First-principles study of crystal structures and superconductivity of ternary YSH\(_6\) and LaSH\(_6\) at high pressures

Xiaowei Liang, Shuotao Zhao, Cancan Shao, Aitor Bergara, Hanyu Liu, Linyan Wang, Rongxin Sun, Yang Zhang, Yufei Gao, Zhisheng Zhao, Xiang-Feng Zhou, Julong He, Dongli Yu, Guoying Gao†, and Yongjun Tian

1Center for High Pressure Science, State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
2School of Physics and Electronic Science, Fuyang Normal University, Fuyang 236037, China
3Departamento de Física de la Materia Condensada, Universidad del País Vasco, UPV/EHU, 48080 Bilbao, Spain
4Donostia International Physics Center (DIPC), 20018 Donostia, Spain
5Centro de Física de Materiales CFM, Centro Mixto CSIC-UPV/EHU, 20018 Donostia, Spain
6Innovation Center for Computational Physics Methods and Software & State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China

(Received 29 June 2019; published 4 November 2019)

We have performed a systematic study on the crystal structures and electronic properties of two ternary hydrides, YSH\(_6\) and LaSH\(_6\), under pressure, using the particle swarm optimization method and first-principles calculations. As a result of extensive structure searches, metallic YSH\(_6\) and LaSH\(_6\) are thermodynamically stable between 195–237 and 170–300 GPa, respectively. Interestingly, in YSH\(_6\), eight neighboring hydrogen atoms form octagons, and the octagons in different layers are connected by four sulfur atoms, forming a cagelike structure with a Y atom at the center, while those octagons in the same layer form polyphenylene-like chains via one shared side. In LaSH\(_6\), however, hydrogen atoms form both curved “H\(_2\)” chains or straight chains when bonded to sulfur atoms. Furthermore, electron-phonon coupling calculations indicate that YSH\(_6\) and LaSH\(_6\) are promising superconductors with estimated \(T_c\) values of 91 and 35 K at 210 and 300 GPa, respectively. These results provide guidance for future experimental studies and stimulate more exploration on ternary hydrides.

DOI: 10.1103/PhysRevB.100.184502

I. INTRODUCTION

The search for high critical (\(T_c\)) or even room-temperature superconductors remains one of the most exciting research topics and has attracted great interest because of their fundamental and practical applications. Since Ashcroft [1] suggested that hydrogen-rich materials might be potential high-\(T_c\) superconductors at lower pressures than that of solid hydrogen due to “precompressing effects,” much experimental and theoretical effort has been devoted to the investigation of many hydrides with high \(T_c\) [2–28]. Encouragingly, hydrides formed by some elements in the chalcogen, alkaline earth, or rare-earth groups have recently been reported to have \(T_c\) values over 200 K [3–11,13–15]. Compressed H\(_2\)S was predicted to have a \(T_c\) of 80 K above 100 GPa [2], which was later confirmed experimentally [4]. Moreover, another “high-temperature sample” was also obtained with a higher \(T_c\) of 203 K at 150 GPa, in agreement with a previous theoretical prediction [3]. CaH\(_6\), YH\(_6\), MgH\(_6\), and recently predicted ternary CaYH\(_{12}\), all with hydrogen clathrate frameworks, were predicted to exhibit even higher \(T_c\) values at high pressure [6–9]. The rare-earth hydrides, YH\(_{10}\) and LaH\(_{10}\), were predicted to be stable in a \(Fm\bar{3}m\) structure with H\(_{32}\) cages and estimated to be superconductors with \(T_c\) values over 280 K [10,11]. These predictions have been recently confirmed, as \(Fm\bar{3}m\) LaH\(_{10}\) was successfully synthesized at 170 GPa on heating to about 1000 K [12], and multiple measurements revealed its high \(T_c\) values of 250–260 K at 170–190 GPa [13,14].

Such achievements enhanced the interest in further searching possible room-temperature superconducting hydrides, and ternary hydrogen-rich compounds are interesting candidates. BaReH\(_9\) was reported experimentally to be a superconductor under pressure, with a \(T_c\) of about 7 K above 100 GPa [22]. Ba(AuH\(_2\)\(_3\)) and Sr(AuH\(_2\)\(_3\)) were predicted to be superconductors below 30 and 10 K at 1 atm, respectively [23]. \(Cmc\bar{2}\), Fe\(_2\)S\(_3\), \(Fm\bar{3}m\) Li\(_2\)BH\(_6\), and \(Pm\bar{3}m\) MgSiH\(_6\) and MgGeH\(_6\) were reported to have \(T_c\) values of 0.3, 100, 63, and 67 K at 173, 100, 250, and 200 GPa, respectively [24–27]. Moreover, three phases of H\(_6\)S\(_2\)Se, similar to \(Im\bar{3}m\) H\(_2\)S\(_2\), were predicted to be superconductors with \(T_c\) decreasing from 195 to 115 K as the strength of the weakest covalent H-S or H-Se bonds in these structures declines [28]. In addition, our recent work on CaYH\(_{12}\) showed that its estimated \(T_c\) might reach 258 K at 200 GPa [9], which encouraged us to search for high-\(T_c\) superconductors in other ternary hydrides.

In this paper, high-pressure structures and superconductivity of YSH\(_6\) and LaSH\(_6\) were investigated by a combination of the particle swarm optimization algorithm and first-principles calculations. Under pressure, rare-earth elements are expected...
to transfer electrons to hydrogen atoms occupying their antibonding orbitals, which might induce the decomposition of H₂ dimers [29] and help the formation of hydrides [7–11]. Meanwhile, S atoms might form covalent bonds with Hs, preventing the formation of H₂ molecules, which might play a critical role in the superconducting transition [3,28]. Interestingly, new cagelike frameworks containing two octagons and four S atoms were predicted to be stable in YSH₆ with $P4_2/mmc$ symmetry. In addition, curved “H$_5$” and straight “H−S” chains were revealed in the $Cmcm$ phase of LaSH₆. Electron-phonon coupling (EPC) calculations suggested that both phases are promising candidates as superconducting materials.

II. COMPUTATIONAL DETAILS

To obtain the stable structures of ternary hydrides YSH₆ and LaSH₆ at high pressures, we conducted structure predictions based on the particle swarm optimization algorithm as implemented in the CALYPSO package [30,31]. This method has been applied successfully to many crystalline systems ranging from elemental solids to binary and ternary compounds and has been proven to be a powerful tool for predicting high-pressure structures [2,32,33]. The structural relaxation and electronic structure calculations were performed in the framework of density functional theory using the Perdew-Burke-Ernzerhof generalized gradient approximation method [34] as implemented in the Vienna ab initio simulation package code [35]. The frozen-core all-electron projector-augmented wave method was used, where $5s^25p^64d^15s^2$, $5s^25p^45d^16s^2$, $3s^23p^4$, and $1s^1$ are treated as valence electrons for Y, La, S, and H, respectively. A plane wave cutoff energy of 600 eV and appropriate Monkhorst-Pack [36] $k$-meshes were tested and converged to less than 1 meV/atom. Phonon dispersion and EPC calculations were performed within the density functional perturbation theory, as implemented in the QUANTUM ESPRESSO package [37], where norm-conserving pseudopotentials for Y, La, S, and H were considered with a kinetic energy cutoff of 80 Ry. 8 × 8 × 3 and 8 × 8 × 4 $q$-meshes in the first Brillouin zones were used in the EPC calculations for $P4_2/mmc$ YSH₆ and $Cmcm$ LaSH₆, respectively.

III. RESULTS AND DISCUSSION

Here crystal structural predictions were performed at pressures of 50, 100, 200, and 300 GPa, with unit cells containing up to four formula units. For YSH₆, three new phases, $Cm$, $P1$, and $C2/m$, were predicted below 200 GPa with H atoms both in the form of “H₂” units and monatomic H (Fig. S1 [38]). However, with increasing pressure, a tetragonal $P4_2/mmc$ structure becomes the preferred one, and H atoms evolve from “H₂” units in low-pressure structures to “H₅” octagons in high-pressure $P4_2/mmc$ [Fig. 1(a)]. There are three types of H-H bonds in the octagon, with distances of 0.893 Å (H₁-H₂), 0.934 Å (H₁-H₄), and 1.254 Å (H₂-H₃) at 200 GPa. The shortest H-H bond length (0.893 Å) is longer than that of 0.743 Å in pure H₂ solid at the same pressure [39]. The longest hydrogen bond of 1.254 Å is close to that in YH₆ (1.241 Å) at 200 GPa [7], indicating the existence of weak covalent interactions. As pressure increases to 300 GPa, the nearest and second-nearest bond lengths in the octagon increase to 0.919 and 0.956 Å, respectively, while the longest one becomes shorter (1.179 Å). Pressure is a useful tool to help the dissociation of H₂ dimers, making H octagons more regular and stable. Moreover, H octagons in different layers are connected with each other by four S atoms, building a cagelike structure with a Y atom at the center, while those octagons in the same layer share one side and form polyphenylene-like chains.

For LaSH₆, three phases, $P1$, $P1$, and $Cmcm$, were predicted at different pressures by means of extensive structure searches. As in YSH₆, the lower-pressure $P1$ and $P1$ structures of LaSH₆ (Fig. S1 [38]) show monoatomic H combined with H₂ and H₃ units. In the higher-pressure $Cmcm$ phase [Fig. 1(b)], some hydrogen atoms form curved “H₅” chains, which is different from the octagonal character presented in $P4_2/mmc$ YSH₆. “H₅” chains and La atoms are arranged alternately along the coordinate axis and present two kinds of H-H bonds, with 0.856 (H₃-H₄) and 1.128 Å (H₂-H₃) lengths. The H-H bond length of 1.128 Å is close to that of 1.109–1.196 Å in LaH₁₀ at 200 GPa [10,11]. The remaining H atoms are bonded with S atoms and form straight chains, which are parallel to each other along the coordinate axis. The length of the H-S bond is 1.60 Å, which is longer than that in $Im\overline{3}m$ H₃S (1.492 Å) [3]. Moreover, the trend of H-H distances in the “H₅” chain with pressure is also similar to those found in the octagon in $P4_2/mmc$ YSH₆. The smallest bond length becomes longer (0.88 Å at 300 GPa), while the longest one becomes shorter (1.09 Å at 300 GPa).

The calculated relative enthalpy curves for the predicted structures of YSH₆ and LaSH₆ as a function of pressure are presented in Fig. 2. On the basis of corresponding binary compounds, the decomposition enthalpies into YS(LaS) + 3H₂, Y(La)H₃ + H₃S, Y(La)H₄ + H₂S, and Y(La)H₅ + S are considered in order to investigate the phase stability of YSH₆ and LaSH₆ at high pressures.
and 3H$_2$ structures for Y(La)SH$_6$ as a function of pressure including zero-point corrections are shown in the insets. Y(La)H$_3$ pressure for (a) YSH$_6$ and (b) LaSH$_6$ with respect to 3H$_2$. The most stable structure at the corresponding pressure for each stoichiometry is considered [3,7,11,39,40]. The enthalpies of some stable phases between 58–183 and 183–300 GPa, respectively, occurs at 58 GPa. For LaSH$_6$, the phase transition from Cm to P1 and C2/m structures at 210 and 200 GPa, respectively (Fig. S2 [38]). According to our calculations, the PV terms of Y(La)SH$_6$ are always higher than those of Y(La)H$_6$ + S, while the U terms show the opposite trend, so that negative ΔU terms are mainly responsible for the overall negative relative enthalpy under pressure. These results indicate that diverse H-S, Y(La)-S, and H-H bonds in YSH$_6$ and LaH$_6$ may be the key driving mechanism for its phase stability.

In order to investigate the phase stability mechanism of P4$_2$/mmc YSH$_6$ and Cmcm LaSH$_6$, we have calculated the internal energies (U) and the product of pressure and volume (PV) contributions to the enthalpy relative to YH$_6$ + S and LaH$_6$ + S, respectively (Fig. S2 [38]). According to our calculations, the PV terms of Y(La)SH$_6$ are always higher than those of Y(La)H$_6$ + S, while the U terms show the opposite trend, so that negative ΔU terms are mainly responsible for the overall negative relative enthalpy under pressure. These results indicate that diverse H-S, Y(La)-S, and H-H bonds in Y(La)SH$_6$ may be the key driving mechanism for its phase stability.

As shown in Fig. 2(a), YSH$_6$ emerges in a Cm structure at 50 GPa and then transforms to P1 and C2/m structures at 80 and 170 GPa, respectively. Above 250 GPa, the P4$_2$/mmc structure is predicted to be energetically preferred. However, it was metastable with higher enthalpies relative to YH$_6$ and S decomposition. Considering that, due to the low mass of hydrogen, including zero-point energy (ZPE) contributions might be essential in determining the structural stability of hydrogen-rich compounds [39]. ZPE corrections for the predicted C2/m and P4$_2$/mmc YSH$_6$, as well as for YH$_6$ and S, were calculated within the quasiharmonic approximation at 150, 200, 250, and 300 GPa [41]. As shown in the inset of Fig. 2(a), with considering ZPE contributions, the transition pressure from C2/m to P4$_2$/mmc decreases from 250 to 195 GPa, and the P4$_2$/mmc phase becomes stable with respect to YH$_6$ and S decomposition between 195 and 237 GPa.

For LaSH$_6$, the phase transition from P1 to P1 structure occurs at 58 GPa. P1 and Cmcm structures become the most stable phases between 58–183 and 183–300 GPa, respectively [Fig. 2(b)]. Including the ZPEs contribution, the predicted P1 and Cmcm structures are still stable with respect to decomposition. Moreover, the stabilization pressure of the Cmcm structure also decreases from 183 to 170 GPa.

In order to explore the bonding information, the electronic localization function (ELF) [42,43] of P4$_2$/mmc YSH$_6$ and Cmcm LaSH$_6$ were calculated at 200 GPa. The ELF slice for P4$_2$/mmc YSH$_6$ containing the hydrogen octagon is shown at the top panel of Fig. 1(c), the ELF values for the H1-H2 and H3-H4 bonds are larger than 0.9, indicating that they are strong covalent bonds. The ELF value at the center of the H2-H3 bond in the octagon is approximately 0.5, which is the corresponding value for the homogeneous electron gas. From the lower panel, we can conclude there is a weak interaction between S and H1 (H2) atoms. Similarly, for Cmcm LaSH$_6$ [Fig. 1(d)], the very large ELF value at the H3-H4 bond (close to 1) and a smaller one at the H2-H3 bond (around 0.6) indicate their covalent characters, as well as the expected S1-H1 covalent bond with an ELF of about 0.7.

Electronic topological analysis was subsequently performed to further investigate their chemical bonding [44]. In P4$_2$/mmc YSH$_6$, there are electron charge transfers from Y to H and S atoms. Each H$_2$ accepts 0.18 electrons on average, as transferred from Y atoms, which occupy their antibonding orbitals, elongating the H-H bond length [6,45]. In addition, H$_2$ intermolecular distances decrease on compression and stretched H$_2$ dimers tend to form octagons under pressure. Compared with rare-earth hydrides with clathrate structures [7,10], in P4$_2$/mmc YSH$_6$, S atoms attract some electrons donated by Ys. Besides, the H content in YSH$_6$ is relatively lower compared with rare-earth hydrides. Thus, in YSH$_6$ there are H octagons rather than denser clathrate structures. For Cmcm LaSH$_6$, La and S atoms act as electron donors and acceptors, respectively. According to our calculations, most of the H atoms accept electrons, except for those in the middle of curved H$_2$ chains, which donate electrons.

FIG. 2. Enthalpy curves per formula unit as a function of pressure for (a) YSH$_6$ and (b) LaSH$_6$ with respect to 3H$_2$ and 3H$_2$+LaS. The decomposition enthalpies for Y(La)SH$_6$ to Y(La)H$_3$+YS, Y(La)H$_3$+H$_2$S, and Y(La)H$_3$+S are also presented. The most stable structure at the corresponding pressure for each stoichiometry is considered [3,7,11,39,40]. The enthalpies of some structures for Y(La)H$_6$ as a function of pressure including zero-point corrections are shown in the insets.

As shown in Fig. 2(a), YSH$_6$ emerges in a Cm structure at 50 GPa and then transforms to P1 and C2/m structures at 80 and 170 GPa, respectively. Above 250 GPa, the P4$_2$/mmc structure is predicted to be energetically preferred. However, it was metastable with higher enthalpies relative to YH$_6$ and S decomposition. Considering that, due to the low mass of hydrogen, including zero-point energy (ZPE) contributions might be essential in determining the structural stability of hydrogen-rich compounds [39]. ZPE corrections for the predicted C2/m and P4$_2$/mmc YSH$_6$, as well as for YH$_6$ and S, were calculated within the quasiharmonic approximation at 150, 200, 250, and 300 GPa [41]. As shown in the inset of Fig. 2(a), with considering ZPE contributions, the transition pressure from C2/m to P4$_2$/mmc decreases from 250 to 195 GPa, and the P4$_2$/mmc phase becomes stable with respect to YH$_6$ and S decomposition between 195 and 237 GPa.

For LaSH$_6$, the phase transition from P1 to P1 structure occurs at 58 GPa. P1 and Cmcm structures become the most stable phases between 58–183 and 183–300 GPa, respectively [Fig. 2(b)]. Including the ZPEs contribution, the predicted P1 and Cmcm structures are still stable with respect to decomposition. Moreover, the stabilization pressure of the Cmcm structure also decreases from 183 to 170 GPa.

In order to explore the bonding information, the electronic localization function (ELF) [42,43] of P4$_2$/mmc YSH$_6$ and Cmcm LaSH$_6$ were calculated at 200 GPa. The ELF slice for P4$_2$/mmc YSH$_6$ containing the hydrogen octagon is shown at the top panel of Fig. 1(c), the ELF values for the H1-H2 and H3-H4 bonds are larger than 0.9, indicating that they are strong covalent bonds. The ELF value at the center of the H2-H3 bond in the octagon is approximately 0.5, which is the corresponding value for the homogeneous electron gas. From the lower panel, we can conclude there is a weak interaction between S and H1 (H2) atoms. Similarly, for Cmcm LaSH$_6$ [Fig. 1(d)], the very large ELF value at the H3-H4 bond (close to 1) and a smaller one at the H2-H3 bond (around 0.6) indicate their covalent characters, as well as the expected S1-H1 covalent bond with an ELF of about 0.7.

Electronic topological analysis was subsequently performed to further investigate their chemical bonding [44]. In P4$_2$/mmc YSH$_6$, there are electron charge transfers from Y to H and S atoms. Each H$_2$ accepts 0.18 electrons on average, as transferred from Y atoms, which occupy their antibonding orbitals, elongating the H-H bond length [6,45]. In addition, H$_2$ intermolecular distances decrease on compression and stretched H$_2$ dimers tend to form octagons under pressure. Compared with rare-earth hydrides with clathrate structures [7,10], in P4$_2$/mmc YSH$_6$, S atoms attract some electrons donated by Ys. Besides, the H content in YSH$_6$ is relatively lower compared with rare-earth hydrides. Thus, in YSH$_6$ there are H octagons rather than denser clathrate structures. For Cmcm LaSH$_6$, La and S atoms act as electron donors and acceptors, respectively. According to our calculations, most of the H atoms accept electrons, except for those in the middle of curved H$_2$ chains, which donate electrons.

In order to investigate the phase stability mechanism of P4$_2$/mmc YSH$_6$ and Cmcm LaSH$_6$, we have calculated the internal energies (U) and the product of pressure and volume (PV) contributions to the enthalpy relative to YH$_6$ + S and LaH$_6$ + S, respectively (Fig. S2 [38]). According to our calculations, the PV terms of Y(La)SH$_6$ are always higher than those of Y(La)H$_6$ + S, while the U terms show the opposite trend, so that negative ΔU terms are mainly responsible for the overall negative relative enthalpy under pressure. These results indicate that diverse H-S, Y(La)-S, and H-H bonds in Y(La)SH$_6$ may be the key driving mechanism for its phase stability.

With the aim to search for metallic and superconducting materials, we explored the electronic band structures for the predicted phases of YSH$_6$ and LaSH$_6$. For YSH$_6$, the Cm, P1, and C2/m structures were calculated to be semiconductors with indirect band gaps of 2.54, 1.12, and 0.14 eV at 50, 100, and 200 GPa, respectively (Fig. S3 [38]). The bands for Cm and P1 phases are quite flat at lower pressures, associated with their strong electronic localization. Similarly, P1 LaSH$_6$ (Fig. S3d [38]) is also a semiconductor with an indirect band gap of 1.56 eV at 50 GPa. Upon compression, P1 LaSH$_6$ becomes a metal at 150 GPa. Additionally, both high-pressure P4$_2$/mmc YSH$_6$ and Cmcm LaSH$_6$ are good metals at 210 and 200 GPa,
respectively, with several bands crossing the Fermi level ($E_f$) (Fig. 3). Band projections onto $Y\ d$ ($La\ d$ and $f$), $S\ p$, and $H\ s$ orbitals are also shown in both band structures. These orbitals are the main contributions to the electronic states near the $E_f$, which mainly contribute to the electron-phonon coupling. In addition to some steep bands crossing the $E_f$, some holelike and electron-like bands are also found near the $E_f$ (around $M$ and $R$ points for $YSH_6$; $Y$, $\Gamma$ points and along the $\Gamma$-$Z$ direction for $LaSH_6$), giving rise to a large density of states (DOS) (Fig. 3 and Fig. S4 [38]), which enhances the electron-phonon coupling strength [46–51].

The dynamical stabilities of $P4_2/mmc\ YSH_6$ and $Cmcm\ LaSH_6$ were investigated by calculating their phonon dispersion curves. As shown in Fig. 4, the absence of any imaginary frequency confirms their dynamical stability at 210 and 200 GPa, respectively. As shown in the projected phonon DOS, the vibrations of the heavier Y and La atoms in $P4_2/mmc\ YSH_6$ and $Cmcm\ LaSH_6$ are associated with the low-frequency phonon branches, while vibrations of $S$ and $H$ atoms are mainly related to the middle- and high-frequency regions, respectively. For $P4_2/mmc\ YSH_6$, the two main ingredients to estimate $T_c$ ($T_c = \frac{\omega_{\text{avg}}}{1 - \exp\left(-\frac{\omega_{\text{avg}}}{k_B T_c}\right)}$) [52], the logarithmic average frequency, $\omega_{\text{avg}}$, and the EPC parameter, $\lambda$, are calculated to be 1048 K and 1.17, respectively. The origin of $\lambda$ can be understood by analyzing the Eliashberg phonon spectral function, $\alpha^2 F(\omega)$. As shown in the right panel of Fig. 4(a), the spectrum of $\alpha^2 F(\omega)$ is roughly proportional to the phonon DOS between 30 and 55 THz, dominated by H modes. Between 20 and 30 THz, the values of phonon DOS are relatively low, but pronounced peaks appear in the $\alpha^2 F(\omega)$ curves, which show the strong coupling strength from phonons in this frequency range. To further explore the contributions of different phonon modes, red circles with the radius proportional to the phonon linewidth are also plotted in the first panel of Fig. 4(a). The high-frequency modes (above 60 THz) at the $\Gamma$ point and the soft modes along $Z$-$R$-$X$-$\Gamma$ (between 20 and 30 THz) and $A$-$M$ (between 5 and 15 THz) directions show quite large phonon linewidths, enhancing the EPC parameter. At 300 GPa, the calculated $\omega_{\text{avg}}$ increases to 1437 K, while $\lambda$ decreases to 0.76 (Fig. 5). It is seen that...
the peaks of $\alpha^2 F(\omega)$ are mainly associated to H vibrations (Fig. S7 [38]), which play a critical role in the EPC, with a 75% contribution to the total $\lambda$. Phonon modes become stiffer with pressure and, therefore, $\omega_{\text{log}}$ increases. Moreover, $\alpha^2 F(\omega)$ at 300 GPa is almost simply shifted to a high-frequency region (Fig. S7 [38]), which weakens $\alpha^2 F(\omega)/\omega$ due to the increase of $\omega$, and thus $\lambda = 2 \int_{0}^{\infty} \alpha^2 F(\omega)/\omega \ d\omega$ decreases with pressure.

For $Cmcm$ LaSH$_6$ [Fig. 4(b)], vibrations of H atoms above 20 THz contribute 56% of the total $\lambda$ of 0.63, whereas the remaining 44% comes from vibrations of other Hs, La, and S atoms. As shown in the $\alpha^2 F(\omega)$ curves, the main peaks emerge between 30 and 50 THz. In this frequency range some modes around $\Gamma$ and $\Gamma$ points give important contributions to $\lambda$, which is different from $P4_2/mmc$ YSH$_6$, where the main peaks show up at the frequency region of the soft modes. Comparing the phonon spectra of $P4_2/mmc$ YSH$_6$ with $Cmcm$ LaSH$_6$, there are many soft modes in $P4_2/mmc$ YSH$_6$, while only one along the $\Gamma$-S-R direction between 20 and 50 THz in $Cmcm$ LaSH$_6$. Although this soft mode also enhances $\lambda$, the vibrations between 30 and 50 THz still remain dominant. As pressure increases to 300 GPa, $\omega_{\text{log}}$ increases from 918 to 1100 K (Fig. 5). Although phonon modes also become stiffer with pressure, $\alpha^2 F(\omega)$ generally increases with pressure and the calculated total $\lambda$ rises a little, from 0.63 to 0.68 (Fig. 5). At 300 GPa the main contribution to $\lambda$ corresponds to H vibrations (63%) (Fig. S7 [38]), so that H-associated phonons are mainly responsible for the EPC parameter $\lambda$ in the Y(La)SH$_4$. This indicates that a large number of electronic states [Y $d$ (La $d$ and $f$), S $p$, and H $s$ for Y(La)SH$_4$] at the $E_f$ are coupled to the H-derived phonon modes, therefore enhancing the superconducting transition.

Superconducting transition temperatures of $P4_2/mmc$ YSH$_6$ and $Cmcm$ LaSH$_6$ are evaluated through the Allen-Dynes modified McMillan equation [52]. The estimated $T_c$ values for the $P4_2/mmc$ YSH$_6$ and $Cmcm$ LaSH$_6$ at 210 and 200 GPa are 80–91 and 17–24 K, respectively, using Coulomb pseudopotential parameter $\mu^*$ of 0.13 and 0.1. As shown in Fig. 5, the trend of $T_c$ as a function of pressure was also investigated for both structures. As pressure increases from 210 to 300 GPa, the estimated $T_c$ for $P4_2/mmc$ YSH$_6$ decreases from 91 to 61 K with $\mu^*$ of 0.1, which follows the trend of $\lambda$ with pressure. $T_c$ reaches a maximum at the pressure in which the crystal structure becomes dynamically unstable, which is similar to some other high-$T_c$ hydrides [10,11]. On the other hand, for $Cmcm$ LaSH$_6$ both $\omega_{\text{log}}$ and $\lambda$ increase with pressure, and therefore the calculated $T_c$ also rises from 24 to 35 K. Moreover, we have also investigated the constituent atomic contributions (non-H atoms and H) to $T_c$ at 300 GPa (Table S1 [38]). Similar to other hydrides [53,54], H atoms have positive effects on increasing both $\lambda$ and $\omega_{\text{log}}$, determining $T_c$. On the other hand, although non-H atoms also increase the total $\lambda$, they decrease $\omega_{\text{log}}$. Our results reveal that the positive effect on $T_c$ of $\lambda$ associated with non-H atoms overcomes the negative effect of $\omega_{\text{log}}$ in both $P4_2/mmc$ YSH$_6$ and $Cmcm$ LaSH$_6$.

As is well known, the corresponding binary hydrides of YSH$_6$ and LaSH$_6$, such as H$_3$S, YH$_6$, YH$_{10}$, and LaH$_{10}$, have been observed or estimated to be excellent superconductors, with $T_c$s over 200 K under pressure. In comparison, YSH$_6$ and LaSH$_6$ have lower $T_c$s, mainly due to their smaller EPC parameter $\lambda$ (Table I). According to the simplified Hopfield expression, $\lambda = N(E_f)/(\omega_{\text{log}})$ [55], where $N(E_f)$ is the calculated electronic DOS at Fermi level, $\langle F \rangle$ is the average over the Fermi surface of the square of the electron-ion matrix element, $M$ is the ion mass, and $\langle \omega^2 \rangle$ is the average of the square phonon frequencies, which could be derived from the spectral function $\alpha^2 F(\omega)$ [56]. $\lambda$ is roughly proportional to $N(E_f)$, and, therefore, a large $N(E_f)$ might enhance $\lambda$. As shown in Fig. S4 [38], the $N(E_f)$ of $P4_2/mmc$ YSH$_6$ is comparable to that of those hydrides with strong EPC, while it is slightly smaller for $Cmcm$ LaSH$_6$. Meanwhile, the values of $\langle \omega^2 \rangle$ (Table I) are smaller overall for $P4_2/mmc$ YSH$_6$ and $Cmcm$ LaSH$_6$ at 210 and 200 GPa. Therefore, the smaller impact of the displacement of the atoms on the electronic structure, as well as the heavier atomic mass resulting from the lower H contents of $P4_2/mmc$ YSH$_6$ and $Cmcm$ LaSH$_6$ become mainly responsible for their lower $\lambda$ and $T_c$ values. Previous studies show that hydrogenic sublattices in hydrides are important to get high $T_c$ values [18,46–48]. However, the presence of isolated hydrogenic motifs (H$^-$ or H$_2^-$) might not imply a high $T_c$, but hydrides containing clathrate H lattices, such as YH$_{10}$ and LaH$_{10}$, show remarkably high $T_c$s. In addition, rare-earth hydrides with one- or two-dimensional hydrogenic lattices (ScH$_9$, ScH$_{10}$, ScH$_{12}$, and LaH$_8$) are also usually estimated to have $T_c$ values intermediate to the other two classes of systems described above [18]. Interestingly, in $C2/m$ LaH$_8$ [11] we found traces of curved H$_5$ units similar to those in $Cmcm$ LaSH$_6$. As they have more H atoms, curved H$_5$ units are linked by other H atoms and form two-dimensional hydrogenic lattices with edge-sharing puckered dodecagons in $C2/m$ LaH$_8$, while there are curved H$_5$ chains in $Cmcm$ LaSH$_6$. Thus, the estimated $\lambda$ in $Cmcm$ LaSH$_6$ at 200 GPa (0.63) is smaller than in $C2/m$ LaH$_8$ at 300 GPa (1.12), and considering that $\omega_{\text{log}}$ is also smaller, it results in a lower $T_c$. In $P4_2/mmc$ YSH$_6$, the H octagons sharing one edge form extended one-dimensional structures, similar to $C2/m$ LaH$_8$. The calculated $\lambda$ in $P4_2/mmc$ YSH$_6$ at 200 GPa (1.17) is close to the values in $C2/m$ LaH$_8$ at 300 GPa (1.12), $Cmcm$ ScH$_{10}$ at 250 GPa (1.17), and $Immm$ ScH$_{12}$ at 350 GPa (1.17).
TABLE I. The calculated EPC parameter $\lambda$, square root of the average square phonon frequencies $\langle \omega^2 \rangle^{1/2}$, logarithmic average frequency $\omega_{\log}$, and critical temperature $T_c$ with $\mu^* = 0.1$ for $P4_2/mmc$ YSH$_6$, Cmcm LaSH$_6$, $\bar{I}m\bar{3}m$ H$_2$S, $\bar{I}m\bar{3}m$ YH$_6$, $Fm\bar{3}m$ YH$_{10}$, and LaH$_{10}$ at different pressures.

<table>
<thead>
<tr>
<th></th>
<th>$P$ (GPa)</th>
<th>$\lambda$</th>
<th>$\langle \omega^2 \rangle^{1/2}$ (K)</th>
<th>$\omega_{\log}$ (K)</th>
<th>$T_c$ with $\mu^* = 0.1$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P4_2/mmc$-YSH$_6$</td>
<td>210</td>
<td>1.17</td>
<td>1428</td>
<td>1048</td>
<td>91</td>
</tr>
<tr>
<td>$P4_2/mmc$-YSH$_6$</td>
<td>300</td>
<td>0.76</td>
<td>1770</td>
<td>1437</td>
<td>61</td>
</tr>
<tr>
<td>Cmcm-LaSH$_6$</td>
<td>200</td>
<td>0.63</td>
<td>1493</td>
<td>918</td>
<td>24</td>
</tr>
<tr>
<td>Cmcm-LaSH$_6$</td>
<td>300</td>
<td>0.68</td>
<td>1739</td>
<td>1100</td>
<td>35</td>
</tr>
<tr>
<td>$\bar{I}m\bar{3}m$-H$_2$S</td>
<td>200</td>
<td>1.95</td>
<td>1551</td>
<td>1349</td>
<td>191, 223$^a$</td>
</tr>
<tr>
<td>$\bar{I}m\bar{3}m$-YH$_6$</td>
<td>200</td>
<td>1.88</td>
<td>1666</td>
<td>1283</td>
<td>177, 209$^a$</td>
</tr>
<tr>
<td>$Fm\bar{3}m$-YH$_{10}$</td>
<td>300</td>
<td>2.06$^a$</td>
<td>1564$^c$</td>
<td>1511$^c$</td>
<td>255$^{ac}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.42$^a$</td>
<td>1751$^d$</td>
<td>1311$^d$</td>
<td>271$^{a-d}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.29$^a$</td>
<td>1325$^c$</td>
<td>1253$^c$</td>
<td>232$^{a-c}$</td>
</tr>
<tr>
<td>$Fm\bar{3}m$-LaH$_{10}$</td>
<td>250</td>
<td>2.46$^a$</td>
<td>1415$^d$</td>
<td>1067$^d$</td>
<td>223$^{a-d}$</td>
</tr>
</tbody>
</table>

$^a$The calculated $T_c$ values are based on the McMillan equation with the strong-coupling and the shape corrections; $^b$Ref. [9]; $^c$Ref. [11]; $^d$Ref. [54].

However, the calculated $T_c$ of $P4_2/mmc$ YSH$_6$ (91 K) is lower than others due to the smaller $\omega_{\log}$, which can be related to its different H content.

**IV. CONCLUSIONS**

In summary, we have systematically analyzed crystal structures and electronic properties of ternary hydrides YSH$_6$ and LaSH$_6$ under pressure. In YSH$_6$, a $P4_2/mmc$ structure is predicted to be stable with pressure and it contains cagelike structures formed by hydrogen octagons connected by sulfur atoms with a Y atom at the center, which is different from the predicted stable phases at low pressure with monoatomic H and H$_2$ units. Similarly, a unique Cmcm structure for LaSH$_6$ is predicted to be stable under pressure with curved “H₂” and straight “H–S” chains. The calculated electronic band structures show the metallic feature of both $P4_2/mmc$ YSH$_6$ and Cmcm LaSH$_6$. Further electron-phonon coupling calculations indicate that both structures become potential superconductors with estimated $T_c$ values of 91 and 35 K at 210 and 300 GPa, respectively, suggesting that cagelike structures favor a high $T_c$. These results might further stimulate future experimental synthesis and more theoretical studies on ternary hydrides.

**ACKNOWLEDGMENTS**

The work was supported by the National Natural Science Foundation of China (Grants No. 11604290 and No. 51732010), National Key R & D Program of China (Grant No. 2018YFA0703400), Funding Program for Recruited Oversea Scholars of Hebei Province (Grant No. CL201729), the Ph.D. Foundation by Yanshan University (Grant No. B970), and the Natural Science Research Project of Education Department of Anhui Province (KJ2018A0342). A.B. acknowledges financial support from the Spanish Ministry of Economy and Competitiveness (FIS2016-76617-P) and the Department of Education, Universities and Research of the Basque Government and the University of the Basque Country (IT756-13).
