Superconductivity of novel tin hydrides (Sn$_n$H$_m$) under pressure

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With the motivation of discovering high-temperature superconductors, evolutionary algorithm USPEX is employed to search for all stable compounds in the Sn-H system. In addition to the traditional SnH$_4$, new hydrides SnH$_8$, SnH$_{12}$ and SnH$_{14}$ are found to be thermodynamically stable at high pressure. Dynamical stability and superconductivity of tin hydrides are systematically investigated. I$_4$m$_2$-SnH$_8$, C$_2$/m-SnH$_{12}$ and C$_2$/m-SnH$_{14}$ exhibit higher superconducting transition temperatures of 81, 93 and 97 K compared to the traditional compound SnH4 with $T_c$ of 52 K at 200 GPa. An interesting bent H$_3$–group in I$_4$m$_2$-SnH$_8$ and novel linear H$_4$ in C$_2$/m-SnH$_{12}$ are observed. All the new tin hydrides remain metallic over their predicted range of stability. The intermediate-frequency wagging and bending vibrations have more contribution to electron-phonon coupling parameter than high-frequency stretching vibrations of H$_2$ and H$_3$.

Molecular hydrogen’s phase transition to a metallic state has been subject of many experimental and theoretical studies$^{1,2}$. Although reaching the metallic state in pure solid hydrogen proved elusive, it is in the main focus of many groups and recently, the progress of bringing pure hydrogen to nearly 400 GPa has been reported$^{3,5}$. Following the pioneering work of Ashcroft$^6$, nearly room-temperature superconductivity was predicted in metallic molecular hydrogen$^{7,8}$.

An alternative approach to metalize hydrogen is to use chemical alloying as a means to exert additional pressure on hydrogen atoms$^9$. Hydrogen-rich compounds such as SiH$_4$ can be metalized at a much lower pressure$^{10}$. For metallic hydrogen, high Debye temperature and strong electron-phonon coupling are anticipated. The same is expected for hydrogen-rich compounds and it has been suggested that hydrogen-rich compounds are good candidates for high-temperature superconductivity$^{9}$. Theoretical studies confirm this idea with predicting superconductivity in high-pressure hydrides such as H-Se$^{11}$, Ca-H$^{12}$, Sn-H$^{13}$, Pt-H$^{14}$ and B-H$^{15}$. A series of hydrogen-rich compounds have been predicted to have remarkably high $T_c$ values (e.g. 235 K for CaH$_4$ at 150 GPa$^{12}$, 191 K for H$_4$S at 200 GPa$^{16}$, 64 K for GeH$_4$ at 220 GPa$^{17}$) while the highest $T_c$ that had been achieved experimentally was in the complex mercury cuprate (138 K at ambient pressure$^{18}$ and 166 K at high pressures$^{19}$). The new record of high $T_c$ was established for H$_4$S, a compound whose existence and superconductivity at 200 K were first predicted theoretically$^{19}$ in 2014 using USPEX and then observed experimentally$^{20}$ in 2015, and started a new wave of interest in hydrogen-rich superconductors.

In a previous theoretical study, Tse et al. reported a high-pressure metallic phase of SnH$_4$ with hexagonal P6/mmm symmetry group, which is a layered structure intercalated with H$_2$ units, and is a superconductor with $T_c$ close to 80 K at 120 GPa$^{21}$. Later, by using evolutionary algorithm USPEX, Gao et al.$^{13}$ reported two novel metallic phases of SnH$_4$ with space groups P6$_3$/mmc and Ama2, which both have hexagonal layers of Sn atoms with semi-molecular H$_2$ units. The reported stability ranges are 96–180 GPa for Ama2, and above 180 GPa for P6$_3$/mmc; with $T_c$ values of 15–22 K at 120 GPa and 52–62 K at 200 GPa for Ama2 and P6$_3$/mmc, respectively$^{13}$.

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While SnH₄ was shown to be a relatively high-\(T_c\) superconductor, the possibility of existence of other tin hydrides were not explored so far. At the same time, by now it is proven²² that totally unexpected compounds become stable under pressure, and this gives hope of finding even better superconductors. Hence, in this study, we systematically search for the stable compounds using the highly efficient variable-composition evolutionary searches (VCES). Apart from the previously reported phases of SnH₄, there is one metastable tetragonal phase of stannane with higher superconducting critical temperature. Other stable superconducting compounds, SnH₈, SnH₁₂ and SnH₁₄, are found to become stable at high pressure. Moreover, we found a semi-molecular group H₃—in the \(\text{I}_4\text{m}2\) structure of SnH₈. Novel H₄—is also present in C2/m-SnH₁₂. We calculate a high \(T_c\) of 81 K at 220 GPa in the newly predicted compound SnH₉, 93 K for SnH₁₂ at 250 GPa, 97 K for SnH₁₄ at 300 GPa and 91 K for the metastable phase of SnH₄ at 220 GPa.

**Results**

Evolutionary variable-composition searches for stable compounds and their structures with up to 20 atoms in the primitive unit cell were performed at 150, 200, 250 and 300 GPa. To further investigate the newly found compounds, fixed-composition structure predictions for the most promising compounds were performed, with one to three formula units per cell. Candidate low-enthalpy structures are metastable \(\text{I}_4\text{mm}3\)-SnH₄, stable \(\text{I}_4\text{m}2\)-SnH₈, \(\text{C}_2\text{m}-\text{SnH}_{12}\) and \(\text{C}_2\text{m}-\text{SnH}_{14}\). In the \(\text{I}_4\text{m}2\)-SnH₈ structure predicted to be stable at pressures above 220 GPa, Sn atoms are packed between H₂ and H₃ molecular groups, in which the bent H₃ units are perpendicular to one another and separated by 1.35 Å. In \(\text{C}_2\text{m}-\text{SnH}_{12}\), Sn atoms form well-separated close-packed layers intercalated with blocks of H₂ and H₄ semi-molecules.

Figure 1(a) shows the enthalpy of formation (\(\Delta H\)) of Sn-H compounds at selected pressures. Significantly, in addition to reproducing various structures of solid SnH₄,³¹, Sn₂³¹ and H₂²⁴, novel compounds SnH₉, SnH₁₂ and SnH₁₄ are found to be stable in a wide pressure range in our systematic evolutionary structure search. It can be seen from Fig. 1(a), that at around 200 GPa the tetragonal SnH₄ with the space group of \(\text{I}_4\text{m}2\) lies above the convex hull, therefore, is metastable with respect to decomposition to \(\text{P}_6/m\text{mc-SnH}_4\) and \(\text{C}_2\text{c}-\text{H}_2\). Between 150 to 300 GPa, we predict stable phases of H₂, SnH₉, SnH₁₀, SnH₁₂, SnH₁₄ and Sn₂³¹. Some metastable forms of SnH₉ and SnH₁₂ are also shown in Fig. 1(a) by open symbols.

SnH₄ is thermodynamically stable at pressures above 108 GPa as was predicted in previous report¹³. It goes through a phase transition at 160 GPa. Upon increasing pressure, at 220 GPa we predict stabilization of SnH₉, SnH₁₂ and SnH₁₄ reach stability at the pressures of 250 GPa and 280 GPa, respectively, and remain stable at least up to 300 GPa. The structures of SnH₉ compounds are found to be dynamically stable within pressure ranges of their stability. In the \(\text{I}_4\text{m}2\)-SnH₈ structure, Sn atoms occupy the 2a Wyckoff site and the H atoms are on the 4e, 8i and 4f sites (detailed structural information is provided in Table 1).

We checked the effects of zero-point energy using phonon calculations²⁵ at 250 GPa. The inclusion of zero-point noticeably lowered the formation enthalpy of SnH₉ with respect to SnH₄ and H₂ (Fig. 1(a)), implying that this compound can be formed at lower pressure. At the same time, SnH₁₂ moves above the convex hull at 250 GPa, suggesting that higher pressure is needed to stabilize \(\text{C}_2\text{m}-\text{SnH}_{12}\). In accord with what we expect, zero-point energy does not change the topology of the phase diagram, but shifts transition pressures.

In \(\text{P}_4\text{m}2\)-SnH₄ structure, the H atoms are split into two categories. Some H atoms form H₂ groups, which were previously observed in solid phases of BaH₆,²⁷ in an unstable structure of H₂Br \((\text{H}_2\text{Br}[\text{H}_2\text{Br}]\text{H}_2)\)²⁸, and in an intriguing linear form with the bond length of 0.92 Å in H₂Te₂.²⁹ In contrast to H₂Br, which has approximately an equilateral triangle form of H₂, here we report the formation of H₂ in a bent geometry with the angle of 146.2° and bond length of 0.86 Å at 220 GPa in the \(\text{I}_4\text{m}2\) structure. The other type of H atoms form H₂ groups which are aligned parallel to each other.

\(\text{I}_4\text{m}2\) structure can be presented as Sn[\(\text{H}_2\text{Br}\)][\(\text{H}_2\text{Br}\)] as shown in Fig. 2(a,b). The bond length in H₂ unit is 0.86 Å, whereas H₂ has a longer bond length of 0.87 Å. Contrary to isolated H₂ molecule, which only has a filled \(\sigma\) bonding orbital, in the H₂ and H₄ semi-molecules, population of anti-bonding orbitals causes lengthening and
Phase | Lattice parameters | Atom | x | y | z
--- | --- | --- | --- | --- | ---
I\text{\textit{4}m\textit{2}} | a = 3.076 Å | Sn(2a) | 0.0000 | 0.0000 | 0.0000
SnH₈ | c = 5.523 Å | H₁(8i) | 0.2729 | 0.0000 | 0.3331 | H₂(4e) | 0.0000 | 0.0000 | 0.6208 | H₃(4f) | 0.0000 | 0.5000 | 0.1701
at 220 GPa | | SnH₁₂ | b = 3.065 Å | H₁(4i) | 0.0495 | 0.0000 | 0.6553
SnH₁₂ | c = 7.388 Å | H₄(8i) | 0.3810 | 0.2399 | 0.1123 | H₅(4g) | 0.0000 | 0.1233 | 0.0000
at 250 GPa | | SnH₁₄ | a = 7.129 Å | Sn(2b) | 0.0000 | 0.5000 | 0.0000 | H₁(4i) | 0.3651 | 0.0000 | 0.7031
SnH₁₄ | b = 2.730 Å | H₅(8i) | 0.2365 | 0.2808 | 0.4035 | H₆(2d) | 0.0000 | 0.5000 | 0.5000 | H₇(2c) | 0.0000 | 0.0000 | 0.5000
at 300 GPa

| C2/m | a = 5.191 Å | Sn(2d) | 0.0000 | 0.5000 | 0.5000 |
| C2/m | b = 3.065 Å | H₁(4i) | 0.0495 | 0.0000 | 0.6553 |
| C2/m | c = 7.388 Å | H₄(8i) | 0.3810 | 0.2399 | 0.1123 |
| C2/m | β = 148.95° |
| C2/m | H₅(4g) | 0.0000 | 0.1233 | 0.0000 |
| C2/m | H₆(2d) | 0.0000 | 0.5000 | 0.5000 |
| C2/m | H₇(2c) | 0.0000 | 0.0000 | 0.5000 |

Table 1. Predicted crystal structures of SnH₈, SnH₁₂ and SnH₁₄ at 220, 250 and 300 GPa, respectively.

Figure 2. Predicted structures of (a,b) SnH₈ [I\text{\textit{4}m\textit{2}}], (c) SnH₁₂ [C2/m] and (d) SnH₁₄ [C2/m]. Large and small spheres represent Sn and H atoms, respectively. Electron localization functions (ELF) for (e) SnH₈ [I\text{\textit{4}m\textit{2}}] at 220 GPa and (f) SnH₁₄ [C2/m] at 250 GPa.
weakening of the covalent bond. The slightly longer H-H bond length compared to isolated H2 molecule (0.74 Å) is caused by charge transfer of 0.42 e− and 0.48 e−, as computed using Bader theory26, from Sn to each H2 and H3 unit, respectively. Charge transfer is an important factor in the formation of H2 and H3 units in the H4Te, GeH4, SnH4, CaH4, H5Te, H5Br, BaH6, Cmcm-H4Te28, where Br translational modes make the largest contribution to the total vibrations, which contribute 10.6% (22.9%) for SnH8 (SnH12). This is different from superconductivity in H-rich compounds, comparable with H3M-Im11. Structures of SnH8, SnH12 and SnH14 are phonon-mediated superconductors with Tc values of 81, 93 and 97 K at pressures of 220, 250, and 300 GPa, respectively. Employing the αF(ω) and electron-phonon integral λ(ω) of: (a) SnH8 [I/m2] at 220 GPa, (b) SnH12 [C2/m] at 250 GPa and (c) SnH14 [C2/m] at 300 GPa.

In conclusion, we explored the energetically stable/metastable high-pressure phases of the Sn-H system in detail by means of ab initio evolutionary structure prediction. The results demonstrate that SnH8, SnH12 and SnH14, reported for the first time in this work, are thermodynamically stable compounds that coexist stably with solid Sn, H2 and SnH4 in a wide pressure range starting from 220 to at least 300 GPa. EPC calculations indicate that high-pressure SnH8, SnH12 and SnH14 are phonon-mediated superconductors with Tc values of 81, 93 and 97 K at pressures of 220, 250, and 300 GPa, respectively. λ is high for SnH4 compounds, comparable with H,M-Im5m, where M = S and Se11. Structures of SnHn compounds contain H2, bent H3, and linear H4 groups. Further experimental studies on the formation of SnHn, n = 8, 12 and 14 at high pressure are needed, and present results will serve as a guide for future experiments.

Figure 3. Phonon band structure, phonon DOS, Eliashberg phonon spectral function αF(ω) and electron-phonon integral λ(ω) of: (a) SnH8 [I/m2] at 220 GPa, (b) SnH12 [C2/m] at 250 GPa and (c) SnH14 [C2/m] at 300 GPa.
Methods

To find stable and low-enthalpy metastable structures, we took advantage of evolutionary algorithm implemented in USPEX code\(^{30-32}\), which has been extensively used to predict stable crystal structures with just a knowledge of the chemical composition and without any experimental information\(^{15,33-35}\).

In this method, the initial generation of structures and compositions is produced with the random symmetric algorithm\(^{34}\), and subsequent generations are produced by carefully designed variation operators. In order to find all stable stoichiometric compounds and the corresponding stable and metastable structures in the Sn-H binary system, we used VCES method implemented in USPEX\(^{30,31}\).

Structure relaxations were carried out using VASP package\(^{36}\) in the framework of density functional theory (DFT) and using PBE-GGA (Perdew-Burke-Ernzerhof generalized gradient approximation)\(^{37}\). The projector-augmented wave approach (PAW)\(^{38}\) was used to describe the core electrons and their effects on valence orbitals. The plane-wave kinetic energy cutoff was chosen as 1000 eV for hard PAW potentials, and we used Γ-centered uniform \(k\)-points meshes to sample the Brillouin zone.

Phonons and thermodynamic properties of Sn-H compounds are calculated using the PHONOPY package\(^{25,39}\). The supercell approach is used with supercell dimensions greater than 10 Å (typically \(3 \times 3 \times 3\) replication of the primitive cell). We used valence electron configurations of 4d\(^{10}\) 5s\(^2\) 5p\(^2\) and 1s\(^1\) for tin and hydrogen, respectively. Phonon frequencies and electron-phonon coupling (EPC) coefficients are calculated using DFPT as implemented in the Quantum ESPRESSO (QE) code\(^{40}\). In the QE calculations, we employed ultrasoft pseudopotentials and PBE-GGA exchange-correlation functional\(^{37}\). A plane-wave basis set with a cutoff of 70 Ry gave a convergence in energy with a precision of 1 meV/atom. The EPC parameter was calculated using \(4 \times 4 \times 3, 5 \times 5 \times 4\) and \(5 \times 5 \times 4 \times 4\)-point meshes for \(I\bar{4}m2\)-Sn\(_{13}\)\(_{1}\), \(C2/m\)-Sn\(_{12}\)\(_{1}\), and \(C2/m\)-Sn\(_{14}\)\(_{1}\), respectively. Denser \(k\)-point meshes, \(8 \times 8 \times 6, 10 \times 10 \times 8\) and \(10 \times 10 \times 8\) were used for convergence checks for the EPC parameter \(\lambda\). The superconducting \(T_c\) was estimated using the Allen-Dynes modified McMillan equation\(^{41}\):

\[
T_c \approx \frac{\omega_{\log}}{1.2} \exp\left(\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right)
\]

where \(\omega_{\log}\) is the logarithmic average frequency and \(\mu^*\) is the Coulomb pseudopotential, for which we used 0.10 and 0.13 values, which often give realistic results. The EPC constant and \(\omega_{\log}\) were calculated as:

| Structure     | Pressure (GPa) | \(\lambda\) | \(\omega_{\log}\) (K) | \(T_c\) (K) |
|---------------|---------------|-------------|-----------------------|--------------|
| \(I\bar{4}m2\)-Sn\(_{13}\)\(_{1}\) | 220           | 1.180       | 1025                  | 91 \((\mu^* = 0.10)\) |
|               |               |             |                       | 80 \((\mu^* = 0.13)\) |
| \(I\bar{4}m2\)-Sn\(_{13}\)\(_{1}\) | 220           | 1.188       | 919                   | 81 \((\mu^* = 0.10)\) |
|               |               |             |                       | 72 \((\mu^* = 0.13)\) |
| \(C2/m\)-Sn\(_{12}\)\(_{1}\) | 250           | 1.250       | 991                   | 93 \((\mu^* = 0.10)\) |
|               |               |             |                       | 83 \((\mu^* = 0.13)\) |
| \(C2/m\)-Sn\(_{14}\)\(_{1}\) | 300           | 1.187       | 1099                  | 97 \((\mu^* = 0.10)\) |
|               |               |             |                       | 86 \((\mu^* = 0.13)\) |

Table 2. The calculated EPC parameter (\(\lambda\)), logarithmic average phonon frequency (\(\omega_{\log}\)) and critical temperature (\(T_c\)) (with \(\mu^* = 0.10\) and 0.13) for metastable Sn\(_{13}\), stable Sn\(_{12}\)\(_{1}\), Sn\(_{12}\)\(_{1}\), and Sn\(_{14}\)\(_{1}\) at 220, 220, 250 and 300 GPa, respectively.

Figure 4. Electronic band structure and projected DOS on Sn and H atoms for Sn\(_{13}\)\(_{1}\) \(I\bar{4}m2\) at 220 GPa.
\[ \lambda = 2 \int_0^\infty \alpha^2 F(\omega) \omega d\omega \]  
(2)

and

\[ \omega_{\text{lag}} = \exp \left[ \frac{2}{\lambda} \int_0^\infty \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln(\omega) \right] \]  
(3)

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Author Contributions
M.M.D.E. performed all the calculations presented in this article with help from Z.W., Q.Z. and H.D. Research was designed by A.R.O. S.W, M. R. and X-F. Z. analyzed data. M.M.D.E., A.R.O. and Z.W. wrote the first draft of the paper and all authors contributed to revisions.

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