Prediction of High-$T_c$ conventional Superconductivity in the Ternary Lithium Borohydride System

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We investigate the superconducting ternary lithium borohydride phase diagram at pressures of 0 and 200 GPa using methods for evolutionary crystal structure prediction and linear-response calculations for the electron-phonon coupling. Our calculations show that the ground state phase at ambient pressure, LiBH$_3$, stays in the $Pnma$ space group and remains a wide band-gap insulator at all pressures investigated. Other phases along the 1:1:x Li:B:H line are also insulating. However, a full search of the ternary phase diagram at 200 GPa revealed a metallic Li$_2$BH$_6$ phase, which is thermodynamically stable down to 100 GPa. This superhydride phase, crystallizing in a $Fmar{3}m$ space group, is characterized by six-fold hydrogen-coordinated boron atoms occupying the $fcc$ sites of the unit cell. Due to strong hydrogen-boron bonding this phase displays a critical temperature of $\sim 100$ K between 100 and 200 GPa. Our investigations confirm that ternary compounds used in hydrogen-storage applications are a suitable choice for observing high-$T_c$ conventional superconductivity in diamond anvil cell experiments, and suggest a viable route to optimize the critical temperature of high-pressure hydrides.

The pioneering prediction of N.W. Ashcroft that hydrogen, the lightest among all elements, could become a high-temperature (high-$T_c$) superconductor at high pressures, can be seen as the foundation of high-pressure superconductivity research$^1$. Hydrogen has long been subject to comprehensive theoretical and experimental investigations,$^1$–$^8$ since it is expected to contain many fascinating properties, including a superconductor to superfluid phase transition.$^9$ In January 2017, Dias and Silvera reported its metallization in a diamond anvil cell under a static pressure of 495 GPa$^{10}$. The heated discussion that this claim has initiated among the experts testifies the relevance and the high actuality of this topic$^{11,12}$. Besides pure hydrogen, it has been demonstrated that also metallic hydrides can become high-$T_c$ superconductors at much lower pressures than those required to metallize hydrogen. Impurities in the hydrogen matrix can influence the bonding properties, and cause a chemical precompression on the H atoms$^{13}$–$^{15}$. This idea has led to the prediction of novel high-pressure hydrides, with remarkable superconducting transition temperatures. The coronation of this predictions was the experimental discovery of SH$_3$, with critical temperatures as high as 203 K at 200 GPa$^{16}$–$^{18}$. In addition to being the current record-holder for superconductivity, SH$_3$ is the first example of a completely unknown compound predicted from first principles. A few months after SH$_3$, high-$T_c$ superconductivity was reported in a second superconducting hydride, PH$_3$$^{19}$–$^{22}$. Besides these two known examples, other hydrides have been predicted to superconduct above liquid nitrogen temperature,$^{14,23}$–$^{28}$ but, in general, the $T_c$’s of binary hydrides are quite scattered and only a few of them surpass the liquid nitrogen threshold.$^{29}$

SH$_3$ has been the object of several $ab$-initio studies, which have established that its record-high $T_c$ is a consequence of high electron-phonon ($ep$) matrix elements enabled by the strong hydrogen-sulfur bonds, electronic van-Hove singularities at the Fermi level, and large vibrational frequencies of the hydrogen modes accompanied by large anharmonic effects$^{18}$, $30$–$37$. The first two aspects are intrinsically related to the $Imar{3}m$ high-pressure structure of SH$_3$, which is a typical example of forbidden chemistry, i.e. a behavior, which typically occurs at high pressures, that defies the usual rules of chemistry. In this structure sulfur forms three $90^\circ$ covalent bonds with hydrogen, which couple strongly to phonons. It has been shown that in binary hydrides the formation of metallic covalent bonds, conducive to high-$T_c$ superconductivity, requires elements with electronegativities close to hydrogen.$^{21,30,31}$ It is conceivable that also other atomic properties, such as valence, atomic radii, etc could have an influence on the high-pressure superconducting behavior of hydrides. Understanding how these properties could be tuned to increase the maximum critical temperatures or decrease the pressure needed to induce high-$T_c$ superconductivity represents a major step forward for the design of better superconductors.

Hydrogen storage research has shown that complex (ternary or higher) hydrides often exhibit improved performances compared to simple hydrides, because by controlling the chemical composition it is possible to improve independently different properties, such as hydrogen density and activation barriers. The same flexibility could be exploited to improve the superconducting behavior at high pressures, for example acting independently on the doping level and on the bonding characteristics to lower the metallization pressure or increase the maximum $T_c$.

Given the large number of ternary hydrides, identifying suitable systems experimentally by trial and error is unfeasible. On the other hand, $ab$-initio methods for crystal structure prediction and thermodynamics, which led to the successful prediction of SH$_3$, $^{18}$ can also be applied to multinary phase diagrams. The phase space and, consequently, the computational cost are much larger as compared to binary hydrides. Therefore, it is not surprising that, although a few examples of $ab$-initio studies of
the phase diagrams of complex hydrides at ambient pressure can be found in literature.\textsuperscript{39} to our knowledge there are no examples of similar studies for superconductivity at high pressures.

In this work, we explore \textit{ab-initio} the high-pressure superconducting phase diagram of a prototypical ternary system, lithium-boron-hydrogen, combining methods for evolutionary crystal structure prediction with linear-response calculations of the electron-phonon (ep) coupling.\textsuperscript{40,41} Our aim is to identify prospective high-\(T_c\) superconductors at high pressures. We show that an accurate sampling of the whole phase diagram is needed to identify the high-\(T_c\) superconducting phases, because these are found for compositions that are not \textit{obvious} in the sense that will be discussed below.

The lithium-boron-hydrogen system is very well characterized at ambient pressures, because the ground-state lithium borohydride (LiBH\(_4\)) is one of the best materials for hydrogen storage applications. This compound combines a weak (Li) and a strong (B) hydrogen former, and this permits to have at the same time a high hydrogen density and a reasonable activation barrier for hydrogenation and dehydrogenation reactions; due to the low masses of Li and B, not only the volumetric density, but also the gravimetric one are extremely high;\textsuperscript{12–49} furthermore, the existence of several possible hydriding and dehydriding reactions provides the possibility to control the H-content in experiments.\textsuperscript{50,51}

Except for the boundary phases, the high-pressure phase diagram is unknown, but there are many reasons to believe that it could host high-\(T_c\) superconductors. First of all, the very light masses of the three constituents imply that the average phonon frequencies of all compounds will be high, which is intrinsically favorable to phonon-mediated superconductivity. In fact Li, B and the corresponding hydrides exhibit interesting superconducting properties under pressure.\textsuperscript{23,52–61} while the binary Li-B system hosts one of the first \textit{ab-initio} predictions of novel superconductors.\textsuperscript{62} Furthermore, strong hydride formers, such as boron, form covalent or ionic bonds, which translate into large intrinsic ep matrix elements, while weak hydrogen formers typically form metallic hydrides; combining the properties of the two elements, therefore a ternary Li-B-H compound could behave as a "covalent metal", similarly to SH\(_3\), already at much lower pressures. The many hydrogen-rich phases which are weakly metastable at ambient pressure are ideal candidates for covalent metallic behavior (and superconductivity): in fact, they could be considered the ternary equivalent of SH\(_3\), which is a hydrogen-rich phase obtained by the hydrating reaction of SH\(_2\) at high pressures.\textsuperscript{16,18}

The aim of this work is to understand whether any of the ternary Li-B-H compounds known at ambient pressure, or any new, still unknown composition, exhibit high-\(T_c\) superconductivity in the Megabar range. We indeed identify a new high-\(T_c\) phase (Li\(_2\)BH\(_6\)), which, similarly to SH\(_3\), can be classified as a highly-symmetric covalent metal. At 200 GPa, this compound exhibits a \(T_c\) of 80 K, i.e. lower than SH\(_3\) but, in contrast to other known hydrides, the high-\(T_c\) behaviour persists down to 100 GPa. We will argue that the possibility to lower the pressure for high-\(T_c\) compared to binary hydrides is an intrinsic property of ternary (or higher) hydrides.

Fig. 1 shows the phase diagram of the Li-B-H system at ambient pressure (\(P = 0\)) and at 200 GPa (\(P = 200\)), calculated using the evolutionary crystal structure prediction method, as implemented in the \textit{Uspex} code.\textsuperscript{63–66} Due to the high computational cost of ternary phase diagrams, we had to restrict our search to representative pressures: 200 GPa was chosen because this is the pressure at which SH\(_3\) exhibits its maximum \(T_c\), and is well beyond the metallization pressure for many binary hydrides. Ambient pressure was mainly intended to check the accuracy of our calculations against literature results.

We first performed a full search of the two ternary phase diagrams, in which we sampled many possible compositions, represented by symbols in the two upper panels. The aim of this preliminary scan is to identify the compositions in the ternary phase diagram that could give rise to high-symmetry metallic structures at high pressure. In order to ensure an optimal trade-off between accuracy and computational time, we restricted the search to structures with all possible compositions, but with a minimum(maximum) number of atoms/unit cell equal to 8(16); a combinatorial argument gives a total of 300 possible stoichiometries. For each pressure, we generated a total of 1800 structures, which gives an average of 6 structures/composition. We would like to remind that this is only an exploratory run, while more accurate runs were used to inspect the most promising compositions.\textsuperscript{67}

Despite the apparently coarse sampling, our preliminary search identified correctly all known Li-B-H phases, both along the boundary lines and in the middle of the phase diagram. Only Li\(_2\)B\(_{12}\)H\(_{12}\), which is an important intermediate product of the hydrogenation process of LiBH\(_4\), has been added by hand, because the unit cell at ambient pressure is larger than the maximum number of atoms employed for our search. At ambient pressure, we reproduce the phase diagram and energetics of previous works; at \(P=200\) GPa, there are no literature data for ternary phases, but we reproduce known results for the Li-H, B-H and Li-B systems.\textsuperscript{23,61,62}

Our previous experience on binary systems taught us that the energies and structures from initial coarse sampling runs need to further be refined to obtain a correct ranking of structures and compositions.\textsuperscript{58} For this reason, after the initial scan, we focused on two specific \textit{Li}:B:H lines, shown in Fig. 1.\textsuperscript{68} These are the 1:1:x line, that contains compounds with chemical formula Li\(_x\)BH\(_{3-x}\), including LiBH\(_4\), and the 2:1:x one, where we found a highly symmetric metallic structure with chemical formula Li\(_2\)BH\(_6\). For these two lines, we ran additional crystal structure prediction runs with tighter settings; the same was done for boundary lines, and for Li\(_2\)B\(_{12}\)H\(_{12}\).
Figure 1. Top: Generalized convex hull for the Li-B-H system at zero (left) and 200 (right) GPa, obtained from evolutionary crystal structure prediction. Points represent compositions sampled in our preliminary run, lines indicate ranges of compositions for which we computed more accurate binary convex hulls (see text). These are shown in the bottom panels. Circles and squares represent compositions that are thermodynamically metastable or stable with respect to other phases on the ternary hull (see text).

The two enthalpy ($\Delta H$) vs. composition ($x$) binary convex hulls are shown in the two lower panels of Fig. 1.

Similarly to what observed in binary hydrides, pressures in the Megabar range stabilize several compositions which are metastable at ambient pressure. In particular, along the $1:1:x$ line LiBH, LiBH$_2$ and LiBH$_6$, besides the ground-state LiBH$_4$, lie close to the hull, while for the $2:1:x$ line there are several compositions close to the hull. Note that compositions on the binary hull are stable with respect to the decomposition into the end members of the line (LiB + H, and Li$_2$B + H); however, in a ternary system other decompositions are also possible. Although computing all possible paths would be prohibitive, we recomputed the enthalpy of formation of all compounds on the binary hulls also with respect to boundary phases; taking this effect into account, a few phases on the binary hull turned out to be metastable. These are shown as (blue) circles in Fig. 1, while genuinely ground state structures are shown as (red) squares. In the following, we will discuss the crystal and electronic structure of the most interesting compositions, with the aim of identifying potential high-$T_c$ superconductors.

We start from the ground-state LiBH$_4$, shown in the upper panel of Fig. 2. For this stoichiometry, we ran evolutionary structure prediction runs at fixed compositions for 0, 100, 200 and 300 GPa with 2,3 and 4 formula units per unit cell. At all pressures, we found as most stable a $Pmna$ structure, in which (BH$_4$)$^-$ tetrahedra are intercalated with Li$^+$ ions. At ambient pressure, the structure is very open, and the BH$_4$ tetrahedra can orient freely in the unit cell. Pressure leads to a more close-packed arrangement, in which the BH$_4$ tetrahedra only acquire two possible orientations around the Li atoms. The high-pressure structure shown in the figure is stable at least up to 300 GPa, where it is still insulating. Thus, LiBH$_4$ cannot support high-$T_c$ conventional superconductivity as in SH$_3$, but other phases on the phase diagrams are strong candidates.

An obvious candidate, due to its high hydrogen content, is Li$_2$B$_2$H$_{12}$. At ambient pressure, this compound crystallizes in an open structure of B-H icosahedra, intercalated with lithium atoms. Icosahedra are found in $\alpha$-boron and in several B-rich phases, including superconducting dodecaborides, such as ZrB$_2$. However, at ambient pressure Li$_2$B$_2$H$_{12}$ is insulating, and hence cannot superconduct. At higher pressures, the icosahedral environment is destabilized, and Li$_2$B$_2$H$_{12}$ acquires a completely different structures, characterized by unidimensional B-H chains, intercalated by lithium. This phase is however metastable (by 200 meV/atom) with respect to elemental decomposition, and we will not consider it further in our study.

Other compounds which have been often discussed in the hydrogenation and rehydrogenation reactions of LiBH$_4$ are those that lie along the 1:1:x Li:B:H line. The bottom left panel of Fig. 2 shows the high-pressure crystal structure of LiBH$_6$. The high-pressure stabilization of a hydrogen-rich phase of LiBH$_4$ could be the analogue of the reaction SH$_2$ + H$_2$ → SH$_3$ that led to the discovery of the first high-pressure conventional superconductor. However, Fig. 2 shows that there is an important difference between SH$_3$ and LiBH$_6$. In SH$_3$ a pressure of 200 GPa is sufficient to break the molecular bonds of SH$_2$ and H$_2$ and stabilize three new directional, covalent bonds between S and H. In LiBH$_6$ one can still recognize a close-packed LiBH$_4$ lattice, and molecular hydrogen intercalated in-between. This structure should thus rather be described as LiBH$_4$ + H$_2$ than LiBH$_6$. Not surprisingly, this structure is insulating.

Our evolutionary runs allowed us to identify at least one hydrogen-rich phase in which the (BH$_4$)$^-$ tetrahedral environment is destabilized, and molecular hydrogen is incorporated into the boron lattice. This is the Li$_2$BH$_6$ structure shown in the bottom right panel of Fig. 2. Here, boron and hydrogen form octahedra, and lithium sits in-between. BH$_6$ octahedra are not common in nature, but an AlH$_6$ octahedral motif is common in alanates. For borohydrides this motif, which is stabilized by $e_g$ ($d$) electrons, has never been observed at ambient pressure, and we consider our finding an example of high-pressure forbidden chemistry; we will come back to this point in the following.

Although unusual in structure and composition, according to our calculations Li$_2$BH$_6$ remains thermodynamically stable with respect to decompositions towards...
all phases on the ternary Gibbs diagram down to 100 GPa. Given the accuracy of our predictions in all other cases for which we had access to experimental data, we believe that this is a strong indication that Li$_2$BH$_{6}$ could be synthesized in experiments. In Fig. 2, superimposed to the crystal structure of Li$_2$BH$_{6}$, we show the 0.7 isocontour of the electronic localization function (ELF); the plot shows that most of the charge resides along the BH$_6$ bonds. Combined with the fact that Li$_2$BH$_{6}$ is metallic, this makes it a very strong candidate for high-$T_c$ conventional superconductivity. Indeed, as we will show, our electronic structure calculations confirm this hypothesis.

Fig. 3 shows the partial Densities of States (DOS) of the most relevant ternary Li-B-H phases in this work, calculated at 200 GPa. The first two panels show LiBH$_4$ and LiBH$_6$; in both compounds a large gap ($\Delta \sim 3$eV) separates bonding and antibonding states derived from the hybridization of B sp$^3$ states with hydrogen. This makes the BH$_4$ environment extremely stable; in fact, in LiBH$_6$ the two excess hydrogens do not bind to boron, but remain in molecular form, and arrange in the interstitials of the structure; the relative electronic states form an additional peak near the top of the valence band. Other structures along the 1:1:x line (not shown) are also insulating for similar reasons at this pressure. Li$_2$B$_2$H$_{12}$, shown immediately below, is a good metal, but metastable.

The two bottom panels show Li$_2$B$_6$H$_6$, which is the most promising candidate for superconductivity identified in this work, and a hypothetical compound in which lithium is replaced by a uniform background of charge ($\Box^{+2}$BH$_6$). The strong similarity between the two DOS’s in the valence region indicates that the main role of lithium in this structure is to donate charge to the boron-hydrogen octahedra, while its contribution to the bonding is only marginal.

We can thus try to understand the electronic structure in terms of the BH$_6$ cluster alone; the states at the Fermi level result from the hybridization of B d $e_g$ states with hydrogen; the two other structures centered at $\sim -8$ eV and $\sim -15$ eV correspond to B s and p states. It has been argued that the octahedral environment is not seen in borohydrides, because the gap between d and p states is too large compared to other hydrides of the third group. In these compounds, the $XH_6$ environment is stable already at ambient pressure, where the bandwidth is much smaller. s, p and $e_g$ states cause clear gaps in the electronic spectrum. Octahedral hydrides typically host 12 valence electrons, corresponding to a complete filling of s, p and $e_g$ shells. On the other hand, according to our calculations, the Li$_3$BH$_6$ phase, which has only 11 valence electrons, is thermodynamically stable down to 100 GPa, where it remains metallic. We believe that the reason why this unusual phase can occur at high pressures is that the boron-hydrogen bandwidth is large enough to overcome the intrinsic gaps in the boron spectrum, giving rise to a metallic DOS, allowing a wider range of dopings. In Li$_2$BH$_6$, the Fermi level sits in a shallow region of this continuum, where $N \sim 0.2$ st/eV f.u.

In order to estimate the actual superconducting characteristics of Li$_2$BH$_6$, we performed linear response calculations of its electron-phonon properties, and estimated the critical temperature through the Mc-Millan Allen-Dynes formula,$^{72,73}$:

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

(1)

The phonon dispersions, decorated with circles whose size is proportional to the partial $ep$ coupling of each branch, are shown in the left panels of Fig. 4: the right panels show the partial Phonon DOS and the $ep$ (Eliashberg) spectral function $\alpha^2 F(\omega)$, which describes how the $ep$ coupling is distributed on phonon modes with energy $\omega$. The top and bottom panels refer to P=100 and P=200 GPa, respectively. The parameters $\lambda$ ($ep$ coupling constant) and $\omega_{\log}$ (logarithmically averaged phonon frequency) in Eq. 1 can be obtained from $\alpha^2 F(\omega)$ as:
\[ \lambda = 2 \int d\omega \alpha^2 F(\omega) \quad \text{and} \quad \omega_{\log} = \exp \left[ \frac{\lambda}{2} \int d\omega \alpha^2 F(\omega) \ln(\omega) \right] \]

\( \mu^* \) is the Coulomb pseudopotential, renormalized to include retardation effects due to the large disparity between the electron and phonon energies.

For \( P=100 \) and 200 GPa, we obtain \( \omega_{\log}=1551 \) and 1940 K and \( \lambda=0.94, 0.76 \), respectively. The corresponding \( T_c \)'s, estimated from Eq. 1 with \( \mu^* = 0.1 \) are 98 and 81 K, comparable to those of PH$_3$. Comparing the \( \alpha^2 F(\omega) \) with the partial phonon DOS next to it, it is clear that the most substantial contribution to the coupling comes from H modes at intermediate frequencies, while octahedral vibrations (above 300 meV), play a very marginal role. The phonon spectrum shifts almost rigidly by \( \sim 50 \) meV going from 100 to 200 GPa, causing a similar increase in \( \omega_{\log} \). On the other hand, the electronic properties worsen with pressure, since the DOS at the Fermi level decreases by 20%, causing a similar decrease in the total \( ep \) coupling constant \( \eta \approx 4.2 \text{ eV f.u.} \), and comparable with SH$_3$ and PH$_3$, where \( \eta \) is 3.6 and 3.8, respectively.\[22\] Fig. 3 shows that the Fermi level in Li$_2$BH$_6$ sits in a shallow region of the DOS, which is weakly affected by pressure; this explains the weak dependence of \( T_c \) on \( P \).

While this weak dependence implies that \( T_c \) cannot be effectively boosted by pressure, as in PH$_3$ and SH$_3$, it also implies that superconductivity survives with remarkable \( T_c \)'s down to pressures which are twice smaller than in SH$_3$. Furthermore, the fact that the atoms that contribute to charge doping and covalent bonding are different (lithium and boron, respectively), offers a simple route to improve the superconducting properties of Li$_2$BH$_6$. Partially replacing lithium with alkaline earths
or vacancies would allow to easily tune the doping level, and hence the value of the DOS, without affecting the stiff boron-hydrogen sublattice responsible for the large ep coupling. Doping on the Li site in ternary hydrides is routinely achieved in hydrogen storage applications, and is most likely much easier to obtain also at high pressures than the iso- or heterovalent substitutions proposed by several authors for covalent hydrides.\textsuperscript{27,31,74} On the other hand, substitutions at the B site could be used to tune other intrinsic properties, such as ep matrix elements or metallization pressures.

In conclusion, in this work we have studied from first-principles the high-pressure superconducting phase diagram of lithium-boron-hydrogen, a prototypical ternary system employed for hydrogen storage applications. Besides the well-known boundary phases, we have identified several new compositions which are stabilized by high pressures. We have shown that neither the ground-state LiBH$_4$, nor any of its direct hydrogenation or dehydrogenation products is a viable candidate for high-$T_c$ superconductivity, but we have identified at least one ternary phase, Li$_2$BH$_6$, which exhibits superconducting properties comparable to those of the best binary hydrides. The Li$_2$BH$_6$ composition is not stable at ambient pressure, but according to our calculations it should become thermodynamically stable for P > 100 GPa. Similarly to SH$_3$, which is a hydrogen-rich phase of sulfur hydride, in which the original molecular bonds are broken and new, directional bonds are formed under pressure, Li$_2$BH$_6$ exhibits a highly symmetric structure in which the original BH$_4$ tetrahedra that are characteristic of boronhydrides rearrange to form BH$_6$ octahedra, with covalent B-H bonds. These determine the valence band structure, while lithium mainly acts as a charge reservoir.

The fact that two different atoms govern the bonding and the charge doping should allow to tune the $T_c$ more easily than in binary hydrides. Our work demonstrates that ternary hydrides can exhibit high-$T_c$ superconductivity and is a first step towards the optimization of superconducting properties in high-pressure hydrides using chemical methods.

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