The Systematic Study on the Stability and Superconductivity of Y-Mg-H Compounds under High Pressure

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Structural stabilities of high-pressure YMgH$_x$ phases ($x = 2 - 10, 12, 14,$ and $16$) and their superconductivities are investigated by employing evolutionary-algorithm-based crystal search combined with first-principles calculations. For predicted candidate structures of YMgH$_x$, the convex hull and phonon analyses reveal seven stable and two metastable phases. For all the predicted phases, superconducting transition temperatures ($T_c$) are also predicted by using the McMillan formula. $P4/mmm$-YMgH$_6$ is found having $T_c = 76$ K at 300 GPa comparable to the boiling temperature of liquid nitrogen, and high-$T_c$ ($\geq 77$ K) being predicted for the H-richer phases, $P4/mmm$-YMgH$_8$ (124 K at 300 GPa), Cmmm-YMgH$_{12}$ (152 K at 250 GPa), and $Fd3m$-YMgH$_{12}$ (190 K at 200 GPa), which possess clathrate structures composed of H$_{14}$, H$_{18}$, H$_{24}$, and H$_{24}$ cages, respectively. To elucidate why the H-rich phases attain high-$T_c$, electronic and phonon band structures as well as electron-phonon coupling strength are analyzed based on Eliashberg spectral functions. The clathrate structures exhibit both a larger H-driven electronic density of states at the Fermi level and a denser H-driven phonon density of states, correlating with larger EPC constants. These structural and chemical bonding analyses reveal that the highest-$T_c$ phase $Fd3m$-YMgH$_{12}$ has H$_4$ units formed in the sodalite cage.

1. Introduction

Recently, with the experimental verification of room temperature superconductivity in C-S-H compounds ($T_c \approx 288$ K at \(\approx 267\) GPa), ternary hydrides have been playing an increasingly important role in the search for novel high-temperature superconductors. However, due to the diversity of ternary hydrides, the difficulty in searching for new superconducting hydrides has increased exponentially, and only about 20 potential superconducting hydrides have been predicted. Compared with binary superconducting hydrides, ternary superconducting hydrides have a higher competitive possibility to achieve the room temperature superconductivity. The successful prediction of room temperature superconductor Li$_3$MgH$_{16}$ is a good demonstration (estimated value of $T_c \approx 473$ K at 250 GPa). Among the discovered ternary hydrides (A-B-H system), they can be classified mainly into three categories: 1) A and B are metal and non-metal elements, respectively, 2) both A and B are non-metal elements, and 3) both A and B are metal elements.

1) In the first category, theoretical calculations show the following compounds with superconductivity, such as YSH$_6$, MgGeH$_6$, FeSeH$_6$, CaBH$_4$, LiBH$_4$, and so on. Interestingly, the introduction of non-metal can reduce the pressure required for stability to a certain extent. For example, LaBH$_4$ was predicted to have a superconducting transition temperature ($T_c$) of 126 K at...
50 GPa. Therefore, it is more promising to search for the potential low-pressure-stabilized high-temperature superconductors in these compounds.

2) In the second category, the theoretically predicted superconducting hydrides include H\textsubscript{5}Se, CSH\textsubscript{4}, and so on.\[^{[7,10,18,28–31]}\] These compounds do not show any particularly obvious structural characteristics. In addition, their phases exhibit instabilities depending on applied pressures. For example, in the CSH\textsubscript{4}, reported by Sun and Cui, there may be phase decomposition relative to CH\textsubscript{4} and H\textsubscript{2}S.\[^{[18,29]}\] For such compounds, chemical doping may be a more feasible way.\[^{[30,31]}\] For example, in the recently reported C-S-H (287.7 K at 267 GPa), the highest \(T_c\) value (270 K) can be achieved when approximately 0.0555 carbon is incorporated into H\textsubscript{2}S, as predicted by the virtual crystal approximation (VCA) method.\[^{[1,32]}\]

3) The currently reported potential superconducting compounds with \(T_c\) greater than 200 K mainly fall into such a combination, such as CaYH\textsubscript{12}, CaMgH\textsubscript{12}, Li\textsubscript{2}MgH\textsubscript{16}, and so on.\[^{[3,8,10,33]}\] Some of these compounds are energetically favorable to form the clathrate structures and also likely to have robust electronic density of states (DOS) at the Fermi level. The structures with robust DOS tend to have a large electron–phonon coupling (EPC) constant (\(\lambda\)). In general, larger \(\lambda\) is easier to show high \(T_c\).\[^{[34]}\] For example, the EPC constant of the room temperature superconductor \(Fd\bar{3}m\)-Li\textsubscript{2}MgH\textsubscript{16} can reach an astonishing value of 3.35.\[^{[8]}\]

Our target is to search for some compounds with extremely high-\(T_c\). Therefore, we pay more attention to the third category of ternary hydrides as mentioned above. Among the binary hydrides discovered, YH\textsubscript{10} has the highest \(T_c\) value (\(T_c = 310\) K at 300GPa).\[^{[35]}\] We first consider the introduction of the second metal element into YH\textsubscript{10}. Indeed, there have been many reports of potential superconducting hydrides such as ScYH\textsubscript{6}, CaYH\textsubscript{12}, LaYH\textsubscript{12}, and YKH\textsubscript{12}.\[^{[10,21,36–38]}\] In the previous studies of binary hydrides, it has been found that the atomic number, atomic mass, atomic radius, number of electrons, etc., have significant impact on the final \(T_c\) value.\[^{[39,40]}\] Lightweight elements usually can have a higher vibration frequency and thus can be helpful to realize a higher \(T_c\) value.\[^{[34]}\] The superconductivity of hydrides would greatly decrease as the number of \(d\) and \(f\) electrons increase. This trend is most obvious in the metal hydrides of the actinides and lanthanides.\[^{[40]}\] Considering the atomic mass and the absence of \(d\) and \(f\) electrons, alkali and alkaline earth metals (Li, Na, Be, Mg, etc) are the most ideal candidate elements to be incorporated into YH\textsubscript{10}. In addition, among the binary hydrides of the aforementioned four candidate elements, MgH\textsubscript{2} has the \(T_c\) value (271 K) closest to room temperature.\[^{[41]}\] Thus, the above facts motivated us to investigate Y-Mg-H systems for high-\(T_c\) candidates. For that purpose, we should first explore crystal structures of MgH\textsubscript{2} compounds because their structures still remain unknown.

In the present study, we performed an evolutionary-algorithm based structural search for YMgH\textsubscript{x} compounds (\(x = 2 – 10, 12, 14, \text{and} 16\)) at 100, 200, and 300 GPa. As a result, several polymorphs were obtained for each \(x\), and the most stable polymorphs depending on the pressures were used to draw the convex hulls, thereby obtaining the thermodynamically stable phases. In addition, we confirmed their dynamical stabilities by performing their phonon simulations. Finally, we acquired a pressure-dependent phase diagram of the Y-Mg-H system. According to the phase diagram, we predicted \(T_c\) values for the most stable YMgH\textsubscript{x} compounds. We found that the strong competition between the phase stability and superconductivity of YMgH\textsubscript{x} and that the superconductivity of YMgH\textsubscript{12} would depend strongly on the hydrogen content and applied high pressure. In addition, we found a metastable phase \(Fd\bar{3}m\)-YMgH\textsubscript{12}, and its superconducting transition temperature could be high up to 190 K at 200 GPa.

## 2. Experimental Section

The crystal-structure search for YMgH\textsubscript{x} (\(x = 2 – 10, 12, 14, \text{and} 16\)) at 100, 200, 300 GPa was performed using the USPEX (Universal Structure Predictor: Evolutionary Xtallography) code.\[^{[42]}\] Each structure underwent four steps of relaxation, in which the force on each atom and the stress tensor were optimized using the VASP code\[^{[43–46]}\] based on the density functional theory (DFT) with the GGA-PBE functional\[^{[47]}\]; the DFT calculations were done with a cutoff energy of 60 Ry and the smallest allowed spacing between the \(k\)-points in Brillouin zone was set to be 0.25 \(\text{Å}^{-1}\). These chemical compositions were created at random, with the first 400 structures being created at random, and each subsequent generation producing 100 structures. These structures were composed of 40% heredity, 40% random, 10% mutation, and 10% soft mutation.

The stable phases under different pressures were determined from predicted polymorphs by comparing relative formation enthalpies in the convex hull diagram. The energy of the produced structures was globally minimized using GGA-PBE functionals\[^{[47]}\] through three DFT computations. Around ten of the structures with the lowest structural energy were chosen for each chemical composition and two higher-precision optimizations undertaken to guarantee that they could converge well under 1 meV. Then, the structure with the lowest energy was chosen as the final contender among these structures. To confirm if the thermodynamically stable phases were dynamically stable, it was checked if they did not have imaginary modes by phonon simulations. Regarding the phonon calculations, the structures of YMgH\textsubscript{x}, with small number of atoms were carried out using the Quantum-ESPRESSO code and the others were performed using the Phonopy\[^{[48]}\] code: The supercell method, as implemented in the Phonopy code,\[^{[48]}\] was used to calculate phonons for YMgH\textsubscript{10}, YMgH\textsubscript{12}, and YMgH\textsubscript{16}. Quantum ESPRESSO was used to compute the phonons of YMgH\textsubscript{2}, YMgH\textsubscript{5}, YMgH\textsubscript{8}, YMgH\textsubscript{10}, and YMgH\textsubscript{12}.\[^{[49–53]}\]

To evaluate superconducting transition temperature (\(T_c\)) of the stable/metastable YMgH\textsubscript{x} compounds, not only phonon calculations, but also electron-phonon coupling (EPC) calculations are necessary. Their EPC was calculated by quantum ESPRESSO with a plane wave basis set with a cutoff energy of 60 Ry and Marzari–Vanderbilt method in the context of linear response theory. The EPC calculation matrix is evaluated with those shown in Table 1. Thus, the \(T_c\) values were calculated using the McMillan formula.\[^{[52]}\] These calculations were done with \(k/q\)-point meshes shown in Table 1.

It was further investigated how the crystal structures and electronic structures (more precisely, chemical bonding nature) of stable/metastable YMgH\textsubscript{x} compounds contribute to \(T_c\) values. In particular, electronic structures at Fermi levels are impor-
Table 1. Setting of k-point meshes in the self-consistent field (SCF) calculations and that of q-point meshes in the phonon calculations for stable/metastable YMgH\textsubscript{2} phases.

| Compound | Space | SCF dense | Phonon group | k-point | q-point |
|----------|-------|-----------|--------------|---------|---------|
| YMgH\textsubscript{2} | I\textsubscript{4} \textsubscript{1/a}nd | 12 x 12 x 12 | 3 x 3 x 3 | 3 x 3 x 3 |
| YMgH\textsubscript{3} | P\textsubscript{6} \textsubscript{1}/mmc | 16 x 16 x 8 | 4 x 4 x 2 | 4 x 4 x 2 |
| YMgH\textsubscript{9} | Imma | 12 x 12 x 12 | 3 x 3 x 3 | 3 x 3 x 3 |
| YMgH\textsubscript{9} | Pmma | 12 x 12 x 12 | 3 x 3 x 3 | 3 x 3 x 3 |
| YMgH\textsubscript{6} | Fmm2 | 12 x 12 x 12 | 3 x 3 x 3 | 3 x 3 x 3 |
| YMgH\textsubscript{8} | P\textsubscript{4}/mmm | 16 x 16 x 12 | 4 x 4 x 3 | 4 x 4 x 3 |
| YMgH\textsubscript{8} | P\textsubscript{4}/mmm | 16 x 16 x 12 | 4 x 4 x 3 | 4 x 4 x 3 |
| YMgH\textsubscript{12} | C\textsubscript{m}mm | 16 x 16 x 12 | 4 x 4 x 3 | 4 x 4 x 3 |
| YMgH\textsubscript{12} | F\textsubscript{d}\textsubscript{3}m | 16 x 16 x 8 | 4 x 4 x 4 | 4 x 4 x 4 |

Figure 1. Pressure-dependent phase diagram of the Y-Mg-H system. The phases shown here are both thermodynamically and dynamically stable, while metastable phases do not appear.

3. Results and Discussion

3.1. Pressure-Dependent Phase Diagram

Figure 1 shows the pressure-dependent Y-Mg-H phase diagram at 100 – 300 GPa. Seven stable YMgH\textsubscript{2} phases were predicted: I\textsubscript{4} \textsubscript{1}/amd-YMgH\textsubscript{2} (100 – 300 GPa), P\textsubscript{6} \textsubscript{1}/mmc-YMgH\textsubscript{2} (100 – 300 GPa), Imma-YMgH\textsubscript{2} (100 – 150 GPa), Pmm2-YMgH\textsubscript{2} (250 – 300 GPa), Fmm2-YMgH\textsubscript{2} (100 – 200 GPa), P\textsubscript{4}/mmm-YMgH\textsubscript{2} (250 – 300 GPa), and C\textsubscript{m}mm-YMgH\textsubscript{12} (250 – 300 GPa) (see Figure S2, Supporting Information, for their structures). We can see that stabilizing hydrogen-richer compounds involves applying higher pressures. In addition, we explored two metastable phases (P\textsubscript{4}/mmm-YMgH\textsubscript{2} and F\textsubscript{d}3m-YMgH\textsubscript{12}). These phases were determined by checking their 1) thermodynamical and 2) dynamical stabilities.

3.1.1. Thermodynamical Stability

A number of candidate polymorphs were proposed by our structure search for every x (x = 2 – 10, 12, 14, 16) at each of the selected pressures (P = 100, 150, 200, 250, 300 GPa). Using these candidate polymorphs for each of the pressures, we depicted the convex hull diagrams of YMgH\textsubscript{2} relative to (I\textsubscript{4} \textsubscript{1}/amd-YMgH\textsubscript{2} + C2\textsubscript{2}/c\textsubscript{2}-H\textsubscript{2}) as reference, as shown in Figure 2a–e; the reference compound, I\textsubscript{4} \textsubscript{1}/amd-YMgH\textsubscript{2}, was determined from its thermodynamical stability relative to its decomposition counterparts (YH\textsubscript{2} + Mg) at 100 – 160 GPa and (\frac{1}{2}YH\textsubscript{4} + 2Y + Mg) over 160 GPa) referring to refs. [55–57], as shown in Figure 2f. Our thermodynamic convex hull analysis indicates that YMgH\textsubscript{x} compounds for x = 10, 14, and 16 lie above the tie lines in the diagrams within the pressure we searched, indicating their thermodynamical instabilities at any pressures. Thus, we concentrated on YMgH\textsubscript{x}, with x = 2 – 9 and 12 for further checking their thermodynamical stabilities relative to decomposition counterparts as shown in Figure S1, Supporting Information, which determines the pressure ranges for their thermodynamical stabilities. Hereafter, we will see below each of them in more detail.

I\textsubscript{4} \textsubscript{1}/amd-YMgH\textsubscript{2}, P\textsubscript{6} \textsubscript{1}/mmc-YMgH\textsubscript{1}, and P2/m-YMgH\textsubscript{2} remain thermodynamically stable in the pressure range from 100 to 300 GPa. Pmmm\textsubscript{2}-YMgH\textsubscript{2} gets instable more than 190 GPa, indicating that it decomposes into (P\textsubscript{6}/mmm-YH\textsubscript{2} \textsuperscript{[56]} + P\textsubscript{6}/mmm-Y\textsubscript{2} \textsuperscript{[58]}). YMgH\textsubscript{5} undergoes a phase transition from Imma to Pmm2 around 175 GPa. For YMgH\textsubscript{6}, we found Fmm2 being thermodynamically most stable at 100 – 200 GPa. In addition, a metastable phase, P\textsubscript{4}/mmm, was found to be almost degenerate with the most stable Fmm2 within 0.005 eV atom\textsuperscript{-1}. The P\textsubscript{4}/mmm structure was also found for ScYH\textsubscript{4} \textsuperscript{[21,59]}, P\textsubscript{4}/mmm-YMgH\textsubscript{9} was found to be thermodynamically stable above 250 GPa. This structure was also found for ScCaH\textsubscript{4} \textsuperscript{[21,59]}, whose T\textsubscript{c} values were predicted to be incredibly high up to 212 K \textsuperscript{[59]}. P2/m-YMgH\textsubscript{9} was the most stable thermodynamically at 100 – 200 GPa. For x = 12, the convex hull analysis exhibits its thermodynamical stability over 250 GPa. Considering the binary hydrides of Y-H and Mg-H, however, a decomposition of C\textsubscript{m}mm-YMgH\textsubscript{12} into (YH\textsubscript{4} (I\textsubscript{4} \textsubscript{1}/amd\textsubscript{3}m) \textsuperscript{[56]} + MgH\textsubscript{2} (P\textsubscript{6}/mmm) \textsuperscript{[58]} + 2H\textsubscript{2} (C2/c) \textsuperscript{[58]})) occurs less than 250 GPa. At 300 GPa, we can also see a metastable F\textsubscript{d}3m phase.

3.1.2. Dynamical Stability

For the above thermodynamically stable phases for x = 2 – 9 and 12, we confirmed whether or not they are dynamically stable at each pressure, thereby obtaining the pressure-dependent phase diagram. Figure 1; the phonon simulations of selected polymorphs at some pressures shown in Figures S4 and S5, Supporting Information. Looking at the compounds exhibiting imaginary modes, Pmm2\textsubscript{2}-YMgH\textsubscript{2}, P2/m-YMgH\textsubscript{2}, and P2/m-YMgH\textsubscript{9} were found to be dynamically instable at all the pressures as considered to be thermodynamically stable; it was found that YMgH\textsubscript{5} exhibited dynamical instabilities between 150 and 250. Eventually, excluding the above dynamically instable phases, we obtained the seven stable phases (Figure 1) and additionally two metastable phases.
Figure 2. Convex hull diagrams of YMgH$_x$ relative to YMgH$_2$ and H-C2 at the pressure of a) 100 GPa, b) 150 GPa, c) 200 GPa, d) 250 GPa, and e) 300 GPa. To ensure the relative stabilities of YMgH$_x$ compounds, the relative stability of YMgH$_2$ against several decomposition possibilities is also given in (f).

Figure 3. The clathrate structure of a) P4/mmm-YMgH$_6$, b) P4/mmm-YMgH$_8$, c) Cmmm-YMgH$_{12}$, and d) Fd3m-YMgH$_{12}$.

Finally, we make remarks on predicted crystal structures of several YMgH$_x$ compounds. In the present study, highly symmetric clathrate structures were found for not only P4/mmm-YMgH$_6$ and Cmmm-YMgH$_{12}$ stable phases, but also P4/mmm-YMgH$_6$ and Fd3m-YMgH$_{12}$ metastable phases, as shown in Figure 3. The hydrogen-rich phases, Cmmm-YMgH$_{12}$ and Fd3m-YMgH$_{12}$ are composed of H$_{14}$ cages with six quadrilaterals and eight hexagons, respectively. On the other hand, P4/mmm-YMgH$_6$ and P4/mmm-YMgH$_8$ consist of H$_{14}$ and H$_{18}$ cages, respectively. They have the same space group as ScCaH$_6$ with clathrate structure exhibiting $T_c = 212$ K at 200 GPa. Therefore, clathrate structures can be expected to be good candidates for high-$T_c$ compounds.

3.2. Superconducting Transition Temperatures

To discover superconducting YMgH$_x$ compounds for $x = 2, 3, 5, 6, 8,$ and 12, we have predicted $T_c$ values at certain pressures based on the McMillan formula\cite{52}:

$$T_c = \frac{\alpha_{\log} }{1.2} \exp \left( - \frac{1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right)$$

where the parameter $\mu^*$ is an effective Coulomb repulsion whose typical values lie between 0.10 and 0.13; $\lambda$ is the electron-phonon coupling (EPC) constant; $\alpha_{\log}$ is the logarithmic average phonon frequency. Both $\lambda$ and $\alpha_{\log}$ can be obtained from the Eliashberg spectral functions $\alpha^2 F(\omega)$ shown in Figure 5. The electronic density of states at Fermi level $N(E_F)$ is also an important factor constructing of $\alpha^2 F(\omega)$, which can be seen in Figure 6. These quantities evaluated for stable/metastable YMgH$_x$ phases in the present study are listed in Table 2. The predicted $T_c$ values of YMgH$_x$ are summarized in Figure 4 as well as Table 2.
The clathrate structures are an important key to discovering high-
terconductivity phases. Thus, hydrogen-rich phases can be regarded as high- 
Tc materials (we will give a detailed analysis of such structures in the 
next subsection). On the other hand, hydrogen-poor materials (x ≤ 5) exhibit no superconductivity or have much smaller Tc values,12,41 whereas YMgH3 does with a small Tc value of 2 K. For YMgH5, the Pmma phase can be stabilized by increasing the pressure (≥ 250 GPa) and the corresponding Tc value also increases slightly (≈ 6 K).

Next, we will see how Tc relate to its constituent quantities entering Equation (1). Comparing the H-rich materials (x ≥ 6) with the H-poor ones, it is evident that the higher Tc generally comes from the higher EPC constants (higher-Λ). For the H-rich materials, Ω0 increases as the H content x increases. For the H-poor materials, however, this is not the case. For example, YMgH3 has a higher Ω0 than YMgH2, but the former exhibits no superconductivity, while the latter does. As for N(EF), it is hard to straightforwardly consider its contribution to Tc, but we can see N(EF) = 0.021 – 0.027 for the H-rich materials. In contrast, the N(EF) values significantly vary (0.005 – 0.029) depending on the system for the H-poor materials. To understand the contribution of Ω0 and N(EF) as well as λ more closely, hereafter, we examine their phonon and electronic bond structures shown in Figures 5 and 6, respectively.

Referring to phonon partial density of states shown in Figure 5, we can see atomic contributions to the phonon modes: Phonon modes with higher frequencies (≥ 25 THz) mainly come from the vibrations of H atoms, whereas lower phonon modes (≤ 25 THz) are attributed to heavier Mg and Y atoms. The distributions/peak positions of the Eliashberg spectral functions with respect to frequency look similar to those of phonon band structures. This implies that the contribution to the Eliashberg spectrum at low/high frequencies originate from low/high-frequency-phonon modes caused by Y or Mg/H atomic vibrations interacting with electrons near EF. For the H-rich YMgHx compounds (x = 8 and 12), their Eliashbarg functions rapidly increase at the high frequencies, indicating that the contributions of the hydrogen vibrations to the EPC are more significant for the H-rich materials.

Figure 6 shows band structures and the corresponding density of states for selected YMgHx compounds, indicating atomic contributions to the electronic states near EF. For a) YMgH3 and b) YMgH5, the Y atoms mainly contribute to the electronic states near EF, though the N(EF) value of the latter is quite small, that is, even the high pressure of 100 GPa cannot metallize the Imma-YMgH5 phase sufficiently. In contrast, for the H-rich materials (d–f), the electronic states near EF consist of hybridization between the H and Y atomic orbitals, though the former is slightly larger than the latter. Remembering that Tc increases when increasing the H content, we can see that the contributions of the H atoms to N(EF) are essential for achieving high-Tc. To understand this, we further demonstrate the structural and the chemical bonding analyses.

### 3.3. Structural and Chemical Bonding Analyses

Herein, we demonstrate their relationships between the structures and the electronic states/chemical bonding for the H-rich YMgHx compounds. As previously demonstrated, the coexistence of different types of hydrogenic motifs formed in hydrogenic lattices (e.g., H−, H+ dimer, square H+2, etc) has been known as an important trigger of high-Tc for other metal hydrides.[60,61] Hence, we may roughly classify chemical bonding natures into two types: one is hydrogen atoms weakly bounded with the other hydrogen or metal atoms, the other is H2x-like co-
valent bonding. Hereafter, we further make detailed analyses on the dimerized hydrogens.

Table 3 lists the first nearest neighbor distance between atomic pairs, Y–H, Mg–H, and H–H lengths (see Figure S2, Supporting Information, for the radial distribution functions of H–H atomic pairs). For the H-rich materials with high-Tc, we can see that the H–H length is always shorter than the Mg–H and Y–H lengths. In general, the shorter H–H length implies that the H–H atomic pair can form stronger chemical bonding. Our concerns are high-Tc compounds, but for comparison, we see the case of the H-poor materials: the H–H lengths are longer than the Mg–H lengths, though we cannot see a clear trend between the H–H and Y–H lengths. Comparing the H-rich with H-poor materials, the former has much shorter H–H lengths than the latter, while there is no clear trend in Y–H and Mg–H lengths. We look into individual hydrogenic motifs in the H-rich materials below.

Figure 7 shows the electron localization function (ELF) of YmGax (x = 6, 8, and 12), with the first nearest neighbor H–H distances specified by arrows. The H–H length in P4/mmm-YmgH8 is 0.86 Å, which is close to the H–H bond length (0.74 Å).
of H₂ molecule. This may be ascribed to the charge transfer from Y and/or Mg atoms to the H–H atomic pair, where the extra electrons occupy the antibonding state of the H₂ molecule, thereby elongating the H–H length. The antibonding state can be also seen from Figure 7b. The H–H length in Cmmm-YMgH₁₂ is 1.04 Å, which is further longer than that in P4/mmm-YMgH₈ as well as H₂ bond length. Note that the H–H lengths in YMgH₁₂ are close to those in YH₆ (1.19 Å) and MgH₆ (1.10 Å). This is because the clathrate structure formed in Cmmm-YMgH₁₂ (Figure 7c) has similarities with those formed in MgH₆ and YH₆; they all consist of H₂₄ cages. Fd3m-YMgH₁₂ with the shortest bond length of 1.10 Å (Figure 7d) has slightly distorted square H₄ units, which has been known for a sodalite-like CaH₆ structure. In contrast, the H–H length in P4/mmm-YMgH₆ (1.54 Å) (Figure 7d) is longer than those in YMgH₁₂ and YMgH₈.

Figure 6. Electronic band structures for a) P6₃/mmc - YMgH₃ (100 GPa), b) Imma - YMgH₅ (100 GPa), c) P4/mmm - YMgH₆ (300 GPa), d) P4/mmm - YMgH₈ (300 GPa), e) Cmmm - YMgH₁₂ (250 GPa), and f) Fd3m - YMgH₁₂ (200 GPa).
Figure 7. The contour plots of electron localization function (ELF) on a) (200) plane of \( P_{4}/mnm - YMgH_{6} \), b) (100) plane of \( P_{4}/mmm - YMgH_{8} \), c) (100) plane of \( Cmmm - YMgH_{12} \), and d) (100) plane of \( Fd\bar{3}m - YMgH_{12} \) with an isosurface value of 0.5.

Table 3. Distances of the first nearest neighboring atomic pairs, Y–H, Mg–H, and H–H for stable/metastable YMgH\(_{x}\) compounds at selected pressures.

| Compound | Space group | \( P \) [GPa] | Y–H [Å] | Mg–H [Å] | H–H [Å] |
|----------|-------------|----------------|---------|----------|---------|
| YMgH\(_{2}\) | \( I_{4}/amd \) | 100 | 1.93 | 1.97 | 1.97 |
| YMgH\(_{3}\) | \( P_{6}_{3}/mmc \) | 100 | 2.03 | 1.70 | 1.78 |
| YMgH\(_{5}\) | \( Imm \) | 100 | 1.94 | 1.65 | 1.78 |
| YMgH\(_{8}\) | \( Pmna \) | 300 | 1.73 | 1.56 | 1.52 |
| YMgH\(_{9}\) | \( Fmm2 \) | 120 | 1.90 | 1.68 | 1.73 |
| YMgH\(_{6}\) | \( P_{4}/mmm \) | 300 | 1.76 | 1.54 | 1.54 |
| YMgH\(_{11}\) | \( P_{4}/mmm \) | 300 | 1.82 | 1.58 | 0.86 |
| YMgH\(_{12}\) | \( Cmmm \) | 250 | 1.88 | 1.73 | 1.04 |
| YMgH\(_{12}\) | \( Fd\bar{3}m \) | 200 | 1.97 | 1.83 | 1.10 |

The units are given in Å.

![Figure 8](image.png)

Figure 8. Partial (electronic) density of states (pDOS) and projected crystal orbital Hamilton population (pCOHP) for a) \( P_{4}/mmm - YMgH_{6} \), b) \( P_{4}/mmm - YMgH_{8} \), c) \( Cmmm - YMgH_{12} \), and d) \( Fd\bar{3}m - YMgH_{12} \).

The hybridization between the H–H atomic pair in \( P_{4}/mmm - YMgH_{8} \) (Figure 8a) is further enhanced than that in \( P_{4}/mmm - YMgH_{6} \). The H–H bonding states have an energy range from the Fermi level \( E_{F} \) to -15 eV. Meanwhile, the hybridization between the H–H atomic pair in \( P_{4}/mmm - YMgH_{8} \) is also further enhanced than that in \( P_{4}/mmm - YMgH_{6} \); the corresponding states become deeper and be centralized around -15 eV. The H–H antibonding states in \( P_{4}/mmm - YMgH_{8} \) appear just below \( E_{F} \) (see Figure 8c,d). Therefore, the H–H atomic pairs form covalent bonding. This can be also seen from the ELF, as shown in Figure 7c,d.
4. Conclusion

We have systematically investigated the stability and superconductivity of the ternary hydride YMgH$_x$ at high pressures. Seven and two phases were predicted to be the most stable and metastable, respectively, in terms of both thermodynamical and dynamical stabilities. We found YMgH$_x$ with $x = 6.8$, and 12 at high pressures having clathrate structures composed of H$_{14}$, H$_{18}$, and H$_{24}$ cages, respectively. Our $T_c$ evaluations based on the McMillan formula combined with electron–phonon coupling simulations predicted all the YMgH$_x$ clathrate structures to exhibit high-$T_c$ superconductivity; the $T_c$ value increases as the H content $x$ increases; the stable $Cmmm$-YMgH$_{12}$ and metastable $Fdar{3}m$-YMgH$_{12}$ sodalite structures exhibit $T_c$ values of 153 K at 250 GPa and 190 K at 200 GPa, respectively. Electronic and phonon band structures clarified that the hydrogen contributions to electronic states near the Fermi level and dense phonon density of states at high frequencies are essential for triggering high-$T_c$. Our structural and chemical bonding analyses further provide an important insight into the origin of high-$T_c$ in the Y-Mg-H system: In the cage structures, there simultaneously exist not only H atoms weakly bounded with other atoms, but also square H$_4$ units having weaker covalent bonding with longer bond lengths than the H$_2$ molecule, which is similar to CaH$_2$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electron-phonon coupling, high-temperature superconductors, superconducting phase transition
