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High-pressure synthesis of lithium hydride

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By compressing elemental lithium and hydrogen in a diamond anvil cell, we have synthesized lithium hydride (LiH) at pressures as low as 50 MPa at room temperature. Combined Raman spectroscopy and synchrotron x-ray diffraction measurements reveal that, once synthesized, LiH remains stable at 300 K up to 160 GPa in the presence of molecular hydrogen. The mixture of lithium hydride and molecular hydrogen and application of pressure alone *cannot* form a higher H_2 content hydride (LiH_x, $x > 1$) as was suggested from the theoretical *ab initio* calculations and therefore, cannot be considered as a route to low-pressure hydrogen rich material metallization.

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Lithium hydride, LiH, is the most elementary ionic compound in terms of electronic structure, having only four electrons per unit cell, and has the highest hydrogen content, in mass percentage, of any saline hydride. Its volumetric and gravimetric hydrogen contents are also very competitive among other hydrides, electing LiH a prospective candidate for hydrogen storage.[1] Hydrogen is a propitious alternative energy source that could be the primary facilitator in the transition from fossil fuels to clean sources of energy. There is, however, a challenge to produce a material capable of both reacting with hydrogen to form a stable state and release a significant quantity on demand, at minimum energy expense. LiH is an industrially versatile compound with applications in hydrogen generators, in the manufacturing of ceramics, and in both the shielding and cooling of nuclear reactors. Because of its high reactivity, LiH is an excellent desiccant and chemical reducing agent, as well as the precursor for the synthesis of binary intermetallic hydrides such as lithium aluminium hydride, another potential candidate for hydrogen storage.[2]

There are various industrial methods in producing pure LiH, all of which involve the hydrogenation of the constituent materials, often in the presence of a catalyst, at elevated temperatures.[3,4] At ambient pressure, hydrogen is absorbed into molten lithium at temperatures ranging between 700 and 1000 K; the melting point of lithium at ambient pressure is 453.7 K while LiH itself melts at 961 K.[5] The synthesis temperatures of NaH and KH also occur above the melting temperature of pure Na and K, motivating investigations into alternative, energy economical, synthesis routes. Surprisingly no synthesis method has been reported involving *cold* (room temperature) synthesis of LiH from its pure constituents. Pressure can have a profound effect on chemical reactivity, inducing changes in atomic and electronic structure. Two different elements that do not react at ambient conditions can form novel compounds if statically compressed, even without additional heating. Pressure alone was sufficient enough to form novel compounds such as PtH, silicon dihydride or rhenium hydride,[6–9] showing that the kinetics of the solid-state reactions could be greatly influenced by the application of high densities. LiH does not decompose into pure elements until heated to above its melting point (>1000 K) at atmospheric pressure, however it easily reacts with water to the corresponding hydroxide liberating hydrogen from water.[10] The decomposition of LiH at high pressures and temperatures has yet to be investigated, which would have direct consequences for the viability of LiH as a hydrogen storage material.

LiH, which crystallizes in the rock-salt structure, is the only known stable point in the Li/H_2 mixture phase diagram, other than the elements at ambient conditions. Recently, there has been much interest in the chemical compression of hydrogen from a fundamental solid state physics perspective. Through theoretical calculations, it has been shown that *a little bit of lithium* could have the profound effect of lowering the metallization pressure of hydrogen through the formation of a higher hydrogen content hydride.[11] Metallic LiH_2, LiH_6, and LiH_8 were predicted to become more stable than the $LiH + H_2$ mixture at pressures above 100 GPa,[11] well within experimental capabilities. Further yet, another theoretical study using *ab initio* random structure searching[12] reported that at a lower pressure of 100 GPa, the lithium-hydrogen compound with much higher hydrogen content (LiH_{16}) is stable against decomposition into LiH_8 and H_2.

Utilizing x-ray diffraction and Raman spectroscopy measurements, we report the synthesis of LiH from the pure constituents at pressures as low as 500 bar, to our knowledge the lowest pressure at which metallic hydride was synthesized at room temperature. In assessment of LiH as a candidate for a hydrogen storage material, we investigate possible high temperature and pressure decomposition. Furthermore we show that at 300 K and in the presence of molecular hydrogen, LiH is a stable compound up to 160 GPa, which *does not* form any of the predicted higher hydrogen content hydrides.

We have conducted two types of experiments: synthesis of LiH from its constituencies and studies of LiH in H_2 up to 160 GPa. To synthesize LiH we have loaded Li (99.9% purity) together with precompressed hydrogen in the Re gasket of a diamond anvil cell with 600 and 300 μm flat and 80 μm diameter bevelled diamonds. Due to the high reactivity of lithium in the presence of oxygen and moisture, all loadings were performed in a glove box under an atmosphere of dry argon. The cell was then gas loaded with hydrogen (99.9% purity) at pressures varying from 50 MPa to 0.2 GPa. We conducted experiments with various Li to H_2 volume ratios ranging from 1:10 to 1:1. We also conducted several experiments loading industrially produced LiH (99.4% purity) by itself together with H_2. Pressure was determined from ruby luminescence, the equation of state of LiH, Li, or from the frequency dependence of the ν_1 vibron mode of hydrogen. Powder x-ray diffraction data for all experiments were collected at beamline ID09 at the ESRF, Grenoble. A focused monochromatic beam was used, with a wavelength between 0.4117 and 0.4130 Å, and the data were recorded on a MAR image plate. Raman spectra were recorded using a custom-constructed Raman microprobe system described in Ref. 13 with both 514.5 and 647.1 nm excitations at room and low temperature.

The pressure in the first cell with $Li + H_2$ after loading was measured to be 0.32 GPa. X-ray diffraction pattern collected at this pressure contained signatures from the *fcc* phase of LiH [Fig. 1(a)]. Lattice parameter of the LiH *fcc* structure is in agreement with the known values from high-pressure study of LiH.[14] In some of our experimental runs we observed the persistence of a signal from pure Li in our x-ray data which we attributed to the large volume ratio of Li to H_2 (1:2) together with the reaction rate. With such a volume ratio, the lithium is often "bridged" between the two diamonds resulting in only a small surface area exposed to the hydrogen. Once lithium hydride is formed on the surface, the rate of absorption is reduced, resulting in a slower rate of reaction (several days to completely transform). Since all known synthesis methods include high temperatures and catalysts we decided to investigate the minimal pressure required to synthesize LiH at room temperature. We loaded pure lithium at a hydrogen pressure of 50 MPa with a Li to H_2 volume ratio of 1:10. No bridging of the sample was observed resulting in the entire surface area of Li exposed to H_2. Immediately after loading x-ray diffraction confirmed the synthesis of lithium hydride [Fig. 1(b)]. Within a reaction period of 48 hours the entire sample became transparent, an indication that the bulk sample transformed to LiH. To our knowledge, this is the lowest pressure synthesis of any metal hydride at pressures above ambient at 300 K, when the whole sample completely transformed. The pressures 50 MPa could be easily generated in large volumes, and therefore our finding could provide the pathway for synthesis of this industrially important material in large quantities without application of temperature.

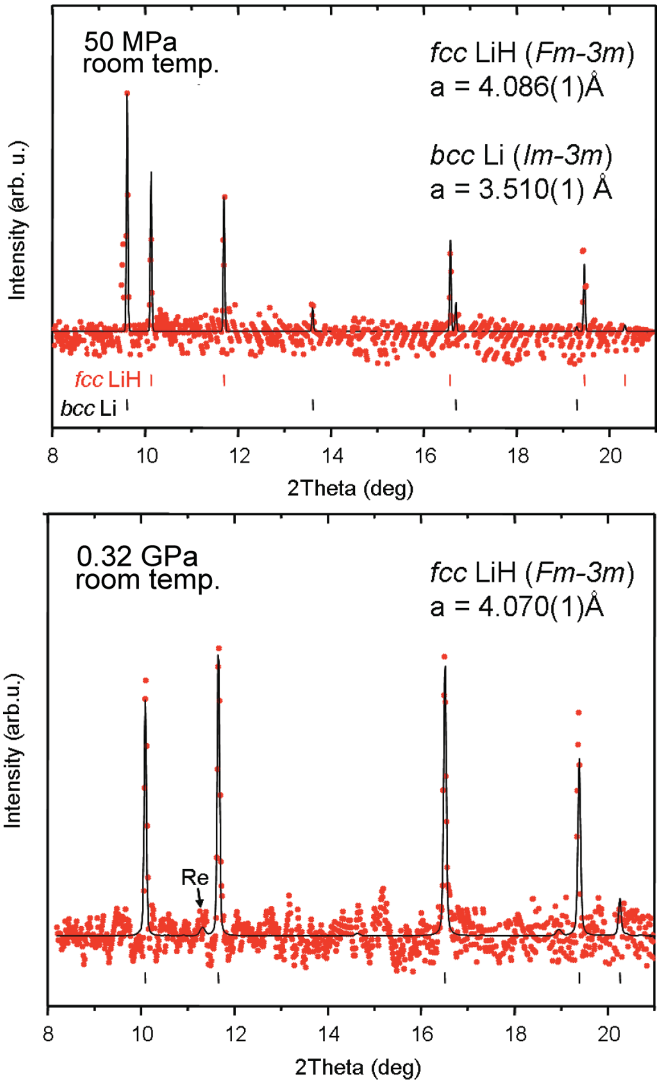

FIG. 1. (Color online) Representative XRD profile collected from $Li + H_2$ phase assembly at 0.05 GPa (top) and 0.32 GPa (bottom) at room temperature (crosses) and its LeBail fit (solid line); the background baseline has been subtracted. Positions of diffraction peaks of *bcc*-Li and *fcc*-LiH are shown by tick marks below; XRD reflections from rhenium gasket are also marked.

LiH exhibits no first-order Raman activity due to the crystal having inverse symmetry about host-lattice ion. However, unusually strong second-order spectra are observed in the region of 500–1500 cm^{-1}, involving combinations of phonons throughout the Brillouin zone.[15,16] In all our loadings, both the second-order LiH Raman band and hydrogen fundamental molecular modes were observed, confirming the presence of both LiH and the fluid H_2 [Figs. 2(a) and 2(b)]. The intensities of the Raman spectra arising from the hydrogen intramolecular

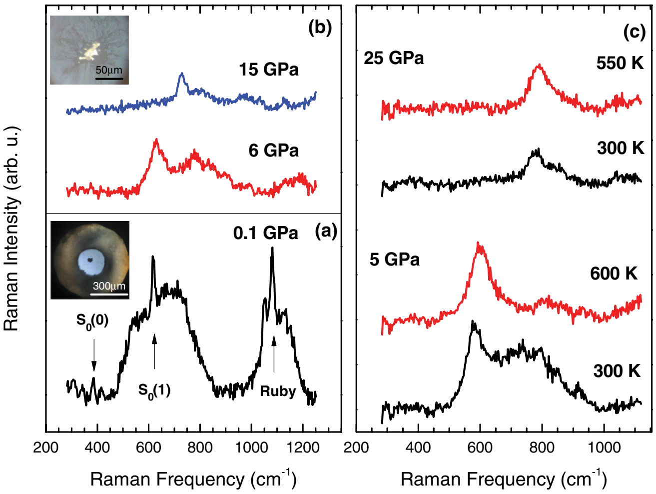

FIG. 2. (Color online) (a) Representative second-order Raman spectra of synthesised $LiH + H_2$. Arrows indicate peaks corresponding to rotational modes from pure hydrogen and ruby fluorescence used as a pressure gauge. Inset: photomicrograph of sample at 0.05 GPa. (b) Raman spectra of recovered synthesized LiH at various pressures. Inset: photomicrograph of recovered transparent LiH sample from (a). (c) High temperature Raman measurements of the recovered synthesized LiH.

rotations (rotons) are far greater than the second-order Raman bands from LiH. In the fluid the hydrogen rotons are sharp and highly intense, however in the solid, the rotons broaden obscuring the LiH Raman signal, restricting Raman measurements of LiH in this pressure regime. As LiH is stable to atmospheric conditions, we resolved this problem by releasing the excess hydrogen in an inert environment and recovering some of our synthesized LiH samples. Figure 2 shows Raman spectra of the recovered synthesized LiH to 25 GPa.

In an attempt to decompose the synthesized LiH, we heated our samples to temperatures of 600 and 550 K at pressures of 5 and 25 GPa respectively [Fig. 2(c)]. We did not observe through heating the appearance of the hydrogen vibrational fundamental mode ν_1, which would be a clear indication of decomposition. It appears that LiH is a very stable compound to which the application of temperature and pressure within the scale of the industrial capabilities is not enough to promote decomposition. According to a computational study, temperatures in excess of 1600 K may be required for decomposition at 25 GPa.[17] In order for LiH to be a viable candidate for a hydrogen storage material, other reaction mechanisms to decompose LiH must be invented.

Through single crystal x-ray diffraction, the LiH rock-salt phase has been shown to be stable at ambient temperature up to 200 GPa.[14,18] However, does a hydrogen media have any affect on the stability of LiH at such high pressures? The results of the present study represent an attempt to experimentally observe the new chemistry recently predicted for hydrogen in the presence of Li. The presence of elemental lithium in a hydrogen medium has been suggested to reduce the pressure required to attain the long sought metallization of hydrogen. We have studied the synthesized LiH sample embedded in H_2 to pressures as high as 160 GPa to investigate the predicted formation of LiH_2, LiH_6, and LiH_8.[11,12] All predicted lithium polyhydride structures contain hydrogen molecules which, as with any structural change, will be observable in x-ray diffraction. However, such light elements as lithium and hydrogen both have very weak x-ray scattering cross sections making x-ray diffraction on $LiH + H_2$ mixtures very challenging to study at high pressures in the diamond anvil cell. A very useful, subtle characteristic of all predicted structures is that they all contain stretched hydrogen molecules. The vibrational intramolecular Raman-active mode ν_1 is extremely sensitive to any structural changes. It is predicted that LiH_6 will have Raman active optical phonons with the highest mode at frequencies of 2920 cm^{-1} at 100 GPa, which would be a significant deviation from the pure hydrogen vibrational mode (4170 cm^{-1}). As LiH_6 is predicted to be metallic, it is expected that the sample would become optically opaque in transmitted light as a result of band-gap closure.

Our x-ray diffraction study up to 65 GPa shows that the mixture of synthesized (or industrially produced) LiH and H_2 do not react and behave according to their known equation of states.[14,18,19] Figure 3 shows the evolution of observed *d* spacings for Li, LiH, and H_2 as observed by x-ray diffraction in the present work, demonstrating a perfect agreement with the known values.[14,20,22,23] In the runs with pure Li as starting

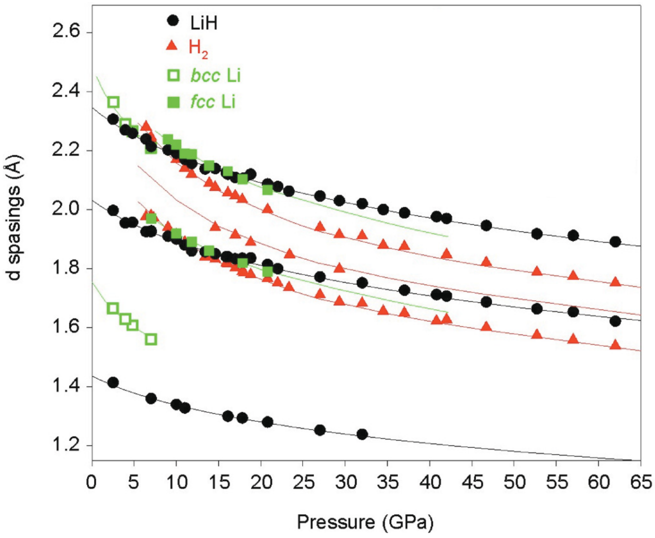

FIG. 3. (Color online) *d* spacings of observed phases as a function of pressure (open and solid symbols) plotted against previously reported compression data of Li (Refs. 20 and 21), LiH (Refs. 14 and 18), and H_2 (Refs. 22 and 23).

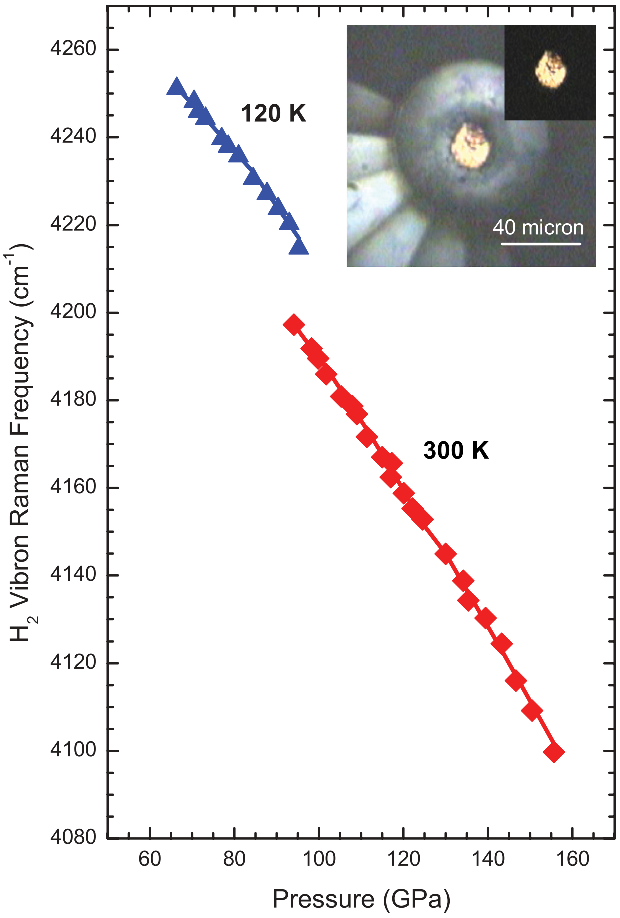

FIG. 4. (Color online) Pressure evolution of the frequency of the H_2 vibron with pressure. Symbols and lines represent measurements on the LiH part and hydrogen part of the sample, respectively. Triangles and line (blue) show measurements at 120 K while diamonds and line (red) represent measurements at room temperature. The inset shows the synthesized LiH sample in hydrogen media at a pressure of 155 GPa.

material we were able to follow Li d spacings up to 25–35 GPa (see Fig. 3). Above these pressures we did not observe Li either due to its melting[24] or to due complete transformation to LiH. At pressures above 65 GPa we utilized Raman spectroscopy and visual observations which would be very sensitive to any chemical changes. The initial reaction to be studied was between pure lithium and hydrogen, thus upon loading we compressed the sample from 0.2 GPa to 20 GPa in a period of seconds in an attempt to avoid complete transformation to LiH. It is well known from our previous studies[24] that prolonged lithium exposure at high pressure causes premature anvil failure to diamonds and that the application of low temperatures can, to an extent, prevent such an occurrence. As such, at pressures above 60 GPa, we cooled our samples to 120 K as a preventative measure. However, above 95 GPa, through visible observations, it was clear that all lithium had reacted to form lithium hydride and cooling was no longer required. Up to the maximum pressure reached (160 GPa), only ν_1 vibron of H_2 has been observed in our Raman spectra (see Fig. 4), and its frequency corresponded very well to the know value of pure H_2 at 120 and 300 K; no additional Raman lines or change of color were detected that would be indicative of the predicted LiH_x compound.[11] One might argue that the appearance of the predicted hydrogen rich compound in the experiment is hindered by the kinetics. The synthesis of silicon dihydride at above 120 GPa took several months to complete,[7] but it is possible that if high temperature were involved it could happen within minutes, e.g., formation of PtN_2 at high P-T.[25] There might be a kinetic barrier, which would allow LiH to persist on compression to much higher pressures than the predicted 110–120 GPa. Possible heating of the $LiH + H_2$ mixtures in the diamond anvil cell at pressures about 120 GPa could accelerate the chemical reaction. However, currently the heating of the transparent material in hydrogen media at above 100 GPa is not a trivial task. Alternatively, our recent experiments at room temperature on pure hydrogen to above 300 GPa showed the clear change of color and closing band gap which reached 1.8 eV at 310 GPa. That demonstrates the possibility of static compression of hydrogen at *hot* temperatures which perhaps is the simpler and more direct approach to achieve the long-sought metallic state of hydrogen.[26]

In conclusion, the synthesis of LiH from the elemental metals at pressures as low as 500 bar at room temperature is undoubtedly a result that will stimulate further experimental studies especially aimed at bringing this process to the large industrial scales. The reported high pressure synthesis of LiH represents an energetically efficient and clean way of producing this compound that has a high industrial demand. Contrary to theoretical predictions, no further reaction takes place between LiH and H_2 to form higher hydrogen content metallic hydrides to the maximum pressure of 160 GPa at 300 K.

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[1] L. George and S. K. Saxena, Int. J. Hydrogen. Energ. **35**, 5454 (2010).

[2] S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, and C. M. Jensen, Chem. Rev. **107**, 4111 (2007).

[3] J. Synder, U.S. Patent Office 3, 387, 949 (1968); R. Lemieux, *ibid.* 4, 007, 257 (1977); B. Bogdanovic, *ibid.* 4, 396, 589 (1983); J. Y. Dumousseau, *ibid.* 4, 605, 547 (1986).

[4] S. Liao, W. Kong, H. Z. Liu, J. K. Li, and Y. Xu, Acta Chimica Sinica **3**, 201 (1985).

[5] C. Messer, E. Damon, P. Maybury, J. Mellor, and R. Seales, J. Phys. Chem. **62**, 220 (1958)

[6] O. Degtyareva, J. E. Proctor, C. L. Guillaume, E. Gregoryanz, and M. Hanfland, Solid State Commun. **149**, 1583 (2009).

[7] M. Hanfland, J. E. Proctor, C. L. Guillaume, O. Degtyareva, and E. Gregoryanz, Phys. Rev. Lett. **106**, 095503 (2011).

[8] T. Scheler, O. Degtyareva, M. Marqrés, C. L. Guillaume, J. E. Proctor, S. Evans, and E. Gregoryanz, Phys. Rev. B **83**, 214106 (2011).

[9] T. Scheler, O. Degtyareva, and E. Gregoryanz, J. Chem. Phys. **135**, 214501 (2011).

[10] A. Züttel, Naturwissenschaften **91**, 157 (2004).

[11] E. Zurek, R. Hoffmann, N. W. Ashcroft, O. R. Oganov, and A. O. Lyakhov, Natl. Acad. Sci. USA Phys. **106**, 17640 (2009).

[12] C. Pickard and R. Needs, J. Phys.: Condens. Matter. **23**, 053201 (2011).

[13] J. E. Proctor, E. Gregoryanz, K. S. Novoselov, M. Lotya, J. N. Coleman, and M. P. Halsall, Phys. Rev. B **80**, 073408 (2009); M. Marqués, M. Santoro, C. L. Guillaume, F. A. Gorelli, J. Contreras-García, R. T. Howie, A. F. Goncharov, and E. Gregoryanz, *ibid.* **83**, 184106 (2011).

[14] P. Loubeyre, R. Le Toullec, M. Hanfland, L. Ulivi, F. Datchi, and D. Hausermann, Phys. Rev. B **57**, 10403 (1998).

[15] A. C. Ho, R. C. Hanson, and A. Chizmeshya, Phys. Rev. B **55**, 14818 (1997).

[16] A. Anderson and F. Luty, Phys. Rev. B **28**, 3415 (1983).

[17] T. Ogitsu, E. Schwegler, F. Gygi, and G. Galli, Phys. Rev. Lett. **91**, 175502 (2003).

[18] P. Loubeyre and F. Occelli, ESRF Report, HS2866 (2005).

[19] A. Lazicki, P. Loubeyre, F. Occelli, R. J. Hemley, and M. Mezouar, Phys. Rev. B **85**, 054103 (2012).

[20] M. Hanfland, K. Syassen, N. E. Christensen, and D. L. Novikov, Nature (London) **408**, 174 (2000).

[21] M. Hanfland, I. Loa, K. Syassen, U. Schwarz, and K. Takemura, Solid State Commun. **112**, 123 (1999).

[22] P. Loubeyre, R. LeToullec, D. Hausermann, M. Hanfland, R. J. Hemley, H. K. Mao, and L. W. Finger, Nature (London) **383**, 702 (1996).

[23] R. J. Hemley, H. K. Mao, L. W. Finger, A. P. Jephcoat, R. M. Hazen, and C. S. Zha, Phys. Rev. B **42**, 6458 (1990).

[24] C. L. Guillaume, E. Gregoryanz, O. Degtyareva, M. I. McMahon, M. Hanfland, S. Evans, M. Guthrie, S. V. Sinogeikin, and H. K. Mao, Nat. Phys. **7**, 211 (2011).

[25] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H. K. Mao, and R. J. Hemley, Nat. Mater. **3**, 294 (2004).

[26] R. T. Howie, C. L. Guillaume, T. Scheler, A. F. Goncharov, and E. Gregoryanz, Phys. Rev. Lett. **108**, 125501 (2012).