Three lines of thought—call them obsessions—impelled this investigation: (i) thinking of new pathways to promote and enhance the metallization of hydrogen, (ii) more generally the potential stability of new compounds with unusual stoichiometries under high pressures, and (iii) proposals for the design of new superconductors. As will be seen, we find two surprising ways (making good chemical sense) for the first, as well as sound theoretical evidence for the second. Based upon what is already known about possible superconductivity in metallic hydrogen, we find indications for the third.

LiH, crystallizing in the NaCl structure with a band gap of 4.99 eV (1), is one stable point in the Li/H phase diagram, the only one other than the elements at ambient conditions. It remains stable at higher pressures; the reaction \( \text{Li} + \frac{3}{2} \text{H}_2 \rightarrow \text{LiH} \) is computed to be exothermic at all of the pressures we have considered. Calculations predict that pressure-induced metallization and transformation to the CsCl structure occur simultaneously at approximately 329 GPa (2). The results of our density functional theory (DFT) calculations on LiH are given in the supporting information (SI).

Hydrogen also vehemently resists metallization. At 320 GPa, it becomes black, indicating considerable reduction of the band gap under compression (3). Yet, it does not become metallic at the highest static pressures reached so far—342 GPa (4). Experimental and theoretical work indicates that combination with tetravalent atoms, as in the group 14 hydrides (5–13), may enhance the metallization of hydrogen, (4) more generally the potential stability of new compounds with unusual stoichiometries under high pressures, and (iii) proposals for the design of new superconductors. As will be seen, we find two surprising ways (making good chemical sense) for the first, as well as sound theoretical evidence for the second. Based upon what is already known about possible superconductivity in metallic hydrogen, we find indications for the third.

In Fig. 1B and C, our two proposals are sketched.

These approaches will be illustrated below in detail for LiH₂ and LiH₆, although we have explored a variety of stoichiometries (LiHₙ, \( n = 2–8 \)) over pressures ranging from 0 to 300 GPa. In all of these phases, extended hydrogen networks begin to emerge at pressures still below those computed for the metallization of pure H₂. Interestingly, between \( \sim 100 \) and 165 GPa, all become stable or metastable. All are metallic.

**LiH₂, Hydrides, and Hydrogen Molecules**

Our DFT calculations indicate that the ground state enthalpy of formation of LiH₂ (relative to LiH and H₂) becomes negative at approximately 120 GPa (or 2.4-fold compression). The best structure we have found, \( P4/mmb \) (space group 127), contains four formula units per cell, and therefore 12 valence electrons. As illustrated in Fig. 2B, a unit cell (Li₄H₈) contains four "guest" hydrogen atoms, all part of H₂ units (white). The H–H bond distance is 0.76 Å at 150 GPa, close to that of an H₂ molecule in the gas phase or in the solid. When the pressure is doubled further to 300 GPa, the H–H bond length decreases only slightly, by 0.02 Å. The shortest distance between hydrogen belonging to two different H₂ units is 1.20/1.06 Å (along the c axis) at 150/300 GPa, indicating that a 1D chain-like network of hydrogen is developing with increasing pressure.

The mauve hydrogens in LiH₂ in Fig. 2B are different. They are part of an LiH "host" sublattice and their nearest neighbors are Li atoms (1.50/1.38 Å), whereas the closest hydrogen neighbors are at least 1.68/1.56 Å at 150/300 GPa. We will therefore refer to these as lone or hydridic hydrogens. LiH₂ can be thought of as containing interpenetrating Li²⁺ and H⁻ sublattices. Its structure is reminiscent of Bi-III, Sb-II, Ba-IV and Sb-V, however in the elemental phases, the guest component is incommensurate with the host (see ref. 15 and references therein). Rb-IV and K-III (15) and the tI9 phase of Na (16) also have similar structures, but the host is made up of 16 atoms instead of 8.

The two types of hydrogens, differing much in their bonding, determine the electronic structure of LiH₂. In Fig. 3A the density of states (DOS) of LiH₂ at 0 GPa is shown: The main contribution to the peak lowest in energy comes from the \( \sigma \) bonding orbitals of the H₂ units (extended Hückel, eH, calculations confirm the H–H bonding in this band), whereas the peak just below \( \mu_0 \) (ranging from approximately −1 to −5.8 eV) is primarily due to the hydridic atoms. There is little Li character in the occupied bands. Indeed, the DOS of LiH₂ agrees well with that computed for the charged hydrogen sublattice (see SI) indicating that the Li–H bonding is primarily ionic. The conduction band can be identified (via eH) as being derived from the \( \sigma_u \) orbitals of the H₂ units, with increasing Li contributions at higher energy. Note the one-dimensional nature of the \( \sigma_g \) (H₂) DOS.

The general features of the electronic structure of LiH₂ (Fig. 3A and B) are represented schematically in Fig. 1B. With increasing pressure, the gap between the H₂ \( \sigma_g \) and H⁻ levels closes. More importantly, the H⁻ and unfilled H₂ \( \sigma_u \) bands approach each other; our DFT calculations predict that \( P4/mmb \)

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LiH$_2$ becomes a semimetal at pressures slightly >50 GPa. By 120 GPa, the system also becomes more stable than LiH + $\frac{1}{2}$H$_2$. The band gaps obtained with DFT are typically too small, and H$_2$ itself is predicted to metalize at ~240 GPa (17) — but it does not do so (3, 4). Given this discrepancy between theory and experiment, it is likely that our calculations also underestimate the pressure necessary to metalize LiH$_2$. Nonetheless, the metallization pressure we calculate is more than four times lower than the corresponding DFT values obtained for pure H$_2$.

**Fig. 3.** DOS (g(E)/valence electron in eV$^{-1}$) of the most stable LiH$_2$ (A and B) and LiH$_6$ (C and D) structures at 0 GPa and 100 GPa. The dashed vertical lines are the zero temperature limit of the electron chemical potential, or the Fermi energy, $E_F$, for metallic states.

Fig. 3B reveals that at 100 GPa LiH$_2$ is just metallic, and the small density of states at the Fermi energy (g($E_F$)/valence electron = 0.001 eV$^{-1}$) is reminiscent of the DOS calculated for compressed Li (19–21), rising only a little to 0.007 eV$^{-1}$ at 300 GPa. For elemental Li, the 1s cores start to overlap with increasing pressure, and the valence electrons are pushed into the interstitial regions (19). Could it be that core overlap also occurs in LiH$_2$? Our calculations show that the width of the core Li 1s bands is 0.76 eV at 100 GPa and rises to 2.16 eV at 300 GPa, strongly indicative of core overlap. Indeed, the LiH$_2$ DOS is characterized by a pseudogap above a valence band maximum at every pressure studied (other than 1 atm). The closest distance between two Li atoms in LiH$_2$ is 2.06 and 1.65 Å at the aforementioned pressures. These distances are somewhat longer than in pure Li: 1.63 Å (cI, 100 GPa), and 1.52 Å (P4$_3$2$_1$, 300 GPa). It is very likely that in LiH$_2$ there are also Li–Li interactions that impel valence electrons into interstitial regions (calculations show that the maximum of the valence electron density for the Li sublattice is near the positions of the hydridic atoms in LiH$_2$, see Fig. S3 in SI). This remains to be explored further.

**LiH$_6$, Metallic Because of Electron Transfer to H$_2$**

By 110 GPa, LiH$_6$ is stable relative to LiH and H$_2$. For P ≥ 150 GPa, it has the most negative enthalpy of formation of all of the
LiH₆ structures we have found. The unit cell contains one formula unit ($R3m$, space group 166) and therefore 7 valence electrons. Unlike LiH₂, in the optimized LiH₆ structure (Fig. 2C), no atoms are hydridic. All of the hydrogens belong to slightly stretched H₂ units. As will be seen, this is a consequence of electron transfer, and it is crucially important for the emerging electronic structure of the material. At 1 atm, the H–H bond length is computed to be 0.81 Å; this stretches slightly by 0.02 Å at a pressure of 50 GPa. Further compression up to 300 GPa has no effect on the shortest H–H distance. H₂ units with slightly stretched bonds have also been found in compressed germane (12). It should be mentioned that for LiH₆, as for the other LiHₓ, we have strong indications that in the low-pressure regime ($P < \approx 100$ GPa), segregation and layering into slabs of LiH and H₂ is preferred.

The DOS of LiH₆ at 1 atm is given in Fig. 3C, (LiH₆ is not yet stable relative to LiH and H₂ at normal pressures) and it shows quite a surprise: The system is metallic. As in LiH₂, the lowest energy peak is traced to the $\sigma$ bands. The Fermi level passes through a nearly free-electron-like region of the DOS, which we have identified (via eH) as being associated with the H₂ $\sigma$ bands. Thus, LiH₆ can be viewed as composed of Li⁺ and (3H₂) fragments. The slightly stretched H–H bond is a result of the partial filling of the $\sigma$ levels. In a molecular calculation, the bond in (H₂)⁹ with a partial charge of $q = -1/3$ optimized to 0.80 Å, in good agreement with the H–H bond length in LiH₆ at 1 atm. Thus, metallicity—even at low pressure—occurs because of electron transfer as illustrated in Fig. 1C. And it is not (at low pressures) a result of the direct overlap of sublattice wave functions with compression, in stark contrast to LiH₂ and the recently studied group 14 hydrides (6–8, 10–12).

The electron-transfer-induced metallicity persists as LiH₆ becomes a stable phase. Also, as the pressure increases, the gap between the $\sigma$ and $\sigma'$ bands closes, as the DOS at 100 GPa in Fig. 3D reveals. Electron transfer from Li to H₂ $\sigma'$ continues to dominate. $g(E_F)$ is particularly high, 0.033 eV⁻¹/valence electron, and remains nearly constant up to 300 GPa. Pressure has a nearly negligible effect on the intramolecular H–H distances. The intermolecular distances, on the other hand, decrease as expected.

The H₂ sublattice of LiH₆ is metallic at 100 GPa (see SI), whereas at the same pressure hydrogen is not. The sublattice is also ~481 meV per proton less stable than the P6₃/m H₂ structure. Why should this be? Consider Fig. 1A, a schematic sketch of metallization by band broadening and eventual overlap. If the H₂ bond is stretched, the energy of the molecular filled orbital will go up, and that of the empty one will go down (similar to Fig. 1C). As bands develop from the $\sigma$ and $\sigma'$ levels under compression, they will merge at a lower pressure than for pure solid H₂.

Interestingly, at 1 atm, the volume of LiH₆ is a factor of two smaller than that of the optimized H₂ lattice, indicating that the ionic attraction between Li⁺ and 3(H₂)⁻ results in “Madelung precompression.” This is the primary reason for the ~6 eV bandwidth of the $\sigma$ in Fig. 3C. However, because of the presence of the Li⁺ core, Madelung precompression is effective only in the low-pressure regime. For example, at 100 GPa, the volume of LiH₆ is ~1.4 times greater than that of pure H₂.

Because of the high ratio of hydrogen in LiH₆, the distances between nearest-neighbor Li atoms are too large for core overlap to occur. The Li 1s bandwidth is 0.51 eV at 300 GPa ($d$(Li–Li) = 2.35 Å), approximately a factor of four less than for LiH₂ at the same pressure.

For LiH₆, the highest phonon frequencies of 2920/3590 cm⁻¹ at 100/300 GPa (see SI) are reduced from the free H₂ vibron of 4,161 cm⁻¹ (22). This is also a consequence of the population of the $\sigma'$, and connected to the H₂ bond stretching, as observed in SiH₆(H₂)₂ (23). The aforementioned frequencies correspond to estimated Debye temperatures of 4,200/5,165 K. The substantial $g(E_F)$, and the large Debye temperatures for LiH₆ suggest that the electron–phonon coupling will be large. Moreover, the bands are wide, so that screening will reduce electron–electron repulsion (which works against pairing). Thus, LiH₆ may be another hydrogen-rich, high-temperature superconductor at experimentally accessible pressures.

**Other Stoichiometries**

We also studied LiHₓ with $n = 3–5, 7, and 8$. Each has its own interesting peculiarities, but the essential underlying features have already been shown for the $n = 2$ and 6 cases above. LiH₃ is similar to LiH₂, with H₂ units and hydridic atoms. LiH₄ and LiH₆ are akin to LiH₆: They contain H₂ units with slightly stretched H–H bonds. In our calculations, LiH₆ shows two structures of nearly equal enthalpies (in the pressure range within which they are stable): one similar to LiH₂, and the other to LiH₆. Finally, LiH₇ also has two structures, one with H₂ units and the other with a complex hydrogenic network.

What we see in the various LiHₓ structures is that some of the H₂ molecules are split up. Here is a way to think about it: Suppose Li transferred its valence electron to a single H₂, creating a fleeting negatively charged (H₂)⁻, populating $\sigma'$ of H₂ weakening the H–H bond. For what $q$ could the poor H₂ maintain bonding, albeit weakened? Molecular calculations supply an answer: $q = -1.2$ (for which H–H is stretched to 1.07 Å). If $q$ is more negative, (H₂)⁻ is not bound. This model suggests that Li₁.₂H₂ is the limit; in a binary phase with more Li, any H₂ molecules are unlikely to exist.

The enthalpic trends of all of the LiHₓ phases studied are shown in Fig. 4, a tie-line representation (18). The essential features of this diagram are the following: (i) of course, there is no stabilization for $n = 1$ and $n = \infty$ in LiH₄; (ii) stabilization begins to occur at ~100 GPa for some $n$; by 200 GPa, all of the phases are stable or metastable relative to LiH and H₂; (iii) LiH₆ is the most stable phase for $P \approx 150$ GPa; at 100 GPa, LiH₆ is
slightly more stable. There are regions of metastability for LiH₂ and LiH₃, and for a given pressure, various structures are within dynamical enthalpies of each other.

The optimum composition of LiₙHₚ must have y > x, given the great donor strength of the electropositive Li, the incentive to stretch—if not break—the H–H bond by populating the σₓ band of the Hₓ, as well as the Madelung stabilization of LiₚHₓ⁻. Why the balancing act is best for LiH₆ is not yet clear to us.

**Conclusion**

Indeed, a little bit of Li does a lot for H₂—under pressure. All of the high-hydride phases with unusual stoichiometries (LiHₓn, n = 2–8) become enthalpically stable relative to LiH and H₂. There is remarkable structural variety in the stable LiHₓn; some contain only Hₓ units, some both Hₓ and H⁻ (or a host LiH lattice with Hₓ guests). Every phase of LiHₓ (n > 1) is computed to become metallic and stable or metastable in the range of approximately 100–165 GPa, a pressure much lower that that required to metalize pure H₂. These structures provide ways to think about metalizing hydrogen by electron transfer from an electropositive element. Indeed, two strategies emerge: (i) stabilization of H⁻, and thereby the introduction of a band between the filled and empty H₂ bands or (ii) population of the σₓ orbital of H₂. The phenomenon may not be limited to Li, and we have preliminary indications of similar behavior in other alkali high-hydride systems.

As a concluding observation, it may be noted that for pressures in the vicinity of 400 GPa, pure hydrogen, i.e., LiHₓ, may metalize as a ground-state quantum liquid (24). This suggests that in an Li–H alloy system, and at a pressure expected to be considerably lower than 400 GPa (based on the findings above), the possibility of eutectic-like behavior may arise for sufficient addition of hydrogen, but with the melting point dropping to temperatures close to zero. These could remain at very low values in the approach to the pure hydrogen limit, again suggesting consequent quantum liquid behavior and with possible quantum orderings now reflecting the statistical properties of the constituents.

**Computational Methodology**

Geometry optimizations and electronic structure calculations were performed by using DFT as implemented in the Vienna ab-initio simulation package (VASP) (25). The Perdew-Burke-Ernzerhof (PBE) exchange–correlation functional (26), an energy cutoff of 500 eV, and all-electron plane-wave basis sets within the projector augmented wave (PAW) method (27) have been used. The k-point grids were generated using the Monkhorst-Pack scheme, and the number of divisions along each reciprocal lattice vector was chosen so that the product of this number with the corresponding real lattice constant was ~50 Å. Phonon calculations were carried out by using VASP combined with PHON (28) on supercells of 189 (LiHₓ) and 324 (LiHₓ) atoms. Symmetry identification of the structures was carried out by using ISOTROPY (http://stokes.byu.edu/isotropy.html). For a given pressure, the lowest-enthalpy structures were found by using the evolutionary algorithm USPEX, which has been successfully tested and applied to many other systems (29–31). It also correctly predicts the rock salt structure for LiH between 0 and 200 GPa. For LiHₓ/LiHₓ⁺, we have considered unit cells containing up to 4 and 2 formula units, respectively. Calculations were carried out between 0 and 300 GPa, in 50-GPa intervals. For a given cell size and stoichiometry, the USPEX calculations found the same space group and unit cell over the whole pressure range within which LiHₓ was stable. The molecular calculations on (Hₓ)ₓ were performed by using ADF (www.scm.com), and the extended Hückel (eH) computations with YaeHMP (http://overlap.chem.cornell.edu:8080/YaeHMP.html).

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