High-temperature superconductivity in clathrate thorium-doped hexahydrides $A_{1-x}Th_xH_6$ (A = La, Ac, and Y) at moderate pressure

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The discovery of high-temperature superconductivity in hydrides provides a promising route to achieve the goal of room-temperature superconductivity, but the ultrahigh pressure required to be synthesized severely limits their application. The next challenge is to find novel hydrides with high T_c at low pressure, even ambient pressure. Here, we propose a strategy that elements with little electronegativity, large atomic volume, and suitable valence electron number can be regarded as a candidate for reducing the stable pressure by summarizing the superconducting rules of the clathrate hexahydrides, and find that thorium is a good "precompressor." Based on the above strategy, we doped thorium into clathrate hexahydrides with a H_{24} cage, and designed a series of hydrides. They could be dynamically stable at moderate pressure, which is much lower than that of the well-known hexahydrides CaH_6. Remarkably, $LaTh_3H_{24}$, $AcTh_3H_{24}$, and $YThH_{12}$ exhibit excellent superconductivity with high T_c of 198 K at 50 GPa, 201 K at 60 GPa, and 208 K at 60 GPa, respectively. This work suggests that thorium doping is an effective method for finding hydrides with high T_c at moderate pressure, and successfully helps us design a series of interesting high-temperature superconducting hydrides.

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I. INTRODUCTION

Since Onnes discovered the superconductivity of 4.2 K in mercury [1], finding superconductors with higher critical temperatures (T_c) had been one of the most attractive researches in condensed matter physics and materials science. According to the Bardeen-Cooper-Schrieffer theory [2], metallic hydrogen is expected to be a potential room-temperature superconductor due to its high Debye temperature and strong electron-phonon coupling (EPC). However, ultrahigh pressure (above 500 GPa) is required to obtain solid metallic hydrogen [3–5], which posed a huge challenge to experiments. In the face of tremendous difficulties in synthesizing metallic hydrogen, Ashcroft suggested in 1983 that the introduction of impurities could lower the energy of the metallic phase and reduce the external pressure [6], and then proposed in 2004 that hydrogen-rich compounds might exhibit high-temperature superconductivity at lower pressure than hydrogen by the chemical "precompression" of other elements [7]. Based on this principle, a series of superconducting hydrides were discovered, through high pressure synthesis following theoretical predictions. Remarkably, the theory-led prediction of H_3S [8–11] and LaH_{10} [12–16] with high T_c above 200 K has been confirmed by experiments, reigniting the century-old dream of room temperature superconductivity.

With further research, a large number of hydrides with high T_c were found under high pressure. According to the arrangement of hydrogen atoms, hydrides were divided into three categories [17]: covalent hydrides [8,18], clathrate hydrides [12], and layered hydrides [19]. Among them, clathrate hydrides are the most abundant and closely associated with high-temperature superconductivity. For example, CaH_6 [20–22] with a H_{24} cage, YH_9 [12,23] with a H_{29} cage, and LaH_{10} [12,15] with a H_{32} cage were predicted with high T_c above 200 K and have been synthesized experimentally. The clathrate hexahydride CaH_6 with symmetry of Im-$3m$ was predicted with a high T_c of 235 K at 150 GPa [22], which has a body-centered-cubic structure with hydrogen that forms an unusual sodalite cage. Subsequently, a series of XH_6 (X = Mg, Sc, Y, Hf, La, Tm, Yb, and Lu) [12,24–31] was successively predicted with excellent superconductivity. The stable pressure of the above-mentioned hydrides is much lower than that of metallic hydrogen, but it still remains too high. Therefore, the next challenge is the pursuit of high-temperature superconductivity in hydrides under relatively mild pressure conditions.

It has been found that doping elements or molecules into binary hydrides is an effective way to reduce the stable pressure. Following the theoretical predictions of "fluorite-type" hydride $LaBeH_8$ at moderate pressure [32], a high T_c of 110 K at 80 GPa was documented experimentally [33] and it is suggested that ternary systems provide more structural prototypes for exploring better superconductivity. Moreover, great progress has been made in ternary hydrides experimentally, such as binary alloy hydrides $(La, Y)H_4$, $(La,Ce)H_9$, and $(La,Y)H_{10}$ [34–37]. For example, Semenok *et al.* synthesized decahydrides $(La,Y)H_{10}$ and hexahydride $(La,Y)H_6$ with a maximum T_c of 253 K [36], which can be considered

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as solid solutions of YH_{10} and LaH_6 in Fm-$3m$-LaH_{10} and Im-$3m$-YH_6, respectively. It is suggested that some ternary hydrides which were designed by substituting metal atoms and adjusting their stoichiometric ratio may host better superconductivity than their parent phases, such as (La,Y)H_6, (Y,Ca)H_6, and (Y,Lu)H_6 [36,38–46].

For further reducing the stable pressure, all of the clathrate hexahydrides are summarized. It is found that the electronegativity (χ) and volume (V) of metal atoms have a linear relationship with minimum stable pressure (P_m) and a different variable Φ_P is proposed for exploring a better "compressor." In this work, we propose a strategy for reducing the stable pressure of clathrate hydrides and identify a better compressor—thorium. Therefore, we introduced the thorium element into the clathrate hexahydrides and designed a series of ternary hydrides (A, Th)H_6 (A = La, Ac, and Y) by using the first-principles method. It is found that the $LaTh_3H_{24}$ with a space group of $P4/mmm$ is predicted to be dynamically stable down to 50 GPa with a high T_c of 198 K, whose stable pressure is much lower than that of the well-known hydrides with the H_{24} cage. In addition, the T_c of $P4/mmm$-$AcTh_3H_{24}$, P-$3m1$-YTh_2H_{18}, Fd-$3m$-$YThH_{12}$, and P-$3m1$-$LaTh_2H_{18}$ are 201 K at 60 GPa, 199 K at 60 GPa, 208 K at 60 GPa, and 199 K at 70 GPa, respectively, which also host excellent superconductivity at moderate pressure. These ternary hydrides with high T_c about 200 K at moderate pressure successfully conform our predictions—thorium doping is an effective method for designing high-temperature superconducting hydrides at moderate pressure. This work not only found some interesting hydrides with high T_c at moderate pressure, but also paves the way to explore high-temperature superconducting hydrides at lower pressure.

II. COMPUTATIONAL DETAILS

We performed the structure searches of $A_{1-x}Th_xH_6$ (A = La, Ac, and Y, $x = 0.25$, 0.33, 0.5, 0.67, and 0.75) with 1–2 formula units at 150 GPa using AIRSS (*Ab initio* random structure searching) code [47] and predicted more than 10 000 structures. The predicted candidate structures were reoptimized by the on-the-fly generation of ultrasoft pseudopotentials in Cambridge Sequential Total Energy Package (CASTEP) code [48]. For making the enthalpy calculations accurately converge to less than 1 meV/atom, the Brillouin zone was sampled with a k-point mesh of $2\pi \times 0.03$ Å^{-1}, and the cutoff energy was set to 800 eV.

The VASP (Vienna *ab initio* simulation packages) code [49] was used to optimize crystal structures and calculate electronic properties. The exchange correlation functional was treated through the Perdew-Burke-Ernzerhof generalized gradient approximation [50] and the cutoff energy was set to 1000 eV. The Monkhorst-Pack k-point meshes with grid spacing of $2\pi \times 0.03$ Å^{-1} and $2\pi \times 0.02$ Å^{-1} were used for high-accuracy structural relaxations and electronic properties calculations with the PAW potentials [51], respectively.

Then Quantum ESPRESSO code [52] was used to calculate the electron-phonon coupling (EPC) and superconductivity. The PAW pseudopotential was selected with a kinetic energy cutoff of 80 Ry. The first Brillouin zone was sampled using $4 \times 4 \times 4$ q-point meshes and $12 \times 12 \times 12$ k-point meshes for ATh_3H_{24}, A_3ThH_{24}, ATh_2H_{18}, and A_2ThH_{18}. Denser $6 \times 6 \times 6$ q-point meshes and $18 \times 18 \times 18$ k-point meshes were used for $AThH_{12}$ and XH_6 (X = La, Y, Ac, and Th). The Coulomb pseudopotential μ^* was set to 0.10–0.13. Considering that the EPC parameters λ are greater than 1.5, their T_c were calculated with the Allen-Dynes modified McMillan equation [53] and Eliashberg equation [54,55].

III. RESULTS

For exploring the way to find hydrides with high T_c at relative low pressure, we summarized the known clathrate hexahydrides, including binary XH_6 and ternary (X,Y)H_6, which always have high T_c and can stable at lower pressure than other clathrate hydrides, such as YH_9 and LaH_{10}. We collected their electronegativity (χ) and volume (V) of metal atoms, and recalculated their minimum stable pressure (P_m) using uniform calculation accuracy. It can be found that χ and V have an obvious linear relationship with the P_m, as shown in Figs. 1(a) and 1(b). Therefore, it is suggested that metal atoms with smaller electronegativity and larger volume could significantly reduce the stable pressure of clathrate hexahydrides from 300 to 100 GPa. Aiming to provide more accurate guidance, we proposed a variable Φ_P, which is defined as the product of χ and reciprocal of V. The fitting result is shown as the red line in Fig. 1(c). The mean absolute error (MAE) of 12.9 GPa suggests that there is a strong linear correlation between the variable Φ_P and P_m, and Φ_P can be used to predict the P_m of clathrate hexahydrides. Meanwhile, the number of valence electrons is also an important factor for the stability and the best range of valence electron number is 2–4. Based on the foregoing analysis, a "precompress" element with less electronegativity, larger atomic volume, and suitable valence electron number of 2–4 should be selected to dope into the clathrate hexahydrides for reducing the stable pressure. Thus, thorium with little electronegativity of 1.3, large atomic volume 24.4 Å^3, suitable valence electron number of 4, and an excellent Φ_P of 0.05 is considered a better "precompressor," superior to other elements, and doping it into the parent phase can reduce the stable pressure.

Next, we performed structure searches for hexahydrides (La, Th)H_6, (Ac,Th)H_6, and (Y,Th)H_6 at 150 GPa and obtained seven structures (see Fig. 2), including Pm-$3m$-$AThH_{12}$, $Cmmm$-$AThH_{12}$, Fd-$3m$-$AThH_{12}$, P-$3m1$-ATh_2H_{18}, P-$3m1$-A_2ThH_{18}, $P4/mmm$-ATh_3H_{24} and $P4/mmm$-A_3ThH_{24} (A = La, Ac, and Y). To determine the thermodynamic stability of these phases, we constructed the convex hulls of La-Th-H, Ac-Th-H, and Y-Th-H ternary systems at 150 GPa (see Figs. S1–S3 of the Supplemental Material (SM) [56]). However, all of the clathrate hexahydrides in our study are metastable phases at 150 GPa. It is found that (La, Th)H_6 are close to the convex hull, and the lowest enthalpies for La_3ThH_{24}, La_2ThH_{18}, $LaThH_{12}$, $LaTh_2H_{18}$ and $LaTh_3H_{24}$, are 7, 9, 12, 13, and 17 meV/atom above the convex hull, respectively. In addition, (Ac,Th)H_6 and (Y,Th)H_6 are less than 40 and 50 meV/atom from the convex hull at 150 GPa, respectively. It does not preclude experimental synthesis of these metastable materials. According to the

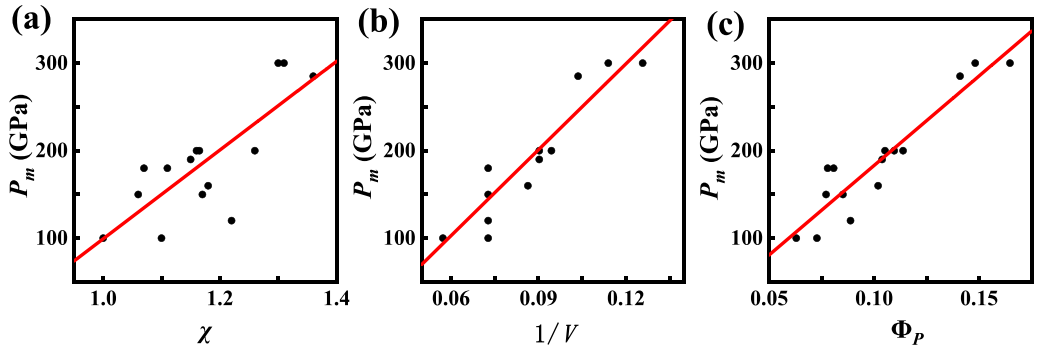

FIG. 1. Variation of the minimum pressure P_m for dynamical stability with the weighted average (a) electronegativity (χ), (b) atomic volume of metal atoms (V), and (c) variable (Φ_P) in clathrate hexahydrides. Black circles correspond to theoretical predictions and red line represents the linear fitting for those data.

inorganic crystal structure database, 20% of materials which have been experimentally synthesized are metastable, and some of them have high positive formation enthalpies even larger than 40 meV/atom [57,58]. Meanwhile, some metastable hydrides were also synthesized experimentally, such as La_4H_{23} and BaH_{12} [29,59].

Then we calculated the T_c and minimum dynamically stable pressure of ternary clathrate hexahydrides, including (La, Th)H_6, (Ac,Th)H_6, and (Y,Th)H_6, as shown in Fig. 3 and Table S1 of the SM [56]. We also recalculated the T_c of binary hydrides LaH_6, YH_6, and ThH_6 in the same way. The results show that the T_c of YH_6 using the Eliashberg equation is in good agreement with the experimental measurements of 224 K at 166 GPa [60,61]. Interestingly, Im-3m-ThH_6 has a high T_c of 159 K at 50 GPa. Such a low pressure is unprecedented in binary clathrate hexahydrides and its T_c is much higher than the boiling point of nitrogen.

Compared with LaH_6, the superconducting properties of (La, Th)H_6 are further improved after incorporation of Th and their T_c improves from 174 to ∼200 K. As shown in Fig. 3(a), with increasing content of thorium, there is a significant decrease in minimum dynamically stable pressure while their T_c also exhibits an apparent decreasing trend. Pm-3m-$LaThH_{12}$ exhibits the highest T_c of 231 K at 100 GPa, followed by $LaTh_2H_{18}$ and $LaTh_3H_{24}$ with a T_c of 199 K at 70 GPa and 198 K at 50 GPa, respectively. Notably, $LaTh_3H_{24}$ can be dynamically stable down to 50 GPa while retaining high-temperature superconductivity. $LaThH_{12}$ and $LaTh_2H_{18}$ also exhibit high-temperature superconductivity at moderate pressure below 100 GPa. La_2ThH_{18} and La_3ThH_{24} cannot be dynamically stable in our studied pressure range. For (La, Th)H_6, it can be found that the content of Th has a great effect on superconducting properties and the doping of Th plays an important role in reducing the dynamically stable pressure.

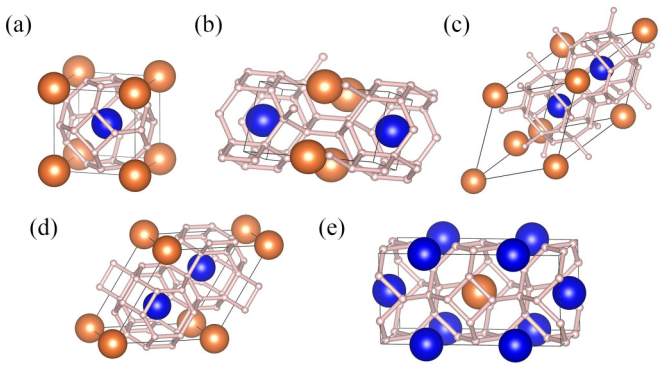

FIG. 2. Crystal structures of (a) Pm-3m-$ATh H_{12}$, (b) $Cmmm$-$ATh H_{12}$, (c) Fd-3m-$ATh H_{12}$, (d) $P-3m1$-ATh_2H_{18}, and (e) $P4/mmm$-ATh_3H_{24}. The orange and blue balls represent precompressor metal atoms A (A = La, Ac, and Y) and Th, respectively. The small pink balls represent H atoms.

For the binary hydride Im-3m-AcH_6, it is dynamically unstable within the pressure range 50–300 GPa, so it is unable to obtain its T_c value. But doping Th can make (Ac,Th)H_6 dynamically stable at moderate pressure, as shown in Fig. 3(b). Note that Pm-3m-$AcThH_{12}$ can be dynamically stable at 110 GPa with a T_c of 243 K, $AcTh_2H_{18}$ can be dynamically stable at 90 GPa with a T_c of 203 K, and $AcTh_3H_{24}$ can be dynamically stable at 60 GPa with a T_c of 201 K. As the proportion of Th increases, the dynamically stable pressure gradually decreases from 110 to 60 GPa. The other way around, a small amount of actinium doping can effectively improve the superconducting properties of ThH_6.

Different from the LaH_6 and ThH_6 with T_c below 200 K, YH_6 was predicted to have a high T_c of 264 K at 120 GPa, so we expect to reduce its stable pressure and retain its high T_c by doping Th. When the content of Y is higher than that of Th, the doping of Th cannot exhibit its advantages in reducing dynamically stable pressure. Y_3ThH_{24} and YTh_3H_{24} are dynamically unstable within the pressure range 50–300 GPa. Y_2ThH_{18} hosts a T_c of 211 K at 150 GPa. With further doping of Th, the dynamically stable pressure of (Y,Th)H_6 begins to decrease rapidly. Fd-3m-$YThH_{12}$ and YTh_2H_{18} are dynamically stable down to 60 GPa with high T_c of 208 and 199 K, respectively. It is suggested that appropriate doping of Th can effectively reduce the stable pressure of YH_6.

With further study of superconducting hydrides, more and more hydrides were predicted to host high T_c above 200 K even room temperature, but the extreme high-pressure synthesis condition makes it difficult for experiment groups. It is necessary to balance the pressure required and T_c, rather than only trying to maximize T_c. In order to quantify the

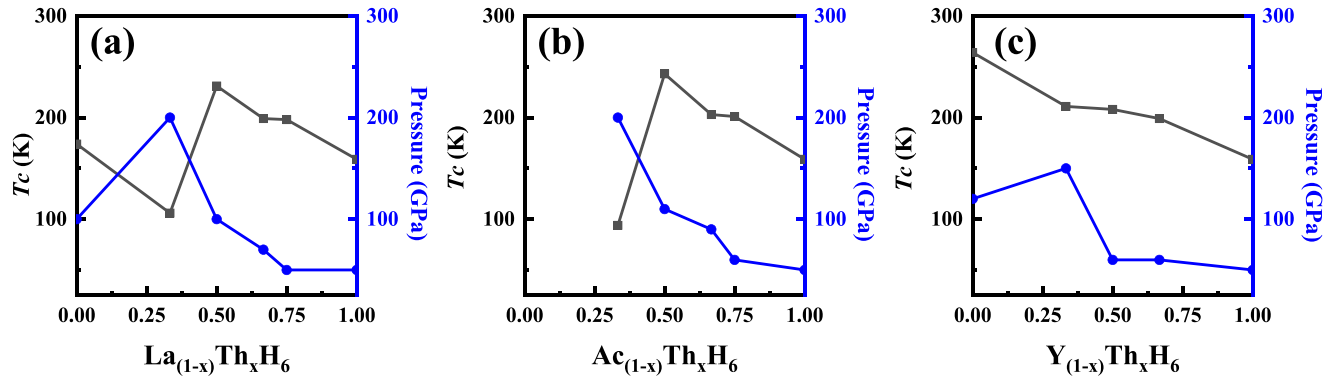

FIG. 3. The calculated superconducting critical temperature T_c using the self-consistent solution of the Eliashberg equation and the minimum dynamical stable pressure as a function of (a) $La_{(1-x)}Th_xH_6$, (b) $Ac_{(1-x)}Th_xH_6$, and (c) $Y_{(1-x)}Th_xH_6$. The Coulomb pseudopotential is using $\mu^* = 0.10$.

compromise explicitly, a figure of merit S [62] was proposed to evaluate the quality of the superconductors. The parameter S is obtained from

$$S = \frac{T_c}{\sqrt{T_{c,\,\mathrm{MgB_2}}^2 + P^2}}, \tag{1}$$

where $T_{c,\mathrm{MgB_2}}$ is the T_c of MgB_2 (39 K) at ambient condition. The S value of $LaTh_3H_{24}$ is larger than 3 (see Fig. 4), which is much better than the well known hydrogen-based superconductor H_3S and LaH_{10}. In addition, it can be found that $YThH_{12}$, $AcTh_3H_{24}$, YTh_2H_{18}, and $LaTh_2H_{18}$ host high-S values of 2.91, 2.81, 2.78, and 2.48, respectively, indicating that they are also excellent superconductors.

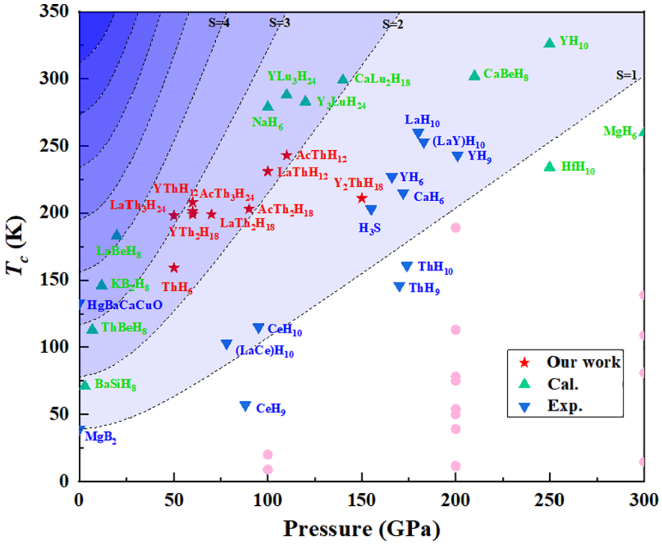

FIG. 4. Pressure dependence of T_c calculated for $(A, Th)H_6$ shown alongside other high T_c superconductors. The results in our work are marked with red stars. Green triangles correspond to theoretical predictions and blue inverted triangles correspond to experimental measurements.

IV. DISCUSSION

For further studying their mechanism of high T_c and relative low pressure, we calculated the electronic band structures and density of states (DOS) for $(La, Th)H_6$, $(Ac,Th)H_6$, and $(Y,Th)H_6$ at 100 GPa, as shown in Fig. 5 and Figs. S9–S13 of the SM [56]. $(La, Th)H_6$ can exhibit high T_c of 200 K which is related to the flat band near the Fermi level, as shown in Figs. 5(a)–5(c). Such flat bands exist in all clathrate hexahydrides in this work, but not all the flat bands are close to the Fermi level, which result in the different T_c values of $(La, Th)H_6$. Different from those room-temperature superconducting clathrate hexahydrides such as $(Mg,Ca)H_6$ and $(Y,Lu)H_6$, Th atoms provide a large contribution to the electronic DOS at the Fermi level which has an adverse effect on superconductivity. For $LaThH_{12}$, the projected DOS at the Fermi level on La, Th, and H is 0.34, 0.44, and 0.42, accounting for 28.3%, 36.7%, and 35.0%, respectively. With the increase of thorium content, the DOS contribution of Th improves from 36.7% to 55.1% and dominates the Fermi level, accompanied by weak H-state occupation. This results in a reduced contribution ratio from hydrogen and could slightly suppress the superconductivity. Consequently, one can try to improve the T_c of hydrides by adjusting the ratio of "precompression" elements. Comparing $LaTh_2H_{18}$ and YTh_2H_{18} [see Figs. 5(b) and 5(c)], it is found that their electronic band structures and DOS are very similar near the Fermi level due to the similar valence electron structures of La and Y, and this is the essential reason for their close T_c.

The minimum dynamically stable pressure of clathrate hexahydrides can be rationalized based on the effective number of transferred electrons in each element. Because of the filled σ bond in the H_2 unit, the extra electrons from the central metal atoms will reside in the antibonding σ orbitals and weaken the H-H bond, which results in the dissociation of H_2 molecular units and form H_4 units. The stability of H_{24} cages in clathrate hexahydrides comes from the formation of H_4 units which are the cornerstones of the construction, and meanwhile the electron transfer is essential to the stability. Figure 6 shows the numbers of electrons that each element donated in $LaThH_{12}$, $LaTh_2H_{18}$, and $LaTh_3H_{24}$ at 50–150 GPa. As the pressure decreases, hydrogen atoms need to adopt

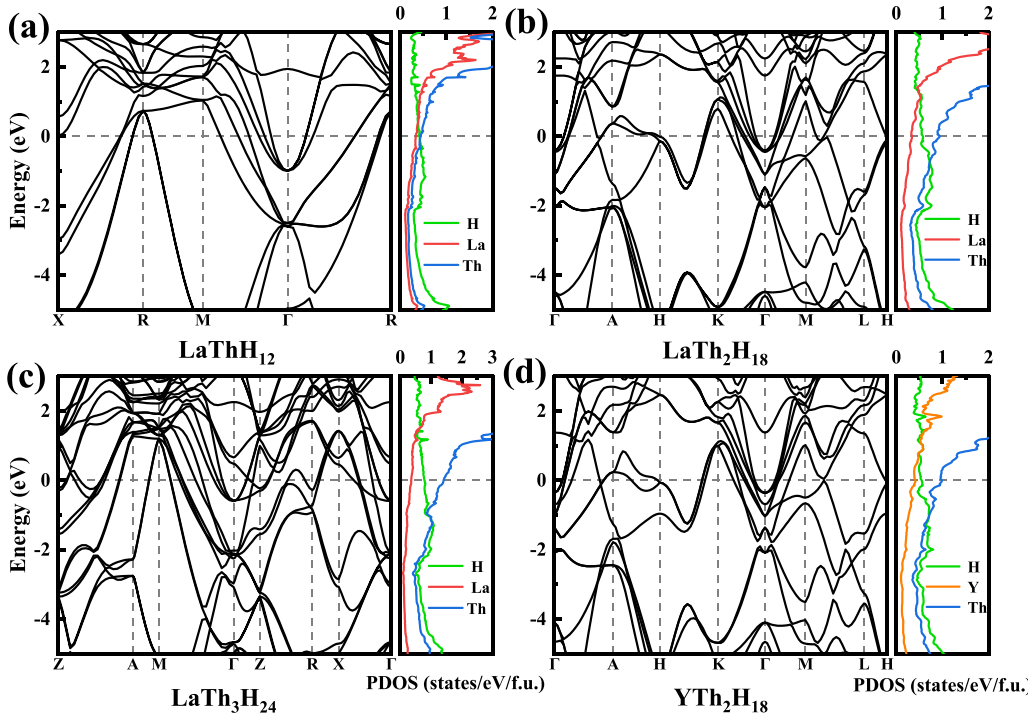

FIG. 5. Electronic band structures and projected DOS of (a) *Pm*-3*m*-$LaThH_{12}$, (b) *P*-3*m*1-$LaTh_2H_{18}$, (c) *P*4/*mmm*-$LaTh_3H_{24}$, and (d) *P*-3*m*1-YTh_2H_{18} at 100 GPa, respectively.

more electrons from metal atoms to keep the structure stable. At the same pressure, it can be found that hydrogen atoms capture more electrons as the thorium content increases, because Th has more valence electrons and is likely to lose more electrons than La. Each Th atom can donate about 1.65–1.85 electrons at 50–150 GPa, while each La atom can only donate 1.25–1.45 electrons. It is suggested that metal atoms with larger volume and less electronegativity, such as Th, are able to donate more electrons to hydrogen. In (La, Th)H_6, Th has a better ability to donate electrons and this is the reason why (La, Th)H_6 can be stable at lower pressure with the increase of thorium content.

To further explore the mechanism of high T_c, we calculated the phonon spectrum, phonon density of states (PHDOS), and EPC parameter λ of our predicted stable clathrate hexahydrides at their minimum dynamically stable pressure (see Fig. 7 and Figs. S4–S8 of the SM [56]). The absence of any imaginary frequency indicates that they are dynamically stable. The high hydrogen content makes the most of the phonon spectrum dominated by vibrations of hydrogen. It can be found that the low frequency region (below 200 cm^{-1}) in the phonon spectrum is mainly from the vibration of metal atoms, and the high frequency region comes from the vibration of hydrogen, which is the main provider of strong electron-phonon coupling. Both the high frequency vibration from hydrogen and softening of the optical branch lead to a strong EPC which is essential for high T_c. The softening of the optical branch along the high-symmetry lines *Z*-*A*-*M*-*L* direction and acoustic branch along the *A*-*M* direction provides a large λ of 3.12 and high T_c for $LaTh_3H_{24}$ at 50 GPa. A similar strong EPC was also observed in (Ac,Th)H_6 and (Y,Th)H_6. $LaTh_2H_{18}$ and YTh_2H_{18} present a similar phonon spectrum, especially the softening mode along the Γ-*A* direction, which leads to a large λ of 2.70 in YTh_2H_{18} and 2.41 in $LaTh_2H_{18}$, respectively. It is known that anharmonicity plays an important role in the calculations of some superconducting hydrides [16,63,64], which always tends to eliminate the pseudodynamic instabilities. The anharmonic effects may stabilize (La, Th)H_6 at lower pressures, but it will not fundamentally revise the main conclusion that the Th doping can reduce the dynamically stable pressure. Therefore, the simulations with anharmonicity are not performed and will be carried out elsewhere.

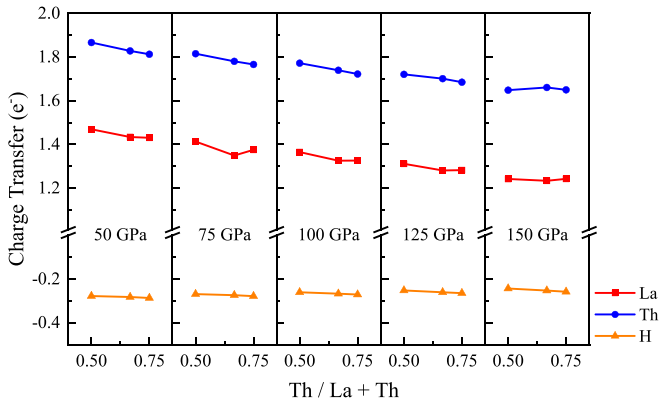

FIG. 6. The donated charges for each element in (La, Th)H_6 as a function of thorium content at pressure range of 50–150 GPa.

V. CONCLUSIONS

In conclusion, we proposed that thorium might be a good candidate to precompress the H_{24} cage by fitting the

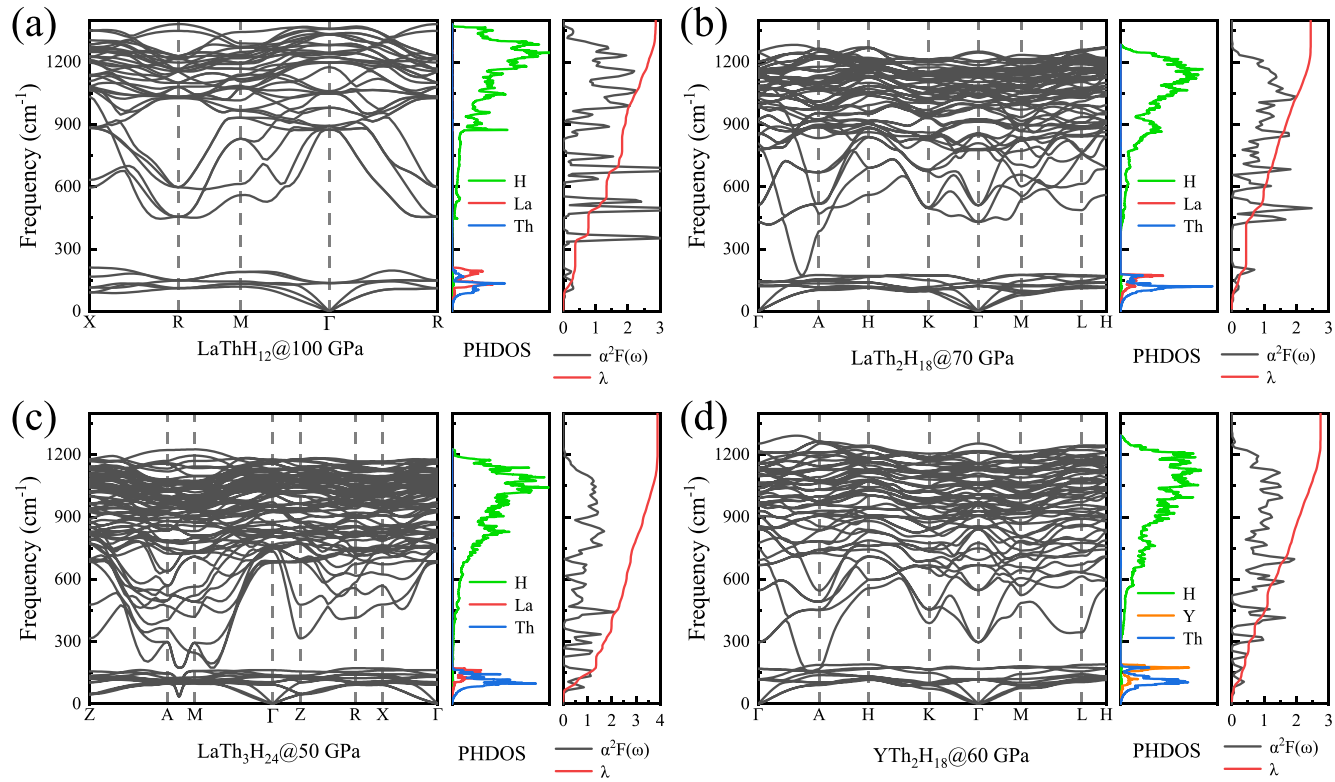

FIG. 7. Phonon dispersion, phonon density of state (PHDOS), and Eliashberg spectral function $\alpha^2F(\omega)$ together with the electron-phonon integral λ of (a) $LaThH_{12}$ at 100 GPa, (b) $LaTh_2H_{18}$ at 70 GPa, (c) $LaTh_3H_{24}$ at 50 GPa, and (d) YTh_2H_{18} at 60 GPa.

electronegativity and atomic volume of the known clathrate hexahydrides. A series of hydrides $(A, Th)H_6$ (A = La, Ac, and Y) were designed and predicted to be stable at moderate pressure. Notably, $LaTh_3H_{24}$ with a space group of *P4/mmm* can be dynamically stable down to 50 GPa and exhibit high-temperature superconductivity with a T_c of 198 K. Furthermore, $LaTh_2H_{18}$, $AcTh_3H_{24}$, $YThH_{12}$, and YTh_2H_{18} also have a high T_c at moderate pressure. We can find that the minimum dynamically stable pressures decrease with the development of Th content in $(A, Th)H_6$. It is suggested that Th is an excellent precompressor and can effectively reduce the dynamically stable pressure. These results suggest that our findings provide a different approach for designing high-temperature superconducting hydrides at moderate pressure and we hope that it is helpful to the research of superconducting hydrides in the future.

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