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Silane plus molecular hydrogen as a possible pathway to metallic hydrogen

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The high-pressure behavior of silane, SiH₄, plus molecular hydrogen was investigated using a structural search method and ab initio molecular dynamics to predict the structures and examine the physical origin of the pressure-induced drop in hydrogen intra-molecular vibrational (vibron) frequencies. A structural distortion is predicted at 15 GPa from a slightly strained fcc cell to a rhombohedral cell that involves a small volume change. The predicted equation of state and the pressure-induced drop in the hydrogen vibron frequencies reproduces well the experimental data (Strobel TA, Somayazulu M, Hemley RJ (2009) Phys Rev Lett 103:065701). The bond weakening in H₂ is induced by intermolecular interactions between the H₂ and SiH₄ molecules. A significant feature of the high-pressure structures of SiH₄(H₂)₂ is the dynamical behavior of the H₂ molecules. It is found that H₂ molecules are rotating in this pressure range whereas the SiH₄ molecules remain rigid. The detailed nature of the interactions of molecular hydrogen with SiH₄ in SiH₄(H₂)₂ is therefore strongly influenced by the dynamical behavior of the H₂ molecules in the high-pressure structure. The phase with the calculated structure is predicted to become metallic near 120 GPa, which is significantly lower than the currently suggested pressure for metallization of bulk molecular hydrogen.

One of the main challenges for condensed matter experimentalists and theoreticians for many decades has been to find the conditions where molecular hydrogen can be transformed to a metallic solid. The properties of metallic hydrogen could include high-temperature superconductivity, a liquid ground state, and conductivity at very high temperatures that gives rise to the strong magnetic fields of Jovian planets. The direct compression of solid molecular hydrogen however may require a pressure in excess of 400 GPa to reach a metallic state and this pressure lies at the upper limit of the current experimental static compression techniques. There have been other approaches to this problem, including the study of hydrogen-rich molecular compounds. Compression of such compounds, in particular those involving group 14 elements, is predicted to lower the pressure required for metallization compared to pure bulk hydrogen.

In these systems, the hydrogen can be viewed as perturbed by “impurities” in the material and “chemically precompressed” (6).

An extension of this approach is to study mixtures of elements or simple molecules with hydrogen under pressure (9, 10). Recently, Strobel et al. (11) reported that by mixing silane (SiH₄) and hydrogen, a stoichiometric compound, SiH₄(H₂)₂, can be formed near 7 GPa. This compound has unique properties under pressure including a surprising weakening of the molecular hydrogen stretching frequencies. Wang et al. (12) also recently presented experimental evidence that vibrational (vibron) frequencies are lowered at low pressures when hydrogen is added to SiH₄. The behavior in SiH₄(H₂)₂ contrasts with that of other mixtures of simple materials (13–16) where hydrogen vibron frequencies increase with pressure in the pressure range below 100 GPa and they remain insulating. This observation indicates that the covalent bond in the H₂ molecules can be effectively modified at relatively low pressure with small change in chemical environment [there is only 11 atom percent Si in SiH₄(H₂)₂], and would perhaps give rise to a unique metal with properties similar to metallic hydrogen.

X-ray diffraction (11) revealed the structure of SiH₄(H₂)₂ to have high symmetry, with the Si atoms forming an fcc framework. Ramzan et al. (17) subsequently estimated the metallization pressure for SiH₄(H₂)₂ but the proposed structure was not completely described. In particular, the locations and orientations of hydrogen atoms in both SiH₄ and H₂ molecules were not given. Theoretical understanding of the interesting physical properties of this and related compounds is therefore currently not yet in hand. In the current study, predictions of the locations and orientations of the hydrogen atoms in SiH₄(H₂)₂ are made, along with a suggestion of a possible lattice distortion at elevated pressure. The predicted structure shows a large decrease in the vibron frequency at pressures significantly lower than that observed in bulk molecular hydrogen (18). This finding is explained by the weakening of the H–H bonds at high pressure, resulting from strong intermolecular interactions between the H₂ and SiH₄ molecules. The phase with the predicted structure is calculated to undergo metallization near 120 GPa, which is about one-third the suggested pressure required for metallization of bulk molecular hydrogen.

Results and Discussion

The structural search results are presented in Fig. 1 where equations of state (EOS) of the most energetically competitive structures are shown and compared with the experimental data (11) over the pressure range 5–40 GPa (the SI Appendix presents computational details). The theoretical predictions show a good agreement with experiment. Because the EOS calculations do not include thermal expansion effects, they yield smaller volumes than the experimental data (obtained at room temperature). At low pressures, the structures obtained have slightly strained fcc frameworks of Si atoms, with four H₂ molecules occupying all four octahedral sites, and the other four occupying four out of eight tetrahedral sites. To minimize the interactions among H₂ molecules, alternate tetrahedral sites are occupied. The SiH₄ molecules form tetrahedrons through sp³ hybridized orbitals. In order to reduce unfavorable repulsive interactions with H₂ molecules in the occupied interstitial sites, the four Si–H axes in the SiH₄ molecules all point to the nearest empty tetrahedral sites, and therefore unambiguously fixes the orientation of SiH₄ molecules. In terms of smallest volume (Fig. 1), there are two favorable structures, with space group I-4m2 and Imm2, obtained at pressures in the 5–15 GPa range. The main difference between these two structures is the orientation of H₂ molecules. In the I-4m2 structure, all H₂ molecules are aligned along the [001] direction of the fcc unit cell (Fig. 24). This alignment results

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These two structures have very close volumes and enthalpies in along the these two directions (orthorhombic distortion, Fig. 2). The SiH₂ molecules deviate from the perfect tetrahedrons, as the sp³ orbitals interact with the nearby H₂ molecular orbitals. These distortions, being in SiH₂ and H₂ molecules, reduced the space group of SiH₂(H₂)₂ to P1. In terms of enthalpy (SI Appendix, Figs. S3 and S4), the P1 structure becomes more favorable than the I-4m2 structure at pressures higher than 22 GPa. The vibrational contribution to free energy, F_vib is estimated (19), for example, at 30 GPa and 300 K (SI Appendix, Fig. S6) and the results shows that the F_vib of the P1 structure is about 0.11 eV/f.u. higher than that of the I-4m2 structure. A rough estimate of Gibbs free energy by adding F_vib to the enthalpy indicates that the I-4m2 structure is only 0.02 eV/f.u. more stable than the P1 structure at 30 GPa. Given that the enthalpy of I-4m2 structure goes up rapidly relative to that of P1 structure with increasing pressure (SI Appendix, Fig. S4), one can expect, when entropy is considered, that the P1 structure is energetically favorable at pressures somewhat greater than 30 GPa.

The structural details of the I-4m2, Imm2, and P1 structures are listed in SI Appendix, Table S1. The calculated X-ray diffraction patterns for both the I-4m2 and Imm2 structures are close to that of the fcc structure, as the Si frameworks in these two structures are only slightly strained (Fig. 2D). These diffraction patterns are in agreement with the experimentally reported diffraction pattern (11). The calculated P1 diffraction pattern however already deviates from that of the fcc lattice at 15.5 GPa (Fig. 2D). As will be discussed in detail later, the H₂ molecules in SiH₂(H₂)₂ rotate in their original site over the pressure range studied in Fig. 1. Any orientation of H₂ molecules derived from a static calculation in this pressure range therefore only corresponds to an instantaneous configuration, and the properties of SiH₂(H₂)₂ represent the collective effects of all possible configurations.

The calculated pressure dependences of H₂ vibron frequencies for the I-4m2, Imm2, and P1 structures are shown in Fig. 3. For all three structures, the vibron frequencies undergo a remarkable weakening in the 5–40 GPa pressure range as was observed in the experimental report (11) except for a single vibron frequency in the experiment that has much lower frequency than in bulk hydrogen but does not weaken up to 35 GPa and could arise from another higher energy structure (12). This weakening of H₂ vibron frequencies in SiH₂(H₂)₂ is significantly greater than that observed in the bulk solid hydrogen (18) over a similar pressure
range. For bulk hydrogen, the vibron frequency weakening occurs at much higher pressures (above 40 GPa) and over a much larger pressure range, from 40 to 120 GPa. This observation suggests that a unique interaction between H₂ and SiH₄ molecules is present in SiH₄(H₂)₂. The H₂ molecules at the tetrahedral sites always have more prominent bond weakening than their counterparts at the octahedral sites (Fig. 3), which indicates the former experience stronger interaction with the SiH₄ molecules than the latter. One may explain the difference in interaction strengths by applying a “short distance = strong interaction” paradigm (20), as the tetrahedral sites are closer to the nearest fcc SiH₄ sites than are the octahedral sites.

A qualitative analysis of the intermolecular interactions in SiH₄(H₂)₂ is provided through the calculated valence charge density for I-4m2 and P1 structures at selected pressures (Fig. 4). At low pressure (6.9 GPa), the intermolecular interactions in the entire system are relatively weak. The SiH₄ molecules remain as tetrahedrons. As the pressure increases, the free space within the cell decreases and forces the molecules (H₂ and SiH₄) to more strongly interact with each other. This interaction goes up rapidly with compression and the valence electrons from neighboring molecules would have to migrate toward the region between molecules to minimize the unfavorable repulsions. As a result, the bonding within the molecules will weaken. For example, at 15.7 GPa (Fig. 4), notable electron density is already built up in the region between SiH₄ molecules and H₂ molecules at the tetrahedral sites, indicating a strong orbital overlap. The interaction with H₂ molecules at the octahedral sites, on the other hand, is much weaker. The orbital overlap distorts the sp³ hybridized orbital and the SiH₄ molecules start to deform progressively from perfect tetrahedrons. This trend is even more prominent at higher pressure. As seen from the valence charge density at 99.2 GPa (Fig. 4), the H₂ molecules at tetrahedral sites are already very close to the Si atoms. The high pressure brings H₂ molecules at tetrahedral sites into the coordination shell of the Si atoms and the SiH₄ tetrahedrons distort significantly. The interaction between SiH₄ and the H₂ molecules at octahedral sites also strengthens.

Another measure of the interactions between SiH₄ and H₂ molecules in SiH₄(H₂)₂ is reflected by the H–H bond length changes. Because phonon frequencies are correlated with the interatomic force constants, the softening of the vibron frequency in Fig. 3 indicates that the H–H bond lengths increase with pressure. For the P1 structure at 15.7 GPa, the calculated H–H bond lengths in the H₂ molecules at tetrahedral and octahedral sites are 0.750 and 0.748 Å, respectively. At 42.6 GPa, the two bond lengths increase to 0.756 and 0.749 Å. Here again one notices that the bond weakening is more prominent for the H₂ molecules at the tetrahedral sites than for their counterparts at octahedral sites. Once the pressure increases to 99.2 GPa, the H–H bond lengths at tetrahedral sites increases significantly to 0.815 Å, while the bond lengths at octahedral sites remain at 0.749 Å. For comparison, the calculated H–H bond lengths in the predicted C2/c structure (21, 22) for phase III of bulk hydrogen at a much higher pressure of 154 GPa are 0.743 and 0.750 Å. Examination of the changes in the H–H bond length show lengthening of 0.0064 Å over a pressure range 7.8–33.7 GPa for the I-4m2 structure and 0.0055 Å over the pressure range 9.6–37.7 GPa for the Imm2 structure.

The valence charge density in Fig. 4 also reveals that, under high pressure, some valence electrons are delocalized among off atoms to interstitial regions (charge density between 0.2 and 0.3 e−/Å³). The “delocalizing” of electrons at high pressure is rather general (23). It is helpful for further understanding to consider the behavior of bulk Si under high pressure. At ambient pressure, bulk solid Si forms a cubic diamond structure (Si-I) through sp³ covalent bonds. With increasing pressure, the 3d orbital energy approaches that of the sp³ orbital, and valence electrons start to fill up the 3d orbital. This results in an orbital rehybridization to a sp² orbital once sufficient electrons are promoted to 3d orbitals. As a result, the Si structure transforms from a cubic diamond structure to a two-dimensional (sp²) structure (for example, Si-XI) at high pressure (24). A similar electron reordering also occurs in SiH₄(H₂)₂. As shown in SI Appendix, Fig. S8, there is already a significant promotion of valence electrons in Si atoms to 3d orbital in the P1 structure at 99.2 GPa.

With the accumulation of valence electrons on the more diffuse interstitial regions, the overall electron mobility and metallic character in SiH₄(H₂)₂ increases with pressure. The next question to address is at what pressure will SiH₄(H₂)₂ become metallic. The answer can be provided from the examination of the calculated electronic density of states (DOS). As shown in SI Appendix, Fig. S7, the band gap of P1 structure starts to close near 120 GPa (the accurate pressure for band gap closure depends on the detailed orientation of the H₂ molecules; see discussion below). It is encouraging to see that the calculated metallization pressure for SiH₄(H₂)₂ is well within the reach of current diamond–anvil techniques. On the other hand, it should be noted that, due to systematic defects for treating the excited states in density functional theory (DFT) calculations (as used in the present study) band gaps are in general underestimated. Thus, it is very likely that actual pressure for band gap closure in SiH₄(H₂)₂ is higher than the DFT estimated values (17). Nevertheless, the metallization pressure calculated here is more than a factor of 3 lower than the currently suggested pressure required for metallization of bulk molecular hydrogen.

Fig. 5 A–D show the evolution of valence bands and band gap closure for SiH₄(H₂)₂ with increasing pressure. Close to the ambient pressure (0.27 GPa, Fig. 5A), van der Waals interactions predominate in the system. The SiH₄ molecules, H₂ molecules at tetrahedral and octahedral sites, have well-separated valence bands. The valence bands for the H₂ molecules at tetrahedral sites interact slightly with their counterparts at the octahedral sites. The rather weak intermolecular interactions, in reality, cannot maintain the SiH₄(H₂)₂ structure at this pressure (11, 12). For the initial pressure range where weak interactions dominate, compression occurs easily, after which intermolecular interactions increase rapidly. At 6.9 GPa, the volume of I-4m2 structure already decreases to about 54% of the initial value at 0.27 GPa, and the intermolecular interactions begin to increase (Fig. 5B).

The behavior of the DOS with pressure from Fig. 5 A–D reveals...
several noteworthy points. As the compression delocalizes the orbitals, the orbitals of the neighboring molecules (being either H₂ or SiH₄) would therefore overlap (Fig. 4) and result in a broad valence band (Fig. 5 A–D). With increasing pressure, the strengthening orbital overlap stabilizes the bonding interactions (lower in energy) and destabilizes the antibonding interactions (higher in energy), and therefore increases the overall bandwidth (25). The bandwidth expansion in energy is a key ingredient for the metallization. A sufficiently large bandwidth expansion eventually forces valence and conduction bands to overlap, and increases the electron velocity near the Fermi level, which is exactly as found for SiH₄(H₂)₂. As seen in Fig. 5D, at 152.7 GPa, some unoccupied DOS of H₂ molecules, through mixing with the SiH₄ conduction band, moves below the Fermi level and overlaps with the occupied DOS, and therefore the system becomes weakly metallic. The weakening of the H–H bonds in the H₂ molecules (Fig. 3) is also closely correlated with the metallization (9). The valence and the nearest conduction bands of H₂ molecules are constructed from bonded states (σ₂) and antibonded states (σ₂'), respectively. Once H–H bonds weaken, the energy of bonded states will increase and those of the antibonded states will decrease. Thus, the energy separation between the bonded states and antibonded states, in other words the energy gap, decreases. The same band overlap and band gap closure will also occur in bulk solid hydrogen, but at much higher pressure.

Another important issue to address is the stability and dynamics of SiH₄(H₂)₂. The calculated phonon dispersion curves for the I-4m2 structure at 10 GPa shows weak instability at 0 K, as indicated by the imaginary frequencies in the Z to Γ and N to Γ directions (SI Appendix, Fig. S5A). The same calculation, however, shows that at elevated pressures, i.e., 30 GPa, the imaginary phonon frequencies disappear and I-4m2 structure becomes stable (SI Appendix, Fig. S5B). The calculations of phonon DOS for both I-4m2 and P1 structures confirmed their mechanical stabilities at 30 GPa (SI Appendix, Fig. S6). There are multiple reasons to account for the phonon softening at low pressure. At low pressure, long-distance weak interactions dominate in the system, which makes the DFT evaluation of the force constants difficult. The small proton mass also poses a problem. The molecular motions (i.e., from quantum effects) can deviate from a harmonic description, which would be important for hydrogen-rich materials (18, 26). To investigate further the stability of SiH₄(H₂)₂, and recognizing that the instability of SiH₄(H₂)₂ at low pressure may be a result of an insufficient harmonic approximation of vibrations in analogy with results reported for elemental Ca (27), room temperature (300 K) Car–Parrinello molecular dynamics (CPMD) (28) were performed on the I-4m2 and P1 structures at 12 and 34 GPa, respectively. The calculated time evolutions of the dimensions and angles of the simulation cells are shown in Fig. 6 A and B obtained from 15 ps isothermal-isobaric (NPT) CPMD trajectories. Both the I-4m2 and P1 structures appear to be stable at 300 K with the dimensions and angles of the simulation cells remaining near their equilibrium values. The static structure factor S(Γ) (q) for I-4m2 and P1 structures were evaluated (29) from the NPT CPMD trajectories and the results are shown in Fig. 6C (computational details in SI Appendix). The S(Γ) (q) for both structures resembles closely to the calculated X-ray diffraction patterns in Fig. 2D, indicating that the molecules in the NPT CPMD trajectories remain at their equilibrium sites, which therefore suggests structural stability at room temperature. The S(Γ) (q) of the I-4m2 structure (Fig. 6C), is clearly associated with that of a fcc cell and agrees very well with the experimentally reported diffraction pattern (11). The slight tetragonal distortion (arising from the alignment of H₂ molecules along c axis) from the static calculation (Fig. 2A), is not readily

![Fig. 5. Calculated electronic DOS projected on SiH₄ and H₂ 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 H₂ molecules at tetrahedral and octahedral sites. The origin “0” in energy corresponds to the highest energy of the occupied states.](https://www.pnas.org/cgi/doi/10.1073/pnas.1006508107)

![Fig. 6. Evolution of the simulation cell dimensions and angles for the (A) I-4m2 and (B) P1 structures of SiH₄(H₂)₂ at 12 and 34 GPa, respectively, from NPT CPMD simulations at 300 K. (C) Calculated static structure factor (X-ray wavelength = 0.5 Å), S(Γ) (q), for the I-4m2 and P1 structures from the calculations indicated in A and B. See text and SI Appendix.](https://www.pnas.org/cgi/doi/10.1073/pnas.1006508107)
apparent at room temperature and is obscured by hydrogen molecular motions.

The dynamics of both SiH$_4$ and H$_2$ molecules are seen from visualization of their individual atomic trajectories. The equilibrated CPMD trajectories were obtained in a microcanonical (NVE) ensemble after an additional temperature equilibration in a canonical (NVT) ensemble and the pressure equilibration in the NPT ensemble described above. In Fig. 7 A and C, the trajectories of SiH$_4$ components are depicted for the I-4/m2 and P1 structures, respectively. The SiH$_4$ molecules remain basically fixed at their original sites and both the H and Si atoms undergo thermal motions about their respective crystallographic symmetry. In contrast, H$_2$ molecules undergo clear rotation at these pressures (Fig. 7 B and D). The rotation of H$_2$ molecules implies a sampling of many possible structures in addition to the lowest enthalpy ones and is the reason that average cell constants and angles in Fig. 6a remain at those for an fcc structure. The CPMD trajectories for the P1 structure indicates that this basic structure is preserved (Fig. 7C and D). In both cases, the H$_2$ molecules remain rotating in their original sites and the structure appears to be stable. The rotation of H$_2$ molecules is also a structural feature of the low-pressure phase I of solid bulk hydrogen that is stable up to pressures of about 110 GPa (18). The clear rotation of H$_2$ molecules seen in the CPMD simulations indicates that the structure is sampling a variety of low-energy sites and therefore a variety of structures which would lead to the complex and somewhat broad Raman spectrum observed in the experiment (11). With increasing pressure, the strong interaction with the SiH$_4$ molecules will reduce the mobility of the H$_2$ molecules and, in particular, the mobility of the H$_2$ molecules at the tetrahedral sites. Additional CPMD calculations show that, at 100 GPa, the H$_2$ molecules at the tetrahedral sites stopped rotating and the ones at octahedral sites have rotations confined mostly to the (110) plane. The rotation of H$_2$ molecules will influence the properties of SiH$_4$($H_2$)$_2$ including the metallization.

Fig. 7. Depicted trajectories of Si (yellow) and H atoms (white) in SiH$_4$ molecules in the (A) I-4/m2 and (C) P1 structures of SiH$_4$($H_2$)$_2$ obtained from NVE CPMD simulations. Depicted trajectories for hydrogen molecules at the octahedral (green) and tetrahedral (blue) sites in the (B) I-4/m2 and (D) P1 structures of SiH$_4$($H_2$)$_2$ from simulations for A and C. The distorted fcc unit cells are identified by solid lines.

Conclusions
In summary, the results of this study of the structure of SiH$_4$($H_2$)$_2$ indicate that interaction of SiH$_4$ with molecular hydrogen at high pressure is unexpectedly strong, in agreement with recent experimental findings. The rapid weakening and lengthening in the H$_2$ bond occurs at pressures far below that seen in bulk hydrogen and takes place in a structure where H$_2$ molecules rotate at tetrahedral and octahedral sites of a distorted fcc lattice of SiH$_4$ units in the pressures in the experimental report. The rotation of hydrogen molecules become partially hindered near the metallization pressure of about 120 GPa. H$_2$ molecules at tetrahedral sites show significantly greater bond weakening than H$_2$ molecules at octahedral sites. This rapid weakening of the H$_2$ bond is also consistent with a predicted metallization pressure near 120 GPa. These results demonstrate that the metallization of SiH$_4$($H_2$)$_2$ may be achieved at relatively low pressure and with properties similar to metallic hydrogen.

Methods
Searches for candidate structures of SiH$_4$($H_2$)$_2$ were performed with an experimental reported fcc lattice (details in SI Appendix). The EOS, valence charge densities, and electronic DOS were calculated using the Vienna ab initio simulation code (30) and projector-augmented plane-wave potentials (31). The Si and H potentials employed 3s3p and 1s as valence states, respectively, with the Perdew–Burke–Ernzerhof exchange-correlation functional (32) (same for all three pseudopotentials used in the present study). An energy cutoff of 910 eV was used. An 8 × 8 × 8 and a 32 × 32 × 32 k-point mesh (33) for Brillouin zone (BZ) samplings were used in the EOS and electronic DOS calculations, respectively. Phonon calculations were performed using the ABINIT program (34) employing the linear response method, Hertwigsen–Goedecker–Hutter pseudopotentials (35) with an energy cutoff of 70 Hartree. A 4 × 4 × 4 q-point and a 10 × 10 × 10 k-point mesh was used for phonon calculations. The CPMD calculations (28) were performed with a supercell of 288 atoms, using the Quantum ESPRESSO package (36) with norm-conserving pseudopotentials (37) with an energy cutoff of 60 Rydberg. A fictitious electron mass of the electronic wave function of 50 a.u. and a time step of 4 a.u. were used for the time integration of the ionic motions (38). The BZ sampling was restricted to the zone center. To check the structural stability, the supercells were first examined for 15 ps in an isothermal-isobaric (NPT) ensemble, after an initial 3-ps temperature equilibration in a canonical (NVT) ensemble. The static structure factor $S_s(q)$ was calculated (see SI Appendix for details) from the NPT CPMD trajectories. The equilibrated trajectories were then obtained in a microcanonical (NVE) ensemble after an additional temperature equilibration (3 ps) in a canonical (NVT) ensemble to avoid temperature drifting. The temperature in the CPMD calculations is controlled by a Nose thermostat (39).

Note
Recently there were several additional reports appearing after our submission (40–42) that address several other properties of SiH$_4$($H_2$)$_2$.

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