I. INTRODUCTION

Exploration of superconductivity in materials at ever-increasing temperatures is a burgeoning research topic in condensed matter physics, chemistry, and materials science. Conventional electron-phonon coupling considerations point to compressed hydrogen-rich materials as excellent candidates for superconductors having high critical temperatures ($T_c$'s) due to the potential for formation of atomic hydrogen lattices in which the low mass leads to both high vibrational frequencies and strong electron-phonon coupling. As originally proposed by Ashcroft [1], this concept has inspired numerous studies (see Refs. [2–6] for reviews), specifically the recent progress on pressurized hydrides predicted and observed to have high $T_c$'s above 200 K in pursuit of superconductivity at, or even above, room temperature [7–22]. However, pressures in the megabar range (>100 GPa) are required to synthesize and stabilize the high-$T_c$ hydrides considered so far. For example, high-$T_c$ superconductivity was established above 170 and 166 GPa for clathrate metal hydrides LaH$_{10}$ and YH$_6$ [17,20], and near 155 and 267 GPa for $p$-block element hydrides H$_3$S and C-S-H [14,22], respectively, where the pressures are those of the reported $T_c$ maxima. Given the very high pressures required to create these high critical temperatures, the pursuit of high-$T_c$ superconductivity in hydrides that can persist in stable or metastable compounds at lower, and even ambient, pressure remains an important goal.

The stability of binary hydrides having potential superconducting $T_c$'s above 100 K has been largely limited to pressures above 100 GPa [23]. For example, synthesis of superhydride UH$_7$ has been reported at a low pressure of 31 GPa, but its $T_c$ is estimated to be 44 K [24,25]. The lowest pressures reported for stabilization of a superhydride include those of CeH$_9$ at 80 GPa [26] and BaH$_{12}$ at 75 GPa [27] for atomic and molecular-based hydrogen structures, respectively. Predictions of lower pressure stability of hydrogen-rich binary hydrides include that of RbH$_{12}$, which is calculated to be stable at 50 GPa with a $T_c$ near 115 K [23]. With the additional degrees of freedom made possible by expanding the chemical space available, ternary hydrides are receiving growing interest as means both to increase $T_c$ and to enhance stability over a broader range of pressures. As such, a $T_c$ of 287 K has been reported in a C-S-H mixture at about 267 GPa, while
the structure and composition for the high-$T_c$ phase remain under study [22]. Theoretical calculations predict that hydride perovskite structures based on the above elements could be a route to stabilizing lower pressure hydride superconductors, for example, by sublattice replacement of SH$_3$ with CH$_4$ in H$_2$S to produce structures of composition CSH$_2$ with predicted dynamical stability, and therefore kinetic stability, at lower pressures than that of pure H$_2$S [28,29]. Lower level CH$_4$ substitution in the material, either as stoichiometric compounds or doped structures, could enhance low-pressure stability, as well as significantly enhance $T_c$ as recently predicted for the C-S-H superconductor [30]. These results further suggest that ternary hydride systems may be a useful venue for discovering high-$T_c$ superconductors at low pressures.

Metal hydrides having clathrate and related structures (e.g., MgH$_6$, CaH$_6$, YH$_6$, LaH$_{10}$, and H$_2$S) [7–10,12,13] have been predicted, and in several cases now observed, to have high-$T_c$ values that are higher than those with higher H content, such as MgH$_{12}$ and MgH$_{16}$ [31]. This trend arises from the different molecules accept electrons, inducing dissociation to form a monoatomic and metallic structure in which there is an increase in the H contribution to the electronic states around the Fermi level and increasing the critical temperature. Therefore, the presence of atomic H in the structure is an important feature of high-$T_c$ superconductivity of hydrides.

Theoretical studies indicate that adding Li and Ca to the B-H binary stabilizes phases that accommodate more atomic H atoms, leading to ternary hydrides with higher $T_c$’s relative to those found for B-H phases [32–36]. Given its larger ionic radius at ambient pressure, La can accommodate more atomic H (e.g., as a superhydride) compared to Li and Ca [12]. Therefore, the stable phases with higher H content might be obtained in the La-B-H system under pressure. Moreover, a recent experimental study reported evidence for superconductivity at and above room temperature in La-hydride samples upon thermal annealing [37]. Given that ammonia borane (NH$_3$BH$_3$) was used as a hydrogen source, the formation of La-H phases containing boron was suggested as giving rise to the high $T_c$ [17,37].

In this paper, we examine theoretically high-pressure structures, stability, and superconducting properties of stoichiometric La-B-H phases, with a focus on lower pressure stability. Detailed study of phases with composition LaBH$_{x}$ (x = 1–10) and La(BH$_4$)$_{y}$ (x = 1–5) reveals intriguing H-rich LaBH$_4$ (Pm3m) and LaB$_5$H$_8$ (Fm$ar{3}$m) structures containing BH$_4$ and BH$_8$ units, respectively. Moreover, LaBH$_4$ and LaB$_5$H$_8$ are dynamically stable at pressures as low as 109 and 48 GPa, with predicted $T_c$’s of 93 and 156 K at 110 and 55 GPa, respectively. Our results indicate that continued exploration of ternary hydrides in these and related chemical systems may be an effective route to realizing a high-temperature superconductivity at lower, or even ambient, pressure.

II. COMPUTATIONAL DETAILS

The structure searches of La-B and La-B-H system were performed under pressure using the particle swarm optimization technique implemented in the CALYPSO code [38,39]. The structural relaxations and electronic properties were calculated using density functional theory with the Perdew-Burke-Ernzerhof generalized gradient approximation as implemented in the VASP code [40,41]. The ion-electron interaction was described by projector-augmented-wave potentials, where 5s$^2$5p$^5$5d$^1$6s$^2$, 2s$^2$2p$^4$, and 1s$^1$ configurations were treated as valence electrons for La, B, and H atoms, respectively [42]. Plane wave kinetic energy cutoff was set to 700 eV and corresponding Monkhorst-Pack (MP) k-point meshes for different structures were adopted to ensure that the enthalpy converges to 1 meV/atom. Phonon calculations were performed by using the supercell method or density functional perturbation theory (DFPT) with PHONOPY [43] and Quantum-ESPRESSO codes [44], respectively. Electron-phonon coupling (EPC) calculations were carried out with the Quantum-ESPRESSO code using ultrasoft pseudopotentials for all atoms. We adopted a kinetic energy cutoff of 60 Ry.

Before investigating the phase stability of ternary La-B-H compounds under pressure, we first assessed information about the La-H, B-H, and La-B binaries. The high-pressure behavior of the B-H [34–36] and La-H [12,13,45–47] binaries has been well-studied in recent years, whereas information on the La-B system under pressure is lacking. We therefore performed structure-search calculations for La$_n$B$_m$ (n = 1, m = 1–8; n = 2, m = 1) with system sizes containing up to 4 or 8 formula units (f.u.) per simulation cell at pressures of 0–300 GPa. To identify the stability of different stoichiometries, convex hulls were constructed by calculating the formation enthalpies for predicted La$_n$B$_m$ structures relative to the elemental La and B (Fig. S1 within the Supplemental Material, SM [48]). All the stoichiometries were found to have negative formation enthalpies within 0–300 GPa, showing that they are thermodynamically stable with respect to decomposition into La and B elements. The increase in formation enthalpy indicates that the stability of the phase decreases with increasing pressure; in addition, a stoichiometry located on the hull is stable with respect to other binary compounds, otherwise it is metastable. At 1 atm and 10 GPa, the experimentally observed LaB$_4$ and LaB$_5$ were predicted to be stable, which confirms the reliability of our method. At 50 GPa, with exception for LaB$_4$ and LaB$_5$, a new stoichiometry LaB$_7$ is also located on the convex hull. With increasing pressure to 100 GPa, we found that LaB$_4$, LaB$_5$, and LaB$_6$ are stable, while LaB$_5$ was predicted to possibly decompose into LaB$_5$ + LaB$_6$. At 200 GPa, only LaB$_4$ and LaB$_5$ remain on the convex hull, and LaB$_5$ has the lowest formation enthalpy. At 300 GPa, LaB$_5$ remains stable, and LaB becomes metastable. The predicted stable structures of La-B compounds under pressure are shown in Fig. S2 [48]. In R$_3$m-LaB, B atoms form graphene-like layers. With increasing B content, the B atoms are apt to form polyhedral configurations with decahedra in...
Cmmm-LaB₄, octahedra in P4/mmm-LaB₅ and octadecahedra in R3m-LaB₈, respectively.

Calculated La-B-H ternary phase diagrams at 100–300 GPa are presented in Fig. 1. All the ternary hydrides are stable relative to dissociation into elements at the pressures studied. Moreover, all the ternary hydrides LaBH₈ studied have lower enthalpies than those of LaB and H₂, suggesting that they are stable against decomposition into LaB and H₂ (Fig. S3 within the SM [48]). We note that LaBH, LaBH₄, LaBH₆, La(BH₄)₂, and La(BH₄)₃ fall on the 3D convex hull at 100 GPa, indicating that they are also stable phases with respect to decomposition into binary and other ternary phases. At 150 GPa, an additional composition, LaBH₇, appears on the convex hull. With further increase in pressure to 200 GPa, the originally stable LaBH, LaBH₆, and La(BH₄)₂ are predicted to decompose into other compounds, and the higher H content LaBH₈ begins to become stable. At 300 GPa, the formation enthalpy of LaBH₈ is increasingly negative. LaBH₇ becomes metastable phases with higher enthalpies relative to 1/4 LaBH₄ + 3/4 LaBH₈. To determine accurate stability pressures, we also plot the specific enthalpy curves of LaBH₄, LaBH₆, LaBH₇, and LaBH₈ relative to other compounds (Fig. S4 within the SM [48]). After including zero-point energy corrections (Fig. S5 within the SM [48]) [49], we found that LaBH₄ remains thermodynamically stable in a P2₁/m structure within the entire pressure range studied. C2/c-LaBH₆ is stable below 134 GPa. For LaBH₇, the P3m1 structure is predicted to become stable against dissociation into other stoichiometries at pressures of 103–233 GPa. LaBH₈ is predicted to crystallize in the cubic Fm3m structure, which is stable relative to LaBH₇ and H₂ above 161 GPa.

More recently, Cataldo et al. [50] reported simulations of the structure, superconductivity, and stability of LaBH₆.

Although the results are largely consistent with our results, several differences should be noted. First, Cataldo et al. predicted that F43m-LaBH₃ and Fm3m-LaBH₈ are thermodynamically stable compositions at 100 and 110 GPa, respectively. On the other hand, we find that F43m-LaBH₃ and Fm3m-LaBH₈ are thermodynamically unstable with respect to decomposition into LaBH₇ + LaBH₆ and LaBH₆ + H₂ at 100 and 110 GPa, respectively. Relative enthalpy-pressure curves for LaBH₅ are shown in Fig. S6 within the SM [48]. Second, we found additional stoichiometries (LaBH, LaBH₄, and LaBH₆) to be stable at 100 GPa that were not mentioned in Ref. [50]. In addition, we explored systematically the crystal structures of different stoichiometries and their stability at different pressures. Stable pressures of the predicted La-B-H compounds were determined that will provide clear guidance for experiments, including specific composition and structure information. Pressure favors the formation of more H-rich compounds in the La-B-H system, e.g., with LaBH₅, LaBH₆, LaBH₇, and LaBH₈, increasing stable under pressure. Finally, we point out interesting structural trends among the La-B-H system are associated with this increase in H content. Specifically, the H atoms gradually bond with the surrounding B atoms, changing from BH units in LaBH₃ and LaBH₄ to BH₁ in LaBH₆, BH₆ in LaBH₇, and eventually BH₈ units in LaBH₈.

The predicted stable structures of the LaBH₄ system are shown in Fig. 2. LaBH adopts the hexagonal P6/mmm structure, in which B atoms form honeycomb sheets and B, La, and H atomic layers are alternately arranged. In LaBH₃ and LaBH₄, zigzag B chains stretch along specific directions while B atoms are surrounded by H atoms to form covalent bonds. Since more H atoms are filled in the adjacent four H atoms. With the increasing H content of LaBH₇, each B atom accommodates six H atom to form BH₆ units. The BH₆ groups are located on the vertices and edges of the hexagonal structure, with the BH₆ units distributed on the edges connected to each other by H atoms. The H-rich LaBH₈ assumes a high-symmetry Fm3m structure in which B atoms accommodate all the H atoms to form BH₈.
covalent units that occupy the octahedral interstices of the face-centered cubic (fcc) lattice formed by La atoms. In H3S, the S atoms located on a body-centered cubic lattice with each S atom covalently bonded to the surrounding six H atoms. The H atoms in LaBH8 are found to bond with B in a manner that is similar to that of S in H3S [51]. In addition, the atomic positions of La and eight H atoms in LaBH8 are the same as those of La and eight of the H atoms in LaH10. Given the high Tc of H3S and LaH10, this similarity in bonding and high symmetry structure suggests interesting superconducting properties of LaBH8 as well. The enthalpy curves and predicted stable structures of La(BH)4 and La(BH)3 are shown in Fig. S7 within the SM [48]. P1-La(BH)4 is stable between 100–265 GPa and transforms to a Cm structure above 265 GPa. In P1-La(BH)3, B atoms bond to each other forming layered structures composed of 4- and 10- membered rings and H atoms locate between layers to bond with the surrounding B atoms. Cm La(BH)3 is an open-framework structure formed by B and H atoms with La-filled channels along the crystallographic b axis. La(BH)3 is stable in the Cm structure between 100 and 150 GPa, where B atoms form chains and bond with surrounding H atoms. As a result, the remaining H atoms adopt the form of H2 units. In addition, several metastable structures are also predicted as shown in Fig. S8 within the SM [48].

At 100 GPa, the F43m structure was predicted to have the lowest enthalpy in LaBH5, although it is metastable relative to other stoichiometries. As the pressure decreases to 50 GPa, the structure tends to become stable. As shown in Fig. S9 within the SM [48], F43m-LaBH5 is constructed by fcc lattices formed by La atoms with BH4 units and H atoms located on the octahedral and tetrahedral interstices respectively. C2/c-LaBH6, which is stable at higher pressures, has a similar structure to F43m-LaBH5 but a little distorted, with more individual H atoms in the lattice. In LaBH6, a low-symmetry P21/m structure is thermodynamically more favorable than the Fm3m structure below 154 GPa, where B atoms bond with seven H atoms forming BH3 units. Under pressure, this structure will transform into more densely packed Fm3m structure with BH4 units. This low-pressure P21/m structure can be viewed as the distorted Fm3m structure. The La and B atoms always maintain NaCl-type structure in F43m-LaBH5, C2/c-LaBH6, P21/m-LaBH6, and Fm3m-LaBH6, showing that pressure has less effect on the La-B bonding. Moreover, these H-rich compounds have common structural features of B-H units, and the number of H atoms bonded to B increases with increasing pressure. To investigate the thermodynamic stability mechanism of Fm3m-LaBH6, we calculated the internal energies (U) and the pressure-volume (P-V) contributions to the enthalpy relative to LaBH7 + H2 and P21/m-LaBH8 (Fig. S10 within the SM [48]). The P-V term of Fm3m-LaBH6 is always lower than those of LaBH7 + H2 and P21/m-LaBH8, while U is opposite, showing that denser structure of cubic Fm3m-LaBH6 is the key factor for its stability.

Lattice dynamics calculations were carried out for the phases in the pressure ranges of their predicted thermodynamic stability. The lack of imaginary frequencies in the calculated phonon dispersion curves indicates that all structures are dynamically stable within the harmonic approximation (Figs. 5 and S11 within the SM [48]). On the other hand, phonon softening is evident for LaBH7 and LaBH8, an effect that can enhance the EPC [12]. With decreasing pressure, these phonon modes further soften and eventually have imaginary frequencies. Figure S12 within the SM [48] shows the frequency of the softest mode as a function of pressure. In contrast to LaH10, however, LaBH7 and LaBH8 maintain dynamical stability to pressures as low as 109.2 and 48.3 GPa, respectively, the latter being much lower than that predicted for other H-rich hydride superconductors.

To understand the origin of relatively low-pressure stability of P3m1-LaBH7 and Fm3m-LaBH8, we explored the bonding of these structures by calculating the electron localization function (ELF) [52,53] and Bader charge transfer [54] among atoms. ELFs with an isosurface of 0.6 are shown in Figs. 3(a) and 3(b) for the two phases at 110 and 55 GPa, respectively. Electron density at the La atoms is due to their inner valence shells. Many electrons are clearly localized between B and H atoms and closer to the H atoms. The ELF slice in the (1 1 0) plane containing La, B, and H atoms for LaBH7 and LaBH8 [Fig. 3(c)] also shows that the ELF values between B and H atoms gradually increase toward H atoms, suggesting the polar covalent character of the B-H bond. For comparison, we calculated the ELF of the well-known hydrogen storage material LiBH4 at 1atm (Fig. S13 within the SM [48]), which contains a strong BH4 covalent unit. The ELFs around B and between B and H atoms in LaBH7 and LaBH8 are similar to those in LiBH4. As shown in Fig. S9 within the SM [48], the bond lengths of the B-H bonds in La-B-H compounds are comparable to those of 1.23 Å in LiBH4 at 1 atm. Moreover, similar results were also found in Inm3m-H3S [7]. In LaBH7, atom H2 appears to form a covalent bond to H1 with an ELF value of 0.64 connecting BH4 units on the edges. In both phases, the ELF values at the center of the shortest La-H and La-B are below 0.3, indicative of an ionic character between La and B-H units.

To provide a deeper insight into the bonding, we calculated the Crystal Orbital Hamilton Population (COHP) and its...
integration ICOHP [55–57] projected onto B-H and H-H pairs in LaBH$_7$ and LaBH$_8$ at different pressures, and H-S bonds in H$_3$S at 200 GPa for comparison. Positive and negative -COHP indicate bonding and antibonding interactions, respectively. The ICOHP up to the Fermi level can describe the atom pair interaction strength. Figure S14 within the SM [48] clearly shows there are strong B-H bonding states below the Fermi level in LaBH$_7$ and LaBH$_8$, which are similar to the case of H-S in H$_3$S. The H1-H2 interaction in LaBH$_7$ is weak and mainly distributed around 10 eV below the Fermi energy, while the interaction strength of H2-H3 in LaBH$_7$ and H-H in LaBH$_8$ are negligible, which suggests that the H-H bond will not play a major role in structural stability and properties. The -ICOHP at the Fermi level increases with pressure, which indicates the enhancement of the B-H interactions. At 200 GPa, the calculated -ICOHP between B and H atoms at Fermi level are 3.34 and 3.18 in LaBH$_7$ and LaBH$_8$, values that are comparable to that of 3.50 between S and H in H$_3$S, indicating the H atoms in LaBH$_7$ and LaBH$_8$ bond with B in a manner as H-S in H$_3$S.

Bader charge calculations show that electrons transfer from La and B to H atoms. In LaBH$_7$, each La atom and B atom located on the vertex and edge of the lattice loses 1.44, 1.37, and 1.16 electrons, respectively. Correspondingly, each H atom in BH$_6$ at the vertex (H3) and edge (H1) accepts 0.45 and 0.39 electrons, respectively. The H atom (H2) that only bonds with a H atom gets 0.15 electrons. The existence of the H1-H2 covalent bond weakens the B-H1 bond connected to it. In LaBH$_8$, each La and B atom transfers 1.47 and 1.04 electrons to eight H atoms, respectively. With increasing pressure, the number of electrons transferred by La and B atom decreases and increases, respectively. Fm$ar{3}$m-LaBH$_8$ possesses the same fcc lattices composed by La atoms as in Fm$ar{3}$m-LaH$_{10}$. The difference is that B and H atoms form strong covalent bonds in LaBH$_8$, while the H atoms in LaH$_{10}$ are connected by weak covalent bonds forming a cage structure. At 200 GPa, the calculated -ICOHP for the B-H bond in LaBH$_8$ is 3.18, which is much higher than 0.17 for the H-H bond, revealing strong interactions between B and H atoms in LaBH$_8$. The calculated -ICOHP for H-H pairs in LaH$_{10}$ (Fig. S15 within the SM [48]) is 1.6, showing weak covalent bonds. By analyzing the eigenvectors of soft modes for LaBH$_8$ and LaH$_{10}$, it is found that their structural stabilities are mainly associated with the vibrations of the B-H and H-H bond, respectively (Fig. S16 within the SM [48]). With decreasing pressure, the distance between atoms becomes longer and the interactions weaker, which eventually leads to a structural instability and phase transition (Fig. S17 within the SM [48]) [12,45]. The results indicated that the B-H bonds in LaBH$_8$ are much stronger than H-H interactions in LaH$_{10}$, and the B and H atoms can maintain a bonding interaction over large pressure range. Therefore, the strong interactions between B and H atoms play an important role in determining its relatively low-pressure dynamical stability.

We further investigated the electronic properties of the stable structures found in the La-B-H system. The calculated electronic density of states (DOS) for P6/mmm-LaBH, Pmmm-LaBH$_3$, P2$_1$/m-LaBH$_4$ and C2/c-LaBH$_6$, within their ranges of pressure stability are shown in Fig. S18 [48]. The electronic DOS at the Fermi level indicates that they are all metallic. P6/mmm-LaBH, Pmmm-LaBH$_3$, and P2$_1$/m-LaBH$_4$ all have relatively high DOS values at the Fermi level. However, this metallicity is mainly derived from the contribution of La and B atoms: there is a negligible H contribution to the DOS at Fermi level, which is unfavorable to superconductivity. In C2/c-LaBH$_6$, the Fermi level falls at the valley of the electronic DOS, showing poor metallicity.

We focused on the H-richer LaBH$_7$ and LaBH$_8$ compounds. Figure 4 illustrates the calculated electronic band structures, DOS and Fermi surface of P3$_3$m1-LaBH$_7$ and Fm$ar{3}$m-LaBH$_8$ at 110 and 55 GPa, respectively. They are the metallic phases with some bands crossing the Fermi level. In LaBH$_7$, a flat band with more localized electronic states appears near the Fermi level at the $\Gamma$ point, which might enhance the electron-phonon interactions. Flat-steep band features are beneficial for superconductivity [58]. As such, the steep and flat bands are found for LaBH$_8$ along the $\Gamma$-X and X-W directions near the Fermi level, respectively. According to the calculated ELFs, the distributions of ELF between H2 and H3 in LaBH$_7$ and H atoms in neighboring BH$_8$ units in LaBH$_8$ can be seen as the picture of two tangent circles, respectively. The ELF values decrease gradually from the center of one atom to the middle point of the two atoms. Therefore, we roughly considered half of the distance between H2 and H3 in LaBH$_7$ and H atoms in neighboring BH$_8$ units in LaBH$_8$ as the H projected radius for the projected DOS calculations. The results show that the contribution of H atoms to the DOS at
the Fermi level exceeds that of La and B atoms in LaBH$_7$, and the metallicity are dominated by H atoms in LaBH$_5$, which suggest that $P3m1$-LaBH$_7$ and $Fm3m$-LaBH$_5$ may be high-$T_c$ superconductors. Both the Fermi surfaces of $P3m1$-LaBH$_7$ and $Fm3m$-LaBH$_5$ are composed of three sheets and one of them is an electron-like ellipsoid and polyhedron around the $\Gamma$ point, respectively. In LaBH$_5$, one Fermi surface sheet is like a tube along the $\Gamma$-$A$ direction and the other is distributed in a large outer region of the Brillouin zone. In LaBH$_7$, with the exception of a cross-like sheet, there are small electron and hole pockets at $L$ and $X$ point, respectively.

Given their promising electronic properties, we calculated the superconducting properties of LaBH$_7$ and LaBH$_8$. We calculated their phonon spectra, projected phonon DOS, Eliashberg phonon spectral function $\alpha^2 F(\omega)/\omega$ and integral $\lambda(\omega)$ for the two phases at 110 and 200 GPa, respectively [Figs. 5(a) and 5(b)]. Similar to the hydrides studied previously, the projected phonon DOS can be separated into three regions. The La atom with the heaviest atomic mass dominates the low-frequency region, whereas the vibrations of the B and H atoms are associated with the mid- and high-frequency phonon branches, respectively. The spectral function $\alpha^2 F(\omega)/\omega$ for LaBH$_7$ is mainly distributed below 30 THz, especially between 8–15 THz [Fig. 5(a)], which results in an EPC constant $\lambda$ of 1.46 at 110 GPa. However, the value of the phonon DOS between 8–15 THz is negligible. Further analysis reveals a soft mode in this frequency range with a potentially large EPC contribution. The distribution of the EPC strength on the different phonon modes are also plotted with the spectra. The soft mode associated to H atoms below 20 THz around the $M$ point shows a quite large EPC. Similarly, for LaBH$_5$, the calculated EPC $\lambda$ is 0.72 at 200 GPa, and the contribution to $\lambda$ of the vibrations related to H atoms above 30 THz accounts for 83% of the total value. The soft mode near 30 THz at $\Gamma$ point makes an important contribution to the EPC. Previous studies of related superconducting hydrides indicate that the total EPC may be enhanced by further phonon softening induced by decompression toward the structural instability predicted by this harmonic approximation of the lattice dynamics [7,12]. Calculations for LaBH$_5$ indicate that $\lambda$ increases to 1.97 and 2.29 near its predicted instability at 55 [Fig. 5(c)] and 50 GPa (Fig. S19 within the SM [48]), which are comparable with the value of 2.19 found for H$_3$S at 200 GPa. As discussed above, our results show that the interaction between B and H atoms is stronger than that between H atoms in LaBH$_5$. The contribution to the strong EPC at 55 GPa arising from soft modes (5–20 THz) is about 59%, which is mainly associated with the vibrations of B-H and H-H [Fig. 5(c)].

We adopted the Allen-Dynes modified McMillan equation to estimate the $T_c$ of $P3m1$-LaBH$_7$ and $Fm3m$-LaBH$_5$ at different pressures (Table I) [59]. For LaBH$_7$, the calculated $\lambda$ and phonon frequency logarithmic average $\omega_{\text{avg}}$ is 1.46 and 837 K at 110 GPa, leading to a $T_c$ of 93 K with $\mu^* = 0.1$. As pressure decreases from 200 to 100, 55, and 50 GPa, the calculated $\lambda$ for LaBH$_5$ increases from 0.72 to 1.11, 1.97, and 2.29, whereas $\omega_{\text{avg}}$ decreases from 1557 to 1189, 807, and 692 K. As a result of these two effects, the calculated $T_c$ first increases from 58 to 115 K and then decreases to 108 K assuming $\mu^* = 0.1$, which follows the trend of $\lambda$ and with pressure, respectively. Since the $\lambda$ of LaBH$_5$ at 55 and 50 GPa are much greater than 1.5, the accuracy of $T_c$ values was improved by considering the strong-coupling and the shape corrections ($f_1$ and $f_2$). The estimated $T_c$ values are 139 and 138 K with $\mu^* = 0.1$. By numerically solving the Eliashberg equation [60], the $T_c$’s increase a little, becoming 156 and 154 K, respectively.

IV. CONCLUSIONS

Density functional theory-based structure-search calculations have identified seven phases in the ternary La-B-H system at pressures of 100–300 GPa that are potential targets for experimental synthesis. Most significant are the predictions of stability of H-rich $P3m1$-LaBH$_7$ at 103–223 GPa and $Fm3m$-LaBH$_5$ above 161 GPa, with the latter calculated to be dynamically stable as low as 48 GPa. Structural trends among these phases are observed as the H content increases. In LaBH$_5$, the B atoms form graphene-like layers, whereas in LaBH$_7$ and LaBH$_4$, the B atoms not only bond with each other to form zigzag chains, but bond with H atoms. In LaBH$_5$ and LaBH$_7$, there are no B-B bonds and B atoms are coordinated by Hs to form BH$_4$ and BH$_6$ units. LaBH$_5$ is stable in the high-symmetry $Fm3m$ structure, in which the B atoms accommodate all the H atoms to form BH$_8$ units. The La
atom acts as an electron donor in the structures to stabilize the higher H content B-H units. Moreover, EPC calculations show that LaBH$_7$ and LaBH$_8$ are potential superconductors. Softening of phonons dominated by H-atom vibrations in these structures makes a large contribution to superconductivity. The estimated $T_c$ of LaBH$_7$ is 93 K at 110 GPa, whereas the $T_c$ of LaBH$_8$ is calculated to be as high as 156 K at 55 GPa. The expanded range of dynamical stability to low pressures together with its predicted relatively high $T_c$ make $Fm\bar{3}m$-LaBH$_8$ a promising candidate superconductor for low-pressure stabilization experiments. Similar results for LaBH$_8$ were reported during the preparation and submission of this paper [50,61,62]. Additional chemical substitution of these phases could be used to enhance both $T_c$ (e.g., by electron or hole doping) or structural stability at still lower pressures. Additional theoretical work could explore potential anharmonic and quantum effects on the stability and the calculated critical temperatures [45,46,63]. The present paper is thus expected to stimulate further research on ternary and more complex superconducting hydrides with high critical temperatures and expanded ranges of stability.

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TABLE I. The calculated electron-phonon coupling parameter $\lambda$, phonon frequency logarithmic average $\omega_{\log}$ and critical temperature $T_c (\mu^* = 0.1-0.13)$ from Allen-Dynes modified McMillan, McMillan with the strong-coupling and the shape corrections ($f_1$ and $f_2$) and Eliashberg equations for $P\bar{3}m1$-LaBH$_7$ and $Fm\bar{3}m$-LaBH$_8$.

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$\lambda$</th>
<th>$\omega_{\log}$ (K)</th>
<th>$T_c$ (K) McMillan $\mu^* = 0.1-0.13$</th>
<th>$T_c$ (K) McMillan ($f_1$ and $f_2$) $\mu^* = 0.1-0.13$</th>
<th>$T_c$ (K) Eliashberg $\mu^* = 0.1$</th>
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<td>LaBH$_7$ ($P\bar{3}m1$)</td>
<td>110</td>
<td>1.46</td>
<td>837</td>
<td>93–85</td>
<td></td>
</tr>
<tr>
<td>LaBH$_8$ ($Fm\bar{3}m$)</td>
<td>200</td>
<td>0.72</td>
<td>1557</td>
<td>58–45</td>
<td></td>
</tr>
<tr>
<td>LaBH$_7$ ($Fm\bar{3}m$)</td>
<td>100</td>
<td>1.11</td>
<td>1189</td>
<td>96–84</td>
<td></td>
</tr>
<tr>
<td>LaBH$_8$ ($Fm\bar{3}m$)</td>
<td>55</td>
<td>1.97</td>
<td>807</td>
<td>115–107</td>
<td></td>
</tr>
<tr>
<td>LaBH$_8$ ($Fm\bar{3}m$)</td>
<td>50</td>
<td>2.29</td>
<td>692</td>
<td>108–102</td>
<td></td>
</tr>
</tbody>
</table>


[48] See Supplemental Material at http://link.aps.org supplemental/10.1103/PhysRevB.104.134501 for formation enthalpies per atom of La,Bn and LaBH4 (x = 1–10) at 100–300 GPa, the predicted stable structures of La-B system under pressure, relative enthalpy-pressure curves for LaBH4, LaBH6, LaBH7, and LaBH8 relative to the corresponding binary hydrides as a function of pressure without and with zero-point energy, the enthalpy curves of structures for LaBH4 relative to other ternary La-B-H compounds as a function of pressure, the enthalpy curves and predicted stable structures of La(BH)3 and La(BH)4, crystal structures of several predicted metastable La-B-H compounds, crystal structures of F43m-LaBH4, C2/c-LaBH6, P21/m-LaBH8, and Fm3m-LaBH8, calculated internal energies U and PV components of the enthalpy of the Fm3m-LaBH8, phonon dispersion relations for the predicted stable structures at different pressures, the calculated frequency of the softest mode of LaBH4 and LaBH6 as a function of pressure, calculated ELF of Pmna LiBH4 and Im3m-H3S, the calculated COHP and its integration ICOHP for B-H and H-S in H3Sa, different distances as a function of pressure for LaBH4, LiBH4, and LaBH10, the calculated B-H, H-H distances as a function of pressure for LaBH4, LiBH4, and LaBH10, electronic density of states (DOS) of predicted stable LaBH4, LaBH6, LaBH8, and LaBH10 at their stable pressures, superconductivity of LaBH4 at 50 GPa, detailed structural parameters of the predicted La-B compounds and La-B-H ternary hydrides.


