**Cage Structure and Near Room-Temperature Superconductivity in TbH$_n$ (n = 1−12)**

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**ABSTRACT:** Hydrogen-rich compounds are considered most likely to achieve room-temperature superconductivity since the critical temperature ($T_c$) above 250 K was observed in lanthanum hydride. Exploring the high-temperature superconductivity in rare-earth metal hydrides becomes very interesting. Based on the particle swarm optimization for crystal structures and first-principles calculations, we investigate the crystal structures, phase stability, metallization, and possible superconducting properties of terbium hydride (TbH$_n$ $n$ = 1−12) under pressure. Our results show that terbium hydride is a potential high-temperature superconductor under high pressures. It stably exists at different pressure conditions by adjusting the H content. Specifically, the H atomic cage structure can be observed in most terbium hydrides, and the number of H atoms in the cage sublattice increases with the stoichiometry of H in TbH$_n$. We demonstrate that the high $T_c$ value is closely related to this cage sublattice and it increases with increasing H content in terbium hydride. The highest $T_c$ above 270 K is predicted in TbH$_{10}$ at 250 GPa for Fm$ar{3}$m and 310 GPa for R$ar{3}$m space group. This result indicates that the superconductivity with $T_c$ close to or beyond lanthanum hydride can be achieved in other rare-earth metal hydrides.

**INTRODUCTION**

In 2004, Ashcroft suggested that hydrogen-rich compounds can become metallic and superconducting at lower pressures than solid hydrogen, presumably because of “chemical compression” of heavy elements. Hydrogen-rich compound is widely regarded as one of the most promising materials to achieve room-temperature superconductivity. Numerous hydrides have been studied. From the aspect of the interaction between H and heavy elements, there are two kinds of hydrides respectively containing the polar covalent bond and the ionic bond. The former includes SiH$_4$, H$_2$S, PH$_3$, GeH$_4$, and so on, while the latter is mainly GeH$_4$(H$_2$)$_2$, SnH$_4$, PbH$_4$(H$_2$)$_2$, CaH$_6$, MgH$_6$, YH$_6$, CaH$_6$, MgH$_6$, YH$_6$, LaH$_{10}$, etc. In 2015, the discovery of superconductivity in H$_2$S (critical temperature $T_c$ $\approx$ 203 K at 155 GPa) is a milestone in the search of room-temperature superconductors, which means that the superconductivity at more than 200 K was observed in hydrides for the first time. Soon in 2019, the superconductivity near room temperature ($T_c$ $\approx$ 250 K at 170 GPa) was discovered, and the research of high-temperature superconductors has attracted much attention. From the existing form of H atom in the hydride, the structure of H atoms in hydrides is highly sensitive on superconductivity. Except H$_2$S, most of the hydrides containing polar covalent bonds exhibit the low $T_c$ such as 75 K of SiH$_4$, 78 K of PH$_3$, 80 K of H$_2$S, 45 K of H$_2$Cl, and 33 K of H$_2$. The formation of H quasi-molecular units in hydrides results in the increase in $T_c$ such as 107 K of SiH$_4$(H$_2$)$_2$, GeH$_4$(H$_2$)$_2$, and PbH$_4$(H$_2$)$_2$, indicating that the H “cluster” can drive higher $T_c$ values. The cage configuration of H atoms in CaH$_6$, YH$_6$, and LaH$_{10}$ supports this idea. The cage sublattice formed by H atoms leads to the $T_c$ near room temperature, even up to 473 K in Li$_2$MgH$_{16}$. This kind of cage structure can be viewed as one kind of H cluster. In fact, the distance of H–H in these H cages is similar to that in metallic hydrogen at high pressures.

Compared to alkaline-earth metal hydrides, previous studies have established that rare-earth metal hydrides easily produce the H cage structure. Expect LaH$_{10}$, the cage character was also observed in other rare-earth metal hydrides such as CeH$_{28,29}$, UH$_{77}$, ACH$_{19}$, ThH$_{10}$, PrH$_{33}$, PaH$_{36}$, etc. It was well known that the transition group rare-earth hydrogen-rich compounds have one thing in common. Almost all of these elements contain empty d or f and form what we call the “lability belt”, in which the electronic structure of elements are
particularly sensitive to the atomic environment because they have empty low-lying orbitals. The population of the orbitals depends on crystal field, making strong electron–phonon coupling possible.\(^\text{35}\) However, the \(T_e\) values of these rare-earth hydrides mentioned above are all lower than that of \(\text{LaH}_{10}\). Analyzing the electronic configuration, we know that the difference between \(\text{La}\) and other rare-earth elements is the absence of the 4f or 5f electrons in \(\text{La}\). Then, it is an interesting issue to explore the superconductivity with higher \(T_e\) values in 4f or 5f rare-earth metal hydrides under high pressures than the \(\text{La}\) case.

Terbium is a member of the lanthanide family. The structures of terbium are all close packed and have a high symmetry. At 40.2 and 155 GPa, the phase transition of terbium changes to \(\text{hR24}\) and \(C2/m\), respectively.\(^\text{57}\) The increase in pressure directly increases the electron density, which leads to the distortion of the \(\text{hR24}\) phase. Upon further compression, the 4f electrons become itinerant. Thus, low symmetry structures can also form at high pressures. This kind of transformation is first-order, which is accompanied by the discontinuous decrease in volume, the decrease in resistivity, and the hardening of lattice. The change of the f-electron behavior under pressure has a significant effect on the superconducting behavior, and f-electron delocalization induces a considerable bond shortening. These effects are observed in rare-earth metals. In addition, the insulator–metal transitions induced by f-electron delocalization are expected in rare-earth monochalcogenides.\(^\text{38}\) Due to the high-pressure behavior of terbium mentioned above, one is interested in the crystal structure, electronic characteristics, and superconducting properties of terbium hydride (\(\text{Tb–H}\)) under high pressures. Can terbium hydride produce better superconductivity than \(\text{LaH}_{10}\)? These are all fascinating and open issues. In this work, we examine the electronic structure and bonding of terbium hydride to understand the crystal chemistry of this system and to look for the possible superconductivity with higher temperatures than \(\text{LaH}_{10}\) by using first-principles calculations.

## COMPUTATIONAL DETAILS

Referring to the previous studies on similar hydrogen-rich systems, we know that the crystal structure with one to six formula units (f.u.) in each unit is frequent. Therefore, we searched for possible structures within the framework of about 200 space groups with the CALYPSO code.\(^\text{39,40}\) Due to the different positions of Wyckooff, we consider as many crystal configurations as possible for each space group. Each cell of the candidate structure of \(\text{Tb–H}\) contains one to six f.u. Then, we calculated their total energy and enthalpy at 0, 50, 100, 150, 200, 250, and 300 GPa. The relatively stable structure was selected and extended to other pressure points. All structural optimization was carried out by using the density functional theory of Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA)\(^\text{41}\) and the projector augmented wave pseudopotential\(^\text{12}\) as implemented in the Vienna ab initio simulation package (VASP).\(^\text{43,44}\) The adopted pseudopotentials of \(\text{Tb}\) and \(\text{H}\) are from files titled “PAW-PBE Tb 23Dec2003” and “PAW-PBE H 15Jun2001”, respectively. Thus, 4f\(^5\)5s\(^2\)5p\(^6\)6s\(^0\) of \(\text{Tb}\) and 1s\(^1\) of \(\text{H}\) were treated as valence electrons. \(\text{Tb–H}\) unit cells were sampled from the Brillouin zone (BZ) by the energy cutoff 600 eV plane wave basis. The \(k\)-point of the Brillouin zone was a 0.04 Å\(^{-1}\) interval distribution of Monkhorst-Pack for the optimization of structures, and the \(k\)-point interval of the total energy self-consistent calculation was 0.02 Å\(^{-1}\) or better. Convergence thresholds were set as \(10^{-5}\) eV in energy and \(10^{-3}\) eV/Å in force.

The QUANTUM ESPRESSO (QE) package\(^\text{45,46}\) was used to examine the dynamical and possible superconducting properties of these compounds. Phonon frequency and electron–phonon coupling (EPC) constant were calculated using density functional perturbation theory,\(^\text{47}\) employing the plane-wave pseudopotential method. The adopted pseudopotentials of \(\text{Tb}\) and \(\text{H}\) are from files titled “\(\text{Tb}\).pbe-spdn-kjpaw-psl.1.0.0.UPF” and “\(\text{H}\).pbe-kjpaw-psl.1.0.0.UPF”, respectively. The 4f\(^\text{2}\) electrons of \(\text{Tb}\) were treated as valence electrons similar to that in VASP. The cutoff energies were set as 80 and 600 Ry, respectively, which were used for wave function and charge density. The forces and stresses of the converged structure were optimized and controlled within the error range between VASP and QE code.

Considering that \(\text{Tb}\) is a heavy element, we have tested the spin-orbit coupling (SOC) effect on total energy of the system. In particular, the influence of SOC effect on total energy mainly reflects in the analysis of crystal stability and phase transition. So, we investigated the difference of calculation results with or without SOC correction in the cases of several structures under different pressures. As shown in Figure S1 of the Supporting Information, the SOC correction does not change the phase transition ordering though the pressure point of phase transition has a slight shift. Thus, we conclude that the SOC effect will not essentially change the stability and phase transition ordering of \(\text{TbH}_n\) under pressure because the SOC is a minor correction in the energy scale. With regard to the electronic correlation effect in \(\text{TbH}_n\), we think it is weak under high pressures. It is well known that systems may have different physical properties under high pressures. Pressure is an important physical quantity for hydrides. The 4f electrons become itinerant, and the energy bands near the Fermi level are just broadening under high pressures. Especially, the Hubbard \(U\) were calculated by using the linear response approach of Cococcioni et al.\(^\text{48}\) to estimate the strength of electronic correlations. For several typical systems, we obtained \(U = 0.74\) eV for \(\text{TbH}_{10}\) at 250 GPa, \(U = 0.96\) eV for \(\text{TbH}_4\) at 150 GPa, and \(U = 2.3\) eV for \(\text{TbH}_2\) at 25 GPa. The results indicate that the electronic correlations in \(\text{TbH}_n\) are weak at higher pressures such as above 100 GPa. Based on these two tests above, the results will be presented and discussed at the GGA functional level in this work, especially for electronic structures and possible superconductivity of \(\text{TbH}_n\) at high pressures.

## RESULTS AND DISCUSSION

### Phase Diagram

Some possible structures of the \(\text{Tb–H}\) system with different \(\text{H}\) contents have been systematically investigated by using the data package provided by CALYPSO and referring to previous studies.\(^\text{14,15,29–36}\) More than 100 configurations were selected from all the structures with different chemical coordination numbers and low energies. The formation enthalpy of terbium hydride was calculated at 0, 50, 100, 150, 200, 250, and 300 GPa. The formation enthalpy of \(\text{Tb–H}\) at different pressures with respect to \(\text{Tb + H}_2\) is shown in the convex hull diagrams of composition–pressure phase diagram (Figure 1). The energetic stability of different terbium hydrides is evaluated by its formation enthalpy. Here, we preferentially explore
terbium hydrides with higher hydrogen contents by compressing the mixture containing Tb and H. For each stoichiometry, up to six formula units are used in the model for calculation at a pressure of $0 - 300$ GPa. The basic information can be summarized as follows: (1) At low pressures ($0 - 100$ GPa), most of the composition compounds are in metastable states, while most of the structures with different stoichiometries are thermodynamically stable above $150$ GPa; (2) Notably, only TbH$_1$ is always stable in the whole pressure range of $0 - 300$ GPa, while TbH$_2$, TbH$_9$, and TbH$_{11}$ are metastable in the whole pressure range considered, which are excluded from later discussion; (3) The higher the ratio of hydrogen to terbium, the lower the formation enthalpy, and the more stable the thermodynamic performance. We will pay more attention to this part of stoichiometry in the later discussion.

Based on the composition–pressure phase diagram above, the stable phases of each TbH$_n$ ($n = 1 - 12$) system are further confirmed. Figure 2 depicts the ordering of phase transition with the increase in pressure for each TbH$_n$ in the pressure range of $0 - 300$ GPa. The phase satisfied as the composition–pressure stable relation shown in Figure 1 is defined as the thermodynamically stable phase and plotted by the solid line in Figure 2. On the contrary, the phase dissatisfied as the composition–pressure stable relation shown in Figure 1 is defined as the thermodynamically metastable phase and plotted by the dotted line in Figure 2. It is found that TbH$_1$, TbH$_2$, and TbH$_3$. TbH$_1$ always has a stable and metastable structure with the space group of Cmcm in the whole pressure range of interest. TbH$_2$ can stably exist below the pressure of $25$ GPa with the Pbcm symmetry, and then it is stabilized with the P6/mmm phase from $175$ to $275$ GPa before transforming to the C2/m phase after $275$ GPa. TbH$_3$ is almost stable in the whole pressure range except for $245 - 255$ GPa. At low pressures, TbH$_3$ stably exists in the form of Pm$m3n$ symmetry up to $245$ GPa, the space group is transformed from Pm$m3n$ to Cmcm at $245$ GPa, and the space group Cmcm is maintained until $300$ GPa. As shown in Figure 2, the stable phases of TbH$_4$, TbH$_9$, TbH$_{10}$, and TbH$_{12}$ appear at the moderate pressures above $125$ GPa. For TbH$_{12}$, there are two stable space groups in the pressure ranges of $145 - 155$ and $155 - 300$ GPa, respectively. The phase transition among stable structures in TbH$_4$ occurs at about $155$ GPa from P321 to I4/mmm. Meanwhile, the single stable phase exists in TbH$_6$ (P1$_i$, >$160$ GPa), TbH$_7$ (Im$3m$, >$145$ GPa), TbH$_8$ (C2/c, >$175$ GPa), and TbH$_9$ (P4$_{2}$/mmc, >$145$ GPa). Interestingly, TbH$_{10}$ is thermodynamically stable in a pressure range of $270 - 300$ GPa. The stable space group R3$m$ is accompanied by a metastable state with the symmetry of Fm$3$m. The enthalpy difference between R3$m$ and Fm$3$m is only $0.06$ eV/f.u. They can be considered as two degenerate states of TbH$_{10}$ at high pressures. Considering that MH$_{10}$ ($M = La, Y, Ac$, and Th) has achieved exciting results in the previous theoretical prediction and experimental research,18-20,31-33 the structure and possible superconductivity in TbH$_{10}$ are also expected in the pressure range of $200 - 350$ GPa. Noticeably, some metastable phases (marked by dotted lines) in their corresponding pressure ranges have been also shown in Figure 2 for comparison.

We now examine the above results. Because zero-point energy (ZPE) has been shown to play an important role in determining the stability of hydrogen-rich materials, we consider its effect. We have recomputed the formation enthalpies of different phases in Tb–H at $250$ GPa by including ZPE (Figure S2). As a result, the phases of Tb–H are still stable; therefore, the above conclusions are not altered by considering zero-point vibrations.

Crystal Structures. The crystal structure characteristics of the stable phases for TbH$_n$ at different pressures are shown in Figures 3 and 4. Correspondingly, their crystal unit cells are presented in Figures S3 and S4, and the crystal lattice parameters are summarized in Table S1 of the Supporting Information. It is found that H atoms have difficulty in forming hydrogen clusters in low H content terbium hydrides and at low-pressure conditions. Below $150$ GPa, the nearest distance of H–H ($d_{H-H}$) in TbH$_n$ is commonly larger than $1.6$ Å. From the calculated electron localization functions (ELFs) shown in Figure S5, the bonding interaction among H atoms appears to be largely covalent-like.
Interaction between them is greatly enhanced. At the same time, the distance between the hydrogen atom and the center atom is compressed, which means that the center atom can get more charge. As a result, the electron–phonon interaction is greatly enhanced. Hence, cage structures of the H atoms in hydrides are viewed as the signal of high-temperature superconductivity.

Figure 3. Optimized crystal structures of TbH₄ with low H contents. (a) Cmcm phase of TbH₁ at 150 GPa, (b) C2/m phase of TbH₂ at 300 GPa, (c) P6/mmm phase of TbH₂ at 200 GPa, (d) Pcmn phase of TbH₂ at 20 GPa, (e) Cmcm phase of TbH₂ at 300 GPa, (f) Pn₃m phase of TbH₁ at 200 GPa, (g) I4/mmm phase of TbH₂ at 200 GPa, (h) P321 phase of TbH₃ at 150 GPa, and (i) P1 phase of TbH₄ at 200 GPa. Big and small balls represent Tb and H atoms, respectively.

Figure 4. Cage-like feature in optimized crystal structures of TbHₓ with high H contents. (a) Im3m phase of TbH₁ at 300 GPa, (b) C2/c phase of TbH₂ at 300 GPa, (c) Pn₃m phase of TbH₁₀ at 300 GPa, (d) R3m phase of TbH₁₀ at 300 GPa, and (e) P42/nmc phase of TbH₁₁ at 300 GPa. Big and small balls represent Tb and H atoms, respectively.

Figure 5. Variation of the nearest H–H distance (d_{H–H}) in cage-like structures of TbHₓ with pressure, comparing with those of CaH₆, MgH₆, YH₁₀, ScH₆, LaH₁₀, TbH₁₀, TbH₁₂, and AcH₁₂. The bar implies the distribution of the d_{H–H} values in the cage configuration.
increasing pressure. Moreover, Pl1 symmetrical TbH6 (Figure 3i) shows a distorted H3m cage configuration at high pressures of 160 – 300 GPa. Differing from I4/mmm-TbH6, the H3m cage in Pl1-TbH6 is made up of six quadrilaterals, two pentagons, and five hexagons. The di-H value varies in the range of 1.27 – 1.51 Å for the pressure of 200 GPa, and the average value of di-H decreases with increasing pressure.

With the cage characteristics, H atoms exhibit visibly bonding interactions as shown in Figures S5g and S5i. However, as shown in Figure S5, the di-H value in the H cage structure of TbH3 is comparatively larger than those of other rare-earth hydrides at the same pressure.

As mentioned above, the cage feature of H atoms was also observed in TbH6 with high H contents (Figure 4), such as TbH6-3, TbH10 and TbH12 at high pressures. As shown in Figure 4a, the sodalite cage structure in Im3m-TbH6 is similar to that in CaH614, MgH615, YH616 and ScH6.51 The H24 cage structure can stably exist in the pressure range of 145 – 300 GPa, composed of six quadrilaterals and eight hexagons. The H6 cage configuration can be also viewed as a result of the interconnection of each H atom on the corner of a quadrilateral with other quadrilaterals, showing the visibly bonding interactions as shown in Figure S6a. Also, two H24 cages connect by sharing a quadrilateral in the periodically repeated direction. The di-H value in the H24 cage of Im3m-TbH6 is respectively 1.28, 1.25, 1.22, and 1.20 Å at pressures of 150, 200, 250, and 300 GPa, which is correspondingly larger than 1.24 Å in CaH6 at 150 GPa14 and 1.15 Å in ScH6 at 250 GPa51 and larger than 1.1 Å in MgH6 at 300 GPa.15 The di-H value in Im3m-TbH6 is 2.02 Å at 150 GPa, and then it decreases to 1.90 Å at 300 GPa, which is obviously larger than the di-H value of 1.7 Å in ScH6 at 200 GPa.

For TbH6, the cage structure of the H29 cluster can be formed in the C2/c phase and is stable in the pressure range of 175 – 300 GPa. As shown in Figure 4b, H29 is composed of five quadrilaterals, six pentagons, and six hexagons. Differing from H24 cages in TbH6, two adjacent H29 cages in TbH6 share a hexagon. In the H29 cage of C2/c-TbH6 as shown in Figure 5, the di-H value varies in a wide range, such as from 1.03 to 1.31 Å at 300 GPa, which implies the difference between H24 and H29 cages. Taking a pressure of 150 GPa, for example, the di-H value of 1.1 – 1.4 Å in C2/c-TbH6 is larger than 1.1 Å in P63/mmc-CeH6.29 The di-H value also decreases from 1.93 Å at 200 GPa to 1.80 Å at 300 GPa. It is noted that the average value of di-H decreases from H18 (TbH18) to H29 (TbH29), through H32 (TbH32) and then to H29 (TbH29) as shown in Figure 5.

As shown in Figures 44d and , at high pressures above 270 GPa, both stable R3m and metastable Im3m phases of TbH10 have the similar cage structure of H32, which is composed of 10 hexagons and six quadrilaterals. In the periodical lattice, two adjacent H13 cages share a hexagon. At 300 GPa, the di-H value in the H13 cage of the R3m phase varies in a small range of 1.04 – 1.14 Å. Similarly, the di-H value in the H12 cage of the Im3m phase is in the almost same range of 1.03 – 1.12 Å at 300 GPa, exhibiting strongly bonding characteristics as shown in Figure S6b. Also, it was found that the length of the H–H bond shared by two adjacent hexagons is less than that shared by two adjacent quadrilaterals. In R3m-TbH10g, the di-H value is about 1.95 Å at 300 GPa, which is larger than 1.80 Å of C2/c-TbH4 and 1.90 Å of Im3m-TbH6 at the same pressure.

For TbH12 with a higher H content, the P42/nmc phase is stable at high pressures above 145 GPa and forms a complicated cage-like structure composed of the H24 cage as shown in Figure 4e. Five H24 cages share a pentagon. Each H24 cage contains 12 quadrilaterals and four heptagons, without a hexagon or pentagon. However, the values of di-H in P42/nmc-TbH12 possess a wide distribution range at every pressure. In the case of 300 GPa, the di-H value covers the range from 0.92 to 1.47 Å. At 300 GPa, the di-H value in P42/nmc-TbH12 is about 1.92 Å, which is slightly smaller than 1.95 Å of R3m-TbH10. Especially, this kind of coupling among H24 cages and the smaller distance of di-H read to the better stability in TbH10, so it can exit at lower pressures than TbH10.

The higher the hydrogen content, the easier the formation of the cage structure of H atoms, and the larger the cage size. Moreover, examining the di-H value of TbH6 shown in Figure S4, we find that the nearest distance of H–H in TbH6, TbH6, and TbH10 has a smaller oscillation than that of TbH6, TbH6, and TbH12. This is possibly due to the presence of pentagons (or heptagons) unit or the existence of more than two kinds of hydrogen units in TbH6, TbH6, and TbH12. For example, there are only quadrilaterals and hexagons in TbH6, TbH6, and TbH10. However, by comparison, the di-H value in terbium hydrides with the H cage structure is larger than those of other rare-earth hydrides and metal hydrides containing the H cage structure in general. In addition, the di-H value is often smaller than 2 Å at high pressures above 150 GPa.

Metallization and Electronic Characteristics. As a traditional superconductor, metallization is a necessary condition to superconduct. Before estimating whether terbium hydride is a superconductor, we have investigated the electronic structures of TbH6 (n = 1 – 12). The electronic total density of states (DOS) and band structures were calculated and are presented in Figures S7–S24. It is found that the thermodynamically stable TbH6 exhibits the metallic behavior in electronic characteristics and energy band structures in the corresponding stable pressure range, even at ambient pressure for TbH1 and TbH2 with low stoichiometric ratios of H. Considering that GGA usually underestimates the energy band gap, we also check the electronic structures with the more accurate hybrid functional method (HSE06)16 in the case of TbH10 shown in Figure S25. Comparing Figure S21 and Figure S25, the result shows that no obvious change occurs in DOSs of TbH10 within the framework of HSE06, especially for the DOS value at the Fermi level. This indicates that the metallization based on the GGA level is reliable. Two or more energy bands cross the Fermi level in each stable phase of terbium hydride, forming the complicated Fermi surface morphology composed of electron-like and hole-like sheets. To investigate the fine characteristics of electronic states, we have presented the total DOS and the projected density of states (PDOS) on atoms and orbitals of several typical cases including different pressures and different stoichiometries in Figure 6. It is found that the state feature of Tb-4f is very prominent. The electronic states near the Fermi level are mainly from Tb-4f, while the electronic states near the Fermi level are comparable with metals in the order of magnitude. Thus, the complicated Fermi surface of TbH6 is just induced by the
polymorphic Tb-4f orbital. Of course, slightly away from the Fermi level, the contribution of H to total electronic states is comparable with Tb, as shown in Figure 6.

Furthermore, Figure 6 indicates that the local characteristics of 4f electrons is obvious in TbH, with low H stoichiometries under low pressures, but 4f electronic states are delocalized under high pressures, which further indicates that the electronic correlation effect in TbH is strong at low pressures while it is weak at high pressures. The broadening of the 4f electronic states with increasing pressure shown in Figure 6 results from the enhancement of hybridization interaction between s and f electrons in TbH upon compression. From the crystal structure shown in Figure S26, the coordination of Tb in TbH is increased with the increase in pressure and components. The charge transfer reduces from 1.3e in TbH2 at 25 GPa to 0.8e in TbH10 at 310 GPa. The Tb–H bond length shortens from 2.19 Å in TbH2 at 25 GPa to 1.93 Å in TbH10 at 310 GPa. From the calculated ELFs at different pressures shown in Figure S27, the hybridization interaction between Tb and H also been shown to be enhanced with the increase in pressure. These are reasons that the electron correlation of TbH decreases under pressure. In a word, pressure is an important physical quantity for hydrides. For the high-pressure phases of TbH, the 4f electron correlations are relatively weak. So, for the following discussion of superconductivity, we will focus on the high-pressure phase of TbH.

**Dynamical Properties and Superconductivity.** For thermodynamically stable Tb–H phases, the calculated phonon spectra shown in Figures S28–S39 also confirm their dynamical stability because there is no imaginary frequency. Then, based on the obtained phonon frequency, we tried to analyze the possible superconductivity for high phases (≥100 GPa) of the Tb–H system by calculating the EPC constant ($\lambda$), the logarithmic average of phonon frequency ($\omega_{\log}$), and the $T_c$. In this work, the $\lambda$ is defined by integration over the entire frequency domain of the Eliashberg electron–phonon spectral function $[\alpha^2 F(\omega)]$, where $\omega$ represents the phonon frequency, expressed as

$$\lambda = 2 \int_0^{\omega} \frac{\alpha^2 F(\omega)}{\omega} d\omega$$

(1)

The $\omega_{\log}$ is written as

$$\omega_{\log} = \exp \left[ \frac{2}{\lambda} \int_0^{\infty} \frac{\alpha^2 F(\omega) \log(\omega)}{\omega} d\omega \right]$$

(2)

The $T_c$ is presented by the Allen–Dynes-corrected McMillan equation

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

(3)

Here, $\mu^*$ in eq 3 is the Coulomb pseudopotential representing the Coulomb repulsion. The typical value of $\mu^*$ is in the range of 0.1 – 0.13 for hydrides. The factor $\omega_{\log}$ is decided by the $\lambda$, $\mu^*$, $\omega_{\log}$ and mean square frequency ($\omega$)

Table 1 summarizes the calculated superconducting parameters of stable TbH, in the form of different phases at high pressures.

From the results listed in Table 1, we can claim that terbium hydride is superconducting under high pressures. In general, the electron–phonon interaction and $T_c$ obviously depend on the H content in TbH. Weak or moderate strength EPCs were obtained in TbH, with low H contents, while a strong EPC of $\lambda > 1.5$ could be driven in TbH, with high H contents such as $n \geq 6$. At the same time, $T_c$ decreases with the increase in H content and reaches the highest value in TbH10 and then it has a slight drop in TbH12. For every TbH, the relation between $T_c$ and pressure is not monotonous. Especially, the graphenelike layer structures formed by H atoms in TbH with C2/m and P6/mmm phases did not have the high $T_c$ values similar to HHH13. However, the cage structure of H atoms obviously leads to higher superconducting critical temperatures, which is consistent with perspectives of Zurek et al.55 In the moderate pressure range of 100 – 200 GPa, the electron–phonon interaction is considerable such as $\lambda = 0.57$ for P6/mmm-TbH12 at 150 GPa, $\lambda = 0.84$ for Pm3m-TbH12 at 150 GPa, $\lambda = 0.72$ for P321-TbH12 at 150 GPa, and $\lambda = 1.95$ for P42/m-nmc-TbH12 at 150 GPa. As a result, the $T_c$ can highly reach to 170.5 K in P42/m-nmc-TbH12 at 150 GPa, indicating that terbium hydride is a promising high-temperature superconducting material. In the higher pressure region above 200 GPa, with help of the stronger EPC of $\lambda > 1.5$, the superconductivity with a $T_c$ beyond 270 K can be achieved in TbH, with Fm3m and R3m symmetries at 250 and 310 GPa, respectively. This $T_c$ value in TbH is caught up with that in LaH close to room temperature. Significantly, this is the highest value ever reported in rare-earth metal hydrides containing f electrons.

Focusing on terbium hydride containing the H cage, as shown in Table 1, we found that the maximum $T_c$ is proportional to the number of atoms in the H cage. The H18 cage in I/mmm-TbH14 can produce $T_c \approx 41.3$ K at 200 GPa, and the H32 cage in P1-TbH2 can push $T_c$ to 79.3 K at 200 GPa; furthermore, the H24 cage in Im3m-TbH10 drives a higher $T_c \approx 148.3$ K at 200 GPa, while H29 and H32 cages in TbH9 and TbH10 respectively create superconductivity with a $T_c$ far beyond 200 K. TbH12 is a special case in which H atoms form three interconnected H24 cages so that the $T_c$ of TbH12 is similar to that of TbH at the same pressure. On one hand, as shown in Figure S5, the nearest $d_{H-H}$ slightly decreases with increasing size of the cage, yielding the highest phonon

**Figure 6.** Calculated DOS and PDOS of terbium hydride. Zero energy denotes the Fermi level. (a) Pm3m-TbH4 at 25 GPa, (b) Im3m-TbH6 at 150 GPa, and (c) R3m-TbH10 at 310 GPa.
frequency induced by H–H vibrations shift in a high level. However, on the other hand, as shown in Figures 3 and 4, from TbH$_4$ to TbH$_{10}$, the increase in number of atoms in H cages increases the size of cages. This leads to the decrease in distance among H atoms so that the phonon vibrations among H atoms become weak. This means that, at the same pressure, the phonon dispersion will spread toward the low-frequency side. As a result, the moderate phonon frequencies become softer with increasing number of atoms in H cages. From the EPC integral $\lambda(\omega)$, the soft modes of phonon mainly contribute to the EPC. Hence, the H cage structure results in the stronger EPC and higher $T_s$ value in terbium hydride, and the $T_s$ will be higher with the increase in the number of atoms in the H cage.

The highest $T_s$ value of terbium hydride was predicted in TbH$_{10}$. As mentioned above, TbH$_{10}$ stably exists in two forms of R3m and Fm3m phases at the pressure of $\geq$270 GPa. R3m and Fm3m phases can be viewed as degenerate states of TbH$_{10}$ in energy. Interestingly, the Fm3m phase is dynamically stable in the relatively low-pressure range of 210 – 270 GPa, though its thermodynamical stability is a little worse in this pressure range. Therefore, the investigation of superconductivity of TbH$_{10}$ has been extended to a larger pressure range. As shown in Table 1, in the pressure range of 270 – 350 GPa, the R3m phase exhibits the superconductivity with $T_s > 200$ K. So, the Fm3m phase does in the pressure range of 210 – 350 GPa. For both R3m and Fm3m phases, the change of $T_s$ with pressure displays a maximum value, namely, 270.9 K at 310 GPa for the R3m phase and 277.8 K at 250 GPa for the Fm3m phase. For this best superconductivity, the $\lambda$ value reaches to 2.13 for R3m and 2.50 for the Fm3m phase, and the $\omega_{bg}$ value is about 1395.6 K for R3m and 1225.1 K for the Fm3m phase, respectively, meaning that a very strong EPC is formed in TbH$_{10}$.

Figure 7. Calculated phonon spectra, phonon density of states (PhDOS), Eliashberg spectral function $\alpha^2F(\omega)$, and EPC integral $\lambda(\omega)$ of R3m and Fm3m phases at pressures of 310 and 250 GPa, respectively. For the R3m phase at 310 GPa, the phonon bands (Figures 7b and c) are visibly divided into two parts of 0 – 250 and 520 – 2578 cm$^{-1}$. The low-frequency region is completely from the Tb vibrations, while the high phonon frequencies above 520 cm$^{-1}$ are mainly contributed by H vibrations. From the Eliashberg spectral function shown in Figure 7c, we can find that the contribution of Tb to total EPC is only 11%, while the H cage contributes about 89% to the total EPC. In terbium hydride, the Tb element mainly provides charge to H atoms, which is the main reason for metallization. Combining the absence of electronic states of H atoms at the Fermi level as shown in Figure 6, we...
can identify that the contribution of Tb is to the electron aspect while the contribution of H is to the phonon aspect during the EPC process. Namely, the superconductivity of terbium hydride can be viewed as the motion of Tb-4f electrons in the lattice field formed by H atoms. The phonon structures and the EPC of the \( \text{Fm}3\text{m} \) phase at 250 GPa shown in Figure 8 are similar to those of the \( \text{R}3\text{m} \) phase at 310 GPa. The \( \text{H} \) cage also contributes about 89% to the total EPC.

Remarkably, when the pressure drops to 230 GPa, the \( T_c \) of the \( \text{Fm}3\text{m} \) phase is still around 270 K. From Table 1, the superconductivity with a \( T_c \) above 250 K covers a wide pressure range, such as from 230 to 350 GPa for the \( \text{Fm}3\text{m} \) phase and from 290 to 350 GPa for the \( \text{R}3\text{m} \) phase. In addition, TbH\(_4\) also exhibits the high-temperature superconductivity of above 200 K in the pressure range of 230 – 300 GPa. Moreover, both TbH\(_{12}\) and TbH\(_6\) have the superconductivity with a \( T_c \) beyond 100 K in a wide pressure range as shown in Table 1. These results show that the high-temperature superconductivity of terbium hydride is very solid and interesting. Reviewing the superconductivity of terbium hydride, we find that the highest \( T_c \) value is almost equal to 274 K of LaH\(_{10}\) at 250 GPa, though it is less than 326 K of YH\(_{10}\). Especially, in rare-earth metal hydrides containing \( f \) electrons, the \( T_c \) is 278 K in TbH\(_{10}\), 274 K of LaH\(_{10}\) at 250 GPa, though it is less than 326 K of YH\(_{10}\). The phonon dispersion broadens and more and more softening modes are formed. Thus, the \( T_c \) increases with increasing the \( \text{H} \) content in TbH\(_n\), especially with the increase in the \( \text{H} \) cage size. \( 1\text{H}/\text{mmm}-\text{TbH}_6 \) exhibits the superconductivity with \( T_c \approx 40 \) K at 200 GPa. \( \text{P}3\text{m}1\)-TbH\(_6\) has \( T_c \approx 80 \) K at 200 GPa. Meanwhile, in \( 3\text{m}3\text{m}\)-TbH\(_{12}\), the \( T_c \) was predicted as \( \sim 150 \) K at 200 GPa. Furthermore, the \( T_c \) around 220 K was presented in \( \text{C}2/\text{c}\)-TbH\(_4\) in the pressure range of 230 – 300 GPa. Excitedly, TbH\(_{10}\) with \( \text{R}3\text{m} \) and \( \text{Fm}3\text{m} \) symmetries both possess the near room-temperature superconductivity of \( T_c \approx 270 \) K, respectively, above 270 and 230 GPa. TbH\(_{12}\) exhibits the similar superconductivity to TbH\(_6\) at the same pressure. The superconductivity of terbium hydride is suggested to be due to the motion of Tb-4f electrons in the lattice field formed by H atoms.

Finally, this study indicates that the superconductivity close to or beyond lanthanum hydride can be achieved in rare-earth metal hydrides TbH\(_n\).

**CONCLUSIONS**

In summary, we have systematically studied the crystal structures, thermodinamical stability, electronic states, dynamical properties, and electron–phonon interactions of binary terbium hydride TbH\(_n\) \((n = 1 – 12)\). The results successfully revealed the structure and superconductivity of the binary terbium hydride under pressure. We predicted the highest \( T_c \approx 278 \) K in terbium hydride. Our findings can be summarized as follows:

1. All of TbH\(_2\), TbH\(_6\), and TbH\(_{10}\) are unable to be stable in our considered pressure range. Three stoichiometric compounds of TbH\(_2\), TbH\(_9\), and TbH\(_{12}\) with low H contents have both high-pressure and low-pressure stable phases, while terbium hydride of other chemical proportions is only stable at high pressures above 150 GPa. Interestingly, the cage configuration was observed in high phases of TbH\(_9\), TbH\(_{10}\), TbH\(_{12}\), TbH\(_{16}\), and TbH\(_{18}\), in which the cage size increases with the increase in H content in TbH\(_n\).

2. TbH\(_n\) exhibits the metallic characteristics under pressure, and the metallization comes from the double effects of charge transfer and pressure. Tb-4f electrons mainly contribute to the states at the Fermi level.

3. The thermodynamically stable TbH\(_2\) is almost dynamically stable. The phonon bands of TbH\(_n\) are obviously divided into two parts, with Tb phonon modes in the low-frequency region and H phonon modes in the high-frequency region. With the increase in H cage size, the phonon dispersion broadens and more and more softening modes are formed. Thus, the \( T_c \) increases with increasing the \( \text{H} \) content in TbH\(_n\), especially with the increase in the \( \text{H} \) cage size. \( 1\text{H}/\text{mmm}-\text{TbH}_6 \) exhibits the superconductivity with \( T_c \approx 40 \) K at 200 GPa. \( \text{P}3\text{m}1\)-TbH\(_6\) has \( T_c \approx 80 \) K at 200 GPa. Meanwhile, in \( 3\text{m}3\text{m}\)-TbH\(_{12}\), the \( T_c \) was predicted as \( \sim 150 \) K at 200 GPa. Furthermore, the \( T_c \) around 220 K was presented in \( \text{C}2/\text{c}\)-TbH\(_4\) in the pressure range of 230 – 300 GPa. Excitedly, TbH\(_{10}\) with \( \text{R}3\text{m} \) and \( \text{Fm}3\text{m} \) symmetries both possess the near room-temperature superconductivity of \( T_c \approx 270 \) K, respectively, above 270 and 230 GPa. TbH\(_{12}\) exhibits the similar superconductivity to TbH\(_6\) at the same pressure. The superconductivity of terbium hydride is suggested to be due to the motion of Tb-4f electrons in the lattice field formed by H atoms.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c00645.

The crystal structures of TbH\(_n\), the crystal lattice parameters of TbH\(_n\), the electronic structures of TbH\(_n\), the zero-point energy effect, the phonon spectra, and superconducting parameters of TbH\(_n\) (PDF).

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Notes

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