# Hydrogen "penta-graphene-like" structure stabilized by hafnium: a high-temperature conventional superconductor

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## Abstract

Recent discovery of $H_3S$ and $LaH_{10}$ superconductors with record high superconducting transition temperatures, $T_c$, at high pressure, has fueled the search for room-temperature superconductivity in the compressed superhydrides. Here we introduce a new class of high $T_c$ hydrides with a novel structure and unusual properties. We predict the existence of an unprecedented hexagonal $HfH_{10}$, with remarkably high value of $T_c$ (around 213-234 K) at 250 GPa. As concerns the novel structure, the H ions in $HfH_{10}$ are arranged in clusters to form a planar "penta-graphene-like" sublattice. The layered arrangement of these planar units is entirely different from the covalent sixfold cubic structure in $H_3S$ and clathrate-like structure in $LaH_{10}$. The Hf atom acts as a precompressor and electron donor to the hydrogen sublattice. This "penta-graphene-like" $H_{10}$ structure is also found in $ZrH_{10}$, $ScH_{10}$ and $LuH_{10}$ at high pressure, each material showing a high $T_c$ ranging from 134 to 220 K. Our study of dense superhydrides with "penta-graphene-like" layered structures opens the door to the exploration of a new class of high $T_c$ superconductors.

The development of room temperature superconductors is the ultimate goal for superconductivity research. The Bardeen-Cooper-Schrieffer theory suggests that metallic hydrogen is likely to be a good candidate for attaining high-temperature superconductivity, due to its high Debye temperature and strong electron-phonon coupling [1,2]. Conceptually, metallization can be achieved in pure hydrogen by dissociating the $H_2$ molecules under extreme conditions. Evidence for molecular dissociation has been found in high-pressure phases of solid hydrogen, where the vibron frequency decreases rapidly with increasing pressure [3], indicating the weakening of the intramolecular bonding. However, although there have been extensive attempts to synthesize metallic hydrogen [4,5], there is a lack of consensus on reported "successes", and superconductivity has not been measured in any of the reported phases.

In the face of tremendous difficulties in synthesizing pure metallic hydrogen, many investigators have suggested that metallization can be achieved by 'precompressing' hydrogen species in simple hydrides [6]. Highly compressed hydrogen-dominant hydrides are predicted to be able to attain a metallic state and may, therefore, exhibit high $T_c$ superconductivity. Recently, the search for high-$T_c$ superconductivity has been expanded from the known [7-9] to hitherto unknown hydrides, through high-pressure synthesis following theoretical predictions [10-23]. Remarkably, two of the predicted hydrides, $H_3S$ [11-13] and $LaH_{10}$ [17-19], have been successfully synthesized recently and exhibit record high $T_c$ above 200 K. $H_3S$ has a *bcc* lattice of S with H atoms located halfway between the S atoms, exhibiting three-dimensional covalent metallic characteristics. $LaH_{10}$ has a three-dimensional clathrate-like structure of H with La atoms filling the clathrate cavities, which has been described as an extended metallic hydrogen host structure stabilized by the guest electron donor (La).

By analyzing the superconducting properties of a large number of hydrides, we have summarized four criteria for finding high $T_c$ superconductors in highly compressed hydrides (Figs. S1 and S2 [24]): (i) high symmetry crystal structure, (ii) absence of $H_2$-like molecular units, (iii) a large H contribution to the total electronic density of states (DOS) at the Fermi level, and (iv) strong coupling of electrons on the Fermi surface with high frequency phonons. The search for high-$T_c$ materials has been focused on two families of binary hydrides (see Table S1 [24]), covalent sixfold cubic structure [10-14] found in $H_3S$ and $H_3Se$, and clathrate structure [15-22] found in rare earth hydrides $REH_{10}$, $REH_9$ and $REH_6$.

These two high-$T_c$ families satisfy the four criteria, with a common feature that they both adopt three-dimensional sublattices of hydrogen. On the other hand, pure solid hydrogen features pronounced layer-like characters. One example is the phase IV of hydrogen that consists of strongly bonded $H_2$ molecules and weakly bonded graphene-like sheets [48-50]. This structure is considered as an important intermediate between the molecular (insulating) and atomic (metallic) crystalline phases of hydrogen. Many hydrides have been predicted to have a layered structure, but their $T_c$ are not very high, *e.g.* $FeH_5$ [51], $TeH_4$ [52], and $KH_6$ [53], etc. One can raise a question: is there a layered structure of hydrogen-rich materials at high pressure that can achieve high $T_c$? This question leads to the search for new physics and, more specifically, new structures and new concepts in this exciting field.

We introduce here a new class of superhydrides with novel structure and a number of unusual properties. We performed an extensive structure searching at high-pressure using AIRSS, USPEX and CALYPSO codes [54-56] and indeed discovered a layered high-$T_c$ hafnium decahydride. In $HfH_{10}$, the H atoms form planar clusters of three $H_5$ pentagons, analogous to penta-graphene, while Hf atoms are intercalated between the clusters on the same plane. A new class of superhydrides, $MH_{10}$ (M = Zr, Sc and Lu), which are isostructural to $HfH_{10}$, have also been predicted to possess high $T_c$.

Our main structure searching results for Hf-H system at high pressure are depicted in the convex hull diagrams of Figs. 1(a) and S3 [24]. Considering the non-negligible quantum effects associated with hydrogen, the zero-point energy (ZPE) was included in the calculation of the formation enthalpies of predicted Hf-H compounds. We analyzed the stability of these compounds with respect to the elemental hafnium and hydrogen. As shown in Fig. 1(a), these searches revealed four stable stoichiometries at various pressures, *e.g.*, HfH, $HfH_3$, $HfH_4$, and $HfH_{14}$, in addition to the previously known $HfH_2$ and $Hf_4H_{15}$ [57,58]. Moreover, $HfH_6$ and $HfH_{10}$ are close to the convex hull (~ 1-2 meV) at 300 GPa. A minor energy difference of this order already approaches the resolution of density functional theory calculation. For high-pressure synthesis, which usually involves high temperatures, the experimentally realized materials are often metastable phases [59]. The recently discovered high-$T_c$ superconducting $LaH_{10}$ [18,19], for example, is a metastable compound lying above the convex hull that was previously predicted by Peng et al. [16].

For $HfH_{10}$, there are two energetically competitive structures, adopting $P6_3/mmc$ and $P\bar{1}$

symmetries (Tables. S2 and S3 [24]). The $P\bar{1}$ structure consists of diatomic hydrogen pairs similar to $H_2$ molecules (Fig. S4 [24]), and this violates criteria (i) and (ii) for attaining high $T_c$. Intriguingly, the $P6_3/mmc$ is a layered structure in which the Hf and H atoms are situated on the same plane [Figs. 1(b) and (c)]. The Hf atoms form a hexagonal sublattice interspersed by H atoms in unique 'H$_5$' pentagons akin to the geometry of penta-graphene: three pentagons are fused by edge-sharing to form a $H_{10}$ unit [Fig. 1(c)]. In the proceeding discussion, the superhydride $P6_3/mmc$-HfH$_{10}$ is the main focus because it satisfies both criteria (i) high crystal symmetry and (ii) absence of $H_2$ molecular unit.
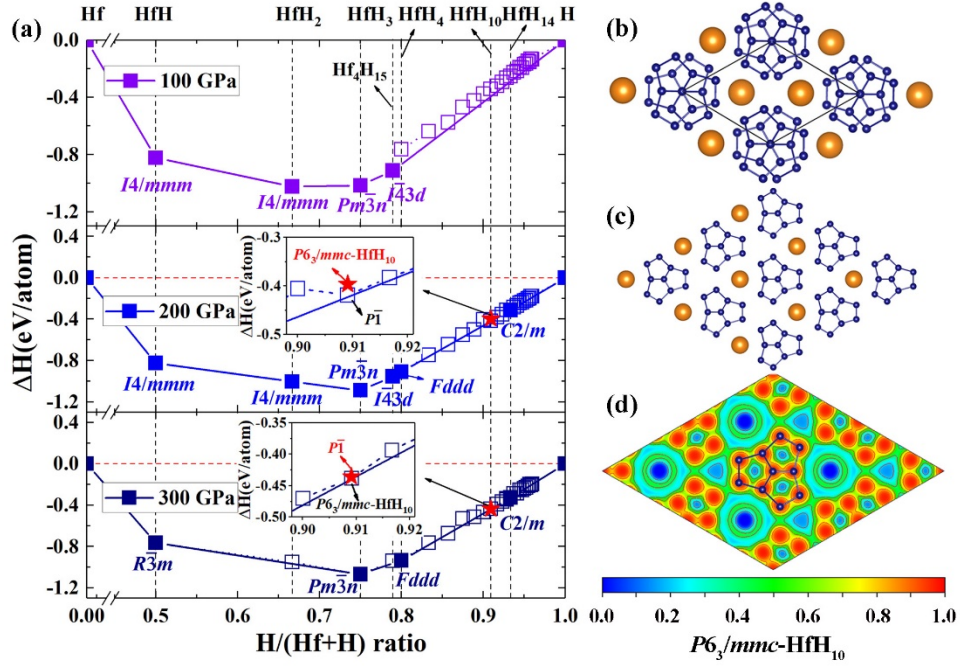


FIG. 1. (a) Formation enthalpies of predicted HfH$_x$ ($x$=1-24), including ZPEs with respect to decomposition into Hf and H under pressure. The $Im\bar{3}m$ structure for hafnium [60], the $P6_3/mc$, $C2/c$ and $Cmca$-12 structures for hydrogen [49] were adopted. Open symbols represent unstable configurations with respect to mixing lines on the convex hull, while solid symbols on the convex hull represent stable configurations. The red star near convex hull represents HfH$_{10}$ phase with higher enthalpy. (b) The crystal structure of layered $P6_3/mmc$ in HfH$_{10}$, where the layers are stacked in an ABAB fashion. (c) A layer of the $P6_3/mmc$ structure. (d) ELF on the (001) plane. Golden (large) and small (blue) spheres represent Hf and H atoms, respectively.

We examine the chemical bonding of layered HfH$_{10}$ by analysing electron localization function (ELF), crystal orbital Hamiltonian population (COHP) and Bader charges. As shown in Figs. 1(d) and S5 [24], there is no charge localization between Hf and H, indicating that the Hf-H bonding is purely

ionic. The ELF values for the $H_{10}$ unit range between 0.6-0.8, showing the evidence for H-H covalent bonding. As depicted in Fig. S6 [24], the calculated COHP shows that most of the states below the Fermi level correspond to H-H bonding, consistent to H-H covalent bonds within the $H_{10}$ unit. Furthermore, Bader charge analysis reveals that the planar $H_{10}$ unit accepts an amount of charge, $e.\ g.$, ~0.13 $e^-$ per H atom, from nearby Hf atoms, which results in longer H-H distances compared to that in free $H_2$ molecule [61]. The additional electrons reside in the H-H antibonding orbital ($\sigma^*$) and therefore weaken the H-H bonding, thus increasing the H-projected density of states (H-PDOS) at the Fermi level ($\varepsilon_f$).

To further explore this new form of hydrogen, we compared the H-H distances in $HfH_{10}$ with those in $LaH_{10}$ [17], atomic H [2] and layered phase-IV of H ($Pc$-48) [48] structures. As shown in Fig. S7 [24], the longest nearest-neighbor H-H distance ($d_{H1-H2}$) in $HfH_{10}$ is close to the shortest H-H distance in $LaH_{10}$ at the same pressure. The distance between H1 and H1 (second nearest neighbor) atoms approaches that of the atomic structure of hydrogen near 200 GPa. As the pressure increases, the shortest H-H bond length ($d_{H2-H3}$) gets progressively closer to the H-H distances of $Pc$-48 H ($d_2$). Therefore, this "penta-graphene-like" hydrogen sublattice lies somewhere between atomic and layered hydrogen.

The discovery of apparently stable or metastable structures of $HfH_{10}$ prompt us to further study the Zr-H system at 300 GPa (see Fig. S8 [24]). As it might be anticipated, $ZrH_{10}$ adopts the same two competitive structures $P\bar{1}$ and $P6_3/mmc$ as $HfH_{10}$. According to the criterion (iii) for high $T_c$ superconductivity, a large contribution by hydrogen to the total electronic DOS at the Fermi level is a critical factor for the development of exceptional superconducting properties. To this end, the projected electronic DOS of $P6_3/mmc$ in $HfH_{10}$ and $ZrH_{10}$ were calculated [Fig. 2]. One can see that both phases are metallic with a large total electronic DOS and significant hydrogen contribution to the electronic DOS at the Fermi level. Remarkably, the electronic DOS exhibits van Hove singularities near the Fermi level, indicating a large electron-phonon coupling (EPC) strength bound up with hydrogen phonon modes. The total DOS of $H_3S$, $LaH_{10}$, $HfH_{10}$ and $ZrH_{10}$ at 300 GPa are compared in Fig. 2(c). It is shown that $HfH_{10}$ and $LaH_{10}$ have a comparable electronic DOS at the Fermi level, and these are notably larger than those of $ZrH_{10}$ and $H_3S$.
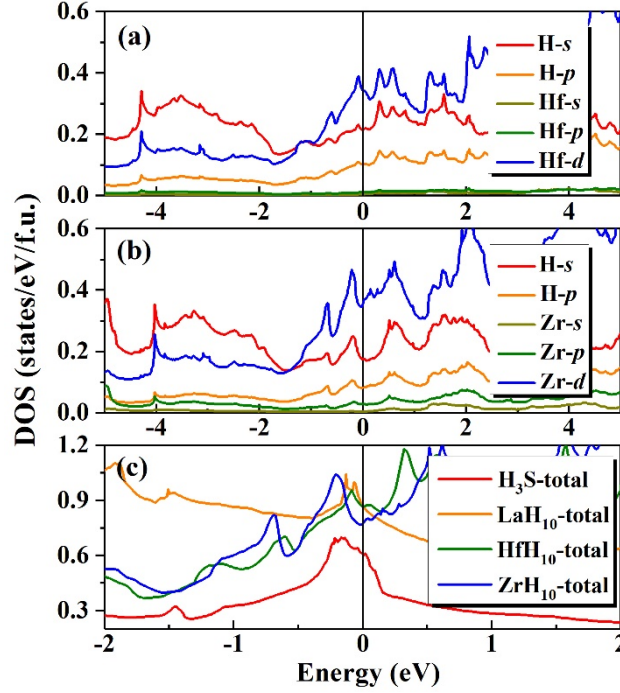
FIG. 2. Projected electronic DOS of (a) $P6_3/mmc$-HfH$_{10}$ and (b) $P6_3/mmc$-ZrH$_{10}$ at 300 GPa. (c) Total electronic DOS of H$_3$S, LaH$_{10}$, HfH$_{10}$ and ZrH$_{10}$ around the van Hove singularities at 300 GPa.

To examine the superconductivity in the layered "penta-graphene-like" structure, we calculate the average phonon frequency and EPC as shown in Table S5. For HfH$_{10}$, our EPC calculation yields a large $\lambda$ of 2.16 at 300 GPa which is benefited from large H-PDOS and high frequency vibrations (above 10 THz) due to hydrogen which contribute 70 % to the value of $\lambda$ [Fig. 3(a)]. It is obvious that the large $\lambda$ satisfies the last criterion (iv). Since $\lambda$ is larger than 1.5, we calculated $T_c$ using three approaches: Allen-Dynes modified McMillan equation (A-D) (Eq. S12 [24]) [62], Matsubara-type linearized Eliashberg equation (LE) [63], and Gor'kov-Kresin equation (G-K) [64], all of which were designed to estimate the $T_c$ for materials with strong electron-phonon coupling. The results show that HfH$_{10}$ is an extraordinary superconductor with a $T_c$ of 151-166 K (A-D), 214-228 K (LE), and 197-220 K (G-K) using $\mu^* = 0.1$-0.13 at 300 GPa. To narrow down the range of $T_c$, we calculated the $T_c$ of H$_3$S and LaH$_{10}$ at 200 GPa and compared them to the experimental values to obtain appropriate parameters for this family of materials. As presented in Fig. S9 [24], the calculated $T_c$ with $\mu^* = 0.13$ using G-K and LE equations are close to the experimental values, while those estimated by A-D equation are much lower. In the following, we will estimate the $T_c$'s using the G-K equation. With the pressure decreased to 250 GPa, $\lambda$ and $T_c$ for HfH$_{10}$ increase to 2.77 and 213-234 K with $\mu^* = 0.1$-0.13,

respectively; these values are higher than those for $H_3S$. For $ZrH_{10}$, a large EPC parameter $\lambda$ of 1.59 is calculated at 300 GPa, of which 74% is due to contributions by H atoms [Fig. 3(b)]. A high $T_c$ of 194-218 K is therefore estimated for $ZrH_{10}$. At 250 GPa, $T_c$ increases to 199-220 K with a stronger $\lambda$ of 1.77. We also calculated the electronic DOS and $T_c$ of $P\bar{1}$-$HfH_{10}$ at 200 GPa (see Fig. S10 and Table S7[24]). It is found that, as expected, the existence of $H_2$ units reduce the electronic DOS at the Fermi level, and a low EPC parameter of 0.72, thereby limiting its superconductivity with $T_c$ of 28.9-37.4 K ($\mu^* = 0.1$-0.13). Therefore, the four criteria for superconductivity provide important guidance in the search for high $T_c$ superconductors in compressed superhydrides. Intriguingly, it is noted that high-$T_c$ hydrides $HfH_{10}$, $ZrH_{10}$, $LaH_{10}$, or ternary $Li_2MgH_{16}$ [65] with strong EPC are off the convex hull, suggesting that maybe one can search high $T_c$ superconductors in compounds that are in the proximity of stability.
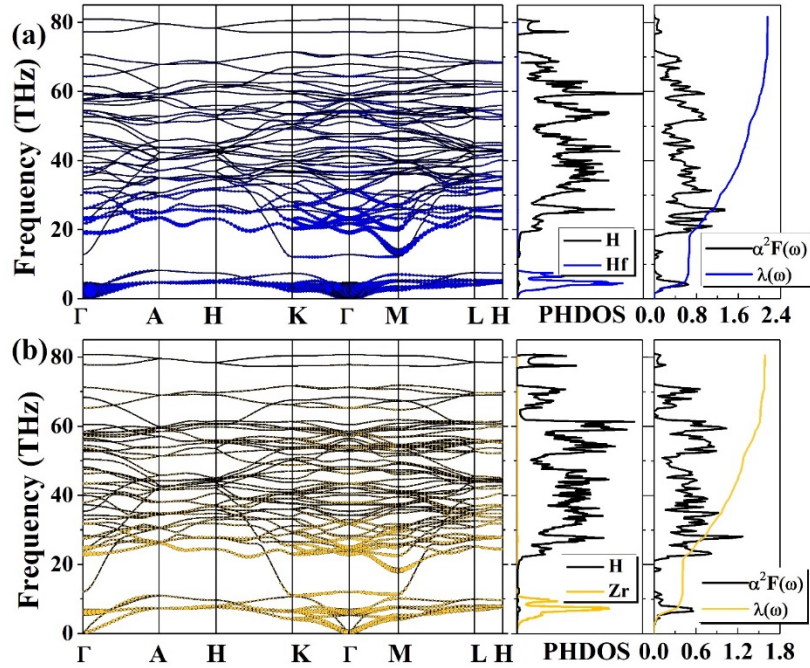


FIG. 3. Phonon dispersion curves (left), density of states (middle) and Eliashberg spectral function $\alpha^2F(\omega)$ together with the electron-phonon integral $\lambda(\omega)$ (right) of (a) $HfH_{10}$ and (b) $ZrH_{10}$ at 300 GPa. The size of the solid dot on phonon spectra signifies the contribution to electron-phonon coupling.

To further understand the superconductivity of the 'clathrate-like' and "penta-graphene like" decahydrides, we compared the calculated $T_c$'s and essential parameters for $YH_{10}$, $LaH_{10}$, $HfH_{10}$ and $ZrH_{10}$ at 300 GPa, illustrated in Fig. 4. We find that $T_c$ decreases in the order of $YH_{10} > LaH_{10} > HfH_{10} > ZrH_{10}$, consistent with the decreasing trend of "optical" superconducting transition temperature caused

by the interaction of electrons with optical phonons ($T_c^0$), the contribution of H-PDOS to the total DOS at the Fermi level ($P_H$) and "optical" electron-phonon coupling ($\lambda_{opt}$). Thus, the high $T_c$ in these hydrides is mainly attributed to the interaction of electrons with optical phonons and high DOS at the Fermi level associated with H atoms, in agreement with both superconducting criteria (iii) and (iv).
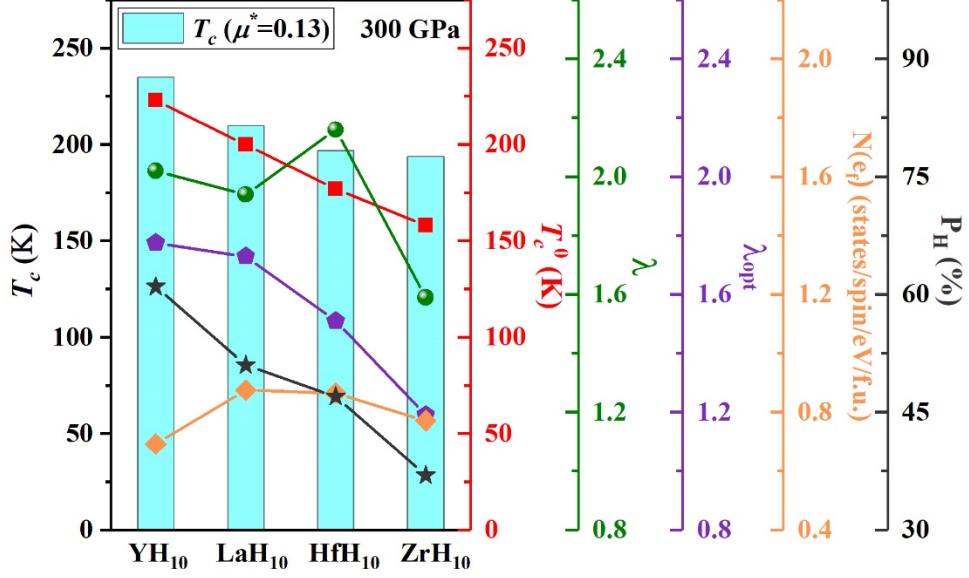


FIG. 4 Calculated superconducting parameters for YH$_{10}$, LaH$_{10}$, HfH$_{10}$ and ZrH$_{10}$ at 300 GPa. The obtained $T_c$ using G-K equation with $\mu^* = 0.13$ ($T_c$), the critical temperature caused by the interaction of electrons with optical phonons ($T_c^0$), EPC parameter ($\lambda$), strength of the interaction of electrons with optical phonons ($\lambda_{opt}$), electronic DOS at the Fermi level $N(\varepsilon_f)$ and the contribution of H atoms DOS to the total DOS at the Fermi energy ($P_H$).

The fact that "penta-graphene like" HfH$_{10}$ and ZrH$_{10}$ have very high $T_c$ naturally raises the question: can any other hydrides adopt the same structure and display high $T_c$ as well? The elements of Hf and Zr have three features in common: similar Pauling electronegativity (~1.3), similar atomic radius (~1.6 Å), and $d$ states in valence subshells. After searching the periodic table of elements, we found that Mg, Sc, Lu and Th have some similar properties. Phonon dispersion relations were calculated to test the stability of the corresponding decahydrides of these metals. The calculations did confirm that both ScH$_{10}$ and LuH$_{10}$ are dynamically stable, while MgH$_{10}$ and ThH$_{10}$ are not. For MgH$_{10}$ (Fig. S11 [24]) its dynamic instability could be due to the absence of $d$ electrons in Mg and insufficient number of electrons transferred to H. For ThH$_{10}$ (Fig. S11 [24]), the large atomic radius of Th (1.8 Å) may be responsible for its dynamic instability. We note that the $P6_3/mmc$ structure was first predicted

by Peng et al. [16] for $ScH_{10}$. However, this work is focused on the structure side, with little discussion on properties. Later, a *Cmcm* structure in $ScH_{10}$ was predicted [66]. We find that these phases are competitive (Fig. S12 [24]). The EPC calculation for the $P6_3/mmc$-$ScH_{10}$ yields a $\lambda$ of 1.16 and $T_c$ ranging 134-158 K at 250 GPa (Figs. S13-S14 [24]). For Lu-H system, we perform extensive structure searching and find that $LuH_{10}$ with $P6_3/mmc$ phase is stable at 300 GPa (Fig. S15 [24]). Phonon calculation shows that it is dynamically stable down to at least 200 GPa (Fig. S18 [24]). At 200 GPa, $LuH_{10}$ is found to be a good superconductor with a relatively high $T_c$ of 134-152 K, comparable with to most other lanthanide hydrides. Although the emergence of $5d$ electron in Lu suppresses the contribution of $4f$ electrons and improves the contribution of hydrogen atoms at the Fermi level (Fig. S19 [24]), the relatively low total DOS at the Fermi level limits to some extent its superconductivity.

All of our calculations were carried out using the harmonic approximation. It is reported that in many hydrides anharmonicity tends to lower phase transition pressure and eliminate the pseudo dynamic instabilities [67,68]. The anharmonic effects may cause the dynamic stabilities of $MgH_{10}$ and $ThH_{10}$, and stabilize $HfH_{10}$ and $ZrH_{10}$ at lower pressures, the analysis of which will be carried out elsewhere.

Since the substitution of deuterium for hydrogen (H→D) affects the optical modes only, whereas the value of $T_c$ is affected by both acoustic and optical modes, the value of the isotope coefficient and its closeness to the $\alpha_{max} = 0.5$ reflect the relative impact of the high frequency optical modes on $T_c$ and the interplay of the optical and acoustic modes. It is worth mentioning that the value of $T_c$ will be reduced upon H→D substitution, since the high frequency hydrogen modes determine the value of the critical temperature in high-$T_c$ hydrides. Thus, the isotope coefficient ($\alpha$) was calculated to estimate the $T_c$ of $MD_{10}$ ($T_c^D$). As shown in Table S5, the coefficients are 0.42-0.43 for $HfH_{10}$ at 250 GPa, 0.38-0.39 for $ZrH_{10}$ at 250 GPa, 0.37-0.38 for $ScH_{10}$ at 250 GPa, and 0.44-0.45 for $LuH_{10}$ at 200 GPa with $\mu^* = 0.1$-0.13, respectively. The $\alpha$ values in these phases are relatively large, suggesting that the pairing, particularly in $HfH_{10}$ and $LuH_{10}$, is dominated by the optical H modes, which yields the relatively low $T_c^D$. The $T_c^D$ was described according to the equation of $T_c/T_c^D = (M_H/M_D)^{-\alpha}$, where $T_c$ is obtained from the G-K equation. In our cases, $T_c^D$ values are 159-174 K for $HfD_{10}$, 153-168 K for $ZrD_{10}$, 104-121 K for $ScD_{10}$, and 99-111 K for $LuD_{10}$, respectively, providing a reference for future experiments.

Our extensive first-principles structure searches have revealed the appearance of stable or metastable layered "penta-graphene like" clustered $H_{10}$ structure in $HfH_{10}$, $ZrH_{10}$, $ScH_{10}$ and $LuH_{10}$. Electronegativity, atomic radius, and valence configuration of the metal element are all found to play critical roles in the stabilization of this novel hydrogen sublattice, and fine-tune the superconductivity of these materials. We want to pay a special attention to $HfH_{10}$ which is predicted to be a high temperature superconductor with estimated $T_c$ of 213-234 K at 250 GPa. It is the first example of the material, which contains two-dimensional structures in hydrogen-rich materials with high $T_c$ above 200 K. It is also a hydride that has the highest $T_c$ to date in the transition metal hydrides. The layered "penta-graphene like" $H_{10}$ structure is a structural model for superconducting hydrides with $T_c$ higher than 200 K which is drastically different from the covalent bonded H structure in $H_3S$ and clathrate H structure in $LaH_{10}$. One can state that at present there are three different model structures for high $T_c$ hydrides. The new structure model described here further establish four criteria for high $T_c$ superconductivity in hydrogen-rich materials proposed in this paper. The emergence of layered "penta-graphene like" clustered $H_{10}$ structure is quite significant, which will stimulate further study of the hydrogen-based family of new superconducting materials and certainly help to develop this promising field. The formulated four criteria for high $T_c$ superconductivity provide a guidance for searching room-temperature superconductors in ternary or quaternary hydrogen-rich materials in the future, which have not been well explored to date.

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