Synthesis of lithium polyhydrides above 130 GPa at 300 K

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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 H₂ units. Measurements have been performed using the nonperturbing technique of synchrotron infrared absorption. The observed vibron frequencies match the predictions for LiH₂ and LiH₆. 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 LiH₆/LiH₂/LiH layers is proposed. Polyhydrides containing an H₂ 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_n 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 H₂ 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 RhH₂ is associated with the change of interstitial hydrogen from octahedral to tetrathedral sites (12). Two novel iron hydrides, FeH₂ and FeH₃, have been discovered under pressure, in the sequence FeH-FeH2-FeH3 that follows the expected drastic increase of hydrogen content upon pressure increase (13). Moreover, FeH₂ and FeH₃ adopt intriguing structures with layers of atomic hydrogen. Finally, a superconducting critical temperature (T_c) of 190 K has been measured in H₂S compressed to about 200 GPa, which breaks the cuprate record of superconductivity temperature (14, 15). The understanding of such a high T_c suggests that decomposition of H₂S sample to form the H₃S 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 LiH₆ and LiH_2 , each containing a sublattice of H_2 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.

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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_n 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⁻¹ under a few gigapascals to 1,900–2,300 cm⁻¹ 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⁻¹ and 3,000 cm⁻¹ while the broad band below 2,000 cm⁻¹ 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⁻¹. Two peaks, denoted v_1 and v_2 , appear around 2,500 cm⁻¹ above 130 GPa. Their intensity increases with pressure. Above 160 GPa, another peak, v_3 , is observed around 4,000 cm⁻¹. The frequency shift with pressure of these three IR peaks and of the absorption band below 2,000 cm⁻¹ could be monitored up to 215 GPa, as plotted in Fig. 3. The v_1 , v_2 , and v_3 peaks are ascribed to vibrons of H₂ entities. We use the calculated phonon density of states in LiH_n 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 H₂ units are synthesized above 130 GPa at 300 K. The observed vibron frequencies are in good agreement with the predictions for LiH₂ and LiH₆.

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Transmitted Intensity (a.u.)



Fig. 1. IR transmission spectra at selected pressures, at 300 K. The broad absorption band corresponding to the LO-TO modes of LiH is visible at low wavenumbers and is framed by the gray cursor as a guide for the eyes. The new absorption peaks originating from LiH₂ and LiH₆ are indicated by black arrows at 201 GPa. The absorption peaks below 3,000 cm⁻¹ can be observed at 155 GPa. (*Inset*) Photograph of the optically transparent sample at 201 GPa. The frequency range of the high two-phonon absorption of the diamond has been masked for clarity purposes.

positive pressure-induced frequency shift of these peaks does not match with the infrared absorption spectra of pure solid H₂ (19). The latter is at higher frequency and exhibits a negative pressure dependence. This rules out the possibility of a dissociation of LiH to form LiH_x (x < 1) and solid H₂ that was recently predicted around 90 GPa (20). LiH₂ is thought of as containing interpenetrating Li⁺H⁻ and H₂ sublattices, with a weak interaction between them. The H–H distance should be similar to the one in pure solid H₂. Thus, the H₂ vibron frequency in LiH₂ is predicted around 4,000 cm⁻¹ with a positive pressure frequency shift. In



Fig. 2. Selected IR absorbance spectra at 300 K above 2,300 cm⁻¹. The absorption peaks labeled v_1 and v_2 both appeared above 130 GPa. A third peak, labeled v_3 , appeared upon further compression above 160 GPa.



Fig. 3. Pressure dependence of the absorption peaks at 300 K and 77 K. Estimation of the LO-TO frequencies from Raman measurements from Lazicki et al. (17) are shown, as well as the most intense calculated frequencies for LiH_2 and LiH_6 by Zurek et al. (1). The measured lower and upper bounds of the LO-TO absorption band of LiH are shown.

contrast to LiH₂, LiH₆ and other LiH_n (n = 4-8) contain H₂ units with slightly stretched H-H bonds, since the Li atom transfers its valence electron to H_2 molecules, hence populating the antibonding state and weakening the H2 molecule. In this case, vibron frequencies are predicted to be in the $3,000 \text{ cm}^{-1}$ range. The predicted vibron frequencies for LiH₂ and LiH₆ are plotted in Fig. 3 and compared with our data. The reasonable agreement between v_1 , v_2 , and v_3 with LiH₆ and LiH₂ vibrons frequencies suggests their formation. In all LiH_n compounds, the other phonon modes, associated with Li atoms or intermolecular vibrations, fall below 2,000 cm⁻¹, i.e., in the measured broad band. As seen in Fig. 3, the evolution of the band is also in good agreement with the evolution of the LO-TO frequencies of LiH, as measured from Raman measurements (17). Therefore, this low-frequency band is not a distinctive criterion for a stoichiometry change in the LiH sample.

The observation of LiH_n products implies that a disproportionation reaction has taken place in the LiH samples under pressure. Other evidence contributes to disclose a possible mechanism of this transformation. In all our LiH compression experiments, the diamond anvils always broke at an unusually low pressure compared with the numerous other studies performed with our DACs. Each failure was identified by a crack propagating from the tip of the anvil. Since no formation of Li could be detected in the sample from a change of the IR absorption, we assume that the excess Li is diffusing into the diamond anvils, as has been reported for pure Li, and so making the crack (21). The convex hull diagram of the relative enthalpies calculated for LiH_n compound indicates that LiH should be always stable if the compressed sample keeps an equal ratio of Li and H (1). In the present case, the affinity of Li with carbon sucks the Li from the LiH sample at the interface with diamond, and the transformed interface layer evolves to the LiH_n compound having the minimum enthalpy, predicted to be LiH₆. The hypothesis of a Li/C chemical reaction was strengthened by



Fig. 4. Temperature dependence of the disproportionation mechanism fitted by an Arrhenius law. The B1–B2 pressure transition in LiH is predicted by Lebègue et al. (22) to take place at 329 GPa and is never intersected by the transition line. The pressure at 18 K corresponds to a lower estimation, as the transition was not observed up to 250 GPa. (*Inset*) Schematic mechanism of the structuration of the sample in layers via the chemical reaction of lithium with the anvils and according to the convex hull proposed by Zurek et al. (1).

performing the LiH compression experiments at low temperature. The appearance of the v_1 and v_2 vibrons, hence the transformation to LiH₆, occurs at higher pressure for lower temperatures—180 GPa at 77 K—and it was not observed up to 250 GPa at 18 K. As seen in Fig. 4, the Arrhenius law fitted for this transition line is indicative of an activation mechanism that is in agreement with the reactivity–diffusion mechanism of Li with diamond. Hence, the Li/C reactivity somehow helps to change the hydrogen composition of the sample and to overcome the energy barrier of the disproportionation reaction [the reaction barrier hindered the transformation of LiH compressed in hydrogen to 160 GPa at 300 K (16)]. It is also interesting to note that the B1–B2 transition, and hence the metallic form of LiH, predicted to occur around 329 GPa (22) might never be observed by compressing pure LiH in a DAC, even at 4K.

By going up in pressure, the appearance of LiH_6 and LiH_2 is, in fact, an illustration of the convexity of the hull diagram. Above

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130 GPa, the diffusion of Li in C favors the formation of a LiH_6 layer in contact with the anvil. However, at the interface between this LiH_6 layer and LiH, the formation of a LiH_2 layer lowers the enthalpy due to the convexity of the hull diagram. This mechanism of the structuration of the sample in layers is illustrated in Fig. 4, *Inset*. The appearance of such layers also explains why the diffraction peaks of LiH were still measured up to 250 GPa, since the central part of the sample was still a single crystal of LiH. However, it should be noted that the detection of the diffraction peaks corresponding to LiH_6 or LiH_2 would be nearly impossible, since only the diffraction of a single crystal can give a measurable signal.

Finally, the compressed LiH sample remained optically transparent up to 215 GPa, and the infrared absorption did not show any characteristic feature of a semimetallic state. Such observation is at odds with calculations, since LiH₆ is predicted to have a structure with one formula unit in the unit cell and so to be a native metal (1, 18). Our observation hence implies either that the structure of LiH₆ has more than one formula unit or that another stoichiometry corresponds to the minimum enthalpy of the convex hull diagram. The band gap of LiH₂ is also predicted to close above 170 GPa (18), but it could be that the metallic transition pressure was underestimated.

To summarize, novel forms of polyhydrides with nontraditional stoichiometry and containing H_2 units, ubiquitously predicted for alkaline and alkaline earth metals, do exist. Such counterintuitive compounds, like LiH₆ (18), are expected to be high- T_c superconductors (8). These experimental results, alongside the recent findings on sulfur hydride (14, 15), should stimulate further experimental and theoretical efforts to achieve their metallization and study their metastability.

Methods

Four different experiments were conducted by compressing LiH in a membrane diamond anvil cell equipped with 40-µm diamond anvil culet size at various temperatures: two at 300 K, one at 77 K, and one at 18 K. Careful loading of high-purity LiH grains was handled in a glove box in an inert argon environment with less than 3 ppm oxygen and water. No pressure medium was used, and LiH was directly compressed in rhenium gaskets coated with gold. A photograph of a sample under white light transmission is shown in Fig. 1. No trace of chemical contamination of the sample could be detected in the IR absorption spectra. The IR experimental configuration is the one used previously for our measurements in solid H_2 to 290 GPa at the SMIS beamline of the SOLEIL synchrotron (23). A home-made horizontal IR microscope, equipped with two Schwarzschild objectives (47-mm working distance, numerical aperture 0.5) enables the use of a He flow cryostat. Infrared spectra were taken with a 4 cm⁻¹ resolution and 512 scans. A Raman system, mounted on the same bench, enables measurement of the highfrequency edge of the T_{2g} Raman band of the diamond at the anvil/sample interface and estimation from it of the sample pressure by using the calibration of ref. 24.

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