

# Synthesis of lithium polyhydrides above 130 GPa at 300 K

Charles Pépin<sup>a</sup>, Paul Loubeyre<sup>a,1</sup>, Florent Occelli<sup>a</sup>, and Paul Dumas<sup>b</sup>

<sup>a</sup>Commissariat à l'Énergie Atomique, Centre DAM - Ile de France, F-91297 Arpajon, France; and <sup>b</sup>Synchrotron SOLEIL, F-91192 Gif-sur-Yvette, France

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**The prediction of novel lithium hydrides with nontraditional stoichiometries at high pressure has been seminal for highlighting a promising line of research on hydrogen-dense materials. Here, we report the evidences of the disproportionation of LiH above 130 GPa to form lithium hydrides containing H<sub>2</sub> units. Measurements have been performed using the nonperturbing technique of synchrotron infrared absorption. The observed vibron frequencies match the predictions for LiH<sub>2</sub> and LiH<sub>6</sub>. These polyhydrides remain insulating up to 215 GPa. A disproportionation mechanism based on the diffusion of lithium into the diamond anvil and a stratification of the sample into LiH<sub>6</sub>/LiH<sub>2</sub>/LiH layers is proposed. Polyhydrides containing an H<sub>2</sub> sublattice do exist and could be ubiquitously stable at high pressure.**

high pressure | hydride chemistry | hydrogen stoichiometry

Over the past 5 y, and since the prediction of stable LiH<sub>n</sub> compounds at high pressure has been proposed (1), numerous calculations have unveiled a novel view on the chemical combination of hydrogen with metals under pressure (2–7). Three remarkable trends have been identified: (i) Hydrogen stoichiometry should drastically increase under pressure in metals. (ii) Polyhydrides with nontraditional stoichiometries, in some cases containing an H<sub>2</sub> sublattice, should be stable. (iii) These hydrogen-dense systems may become metallic at much lower pressure than expected for metallic hydrogen and could have a high-temperature superconductivity (8, 9). These theoretical results have impelled an active experimental search (e.g., refs. 10 and 11).

Very recently, a few experimental results have particularly illustrated the richness of this line of research. A significant change of the H content in a transition metal has been reported by directly compressing rhodium in fluid hydrogen. The transition from RhH to RhH<sub>2</sub> is associated with the change of interstitial hydrogen from octahedral to tetrahedral sites (12). Two novel iron hydrides, FeH<sub>2</sub> and FeH<sub>3</sub>, have been discovered under pressure, in the sequence FeH–FeH<sub>2</sub>–FeH<sub>3</sub> that follows the expected drastic increase of hydrogen content upon pressure increase (13). Moreover, FeH<sub>2</sub> and FeH<sub>3</sub> adopt intriguing structures with layers of atomic hydrogen. Finally, a superconducting critical temperature (*T<sub>c</sub>*) of 190 K has been measured in H<sub>2</sub>S compressed to about 200 GPa, which breaks the cuprate record of superconductivity temperature (14, 15). The understanding of such a high *T<sub>c</sub>* suggests that decomposition of H<sub>2</sub>S sample to form the H<sub>3</sub>S superconducting phase occurs at high pressure in the diamond anvil cell. Here, we directly show the existence under pressure of novel forms of lithium polyhydrides, possibly LiH<sub>6</sub> and LiH<sub>2</sub>, each containing a sublattice of H<sub>2</sub> units.

## Results and Discussion

Previous works have investigated the stability of new Li–H compounds by compressing pure Li in hydrogen, LiH in hydrogen, or pure LiH (16, 17). Stoichiometric LiH is invariably formed. Solid LiH has a rock salt structure (B1) that was observed to remain stable up to 160 GPa and 250 GPa, using Raman spectroscopy and X-ray diffraction, respectively. Any appearance of the predicted hydrogen-rich compounds in these experiments might have been

either hindered by the kinetics or not detected because the probing techniques were not sensitive enough. Heating of these Li–H samples in the diamond anvil cell (DAC) could help to overcome a possible kinetic barrier, but, since Li–H systems form transparent and reactive materials, a controlled heating without chemical contamination by the confinement materials is quite difficult to avoid. Instead we have chosen to perform the measurements using a noninvasive probing technique that has a great sensitivity to chemical changes, namely infrared (IR) absorption measurements. Moreover, IR absorption is ideally suited to detect a metallic character of the sample.

The pressure evolution in the IR transmission spectra of LiH collected at 300 K is illustrated in Fig. 1. The IR transmission of the unloaded empty DAC is used as the reference to obtain the IR absorption bands of the LiH<sub>n</sub> sample. Up to 130 GPa, the only observed feature is a broad absorption band that rapidly shifts upward under pressure, from 800–1,200 cm<sup>−1</sup> under a few gigapascals to 1,900–2,300 cm<sup>−1</sup> at 100 GPa. This band corresponds to the longitudinal and transverse optical (LO–TO) modes of solid LiH that merge into a band due to nonhydrostatic pressure stress broadening, since no pressure-transmitting medium was used. Above 130 GPa, two well-resolved peaks become clearly identified between 2,500 cm<sup>−1</sup> and 3,000 cm<sup>−1</sup> while the broad band below 2,000 cm<sup>−1</sup> is still present. We also note that there is no significant absorption in the lower wave numbers domain, indicating no sign of a semimetallic state. A chemical and/or structural change in the sample clearly occurs above 130 GPa at 300 K and was successfully reproduced in two independent experiments.

Fig. 2 shows more specifically the representative absorption spectra of LiH samples above 2,300 cm<sup>−1</sup>. Two peaks, denoted  $\nu_1$  and  $\nu_2$ , appear around 2,500 cm<sup>−1</sup> above 130 GPa. Their intensity increases with pressure. Above 160 GPa, another peak,  $\nu_3$ , is observed around 4,000 cm<sup>−1</sup>. The frequency shift with pressure of these three IR peaks and of the absorption band below 2,000 cm<sup>−1</sup> could be monitored up to 215 GPa, as plotted in Fig. 3. The  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  peaks are ascribed to vibrons of H<sub>2</sub> entities. We use the calculated phonon density of states in LiH<sub>n</sub> compounds to interpret our data and provide an assignment for these various peaks (1, 18). It should be noted first that the frequency as well as the

## Significance

High hydrides with unusual stoichiometries have been predicted to become energetically favored in various hydrides of alkali and alkali earth metals under pressure. This paper reports on synchrotron infrared spectroscopic measurements on lithium hydride (LiH) compressed in a diamond anvil cell up to 215 GPa, showing that insulating lithium polyhydrides containing H<sub>2</sub> units are synthesized above 130 GPa at 300 K. The observed vibron frequencies are in good agreement with the predictions for LiH<sub>2</sub> and LiH<sub>6</sub>.

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<sup>1</sup>To whom correspondence should be addressed. Email: paul.loubeyre@cea.fr.





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