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## Superconductivity of novel tin hydrides ( $\text{Sn}_n\text{H}_m$ ) under pressure

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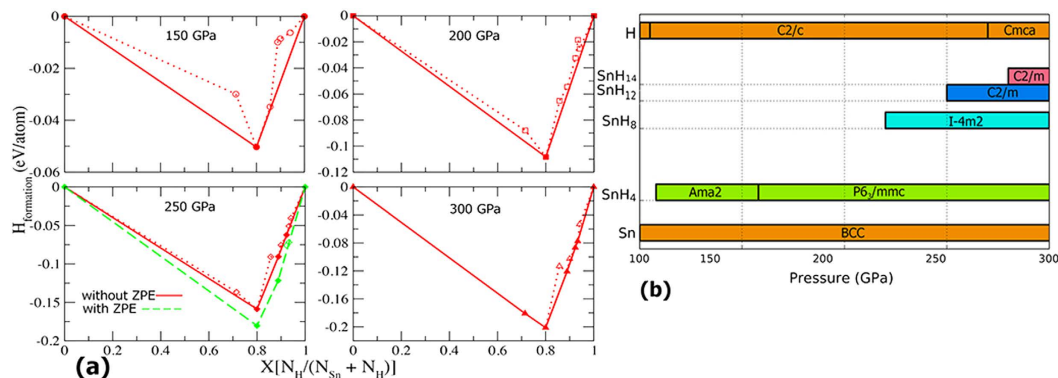
With the motivation of discovering high-temperature superconductors, evolutionary algorithm USPEX is employed to search for all stable compounds in the Sn-H system. In addition to the traditional  $\text{SnH}_4$ , new hydrides  $\text{SnH}_8$ ,  $\text{SnH}_{12}$  and  $\text{SnH}_{14}$  are found to be thermodynamically stable at high pressure. Dynamical stability and superconductivity of tin hydrides are systematically investigated.  $\sqrt{3}\times\sqrt{3}\times\sqrt{3}$ - $\text{SnH}_8$ ,  $\text{C2/m-SnH}_{12}$  and  $\text{C2/m-SnH}_{14}$  exhibit higher superconducting transition temperatures of 81, 93 and 97 K compared to the traditional compound  $\text{SnH}_4$  with  $T_c$  of 52 K at 200 GPa. An interesting bent  $\text{H}_3$ -group in  $\sqrt{3}\times\sqrt{3}\times\sqrt{3}$ - $\text{SnH}_8$  and novel linear  $\text{H}_4$  in  $\text{C2/m-SnH}_{12}$  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  $\text{H}_2$  and  $\text{H}_3$ .

Molecular hydrogen's phase transition to a metallic state has been subject of many experimental and theoretical studies<sup>1,2</sup>. 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<sup>3-5</sup>. Following the pioneering work of Ashcroft<sup>6</sup>, nearly room-temperature superconductivity was predicted in metallic molecular hydrogen<sup>7,8</sup>.

An alternative approach to metalize hydrogen is to use chemical alloying as a means to exert additional pressure on hydrogen atoms<sup>9</sup>. Hydrogen-rich compounds such as  $\text{SiH}_4$  can be metalized at a much lower pressure<sup>10</sup>. 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<sup>9</sup>. Theoretical studies confirm this idea with predicting superconductivity in high-pressure hydrides such as H-Se<sup>11</sup>, Ca-H<sup>12</sup>, Sn-H<sup>13</sup>, Pt-H<sup>14</sup> and B-H<sup>15</sup>. A series of hydrogen-rich compounds have been predicted to have remarkably high  $T_c$  values (e.g. 235 K for  $\text{CaH}_6$  at 150 GPa<sup>12</sup>, 191 K for  $\text{H}_3\text{S}$  at 200 GPa<sup>16</sup>, 64 K for  $\text{GeH}_4$  at 220 GPa<sup>17</sup>) while the highest  $T_c$  that had been achieved experimentally was in the complex mercury cuprate (138 K at ambient pressure<sup>18</sup> and 166 K at high pressures<sup>19</sup>). The new record of high  $T_c$  was established for  $\text{H}_3\text{S}$ , a compound whose existence and superconductivity at 200 K were first predicted theoretically<sup>16</sup> in 2014 using USPEX and then observed experimentally<sup>20</sup> 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  $\text{SnH}_4$  with hexagonal  $\text{P6/mmm}$  symmetry group, which is a layered structure intercalated with  $\text{H}_2$  units, and is a superconductor with  $T_c$  close to 80 K at 120 GPa<sup>21</sup>. Later, by using evolutionary algorithm USPEX, Gao *et al.*<sup>13</sup> reported two novel metallic phases of  $\text{SnH}_4$  with space groups  $\text{P6}_3/\text{mmc}$  and  $\text{Ama2}$ , which both have hexagonal layers of Sn atoms with semi-molecular  $\text{H}_2$  units. The reported stability ranges are 96–180 GPa for  $\text{Ama2}$ , and above 180 GPa for  $\text{P6}_3/\text{mmc}$ ; with  $T_c$  values of 15–22 K at 120 GPa and 52–62 K at 200 GPa for  $\text{Ama2}$  and  $\text{P6}_3/\text{mmc}$ , respectively<sup>13</sup>.

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**Figure 1. Thermodynamics of the Sn-H system.** (a) Predicted formation enthalpy of  $\text{Sn}_n\text{H}_m$  compounds. Solid red lines denote the convex hull and green dashed line shows the effect of ZPE inclusion at 250 GPa. (b) Predicted pressure-composition phase diagram of the Sn-H system.

While  $\text{SnH}_4$  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 proven<sup>22</sup> 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  $\text{SnH}_4$ , there is one metastable tetragonal phase of stannane with higher superconducting critical temperature. Other stable superconducting compounds,  $\text{SnH}_8$ ,  $\text{SnH}_{12}$  and  $\text{SnH}_{14}$ , are found to become stable at high pressure. Moreover, we found a semi-molecular group  $\text{H}_3^-$  in the  $\bar{1}4m2$  structure of  $\text{SnH}_8$ . Novel  $\text{H}_4^-$  is also present in  $\text{C2/m-SnH}_{12}$ . We calculate a high  $T_c$  of 81 K at 220 GPa in the newly predicted compound  $\text{SnH}_8$ , 93 K for  $\text{SnH}_{12}$  at 250 GPa, 97 K for  $\text{SnH}_{14}$  at 300 GPa and 91 K for the metastable phase of  $\text{SnH}_4$  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  $\bar{1}4/mmm\text{-SnH}_4$ , stable  $\bar{1}4m2\text{-SnH}_8$ ,  $\text{C2/m-SnH}_{12}$  and  $\text{C2/m-SnH}_{14}$ . In the  $\bar{1}4m2\text{-SnH}_8$  structure predicted to be stable at pressures above 220 GPa, Sn atoms are packed between  $\text{H}_2$  and  $\text{H}_3$  molecular groups, in which the bent  $\text{H}_3$  units are perpendicular to one another and separated by 1.35 Å. In  $\text{C2/m-SnH}_{12}$ , Sn atoms form well-separated close-packed layers intercalated with blocks of  $\text{H}_2$  and  $\text{H}_4$  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  $\text{SnH}_4$ <sup>13,21</sup>,  $\text{Sn}^{23}$  and  $\text{H}_2$ <sup>24</sup>, novel compounds  $\text{SnH}_8$ ,  $\text{SnH}_{12}$  and  $\text{SnH}_{14}$  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  $\text{SnH}_8$  with the space group of  $\bar{1}4m2$  lies above the convex hull, therefore, is metastable with respect to decomposition to  $\text{P6}_3/mmc\text{-SnH}_4$  and  $\text{C2/c-H}_2$ . Between 150 to 300 GPa, we predict stable phases of  $\text{H}_2$ ,  $\text{SnH}_4$ ,  $\text{SnH}_8$ ,  $\text{SnH}_{12}$ ,  $\text{SnH}_{14}$  and  $\text{Sn}^{23}$ . Some metastable forms of  $\text{SnH}_6$ ,  $\text{SnH}_9$  and  $\text{SnH}_{16}$  are also shown in Fig. 1(a) by open symbols.

$\text{SnH}_4$  is thermodynamically stable at pressures above 108 GPa as was predicted in previous report<sup>13</sup>. It goes through a phase transition at 160 GPa. Upon increasing pressure, at 220 GPa we predict stabilization of  $\text{SnH}_8$ .  $\text{SnH}_{12}$  and  $\text{SnH}_{14}$  reach stability at the pressures of 250 GPa and 280 GPa, respectively, and remain stable at least up to 300 GPa. The structures of  $\text{SnH}_n$  compounds are found to be dynamically stable within pressure ranges of their stability. In the  $\bar{1}4m2\text{-SnH}_8$  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).

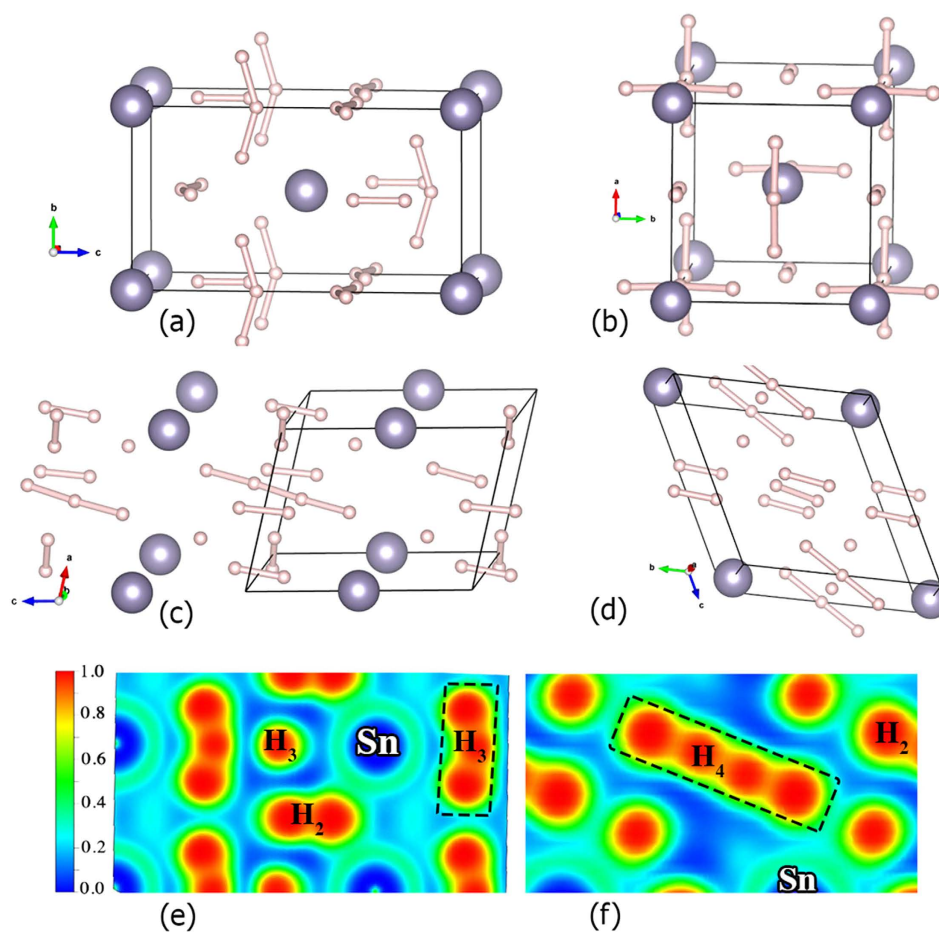
We checked the effects of zero-point energy using phonon calculations<sup>25</sup> at 250 GPa. The inclusion of zero-point noticeably lowered the formation enthalpy of  $\text{SnH}_8$  with respect to  $\text{SnH}_4$  and  $\text{H}_2$  (Fig. 1(a)), implying that this compound can be formed at lower pressure. At the same time,  $\text{SnH}_{12}$  moves above the convex hull at 250 GPa, suggesting that higher pressure is needed to stabilize  $\text{C2/m-SnH}_{12}$ . In accord with what we expect, zero-point energy does not change the topology of the phase diagram, but shifts transition pressures.

In  $\bar{1}4m2\text{-SnH}_8$  structure, the H atoms are split into two categories. Some H atoms form  $\text{H}_3$  groups, which were previously observed in solid phases of  $\text{BaH}_6$ <sup>27</sup>, in an unstable structure of  $\text{H}_3\text{Br}$  ( $[\text{H}_3]\text{Br}[\text{H}_2]$ )<sup>28</sup>, and in an intriguing linear form with the bond length of 0.92 Å in  $\text{H}_3\text{Te}_2$ <sup>29</sup>. In contrast to  $\text{H}_3\text{Br}$ , which has approximately an equilateral triangle form of  $\text{H}_3$ , here we report the formation of  $\text{H}_3$  in a bent geometry with the angle of 146.2° and bond length of 0.86 Å at 220 GPa in the  $\bar{1}4m2$  structure. The other type of H atoms form  $\text{H}_2$  groups which are aligned parallel to each other.

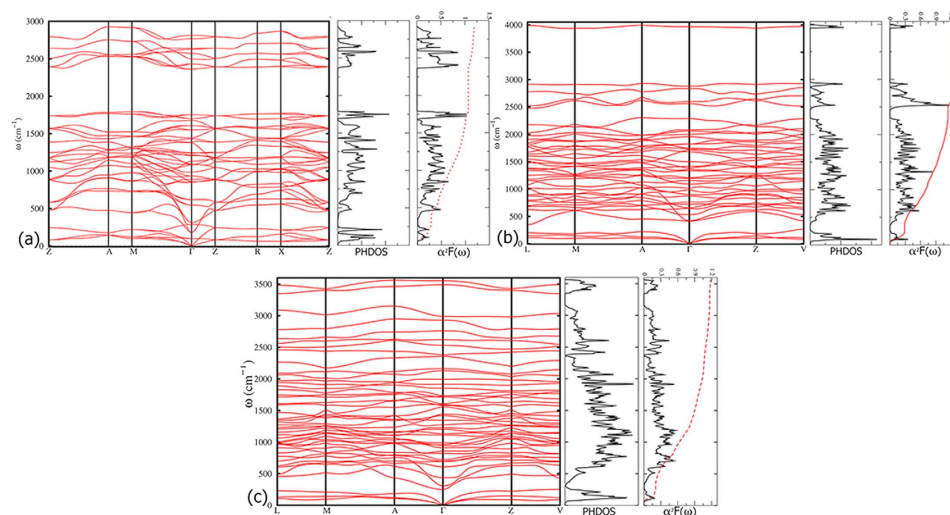
$\bar{1}4m2$  structure can be presented as  $\text{Sn}[\text{H}_2][\text{H}_3]_2$  as shown in Fig. 2(a,b). The bond length in  $\text{H}_3$  unit is 0.86 Å, whereas  $\text{H}_2$  has a longer bond length of 0.87 Å. Contrary to isolated  $\text{H}_2$  molecule, which only has a filled  $\sigma$  bonding orbital, in the  $\text{H}_2$  and  $\text{H}_3$  semi-molecules, population of anti-bonding orbitals causes lengthening and

Phase	Lattice parameters	Atom	x	y	z
$I\bar{4}m2$	$a = 3.076 \text{ \AA}$	Sn(2a)	0.0000	0.0000	0.0000
SnH <sub>8</sub>	at 220 GPa	H <sub>1</sub> (8i)	0.2729	0.0000	0.3331
		H <sub>2</sub> (4e)	0.0000	0.0000	0.6208
		H <sub>3</sub> (4f)	0.0000	0.5000	0.1701
C2/m	$a = 5.191 \text{ \AA}$	Sn(2d)	0.0000	0.5000	0.5000
SnH <sub>12</sub>	at 250 GPa	H <sub>1</sub> (4i)	0.0495	0.0000	0.6553
		H <sub>2</sub> (4i)	0.4564	0.0000	0.7226
	H <sub>3</sub> (4i)	0.3428	0.0000	0.8832	
	H <sub>4</sub> (8i)	0.3810	0.2399	0.1123	
	H <sub>5</sub> (4g)	0.0000	0.1233	0.0000	
C2/m	$a = 7.129 \text{ \AA}$	Sn(2b)	0.0000	0.5000	0.0000
SnH <sub>14</sub>	at 300 GPa	H <sub>1</sub> (4i)	0.3651	0.0000	0.7031
		H <sub>2</sub> (4i)	0.1857	0.0000	0.9852
		H <sub>3</sub> (4i)	0.0732	0.0000	0.6252
	H <sub>4</sub> (4i)	0.8063	0.0000	0.8090	
	H <sub>5</sub> (8i)	0.2365	0.2808	0.4035	
	H <sub>6</sub> (2d)	0.0000	0.5000	0.5000	
	H <sub>7</sub> (2c)	0.0000	0.0000	0.5000	

**Table 1.** Predicted crystal structures of SnH<sub>8</sub>, SnH<sub>12</sub> and SnH<sub>14</sub> at 220, 250 and 300 GPa, respectively.



**Figure 2.** Predicted structures of (a,b) SnH<sub>8</sub> [ $I\bar{4}m2$ ], (c) SnH<sub>12</sub> [C2/m] and (d) SnH<sub>14</sub> [C2/m]. Large and small spheres represent Sn and H atoms, respectively. Electron localization functions (ELF) for (e) SnH<sub>8</sub> [ $I\bar{4}m2$ ] at 220 GPa and (f) SnH<sub>12</sub> [C2/m] at 250 GPa.



**Figure 3.** Phonon band structure, phonon DOS, Eliashberg phonon spectral function  $\alpha^2F(\omega)$  and electron-phonon integral  $\lambda(\omega)$  of: (a) SnH<sub>8</sub> [I $\bar{4}$ m2] at 220 GPa, (b) SnH<sub>12</sub> [C2/m] at 250 GPa and (c) SnH<sub>14</sub> [C2/m] at 300 GPa.

weakening of the covalent bond. The slightly longer H-H bond length compared to isolated H<sub>2</sub> molecule (0.74 Å) is caused by charge transfer of 0.42 e<sup>-</sup> and 0.48 e<sup>-</sup>, as computed using Bader theory<sup>26</sup>, from Sn to each H<sub>2</sub> and H<sub>3</sub> unit, respectively. Charge transfer is an important factor in the formation of H<sub>2</sub> and H<sub>3</sub> units in the H<sub>4</sub>Te, GeH<sub>4</sub>, SnH<sub>4</sub>, CaH<sub>4</sub>, H<sub>5</sub>Te<sub>2</sub>, H<sub>5</sub>Br, BaH<sub>6</sub><sup>12,17,27–29</sup>

Analysis of electron localization function (ELF) shows a high ELF value of 0.88 between H atoms within the unit, indicating strong covalent bonding features (Fig. 2(e)). At the same time, the ELF value on the Sn-H bond is very low, reaching just 0.37.

In C2/m-SnH<sub>12</sub>, intriguing formation of novel H<sub>4</sub> semi-molecules are observed; at 250 GPa, they can be represented as two H<sub>2</sub>-groups separated by just 0.99 Å. Higher pressure of 300 GPa decreases the distance to 0.88 Å, leading to a strong covalent bond in the H<sub>4</sub> units. Fig. 2(f) demonstrates covalent bonds in the linear H<sub>4</sub> units with the ELF magnitude of 0.85.

The calculated phonon dispersion curves and phonon density of states for I $\bar{4}$ m2 structure of SnH<sub>8</sub> at 220 GPa are shown in Fig. 3(a). Dynamical stability is clearly evidenced by the absence of any imaginary frequencies in the whole Brillouin zone. The low-frequency bands below 250 cm<sup>-1</sup> are mainly from the vibrations of Sn atoms. Modes between 300 and 1700 cm<sup>-1</sup> are mainly from the H-H wagging vibrations, and higher frequency vibrations above 2300 cm<sup>-1</sup> are due to H-H stretching vibrations in H<sub>2</sub> and H<sub>3</sub> units.

Low-frequency translational modes, mostly from Sn atom, contribute 23.7% (9.2%) to the total  $\lambda$ . Intermediate H-H wagging vibrations make a significant contribution of 65.7% (67.9%), and the rest is from stretching H vibrations, which contribute 10.6% (22.9%) for SnH<sub>8</sub> (SnH<sub>12</sub>). This is different from superconductivity in Cmcm-H<sub>2</sub>Br<sup>28</sup>, where Br translational modes make the largest contribution to the total  $\lambda$  and similar to the R $\bar{3}$ m-H<sub>4</sub>Te<sup>29</sup> and P4/mmm-BaH<sub>6</sub><sup>27</sup>, where medium-frequency H-wagging and bending modes contribute the most to the EPC. In accord with our expectation,  $\lambda$  increases almost linearly with hydrogen content, where we found 60.2%, 72.2% and 77.1% contribution of H vibrations to the total  $\lambda$  of SnH<sub>4</sub>, SnH<sub>8</sub> and SnH<sub>12</sub>, respectively. This highlights the dominant role of H in the superconductivity of H-rich compounds.

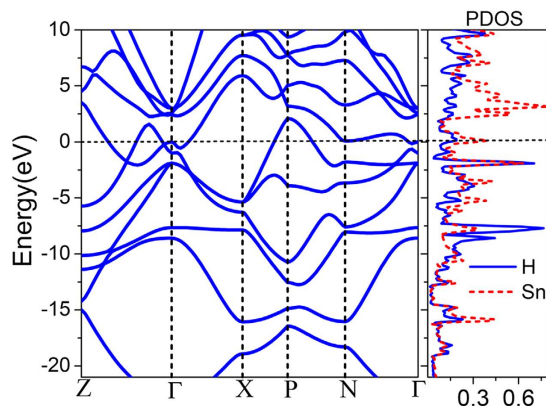
Electronic band structure of I $\bar{4}$ m2-SnH<sub>8</sub> is depicted in Fig. 4. Occurrence of flat and steep bands near the Fermi level has been suggested as a condition for enhancing electron-phonon coupling (EPC) and the formation of Cooper pairs.

We can calculate  $T_c$  based on the spectral function  $\alpha^2F(\omega)$  and taking advantage of Allen-Dynes modified McMillan equation (Eq. 1.) by using Coulomb pseudo-potential  $\mu^*$  of 0.10 and 0.13 as widely accepted values (see Table 2). At 220 GPa, the predicted  $T_c$  values for I $\bar{4}$ m2-SnH<sub>8</sub> are 81 K and 72 K using  $\mu^*$  values of 0.10 and 0.13, respectively. The calculated  $T_c$  slightly decreases with pressure (82 K at 200 GPa and 79 K at 300 GPa using  $\mu^* = 0.10$ ) with a pressure coefficient of  $-0.023$  K/GPa  $\left(\frac{dT_c}{dP}\right)$ . Reported  $\lambda$  is comparable to H<sub>3</sub>Se ( $\lambda = 1.09$ ) at 200 GPa<sup>11</sup>, but in I $\bar{4}$ m2-SnH<sub>8</sub> structure, we have a lower  $\langle \omega_{\log} \rangle$  of 919 K (1477 K for H<sub>3</sub>Se), resulting in a lower  $T_c$  value.

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 SnH<sub>8</sub>, SnH<sub>12</sub> and SnH<sub>14</sub>, reported for the first time in this work, are thermodynamically stable compounds that coexist stably with solid Sn, H<sub>2</sub> and SnH<sub>4</sub> in a wide pressure range starting from 220 to at least 300 GPa.

EPC calculations indicate that high-pressure SnH<sub>8</sub>, SnH<sub>12</sub> and SnH<sub>14</sub> are phonon-mediated superconductors with  $T_c$  values of 81, 93 and 97 K at pressures of 220, 250, and 300 GPa, respectively.  $\lambda$  is high for SnH<sub>n</sub> compounds, comparable with H<sub>3</sub>M-Im $\bar{3}$ m, where M = S and Se<sup>11</sup>. Structures of SnH<sub>n</sub> compounds contain H<sub>2</sub><sup>-</sup>, bent H<sub>3</sub><sup>-</sup>, and linear H<sub>4</sub><sup>-</sup> groups. Further experimental studies on the formation of SnH<sub>n</sub>, n = 8, 12 and 14 at high pressure are needed, and present results will serve as a guide for future experiments.





**Figure 4.** Electronic band structure and projected DOS on Sn and H atoms for SnH<sub>8</sub> [ $I\bar{4}m2$ ] at 220 GPa.

Structure	Pressure (GPa)	$\lambda$	$\omega_{log}$ (K)	$T_c$ (K)
I4/mmm SnH <sub>4</sub>	220	1.180	1025	91 ( $\mu^* = 0.10$ )
				80 ( $\mu^* = 0.13$ )
$I\bar{4}m2$ -SnH <sub>8</sub>	220	1.188	919	81 ( $\mu^* = 0.10$ )
				72 ( $\mu^* = 0.13$ )
C2/m-SnH <sub>12</sub>	250	1.250	991	93 ( $\mu^* = 0.10$ )
				83 ( $\mu^* = 0.13$ )
C2/m-SnH <sub>14</sub>	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 SnH<sub>4</sub>, stable SnH<sub>8</sub>, SnH<sub>12</sub> and SnH<sub>14</sub> at 220, 220, 250 and 300 GPa, respectively.

## Methods

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

In this method, the initial generation of structures and compositions is produced with the random symmetric algorithm<sup>34</sup>, 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<sup>30,31</sup>.

Structure relaxations were carried out using VASP package<sup>36</sup> in the framework of density functional theory (DFT) and using PBE-GGA (Perdew-Burke-Ernzerhof generalized gradient approximation)<sup>37</sup>. The projector-augmented wave approach (PAW)<sup>38</sup> 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  $\Gamma$ -centered uniform  $k$ -points meshes to sample the Brillouin zone.

Phonons and thermodynamic properties of Sn-H compounds are calculated using the PHONOPY package<sup>25,39</sup>. 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<sup>40</sup>. In the QE calculations, we employed ultrasoft pseudopotentials and PBE-GGA exchange-correlation functional<sup>37</sup>. 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  $5 \times 5 \times 4$   $q$ -point meshes for  $I\bar{4}m2$ -SnH<sub>8</sub>, C2/m-SnH<sub>12</sub> and C2/m-SnH<sub>14</sub>, 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<sup>41</sup>:

$$T_c = \frac{\omega_{log}}{1.2} \exp\left(\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right) \quad (1)$$

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:

$$\lambda = 2 \int_0^{\infty} \frac{\alpha^2 F(\omega)}{\omega} d\omega \quad (2)$$

and

$$\omega_{\log} = \exp \left[ \frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln(\omega) \right] \quad (3)$$

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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.

### Additional Information

**Competing financial interests:** The authors declare no competing financial interests.

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