Potential Room Temperature Superconductivity in Clathrate Lanthanide/Actinides Octadechydrides at Extreme Pressures

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Abstract

Atomic metallic hydrogen (AMH) hosting high-temperature superconductivity has long been considered a holy grail in condensed matter physics and attracted great interest, but attempts to produce AMH remain in intense exploration and debate. Meanwhile, hydrogen-rich compounds known as superhydrides offer a promising route toward creating AMH-like state and property, as showcased by the recent prediction and ensuing synthesis of LaH\(_{10}\) that hosts extraordinary superconducting critical temperatures (\(T_c\)) of 250-260 K at 170-190 GPa. Here we show via advanced crystal structure search a series of hydrogen-superrich clathrate compounds MH\(_{18}\) (M: rare-earth/actinide metals) comprising H\(_{36}\)-cage networks, which are predicted to host \(T_c\) up to 329 K at 350 GPa. An in-depth examination of these extreme superhydrides offers key insights for elucidating and further exploring ultimate phonon-mediated superconductivity in a broad class of AMH-like materials.

Introduction

First predicted 86 years ago by Wigner and Huntington,\(^1\) metallic hydrogen has been attracting great interest, especially after the conjecture of its ability to host high-temperature superconductivity.\(^2\)–\(^5\) The quest for ultimate atomic metallic hydrogen (AMH), however, has proven extremely challenging due to stringent synthesis requirements of ultrahigh pressures and supersensitive characterizations that push experimental limits.\(^6\)–\(^8\) An early study of Th\(_4\)H\(_{15}\) found this metal hydride superconducting with a critical temperature \(T_c\) of 8 K at ambient pressure;\(^9\) a proposal was also made to use chemical pre-compression to stabilize hydrogen-containing compounds that may host metallic and superconducting hydrogen states.\(^10\) This line of work has been most actively pursued after Ashcroft’s suggestion\(^11\) that hydrogen dominant metallic alloys may serve as surrogate materials for AMH in probing ultimate phonon-mediated superconductivity. Recent years have seen concerted efforts in exploring compressed metal hydrides.\(^12\)–\(^14\) Hydrogen sulfides with \(T_c\) of 203 K at 150 GPa was discovered\(^15\) following theoretical predictions of high-\(T_c\) superconductivity in H\(_2\)S\(_6\) and H\(_3\)S.\(^17\) On the other route, a distinct class of clathrate superhydrides has been predicted to possess higher \(T_c\) values\(^18\)–\(^20\) with CaH\(_6\) being the first of such examples ever predicted,\(^21\) culminating with the experimental realization of LaH\(_{10}\) that exhibit high \(T_c\) of 250-260 K at pressures of 170-190 GPa,\(^22\)\(^23\) YH\(_9\) with a \(T_c\) of 243 K at 201 GPa,\(^24\) YH\(_6\) with a \(T_c\) of 220 K at 166 GPa or 237 GPa\(^24\)\(^25\) and CaH\(_6\) with a \(T_c\) of 215 K at 170 GPa.\(^26\)\(^27\) Other notable cases for clathrate structured high-\(T_c\) superhydrides include CaH\(_6\),\(^21\) YH\(_{10}\),\(^19\)\(^20\) Li\(_2\)MgH\(_{16}\),\(^28\) and CaYH\(_{12}\),\(^29\)\(^30\) from theory and ThH\(_9\) and ThH\(_{10}\)\(^31\) from experiment. An overriding idea in this area of research is to raise the hydrogen content so that the superhydrides may more closely resemble AMH in bonding environments and physical properties. A major task is to find superhydrides with proper metal elements that are capable of holding higher hydrogen contents in the nonmolecular form (i.e., hydrogen atomization) that can potentially help generate higher \(T_c\) exceeding that of LaH\(_{10}\).\(^12\)\(^21\)\(^28\)\(^32\)\(^33\) Recent studies\(^14\)\(^19\)\(^20\)\(^31\) show that rare-earth (RE) and actinide (An) elements are capable of holding a large amount of hydrogen by forming
clathrate compounds at high pressures, and the resulting hydrides host high-$T_c$ values. These results raise the prospects of finding RE/An hydrides containing even higher hydrogen contents, and such superhydrides may possess further increased $T_c$ approaching or even exceeding room temperature. Based on these considerations, we have chosen a series of electron-rich rare-earth and actinide elements as hosts to provide electrons to dissociate molecular hydrogen pairs, thereby creating an AMH-like environment conducive to harboring higher $T_c$ superconductivity.

Here, we report on the finding of a series of hydrogen-superrich MH$_{18}$ compounds, where M stands for RE or An elements, identified using our developed structural search algorithm.$^{34,35}$ These extreme superhydrides comprise conspicuous H$_{36}$ clathrate cages providing an excellent platform for probing the effect of rising hydrogen content on superconducting properties in superhydrides. First-principles calculations reveal unexpectedly diverse $T_c$ values among the MH$_{18}$ compounds that share the same stoichiometry and bonding structure, suggesting intricate underlying mechanisms. Of the identified superhydrides, CeH$_{18}$ is predicted to exhibit remarkable above-room-temperature high $T_c$ of 329 K at 350 GPa, while other compounds possess widely variable $T_c$ from 50 K to 321 K. These intriguing results provide a wealth of information on rich material behaviors and key physics insights that allow an in-depth study of factors with major influence on approaching ultimate phonon-mediate superconductivity. This work opens a promising path for further exploration of binary and higher order superhydrides that can meet or even exceed AMH in hosting superconducting states with higher $T_c$ values.

Results

Phase diagram. We have performed structure searches in binary hydrides MH$_m$ ($m=2$–24) over a wide range of hydrogen contents to predict stable structures at high pressures. This search process has led to the discovery of a series of hydrogen-superrich compounds. Particularly noteworthy among these are new stoichiometric Ce and Th superhydrides Ce/ThH$_{18}$ that stabilize at experimentally accessible but technically very challenging pressure range around 400 GPa without considering the zero-point energy (ZPE), as shown in Figure 1(a). Further calculations of the formation enthalpy with the inclusion of ZPE show that CeH$_{18}$ and ThH$_{18}$ become stable at notably reduced pressures of 315 and 281 GPa (Figure 1(b)), respectively, making the experimental synthesis and characterization more feasible. A systematic comparison of the stability pressure ranges calculated without and with the inclusion of ZPE is given in Figure S1. We examined a broad range of RE and An superhydrides up to 700 GPa, and the results reveal that this MH$_{18}$ stoichiometry is ubiquitous among diverse RE and An superhydrides for RE/An=Y, La, Ce, Ac, and Th, which are stable over variable extended ranges of pressures as shown in Figure 1(b). Details of the computational methods for the structure search and property calculations are provided in the Supplemental Material.$^{36}$

Crystal structures. The predicted extreme superhydrides MH$_{18}$ contain conspicuous H$_{36}$ clathrate units in its crystal structures. Figure 2(a) shows the crystal structure that comprises a peculiar three-dimensional hydrogen clathrate structure of space group $Fdddd$, where each M atom is located at the center of a
clathrate H$_{36}$ cage that, as shown in Figure 2(c), consists of a 6H$_{6}$ ribbon-ring structure with two wrinkled H$_{6}$ hexagons above and below with bridge bonds connecting the H$_{6}$ hexagons to the 6H$_{6}$ ribbon-ring structure. At higher pressures, which vary for different M atoms, this H$_{36}$ clathrate units rearrange and stabilize in another structure of space group *Fmmm* shown in Figure 2(b). Below we focus our analysis mainly on CeH$_{18}$ to showcase its prominent properties while also discussing key data and trends involving other MH$_{18}$ compounds.

**Discussion**

**Band/Dos character and Superconductivity of CeH$_{18}$.** To assess superconducting properties of CeH$_{18}$, we first evaluate its electronic band structure, taking 400 GPa as a representative case study. Calculated results clearly indicate the metallic nature of CeH$_{18}$ with several band crossing the Fermi level, as shown in the left panel of Figure 3(a). Results in the right panel of Figure 3(a) show that the hydrogen atoms make a substantial contribution to the electronic density of states (DOS) near the Fermi level, which is almost identical to the DOS contributed by the electrons from Ce. It is seen that the DOS is essentially flat around the Fermi energy, which is notably different from the DOS of LaH$_{10}$ that hosts van Hove singularity around the Fermi energy $^{19}$. To examine the changes of the band-filling states, we have calculated the band structures at different pressures, and the results (see Figure S2) show that the hole-bands at the X-point, along the Z–X path, and at the Y–point move downward with rising pressure, indicating a systematic pressure driven electron transfer, which provides an explanation for the decreasing trend of $T_c$ with increasing pressure. We next examine the phonon and electron-phonon coupling in CeH$_{18}$. Calculated phonon dispersion results are shown in the left panel of Figure 3(b). No imaginary phonon modes are present in the entire Brillouin zone, indicating the dynamic stability of this crystal structure. We then computed the Eliashberg spectral function $\alpha^2 F(\omega)$, from which the electron-phonon coupling parameter can be obtained via a simple integration in the frequency domain.$^{37-40}$ The resulting integrated electron-phonon coupling parameter $\lambda = 2.3$ is quite large and comparable to the value of $\lambda = 2.2$ for H$_3$S.$^{17}$ It is noted that such strong electron-phonon couplings make various approximate weak-coupling $T_c$ formulas generally unreliable, and an accurate description necessitates direct numerical solutions to the Eliashberg equations.$^{37-40}$ We have employed this approach to calculate superconducting energy gap and transition temperature using the typical Coulomb pseudopotential $\mu^* = 0.10$; we also checked results with $\mu^* = 0.13$ to estimate a reasonable range of $T_c$ values. The resulting $T_c$ of 309-329 K (for $\mu^* = 0.10$ and 0.13) at 350 GPa, where CeH$_{18}$ is stable, is well above the room temperature and represents the highest hitherto reported $T_c$ among binary superhydrides.

**Superconductivity of MH$_{18}$.** To explore systematic trends and elucidate the underlying mechanisms for superconductivity in the predicted extreme superhydrides, we have calculated key electronic, phonon and electron-phonon coupling parameters and the resulting $T_c$ values from solving the Eliashberg equations of selected MH$_{18}$ compounds. We also have calculated, for the purpose of comparison, under the same
parameters employing the same computational approach for the $I\bar{4}_1/amd$ phase of solid hydrogen that is known to stabilize in the pressure range of interest here.\textsuperscript{41} Moreover, we have systematically examined energetic and phonon dispersion aspects of the MH\textsubscript{18} compounds beyond their stability fields indicate in Figure 1(b), and we have identified several metastable phases that extend the structural viability to lower pressures with enhanced superconducting transition temperatures. All the key parameters and properties for the identified stable and metastable phases of MH\textsubscript{18} and hydrogen in $I\bar{4}_1/amd$ phase are summarized in Table I with the $T_c$ data plotted in Figure 4.

Calculated results show that the electron-phonon coupling parameter $\lambda$ and the resulting $T_c$ vary considerably among the MH\textsubscript{18} superhydrides at the same pressure points (see Table I and Figure 4). This phenomenon reflects the broadly variable lattice dynamics and electronic states in different MH\textsubscript{18} compounds, despite that they all share the same stoichiometry and clathrate structures. These contrasting properties indicate substantial differences in their bonding strengths and charge distributions, which are manifested in the large disparities of their characteristic vibrational frequencies and electronic density of states at the Fermi level as listed in Table I.

It is noted that the MH\textsubscript{18} compounds host $T_c$ values that distribute over a large range, from 50 K for $Fddd$-AcH\textsubscript{18} at 700 GPa up to 329 K for $Fddd$-CeH\textsubscript{18} at 350 GPa ($T_c$ quoted for discussion are all taken at $\mu^* = 0.10$). These results offer important clues for understanding the trends in $T_c$ values that approach the result of the $I\bar{4}_1/amd$ phase of solid hydrogen at high pressures. Among the extreme superhydrides, CeH\textsubscript{18} exhibits the highest $T_c$ in the entire pressure range, and this compound hosts H–H distances in the range of 0.85–1.17 Å that is close to that of AMH (1.0 Å) at 500 GPa. These results show that these newly identified extreme MH\textsubscript{18} superhydrides represent a series of compounds that approach AMH in superconducting properties, confirming Ashcroft’s original conjecture.\textsuperscript{11} We have calculated the projected phonon density of states (PHDOS) from Ce and H atoms. The results given in the middle panel of Figure 3(b) show that the main contributions to the EPC come from the mid– and high–frequency hydrogen vibrations in the range of 500–2500 cm$^{-1}$. It is also seen from the results in Figure 4 that most MH\textsubscript{18} compounds exhibit monotonically decreasing $T_c$ with increasing pressure with the exception of $Fddd$-ThH\textsubscript{18} that hosts a slightly upward trend in its $T_c$ versus rising pressure. This pressure induced reduction of $T_c$ is reminiscent of the behavior of solid hydrogen at higher pressures (700-1,000 GPa),\textsuperscript{5} which is consistent with the idea that chemical pre-compression in hydrogen compounds would shift material behaviors toward lower pressures. These insights are helpful for rational exploration and elucidation of optimal superconducting superhydrides.

**Taking potential effects into consideration.** Additional effects, such as spin-orbit coupling (SOC), magnetism and electron correlation, may affect the estimated $T_c$ of the predicted MH\textsubscript{18} compounds. We have taken CeH\textsubscript{18} and ThH\textsubscript{18} as case studies to assess the effect of SOC. Our calculations reveal that the $T_c$ values are insensitive to SOC (see Table I), which is consistent with the nearly identical band structures with and without the SOC (Figure 3a). We have examined the energetics of the magnetic structures of the
predicted MH$\textsubscript{18}$ compounds by considering six possible magnetic configurations (one ferromagnetic and five antiferromagnetic configurations). The results show that the nonmagnetic state is the most stable for all the predicted MH$\textsubscript{18}$ compounds. We have not considered electron correlation effects on the EPC due to a lack of available computational tools for this purpose. We note, however, that previous studies$^{17,19−21}$ have shown that the experimental results on several superhydrides (e.g., La, Y, Th, and Ca hydrides$^{15,22−25,29,30,42}$) are well described by the theoretical results obtained within the current EPC computation scheme without considering the electron correlation effects. On this basis, it is expected that the results in the present work offer a reasonably accurate description of the superconductivity in the newly predicted MH$\textsubscript{18}$ compounds.

In summary, we have identified a series of MH$\textsubscript{18}$ compounds containing the highest atomic hydrogen content among metal hydrides reported to date. These extreme superhydrides comprise unique H$_{36}$ clathrate units stabilized at high pressures starting around 300–400 GPa. Favorable conditions of electronic density of states near the Fermi level and lattice vibrational modes that set large phonon energy scale and strong electron-phonon coupling in CeH$_{18}$ generate high $T_c$ of 329 K at 350 GPa. Meanwhile, other MH$_{18}$ compounds exhibit a wide range of $T_c$ with variable electronic, phonon and electron-phonon coupling combinations. These results offer insights into intricate mechanisms for superconductivity in superhydrides, establishing a promising platform for further exploration and optimization of diverse superhydrides that approach and may even exceed high-temperature superconductivity predicted for atomic metallic hydrogen.

**Methods**

**Structural predictions.** Our structure search is based on PSO algorithm$^{43,44}$ using the CALYPSO methodology.$^{34,35,45}$ We performed structure searches at 400 GPa with 1–4 formula units (f. u.) per cell of MH$_x$ ($x=2−24$). Most searches converge in 50 generations with about 2,500 structures generated.

**Ab initio calculations.** Structural optimization and computations of enthalpy, phonon, electronic structures, and spin-orbital coupling (SOC) were all performed in the framework of density-functional theory (DFT) as implemented in the VASP code.$^{46}$ The Perdew-Burke-Ernzerhof$^{47}$ generalized gradient approximation$^{48}$ was employed, and a kinetic cutoff energy of 500 eV was adopted to ensure that the calculated enthalpy converges to better than 1 meV/atom. The ZPE of predicted compounds were obtained from lattice dynamic calculations as implemented the PHONOPY code.$^{49}$

**EPC calculations.** The electron-phonon coupling (EPC) calculations were carried out using the QUANTUM ESPRESSO code.$^{50}$ Ultrasoft pseudopotentials for RE/An and H elements were used with a kinetic energy cutoff of 80 Ry. To reliably calculate the electron-phonon coupling in metallic systems, we have employed $k$-meshes of $2\pi \times 0.045 \text{ Å}^{-1}$ for the electronic Brillouin zone integration and $q$-meshes of $2\pi \times 0.09 \text{ Å}^{-1}$ for all the phonon calculations of MH$_{18}$ compounds. We have employed the Migdal-Eliashberg theory$^{51}$ to calculate superconducting energy gap and transition temperature.
Data availability

The authors declare that the main data supporting the findings of this study are contained within the paper and its associated Supplementary Information. All other relevant data are available from the corresponding author upon reasonable request.

Declarations

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Author Contributions

Y.M. and H.L. designed the research; X.Z., and Y.S. performed the calculations; X.Z., Y.S., T.I., M.X., H.L., C.C., and Y.M. analyzed and interpreted the data, and contributed to the writing of the paper.

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Competing interests

The authors declare no competing interests.
Supplementary Information is available for this paper at xxxxxx

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Table

Calculated pressure (P, GPa) variation of $\lambda$, $\omega_{\log}(K)$, $N(E_I)$ (states/Ry/f.u./spin) and $T_c$ (K) for $\mu^*=0.10(0.13)$ for selected MH$_{18}$ compounds in $Fmmm$ or $Fddd$ phase [(M) indicates metastable phase] and hydrogen in $I_4_1/amd$ phase. The values of $T_c$ for $Fddd$–CeH$_{18}$ and $Fmmm$-ThH$_{18}$ with the inclusion of SOC are also listed.
| Compound       | P   | $\lambda$ | $\omega_{\text{log}}$ | $N(E_f)$ | $T_c$  | $T_c$(SOC) |
|---------------|-----|-----------|-------------------|--------|------|-----------|
| H-$I4_1$/amd(M) | 300 | 2.34      | 1577              | 0.23   | 339(320) | -         |
| H-$I4_1$/amd(M) | 400 | 2.39      | 1719              | 0.25   | 383(362) | -         |
| H-$I4_1$/amd   | 500 | 2.24      | 1806              | 0.23   | 380(356) | -         |
| H-$I4_1$/amd   | 600 | 2.10      | 1953              | 0.23   | 388(362) | -         |
| H-$I4_1$/amd   | 700 | 2.08      | 2021              | 0.25   | 401(375) | -         |
| YH$_{18}$-Fddd | 500 | 1.50      | 1082              | 4.21   | 183(165) | -         |
| YH$_{18}$-Fddd | 600 | 1.28      | 1467              | 3.96   | 176(158) | -         |
| YH$_{18}$-Fddd | 700 | 1.10      | 1704              | 3.74   | 162(140) | -         |
| LaH$_{18}$-Fddd | 600 | 0.74     | 1638              | 3.05   | 70(55)   | -         |
| LaH$_{18}$-Fddd | 700 | 0.78     | 1642              | 3.21   | 79(64)   | -         |
| LaH$_{18}$-Fmmm | 300 | 2.46     | 1156              | 4.66   | 271(255) | -         |
| LaH$_{18}$-Fmmm | 350 | 1.68     | 1491              | 4.40   | 239(222) | -         |
| LaH$_{18}$-Fmmm | 400 | 1.28     | 1649              | 4.13   | 192(174) | -         |
| LaH$_{18}$-Fmmm | 500 | 0.82     | 1663              | 3.23   | 93(76)   | -         |
| CeH$_{18}$-Fddd(M) | 300 | 2.03     | 985               | 5.04   | 223(207) | 224(208) |
| CeH$_{18}$-Fddd | 350 | 2.80     | 919               | 6.04   | 329(309) | 330(310) |
| CeH$_{18}$-Fddd | 400 | 2.32     | 1294              | 6.19   | 312(292) | 310(290) |
| CeH$_{18}$-Fddd | 500 | 1.85     | 920               | 5.09   | 240(212) | -         |
| CeH$_{18}$-Fddd | 600 | 1.64     | 844               | 4.88   | 216(194) | -         |
| CeH$_{18}$-Fmmm(M) | 400 | 2.21     | 1260              | 4.17   | 285(265) | -         |
| CeH$_{18}$-Fmmm | 600 | 1.76     | 1388              | 4.20   | 285(262) | -         |
| AcH$_{18}$-Fddd | 400 | 0.92     | 1411              | 3.45   | 99(83)   | -         |
| AcH$_{18}$-Fddd | 500 | 0.80     | 1480              | 3.31   | 76(62)   | -         |
| AcH$_{18}$-Fddd | 600 | 0.65     | 1718              | 3.29   | 53(40)   | -         |
|              |       |       |       |       |           |
|--------------|-------|-------|-------|-------|-----------|
| AcH_{18} Fddd | 700   | 0.62  | 1844  | 3.43  | 50(37)    |
| AcH_{18} Fmmm | 300   | 1.68  | 1217  | 4.39  | 206(190)  |
| AcH_{18} Fmmm | 400   | 1.36  | 904   | 3.73  | 134(119)  |
| ThH_{18} Fddd | 300   | 1.15  | 1227  | 4.01  | 131(116)  |
| ThH_{18} Fmmm | 400   | 3.39  | 568   | 7.09  | 296(277)  |
| ThH_{18} Fmmm | 500   | 1.92  | 1573  | 7.55  | 306(284)  |
| ThH_{18} Fmmm (M) | 600   | 2.13  | 1331  | 7.92  | 321(299)  |

**Figures**

(a) Calculated convex-hull of newly identified extreme superhydrides CeH_{18} and ThH_{18}, both in the Fddd phase, with respect to decomposition into Ce/ThH_{1020}, 31 and H_{241}, 52 at 400 GPa. Data points located on the convex hull (solid lines) represent stable species against possible decomposition. The open symbols represent some metastable/unstable compositions identified by the search process. (b) Stable pressure ranges of the predicted series of extreme superhydrides MH_{18} with respect to decomposition into known MH_{x} (x = 2, 4, 6, 9, 10, 12, 16, and 17) and Cmca H_{2}, and these results are obtained via calculations with the inclusion of the zero-point energy (ZPE).
Figure 2

The crystal structure of MH18 in (a) Fddd and (b) Fmmm phase. (c) The building units of the Ce@H36 hydrogen clathrate cage, including a 6H6 ribbon-ring and two H6 hexagons, which are connected by pertinent bridge bonding networks. The large and small spheres represent the metal and hydrogen atoms, respectively.
Figure 3

(a) Electronic band structure (left) and projected density of states (right) of CeH18 at 400 GPa. The band structures without and with the inclusion of SOC are plotted with black and red lines, respectively. (b) Phonon dispersion curves with the strength of q resolved λq indicated by circle size (left), phonon density of states (PHDOS), Eliashberg spectral function αF (ω) and EPC parameter λ(ω) (middle), and superconducting energy gap (right) of CeH18 at 400 GPa.
Figure 4

Calculated $T_c (\mu^*=0.10)$ for selected extreme superhydrides MH18 compared with the results for the I41/amd phase of solid hydrogen at high pressures. Solid (open) symbols represent the $T_c$ data for stable (metastable) structural phases of the indicated MH18 compounds and solid hydrogen.

Supplementary Files

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