375 Å	Mn 4 <i>e</i> 0 0 0.152	Exp
	150	<i>I4/mmm</i> <i>a</i> = 2.378 Å <i>c</i> = 7.869 Å	Mn 4 <i>e</i> 0 0 0.152 H1 4 <i>c</i> 0 1/2 0 H2 4 <i>e</i> 0 0 0.352	DFT, [36]
<i>cP3</i> -MnH(D) _{3.67}	100	<i>Pm</i> $\bar{3}$ <i>m</i> <i>a</i> = 3.570 Å	Mn 3 <i>c</i> 0 1/2 1/2	Exp
		<i>P4/mmm</i> <i>a</i> = 3.596 Å <i>c</i> = 3.534 Å	Mn1 1 <i>a</i> 0 0 0 Mn2 2 <i>e</i> 0 1/2 1/2 H1 1 <i>b</i> 0 0 1/2 H2 2 <i>f</i> 0 1/2 0 H3 8 <i>r</i> 0.295 0.295 0.769	DFT
<i>tI2</i> -MnH(D) ₇	100	<i>I4/mmm</i> <i>a</i> = 2.537 Å <i>c</i> = 7.142 Å	Mn 2 <i>a</i> 0 0 0	Exp
		<i>Pbcn</i> <i>a</i> = 3.516 Å <i>b</i> = 3.613 Å <i>c</i> = 7.078 Å	Mn 4 <i>c</i> 0 0.748 1/4 H1 4 <i>c</i> 0 0.319 1/4 H2 8 <i>d</i> 0.762 -0.039 0.608 H3 8 <i>d</i> 0.282 0.459 0.616 H4 8 <i>d</i> 0.044 0.732 0.462	DFT

TABLE 2 | Equation of state parameters for Mn and Mn–H phases.

Phase	Pressure (GPa)	<i>V</i> ₀ (Å ³ /Mn atom)	<i>B</i> ₀ (GPa)	<i>B</i> ' ₀	EoS type	Source
α-Mn	0–190	12.21	158(3)	4.6(1)	Vinet	[43]
<i>hcp</i> -MnH(D)	0–141	13.61(3)	201(6)	4 (fixed)	B–M	this study
<i>cP3</i> -MnH(D) _{3.67}	33–149	19.17(6)	267(10)	4 (fixed)	B–M	this study
<i>tI2</i> -MnH(D) ₇	33–182	39.5(20)	62(20)	4 (fixed)	B–M	this study

– ZPE(*Pbcn*-MnH₇) ≈ 13 meV/atom. When ZPE contribution is added, *Pbcn*-MnH₇ (red circle) replaces *P6/mmm*-MnH₇ (red star) on the convex hull (see Figure 2a).

Hydrogen substitution with its heavier deuterium isotope has a dramatic effect on the vibrational and superconducting properties of hydrides. Moreover, there are thermodynamic implications of the isotope effect on ZPE, and there are at least two metals—vanadium [46] and lanthanum [15]—whose deuterides are structurally different from hydrides. To date, the studies of superdeuterides are very scarce, and only yttrium, lanthanum and cerium deuterides have been studied so far [10, 15, 18]. To explore if the predicted *P6/mmm*-MnH₇ could be stabilised if its ZPE is reduced, we performed an experiment with deuterium instead of hydrogen. However, after laser heating, we observed the formation of a *tI2*-MnD₇ phase,

identical to *tI2*-MnH₇, as illustrated by the XRD pattern in Figure S1.

2.3 | Formation of MnH_{3.67} and MnH_{~2}

In addition to *tI2*-MnH(D)₇, we observed a cubic phase with a Pearson symbol *cP3* and a space group *Pm* $\bar{3}$ *m*. The x-ray diffraction pattern and the results of the Rietveld refinement of the crystal structure of this phase are shown in Figure S1. The crystal structure of the metal lattice of this phase is isomorphic to that of *cP3*-Ru₃H₈ [47], and the metastable *R32*-MnH₄ predicted in Ref. [36]. Additionally, a *P4/mmm*-Mn₃H₁₁ compound has recently been predicted in Ref. [35], but no structural information was given. The experimental volume, shown by the yellow squares and the dashed yellow curve in Figure 1c, is somewhat

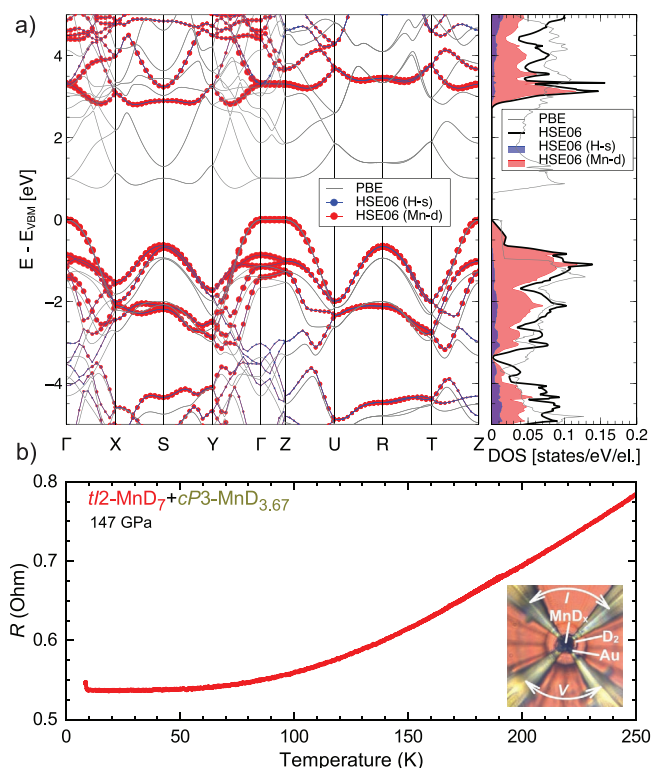


FIGURE 3 | (a) Electronic dispersion curves and density of states of *Pbcn*-MnH₇, calculated at 100 GPa with PBE (grey) and HSE06 functionals (blue and red show the projection onto the H-s and Mn-d states, respectively). (b) Temperature dependence of the electrical resistance of the MnD₇ + MnD_{3.67} sample upon warming from 8.5 K at the pressure of 147 GPa. Photomicrograph of the samples with the electrode configurations are shown in the insets.

smaller than the predicted volume of R32-MnH₄ (black barred square in Figure 1c), indicating that $3 < \text{H/Mn} < 4$ for this hydride. Upon decompression, this phase persists down to about 30 GPa.

The *cP3* lattice features three types of interstitial sites, which can be occupied by hydrogen—1*b* octahedral, 3*d* planar square, and 8*g* cuboctahedral. In the predicted R32-MnH₄ compound from Ref. [36], all of these are fully occupied. In contrast, only 8*g* interstitials are occupied in *cP3*-Ru₃H₈ [47]. Because H/Mn in the *cP3* manganese hydride is between that of *cP3*-Ru₃H₈ and R32-MnH₄, it is natural to assume that its 8*g* interstitials are also fully occupied, and it is either 1*b* or 3*d* interstitials which accommodate vacancies.

Our DFT calculations demonstrated that the resulting structure with the 1*b* vacancy was not energetically competitive, however. On the other hand, emptying all 3*d* interstitials would result in H/Mn = 3, which is too low from experimental volumetric considerations, drawing us to the conclusion that these interstitials are occupied partially. In order to model partial occupancy, it is necessary to break the *Pm* $\bar{3}$ *m* symmetry. The easiest way to do this is realised in the tetragonal *P4/mmm* subgroup, which splits the hydrogen population in 3*d* sites into independent 1*b* and 2*f* sites. Emptying these produced the candidate structures *P4/mmm*-MnH_{3.67}, shown in Figure 2d, and *P4/mmm*-MnH_{3.33}, respectively. The structural parameters for the former *P4/mmm*-

MnH_{3.67} are listed in Table 1, and the corresponding *V(P)* dependence, shown by the black dashed curve in Figure 1c, is in a good agreement with the experimental data (yellow squares), which justifies the assignment of the composition of H/Mn = 3.67 for this phase. When no ZPE correction is taken into account, the formation enthalpies of all of these MnH₄-derived phases at 100 GPa are above that of a *I4/m*-MnH₃ + *P6/mmm*-MnH₇ mixture, which is on the convex hull, as shown by the grey symbols and lines in Figure 2a. However, when ZPE is included (red symbols and lines in Figure 2a), *I4/m*-MnH₃ is replaced by *P4/mmm*-MnH_{3.67} on the convex hull.

In one of our samples with a hydrogen deficiency, we observed the formation of yet another phase after laser heating at 126 GPa. As evidenced from the refinement of its crystal structure shown in Figure S4a, this phase is isomorphic to FeH₂ [48], and to the previously predicted *I4/mmm*-MnH₂ [36] (Figure 2c). It should be noted, however, that the volume of this phase, shown by the solid olive diamonds in Figure 1c is somewhat higher than the volume of *I4/mmm*-MnH₂ calculated with DFT in Ref. [36] (black diamond) and this study (black dash-dotted curve). Volumetric considerations indicate that the hydrogen content of this phase is H/Mn > 2.15. We tried to explore the possible incorporation of extra hydrogen in the crystal structure of *I4/mmm*-MnH₂ with DFT-based crystal structure search but did not find any energetically feasible candidate structures. For this reason, we call this phase MnH_{~2}.

2.4 | Electrical Conductivity of Manganese Hydrides

The electron density of states of the experimentally observed manganese hydrides, calculated with DFT, is shown in Figures 3a and S5. Our calculations indicate that *hcp*-MnH, *I4/mmm*-MnH₂, and *P4/mmm*-MnH_{3.67} are metallic, and *Pbcn*-MnH₇ is a semiconductor with a bandgap 0.6 eV (PBE) or 2.5 eV (HSE06) at 100 GPa. The calculations also correctly reproduce the antiferromagnetic ground state of *hcp*-MnH below 50 GPa (Figure S5a) in agreement with the literature [42].

To explore conductivity experimentally, we have measured the electrical resistance of our MnD₇ + MnD_{3.67} sample with a four-probe technique at 147 GPa, as shown in Figure 3b. We observed that the sample is metallic, but no anomalies were detected above 8.5 K. Given that our calculations indicate that MnH₇ is a semiconductor at such pressures, most likely the conductivity arises from metallic MnD_{3.67}. Previously, no superconductivity has been detected in FeH₅ above 1.5 K [49].

Electrical resistance measurements of a MnH_{~2} + MnH at 107 GPa revealed a drop at 4.7 K (Figure S4b), which could be indicative of a superconductivity onset. On the other hand, we calculated the expected *T_c* of *hcp*-MnH and stoichiometric *I4/mmm*-MnH₂ at 100 GPa using density functional perturbation theory (DFPT), but found the *T_c* to be less than 0.1 K. Further studies would be insightful to account for this discrepancy and to explore potential superconductivity in these manganese hydrides.

3 | Conclusions

In summary, we have explored the Mn-H system under high pressures up to 182 GPa, discovering three new compounds, MnH_7 , $\text{MnH}_{3.67}$ and $\text{MnH}_{\sim 2}$. Surprisingly, the body-centred tetragonal crystal structure of MnH_7 is different from the lowest enthalpy structure found with DFT. Instead, our calculations demonstrate that the inclusion of ZPE is essential to renormalise the energy rankings and correctly predict the crystal structure of this new material. Intrinsically stabilised by nuclear quantum effects, MnH_7 is only the second transition metal superhydride to be discovered and could indicate that more hydrogen-rich transition metal compounds could be synthesised at high pressure high-temperature conditions.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this article are available in the Supporting Information, which includes Refs. [50–64], the experimental details, sample table, x-ray diffraction data, electrical resistance measurements, and DFT calculations. Raw data will be made available upon request.

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