**Potential high-$T_c$ superconductivity in CaYH$_{12}$ under pressure**

Xiaowei Liang,1 Aitor Bergara,2,3,4 Linyan Wang,1 Bin Wen,1 Zhisheng Zhao,1 Xiang-Feng Zhou,1 Julong He,1 Guoying Gao,1,* and Yongjun Tian1

1Center for High Pressure Science, State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
2Department of Física de la Materia Condensada, Universidad del País Vasco, UPV/EHU, 48080 Bilbao, Spain
3Donostia International Physics Center (DIPC), 20018 Donostia, Spain
4Centro de Física de Materiales CFM, Centro Mixto CSIC-UPV/EHU, 20018 Donostia, Spain

(Received 3 November 2018; revised manuscript received 8 March 2019; published 25 March 2019)

The high-pressure phases and superconductivity of CaYH$_{12}$ have been explored by using a particle swarm optimization structure prediction methodology in combination with first-principles calculations. Our results show that CaYH$_{12}$ becomes stable with a cubic $Fd\bar{3}m$ structure above 170 GPa, where metal atoms form body-centered-cubic (bcc) lattices and hydrogens occupy all the tetrahedral interstices of these bcc lattices, completing sodalilite-like cages. The electron-phonon coupling calculations indicate that the $Fd\bar{3}m$ structure is a potential high-temperature superconductor, with a calculated $T_c$ of 258 K at 200 GPa. Our current study provides a possibility for searching new high-$T_c$ superconductors in ternary hydrides.

DOI: 10.1103/PhysRevB.99.100505

Looking for room-temperature superconductivity remains one of the most important topics in condensed matter physics. As the lightest element, hydrogen has been extensively analyzed for its potential high-$T_c$ superconductivity [1–10]. However, many theoretical and experimental studies indicate that extraordinary high pressures are required to metallize hydrogen. Even though metallic hydrogen has been recently reported to be observed at 495 GPa, it still remains highly controversial [10]. In 2004 Ashcroft [11] predicted that hydrogen-rich compounds might also become high-temperature superconductors but at much lower pressures than those required for hydrogen, due to the chemical “precompression” by alloying hydrogen with other elements. This prediction stimulated extensive research [12–37], and since then many hydrides have been predicted to become superconductors under high pressure with $T_c$ values over 100 K [12–21]. Interestingly, these predictions have been recently confirmed, as hydrogen sulfide and lanthanum hydride have been experimentally observed to superconduct with critical temperatures above 200 K [22–26]. H$_2$S was first predicted to be stable in a cubic $Im\bar{3}m$ structure [16] with a remarkably high $T_c$ of 204 K. These predictions were later experimentally confirmed by compressing a H$_2$S sample [22]. Different from the pure covalent structure of H$_2$S, another class of metal hydrides containing H clathrates were predicted with higher $T_c$ values than that of H$_2$S. In these hydrides, $Im\bar{3}m$ CaH$_6$ [17] was first proposed with a $T_c$ of 235 K at 150 GPa and then YH$_6$ [18] was predicted to have the same cubic $Im\bar{3}m$ structure with a $T_c$ of 264 K at 120 GPa, where metal atoms form a bcc lattice, and hydrogens occupy all the tetrahedral interstices of the bcc lattice, forming a sodalilite cage. Recently, Liu et al. [19] and Peng et al. [20] predicted separately that LaH$_{10}$ and YH$_{10}$ are stable in a cubic $Fm\bar{3}m$ structure with H$_{32}$ cages under pressure. The estimated $T_c$ values by both groups are 286 K (at 210 GPa) [19] and 288 K (at 200 GPa) [20] for LaH$_{10}$, while 326 K (at 250 GPa) [19] and 303 K (at 400 GPa) [20] for YH$_{10}$, respectively. Theoretical studies show that strong electron-phonon coupling (EPC) of these phases is closely related to the phonon modes of H-H bonds within the cages. Guided by these theoretical predictions, $Fm\bar{3}m$ LaH$_{10}$ was subsequently synthesized by using laser-heated diamond anvil cell techniques at 170 GPa and 1000 K [24]. More recently, the superconducting transition of this clathrate lanthanum superhydride has been measured almost simultaneously by Somayazulu et al. [25] and Drozdov et al. [26] with $T_c$ of about 260 and 250 K at 190 and 170 GPa, respectively. These exciting results have greatly encouraged us to further explore clathrate hydrogen-rich hydrides.

As we discussed above, CaH$_6$ was first predicted to be stable in the H-clathrate structure with a high $T_c$ and then the same structure was later predicted in YH$_6$. However, a report on their synthesis is still missing. As we know, Ca and Y atoms have a similar atomic radius and electronegativity, which might prevent the H cages from collapsing and thus might maintain excellent superconductivity when we mix them together with H atoms. Thus, here we focus on exploring the crystal structures and superconductivity of the ternary hydride CaYH$_{12}$ under pressure. Simultaneously, this might also provide alternative routes to synthesize these kinds of hydrides, such as CaH$_6$ and YH$_6$.

In this Rapid Communication, we used a particle swarm optimization structural search combined with first-principles calculations to study the high-pressure phases and superconductivity of CaYH$_{12}$. Starting from the $Im\bar{3}m$ phase of CaH$_6$ and considering the substitution method for metal atoms, the $a$ priori simplest structure for CaYH$_{12}$ would be $Pm\bar{3}m$. However, although this structure is also highly competitive, a very similar cubic $Fd\bar{3}m$ structure is predicted to be the most stable...
one above 170 GPa. Interestingly, EPC calculations revealed that \( Fd\bar{3}m \) \( \text{CaYH}_{12} \) is a potential high-temperature superconductor with a \( T_c \) of 258 K at 200 GPa, which is slightly higher than those of \( \text{CaH}_6 \) and \( \text{YH}_6 \) at the same pressure.

Structure searches were performed using the particle swarm optimization technique as implemented in the \text{CA-LYPSO} code [38,39]. This method has successfully predicted the high-pressure structures of various systems [31,40,41]. Structural relaxations were based on density functional theory within the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation [42] as implemented in the Vienna \textit{ab initio} simulation package [43]. The EPC calculations of the \( Fd\bar{3}m \) and \( Pm\bar{3}m \) structures were performed with density functional perturbation theory with the \text{QUANTUM ESPRESSO} code [44], where ultrasoft pseudopotentials for Ca, Y, and H with a kinetic energy cutoff of 60 Ry were employed. The \( 7 \times 7 \times 7 \) and \( 9 \times 9 \times 9 \) \( q \)-point meshes in the first Brillouin zone were used in the EPC calculation for the \( Fd\bar{3}m \) and \( Pm\bar{3}m \) phases, respectively. Correspondingly, Monkhorst-Pack grids of \( 28 \times 28 \times 28 \) and \( 36 \times 36 \times 36 \) were used to ensure \( k \)-point sampling convergence with Gaussians of width 0.02 Ry.

Here, crystal structural predictions are performed for \( \text{CaYH}_{12} \) at 10, 50, 100, 150, 200, 250, 300, and 350 GPa, respectively, with system sizes containing up to 2 formula units (f.u.) per simulation cell. Below 100 GPa, three structures, \( P\bar{1}(1) \), \( P\bar{1}(2) \), and \( P\bar{1} \) (Fig. S1 [45]), are predicted, where the hydrogen atoms exist both in the form of \( \text{H}_2 \) dimers and monoatomic H. The existence of \( \text{H}_2 \) dimers in these structures shows a trend to decomposition of \( \text{CaYH}_{12} \) at low pressure (Fig. S2 [45]). At higher pressures, when we just consider 1 f.u. in the simulation cell, a cubic \( Pm\bar{3}m \) phase is predicted to be stable above 200 GPa [Fig. 1(a)]. In this structure, Ca and Y atoms together form a bcc lattice, and hydrogen atoms occupy all the tetrahedral interstices of the bcc lattice forming a sodalitelike cage. Actually, this structure can be easily derived by a direct substitution of metal atoms in the predicted \( \text{Im\bar{3}}m \) phase for \( \text{CaH}_6 \) and \( \text{YH}_6 \).

When extending the structural search to 2 f.u. in the simulation cell, a different cubic \( Fd\bar{3}m \) structure is predicted to be the most stable one at 200 GPa [Fig. 1(b)]. Interestingly, both \( Fd\bar{3}m \) and \( Pm\bar{3}m \) are very similar. However, in the \( Fd\bar{3}m \) structure, Ca alternates with Y in all the directions in the bcc lattice, which leads to a much bigger conventional cell (\( \text{Ca}_2\text{Y}_2\text{H}_{10} \)) than in \( Pm\bar{3}m \) (\( \text{CaYH}_{12} \)). The first and second nearest H-H distances in \( Fd\bar{3}m \) are 1.18 and 1.26 Å at 200 GPa (Fig. S3 [45]). Added electrons from the metal atoms will occupy antibonding orbitals of the H-H unit, elongating its bond length [17,18]. As it will be discussed below, the number of electrons transferred from the metal atoms considerably affects the H-H separation. In addition, several very competitive metastable \( \text{Cmmm} \), \( \text{P2}_1/\text{m} \), \( \text{Imma} \), and \( \text{P4}_n/\text{mmm} \) structures are also predicted (see Fig. S4 [45]). Interestingly, all these structures are based on bcc metal lattices and H clathrates.

Figure 1(c) shows the calculated enthalpy curves for the predicted structures with respect to the \( Pm\bar{3}m \) phase as a function of pressure. The enthalpies of the decomposition to binary hydrides were also taken into account. As \( \text{CaH}_4 \) was predicted to be the most stable stoichiometry in the Ca-H system [17] below 150 GPa and \( \text{YH}_3 \) is the experimentally known yttrium hydride at lower pressure, we have considered \( \text{CaH}_4(\text{I}\text{4}_\text{mmm}) + \text{YH}_3(\text{Fm\bar{3}m}) + \text{H}_2(\text{C}2/\text{c}) \) as a possible decomposition route. On the other hand, as above 150 GPa \( \text{CaH}_6 \) and \( \text{YH}_6 \) were calculated to become more stable than \( \text{CaH}_4 \) and \( \text{YH}_3 \) [18], respectively, the enthalpy decomposition to \( \text{CaH}_6(\text{I}\text{m}\bar{3}m) + \text{YH}_6(\text{I}\text{m}\bar{3}m) \) was also presented in Fig. 1(c). \( Fd\bar{3}m \) \( \text{CaH}_6 \) becomes thermodynamically stable above 135 GPa. However, it is dynamically unstable below 170 GPa. In this intermediate-pressure range, the H clathrate in \( Fd\bar{3}m \) becomes gradually distorted, as the \( \text{P2}_1/c \) structure in Fig. S1(d) [45], and breaks down into messy configurations, so that much bigger unit cells are needed to predict the correct structures at this pressure, which goes beyond our current computational capabilities. Even though the most stable structure is uncertain, our results can still show \( \text{CaYH}_{12} \) is stable with respect to \( \text{CaH}_4 + \text{YH}_3 + \text{H}_2 \) above 116 GPa at least (Fig. S2 [45]). Additionally, due to the low mass of the hydrogen atom, we have also considered the zero-point energy (ZPE) contribution, which might influence the stability of hydrogen-rich materials. After considering ZPE, \( \text{CaYH}_{12} \)
starts to be thermodynamically stable at a lower pressure of about 106 GPa, which is lower than those required by CaH₆ and YH₆. Due to the uncertainty of low-pressure structures, we will center our next analysis in the higher-pressure range. From 170 to 400 GPa, the predicted Fd3m structure is the most stable one. Additionally, the ZPEs for the predicted structures at 150, 200, and 400 GPa were calculated within the quasiharmonic approximation. According to our calculations, the Fd3m structure remains as the most stable one.

It is very complicated to construct the complete phase diagram for ternary hydrides, which is also beyond the reach of the current study. However, we have checked the stability of CaYH₁₂ relative to other possible ternary hydrides with different ratios of CaH₆ and YH₆. As shown in Fig. S5, CaYH₁₂ is the most stable stoichiometry from 150 to 400 GPa. In addition, the current study also shows that there might exist other ternary hydrides with similar cubic structures, such as Ca₃YH₂₄, Ca₅Y₃H₄₈, and others.

As it is well known and has been experimentally observed, high temperature and high pressure usually promote the formation of hydrides with high H content and make them stable. Thus, under high temperature and high pressure, CaYH₁₂ might be synthesized from the experimentally available materials Ca + Y + H₂ or CaH₂ + YH₂ + H₂.

To explore the bonding information, we calculated the electron localization functions (ELFs) for the high-pressure structures of CaYH₁₂ [Fig. 2(a) and Fig. S6]. As shown in Fig. 2(a), the ELF values at the center of the shortest H-metal separations in the Fd3m structure are very low, showing there is no covalent bonding between them. The ELF values between hydrogen atoms are 0.64 and 0.56, indicating the existence of weak covalent bonds, which are consistent with those in Im3m CaH₆ and YH₆, respectively. As it is shown below, the difference in these ELF values comes from the different number of electrons accepted by the H-H bonds. One bond, marked with a black line (bond length of 1.18 Å and ELF value of 0.64), is adjacent to two Ca atoms and one Y, while the other one, marked with a dark green line (bond length of 1.26 Å and ELF value of 0.56), is close to one Ca atom and two Y. Subsequent Bader charge calculations show that each Ca and Y atom donates 1 and 1.4 electrons to H atoms at 200 GPa, respectively. Therefore, one Ca and two Y atoms transfer more valence electrons to the H-H unit than two Ca and one Y, which results in a longer bond length and smaller ELF values of the H-H bond. In addition, the results of the crystal orbital Hamilton population (Fig. S7) are consistent with the ELF calculations.

The calculated electronic band structures for the Fd3m CaYH₁₂, Im3m CaH₆, and YH₆ are shown in Fig. 2. There are many bands crossing the Fermi level steeply in Fd3m CaYH₁₂, which reveals its metallic character. Moreover, there are also some flatter bands near the Fermi energy, associated with more localized electronic states, which might help to enhance the electron-phonon interaction. Additionally, the electronic density of states (DOS) for both Fd3m and Pm3m CaYH₁₂ are shown in Fig. S8. Remarkably, hydrogen atoms have a large contribution to the DOS at the Fermi level, so that we might expect a strong electron-phonon interaction associated with hydrogen phonon modes.

To explore the superconductivity in CaYH₁₂, lattice phonons and EPC calculations were carried out for the Fd3m structure at 200 GPa (Fig. 3). We can clearly separate its phonon DOS into three regions. The low-frequency modes (0–8.5 THz) are associated with vibrations of heavy Y atoms, the intermediate-frequency branches (8.5–12.5 THz) are related to Ca atoms, and the high-frequency modes (12.5–56 THz) come mainly from H atoms. The calculated logarithmic average frequency ωₐ₀ is 1230 K and the EPC parameter λ is 2.2 (Fig. 3(c), which is higher than that in YH₆ (1.88 at 200 GPa) (Table S1). This large λ mainly comes from the EPC of H modes (82%), especially from the isolated soft modes between 15 and 35 THz. With increasing pressure, these soft modes become harder (Fig. S11(d)), while they are softened with decreasing pressure, until they become unstable below 170 GPa. When lowering the pressure the mechanical energy (PV) is not big enough to break the H₂ dimers, so that they can be formed and the predicted cage-like structures become gradually unstable. Interestingly, as can be seen in Fig. 3(a), besides the optical modes at around 35 and 52 THz at the Γ point, the soft modes between 15 and 35 THz show
to analyze the pressure dependence of demanding, we have considered the pressure. To calculate the Eliashberg spectral function is inversely proportional to the phonon frequency, and an increasing of $\omega_{\text{log}}$. As a result of these two effects, the calculated $T_c$ first increases with pressure and then decreases, reaching the highest value of 215 K at 200 GPa. Below 200 GPa, the value of $\lambda$ is so high that, as $T_c$ saturates with $\lambda$ for high values of $\lambda$, $\omega_{\text{log}}$ plays a major role on the evolution of $T_c$ with pressure. Therefore, for pressures below 200 GPa, $T_c$ follows the trend of $\omega_{\text{log}}$, so that it increases with pressure. However, above 200 GPa, $\lambda$ decreases with pressure and goes out of the saturation range, so that its evolution dominates over the increase of $\omega_{\text{log}}$ with pressure. Therefore, above 200 GPa, $T_c$ follows the trend of $\lambda$ and decreases with pressure.

It is important to note that our calculations were based on the harmonic approximation, and the soft modes in the phonon spectra of CaYH12 might be affected by anharmonic effects. Some studies, e.g., on AlH3 [54], PdH [55], and PtH [56], show that anharmonicity strongly renormalizes the phonon frequencies and suppresses the $\lambda$. However, anharmonicity seems to have little effect on the EPC of pure hydrogen [8] and even can enhance it [57]. More importantly, the LaH10 clathrate was predicted to be a good superconductor with a $T_c$ of 274–286 K at 210 GPa within the harmonic approximation [19], which is in good agreement with the recent experimental measurement of $T_c$, 250–260 K [25,26]. Actually, the high-pressure clathrate structure of CaYH12 and the phonon softening appearing in its phonon spectra are very similar to those of LaH10. Therefore, according to our calculations, we believe that CaYH12 is also a potential high-$T_c$ superconductor.

In summary, we have extensively investigated the crystal structures and superconductivity of ternary hydride CaYH12 under pressure. A cubic $Fd\bar{3}m$ structure is predicted to be stable above 170 GPa, where Ca and Y atoms together form a bcc lattice and hydrogen atoms adopt a clathrate structure, which retains the similar H-clathrate structures as $Im\bar{3}m$ CaH6 and YH6. Moreover, the estimated $T_c$ of cubic CaYH12 is even somewhat higher than those of CaH6 (201 K) [17] and YH6 (233 K) at 200 GPa with $\mu^*$ of 0.13.

Considering the similarities between $Fd\bar{3}m$ and $Pm\bar{3}m$ CaYH12 structures, and having in mind the complexity of the $Fd\bar{3}m$ structure makes the EPC calculations very time demanding, we have considered the $Pm\bar{3}m$ structure in order to analyze the pressure dependence of $T_c$. As it is shown in Fig. 4, the two main ingredients to estimate $T_c$, $\omega_{\text{log}}$ and $\lambda$, present an opposite trend with pressure: $\omega_{\text{log}}$ increases with pressure while $\lambda$ decreases. Actually, this behavior can be easily understood in terms of the evolution with pressure of the intermediate soft modes we have described above. With increasing pressure these soft modes become stiffer (Fig. S9 [45]), which induces both a lowering on $\lambda$, as the Eliashberg spectral function is inversely proportional to the phonon frequency, and an increasing of $\omega_{\text{log}}$. It is important to note that our calculations were based on the harmonic approximation, and the soft modes in the phonon spectra of CaYH12 might be affected by anharmonic effects. Some studies, e.g., on AlH3 [54], PdH [55], and PtH [56], show that anharmonicity strongly renormalizes the phonon frequencies and suppresses the $\lambda$. However, anharmonicity seems to have little effect on the EPC of pure hydrogen [8] and even can enhance it [57]. More importantly, the LaH10 clathrate was predicted to be a good superconductor with a $T_c$ of 274–286 K at 210 GPa within the harmonic approximation [19], which is in good agreement with the recent experimental measurement of $T_c$, 250–260 K [25,26]. Actually, the high-pressure clathrate structure of CaYH12 and the phonon softening appearing in its phonon spectra are very similar to those of LaH10. Therefore, according to our calculations, we believe that CaYH12 is also a potential high-$T_c$ superconductor.

In summary, we have extensively investigated the crystal structures and superconductivity of ternary hydride CaYH12 under pressure. A cubic $Fd\bar{3}m$ structure is predicted to be stable above 170 GPa, where Ca and Y atoms together form a bcc lattice and hydrogen atoms adopt a clathrate structure, which retains the similar H-clathrate structures as $Im\bar{3}m$ CaH6 and YH6. Moreover, the estimated $T_c$ of cubic CaYH12 is even somewhat higher than those of CaH6 (201 K) [17] and YH6 (233 K) at 200 GPa with $\mu^*$ of 0.13.

Considering the similarities between $Fd\bar{3}m$ and $Pm\bar{3}m$ CaYH12 structures, and having in mind the complexity of the $Fd\bar{3}m$ structure makes the EPC calculations very time demanding, we have considered the $Pm\bar{3}m$ structure in order to analyze the pressure dependence of $T_c$. As it is shown in Fig. 4, the two main ingredients to estimate $T_c$, $\omega_{\text{log}}$ and $\lambda$, present an opposite trend with pressure: $\omega_{\text{log}}$ increases with pressure while $\lambda$ decreases. Actually, this behavior can be easily understood in terms of the evolution with pressure of the intermediate soft modes we have described above. With increasing pressure these soft modes become stiffer (Fig. S9 [45]), which induces both a lowering on $\lambda$, as the Eliashberg spectral function is inversely proportional to the phonon frequency, and an increasing of $\omega_{\text{log}}$. As a result of these two effects, the calculated $T_c$ first increases with pressure and then decreases, reaching the highest value of 215 K at 200 GPa. Below 200 GPa, the value of $\lambda$ is so high that, as $T_c$ saturates with $\lambda$ for high values of $\lambda$, $\omega_{\text{log}}$ plays a major role on the evolution of $T_c$ with pressure. Therefore, for pressures below 200 GPa, $T_c$ follows the trend of $\omega_{\text{log}}$, so that it increases with pressure. However, above 200 GPa, $\lambda$ decreases with pressure and goes out of the saturation range, so that its evolution dominates over the increase of $\omega_{\text{log}}$ with pressure. Therefore, above 200 GPa, $T_c$ follows the trend of $\lambda$ and decreases with pressure.

It is important to note that our calculations were based on the harmonic approximation, and the soft modes in the phonon spectra of CaYH12 might be affected by anharmonic effects. Some studies, e.g., on AlH3 [54], PdH [55], and PtH [56], show that anharmonicity strongly renormalizes the phonon frequencies and suppresses the $\lambda$. However, anharmonicity seems to have little effect on the EPC of pure hydrogen [8] and even can enhance it [57]. More importantly, the LaH10 clathrate was predicted to be a good superconductor with a $T_c$ of 274–286 K at 210 GPa within the harmonic approximation [19], which is in good agreement with the recent experimental measurement of $T_c$, 250–260 K [25,26]. Actually, the high-pressure clathrate structure of CaYH12 and the phonon softening appearing in its phonon spectra are very similar to those of LaH10. Therefore, according to our calculations, we believe that CaYH12 is also a potential high-$T_c$ superconductor.

In summary, we have extensively investigated the crystal structures and superconductivity of ternary hydride CaYH12 under pressure. A cubic $Fd\bar{3}m$ structure is predicted to be stable above 170 GPa, where Ca and Y atoms together form a bcc lattice and hydrogen atoms adopt a clathrate structure, which retains the similar H-clathrate structures as $Im\bar{3}m$ CaH6 and YH6. More importantly, CaYH12 is energetically favored relative to CaH6 and YH6 within a certain pressure range. Electron-phonon coupling calculations show that the cubic $Fd\bar{3}m$ CaYH12 could be a high-$T_c$ superconductor, with the highest one among the already studied ternary hydrides. Our findings might provide a possible route to synthesize hydrides such as CaH6 and YH6, and will further stimulate more theoretical and experimental studies on high-$T_c$ superconductors in ternary hydrides.

The work was supported by National Natural Science Foundation of China (Grants No. 11604290 and No. 51732010), the Science Foundation for the Youth Top-notch Talent from Universities of Hebei Province (Grant No. B2017023), Funding Program for Recruited Oversea Scholars of Hebei Province (CL201729), and the Ph.D. Foundation by Yanshan University (Grant No. B970). 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).