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PERSPECTIVE

Metallization of solid hydrogen: the challenge and possible solutions**Dennis D. Klug and Yansun Yao***Received 1st June 2011, Accepted 11th August 2011*

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The search for the means to convert molecular hydrogen to a metal under static conditions at high pressure is reviewed with emphasis on selected recent developments in both experimental studies and theoretical approaches. One approach suggested recently makes use of mixtures of hydrogen and suitable impurities. In these materials hydrogen is perturbed by impurities with the goal of obtaining the metallization of hydrogen at moderate pressures. This approach has also been extensively examined through the use of first-principles methods and we review this recently explored experimental approach and several theoretical studies that have provided an atomic-scale picture of the interaction of hydrogen with impurities under pressure. The objective of this novel approach is to help determine if metallization of hydrogen at pressures is attainable with currently available experimental techniques.

Introduction

Solid molecular hydrogen and the possibility of its metallization has fascinated and challenged condensed matter researchers for many decades since the prediction of the pressure required for metallization was made by Wigner and Huntington in 1935.¹ Their prediction was that metallization of hydrogen could occur at 25 GPa which was outside the range of techniques

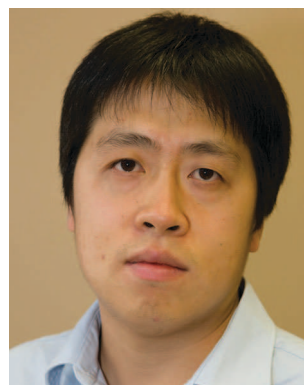
available at that time. There were subsequent studies that suggested that metallic hydrogen may be a superconductor with a fairly high superconducting transition temperature.² This seemed to be a very reasonable suggestion since it is known that the planet Jupiter, has a strong magnetic field and is primarily composed of hydrogen at its core where the temperature may be of the order of 100 K or even higher. At that time, it was thought that pressures of “somewhat less than a megabar” were reasonable estimates for the metallization of hydrogen. The development of the diamond anvil technique and the ability to reach pressures in the megabar range³ meant that a serious search for metallic hydrogen could be pursued.

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The search for metallic hydrogen was therefore intensified by both experimentalists and theoreticians with results that only showed that metallization of hydrogen had not occurred under static conditions close to the highest pressures so far attainable in diamond anvil high-pressure cell.

In this brief review, we attempt to provide a summary of a selection of studies that pursued the goal of metallization of hydrogen under static pressure conditions. We do not attempt to present an exhaustive review but only hope to give the reader a survey of studies that represent the types of recent efforts in this area. We then focus on our recent studies that have examined the electronic structure of two materials that originally had been considered for possible hydrogen metallization.

Since the metallization of pure solid hydrogen under static pressure conditions was not achieved, theoreticians and experimentalists have suggested and tried other novel ways of preparing metallic hydrogen. On the experimental side for example, an early suggestion was made to use mixtures of argon and hydrogen to perhaps yield a molecular dissociation of H_2 below 200 GPa. An early example of this approach was employed by P. Loubeyre *et al.* (1994)⁴ using mixtures of argon and hydrogen which forms an ordered crystalline compound at low pressures. The early study suggested that the H_2 in this compound started to dissociate and become metallic at much lower pressures than thought to be required for pure hydrogen. This very interesting suggestion stimulated much interest but was unfortunately not confirmed and controversy resulted.^{5–8} Since the full characterization of the behavior of argon with hydrogen at the atomic level requires knowledge of the actual structure, this led to a new search for possible structures that may yield the answer to this question.⁹ This will be discussed in more detail below since it provides a very useful contrast with some of the other most recent theoretical studies on this subject of mixtures of hydrogen with impurities.

The possibility of forming metallic hydrogen using hydrogen rich materials was subsequently studied and discussed by theoreticians, recognizing that metallic hydrogen could be produced through alternative paths that result in molecular dissociation of H_2 and/or introduction of band overlap between H_2 molecules. There was strong evidence, for example, from the summary of earlier experimental work by Mao and Hemley¹⁰ which showed that the vibron mode for molecular hydrogen began to decrease rapidly in frequency at high pressures indicating that the H_2 was beginning to dissociate on the way to forming the metallic state. This decrease in the Raman frequency at pressures below 150 GPa was initially interpreted as resulting from pressure-induced bond destabilization but later suggested to be related to vibrational coupling effects consistent with infrared measurements.¹¹ In this perspective article, the main focus is on describing some of the recent attempts to find ways to achieve the preparation of metallic hydrogen through the use of hydrogen-rich compounds.

Recent approaches for metallization of hydrogen

The pathway to metallization of hydrogen that occurs by band overlap in hydrogen bands through the introduction of an impurity has also been considered with the suggestion that

some hydrogen rich compounds or alloys could be used that contain hydrogen as an already pre-compressed component.^{12,13} The idea of pre-compression or chemical pre-compression as used for hydrogen meant that hydrogen in certain materials would already have the properties of band overlap and/or molecular dissociation that are expected in compressed bulk hydrogen near where it becomes metallic. Hydrogen might, for example, be densified or “chemically pre-compressed” in a hydrogen rich material or alloy. Simple hydrides such as silane,¹³ SiH_4 , were examined in this theoretical study and suggested to both metallize and be possible superconductors as well. The hydrogen rich material, silane could perhaps become metallic,^{14–17} perhaps at higher pressures than originally thought^{18,19} but the results so far have been controversial.^{20,21} Other hydrides have also been considered including hydrides of lithium²² which was suggested as an interesting potential example of metallization of solid hydrogen through the introduction of impurity bands between the occupied σ_g bonding orbitals in H_2 molecules and its neighboring unoccupied σ_u^* antibonding orbitals. As another suggestion for these solid phases, certain impurities could donate electrons into σ_u^* antibonding orbitals of H_2 molecules resulting in metallization.

The report of T. A. Strobel, M. Somayazulu, and R. J. Hemley²³ using structural, infrared, and Raman spectroscopic data on a mixture of SiH_4 and molecular hydrogen showed a remarkable lowering of H_2 intramolecular vibrational (vibron) frequencies with increasing pressure similar to that observed in pure bulk hydrogen and predicted for high pressure structures of hydrogen. At nearly the same time, Wang *et al.*²⁴ also reported on the potential importance of mixtures of SiH_4 and hydrogen and noted a lowering of hydrogen vibron frequencies in this material. Other compositions of SiH_4 with H_2 than that used by Strobel *et al.* such as 5 : 1 H_2 : SiH_4 and 1 : 1 H_2 : SiH_4 were examined and although they indicated a lowering of the H_2 vibron frequency from that of pure H_2 , a drop in the vibron frequencies was not observed with increasing pressure. This latter study seemed to confirm that a higher concentration of H_2 than 1 : 1 is required for the strong weakening of H_2 vibron frequencies since a study of the SiH_4 · H_2 mixture showed a strengthening of vibron frequencies with increasing pressure. This contrasted with the vibron pressure dependence reported in inert-gas mixtures with hydrogen^{25,26} or other gases mixed with hydrogen^{27,28} where hydrogen vibron frequencies increase with pressure below 100 GPa and the mixtures remained insulating.

These studies in particular led theoretical and experimental groups to investigate further these types of hydrogen-rich materials that may provide pathways to metallic hydrogen and good superconductors.^{29–35} Most of the very recent theoretical studies, that were published at very similar times, addressed the question of understanding the interesting results with $SiH_4(H_2)_2$ which indicated that the hydrogen molecule covalent bond could indeed be perturbed in a manner similar to that found in pure bulk hydrogen at higher pressure. Many of the publications noted above addressed this finding and all provided valuable insight. There was also significant agreement among the authors regarding the basic understanding and implications of the published experimental results. The theoretical analysis presented in these studies provides an excellent

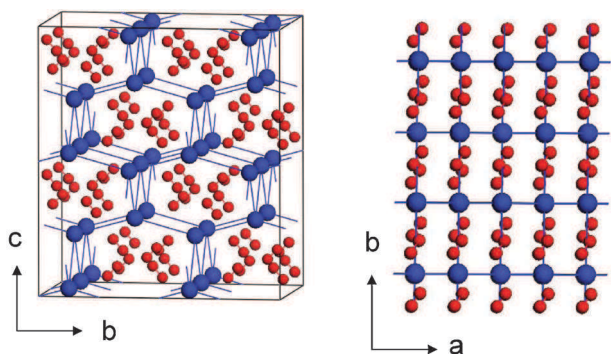


Fig. 1 The predicted CeCu_2 structure of $\text{Ar}(\text{H}_2)_2$. The basic CeCu_2 structure is shown in two views with Ar atoms represented by larger blue balls and the H_2 molecules represented by red dumbbells.

contrast with the results obtained in the study on an inert-gas Ar plus hydrogen mixture.⁹ These studies provide insight into contrasting behavior of mixtures of molecular hydrogen with impurities and perhaps provide a guide for future work.

Other mixtures of H_2 with simple molecules or inert gases have been studied in detail. For example, CH_4 , Xe, Ne, and GeH_4 mixed with H_2 have been examined using structural and spectroscopic methods such as Raman and infrared spectroscopy.^{36,37} Each of these studies revealed new molecular compounds and $\text{GeH}_4(\text{H}_2)_2$ in particular,³⁶ showed evidence of H_2 vibron softening with increasing pressure. The $\text{GeH}_4(\text{H}_2)_2$ however became unstable with respect to decomposition at moderately high pressures so that the dramatic drop of vibron frequencies was not obtained in this material, in contrast to $\text{SiH}_4(\text{H}_2)_2$.

Since a primary goal of this review is to provide the reader with a summary of several ideas and results that have addressed the search for alternate ways to obtain metallic hydrogen or a close approximation to pure bulk hydrogen, two systems, SiH_4 plus hydrogen and Ar plus hydrogen provide significantly different behaviors and illustrate several of the basic ideas from results so far published. One key to understanding whether mixtures of hydrogen with other impurities can provide an alternate path towards the metallization of hydrogen at pressures presently achievable or in the near future is to have an atomic scale picture of the hydrogen-impurity interactions. With this information, one might then “fine-tune” the material and methods to reach the goal of metallic hydrogen or at least a good approximation to metallic hydrogen.

Comparison of approaches to metallize hydrogen

The study of Ar plus hydrogen is an example that provides an excellent contrast with the SiH_4 plus hydrogen system. Although the Ar plus hydrogen system has become controversial, it nevertheless provides a good example of how theory and experiment can provide complementary information to resolve basic issues. In early studies on Ar plus H_2 , it was shown that at 4.3 GPa, an Ar + H_2 mixture with 2/3 mole fraction of H_2 forms an ordered compound $\text{Ar}(\text{H}_2)_2$. Based on the original Raman measurements, it was suggested that H_2 in this structure started to dissociate near 175 GPa to reach the metallic state.⁴ This experimental result suggested an alternate approach to achieve metallic hydrogen at pressures below that of current

experimental techniques. This work stimulated considerable further studies but later infrared (IR) measurements failed to confirm the Raman results. The IR results indicated that the molecular phase of $\text{Ar}(\text{H}_2)_2$ was stable to at least 220 GPa.³⁸

The primary difficulty in providing a correct picture of the high pressure properties of Ar plus H_2 can be attributed to the lack of knowledge regarding the structures of compounds formed by Ar plus H_2 at high pressures. Although several earlier theoretical predictions were published,^{6–8} the recent study⁹ addressed this issue again by performing structure searches using a “random search” method.¹⁹ With this method small cells containing 2 and 4 units of $\text{Ar}(\text{H}_2)_2$ were used to find candidate structures that could then be examined for their enthalpies. The lowest enthalpy structures over a range of pressures could then be tested to determine if they were indeed stable structures. A candidate structure was found that could evolve from the well characterized low-pressure phase structure is isomorphous to a CeCu_2 structure, and was found to exhibit a clear lower enthalpy above about 66 GPa. This predicted CeCu_2 structure is illustrated in Fig. 1 and is described by the orthonorhombic space group *Imma*. This channel-like structure has H_2 molecules located in hexagonal channels consisting of Ar atoms. At low pressures, the H_2 molecules rotate freely, but at high pressures they remain fixed in a particular orientation and therefore lowered the symmetry to a $C2/c$ space group. It was noted that the calculated band gap of the CeCu_2 structure with the $C2/c$ space group obtained when H_2 molecular orientations were fixed did not close until about 350 GPa. Although this estimate was limited by well known deficiencies in DFT theory for estimating band gaps, it was a higher pressure than the DFT value predicted for pure hydrogen.^{39,40}

It should be noted that some of the low enthalpy structures predicted for bulk hydrogen in the latter references using different approaches on small unit cells were identical $C2/c$ space group structures. The lowest enthalpy pure hydrogen structure at 300 GPa was however obtained with a larger unit cell³⁹ and is predicted to be slightly more stable than the $C2/c$ structures obtained with smaller unit cells. It is described by a $B2/n$ space group notation, which is a non-standard $C2/c$ structure description. The large unit cell $B2/n$ and smaller unit cell $C2/c$ structures are very similar layered structures but their calculated X-ray diffraction patterns differ as a result of a difference in packing of layers. A definitive characterization of the structure of bulk hydrogen in this pressure range has not yet however been made by experiment.

To further understand the $\text{Ar}(\text{H}_2)_2$ result and to obtain a more detailed picture of the interaction of Ar with molecular hydrogen for comparison with silane plus hydrogen, an investigation of calculated valence charge densities (Fig. 2a) and the intra- and intermolecular distances in hydrogen molecules in the mixture $\text{Ar}(\text{H}_2)_2$ proves to be useful. The calculated valence charge densities at 300 GPa show weak interactions between Ar and H_2 molecules. Ar acts to maintain separation of H_2 molecules. The valence charge densities for pure hydrogen (Fig. 2b) for a predicted phase at 300 GPa^{39,40} show a much denser packing of H_2 molecules and this accompanies an increase in H–H intramolecular bond lengths. In comparison, the calculated intramolecular H–H distances actually decreases in the $\text{Ar}(\text{H}_2)_2$ with increasing pressure.

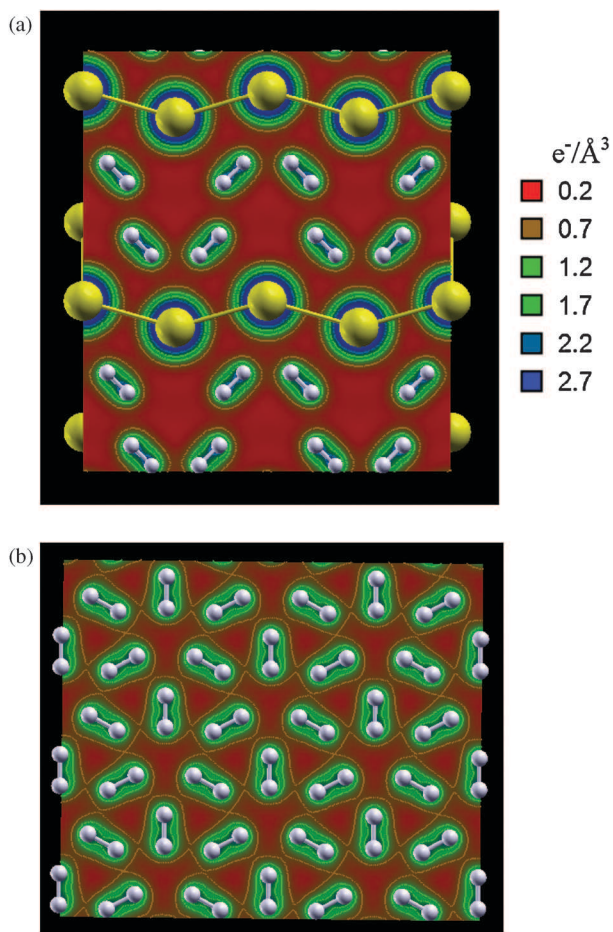


Fig. 2 The calculated valence charge density for (a) $\text{Ar}(\text{H}_2)_2$ and (b) pure hydrogen at 300 GPa differentiated by a color scheme from red (low density, $0.2 \text{ e}^-/\text{\AA}^3$ or lower) to blue (high density, $2.7 \text{ e}^-/\text{\AA}^3$ or higher). The Ar atoms and H_2 molecules are shown as large (yellow) and small (white) spheres, respectively.

The presence of Ar acts to separate the H_2 molecules in contrast to what occurs with silane plus H_2 as will be illustrated below.

Silane plus hydrogen provides an interesting and important contrast to the Ar plus hydrogen compound and may be useful for further exploration of the use of mixtures or alloys with hydrogen to promote metallization of hydrogen. In addition to metallization, there may be important consequences for preparation of superconductive materials as has been noted in the literature.⁴¹ As noted above, silane plus hydrogen has been studied by a large number of groups and we will review only a selection of these studies since there is basic agreement among the recent studies. One of the first theoretical studies to be published presented predictions of the pressure for band gap closure in $\text{SiH}_4(\text{H}_2)_2$ and reemphasized that DFT underestimates the band gap in this material.²⁹ This study indicated that the transition to a metal could be underestimated by almost 20 GPa from 164 GPa predicted for a SiH_4 plus hydrogen structure that was not fully specified.

A number of publications on SiH_4 plus hydrogen quickly followed.^{30–35} All structures in the theoretical studies were based initially on the face-centered (fcc) space group ($F\bar{4}3m$)

for the $\text{SiH}_4(\text{H}_2)_2$ composition that was initially obtained in the experimental study. The structural search methods employed differed but the basic results were in fairly close agreement for the lowest energy structures. The methods used to search for lowest energy structures included an application of the genetic algorithm method⁴² and random search methods where many hundreds of structures were examined with H_2 occupying tetrahedral and octahedral sites in the fcc lattice with SiH_4 molecules located at the fcc unit cell sites. Although the lowest energy structure found within this basic framework was one with four H_2 molecules occupying all four octahedral sites and four others occupying four of the eight tetrahedral sites, it was recognized that the H_2 molecules were in fact rotating at the lower pressures.^{30,34} This rotation was predicted to be only hindered or stopped at pressures greater than 100 GPa for H_2 molecules at tetrahedral sites and the H_2 molecules at octahedral sites had their rotations confined to planes. At pressures up to about 22 GPa, a structure with space group, $I\bar{4}m2$ was predicted to be the most stable structure. This structure was very close in free energy to another structure with $Imm2$ space group. The only difference between these two structures was the orientations of the H_2 molecules and an examination of the dynamics showed that the H_2 molecules were, in any case, rotating at the pressures where these structures were predicted to be the most stable. At pressures greater than about 22 GPa, a $P1$ structure was predicted (Fig. 3) as the lowest energy structure and this structure deviates slightly from the fcc structure identified at lower pressures. This structure forms as a result of distortions of the SiH_4 molecules from perfect tetrahedrons that result from interactions of its Si sp^3 orbitals with neighboring H_2 molecules. In addition to the $P1$ structure, two other structures that were energetically competitive were identified. In the $\text{SiH}_4(\text{H}_2)_2$ system, the H_2 molecules rotated rapidly, at least up to pressures of about 100 GPa, as found in the high-pressure $\text{Ar}(\text{H}_2)_2$ compound. The rapid decrease with

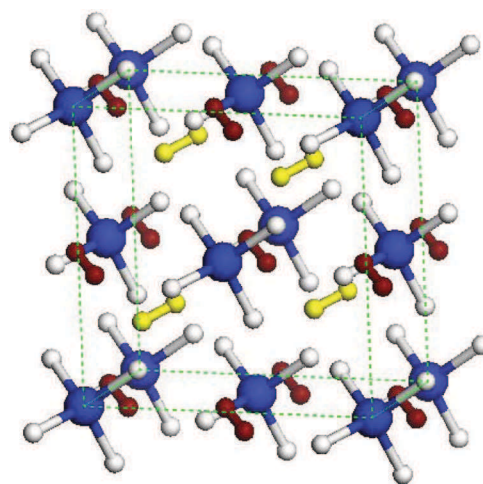


Fig. 3 The $P1$ structure of $\text{SiH}_4(\text{H}_2)_2$ is shown in a distorted fcc unit cell. The SiH_4 molecules are located at the corners and face centers of the unit cell with the Si atom indicated by the larger spheres. The H_2 molecules at the octahedral and tetrahedral sites are colored brown (dark) and yellow (light), respectively.

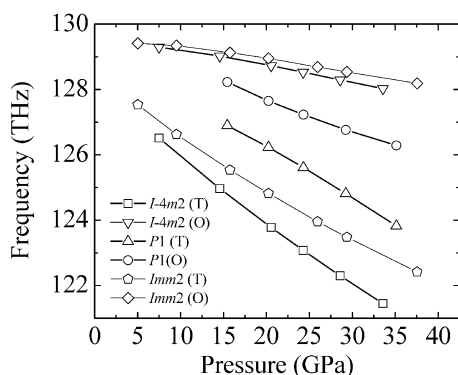


Fig. 4 Calculated pressure dependences of the H_2 vibron frequencies of $I\text{-}4m2$, $Imm2$, and $P1$ structures of $\text{SiH}_4(\text{H}_2)_2$. The $I\text{-}4m2$ and $Imm2$ structures were other energetically competitive structures found for $\text{SiH}_4(\text{H}_2)_2$ (ref. 34). The notations T and O refer to the H_2 molecules at tetrahedral and octahedral sites.

increasing pressure in vibron frequencies was calculated for each of these structures (Fig. 4).

There is basic agreement among authors regarding interactions at pressures below about 35 GPa which is significantly below the predicted pressure for metallization. In the low end of this pressure range, the SiH_4 molecules remain as tetrahedrons but the interaction with H_2 molecules strengthens rapidly. At the lowest pressure, 6.9 GPa, shown in Fig. 5a, the interactions between component molecules is relatively weak and the SiH_4 molecules remain as tetrahedrons. As one progresses upward in pressure to 15.7 GPa, (Fig. 5b) one sees a buildup of electron density and the interaction between H_2 molecules located at tetrahedral sites around SiH_4 is now beginning to distort the sp^3 orbitals of SiH_4 . At 99.2 GPa, as seen in Fig. 5c, there is a clear increase in the calculated valence electron density between SiH_4 and H_2 . The sp^3 orbitals of the SiH_4 molecules distort significantly from their original tetrahedral geometry and there is a significant promotion of valence electrons to 3d orbitals. At 99.2 GPa, the H_2 molecules at tetrahedral sites are well within the coordination shells of Si atoms and the H_2 molecules at the octahedral sites are also interacting strongly with SiH_4 . The next feature appearing at high pressure is the accumulation of valence electrons in the interstitial regions between molecules leading to the metallic state. That is, this system consisting of distorted $\text{SiH}_4(\text{H}_2)_2$ approaches a metallic state.

The result of the strong interaction between SiH_4 and H_2 is that the intramolecular bond length in H_2 molecules at tetrahedral sites lengthens significantly and, in fact, reaches values much greater than that predicted in pure bulk hydrogen structures at a similar pressure. This is precisely what one could expect for the onset of molecular dissociation as metallic hydrogen is formed. Although the true high pressure structure is not yet known, the recent predictions of solid hydrogen structures^{39,40} for the phase existing immediately before metallization provides a very useful comparison. In the predicted structure of pure solid hydrogen, the calculated H–H bondlengths are about 0.75 Å at pressures of 154 GPa whereas in $\text{SiH}_4(\text{H}_2)_2$ the calculated H–H bondlengths increase from about 0.75 to 0.815 Å in the pressure range 15.7 to 99.2 GPa for H_2 molecules located

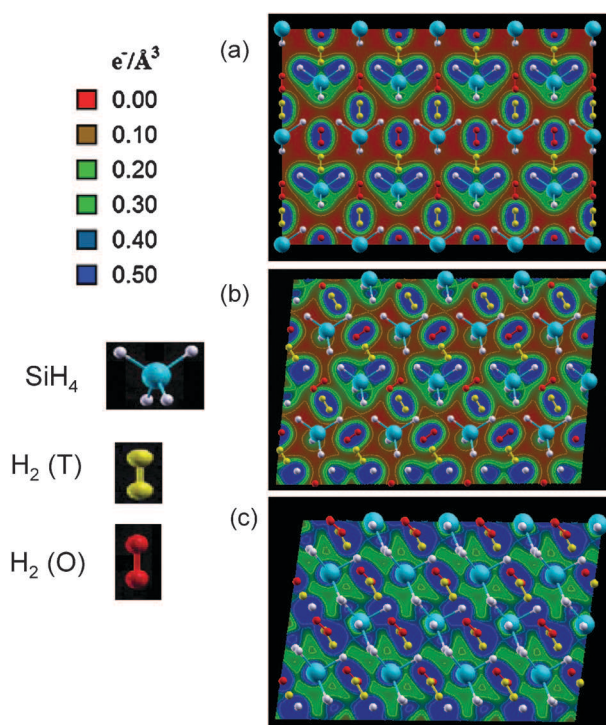


Fig. 5 Calculated valence charge density of $\text{SiH}_4(\text{H}_2)_2$ in the (110) plane of the fcc lattice (distorted accordingly) for a) $I\text{-}4m2$ structure at 6.9 GPa, b) $P1$ structure at 15.7 and c) $P1$ structure at 99.2 GPa. The atoms that are not surrounded by charge densities belong to the nearest plane above the plane shown.

at the tetrahedral sites. In pure solid hydrogen, H_2 vibron frequencies do not show the decrease in frequencies until much higher pressures than that seen in $\text{SiH}_4(\text{H}_2)_2$. The H_2 molecules therefore have a unique interaction with the SiH_4 resulting in a much more prominent weakening of the H–H bond.

The electronic density of states (DOS) as depicted in Fig. 6 can also be used to describe the approach of metallization but here it is essential to emphasize the magnitude of the contributions from each of the various components contributing to the DOS as the $\text{SiH}_4(\text{H}_2)_2$ becomes metallic. As pressure increases, the strengthening of the orbital overlap stabilizes the bonding interactions at lower energies and destabilizes the anti-bonding interactions at higher energies resulting therefore in an increase the overall bandwidth which is one of the key ingredients for metallization. This is what could be expected to occur in bulk hydrogen at pressures predicted to be about 4 Mbar. This bandwidth expansion forces the valence and conduction bands to overlap and is exactly as found for $\text{SiH}_4(\text{H}_2)_2$. The predicted result was that certain unoccupied DOS of H_2 molecules, through mixing with the SiH_4 conduction band, would move below the Fermi level and overlap with the occupied DOS region, and therefore the system becomes weakly metallic. The valence and the lowest lying conduction bands of H_2 molecules are constructed from bonding states (σ_g) and anti-bonded states (σ_u^*), respectively. As the H–H bonds weaken, the energy of bonded states increase and those of the anti-bonded states will decrease. The energy separation between the bonded states and anti-bonded states then decreases just as in bulk solid hydrogen at much higher pressures. This feature is

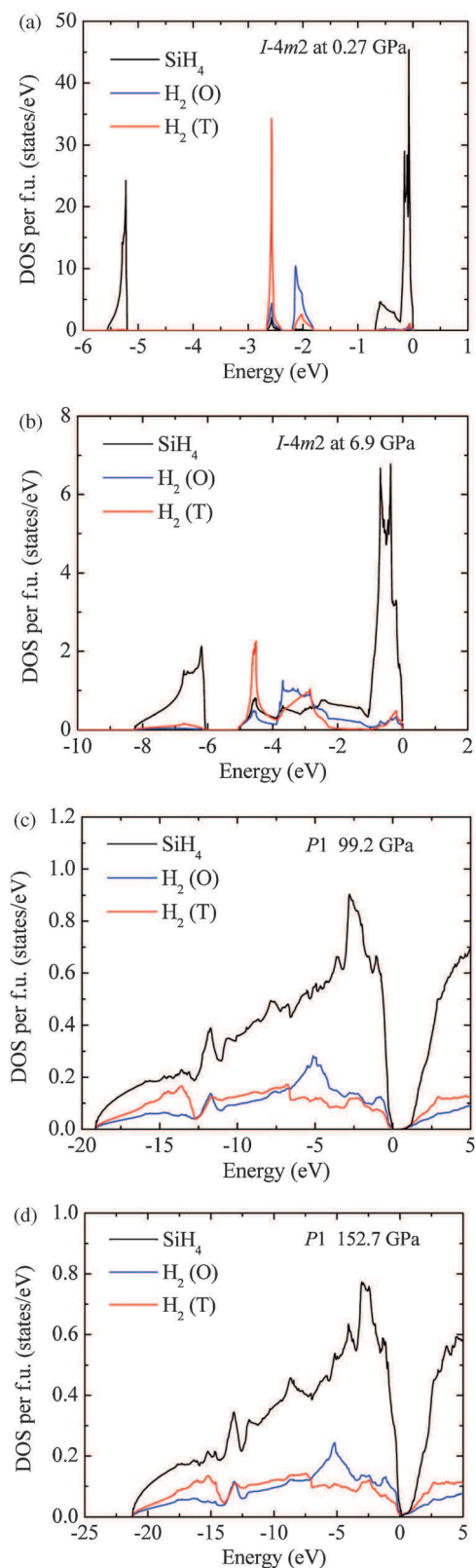


Fig. 6 Calculated electronic DOS projected on SiH₄ unit and H₂ molecules for (a) *I*-4*m*2 structure at 0.27 GPa, (b) *I*-4*m*2 structure at 6.9 GPa, (c) *P*1 structure at 99.2 GPa, and (d) *P*1 structure at 152.7 GPa. The notations T and O refer to the H₂ molecules at tetrahedral and octahedral sites. The origin '0' in energy corresponds to the highest energy of the occupied states.

directly correlated with the weakening of the H–H bonds within the H₂ molecules in SiH₄(H₂)₂ and these are two features similar to that leading to metallization of pure hydrogen.

There is other information that needs to be considered in the evaluation of whether a theoretically predicted material can exist and can be obtained in experiments. The issue of a materials stability is, for example, of primary importance and this is investigated in theoretical studies through the calculation of the phonon dispersion curves and/or through the simulation of its atomic dynamics. Although several studies identified the same or similar low-energy structures for SiH₄(H₂)₂, it was known from the original experimental X-ray diffraction study that the H₂ molecules are rotating in the crystalline phase stable near 7 GPa, although the exact positions of the H₂ molecules could not be determined. Since the H₂ molecules are rotating, at least at the lower pressures in the calculations^{30,34} stability, as indicated through lattice dynamics based phonon calculations, could only be verified at fixed H₂ orientations. The stabilities of high pressure phases of SiH₄(H₂)₂ were therefore also investigated using *ab initio* molecular dynamics.⁴³ The stability and dynamics of SiH₄(H₂)₂ could then be tested, at least for the short time scales allowed in these simulations. These calculations suggested that H₂ molecules remain at their equilibrium sites but that they were rotating as seen from the calculated trajectories shown in Fig. 7. The SiH₄ molecular orientations were however fixed and underwent normal vibrational and librational motions as seen in Fig. 7 for both the lower and higher pressure phases of SiH₄(H₂)₂ at 12 and 34 GPa, respectively. At higher pressures above 100 GPa, it was predicted that the H₂ molecules located at the tetrahedral sites surrounding SiH₄ molecules will stop rotating due to the strong interaction with the SiH₄. The H₂ molecules located at the octahedral sites can still rotate but their rotation is predicted to be confined to planes. This rotation of H₂

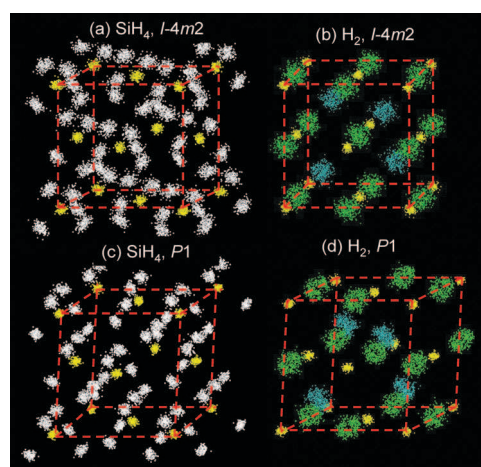


Fig. 7 Depicted trajectories of Si (yellow) and H atoms (white) in SiH₄ molecules in the (a) *I*-4*m*2 and (c) *P*1 structures of SiH₄(H₂)₂ obtained from NVE CPMD simulations. Depicted trajectories for hydrogen molecules at the octahedral (green) and tetrahedral (blue) sites in the (b) *I*-4*m*2 and (d) *P*1 structures of SiH₄(H₂)₂ from simulations for (a) and (c). The distorted fcc unit cells are identified by dashed lines.

molecules would influence the exact pressure of metallization but it was nevertheless suggested that the metallization pressure is less than one-third of that required for pure hydrogen.

Another important property that has been considered for $\text{SiH}_4(\text{H}_2)_2$ is that of high-temperature superconductivity. This is one of the properties originally considered for pure hydrogen and has been examined in combination with the evolutionary algorithm method for prediction of high pressure structures.³¹ In this study, a layered structure with a distorted fcc lattice of Si and significantly large intramolecular H–H bonds was predicted to be stable at pressures greater than 248 GPa and described with a *Ccca* space group. The lower pressure structures predicted were very similar to those of ref. 34. This structure was shown to be mechanically and dynamically stable by phonon dispersion calculations. The authors then applied the Allen-Dynes modified McMillan equation⁴⁴ with the implicit assumption that this structure would be a conventional BCS superconductor to predict a high superconducting temperature of 98–107 K. This interesting result should certainly encourage future experiments on this and similar materials.

Has metallic hydrogen been achieved?

The critical question remaining with all of these studies is however, have we in fact reached the metallic state of hydrogen with $\text{SiH}_4(\text{H}_2)_2$, at least in the theoretical studies? The correct answer is unfortunately a definite no since the DOS at the Fermi level when metallization of $\text{SiH}_4(\text{H}_2)_2$ occurs is dominated by the SiH_4 DOS itself as seen from Fig. 4. A significant fraction of valence electrons in Si atoms have been promoted to 3-d orbitals even by 100 GPa, resulting in an extensive orbital re-hybridization. Thus the Si atom orbitals would in fact contribute significantly to the onset of metallization of $\text{SiH}_4(\text{H}_2)_2$. In view of the recent results on pure SiH_4 that indicates decomposition of this pure material and the results on SiH_4 plus hydrogen mixtures, one may however still suggest this as a template for the potential pathway to metallic hydrogen. The silane-molecular hydrogen compound, $\text{SiH}_4(\text{H}_2)_2$, has shown unique properties under pressure including a surprising weakening of the hydrogen molecular vibron band frequencies. This behavior contrasts with that found in other mixtures of simple materials or gases such as shown for $\text{Ar}(\text{H}_2)_2$ where hydrogen vibron frequencies increase with pressure and H_2 – H_2 interactions are prevented and they remain insulating. The $\text{SiH}_4(\text{H}_2)_2$ crystalline solid at high pressures therefore shows some of the required properties that would perhaps be consistent with the metallization of the molecular hydrogen in this material although it is clear that true metallization of hydrogen has not actually occurred.

In this review, the high-pressure structures and electronic properties of $\text{SiH}_4(\text{H}_2)_2$ and $\text{Ar}(\text{H}_2)_2$ were contrasted to illustrate how theory and experiment were combined to provide an analysis of possible alternate routes to the production of metallic hydrogen. By describing the contrasting studies of high-pressure properties of $\text{SiH}_4(\text{H}_2)_2$ and $\text{Ar}(\text{H}_2)_2$, the basic ideas of using impurities in hydrogen were examined. The basic ideas that have been suggested for “pre-compressing”

hydrogen or introducing appropriate impurities that may enhance the metallization of solid hydrogen have not yet yielded the ultimate goal of metallic hydrogen. These ideas however remain basically valid and will undoubtedly continue to challenge researchers to find alternate routes for the metallization of solid hydrogen.

References

- 1 E. Wigner and H. B. Huntington, *J. Chem. Phys.*, 1935, **3**, 764–770.
- 2 N. W. Ashcroft, *Phys. Rev. Lett.*, 1968, **21**, 1748–1749.
- 3 H. K. Mao and P. M. Bell, *Science*, 1976, **191**, 851–852.
- 4 P. Loubeyre, R. LeToullec and J.-P. Pinceaux, *Phys. Rev. Lett.*, 1994, **72**, 1360–1363.
- 5 R. J. Hemley, *Annu. Rev. Phys. Chem.*, 2000, **51**, 763–800.
- 6 S. Bernard, P. Loubeyre and G. Zerah, *Europhys. Lett.*, 1997, **37**, 477–482.
- 7 N. Matsumoto and H. Nagara, *J. Phys.: Condens. Matter*, 2007, **19**, 365237–365245.
- 8 C. Cazorla and D. Errandonea, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 104108.
- 9 Y. Yao and D. D. Klug, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 020105R.
- 10 H. K. Mao and R. J. Hemley, *Rev. Mod. Phys.*, 1994, **66**, 671–692.
- 11 M. Hanfland, R. J. Hemley, H. K. Mao and G. P. Williams, *Phys. Rev. Lett.*, 1992, **69**, 1129–1132.
- 12 N. W. Ashcroft, *Phys. Rev. Lett.*, 2004, **92**, 187002.
- 13 J. Feng, W. Grochala, T. Jaron, R. Hoffmann, A. Bergara and N. W. Ashcroft, *Phys. Rev. Lett.*, 2006, **96**, 017006.
- 14 Y. Yao, J. S. Tse, Y. Ma and K. Tanaka, *Europhys. Lett.*, 2007, **78**, 37003.
- 15 M. I. Erements, I. A. Trojan, S. A. Medvedev, J. S. Tse and Y. Yao, *Science*, 2008, **319**, 1506–1509.
- 16 X. J. Chen, V. V. Struzhkin, Y. Song, A. F. Goncharov, M. Ahart, Z. Liu, H. K. Mao and R. J. Hemley, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 20–23.
- 17 X. J. Chen, J. L. Wang, V. V. Struzhkin, H. K. Mao, R. J. Hemley and H. Q. Lin, *Phys. Rev. Lett.*, 2008, **101**, 077002.
- 18 M. Martinez-Canales, A. R. Oganov, Y. Ma, Y. Yan, A. O. Lyakhov and A. Bergara, *Phys. Rev. Lett.*, 2009, **102**, 087005.
- 19 C. J. Pickard and R. J. Needs, *Phys. Rev. Lett.*, 2006, **97**, 045504.
- 20 M. Hanfland, J. E. Proctor, C. L. Guillaume, O. Degtyareva and E. Gregoryanz, *Phys. Rev. Lett.*, 2011, **106**, 095503.
- 21 T. A. Strobel, A. F. Goncharov, C. T. Seagle, Z. Liu, M. Somayazulu, V. V. Struzhkin and R. J. Hemley, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 144102.
- 22 E. Zurek, R. Hoffmann, N. W. Ashcroft, A. R. Oganov and A. O. Lyakhov, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 17640–17643.
- 23 T. A. Strobel, M. Somayazulu and R. J. Hemley, *Phys. Rev. Lett.*, 2009, **103**, 065701.
- 24 S. Wang, H. K. Mao, X. J. Chen and W. L. Mao, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 14673–14677.
- 25 M. Somayazulu, P. Dera, A. F. Goncharov, S. A. Gramsch, H. P. Liermann, W. Yang, Z. Liu, H. K. Mao and R. J. Hemley, *Nat. Chem.*, 2009, **2**, 50–53.
- 26 P. Loubeyre, R. LeToullec and J.-P. Pinceaux, *Phys. Rev. B: Condens. Matter*, 1992, **45**, 12844–12853.
- 27 M. Somayazulu, L. W. Finger, R. J. Hemley and H. K. Mao, *Science*, 1996, **271**, 1400–1402.
- 28 R. S. Chellappa, M. Somayazulu, V. V. Struzhkin, T. Autrey and R. J. Hemley, *J. Chem. Phys.*, 2009, **131**, 224515.
- 29 M. Ramzan, S. Lebegue and R. Ahuja, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 233103.
- 30 W. L. Yim, J. S. Tse and T. Iitaka, *Phys. Rev. Lett.*, 2010, **105**, 215501.
- 31 Y. Li, G. Gao, Y. Xie, Y. Ma, T. Cui and G. Zou, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 15708–15711.
- 32 Y. Li, G. Gao, Q. Li, Y. Ma and G. Zou, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 064104.
- 33 K. Michel, Y. Liu and V. Ozolins, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 174103.

- 34 Y. Yao and D. D. Klug, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 20893–20898.
- 35 X. Q. Chen, S. Wang, W. L. Mao and C. L. Fu, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 104115.
- 36 T. A. Strobel, X. J. Chen, M. Somayazulu and R. J. Hemley, *J. Chem. Phys.*, 2010, **133**, 164512.
- 37 W. L. Mao, V. V. Struzhkin, H.-K. Mao and R. J. Hemley, *Chem. Phys. Lett.*, 2005, **402**, 66–70.
- 38 F. Datchi, *et al.*, *Bull. Am. Phys. Soc.*, 1996, **41**, 564.
- 39 C. J. Pickard and R. J. Needs, *Nat. Phys.*, 2007, **3**, 473–476.
- 40 J. S. Tse, D. D. Klug, Y. Yao, Y. Le Page and J. M. Rodgers, *Solid State Commun.*, 2008, **145**, 5–10.
- 41 N. W. Ashcroft, *Physics*, 2009, **2**, 65.
- 42 A. R. Oganov and G. W. Glass, *J. Chem. Phys.*, 2006, **175**, 713–720.
- 43 R. Car and M. Parrinello, *Phys. Rev. Lett.*, 1985, **55**, 2471–2474.
- 44 P. B. Allen and R. C. Dynes, *Phys. Rev. B: Solid State*, 1975, **12**, 905–922.