

Structures and Potential Superconductivity in SiH₄ at High Pressure: En Route to “Metallic Hydrogen”

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A way to circumvent the high pressures needed to metallize hydrogen is to “precompress” it in hydrogen-rich molecules, a strategy probed theoretically for silane. We show that phases with tetrahedral SiH₄ molecules should undergo phase transitions with sixfold- and eightfold-coordinate Si appearing above 25 GPa. The most stable structure found can be metallized at under a megabar and at a compression close to the prediction of Goldhammer-Herzfeld criterion. According to a BCS-like estimate, metallic silane should be a high-temperature superconductor.

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Metallic—and superconducting—hydrogen [1] remains elusive, despite considerable ongoing experimental effort up to pressures of ~ 342 GPa [2,3]. Goldhammer-Herzfeld theory [4,5] suggests that pressure-induced metallization of H₂ will be as difficult as that of Cl₂, F₂, or Kr, the very few genuine nonmetals which have not yet been impelled by pressure into a metallic state. It has recently been pointed out that dense, metallic hydrogen-rich compounds, in particular, pressurized hydrides of group 14 elements (C, Si, and Ge), are likely candidates for high-temperature superconductors [6–8]. One can view the hydrogen in these systems as being “chemically precompressed,” and we now examine this possibility in detail, along the way predicting the metallization pressure of SiH₄ and estimating the key quantities associated with the critical superconducting temperature (T_c) of metallic SiH₄. Indeed, as our study will show, in contrast to pure hydrogen SiH₄ becomes metallic close to 91 GPa. It is also expected to be a potential candidate for high- T_c superconductivity because of the high dynamical scale of the protons and the rather rapid stiffening of phonon modes with pressure.

Structures.—Since the crystal structure of solid SiH₄ is not known at high pressures, we have considered a total of 13 quite different structures in our theoretical study [9], in order to survey a range of possible coordination and packing modes. Our calculations indicate that, among these, the most important structures (judged by the ground-state enthalpy at 0 K, and in the 0–160 GPa pressure range) include (a) tetrahedrally H-coordinated Si atoms with bcc, simple cubic, and fcc packings [**T1**, **T2**, and **T3**, respectively, in Fig. 1(a)]; (b) “1D” chains of edge-sharing SiH₆ octahedra (structure **O1**), or quasi-2D sheets of corner-sharing SiH₆ octahedra (**O2** and **O3** in Fig. 1; (c) a bcc arrangement of Si atoms in cubic coordination (**M1** in Fig. 1(a)). Structure **T1** is, in fact, that of GeF₄ [10]. **O1** has 1D chains similar to those adopted by the CuF₄²⁻

sublattice of Na₂CuF₄ [11]. Structure **O2** is taken up by SnF₄ and PbF₄ [12,13], while **M1** has been observed for Hg₄Pt [14]. Six other structures, which were considered but did not emerge as enthalpically competitive, are shown and described in the auxiliary material to this Letter [9].

Theoretical methodology.—Ground-state enthalpies were obtained using density functional theory with the Perdew-Wang exchange-correlation functionals [15], a generalized gradient approximation with ultrasoft Vanderbilt-type pseudopotentials for Si and H [16] (only *s* and *p* electrons were included), the Blöchl’s projector-augmented wave method, and all implemented in the

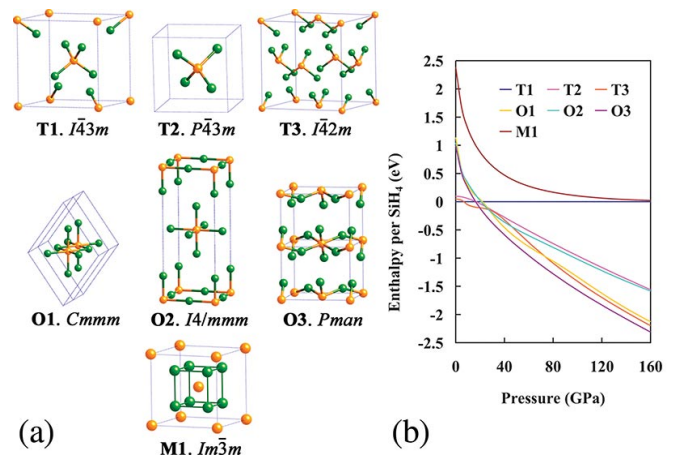


FIG. 1 (color). (a) The energetically most favorable structures computed for SiH₄ in the pressure range 0–160 GPa. The golden spheres are silicon atoms and green are hydrogen atoms. (b) Enthalpies per SiH₄ unit of the most important silane structures are plotted as functions of pressure. The enthalpies are referenced to that of **T1**. Observe for **O2** the SiH₂ planes resemble closely the CuO₂ planes in the high- T_c cuprate superconductors. A puckered variant of this square net occurs in **O3**, the most stable structure over a large pressure range under consideration.

VASP and CASTEP codes. For each structure we relaxed both cell parameters and atomic positions, while fixing the unit cell volume; we also determined the stress tensor. The electronic density of states (DOS) and band structure were subsequently calculated for the optimized unit cell. The \mathbf{k} -point grids for zone sampling were generated via the Monkhorst-Pack scheme [17]. For comparison of different structures, the number of divisions along each reciprocal lattice vector was chosen in such a way that the product of this number with corresponding real lattice constant was approximately equal to 50 \AA for each structure at zero pressure (VASP calculations). These numbers were fixed for each structure as pressures were increased. The \mathbf{k} -point sampling used by CASTEP at pressures 9–202 GPa was $17 \times 17 \times 21$ (structure **O1**), $17 \times 17 \times 8$ (structure **O2**), and $12 \times 15 \times 15$ (structure **O3**). We used a 450 eV cutoff of the kinetic energy of the plane waves and an self-consistent field tolerance of 2×10^{-6} eV/atom (CASTEP calculations) and 1×10^{-5} eV/unit cell for VASP.

Our calculations are formally for a ground state, with infinitely massive ions. Thus, the internal energy contains electronic contributions but no zero-point vibrational energy terms, or the coupling of electrons to the latter. In Fig. 1(b) we plot the calculated enthalpy per SiH_4 unit as a function of pressure (up to 160 GPa), for the seven structures shown in Fig. 1(a) (plots of internal energy vs pressure and enthalpy vs pressure for the structures scrutinized, 13 in all, up to 350 GPa, can be found in the auxiliary material [9]). The enthalpy has been computed using the total internal energy supplemented by the standard pV term. A summary of the results now follows:

The low pressure regime.—The lowest-enthalpy polymorphs of SiH_4 at zero pressure are those with tetrahedral coordination of Si (**T1**, **T2**, and **T3**). Not unexpectedly these are insulating molecular crystals of covalently bonded SiH_4 . There is a confluence of enthalpy curves, for both **T**- and **O**-type structures, at low pressures (around 20 GPa) for these structures, indicating that they will compete as pressure is applied. Phase transitions (including possible amorphous phases with freely rotating SiH_4 molecules) are very likely to occur in this pressure regime.

Higher pressure, higher coordination.—As pressure is applied, a large volume reduction is expected for the molecular crystals, and this is found; the shallow van der Waals intermolecular well is quite easily overcome. Subsequently, as the filled orbitals of adjacent molecules begin to really overlap and the existing Si-H bonds are compressed, squeezing becomes increasingly difficult.

In molecular chemistry, silicon easily goes to fivefold or sixfold coordination, so an analogous extended transformation under pressure makes chemical sense. As the pressure is increased above 25 GPa, structures with sixfold coordination for Si atoms, **O1**, **O2**, or **O3**, indeed take over. Structures **O1** and **O3** are computed to remain very close in enthalpy up to a pressure of about 160 GPa. In the pressure range from 25 to 50 GPa **T3** becomes less stable compared

to the sixfold-coordinate **O1** and **O3** structures. However, as the pressure is further increased (above 70 GPa), **T3** reemerges as enthalpically competitive. As will be clear shortly, this phase no longer contains fourfold-coordinate Si, but is eightfold coordinated in this high pressure regime. It is possible that the molecular SiH_4 structures make a transition to the 1D chain phase (**O1**) when the pressure is above 25 GPa, at which point **O1** is already a metal (the metallization of 1D chain structure occurs at 20 GPa). The volume reduction during this phase transition is about -13% ; an analogous phase transition (-16%) has been observed for methane at 301 GPa [18].

The H-H separations in these structures can become quite short. Figures 2(a) and 2(b) show the evolution of the **O1** structure: the chains of hollow octahedra formed by the hydrogens in **O1** change to edge-sharing tetrahedral cages of H atoms at 159 GPa, some H-H separations as

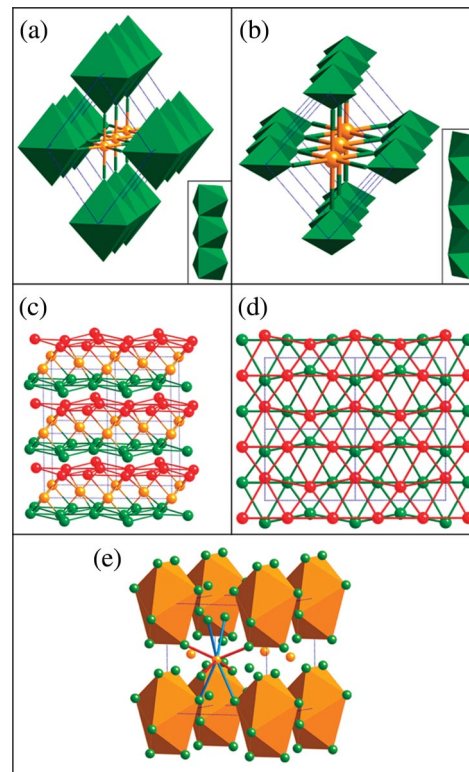


FIG. 2 (color). Structural and dimensional features of **O1**, **O3** and **T3** under pressure. (a) The structure of **O1** at 0 GPa viewed a little off the $[001]$ direction. H atoms from different adjacent unit cells form octahedral cages, shown in green. In the inset is the chain of octahedra viewed from the side. (b) **O1** at 159 GPa. At this pressure, the chains of octahedra become so distorted that they are best seen as chains of tetrahedra. (c) and (d) show the structure of **O3** at 150 GPa. The red and green spheres are the H atoms, and golden spheres are Si atoms. It is clear in (c) (viewed from the $[100]$ direction) that the H atoms form slightly puckered 2-dimensional sheets. Shown in (d) is a view of **O3** along the c direction with only two sheets (red and green) formed by H atoms. (e) The dodecahedral coordination around Si atoms for the **T3** structure at 144 GPa. Golden dodecahedra are shown for the eight silicons on the corners of the unit cell.

small as 1.31 Å. At $p = 150$ GPa in **O3**, there are strong interactions between the layers of corner-sharing octahedra; see Figs. 2(c) and 2(d). At this pressure, the structure can be described as sheets of octahedrally coordinated Si atoms sandwiched between layers formed by H double sheets. The shortest H-H contact is 1.38 Å, occurring between two sheets. As expected, there is strong interaction between quasi-two-dimensional sheets and an increase in electronic dimensionality at high pressures [9].

Higher coordination of Si is also a factor that makes the **T3** structure energetically competitive at elevated pressures. Under pressure, four additional H's from neighboring SiH_4 units move into the coordination shell of Si, making every Si effectively eight coordinate by 90 GPa. The polyhedron formed by the first coordination shell of Si is a classical one for eight coordination in molecules, a D_{2d} dodecahedron [19]. The structure of **T3** at 144 GPa is depicted in Fig. 2(e), where the dodecahedra are shown for the corner Si atoms and a ball-and-stick model is again used for one of the symmetry-equivalent Si atoms. The eight hydrogen neighbors of one Si make up two interpenetrating, distorted (nonidentical) tetrahedra, indicated by blue and red bonds in Fig. 2(e). These structural features persist to higher pressure.

Metallization and the Goldhammer-Herzfeld criterion.—In Fig. 3 we show the computed electronic band gap of SiH_4 (for structures **T1**, **T2**, **T3**, **O1**, **O2**, and **O3**) as a function of the radius of the free-electron sphere, r_s . Here, r_s is given by the usual definition [20]: $4\pi r_s^3/3 = 1/n$, where n is the average density of valence electrons.

As expected, on compression the band gaps generally decrease. Indeed, for all the structures shown the electronic band gaps close when r_s is in the range from 0.80 to 0.95 Å. These values are close to the theoretical value of $r_s \approx 0.88$ Å, derived on the basis of the Goldhammer-Herzfeld metallization criterion for cubic systems [9,21].

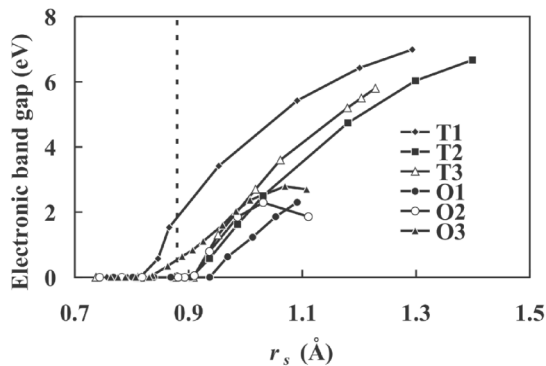


FIG. 3. The band gaps are shown as functions of the radii of a free-electron sphere for structures **T1**, **T2**, **O1**, **O2**, and **O3**. Structure **O3** is computed to be the lowest-enthalpy structure in the 25–160 GPa regime, which should become metallic at $r_s = 0.83$ Å. The dotted line indicates the theoretical r_s at the metallization onset (0.88 Å) predicted based on the Goldhammer-Herzfeld criterion, where a polarizability of 5.44 \AA^3 for free SiH_4 is assumed [21].

Alternative structures that contain highly coordinated Si (**M1**, **M2**, **M3**, and **M4**, [9]) are computed to be metallic even at ambient pressure. In accord with chemical intuition, they cannot compete energetically at low pressure; nevertheless, some of them may be relevant at pressures exceeding 185 GPa.

Electronic dimensionality.—Given that the metallization of silane is predicted to take place for a layered structure [**O3** in Fig. 1(a)], we looked at the electronic dimensionality of this structure by examining plots of the electron density at the Fermi level [9]. At the onset of band overlap (**O3** at 91 GPa) the state may be described as a layered semimetal; the layers composed of terminal H atoms (protruding from the $[\text{SiH}_2]_n$ sheet) are responsible for the low density of states at Fermi level (N_F), which amounts to just $2.1 \times 10^{-6} \text{ eV}^{-1}/\text{electron}$. The N_F value then rises sharply with pressure. At 202 GPa ($r_s/a_0 = 1.44$) the contributions from bridging H and the s and p states of Si (which are strongly mixed at all energies) increase. N_F at 202 GPa attains a value of $2.5 \times 10^{-2} \text{ eV}^{-1}/\text{electron}$, which is already 40% of its nearly free-electron value ($6.2 \times 10^{-2} \text{ eV}^{-1}/\text{electron}$). This is quite high, in comparison, for example, with Pb, whose average electron density is just 25% of that of **O3** at 202 GPa. The conductivity tensor of **O3** SiH_4 at 202 GPa (now orders of magnitude larger) still preserves its 2D character. The conductivity should then be strongly anisotropic, with a very small component along the crystallographic c axis (the van der Waals “gap”).

Superconductivity.—Accurate predictions of superconducting transition temperatures are difficult. In order to derive a first estimate of T_c we have simply used a BCS approach [22]. We examined the phonons (at the zone center) of several of the metallic forms of SiH_4 (**O1**, **O2**, and **O3**), at the onsets of metallization and at higher compression [9].

For structure **O3**, favored in the enthalpy landscape at pressures beyond 25 GPa, the calculated cutoff energy of the phonon spectrum is 2435 cm^{-1} (302 meV) at 91 GPa, 2538 cm^{-1} (315 meV) at 150 GPa, and 2588 cm^{-1} (321 meV) at 202 GPa. The quasi-2D appearance of the metallic form of SiH_4 of **O3** [9] suggests that the motion of terminal H atoms parallel to the puckered $[\text{SiH}_2]$ plane (i.e., the $\text{Si-H}_{\text{term}}$ deformation mode at ca. 167–178 meV) should have the greatest influence on pairing of mobile charge carriers at the onset of metallization. For **O2**, the motions of H atoms in the SiH_2 plane corresponding to stretching of the Si-H bonds (E_u phonon mode, at 2272 cm^{-1} at 56 GPa) should have the largest influence on the pairing of mobile charge carriers. For the subsequent estimates of T_c we will neglect variable coupling strengths for different phonons and will simply use the cutoff phonon energy.

T_c estimates can be obtained by assuming that metallized silane at 91 GPa behaves as a typical metal that conforms to the BCS theory (in the weak coupling limit) [9]. Typically, the $N_F V$ product is 0.25 for Sn, 0.30 for In,

and 0.39 for Pb [23,24]. The density of states *per volume* [9] for structure **O2** at 115 GPa, for **O1** at 108 GPa, and for **O3** at 202 GPa, is of the same characteristic scale as that calculated for Pb in its experimental structure under ambient pressure. To illuminate the important role of dynamics, principally reflected in the light mass of the proton (as revealed in the Debye temperature), we have taken V to be typical of lead. We note, however, the increasingly favorable role played by umklapp processes in metallic SiH₄, these arising from the large number of electrons (at least 8) per unit cell.

The calculated Debye temperature of silane is superior by 2 orders of magnitude to that for Pb [9], a classical strong-coupling superconductor with a T_c of 7.2 K ($\Theta_D = 89$ K [25]). Indeed, the estimated value of T_c for the most stable structure **O3**, rises steeply with pressure, from ~ 0 K at the metallization onset (91 GPa) up to 166 K at 202 GPa (5.3-fold compression). Two factors contribute to this dramatic increase in T_c . As a result of increased band overlap through compression, the density of states at the Fermi level [9] increases dramatically with pressure. The stiffening of phonon modes also has a role, though to a lesser extent.

In view of the well-known shortcomings of density functional theory, in that it tends to underestimate band gaps, even if gradient corrections are introduced [26], we think that the metallization pressure of SiH₄ is likely to be larger than the value of $p_{\text{met}} = 91$ GPa estimated here. Nevertheless, as hydrogen continues to remain a reluctant alkali [27], and since CH₄ has so far not been metallized at pressures up to 301 GPa [17,28], SiH₄ offers an attractive possibility for a hydrogen-rich high- T_c superconductor at accessible pressures [29].

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 [29] Unlike CH₄, SiH₄ is thermodynamically unstable [with respect to decomposition into Si(s) and H₂(g)], yet kinetically persistent. Decomposition of SiH₄ might yield SiH₂(s) (structure not yet known), as divalent Si species are quite stable. Lack of thermodynamic stability contributes to the ease of metallizing silane; but it may also cause technical problems, due to possible hydrogenation of the diamond surface in the diamond anvil cell. Care is advised in analyzing the spectra of compressed silane, as the SiH₂ by-product might metallize at much smaller pressures than SiH₄.