

SUPPORTING INFORMATION

A little bit of lithium does a lot for hydrogen

Eva Zurek^{1*}, Roald Hoffmann¹, N. W. Ashcroft², Artem R. Oganov^{3,4}, Andriy O. Lyakov³

¹ Department of Chemistry and Chemical Biology, Cornell University, Baker Laboratory, Ithaca, NY, 14853-1301, USA

² Laboratory of Atomic and Solid State Physics and Cornell Center for Materials Research, Cornell University, Clark Hall, Ithaca, NY, 14853-2501, USA

³ Department of Geosciences and New York Center for Computational Science, State University of New York at Stony Brook, Stony Brook, NY, 11794-2100, USA

⁴ Geology Department, Moscow State University, Moscow, 11992, Russia

*Correspondence should be addressed to E.Z., R.H. and N. W. A. (ez56@cornell.edu, ezurek@buffalo.edu, rh34@cornell.edu, nwa@ccmr.cornell.edu)

Unless otherwise stated, the results below were obtained from VASP calculations.

Contents of the SI

1. LiH

- discussion of stability, metallization and transformation to the CsCl structure
- enthalpy of formation as a function of pressure (Figure S1)
- densities of states at 0 and 300 GPa (Figure S2)

2. LiH₂

- discussion of core overlap
- valence electron densities (Figure S3)
- band structures at 50 and 100 GPa (Figure S4)
- eH partial densities of states at 100 and 300 GPa (Figure S5)
- DOS of LiH₂ and of its hydrogen sublattice at 0 and 100 GPa (Figure S6)
- phonon densities of states at 100 and 300 GPa (Figure S7)

3. LiH₆

- discussion about the hydrogen sublattice
- DOS of LiH₆ and of its hydrogen sublattice at 0 and 100 GPa (Figure S8)
- eH partial densities of states at 0 and 100 GPa (Figure S9)
- VASP band structures at 0 and 100 GPa (Figure S10)
- eH band structures at 0 and 100 GPa (Figure S11)
- phonon densities of states at 100 and 300 GPa (Figure S12)

4. LiH_n

- enthalpies of formation as a function of pressure (Figure S13)

1. LiH

At 1 atm, LiH crystallizes in the NaCl structure with an equilibrium lattice constant of $a = 4.09 \text{ \AA}$. We calculate $a = 4.01 \text{ \AA}$. The bonding is ionic, Li^+/H^- , and accordingly the valence band is dominated by H s -character. Some Li p is also mixed in. The band gap is 4.99 eV, which is not surprisingly underestimated by our DFT calculations (2.97 eV).

The other alkali hydrides also crystallize in the rocksalt structure, and experiments have shown that they transform to the CsCl structure under pressure. For LiH, this structural transition has not been observed experimentally. However, it has been studied theoretically, and so has the pressure-induced metallization.

In Fig. S1 we illustrate the enthalpy (meV/atom) of LiH in the rocksalt structure as a function of pressure. It is given with respect to H_2 in the $P6_3/m$ (0-100 GPa), $C2/c$ (150-250 GPa), $Cmca-12$ (300-350 GPa) structures (as found in Ref. S1), and Li bcc (0 GPa), $cI16$ (50-250 GPa), and $P4_132$ (300-350 GPa, see Ref. S2) structures.

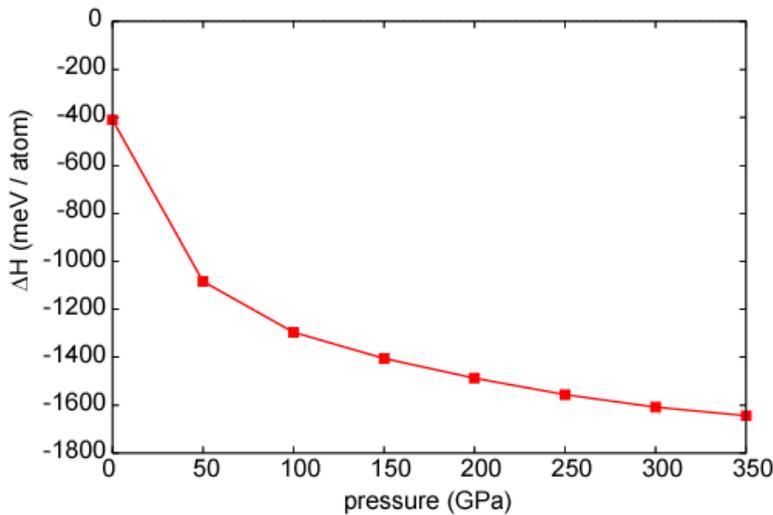


Figure S1 Enthalpy of formation (meV/atom) of LiH in the rocksalt structure from Li and H_2 , as a function of pressure.

Our DFT results indicate that LiH becomes metallic around 300 GPa, and transforms to the CsCl structure at 360 GPa (31% and 29% of the 1 atmosphere cell volume, respectively). It should be noted that the reaction $n(\text{LiH}) \rightarrow (n-1) \text{Li} + \text{LiH}_n$ ($n = 2-8$) was found to have a positive enthalpy at pressures ranging from 0-300 GPa.

Therefore, our calculations indicate that this decomposition reaction will not occur. We have not performed calculations on systems containing more lithium than hydrogen, so we do not know with certainty if reactions such as $8(\text{LiH}) \rightarrow \text{H}_2 + 2(\text{Li}_4\text{H}_3)$ may occur.

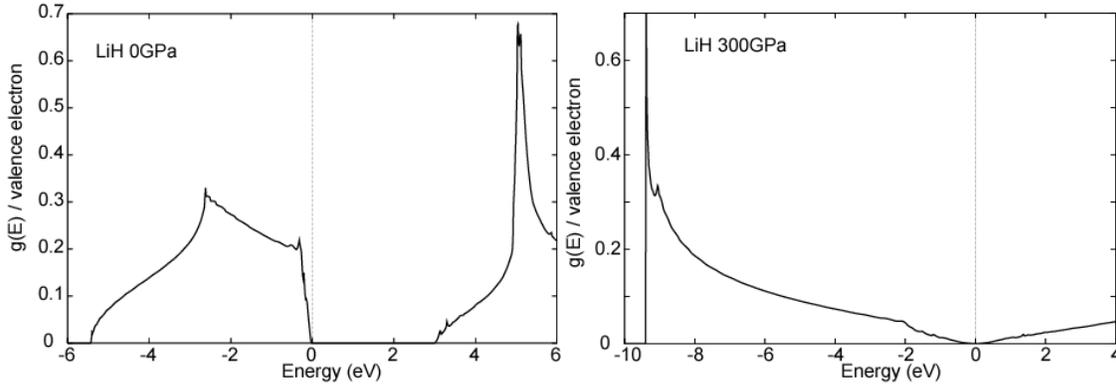


Figure S2 Densities of states ($g(E)/\text{valence electron } eV^{-1}$) of LiH at 0 and 300 GPa. The dashed line denotes the highest occupied level.

2. LiH_2

The best structure we have found $P4/mbm$ (space group 127), contains four formula units per cell. At 150 GPa, $a = 4.10 \text{ \AA}$, $c = 1.96 \text{ \AA}$ with the Li at (0.155, 0.344, 0) and two inequivalent hydrogens at (0.352, 0.148, 0.5) and (0, 0, 0.806).

For elemental Li, with increasing pressure the $1s$ cores start to overlap and the valence electrons are pushed into the interstitial regions. As a result, compressed Li exhibits semiconducting or even insulating behaviour. We find that the width of the core Li $1s$ bands in LiH_2 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 is 2.06 and 1.65 \AA at the aforementioned pressures. It is therefore very likely that in LiH_2 there are also Li-Li interactions that impel valence electrons into interstitial regions. In Figure S3 we illustrate the valence electron density of LiH_2 at 150 GPa, and also that of a neutral Li sublattice with the same structure. The latter shows that the valence electrons reside in the regions where the hydridic atoms in LiH_2 are found.

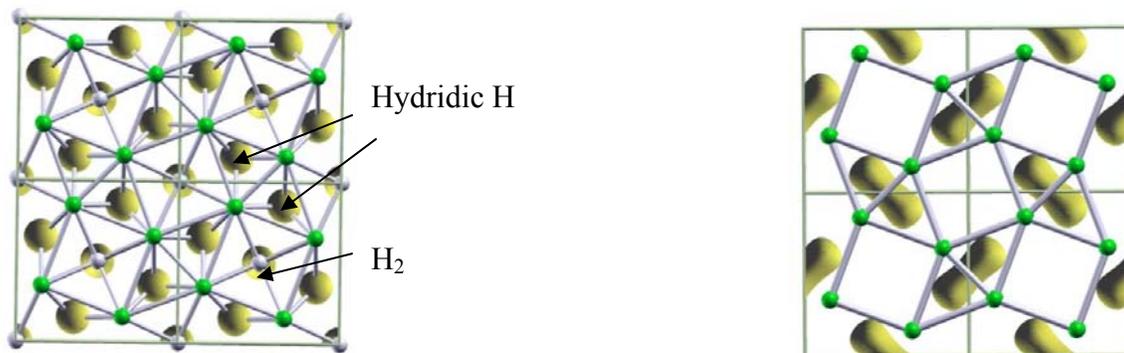


Figure S3 Left: Valence electron density of LiH₂ at 150 GPa. Right: Valence electron density of the neutral lithium sublattice. Lithium atoms are colored green, hydrogen atoms white.

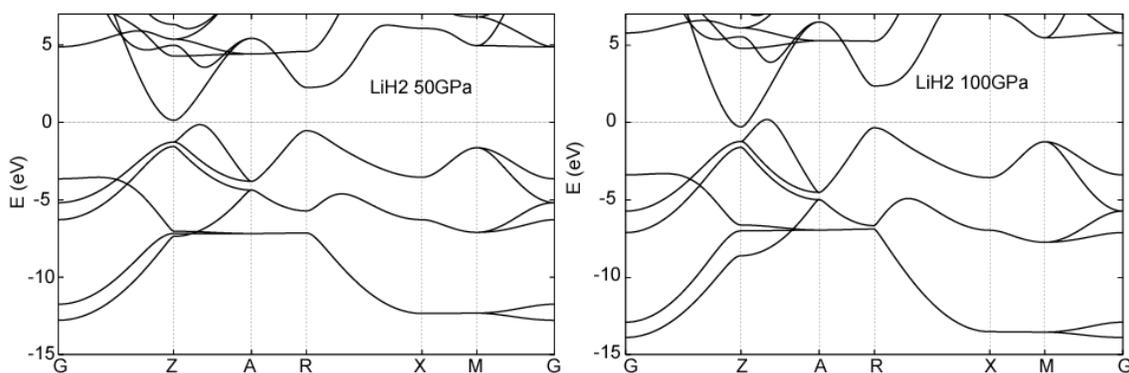


Figure S4 Band structure of LiH₂ at 50 GPa (left) and 100 GPa (right).

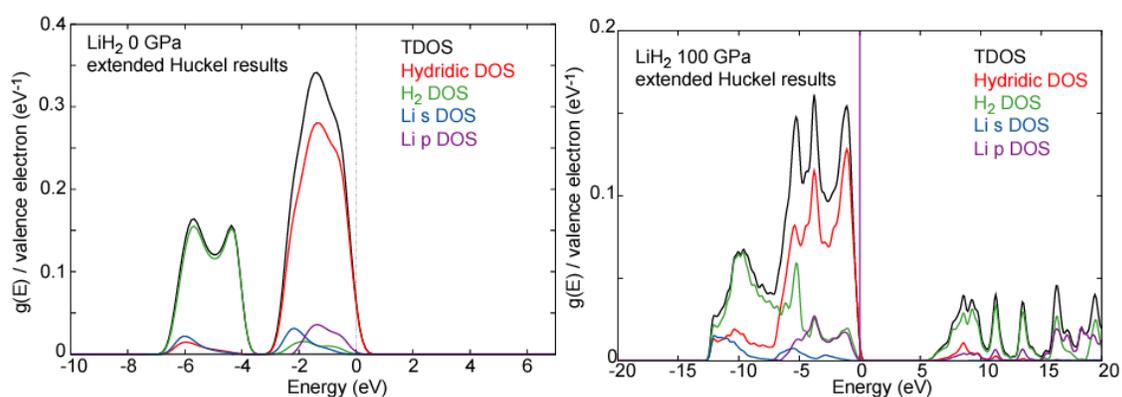


Figure S5 Partial densities of states ($g(E)/\text{valence electron } eV^{-1}$) of LiH₂ as obtained from extended Hückel calculations at 0 GPa (left) and 100 GPa (right).

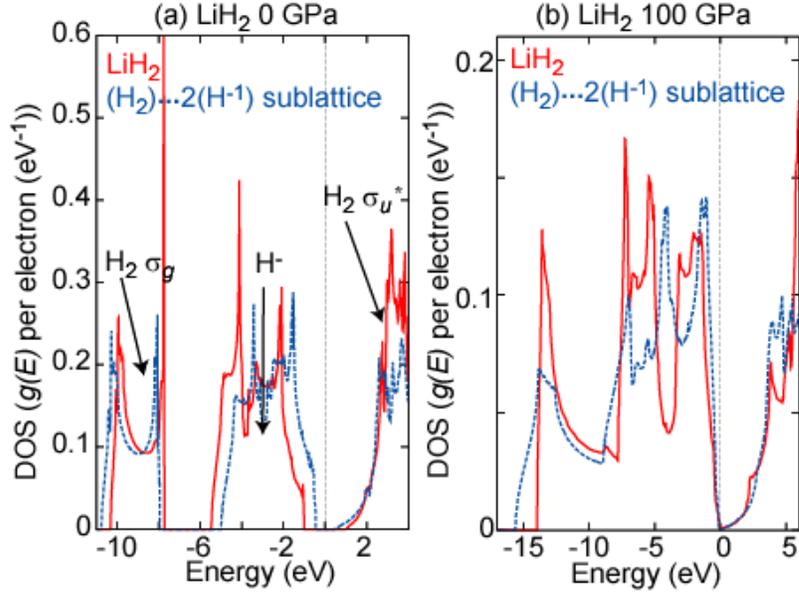


Figure S6 ($g(E)$ /valence electron in eV^{-1}) of the most stable LiH_2 structures at 0 and 100 GPa are given in red. The blue DOS curves were calculated for the hydrogen sublattice, which was charged so that the total number of valence electrons is the same as in LiH_2 . The similarity between the blue and red DOS gives further evidence that the bonding is primarily ionic.

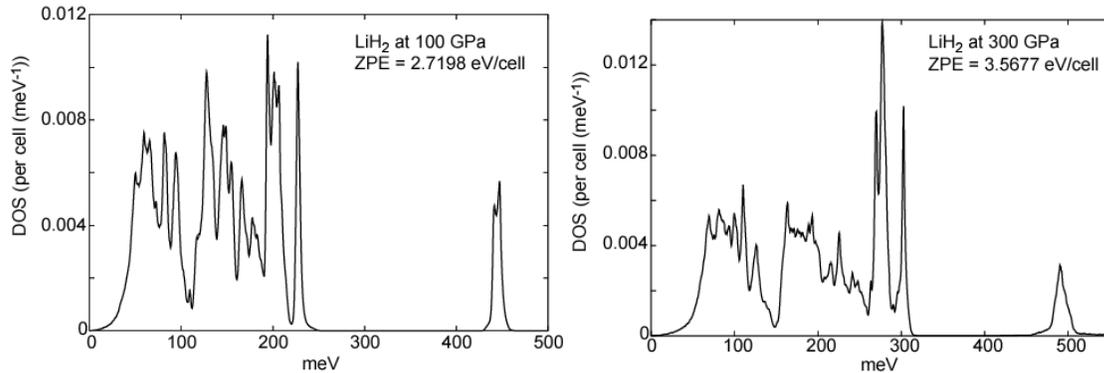


Figure S7 Phonon DOS' for LiH_2 at 100 and 300 GPa calculated using the PHON program and the forces obtained with VASP. No imaginary frequencies were found, indicating this structure is a local minimum. The zero-point energies are 0.227 and 0.297 eV/atom at these pressures, respectively. The zero-point energies will have a negligible effect on the enthalpies of formation (Figure S13), being less than ~ 7 meV/atom (ie. $\Delta ZPE = ZPE(\text{LiH}_n) - (n-1)/2 ZPE(\text{H}_2) - ZPE(\text{LiH})$ is less than 7 meV/atom).

3. LiH₆

The best structure we have found $R\bar{3}m$ (space group 166), has one formula unit per cell. At 150 GPa, $a = 3.13 \text{ \AA}$, $c = 5.47 \text{ \AA}$ with the Li at (0, 0, 0.5) and H at (0.668, 0.834, 0.758). Because of the high ratio of hydrogen in this system, the distances between nearest neighbour Li atoms are too large for the cores to overlap. Indeed, the Li $1s$ bandwidth is 0.51 eV at 300 GPa ($d(\text{Li-Li}) = 2.35 \text{ \AA}$), about a factor of four less than for LiH₂ at the same pressure.

The nearest neighbour separations between two H₂ units are 1.45/1.19 Å at 100/300 GPa, which are very similar to those we calculate for the most stable forms of pure solid H₂: 1.49/1.10 Å at the aforementioned pressures (the structures predicted to be the most stable in Ref. S2 were used). However, even though the distances are very similar, the underlying hydrogen is different. As the blue DOS in Figure S8 (b) reveals, even without the lithiums, the hydrogen sublattice by itself would be metallic at 100 GPa (and ~481 meV/proton less stable than the $P6_3/m$ H₂ structure).

Some comments on the electronic structure of LiH₆ $P = 1 \text{ atm}$: There are some interesting points in the LiH₆ DOS (Figure S8/S9) and band structures (Figure S10/S11). The band structure corresponding to the $P = 1 \text{ atm}$ VASP calculation is shown below in Figure S10 (left panel); the eH band structure in Figure S11 (left panel).

1. The energy scales for the VASP DOS and the band structure are off by 0.5-1.0 eV. This discrepancy has two origins. The DOS has been calculated using the tetrahedron method with Blochl corrections, in order to obtain a smooth DOS curve. It is not possible to use this option to calculate the band structure. Moreover, in the band structure calculations, the k -mesh employed is along the lines connecting the high-symmetry points, whereas in the DOS calculation, the Monkhorst-Pack scheme is used.
2. The large peak at ~-6.5 eV in the VASP DOS (Fig. 3(c) main text) comes from the flat band, the topmost one of the three occupied H₂ σ_g bands in Figure S10. There is also a corresponding flat band in the eH calculation (see Figure S11).
3. The small band gap at -9.2 eV in the VASP calculation is not really a band gap, as the band structure shows; k -point sampling is responsible for the discrepancy.

4. The jagged structure at the Fermi level in the DOS is not obvious from the band structure. Very likely a Jones plane is active along some special direction in the Brillouin Zone that is not shown in Figure S10.

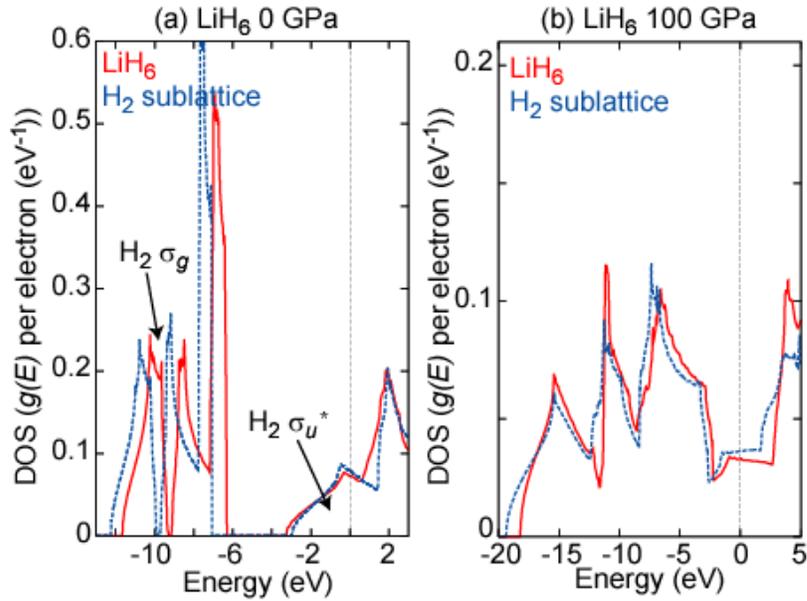


Figure S8 ($g(E)/\text{valence electron in } eV^{-1}$) of the most stable LiH_6 structures at 0 and 100 GPa are given in red. The blue DOS curves were calculated for a neutral hydrogen sublattice. However, the DOS and E_F were calculated for a system containing 7 valence electrons. The similarity between the blue and red DOS gives further evidence that the bonding is primarily ionic.

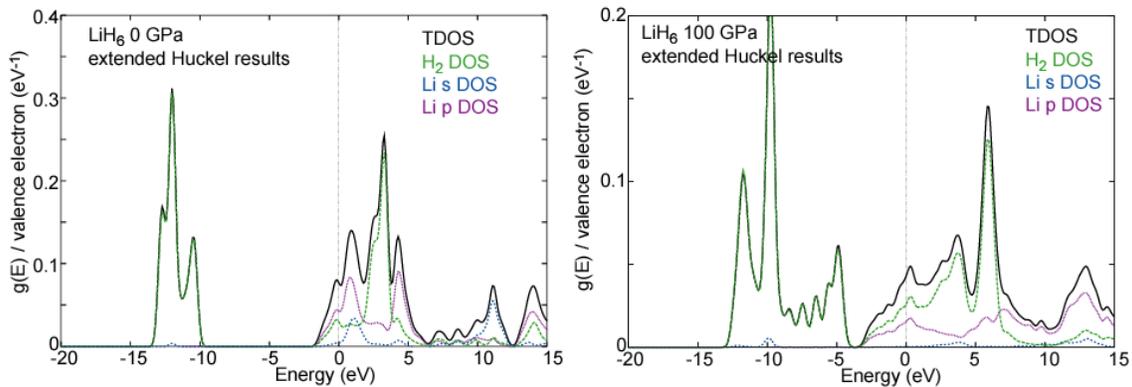


Figure S9 Partial densities of states ($g(E)/\text{valence electron } eV^{-1}$) of LiH_6 as obtained from extended Hückel calculations at 0 GPa (left) and 100 GPa (right).

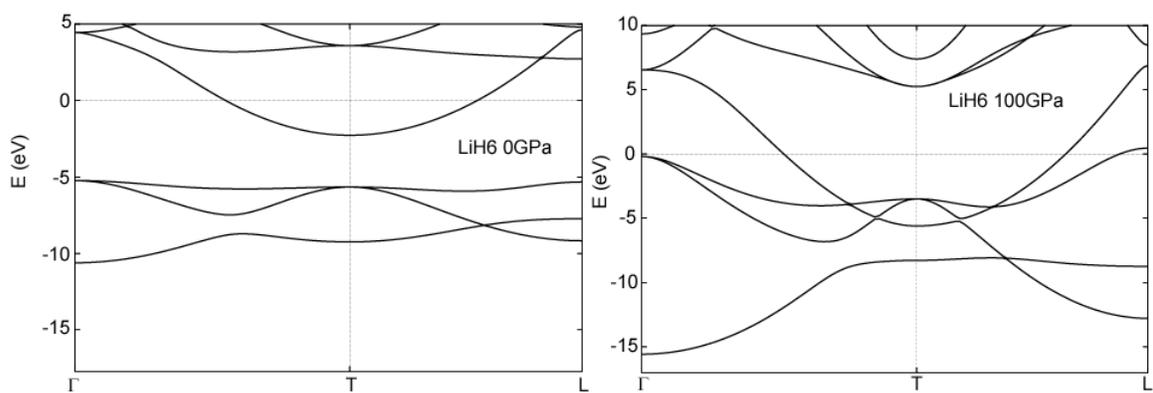


Figure S10 Band structure of LiH_6 at 0 GPa (left) and 100 GPa (right) obtained from VASP.

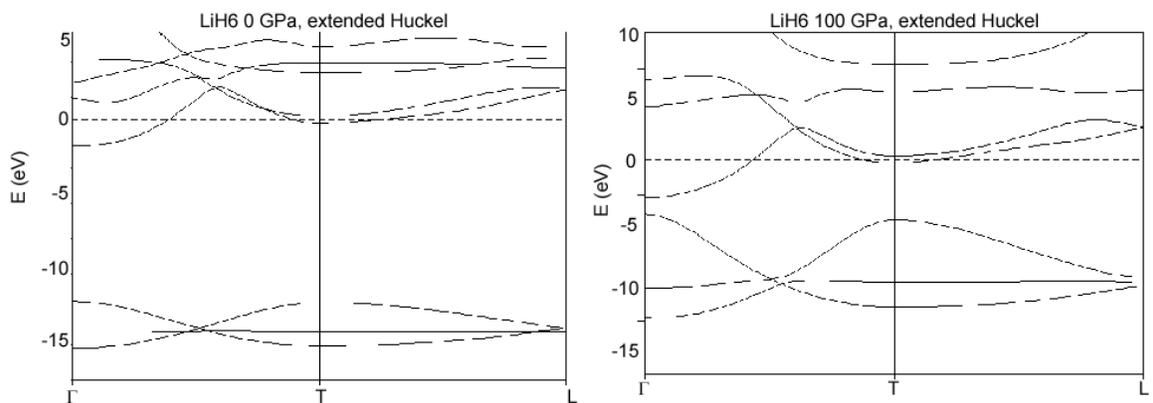


Figure S11 Band structure of LiH_6 at 0 GPa (left) and 100 GPa (right) obtained from extended Hückel calculations.

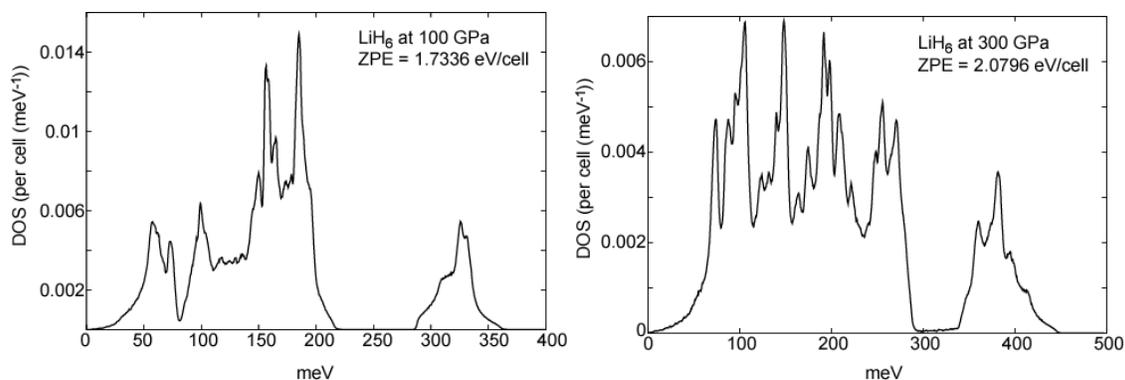


Figure S12 Phonon DOS' for LiH_6 at 100 and 300 GPa calculated using the PHON program and the forces obtained with VASP. No imaginary frequencies were found, indicating this structure is a local minimum. The zero-point energies are 0.248 and 0.297 eV/atom at these pressures, respectively. For LiH in the rocksalt structure we calculated the zero-point energies to be 0.215/0.287 eV/atom at 100/300 GPa, whereas for H_2 they are roughly 0.25 – 0.28 eV/proton, depending on the pressure (*SI*). The zero-point energies will have a negligible effect on the enthalpies of formation (Figure S13), being less than ~ 1 meV/atom (ie. $\Delta ZPE = ZPE(\text{LiH}_n) - (n-1)/2 ZPE(\text{H}_2) - ZPE(\text{LiH})$ is less than 1 meV/atom).

4. LiH_n

In Figure S13 we provide the enthalpies of formation of LiH_n ($n = 2-8$) for all of the stable structures found using USPEX.

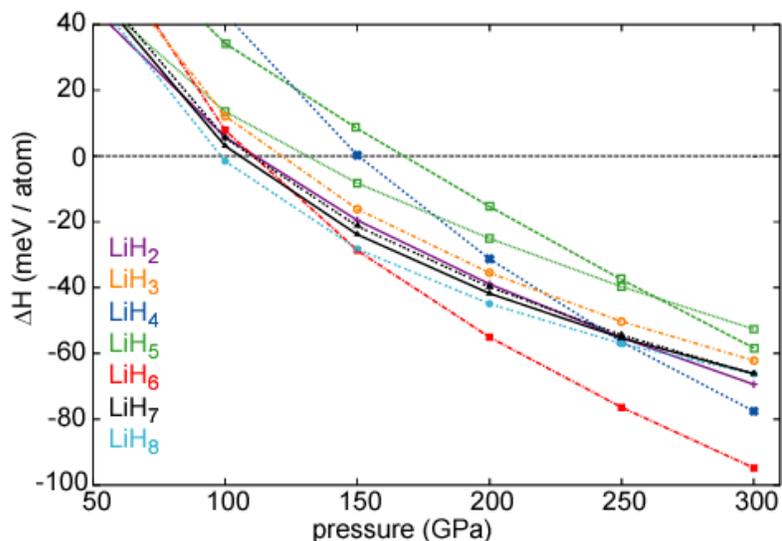


Figure S13 Relative enthalpy with respect to LiH and H_2 (meV/atom) of the most stable LiH_n ($n = 2-8$) solids as a function of pressure. Note, that for LiH_5 and LiH_7 two nearly isoenthalpic structures were found. For these two systems, Figure 4 in the main text gives the relative enthalpies of the structures most stable at 150 GPa.

References

- S1. Pickard, CJ, Needs, RJ (2007) Structure of phase III of solid hydrogen. *Nature Phys* 3:473-476.
- S2. Ma, Y, Oganov, AR, Xie, Y (2008) High-pressure structures of lithium, potassium, and rubidium predicted by an ab initio evolutionary algorithm. *Phys Rev B* 78:014102.