Layered Structures Favor Superconductivity in Compressed Solid SiH$_4$

X. J. Chen$^{1,2,3}$, J. L. Wang$^1$, V. V. Struzhkin$^2$, H. K. Mao$^2$, R. J. Hemley$^2$, and H. Q. Lin$^1$

$^1$Department of Physics and Institute of Theoretical Physics, Chinese University of Hong Kong, Hong Kong, China
$^2$Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA
$^3$School of Physics, South China University of Technology, Guangzhou 510640, China

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The electronic and lattice dynamical properties of compressed solid SiH$_4$ have been calculated in the pressure range up to 300 GPa with density functional theory. We find that structures having a layered network with eight-fold SiH$_8$ coordination favor metallization and superconductivity. SiH$_4$ in these layered structures is predicted to have superconducting transition temperatures ranging from 20 to 80 K, thus presenting new possibilities for exploring high temperature superconductivity in this hydrogen-rich system.

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SiH$_4$ offers a source for high purity silicon in epitaxial and thin film deposition which is at the base of electronics and microdevices. There is ongoing interest in this material as well due to the suggestion of Ashcroft [1] that SiH$_4$ would eventually undergo a transition to metallic and then a superconducting state at pressures considerably lower than may be necessary for solid hydrogen. Exploring the possibility of metallic hydrogen has long been a major driving force in high-pressure condensed matter science and remains an important challenge in modern physics and astrophysics. Recent experimental work on SiH$_4$, using diamond-anvil cell techniques, has revealed an enhanced reflectivity with increasing pressure [2, 3]. It was found [3] that solid SiH$_4$ becomes opaque at 27-30 GPa and exhibits Drude-like behavior at around 60 GPa, signalling the onset of pressure-induced metallization. Structural information is the primary step toward understanding these observed electronic properties.

SiH$_4$ has a rich phase diagram with at least seven known phases [4-6]. Only one solid phase has been reported in the pressure range of 10 and 25 GPa and at room temperature, with a monoclinic structure (Space group P2$_1$/c) [4]. The very low hydrogen scattering cross section of hydrogen-containing materials in all diffraction methods makes structural determination very difficult, specifically in determining the H positions. Although the neutron diffraction is powerful in detecting the H-bonding structures, the current accessible pressure range of this technique is limited to 30 GPa [7]. Therefore it is still impossible to use neutron diffraction to obtain the interesting structural information of SiH$_4$ in the metallic state. The challenge of experimentally or theoretically determining the high-pressure structures of SiH$_4$ is still enormous.

The sequence of SiH$_4$ structures provides the basis for understanding whether the material is a favorable candidate of a high temperature superconductor. For a metallic $Pmmn$ SiH$_4$ phase, Feng et al. [8] obtained a superconducting transition temperature $T_c$ of 166 K at 202 GPa by using the electron-phonon coupling strength for lead under ambient pressure as both materials have the same characteristic density of states per volume at relevant pressures. Pickard and Needs [9] also studied the structural properties of SiH$_4$ and mentioned the possibility of superconductivity in a C2/$c$ phase. All previous work [6, 8, 9] was done without including the calculations of the phonon spectra and electron-phonon coupling parameters. Later phonon calculations by Yao et al. [10] showed that the $Pmna$ structure is in reality not stable and that a new C2/$c$ structure is dynamically stable from 65 to 150 GPa. This C2/$c$ SiH$_4$ phase was predicted to exhibit superconductivity close to 50 K at 125 GPa [10]. It is not known whether there exists a common structural feature that favors superconductivity in metallic SiH$_4$, and no study on superconductivity with other stable structures has been attempted.

In this Letter we report a theoretical study of superconductivity in compressed solid SiH$_4$ including structural, electronic, and vibrational calculations. We find six energetically favorable structures in which the $I\bar{T}$, Cmca, and C2/$c$ structures have layered networks with eight-fold SiH$_8$ coordination. This layered feature favors metallization and superconductivity. The layered phases are predicted to have $T_c$’s in the range of 20 and 80 K, suggesting that SiH$_4$ is indeed a good candidate for high-temperature superconductivity.

To study the structural and electronic behavior of SiH$_4$ over a wide range of pressure, we used the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) density functional and projector augmented wave method as implemented in the Vienna ab initio simulation package (VASP) [12]. An energy cutoff of 450 eV is used for the plane wave basis sets, and 16×16×16 and 8×8×8 Monkhorst-Pack $k$-point grids are used for Brillouin zone sampling of two SiH$_4$ molecular cells and four SiH$_4$ molecular cells, respectively. The lattice dynamical and superconducting properties were calculated by the Quantum-Espresso package [12] using Vanderbilt-type ultrasoft potentials with a cut-off energy of 25 Ry and 200 Ry for the wave functions and the charge density, respectively. 12×12×12 Monkhorst-Pack $k$-point grids with Gaussian smearing of 0.02 Ry were used for the phonon calcula-
We performed a systematic study of the phase stability of SiH$_4$ based on $ab$ initio first-principles calculations. Out of more than one hundred structures we studied, six new polymorphs of SiH$_4$ with low enthalpies are found in the pressure range from 0 to 300 GPa. In Fig. 1 we plot the pressure dependence of their enthalpies along with the results for the $C2/c$ and $I4_1/a$ structure reported previously [9]. A monoclinic structure with $P2_1/c$ symmetry has the lowest enthalpy below 27 GPa, in good agreement with the recent experiments [6]. The $P2_1/c$ structure consists of four isolated covalently bonded SiH$_4$ tetrahedra with the H atom of one molecule pointing away from the H atoms of a neighboring molecule. We find that a face-centered orthorhombic structure with $Fd2$ symmetry appears stable from 27 to 60 GPa. These two phases are insulating.

Near 50 GPa, there are three other competitive, low-enthalpy structures with the $C2/c$, $I4_1/amd$, and $I4_1/a$ symmetry. Our $C2/c$ structure was based on the UI$_4$ arrangement, which as exhibits a layered structure. However, the $C2/c$ structure predicted by Pickard and Needs [9] forms three-dimensional networks at high pressures. For clarification, we name their structure as $C2/c$(3D) and our layered structure as $C2/c$(2D). There are subtle differences in band structures between the $C2/c$ predicted by Yao et al. [10] and our $C2/c$(2D). Our $C2/c$(2D) structure is composed of six-fold coordinated SiH$_6$ octahedra inside a layer, but Si-H bonding between different layers is absent. It is still dynamically stable up to 250 GPa. However, the stability of the $C2/c$ phase of Yao et al. [10] is only stable up to 150 GPa. On compression, the six-fold coordinated SiH$_6$ octahedra are transformed into eight-fold coordinated SiH$_8$ dodecahedra with a S$_2$H$_2$ bridge-like bonding arrangement within the layer. Above 110 GPa, the $C2/c$(2D) structure becomes metallic. The $I4_1/amd$ SiH$_4$ phase is composed of eight-fold coordinated SiH$_8$ dodecahedra and every Si atom shares two H atoms with other Si atoms, as in the $I4_1/a$ structure. The $I4_1/amd$-type SiH$_4$ is a semimetal between 40 and 70 GPa.

The $I4_1/a$ structure was found to have the lowest enthalpy over a wide pressure range (60 to 220 GPa), consistent with previous calculations [9]. In an early powder x-ray diffraction study [14], $I4_1/a$ was considered as one of the most plausible structures for the low-temperature phase II. Raman measurements [3] indicate that this structure
FIG. 3: (color online) (a) Electronic band structure for the \textit{Cmca} SiH$_4$ phase at 250 GPa. The horizontal line shows the location of the Fermi level. (b) The phonon dispersion and phonon density of states (PDOS) projected on Si and H atoms for \textit{Cmca} SiH$_4$ at 250 GPa.

may not exist for SiH$_4$ under high pressure and at room temperature. SiH$_4$ in the \textit{I4$_1$/a} structure is believed to be stable only at low temperature. Between 220-270 GPa, a metallic \textit{Cmca} structure has the lowest enthalpy. Upon further compression, the \textit{C2/c(3D)} phase possesses the lowest enthalpy between 270-300 GPa, which confirms the previous calculations \cite{9}. The \textit{Cmca} phase is also a layered structure that consists of eight-fold coordinated SiH$_8$ dodecahedra. In each layer, the Si-H bonding arrangement is the same as that in the \textit{I4$_1$/a} structure. Thus, the \textit{Cmca} phase can be viewed as the two-dimensional analogue of the \textit{I4$_1$/a} phase.

In the 60 to 100 GPa range, we found a metallic triclinic structure with \textit{P1} space group with eight-fold SiH$_8$ coordination. It has almost the same enthalpy as the \textit{Cmca} structure between 60 and 100 GPa. Both of their enthalpies are within 0.25 eV of the insulating \textit{I4$_1$/a} structure. As pressure is increased, the \textit{P1} structure transforms gradually into the \textit{Cmca} structure. It is instructive to note that the \textit{P1} and \textit{Cmca} phases are metallic over the pressure regime between 60 GPa and 270 GPa, which is in a good agreement with recent experiments \cite{3}. Although the insulating \textit{I4$_1$/a} phase has the lowest enthalpy between 60 and 220 GPa, both \textit{P1} and \textit{Cmca} are good candidates for metallic phases in this regime. We thus obtain six energetically favorable structures for SiH$_4$ at high pressures. The atomic arrangements for each of these structures is shown in Fig. 2. The \textit{P1}, \textit{Cmca}, and \textit{C2/c(2D)} phases have layered structures and are metallic.

Figure 3(a) shows the calculated band structure for \textit{Cmca} SiH$_4$ at 250 GPa. It can be seen that the \textit{Cmca} structure is metallic. The valence bands cross the Fermi level \(E_F\) along the YΓ direction, while the conduction bands cross \(E_F\) near the Γ point. Upon compression, the conduction band crossing \(E_F\) at the Γ point shifts lower in energy, while the valence band across \(E_F\) along the YT direction only moves up slightly in energy. The net effect of the pressure-induced band shifts is to increase the volume of the Fermi surface and the phase space for the electron-phonon interaction.

The structural stability of each SiH$_4$ phase has been examined through lattice dynamics calculations. The typical results of the phonon dispersion and projected phonon density of states for the \textit{Cmca} SiH$_4$ at 250 GPa are displayed in Fig. 3(b). The \textit{Cmca} stability is con-
firmed by the absence of imaginary frequency modes. There are weak interactions between the Si framework and H atoms over the whole frequency range. The heavy Si atoms dominate the low-frequency vibrations, and the light H atoms contribute significantly to the high-frequency modes. Three separate regions of bands can be recognized. The modes for the frequencies below 750 cm$^{-1}$ are mainly due to the motions of Si. The bands around 200 cm$^{-1}$ are caused by acoustic phonons. The Si-H-Si bending vibrations dominate the intermediate-frequency region between 750 and 1200 cm$^{-1}$. At high frequencies above 1200 cm$^{-1}$, the phonon spectrum belongs to the Si-H bond stretching vibrations.

The electron-phonon spectral function $\alpha^2 F(\omega)$ is essential in determining the electron-phonon coupling strength $\lambda$ and logarithmic average phonon frequency $\omega_{\log}$. We have calculated $\alpha^2 F(\omega)$ for the metallic SiH$_4$ phases in the pressure range of interest. Figure 4 shows the results for the $Cmca$, $C2/c$ (2D) and $C2/c$ (3D) structures over the pressure range from 70 to 300 GPa. Below 600 cm$^{-1}$ the major contributions to $\alpha^2 F(\omega)$ come from the phonon modes involving Si-Si vibrations, and the remaining part of the electron-phonon coupling is mainly due to the phonon modes involving H-H vibrations. The $\alpha^2 F(\omega)$ on the wide high-energy side is significantly higher than that on the narrow low-energy side. Thus the high-energy H-H vibrations dominate the total $\lambda$ value. Among these metallic structures, the $C2/c$ (2D) phase at 250 GPa has a relatively large $\alpha^2 F(\omega)$ over the entire frequency range studied, resulting in a large $\lambda$.

We now examine whether superconductivity in metallic SiH$_4$ is possible, using the $T_c$ equation derived by Allen-Dynes [13]. In the calculations, we took the Coulomb pseudopotential $\mu^*$ to be 0.1 which was found to reproduce $T_c$ in MgB$_2$ [16]. Figure 5 shows the pressure dependence of $\omega_{\log}$, $\lambda$, and $T_c$ for SiH$_4$ with the metallic $Cmca$, $C2/c$ (2D) and $C2/c$ (3D) structures. The calculated $\omega_{\log}$ decreases [increases] with pressure for the $C2/c$ (2D) [$C2/c$ (3D)] structure. However, $\lambda$ changes with pressure in an opposite sense to $\omega_{\log}$ for both structures. For the $Cmca$ structure, both $\omega_{\log}$ and $\lambda$ do not show a monotonic pressure dependence. In these metallic phases studied, the variation of $T_c$ with pressure is found to resemble the $\lambda$ behavior. It is therefore indicated that the pressure effect on $T_c$ in SiH$_4$ is primarily controlled by $\lambda$. The $Cmca$ phase has a $T_c$ of 75 K even at 70 GPa. For the $C2/c$ (2D) phase, we calculate a relatively large $T_c$ as high as 80 K at 250 GPa. A decreasing $T_c$ from 47.7 K at 200 GPa to 26.1 K at 300 GPa is obtained for the $C2/c$ (3D) phase. The $P\bar{T}$ structure is also estimated to have a $T_c$ of 46.6 K at 70 GPa. The current results thus suggest new possibilities for exploring high temperature superconductivity in this hydrogen-rich system.

In summary, we have investigated the structural stability of silicon under pressure up to 300 GPa. The $P2_1/c$ phase is confirmed to be a good candidate for the low-pressure insulating phase. Between 27 and 60 GPa, $Fd\bar{d}2$ is predicted to be the structure of another insulating phase. At higher pressures, silicon enters the metallic state having a structure with $P\bar{T}$ symmetry. As pressure is further increased, the $P\bar{T}$ structure transforms gradually into the $Cmca$ structure. The three-dimensional $C2/c$ structure is most stable only after 270 GPa. The layered feature of this material favors metallization and superconductivity. The relatively high transition temperatures in metallic silicon are mainly attributed to the strong electron-phonon coupling due to the phonon modes involving H-H vibrations.

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