Pressure-induced bonding and compound formation in xenon-hydrogen solids

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Closed electron shell systems, such as hydrogen, nitrogen or group 18 elements, can form weakly bound stoichiometric compounds at high pressures. An understanding of the stability of these van der Waals compounds is lacking, as is information on the nature of their interatomic interactions. We describe the formation of a stable compound in the Xe-H₂ binary system, revealed by a suite of X-ray diffraction and optical spectroscopy measurements. At 4.8 GPa, a unique hydrogen-rich structure forms that can be viewed as a tripled solid hydrogen lattice modulated by layers of xenon, consisting of xenon dimers. Varying the applied pressure tunes the Xe-Xe distances in the solid over a broad range from that of an expanded xenon lattice to the distances observed in metallic xenon at megabar pressures. Infrared and Raman spectra indicate a weakening of the intramolecular covalent bond as well as persistence of semiconducting behaviour in the compound to at least 255 GPa.

Hydrogen occupies a unique position in the periodic table as a result of its quantum nature and simple electronic structure, and the prediction of unusual chemical, electronic and dynamical properties at very high pressures. There is great interest in the behaviour of hydrogen-rich materials over a broad range of thermodynamic conditions^{1,2}. In addition to the novel phenomena predicted in their dense metallic phases^{3,4}, the introduction of electronic levels in the bandgap by doping with impurity atoms, thereby facilitating changes in the electronic properties at lower pressures, has been predicted⁵. Xenon has the lowest measured metallization pressure among the rare gas solids, and optical measurements have established bandgap closure and concurrent metallization of xenon at 130–150 GPa (refs 6–8). Evidence for xenon doping of hydrogen in matrix isolation experiments at ambient pressure has been reported^{9,10}, but the nature of the bonding in these metastable phases is not well understood. There has been growing interest in the chemistry of xenon to form bulk compounds at high pressures¹¹ as well as recognition of the biological effects of xenon at high pressures¹². During the course of investigating the Xe-H₂ system, we have discovered novel compound formation in Xe and H₂. High-pressure van der Waals compounds formed in simple molecular systems were reported in the early 1990s (refs 13,14). In addition to revealing new compounds involving xenon, our data provide the first experimental signatures of pressure-induced bonding states in these materials.

A series of H₂-Xe gas mixtures was prepared and loaded into diamond anvil cells using a high-pressure gas loading system. Single crystals of the H₂-rich mixtures were grown using a combination of varying pressure and temperature. At 4.1 GPa, a xenon-rich solid was observed to form. Transitions were optically observed at 4.4, 4.9 and 5.4 GPa with accompanying changes in stoichiometry as inferred from relative volume changes of the phases in the cell (see Supplementary Information). Synchrotron X-ray diffraction data were collected at selected pressures. In the diffraction pattern taken at 4.9 GPa, a total of 201 reflections (Fig. 1a) could be indexed on a hexagonal unit cell with cell constants $a = 8.654(3)$ Å and $c = 12.357(7)$ Å and the systematic absences yielded the space

group R3̄. The structure of the xenon sublattice could be successfully solved using direct methods, which resulted in an excellent refinement ($R_1 = 3.78\%$) for 120 unique observed reflections (see Supplementary Information). A remarkable feature of the xenon sublattice is the presence of two different sets of Xe-Xe distances. The six xenon atoms in the unit cell are arranged into three Xe-Xe pairs oriented along the c axis of the unit cell, giving rise to an array of dimers (Fig. 1b). At 4.9 GPa the distance between the xenon atoms within each pair is 3.875(1) Å, whereas the closest Xe-Xe inter-dimer distance is 4.915(1) Å. Remarkably, the Xe-Xe distance in the dimer at this pressure is close to that of neutral dimers in the gas phase (3.84 Å; ref. 15), which is also close to the nearest-neighbour Xe-Xe distance of 3.83 Å in solid fcc xenon at 5 GPa and room temperature¹⁶. In comparison, the nearest-neighbour distance at 4 K (at ambient pressure) determined from X-ray diffraction measurements is 4.34 Å in the LT, fcc phase (ref. 17). The structure of the xenon sublattice determined from an analysis of the X-ray diffraction data at 4.9 and 7.1 GPa remained unchanged across the transitions. The transitions therefore arise from changes in the amount of hydrogen assimilated into the material.

Raman and infrared (IR) spectra provide further information about the nature of the high-pressure phases. A total of five vibron modes for H₂ were observed in the Raman spectrum (Fig. 2a), indicating that the H₂ molecules are intact. The low-frequency Raman spectrum is found to be indistinguishable from that of pure solid H₂ at the same conditions, indicating rotational disorder of the molecules. No signature of Xe-H bonding is observed in the vibrational spectra⁹. A total of five IR-active vibron modes are observed (Fig. 2b). Of these, two are simultaneously Raman and IR active. A $3 \times 3 \times 3$ superstructure based on the hcp lattice of solid hydrogen would give rise to similar activity and result in the appearance of additional vibron bands compared to pure H₂ as a result of Brillouin zone folding^{18,19}. The IR spectrum shows that the compound remains an insulator at 255 GPa.

The stoichiometries of the compounds were estimated as follows. The change in hydrogen content occurs at discrete pressures

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Figure 1 | X-ray single-crystal diffraction of Xe-H₂ compound. **a**, Oscillation photograph of a single crystal of the Xe-H₂ compound obtained at 4.9 GPa (see Supplementary Information for details of indexing). **b**, Corresponding structure of the xenon sublattice deduced from these data.

Figure 2 | Raman and infrared spectra of Xe-H₂. **a**, **b**, Representative Raman spectra (**a**) and IR spectra (**b**) of the Xe-H₂ compound. The Raman spectrum of pure H₂ at 4.9 GPa is shown in **a** as a dotted curve. The vibron spectrum of the Xe-H₂ compound shows a multiplet structure that becomes evident at higher pressures, in contrast to the behaviour of pure H₂. The low-pressure IR spectrum is shown in the inset of **b**. The IR spectra at the highest pressure show no evidence of Drude absorption. The small increase at the longest wavelengths is indicative of diffraction effects due to decreasing sample size. Transmission at the longest wavelengths places an upper bound on the possible carrier density, with a corresponding upper bound for the plasma frequency of 0.2 eV (ref. 29). The frequency range of the high two-phonon absorption of the diamond is blocked.

(4.9 and 5.4 GPa), and there is no evidence for major changes in stoichiometry at higher pressures based on the continuity of the vibrational frequency shifts to 255 GPa and the volume compression obtained from X-ray data to 50 GPa. The hydrogen content was bounded at these pressures based on the equations of state of the component elements Xe (ref. 16) and H₂ (ref. 20). The space group R3 constrains the number and placement of H₂ molecules in the compound formed at 4.9 GPa. The observed unit cell volume of 801.4 Å³ is ~2% smaller than the sum 6Xe + 42H₂, suggesting a stoichiometry Xe(H₂)₇ for this phase. In comparison, the observed volume of 831.7 Å³ at 7.1 GPa suggests a stoichiometry Xe(H₂)₈ for all pressures above 5.4 GPa. The systematic absences observed at 7.1 GPa suggest that the space group changes from R3 to P3, with the accompanying change in hydrogen stoichiometry. Simulated annealing reverse Monte-Carlo calculations^{21,22} were performed with the diffraction intensity data used in the single-crystal refinement to further constrain the H₂ positions. Xenon atoms were fixed at the positions (in R3) obtained from the original refinement, and H₂ locations were optimized from an initial random placement. Simulations with 42 H₂ molecules (Xe(H₂)₇) yielded a structure that improved the refinement quality factor (in comparison to the model with only xenon atoms) *R*₁ by 0.5%. The structure is shown in Fig. 3. The assumption of 42 H₂ molecules in the unit cell agrees qualitatively with the highest peaks in the difference Fourier map obtained from a refinement that excluded hydrogen atoms.

The structural refinement provides direct information on the origin of the stability of this compound. Making use of the observed structure factors, we calculated the electron density maps. The single crystal at 4.9 GPa was immersed in a hydrostatic liquid hydrogen medium, and the use of Boehler-Almax-type seats with an opening angle of 70° allowed data to be collected over a large angular range. The resulting inherent high quality of the data and the span of the reciprocal space covered gave rise to electron density maps of very good quality. As described above, the xenon atoms are distributed as dimers rather than distinct atoms, with a uniform Xe-Xe distance. Examination of the electron density maps shows no significant distortion of electron density between the xenon atoms at low pressures and therefore no interaction between them (Fig. 4a,b). However, a striking spread of electron

Figure 3 | Model structure of $\text{Xe}(\text{H}_2)_7$. The xenon atoms are surrounded by dumbbell-shaped, freely rotating hydrogen molecules represented by the spherical shells.

density into the interstitial space between the xenon atoms and from the Xe_2 pairs towards the surrounding hydrogen molecules is observed at lower cutoff (Fig. 4c). We interpret these changes in electron density with pressure as arising from increasing chemical

interaction between the xenon atoms in each pair as well as between Xe_2 pairs and the surrounding array of hydrogen molecules. The spread of electron density from the xenon atoms (located on 3a positions) to the surrounding hydrogen molecules serves to stabilize the Xe_2 pairs by depopulating a fully filled σ^* molecular orbital of the Xe_2 unit, creating a Xe–Xe bond. In xenon–halogen compounds, a gradual transition from van der Waals to covalent bonding between xenon atoms and the X_2 halogen molecules is inferred and this depends on the extent of the overlap of the valence orbitals of Xe with the antibonding orbitals of the neighbouring molecule²³. In a similar way, a gradual transition from a neutral Xe_2 to an ionic Xe_2^+ seem to take place with pressure in the Xe– H_2 system²⁴. In other systems, this change in ionicity is initiated by either chemical means²⁵ or xenon partial pressure²⁶. Our data indicate that the Xe–Xe bond length in the dimers attains the value observed in Xe_2^+ at ~ 50 GPa. The formation of ionic xenon dimers is expected to give rise to charge transfer to the high-lying σ^* antibonding states of the H_2 molecules, and results in additional weakening of the H–H bond. Because the bond weakening (inferred from the observed decrease in vibrational frequencies) is similar to that found in pure H_2 (ref. 18), the charge must be localized elsewhere (see Supplementary Information). This conclusion is consistent with the unusual spread in electron density distribution deduced from the refinement of X-ray data at lower pressures (Fig. 4c).

The lowest H_2 vibron frequency decreases and shows a monotonic decrease with increasing pressure above 60 GPa. The decreasing vibron frequencies indicate a weakening of the covalent

Figure 4 | Changes in the electron density of xenon. **a**, Electron density calculated from the observed structure factors (Beever–Lipson maps)³⁰. The projection along y obtained at the first level (**a**) shows the xenon pairs. **b, c**, Three-dimensional equal-energy contours obtained at different cutoff levels, 15e (**b**) and 5e (**c**), show the spread of electron density between the Xe atoms and in the direction of coordinated H_2 molecules lying within the first coordination sphere of the Xe atoms.

intramolecular bond at the highest pressures (that is, above 120 GPa), as observed in pure, solid hydrogen^{18,27}. The observed vibron shift under pressure is similar to that found for H₂ molecules dispersed in rare gas matrices under pressure²⁸. The high-pressure compound formation reported here contrasts with the photochemically induced Xe–H bond formation documented as impurities in cold rare gas matrices near ambient pressure^{9,10}, because no spectroscopic evidence for the formation of Xe–H bonds has been observed at any of the pressures studied. The IR measurements at the highest pressure show no evidence of Drude absorption ($\omega_p < 0.2$ eV) and therefore provide no indication of metallization (volume compression $V/V_0 \approx 0.2$). Nevertheless, the measured variation of the structure on compression suggests the existence of xenon dimers forming a one-dimensional metal at still higher pressures. In addition to the fundamental interest in forming novel, hydrogen-rich compounds as simple molecular quantum systems, the search for such new materials is important technologically (for example, in hydrogen storage); the unexpected stability of the compound described in the present study points to a new family of materials in hitherto unexplored regions of the temperature–pressure–composition space.

Received 29 May 2009; accepted 15 October 2009;
published online 22 November 2009

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Acknowledgements

The authors thank V. V. Struzhkin, G. Shen, Y. Meng and S. Sinogeikin for assistance and discussions. This work was supported by DOE-BES (DE-FG02-06ER46280), DOE-NNSA (CDAC), NSF-DMR (DMR-0805056), NSF-EAR (COMPRES) and the Balzan Foundation. A.P.S. is supported by DOE-BES under contract DE-AC02-06CH11357 and N.S.L.S. is supported by DOE-BES under contract no. DE-AC02-98CH10886.

Author contributions

M.S. and R.J.H. designed the project. M.S., A.F.G. and S.A.G. conducted the sample loading, spectroscopic studies and analysis. M.S., P.D., P.L., W.Y. and H.K.M. conducted the synchrotron X-ray diffraction measurements and analysis. Z.L. performed the synchrotron IR measurements. M.S., P.D., R.J.H., A.F.G. and S.A.G. wrote the manuscript.

Additional information

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