High pressure structures of disilane and their superconducting properties

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A systematic ab initio search for low enthalpy phases of disilane (Si$_2$H$_6$) at high pressures was performed based on the minima hopping method. We found a novel metallic phase of disilane with $C_{mcm}$ symmetry, which is enthalpically more favorable than the recently proposed structures of disilane up to 280 GPa, but revealing compositional instability below 190 GPa. The $C_{mcm}$ phase has a moderate electron-phonon coupling yielding a superconducting transition temperature $T_c$ of around 20 K at 100 GPa, decreasing to 13 K at 220 GPa. These values are an order of magnitude smaller than previously predicted $T_c$ for disilane, and cast strong doubts on the possibility of high-$T_c$ superconductivity in these systems as well as in other hydrogen-rich compounds under moderate pressure.

Superconductivity in elemental hydrogen was predicted by Ashcroft [1] already in 1968. More recently, and with the use of novel theoretical techniques [2, 3], the calculated $T_c$ was estimated to be as high as 240 K at pressures of around 450 GPa [4]. However, the synthesis of metallic hydrogen has been found to be experimentally challenging, and even at extremely high pressures (below 342 GPa) metallization has not yet been observed [5, 6]. This is in agreement with theoretical calculations, that predict the metallic transition above 400 GPa — a pressure beyond the reach of current experimental capabilities.

To circumvent this problem, it was recently suggested that metallization pressures could be achieved in hydrogen rich materials where the hydrogen is chemically “pre-compressed” [7]. Several investigations of such compounds have appeared in the literature, primarily focusing on group IV-hydrides. Calculations on phases of highly compressed silane [8–13], germane [14] and stannane [15, 16] have shown the possibility of metallic phases with high $T_c$ at moderate pressures. From the experimental point of view, silane SiH$_4$ has been reported to crystallize and attain metallicity above 50–60 GPa [17, 18] with a superconducting behavior. However, more recent studies ascribe the observed metallicity to the formation of metal hydrides [19], and metallization of silane was found not to occur at least below 130 GPa [20].

Another hydrogen rich compound of the same family is disilane Si$_2$H$_6$. This compound has attracted attention as a hydrogen rich material due to its experimental availability. Moreover, in a recent theoretical study, Jin et al. [21] performed random searches in order to find stable structures of disilane. They reported three different structures covering a pressure range from 50 to 400 GPa. Crystallization of disilane into a metallic phase with a $P$–1 lattice was predicted to occur at 135 GPa. The $T_c$ of this phase was predicted to be 64.6 K at 175 GPa, and 80.1 K at 200 GPa. Beyond 175 GPa, the lowest enthalpy phase becomes a cubic $Pm\bar{3}m$ structure that reaches the remarkable superconducting transition temperature of $T_c = 139$ K at 275 GPa, a $T_c$ much higher than any other predicted transition temperature of group IV-hydrides. Unfortunately, these results have not been experimentally confirmed.

In this letter, we report on our investigations of the disilane system under pressure by using the recently developed minima hopping method (MHM) [22, 23] for the prediction of low enthalpy structures. This method has been successfully used for global geometry optimization
in a large variety of applications [24–28]. Given only the chemical composition of a system, the MHM aims at finding the global minimum on the enthalpy surface, while gradually exploring low lying structures. Moves on the enthalpy surface are performed using variable cell shape molecular dynamics with initial velocities approximately chosen along soft mode directions. The relaxations to local minima are performed by the fast inertia relaxation engine (FIRE) [29] taking into account both atomic and cell degrees of freedom.

We performed simulations for cells containing 1, 2, and 3 formula units of disilane Si₂H₆ under several different pressures between 40–400 GPa. The initial sampling of the enthalpy minimum was carried out employing the MHM together with Lenosky’s tight-binding scheme [30], extended to include hydrogen. The most promising candidate structures found during the initial sampling were further studied [31, 32] at the density functional theory (DFT) level using the Perdew-Burke-Erzernhof (PBE) exchange-correlation functional [33] and norm-conserving HGH-pseudopotentials [34]. The plane-wave cut-off energy was set to 1400 eV, and carefully converged Monkhorst-Pack k-point meshes [35] with grid spacing denser than 2π × 0.025 Å were used. Finally, in order to confirm that the tight-binding scheme was able to sufficiently sample the enthalpy surfaces, we performed MHM simulations for selected pressures of 100 GPa, 200 GPa, 280 GPa, and 320 GPa at the DFT level.

In Fig. 2 the enthalpy of the different phases found in our MHM simulations are shown with respect to decomposition towards elemental silicon and hydrogen. At pressures above 280 GPa, the Pm–3m phase is favored, competing with several other structures reported by Jin et al. [21]. In addition to the structures reported in Ref. [21] our simulations revealed another low-lying phase with P–1 symmetry (Fig. 1b). However, all these structures lie in a very small energy range which is within our numerical precision. Furthermore, as seen in Fig. 2 crystalline disilane is enthalpically unstable towards decomposition to elemental silicon and hydrogen below 95 GPa. A decomposition to silane SiH₄ together with elemental silicon and hydrogen is enthalpically possible up to pressures of 190 GPa. This compositional instability could pose challenges en route to synthetization of crystalline disilane, depending on barrier heights and on the dynamics of the decomposition.

Yet another low-enthalpy metallic phase of disilane was found during our MHM simulations (see Fig. 1a). It belongs to the Cmcm space group, and is the lowest enthalpy structure up to 280 GPa. At 200 GPa, its conventional cell parameters are a = 7.965 Å, b = 2.705 Å, and c = 4.728 Å, with one silicon atom occupying the 8c crystallographic site at (0.141, 0, 0) and three hydrogen atoms occupying 8g, 8g and 8f sites at coordinates (0.293, 0.173, 0.250), (0.086, 0.302, 0.250) and (0, 0.311, 0.895), respectively. The hydrogen atoms are embedded into a framework of five-fold coordinated silicon atoms. The average silicon-silicon bond length is 2.28 Å, and each silicon atom is surrounded by six hydrogen atoms at a mean distance of 1.52 Å.

We further characterized the Cmcm structure by performing calculations of the phonon-spectrum, the electron-phonon coupling and the superconducting transition temperature Tc. The phonon spectrum and the electron-phonon matrix elements were obtained from density-functional perturbation theory [36]. The spectral function α²F(ω) was integrated over the Fermi surface by applying the tetrahedron technique. Convergence of the
The phonon band dispersion of the Cmcm phase at 200 GPa can be seen in the left panel of Fig. 3 while the partial phonon density of states is shown in the right panel. As expected, the low frequencies (<700 cm$^{-1}$) are dominated by the vibrations of the silicon framework whereas the high end of the spectrum extending up to 2300 cm$^{-1}$ is solely due to the light hydrogen atoms. We found the structure to be dynamically stable up to 220 GPa. However, if the pressure is increased beyond 225 GPa a dynamical instability arises. The phonon band dispersion at 230 GPa can be found in the Supplementary Material [40]. It shows an imaginary (plotted as negative) frequency at the Γ-point, indicating an unstable phonon mode. Following the eigendisplacements of this mode, we use McMillan’s approximation for the superconducting transition temperature $T_c$ [41, 42]. McMillan’s formula requires the Eliashberg spectral function $\alpha^2F(\omega)$, which was obtained from $ab\ initio$ calculations performed with the abinit code [31, 32]. In the right panel of Fig. 3 the solid lines represent the Eliashberg spectral function of the Cmcm phase at 200 GPa. It has three main features: (i) low optical modes of the silicon framework, (ii) two intense hydrogen peaks around 1500 cm$^{-1}$ and 1600 cm$^{-1}$, and (iii) high frequency modes of hydrogen around 2000 cm$^{-1}$.

The superconducting properties of the Cmcm phase at several pressures are summarized in Table I using two different values for the Coulomb pseudopotential $\mu^* = 0.1$ and $\mu^* = 0.13$. Assuming the larger of those values, the superconducting transition temperature $T_c$ is 20.1 K at 100 GPa and decreases to 13.0 K at 220 GPa. A decreasing $T_c$ with respect to increasing pressure is a general feature observed in hydrogen rich materials [17, 43, 44]. We should emphasize that the $T_c$ of the Cmcm phase is approximately one order of magnitude smaller than in previously reported structures, and that the Cmcm phase is the lowest enthalpy phase. This raises serious doubts if high-$T_c$ superconductivity will ever be achieved in silane materials under reasonable pressure.

The superconducting properties of the Cmcm phase are strongly linked to its electronic structure. In Fig. 4 the evolution of the Fermi surface is shown as a function of pressure. Three states cross the Fermi surface. The first (magenta) and the second (yellow) states cover an important portion of the Brillouin zone and remain nearly unaltered as the pressure increases, whereas the third (cyan) changes substantially. The contribution of this third state to the Fermi surface consists of spherical regions near the Γ-point. This band connects two main portions of the Fermi surface. Therefore, we can expected high superconducting values for low pressures; $\lambda = 0.84$ and $\omega_{\text{log}} = 480$ with a $T_c$ of 20 K at 100 GPa. However, as the volume of the structure decreases with increas-

| Pressure (GPa) | $\lambda$ | $\omega_{\text{log}}$ (cm$^{-1}$) | $T_c^*$ (K) | $T_c$ (K) |
|---------------|---------|-------------------------------|------------|---------|
| 100           | 0.84    | 478                           | 24.5       | 20.1    |
| 140           | 0.80    | 553                           | 18.0       | 13.0    |
| 160           | 0.66    | 556                           | 16.9       | 12.8    |
| 200           | 0.68    | 501                           | 16.4       | 12.4    |
| 220           | 0.76    | 384                           | 16.4       | 13.0    |

TABLE I. Superconducting properties of the Cmcm phase at different pressures. The transition temperatures were calculated using McMillan’s formula.
ing pressure, this sphere-like feature of the Fermi surface is abruptly reduced. Consequently, at 160 GPa the superconducting parameters clearly decrease; $\lambda = 0.66$, $\omega_{\text{log}} = 556$ and $T_c = 12.4$ K.

In conclusion, we performed a thorough investigation of the high pressure phases of disilane using first principles calculations. Applying our minima hopping method to explore the potential energy surface of disilane, we found a metallic structure which is enthalpically favorable compared to the previously proposed structures of disilane. Additionally, the systematic study of the superconducting properties as a function of pressure shows that the $Cmcm$ phase possesses a moderate electron-phonon coupling, leading to a superconducting transition temperature in the 10–20 K range. This result stands in sharp contrast with the structures previously proposed of disilane under pressure. Moreover, we observed that the transition temperature of the $Cmcm$ structure has the tendency to decrease monotonically with applied pressure (for $\mu^* = 0.1$), which can be understood by the shrinking of a part of the Fermi surface. This decrease of the $T_c$ is in agreement with most theoretical and experimental results of hydrogen rich materials, including silane \[17, 42, 44\]. Certainly, this does not imply that superconductivity in hydrogen rich materials is limited to relatively low values of $T_c$, but our results do impose strong constraints on the possibility of high-$T_c$ superconductors in silicon-hydrogen systems.

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