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PERSPECTIVE

Metallization of solid hydrogen: the challenge and possible solutions

Dennis D. Klug and Yansun Yao

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

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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 known that the plane 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 range[3] meant that a serious search for metallic hydrogen could be pursued.

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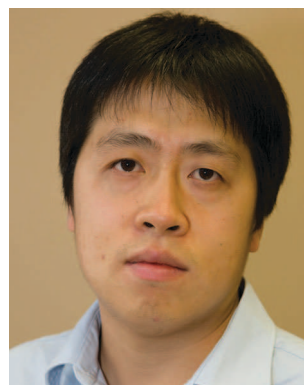
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The search for metallic hydrogen was therefore intensified by both experimentalists and theoreticians with results that only showed that metallization of hydrogen had not occurred under static conditions close to the highest pressures so far attainable 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 Hemley[10] 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 lithium[22] 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. Hemley[23] 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 $SiH_4 \cdot H_2$ 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
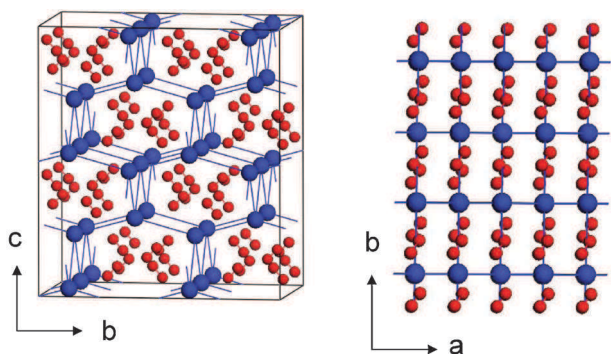
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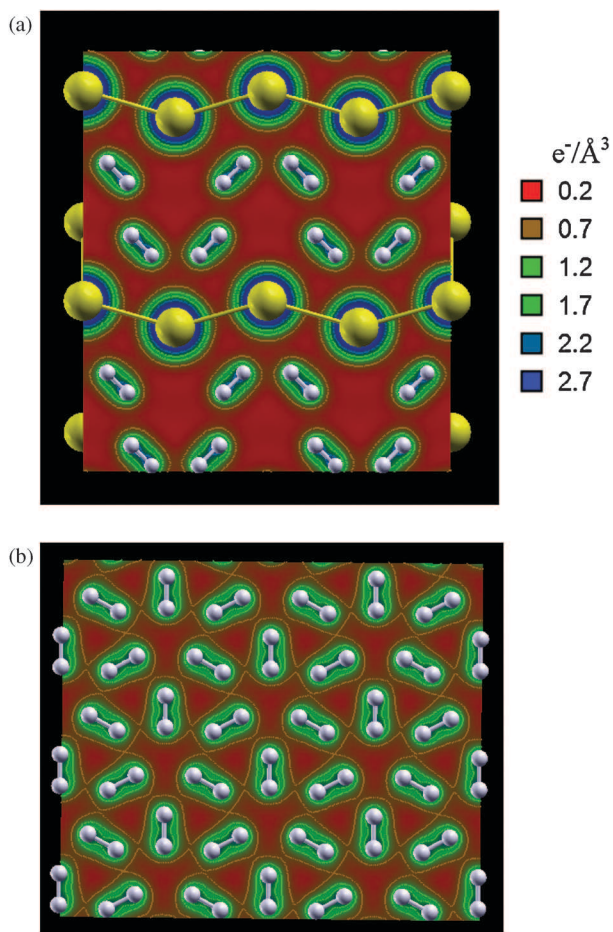
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Fig. 2 The calculated valence charge density for (a) $Ar(H_2)_2$ and (b) pure hydrogen at 300 GPa differentiated by a color scheme from red (low density, $0.2\,e^-/Å^3$ or lower) to blue (high density, $2.7\,e^-/Å^3$ or higher). The Ar atoms and H_2 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 $SiH_4(H_2)_2$ 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-43m)

for the $SiH_4(H_2)_2$ 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 method[42] 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-4m2 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 $SiH_4(H_2)_2$ system, the H_2 molecules rotated rapidly, at least up to pressures of about 100 GPa, as found in the high-pressure $Ar(H_2)_2$ compound. The rapid decrease with

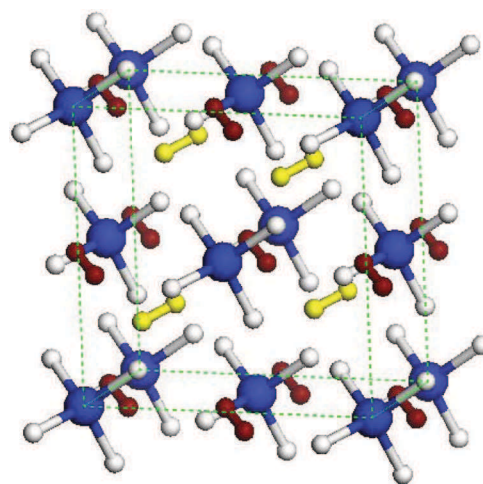**Fig. 3** The P1 structure of $SiH_4(H_2)_2$ is shown in a distorted fcc unit cell. The SiH_4 molecules are located at the corners and face centers of the unit cell with the Si atom indicated by the larger spheres. The H_2 molecules at the octahedral and tetrahedral sites are colored brown (dark) and yellow (light), respectively.
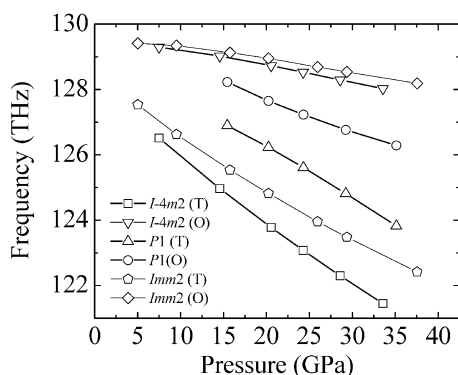
Fig. 4 Calculated pressure dependences of the H_2 vibron frequencies of $I\text{-}4m2$, $Imm2$, and $P1$ structures of $SiH_4(H_2)_2$. The $I\text{-}4m2$ and $Imm2$ structures were other energetically competitive structures found for $SiH_4(H_2)_2$ (ref. 34). The notations T and O refer to the H_2 molecules at tetrahedral and octahedral sites.

Fig. 5 Calculated valence charge density of $SiH_4(H_2)_2$ 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.

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 $SiH_4(H_2)_2$ 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 $SiH_4(H_2)_2$ 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

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 $SiH_4(H_2)_2$. 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 $SiH_4(H_2)_2$ 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 $SiH_4(H_2)_2$. 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-bonding 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 SiH_4 unit and H_2 molecules for (a) $I-4m2$ structure at 0.27 GPa, (b) $I-4m2$ structure at 6.9 GPa, (c) $P1$ structure at 99.2 GPa, and (d) $P1$ structure at 152.7 GPa. The notations T and O refer to the H_2 molecules at tetrahedral and octahedral sites. The origin '0' in energy corresponds to the highest energy of the occupied states.

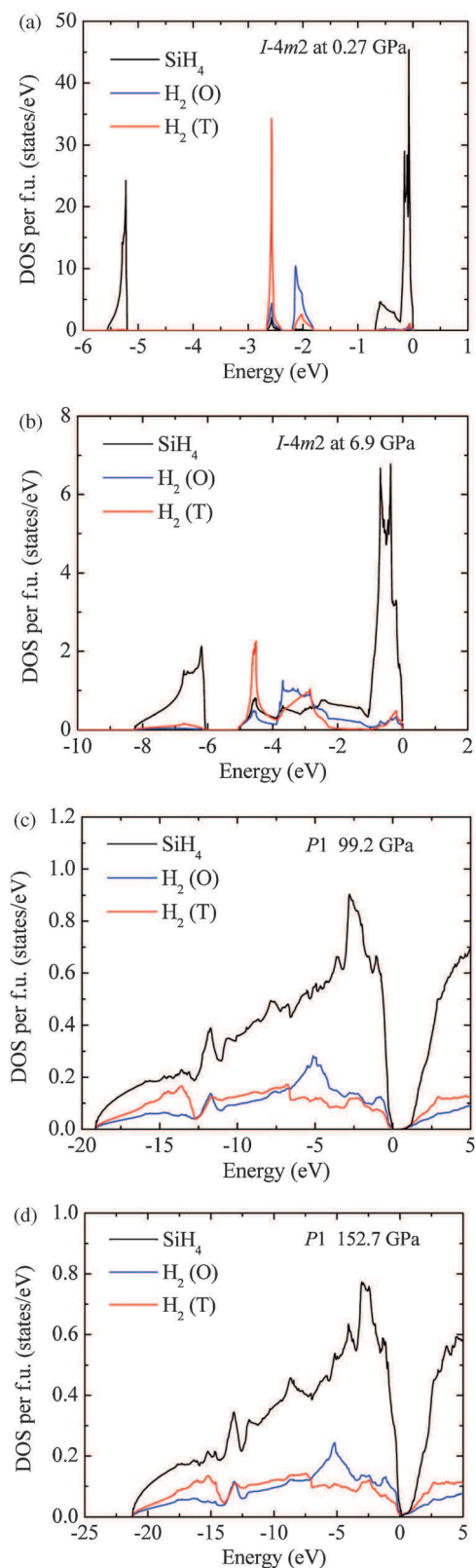directly correlated with the weakening of the H–H bonds within the H_2 molecules in $SiH_4(H_2)_2$ and these are two features similar to that leading to metallization of pure hydrogen.

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 it atomic dynamics. Although several studies identified the same or similar low-energy structures for $SiH_4(H_2)_2$, it was known from the original experimental X-ray diffraction study that the H_2 molecules are rotating in the crystalline phase stable near 7 GPa, although the exact positions of the H_2 molecules could not be determined. Since the H_2 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 H_2 orientations. The stabilities of high pressure phases of $SiH_4(H_2)_2$ were therefore also investigated using *ab initio* molecular dynamics.[43] The stability and dynamics of $SiH_4(H_2)_2$ could then be tested, at least for the short time scales allowed in these simulations. These calculations suggested that H_2 molecules remain at their equilibrium sites but that they were rotating as seen from the calculated trajectories shown in Fig. 7. The SiH_4 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 $SiH_4(H_2)_2$ at 12 and 34 GPa, respectively. At higher pressures above 100 GPa, it was predicted that the H_2 molecules located at the tetrahedral sites surrounding SiH_4 molecules will stop rotating due to the strong interaction with the SiH_4. The H_2 molecules located at the octahedral sites can still rotate but their rotation is predicted to be confined to planes. This rotation of H_2
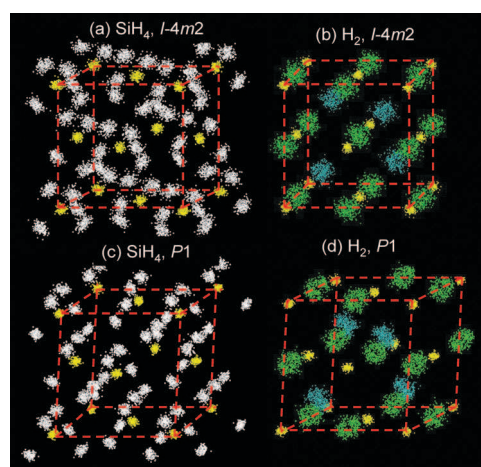
Fig. 7 Depicted trajectories of Si (yellow) and H atoms (white) in SiH_4 molecules in the (a) $I-4m2$ and (c) $P1$ structures of $SiH_4(H_2)$ obtained from NVE CPMD simulations. Depicted trajectories for hydrogen molecules at the octahedral (green) and tetrahedral (blue) sites in the (b) $I-4m2$ and (d) $P1$ structures of $SiH_4(H_2)_2$ 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 that one-third of that required for pure hydrogen.

Another important property that has been considered for $SiH_4(H_2)_2$ 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 equation[44] 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 $SiH_4(H_2)_2$, at least in the theoretical studies? The correct answer is unfortunately a definite no since the DOS at the Fermi level when metallization of $SiH_4(H_2)_2$ 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 $SiH_4(H_2)_2$. 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, $SiH_4(H_2)_2$, 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 $Ar(H_2)_2$ where hydrogen vibron frequencies increase with pressure and $H_2–H_2$ interactions are prevented and they remain insulating. The $SiH_4(H_2)_2$ 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 $SiH_4(H_2)_2$ and $Ar(H_2)_2$ 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 $SiH_4(H_2)_2$ and $Ar(H_2)_2$, 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.

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