Superconductivity in Hydrides Doped with Main Group Elements Under Pressure

Andrew Shamp and Eva Zurek*

Abstract: A priori crystal structure prediction techniques have been used to explore the phase diagrams of hydrides of main group elements under pressure. A number of novel phases with the chemical formulas \( \text{MH}_n, n > 1 \) and \( M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs} \); \( \text{MH}_n, n > 2 \) and \( M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba} \); \( \text{H}_n\text{I} \) with \( n > 1 \) and \( \text{PH}, \text{PH}_2, \text{PH}_3 \) have been predicted to be stable at pressures achievable in diamond anvil cells. The hydrogenic lattices within these phases display a number of structural motifs including \( \text{H}_{2}\delta^- \), \( \text{H}^- \), \( \text{H}_3 \), as well as one-dimensional and three-dimensional extended structures. A wide range of superconducting critical temperatures, \( T_c \), are predicted for these hydrides. The mechanism of metallization and the propensity for superconductivity are dependent upon the structural motifs present in these phases, and in particular on their hydrogenic sublattices. Phases that are thermodynamically unstable, but dynamically stable, are accessible experimentally. The observed trends provide insight on how to design hydrides that are superconducting at high temperatures.

Keywords: superconductivity, hydrides, high pressure, density functional theory, materials prediction

1 Introduction

In a seminal work Ashcroft proposed that because the hydrogen is “chemically precompressed” in solids composed of the group 14 hydrides, less physical pressure would be required to metallize them as compared to pure hydrogen [1, 2]. Moreover, he hypothesized that these phases have the potential to be superconducting at high temperatures. Ashcroft’s predictions led to a plethora of theoretical, and a few experimental, studies that searched for superconductivity in hydrides that are known to exist at atmospheric conditions, such as \( \text{SiH}_4 \) [3–10], \( \text{GeH}_4 \) [11–14], and \( \text{AlH}_3 \) [15–17]. He also pointed out that a second component, which can be seen as an impurity, may potentially reduce the pressure required to metallize hydrogen [18].

Pressure can affect which combinations of elements form stable phases, and the chemical compositions of these phases. Therefore, building on Ashcroft’s proposals, density functional theory (DFT) calculations were carried out to predict the structures of hydrides with stoichiometries that are not stable at atmospheric conditions, in the hopes of uncovering hitherto unknown superconductors [19]. Since then, numerous theoretical studies have been performed that investigate the phase diagrams of hydrogen doped with the electronegative alkali metals or alkaline earth metals [20–34], as well as the electronegative element iodine [35, 36] under pressure. Experimental work on the hydrides of lithium and sodium confirmed that species with unique stoichiometries such as \( \text{NaH}_3 \) and \( \text{NaH}_2 \) can be synthesized in diamond anvil cells, but the phases that have been reported to date do not exhibit superconductivity [21, 37]. Nonetheless, as summarized in this short review, the aforementioned theoretical explorations have: revealed that rich structural variety may be found in the hydrogenic sublattices, suggested a number of ways that hydrogen may be metallized via doping, and shown that the propensity for superconductivity is linked to the nature of the hydrogenic motifs.

Recent experimental studies carried out by Drozdov, Eremets, and Troyan on hydrides containing a p-block element have yielded exciting results. It was shown that when hydrides of sulfur were prepared at \( T \geq 300 \text{ K} \) they become superconducting with a critical temperature, \( T_c \), of 203 K at 150 GPa [38], and at 207 GPa compressed phosphine yielded a \( T_c \) of 103 K [39]. Theoretical studies, which have shown that the superconductivity observed in Ref. [38] arises primarily from an \( \text{H}_2\text{S} \) phase [40–55] whose structure has been recently confirmed experimentally [56], will not be described within this short review. We will, however, discuss the results of first principles calculations carried out for the hydrides of phosphorus [57–59]. Importantly, these studies revealed that the phases made in experiment are not necessarily the thermodynamic minima,
and that a mixture of phases could yield the observed superconductivity.

These studies highlight that new hydrogen-rich materials, some of which may have a $T_c$ higher than those previously thought possible for Bardeen-Cooper-Schrieffer (BCS)-type superconductors, can be attained under pressure, and they have reinvigorated the search for high-temperature superconductivity in high-pressure hydrides.

### 2 How to Metallize with an Electropositive Element

A number of chemical trends have been observed for compressed alkali metal and alkaline earth polyhydrides [33]. The pressure at which the polyhydrides were calculated to become stable with respect to decomposition into the “classical” hydride (of MH or MH$_2$ stoichiometry) and H$_2$ decreases with decreasing ionization potential of the dopant metal. For example, whereas LiH$_n$ phases are thermodynamically stable above 100 GPa, CsH$_n$ structures are accessible above 2 GPa. The stoichiometries of the thermodynamically stable polyhydrides, eg. those which comprised the convex hull, possessed an odd number of hydrogen atoms if the dopant atom was from Group I, and an even number it was from Group II. The only exception to this trend was lithium, wherein LiH$_2$, LiH$_6$, and LiH$_8$ were found to be thermodynamically stable. In general, past a threshold pressure the hydrogen content in the structure with the most negative enthalpy of formation, $\Delta H_F$, decreased with increasing pressure for the alkali metal polyhydrides, whereas for the alkaline earth polyhydrides it increased. Thus, it is likely that at very high pressures the mole % ratio of hydrogen found in the structure that corresponds to the lowest point on the convex hull will be larger in the alkaline earth polyhydrides than in the alkali metal polyhydrides.

Whereas “chemical precompression” can be employed to metallize covalent hydrides at pressures lower than those required for elemental hydrogen, different ways to metallize become important for ionic hydrides. We have found five mechanisms that hasten band gap closure, and four of these are explicitly illustrated schematically in Fig. 1. Which route is taken depends upon the nature of the hydrogenic motifs present in the lattice, and this in turn is governed by the nature of the dopant element. In the paragraphs that follow these five approaches are described by way of example.

1. In the phases that contained only hydrogen molecules, such as R3m-LiH$_6$ shown in Fig. 1(a), valence electrons are transferred from the electropositive metal to the H$_2$ $\sigma^*$-orbitals, which become partially filled [19]. As a consequence, these systems are already good metals at 1 atm (but they are not stable). This mechanism of metallization yields phases with a high density of states (DOS) at the Fermi level, $E_F$.

2. At 1 atm the volume of the R3m-LiH$_6$ unit cell was calculated to be a factor of two smaller than an optimized H$_6$ lattice because ionic attraction between Li$^+$ and three (H$_2$)$^{1/3}$ molecules leads to “Madelung precompression”. However, this method of precompression was only effective at low pressures because the presence of the Li$^+$ core yielded a structure with a volume larger than that of elemental H$_2$ at high pressures. Therefore, this metallization mechanism is likely only effective for ionic compounds that undergo pressure-induced band gap closure at relatively low pressures.

3. The valence electrons of the electropositive element can be transferred to a single hydrogen atom yielding a hydridic hydrogen, H$^-$, within a lattice of H$_2$ molecules, as in the Pm-NaH$_2$ structure illustrated in Fig. 1(b) [26].Because an H$^-$ impurity donor band forms between the H$_2$ $\sigma^*$- and $\sigma_0$-levels, the band gap of this system is smaller at 1 atm than in elemental H$_2$. Therefore, phases possessing H$^-$ should undergo metallization due to band broadening and overlap at lower pressures than those required to metallize pure hydrogen. However, calculations have shown that the DOS at $E_F$ in the metallized systems is generally quite low.

4. Because H$^-$ is a soft base it can interact with H$_2$, an extremely weak acid, to form H$_3^-$, the simplest example of a three–center four–electron (3c-4e) bond. Calculations carried out with a variant of the configuration interaction (CI) method have shown that H$_3^-$ is asymmetric with H–H distances measuring 0.75 and 2.84 Å, and the barrier between the two possible minima is symmetric, with H–H distances measuring ~1.06 Å [60]. Symmetric and asymmetric H$_3^-$ motifs have been observed in polyhydrides containing Na [21], K [28], Rb [27], Cs [29], Sr [23, 32] and Ba [31]: one example is the RbH$_3$ phase illustrated in Fig. 1(c) [27]. In these species metallization occurs via the pressure induced broadening and eventual overlap of the filled H$_3^-$ non-bonding band with the H$_3^-$ anti-bonding bands and/or
the metal $d$-bands. As a result, the DOS at $E_F$ in the metallic phases is typically low.

The $M^+$–$H^-$ interaction decreases the basicity of the hydride, so the formation of $H_3^-$ is easiest in the gas phase, followed by the polyhydride containing the softest metal cation [28]. This explains why $H_3^-$ units were not observed in the polyhydrides of lithium, magnesium and calcium. Under pressure the $H_3^-$ motif tends to symmetrize in many of the structures that were found, and both bent and linear units have been observed.

5. Perhaps the most important mechanism of metallization was found to occur in only a few phases, for example CaH$_6$ above 150 GPa [22] and the $R3m$-SrH$_6$ structure shown in Fig. 1(d) [23, 32]. All of the hydrogens within these systems were partially negatively charged, $H^{6-}$, and they were close enough for their electron densities to overlap and form extended lattices. In CaH$_6$ the hydrogenic lattice was three-dimensional and resembled the framework of the sodalite clathrate, whereas in SrH$_6$ the hydrogen atoms formed one-dimensional hydrogenic helices, $\ldots[H^{6-}]$. The presence of the extended hydrogenic lattices gave rise to metallicity in these phases, and yielded a high DOS at $E_F$. Calculations have predicted that hydrogenic sodalite-like lattices will also be found in MgH$_6$ around 260 GPa [34] and YH$_6$ at 120 GPa [61].

### 3 Metallization in the Presence of $p$-Block Elements

Many of the known hydrides of a $p$-block element form covalent bonds with hydrogen, so they can hasten its metallization by “chemical precompression”. In this section we show that the non-hydrogenic lattice can be important for the metallization of an ionic hydride containing a $p$-block element wherein the hydrogen is the more electropositive species. And, metastable covalent hydrides composed of one-dimensional chains or two-dimensional layers that have nearly free electron like behavior are described.

1. All of the strategies that can be utilized to accelerate band gap closure via doping hydrogen with an electronegative element involve metallizing the hydrogenic sublattice. However, theoretical investigations of $H_nI$, $n > 1$, revealed that it is not only the hydrogenic sublattice which is important for inducing metallization [35].

The stable polyhydrides of iodine contained the following structural motifs: $I^{5+}$, $I^{6+}$, and $H^+_5$ molecules as in $H_2I$, or $I^{6+}$ and $H^{5+}$ molecules as in $H_3I$ and $H_4I$; these phases are illustrated in Fig. 2 [35]. The former could be thought of as a HI lattice with excess $H_2$ molecules, whereas the latter two consisted of an atomistic iodine...
host lattice within which H₂ molecules were guests. The metallic behavior of these phases was found to originate from the HI or iodine sublattices. Atomistic hydrogen was present in a \( R\bar{3}m \)-H₂I phase at 246 GPa [36].

Figure 2: Supercells of (a) P1-H₂I, (b) Cmcm-H₂I and (c) P6/mmm-H₂I from Ref. [35].

The P1 symmetry H₂I phase shown in Fig. 2(a) was stable between 50-90 GPa. It contained zigzag [HI]∞ chains within which every iodine atom was bound to two hydrogen atoms. The H–I distances were nearly equivalent, indicative of multi-center bonding. This zigzag structural motif, and the equalization of inter- and intra-molecular H-X bonds under pressure, occurs in the halogen hydrides with traditional stoichiometries, HX (X=F, Cl, Br) [62]. H₂ molecules bearing a slight negative charge surrounded the hydrogens comprising the [HI]∞ chains in H₂I.

Experiments have shown that HI undergoes a pressure induced insulator to metal transition below 50 GPa [63]. At this pressure the PBE band gap of H₂I was calculated to be \( \sim 0.5 \) eV. By 65 GPa H₂I became metallic, however it is well known that the PBE functional underestimates the pressure at which band gap closure occurs. The metallization of H₂I is a result of the pressure induced broadening of the valence band, primarily of iodine p-character, and the conduction band, exhibiting mainly \( \text{H}^{5+} \) s-character, and the system had a low DOS at \( E_F \). Thus, the mechanism of metallization is the same in H₂I and HI, but because the volume of the former is larger at a given pressure than that of the latter (due to the excess H₂ molecules), higher pressures are required to metallize the polyhydride.

The Cmcm-H₂I and P6/mmm-H₂I phases illustrated in Fig. 2(c,d) lay on the 100, 150, and 200 GPa convex hulls. H₂I consisted of a three-dimensional iodine lattice with two rows of H₂ molecules arranged in a zigzag fashion that run through channels formed by the iodine host. H₄I was composed of parallel one-dimensional chains of iodine atoms and H₂ molecules. In both phases there was a slight transfer of charge from iodine to H₂. These systems were good metals already at 1 atm, even though they were not thermodynamically or dynamically stable at this pressure. The high DOS at \( E_F \) was primarily due to iodine p-states, with an admixture of hydrogen s.

Within elemental iodine, pressure causes the I–I bonds to stretch, and the intermolecular distances to decrease. At \( \sim 16 \) GPa iodine undergoes an insulator to metal transition [64], and by 30 GPa a monoatomic metallic phase forms wherein the I–I distances are equalized [65]. Thus, the metallicity within H₂I and H₄I originates from the fact that their iodine sublattices are atomistic. Single point calculation on these geometries at 100 GPa, but where the hydrogens were removed, illustrated that they were metallic. Interestingly, the DOS at \( E_F \) of the iodine lattice alone was slightly higher than that of the iodine polyhydrides. Whereas the H₂I lattice of H₂I was insulating, the one for H₄I had a small, but non-negligible DOS at \( E_F \).

2. Recently, Drozdov, Eremets, and Troyan observed superconductivity in phosphine, PH₃, which was liquefied and compressed in a diamond anvil cell [39]. The \( T_c \) was measured to be 30 K at 83 GPa and 103 K at 207 GPa via resistance measurements. Because PH₃ is a covalent hydride at atmospheric conditions, the hydrogen within it is "chemically precompressed".

Three different groups nearly simultaneously studied the phase diagram of PHₙ, \( n = 1 - 6 \), at these pressures via first principles calculations [57–59]. These studies found that even though the phosphate polyhydrides are unstable with respect to decomposition into solid phosphorus and H₂ at the pressures considered experimentally, a number of phases were dynamically stable. Many of the structures that were identified via \textit{a priori} crystal structure pre-
diction techniques consisted of one-dimensional chains or two-dimensional layers wherein the environment around the phosphorus atoms resembled that in the hypervalent PCl$_5$ or PCl$_{6}^-$ molecules. Typically, the phosphorus atoms were octahedrally coordinated to phosphorus and hydrogen atoms, but in some structures trigonal bipyramidal coordination was observed.

Consider, for example, the three PH$_2$ phases illustrated in Fig. 3 that had nearly the same (non-zero-point corrected) enthalpies at 150 GPa. A C2/m symmetry structure with five formula units in the primitive cell, 5FU-C2/m PH$_2$, consisted of PH$_3$-PH-PH$_2$-PH-PH$_3$ oligomers that were 1D periodic along the a-axis. Whereas the terminal and central phosphorus atoms in this phase were octahedrally coordinated, the phosphorus atoms within the -PH-segment were nearly trigonal bipyramidal. The phosphorus atoms in a two formula unit C2/m symmetry phase and an I4/mmm structure were all octahedrally coordinated by four phosphorus atoms in the equatorial positions and two hydrogen atoms in the axial positions.

Isosurfaces of the electron localization function (ELF) confirmed covalent P-P and P-H bonding. The occupied bands were parabolic and the DOS nearly free electron like. As a result, these phases had a high DOS at EF. A single point calculation on a geometry wherein the layers in I4/mmm-PH$_2$ were separated by about 10 Å showed that such a system would be a good metal, with a DOS at EF slightly higher than that of the optimized phase. This computational experiment indicates that the metallicity is a result of the structure assumed by the two-dimensional sheet and that the mobile electrons move primarily within the 2D layers, and along the P-P bonds. It is likely that the metallicity within the other PH$_2$ structures containing one-dimensional chains and two-dimensional sheets has the same origin.

Because a number of the dynamically stable PH$_n$ phases gave rise to $T_c$ values in-line with those found experimentally, the computations illustrate that the observed superconductivity is likely due to a mixture of metastable phases that form from the decomposition of phosphine under pressure. These studies also highlight that pressure can lead to the formation of (meta)stable phases with stoichiometries that are not observed at atmospheric conditions.

4 Characteristic Phonon Modes and Superconductivity

Structural characterization of the phases formed in diamond anvil cells can be quite challenging, especially for systems containing light elements. Often Raman or IR spectroscopy is utilized to monitor the behavior of select phonon modes as a function of pressure. By comparing the spectra with those of known structures one can determine if a new phase has been made. In addition, the experimental vibrational frequencies can be compared with those calculated for potential structural candidates via first principles. Importantly, because the hydrogenic motifs found in the polyhydrides give rise to characteristic vibrational modes, they can be used as spectroscopic fingerprints to aid in the identification of the species that are formed.

For example, the H$_2$ stretching mode is typically found between 3000–4500 cm$^{-1}$. Its frequency depends upon the H–H distance, with longer bonds yielding lower frequency vibrations. Both the pressure and the nature of the interaction between H$_2$ and the dopant element influence the bond strength. For example, in H$_6$I at 100 GPa the H–H distances measure 0.799 Å (as compared to the gas phase value of ∼0.75 Å) and the H$_2$ vibron peak is found at 3000–3300 cm$^{-1}$, as illustrated in Fig. 4(a). The weakening of the H–H bond is, at least in part, a result of electron transfer from iodine to H$_2$, which leads to a partial filling of the $\sigma_u^*$ levels.

The bending and asymmetric/symmetric stretching modes of the H$_3$ motif are located between 1500–2500 cm$^{-1}$, and their frequency also depends upon the H–H distances. The symmetric vibration typically has a higher frequency. For example, in CsH$_3$ at 50 GPa it is centered around 2200 cm$^{-1}$, whereas modes associated with the asymmetric stretch are near 1700 cm$^{-1}$, as shown in Fig. 4(b).

Phases that contain extended hydrogenic lattices only, whether they be three-dimensional as in CaH$_4$ or one-dimensional as in SrH$_6$, do not exhibit any vibrations past ∼2250 cm$^{-1}$. This is evident in, the phonon DOS calculated for SrH$_6$ at 250 GPa in Fig. 4(c).

In the phosphorus polyhydrides above 100 GPa, hydrogen bonds covalently to phosphorus and the aforementioned hydrogenic motifs are absent. For the PH$_n$ phases with $n = 1–3$ at 200 GPa the P-H stretching mode was found between 1800–2500 cm$^{-1}$ [57–59]; for example see the phonon DOS for 2FU-C2/m PH$_2$ in Fig. 4(d). The frequencies of X-H vibrations will depend on the pressure and the identity of element X, but they will be found at values lower than that of the hydrogen vibron due to the heavier mass of the dopant element.

Table 1 provides the electron-phonon coupling (EPC) parameter, $\lambda$, the logarithmic average frequency, $\omega$$_{log}$, and the calculated $T_c$ of various alkali metal and alkaline earth polyhydrides, YH$_6$, Im3m-H$_3$S, as well as the aforementioned H$_2$I, H$_6$I, PH, PH$_2$ and PH$_3$ phases. The data has
been organized loosely according to the structural motifs that are present in the hydrogenic lattices, and, in part, the computed \( \lambda \). Most studies employed the Allen-Dynes modified McMillan equation [66] to estimate the superconducting critical temperature. The Coulomb pseudopotential, \( \mu' \), was typically chosen to fall within 0.1 to 0.13. Because we would like to gain a better understanding of how the structural motifs present within the polyhydrides, and the mechanisms by which they become metallic influence \( T_c \), data is provided for a uniform value of \( \mu' = 0.1 \). The only exception are the results from Ref. [58], wherein density functional theory for superconductors (SCDFT) was employed to calculate \( T_c \) for the PH\(_4\) phases.

Generally speaking, \( T_c \) was higher for the alkali metal and alkaline earth polyhydrides than for the polyhydrides of iodine, whose metallicity arises from their monoatomic iodine lattices. LiH\(_2\), which did not superconduct at 150 GPa, was the only exception. This phase becomes metallic due to pressure induced broadening and overlap of the H\(^+\) and H\(^2\) \( \sigma_u \)-bands. However, at this pressure the Li 1s cores overlap so the valence electrons are impelled into interstitial regions thereby reducing the metallicity of LiH\(_2\). MgH\(_4\) and BaH\(_6\) also contained H\(^2\) and H\(^-\) units, so they metalized via the same mechanism as LiH\(_2\). But, the EPC parameters, and therefore \( T_c \)'s, of MgH\(_2\) and BaH\(_6\) were significantly higher than those of LiH\(_2\). The superconducting critical temperatures of phases containing H\(^3\) motifs have not yet been calculated, but we suspect they may be somewhat lower than those of MgH\(_2\) and BaH\(_6\) because the H\(^3\) stretching modes occur at lower frequencies than the vibration of H\(_2\), but the two classes of structures have a similar DOS at \( E_F \).

The EPC parameters of phases that become metallic because of partial filling of the H\(^2\) \( \sigma_u \)-bands, such as LiH\(_4\), LiH\(_8\) and MgH\(_{12}\), ranged from 0.6-0.9 and their \( T_c \)'s fell between 47 K to 70 K (for the pressures listed herein). In comparison, the \( T_c \)'s of MgH\(_6\) and BaH\(_6\) were somewhat lower, and this is primarily a result of their smaller \( \omega_{\text{log}} \) values. The largest contribution to \( \lambda \) in phases that metallize via partial filling of the H\(^2\) \( \sigma_u \)-bands or the overlap of the H\(^-\) and H\(^2\) \( \sigma_u \)-levels was due to vibrations of the hydrogen and dopant atoms.

\( T_c \) is pressure dependent; for example it is predicted to range from 38-82 K for LiH\(_8\) between 150 and 300 GPa [24]. Calculations of the electronic structure of sulfur hydrides as a function of pressure have reported the presence of electronic topological transitions (ETT) at critical values of the pressure. At the ETT the chemical potential will be close to a band edge resulting in the appearance of a new Fermi surface with a small local Fermi energy [2]. These \( k \)-spots could be relevant for the scenario of multiband superconductivity in hydrides proposed by some authors [54, 55]. However, based on the trends observed so far it is unlikely that phases which metallize via the first or third mechanism described in Sec. 2, or the first mechanism outlined in Sec. 3, will be able to attain \( T_c \) values significantly higher than the boiling point of liquid nitrogen at any pressure.

Comparison of the results obtained for the hydrides of phosphorus with the alkali metal and alkali earth polyhydrides that contained H\(^-\) and/or H\(^2\) \( \sigma_u \)-motifs revealed that the PH\(_n\) phases had a slightly higher \( \lambda \), which ranged from 1.0-1.46 but their \( \omega_{\text{log}} \) were generally smaller. The vibrational modes that furnished the main contribution to the EPC parameter consisted of the motions of the phosphorus and hydrogen atoms. The computed \( T_c \)'s of the PH\(_n\) phases fell between 30-80 K in the range of 100-250 GPa, and in general they increased with increasing pressure [58], in agreement with experimental observations [39].

The phases that had the highest \( T_c \) values were comprised of three-dimensional hydrogenic lattices. In fact, the calculated \( T_c \) of CaH\(_6\), MgH\(_4\) and YH\(_6\) wherein the hydrogenic lattice resembled that of the sodalite clathrate rivaled that of the \( \text{Im} \bar{3}m\)-H\(_3\)S phase at 200 GPa. The reason why the former had a higher critical superconducting temperature than the latter was because of the larger EPC parameter, which ranged from 2.69-3.29 for the sodalite-like phases, as compared to 2.19 for H\(_3\)S. The \( T_c \) of a \( \text{R} \bar{3}m \)-SrH\(_6\) phase that contained one-dimensional hydrogenic helices was not calculated [23, 32], but we expect it to be high be-
Table 1: The electron-phonon coupling parameter ($\lambda$), logarithmic average phonon frequency ($\omega_{\text{log}}$) and computed superconducting transition temperature ($T_c$) calculated for $\mu' = 0.1$ (except for Ref. 58) of various polyhydrides at select pressures. The motifs present in the hydrogenic lattices are also provided.

<table>
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<th>System</th>
<th>Pressure (GPa)</th>
<th>$\lambda$</th>
<th>$\omega_{\text{log}}$ (K)</th>
<th>$T_c$ (K)</th>
<th>Hydrogenic Motifs</th>
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<td>61.0</td>
<td>P-H</td>
</tr>
<tr>
<td>PH$_2^{t,h}$</td>
<td>220</td>
<td>1.35</td>
<td>763.6</td>
<td>78.0</td>
<td>P-H</td>
</tr>
<tr>
<td>PH$_2^{t,h}$</td>
<td>180</td>
<td>1.00</td>
<td>884.0</td>
<td>50.5</td>
<td>P-H</td>
</tr>
<tr>
<td>PH$_2^{t,h}$</td>
<td>220</td>
<td>1.09</td>
<td>734.4</td>
<td>55.7</td>
<td>P-H</td>
</tr>
<tr>
<td>PH$_2^{t,h}$</td>
<td>200</td>
<td>1.46</td>
<td>826.0</td>
<td>91.7</td>
<td>P-H</td>
</tr>
<tr>
<td>Im$3$m-SH$_6^m$</td>
<td>200</td>
<td>2.19</td>
<td>1334.6</td>
<td>204.0</td>
<td>atomistic (S-H-S)</td>
</tr>
<tr>
<td>MgH$_6^e$</td>
<td>300</td>
<td>3.29</td>
<td>1450.0</td>
<td>271.0</td>
<td>3-D</td>
</tr>
<tr>
<td>CaH$_6^{T,j}$</td>
<td>150</td>
<td>2.69</td>
<td>-</td>
<td>235.0</td>
<td>3-D</td>
</tr>
<tr>
<td>YH$_6^e$</td>
<td>120</td>
<td>2.93</td>
<td>-</td>
<td>264.0</td>
<td>3-D</td>
</tr>
</tbody>
</table>

$^*$These values are estimates; they were taken from plots found in the original papers. $^\dagger$ $T_c$ was predicted using SCDF (Ref. 58) or solving the Eliashberg equations numerically (Ref. 22). $^a$ Ref. 35, $^b$ Ref. 36, $^c$ Ref. 24, $^d$ Ref. 30, $^e$ Ref. 31, $^f$ Ref. 25, $^g$ Ref. 57, $^h$ Ref. 58, $^i$ Ref. 59, $^j$ Ref. 22, $^k$ Ref. 34 $^l$ Ref. 61, $^m$ Ref. 40.

5 Conclusions

First principles calculations have been carried out to study the phase diagrams, as a function of composition and pressure, of a wide variety of hydrides. A number of phases with unique stoichiometries that contain either H$_2^\delta^+$, H$^-$, H$_3^\delta^-$, extended hydrogenic lattices, or atomistic hydrogen stabilized by bonding to another element have been predicted to become stable at pressures accessible within diamond anvil cells. The mechanism by which these phases become metallic include: chemical and Madelung precompression, pressure induced broadening and overlap of H$^-$ and H$_2$ $\sigma^*$-bands or the overlap of the H$_3$ non-bonding and anti-bonding bands, partial filling of the H$_2$ $\sigma^*$-bands, met-
alization of non-hydrogenic sublattices, or simply by the presence of extended hydrogenic motifs and the absence of molecular ones.

The phases which had the highest estimated superconducting critical temperatures did not contain discrete hydrogenic units such as $H^-$, $H_2^-$ or $H_2$. Instead, they were comprised of extended hydrogenic lattices such as those found in $\text{MgH}_2$, $\text{CaH}_6$, $\text{SrH}_2$, and $\text{YH}_6$, or atomic hydrogen stabilized by bonding to a $p$-group element such as in $\text{H}_2\text{S}$ or $\text{PH}_3$. $n = 1, 2, 3$. Importantly, comparison of the theoretical [57–59] and experimental [39] studies of the polyhydrides of phosphorus revealed that metastable phases may be made experimentally and that superconductivity can result from a mixture of phases. Thus, theoretical studies should not only focus on examining the properties of those systems that are thermodynamically stable, but also on searching for metastable phases with the aforementioned hydrogenic lattices that are conducive for high-temperature superconductivity.

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References


