Crystal structure of the pressure-induced metallic phase of SiH₄ from ab initio theory

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Metallization of pure solid hydrogen is of great interest, not least because it could lead to high-temperature superconductivity, but it continues to be an elusive goal because of great experimental challenges. Hydrogen-rich materials, in particular, CH_4, SiH_4, and GeH_4, provide an opportunity to study related phenomena at experimentally achievable pressures, and they too are expected to be high-temperature superconductors. Recently, the emergence of a metallic phase has been observed in silane for pressures just above 60 GPa. However, some uncertainty exists about the crystal structure of the discovered metallic phase. Here, we show by way of elimination, that a single structure that possesses all of the required characteristics of the experimentally observed metallic phase of silane from a pool of plausible candidates can be identified. Our density functional theory and GW calculations show that a structure with space group *P4/nbm* is metallic at pressures >60 GPa. Based on phonon calculations, we furthermore demonstrate that the *P4/nbm* structure is dynamically stable at >43 GPa and becomes the ground state at 97 GPa when zero-point energy contributions are considered. These findings could lead the way for further theoretical analysis of metallic phases of hydrogen-rich materials and stimulate experimental studies.

hydrogen-rich | metallization

High-pressure experiments on hydrogen-rich materials such as CH_4, SiH_4, and GeH_4 represent a model for study of metallic hydrogen (1) because enormous technical difficulties still prevent the achievement of metallization in pure solid hydrogen (2, 3). In these hydrogen-rich materials, chemical pressure leads to a collapse of the hydrogen network, which is predicted to induce metallization and even superconductivity (1).

Recently, it has been observed from infrared-reflectivity measurements in silane (SiH_4) at room temperature that the reflectivity increases at 60 GPa, pointing toward the existence of a Drude-like metallic phase (4). In the subsequent experiments (5), the transition from insulating molecular solid to metallic state was confirmed for even lower pressures of 50 GPa. Furthermore, the critical temperature for superconductivity was determined at 96 GPa and 120 GPa as $T_c = 17$ K. Based on X-ray diffraction measurements, the hexagonal $P6_3$ space group was suggested for this phase. Precise positions could only be deduced with certainty for silicon atoms, because the assignment of hydrogen sites is almost not possible from the X-ray data.

Before these experimental findings, several theoretical studies were carried out on the subject of metallic silane. Feng *et al.* (6) suggested the existence of a semimetallic phase with the *Pmna* structure at 91 GPa, which becomes superconducting at higher pressure. However, it is important to note that the authors stated that a correction for the band gap would shift the transition toward higher pressure. Another theoretical article (7) focused on a comparison of the enthalpies of random atomic configurations and determined several phases that possess lower enthalpies than that of the *Pmna* structure. In particular, the insulating phase having the

$I4_1/a$ structure was found to have the lowest enthalpy among the tested structures in the pressure range of 50–200 GPa, which has become the accepted ground state of silane in this pressure regime assured by many researchers. Interestingly, in the work above (7), it was also predicted that at >260 GPa, a metallic phase having *C2/c* symmetry becomes stabilized; we refer to this structure in the following as *C2/c* (1). A different structure also belonging to the *C2/c* space group was introduced as a potential metallic phase for pressures <150 GPa (12); for distinction, this structure is referred to as *C2/c* (2) in the following. Even though the *C2/c* (2) structure could not be stabilized against the $I4_1/a$ structure when solely comparing enthalpies, the calculated zero-point energy correction leads to a reduction of the energy difference by 0.068 eV/f.u. at 150 GPa (12).

Despite two successive experimental findings of metallic silane at <100 GPa (4, 5), theoretical predictions have focused mainly on pressure regimes >150 GPa. Because hydrogen contributes considerable zero-point energy to the system, it is essential to include zero-point corrections in any enthalpy comparison of different phases (8). Even if we assume that the $I4_1/a$ structure is indeed the ground state <100 GPa, there remains the possibility for a dynamically stabilized phase to appear as a metastable one, which is a common phenomenon observed in materials under high pressure (9–12).

Here, we present a systematic theoretical approach to determine the structure of a metallic phase of silane for pressure <100 GPa. For a large pool of suggested space groups, we performed a series of tests to eliminate candidates that do not meet criteria that the correct metallic phase of silane should fulfill. Because of the well-known shortcoming of standard density functional theory (DFT) for underestimating the band gap, we can safely discard any phase that is found to be nonmetallic from DFT. Phonon calculations can provide a critical assessment of the dynamical stability in a given system, whereas zero-point energy corrections to the enthalpy can be decisive when it comes to small differences in enthalpy. Finally, the GW correction yields a reliable band structure of any candidate structure to ensure that it is indeed metallic.

In the present study, we have used DFT (further details are presented in *Methods*) to solve the electronic Schrödinger equation. It has recently been noted (13) that the high-pressure phases of solid hydrogen can be treated by using DFT (8). Specifically for silane, recent computational investigations have successfully used the DFT method (6, 7, 12). In one particularly

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