

# High-pressure crystal structures and superconductivity of Stannane (SnH<sub>4</sub>)

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There is great interest in the exploration of hydrogen-rich compounds upon strong compression where they can become superconductors. Stannane (SnH<sub>4</sub>) has been proposed to be a potential high-temperature superconductor under pressure, but its high-pressure crystal structures, fundamental for the understanding of superconductivity, remain unsolved. Using an *ab initio* evolutionary algorithm for crystal structure prediction, we propose the existence of two unique high-pressure metallic phases having space groups *Ama2* and *P6<sub>3</sub>/mmc*, which both contain hexagonal layers of Sn atoms and semimolecular (perhydride) H<sub>2</sub> units. Enthalpy calculations reveal that the *Ama2* and *P6<sub>3</sub>/mmc* structures are stable at 96–180 GPa and above 180 GPa, respectively, while below 96 GPa SnH<sub>4</sub> is unstable with respect to elemental decomposition. The application of the Allen-Dynes modified McMillan equation reveals high superconducting temperatures of 15–22 K for the *Ama2* phase at 120 GPa and 52–62 K for the *P6<sub>3</sub>/mmc* phase at 200 GPa.

hydrogen-rich compounds | metallization | electron-phonon coupling

Relatively high-temperature superconductivity is now documented in light-element metals such as Li under pressure (1–3) and MgB<sub>2</sub> (4), where transition temperatures  $T_c$  up to 20 K and 39 K, respectively, are observed. There is great interest in exploration of unique superconducting phases in other light-element materials because their high phonon frequencies can enhance electron-phonon coupling (see ref. 5). As the lightest element, hydrogen at very high densities is also predicted to be a superconductor with high transition temperatures (6–8). Experiments indicate that the predicted metallic and superconducting states of hydrogen remain above ~300 GPa (9–11). It has been proposed that hydrogen-rich compounds (e.g., group IVa hydrides (12)) are expected to metallize at pressures considerably lower than pure hydrogen due to the chemical “precompression” caused by heavier elements; these metallization pressures may fall within the range of current capabilities of static compression techniques. The exploration of potential superconductivity in these hydrogen-rich compounds (e.g., SiH<sub>4</sub>, GeH<sub>4</sub>, and SnH<sub>4</sub>) is thus desirable and numerous studies have been performed (13–25). Strikingly, recent experiments (15, 18) show that SiH<sub>4</sub> transforms to a metallic phase near 50–60 GPa with a superconducting  $T_c$  of 17 K at 96 and 120 GPa, though debate remains (26). We have recently predicted (17) that GeH<sub>4</sub> becomes a high-temperature superconductor with a  $T_c$  of 64 K at 220 GPa. A theoretical study of SnH<sub>4</sub> (21) predicts that its  $T_c$  can be even higher, reaching the value of 80 K. Using simulated annealing and geometry optimization, that study found that the high-pressure phase of SnH<sub>4</sub> has *P6/mmm* symmetry with a layered structure intercalated by molecular H<sub>2</sub> units, wherein the nearest H-H distance, 0.84 Å, is short enough to be considered as covalent bonding, but significantly longer than the 0.74 Å in the free H<sub>2</sub> molecule. This prediction of extremely high  $T_c$  is

fully dependent on the correctness of the structural model. Therefore, if some other structures are more stable, the picture of superconductivity in SnH<sub>4</sub> may be completely altered.

Here we undertake a different route to explore the high-pressure structures of SnH<sub>4</sub> and use our newly developed *ab initio* evolutionary simulation method (27–29) to address the above question. This method has proven its reliability and efficiency in predicting stable structures with knowledge only of the chemical composition (17, 30–36). We then performed the calculations on the total energy, band structure, phonons, and electron-phonon coupling of the predicted high-pressure structures. Our results reveal the appearance of unique chemistry of SnH<sub>4</sub> at high-pressure and suggest the high superconductivity of SnH<sub>4</sub> under pressures that are accessible by current experimental technique.

## Results and Discussion

We performed evolutionary variable-cell structure prediction simulations with one to four SnH<sub>4</sub> formula units per cell at 30, 70, 120, 200, and 250 GPa. Analysis of the predicted structures gave us a shortlist of candidate structures with space groups *Cmcm*\* (4 molecules/cell), *P2<sub>1</sub>/m*<sup>†</sup> (2 molecules/cell), *Ama2* (4 molecules/cell) and *P6<sub>3</sub>/mmc* (2 molecules/cell), respectively. In the *Cmcm* and *P2<sub>1</sub>/m* structures predicted at 30 and 70 GPa, the Sn atoms are packed in zigzag chains between which nonbonded H<sub>2</sub> molecules are located. This strongly indicates a tendency to decomposition into Sn + 2H<sub>2</sub>. Indeed, enthalpy calculations (Fig. 2) show that decomposition occurs below 96 GPa.

In the *Ama2* phase, Sn atoms form a simple hexagonal packing, where the trigonal prismatic holes are filled with semimolecular H<sub>2</sub> units (H-H distance 0.79 Å, which is longer than the 0.74 Å in the isolated H<sub>2</sub> molecule). The H<sub>2</sub> units are aligned either along the pseudohexagonal axis, or perpendicular to it, and these two orientations alternate (Fig. 1A). Note that the simple hexagonal structure is a high-pressure form of silicon (*P6/mmm*, ref. (37)), but it is not particularly dense. The *P6<sub>3</sub>/mmc* phase here is based on the much denser hexagonal close packing of the Sn atoms ( $c/a = 1.84$  at 200 GPa, relatively close to the ideal value of

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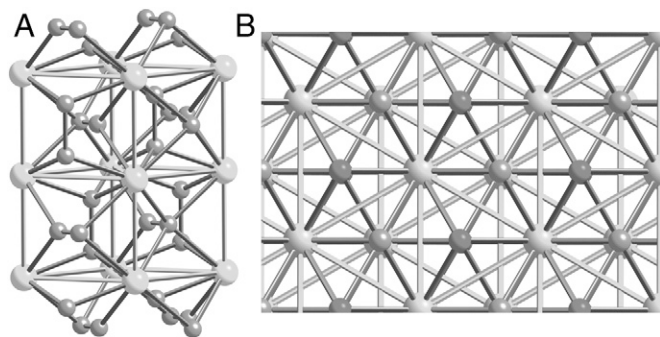
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\*For *Cmcm* structure at 20 GPa, the lattice parameters are  $a = 3.63$  Å,  $b = 9.88$  Å, and  $c = 4.12$  Å with atomic positions of Sn at  $4c$  (0, 0.29142, 0.25) and H at  $4c$  (0, 0.50191, 0.75), (0, 0.42112, 0.75) and  $8f$  (0.96117, 0.49332)

<sup>†</sup>For *P2<sub>1</sub>/m* structure at 70 GPa, the lattice parameters are  $a = 4.89$  Å,  $b = 3.17$  Å,  $c = 3.48$  Å and  $\beta = 89.19^\circ$ , with atomic positions of Sn at  $2e$  (0.64826, 0.25, 0.74596) and H at  $2e$  (0.92488, 0.25, 0.32702), (0.08651, 0.25, 0.38317), (0.02506, 0.25, 0.89266), and (0.18168, 0.25, 0.82398).

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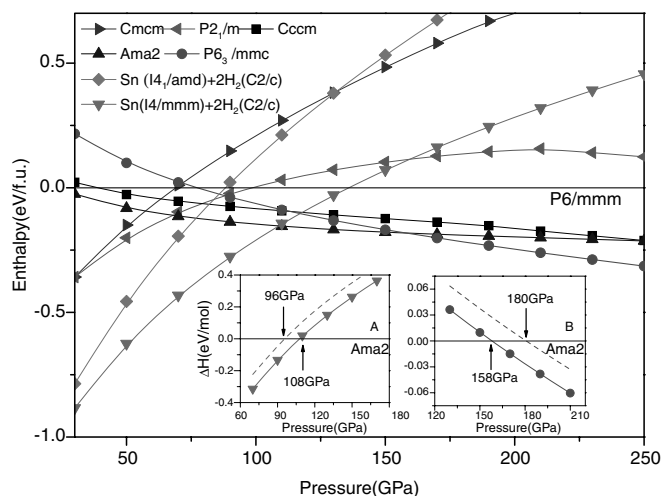


**Fig. 1.** (color online). (A) and (B) *Ama2* and *P6<sub>3</sub>/mmc* structures. For *Ama2* structure at 120 GPa, the lattice parameters are  $a = 5.381 \text{ \AA}$ ,  $b = 5.421 \text{ \AA}$ ,  $c = 3.074 \text{ \AA}$  with atomic positions of Sn at 4a (0, 0, 0.0001) and three inequivalent H atoms at 4b (0.75, 0.58823, 0.00586), 4b (0.75, 0.73278, 0.98835) and 8c (0.87773, 0.32159, 0.99613), For *P6<sub>3</sub>/mmc* structure at 200 GPa the lattice parameters are  $a = b = 2.9024 \text{ \AA}$ ,  $c = 5.3274 \text{ \AA}$ , and  $\gamma = 120^\circ$  with atomic positions of Sn at 2c (2/3, 1/3, 3/4) and H at 4e (0, 0, 0.92278) and 4f (1/3, 2/3, 0.57982), respectively. The large and small spheres represent Sn and H atoms, respectively.

1.63). In this structure, the ordered H atoms are clearly split into two categories. One sort forms semimolecular H<sub>2</sub> units (the magenta atoms in Fig. 1B) occupying hexagonal channels of the hexagonal close packing structure, whereas the other sort of H atoms occupies positions just below and above Sn atoms, forming chains Sn-H...H-Sn-H...H-Sn-H running along the c axis (Fig. 1B).

In both the *Ama2* and *P6<sub>3</sub>/mmc* phases Sn-H distances are about 1.8–1.9 Å, and Sn-Sn distances about 2.9 Å. The main differences are in the topology of the Sn framework and the relative proportion of the H<sub>2</sub> semimolecular units and monatomic hydrogen species. The transition *Ama2* → *P6<sub>3</sub>/mmc* is accompanied by a major electronic reorganization due to the appearance of monatomic hydrogen and the likely change of Sn valence. In the bond valence model the bond order is  $v_{ij} = \exp[-(R_{ij} - R_{0,ij})/b]$ , where  $R_0$  is a bond-specific parameter,  $R$  the bond length, and  $b$  a constant. Taking  $b = 0.25 \text{ \AA}$  (typical of strong covalent bonds (38)), we find that the H-H bond order in the H<sub>2</sub> semimolecular units is 0.82. Thus, hydrogen atoms in these H<sub>2</sub> units are underbonded and tend to acquire the missing electrons from the metal atoms by charge transfer. We propose to call these chemically active H<sub>2</sub> units perhydride groups; they have so far not been observed at ambient conditions, but predicted to exist at high pressures in GeH<sub>4</sub> (ref. 17) and unique lithium hydrides LiH<sub>2</sub>, LiH<sub>6</sub> and LiH<sub>8</sub> (39). Perhydride groups were also predicted in the structures of SnH<sub>4</sub> calculated in refs. 21 (*P6/mmm*) and 40 (*Cccm*), which are otherwise different from our structures. The need for charge transfer implies that perhydrides can only be formed with rather electropositive metals, such as Ge, Sn, and Li, but not Si or C. We believe that perhydrides of alkali and alkali earth metals are likely to exist and are worth exploring. Coming back to SnH<sub>4</sub> and using the estimated H-H bond order (0.82), we find that each Sn atom transfers to all four H atoms 0.72 e in the *Ama2* phase and 2.36 e in the *P6<sub>3</sub>/mmc* phase. The remaining valence is used for Sn-Sn bonds (~0.15 e per bond, and there are eight and 12 such bonds in the *Ama2* and *P6<sub>3</sub>/mmc* phases, respectively), leading us to propose the Sn(II) valence state in *Ama2* and Sn(IV) in *P6<sub>3</sub>/mmc*.

Enthalpy curves of our predicted structures as a function of pressure are presented in Fig. 2. It is noteworthy that the currently predicted structures are energetically much more favorable than the *P6/mmm* (21) and *Cccm* (40) structures. Considering the tendency to decomposition found in structure searches performed at low pressure, the enthalpy of the decomposition (Sn + 2H<sub>2</sub>, with structures of pure elements taken from refs. (41, 42) as a function of pressure) is also shown in Fig. 2. A wide



**Fig. 2.** (color online). Enthalpies per SnH<sub>4</sub> unit of various structures as a function of pressure, referenced to the *P6/mmm* phase (21). The decomposition (Sn + 2H<sub>2</sub>) enthalpies are calculated by adopting the C2/c (Ref. (41)) structure for H<sub>2</sub> and *Fd-3m*, *I4<sub>1</sub>/amd*, *I4/mmm*, and *Im-3m* (Ref. (42)) for Sn, respectively. Inset: (A) and (B) Enthalpy of decomposition (*I4/mmm*-Sn + 2C2/c-H<sub>2</sub>) and the *P6<sub>3</sub>/mmc* structure relative to the *Ama2* phase without (solid line and symbols) and with (dashed line) the zero-point motion corrections, respectively.

region of decomposition into Sn + 2H<sub>2</sub> is indeed confirmed below 108 GPa, above which *Ama2* becomes stable in the pressure of 108–158 GPa and then *P6<sub>3</sub>/mmc* structure takes over above 158 GPa. As divalent Sn(II) species are quite stable, decomposition of SnH<sub>4</sub> might also yield SnH<sub>2</sub>, the structure of which is unknown. We thus searched for the most stable high-pressure phases of SnH<sub>2</sub> at 50 and 100 GPa using the same evolutionary methodology. However, we found that SnH<sub>2</sub> + H<sub>2</sub> is 0.15 eV (0.17 eV) per SnH<sub>4</sub> unit higher in enthalpy than Sn + 2H<sub>2</sub> at 50 GPa (100 GPa). This eliminates the possibility that SnH<sub>4</sub> decomposes into SnH<sub>2</sub> + H<sub>2</sub>. One should keep in mind, however, the importance of dynamical effects stemming from the high vibrational frequencies of light hydrogen atoms, as can be seen from the phonon density of states (DOS) (Fig. 3B, D), which implies a large zero-point (ZP) energy. This has already been found to affect the relative stabilities of hydrogen and hydrides (14, 17, 41). Therefore, we estimated the ZP vibrational energies for C2/c H<sub>2</sub> (41), *I4/mmm* Sn (42), *Ama2* and *P6<sub>3</sub>/mmc* SnH<sub>4</sub> at 120 GPa using the quasi-harmonic approximation (43). It turns out that the inclusion of ZP effects does not change the topology of the phase diagram but extends the stability fields of the *Ama2* and *P6<sub>3</sub>/mmc* structures to be 96–180 GPa and above 180 GPa, respectively (insets of Fig. 2).

The calculated electronic band structures and DOS for the *Ama2* structure at 120 GPa (Fig. 3A) and *P6<sub>3</sub>/mmc* structure at 200 GPa (Fig. 3C) reveal that both phases are metallic. We found that the calculated valence bandwidths are very broad and show strong hybridization between the Sn and H orbitals. In particular, both H and Sn atoms participate in *common overlapping* bands, which is in agreement with previous theoretical prediction (12). Note that the *P6<sub>3</sub>/mmc* structure has less dispersive band structure and more bands crossing  $E_f$ , which lead to a larger electronic DOS ( $2.18 \times 10^{-2}$  states/eV/Å<sup>3</sup>) at the Fermi level  $N(E_f)$  than that ( $1.48 \times 10^{-2}$  states/eV/Å<sup>3</sup>) of the *Ama2* structure. This larger  $N(E_f)$  contributes to a higher  $T_c$ . The phonon DOS for *Ama2* SnH<sub>4</sub> at 120 GPa and *P6<sub>3</sub>/mmc* SnH<sub>4</sub> at 200 GPa are depicted in Fig. 3B, D, respectively. The absence of imaginary frequencies in the phonon DOS and phonon dispersion curves suggests that the *Ama2* and *P6<sub>3</sub>/mmc* structures are both dynamically stable. Three separate regions of phonon bands



and the two-component plasma state predicted for pure hydrogen, might also exist in these compounds.

## Materials and Methods

Ab initio evolutionary simulation for crystal structure prediction done with the Universal Structure Predictor: Evolutionary Xtallography code (27–29) searches for the structure possessing the lowest free energy at given Pressure-Temperature conditions and is capable of predicting the stable structure of a given compound for a given composition. The first generation of structures is produced randomly. Each subsequent generation is produced from 65% of the lowest-enthalpy structures of the preceding generation; in addition, the lowest-enthalpy structure always survived into the next generation. The variation operators used for producing offspring included heredity (65% structures), lattice mutation (20%), and atomic permutation (15%). The underlying structure relaxations were performed using density-functional theory (46, 47) within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) (48), as implemented in the Vienna Ab-initio Simulation Package code (49). The frozen core all-electron projector-augmented wave (50) method was adopted. The use of a plane-wave kinetic energy cutoff of 600 eV and dense  $k$ -point sampling were shown to give excellent convergence of the energy differences and stress tensors. EPC have been explored using the pseudopotential plane-wave method within the PBE-GGA, through the Quantum-*opEn* Source Package for Research in Electronic Structure, Simulation, and Optimization (ESPRESSO) package (51). Forces and stresses for the converged structures are optimized and checked

to be within the error between the VASP and Quantum-ESPRESSO code. Pseudopotentials for H and Sn were generated by a Troullier-Martins norm-conserving scheme (52) and tested by comparing the electronic band structures and phonon spectra with the results calculated from VASP code. In these calculations we used a kinetic energy cutoff of 50 Rydberg and a  $12 \times 12 \times 6$  Monkhorst-Pack (53)  $k$ -point grids for  $Ama2$  and  $P6_3/mmc$ , for which tests showed excellent convergence of the computed properties. The phonon spectra were calculated within density-functional perturbation theory using the Quantum-ESPRESSO package. A  $4 \times 4 \times 2$  grid of  $q$  points in the first Brillouin zone was used in the interpolation of the force constants for the phonon dispersion curve calculation. The technique for the calculation of EPC has been described in detail in our previous publication (17).

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