# Theoretical study of stability and superconductivity of $ScH_n$ (n = 4-8) at high pressure

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The synthesis of hydrogen sulfides, with the potential of high-temperature superconductivity, was recently proposed at high  $T_c = 203$  K. It motivated us to employ an *ab initio* approach for the predictions of crystal structures to find the stable scandium hydrides. In addition to the earlier predicted three stoichiometries of ScH, ScH<sub>2</sub>, and ScH<sub>3</sub>, we identify three other metallic stoichiometries of ScH<sub>4</sub>, ScH<sub>6</sub>, and ScH<sub>8</sub>, which show superconductivity at significantly higher temperatures. The phases of ScH<sub>4</sub> and ScH<sub>6</sub>, whose stability does not require extremely high pressures (<150 GPa with ZPE), are primarily ionic compounds containing exotic quasimolecular H<sub>2</sub> arrangements. The present electron-phonon calculations revealed the superconductive potential of ScH<sub>4</sub> and ScH<sub>6</sub> with estimated  $T_c$  of 98 K and 129 K at 200 GPa and 130 GPa, respectively. The superconductivity of ScH<sub>n</sub> stems from the large electron-phonon coupling associated with the wagging, bending, and intermediate-frequency modes attributed mainly to the hydrogen atoms.

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### I. INTRODUCTION

The design of high-temperature superconductors has posted a challenging scientific and engineering problem since superconductivity was first observed and explained. According to the Bardeen-Cooper-Schrieffer (BCS) theory [1], hydrogen could form a metallic solid with a high Debye temperature and a strong electron-phonon coupling required for high-temperature phonon-mediated superconductivity. Unfortunately, experimental studies at up to 388 GPa failed to realize that prediction and observe solid H [2]. A recent contribution on the metallization of solid H at 495 GPa has received great attention [3]. However, there are still some controversies [4,5] related to the work reported in Ref. [3] requiring additional experimental and theoretical efforts to further confirm this extraordinary claim.

In 2004, Ashcroft showed that the hydrogen-dominated materials can also exhibit high- $T_c$  superconductivity, but could metallize at much lower pressures [6]. This proposal motivated numerous theoretical studies predicting that compressed H-rich materials would show high- temperature superconductivity (for example,  $T_c = 166$  K was predicted for SiH<sub>4</sub> [7,8], 20 K for Si<sub>2</sub>H<sub>6</sub> [9], 64 K for GeH<sub>4</sub> [10], 100 K for SiH<sub>4</sub>(H<sub>2</sub>)<sub>2</sub> [11], 235 K for CaH<sub>6</sub> [12], and 264 K for YH<sub>6</sub> [13]). In addition, a recent breakthrough finding in this field was the observation of superconductivity ( $T_c$  up to 203 K) in hydrogen sulfide (H<sub>2</sub>S) under pressure [14]. This was achieved by a direct investigation on a theoretical prediction of high  $T_c$ superconductivity in compressed solid H<sub>2</sub>S [15]. Following this discovery, scientists have also made great progress in studies of phosphorus hydrides both theoretically and experimentally [16-20]. These discoveries raised hope for achieving room-temperature superconductivity in the H-rich materials.

Transition metal hydrides have been studied for many decades to address a broad range of applied and fundamental

problems [21–23]. The current emphasis is mainly related to compounds with a high hydrogen content, due to the increasing demand for hydrogen storage materials for mobile applications [24,25], however the hydrogen-dominated metallic alloys may also have potential as the high temperature superconductors [6,13,26,27].

Scandium is the lightest element among transition metals and it displays interesting changes in electronic structure induced by different concentrations of hydrogen. Hence scandium is a perfect candidate to obtain a detailed comprehension of the superconducting properties of hydrides. Ye *et al.* [28] have shown rich structures and properties of ScH<sub>n</sub> (n = 1 - 3) from 1 atm to 400 GPa. The superconductivity of scandium hydrides also have been explored by Wei *et al.* [29]. It was shown that the superconducting  $T_c$  of ScH<sub>2</sub> reaches 38.11 K at 30 GPa, while the superconducting behavior of ScH<sub>3</sub> is not obvious under low pressures (P < 46 GPa), and it almost disappears under higher pressures.

At high pressures, it is expected that the valence electronic state of Sc atom will change and therefore provide a possibility for bonding with more H atoms. More recently, Liu *et al.* [27] have shown that yttrium and lanthanum atoms can bond with more than three hydrogens under pressures. The electron-phonon calculations revealed that the superconducting  $T_c$  of YH<sub>10</sub> is 326 K at 250 GPa. This value is much higher than the predicted maximal  $T_c$  of 40 K in YH<sub>3</sub> [13]. Due to the similar valence electronic configuration of scandium and yttrium, scandium hydrides with higher hydrogen concentration at high pressure may also show high-temperature superconductivity.

In this work, we have studied the structures, electron properties, and potential superconductivity of  $\text{ScH}_n$  (n = 4-8) on the basis of first-principle density functional theory. This paper is organized as follows. In the following sections, we first describe details regarding the computational techniques used. Then the results are reported and discussed in the Results and Discussion section. Finally, the paper is closed with the conclusions.

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# **II. COMPUTATIONAL METHODS**

The main body of this work consists of two parts: (1) exploration of the stable structures of  $ScH_n$  (n = 4-8) relative to  $ScH_3$  and  $H_2$ , (2) detailed investigation of the superconductivity of the identified, stable structures.

We search for ScH<sub>n</sub> (n = 4-8) static, ground-state structures using the crystal structure analysis by particle swarm optimization methodology [30] as implemented in the CA-LYPSO code [31], which has been successfully applied to predict the structure of many systems [32–35]. Our structure search, with system sizes containing up to 4 formula units (f.u.) per simulation cell, were performed at pressures of 100, 200, 300, and 400 GPa. To relax the structures and calculate the electronic structures, we employ the planewave basis projector augmented wave (PAW) formalism [36] in the framework of DFT within the generalized gradient approximation as implemented in the VASP code [37]. The use of energy cutoff of 850 eV and Monkhorst-Pack k meshes with grid spacing of  $2\pi \times 0.02 \text{ Å}^{-1}$  are then adopted to ensure that the enthalpy converges to an accuracy better than 1 meV/atom. The convergence threshold was set as  $10^{-6}$  eV in energy and  $10^{-3}$  eV in force. Sc  $3s^23p^63d^14s^2$  and H  $1s^1$ are treated as valence electrons for PAW pseudopotentials. Phonon dispersions and projected phonon density of states were calculated by using density function perturbation theory (DFPT) [38] on a  $3 \times 3 \times 3$  supercell as implemented in the PHONOPY code [39]. The bader charge analysis [40] was employed to perform charge calculation.

The electron-phonon coupling parameter (EPC) of the stable compounds are calculated within the framework of linear response theory using the QUANTUM-ESPRESSO code [41]. We employ the norm-conserving pseudopotentials with  $1s^1$  and  $3d^14s^2$  as valence electrons for H and Sc, respectively. The convergence tests concluded that suitable calculation parameters are 80 Ry for kinetic energy cutoff,  $16 \times 16 \times 16$  k-point sampling mesh, and  $4 \times 4 \times 4$  q mesh in the Brillouin zone.

### **III. RESULTS**

#### A. Structures of ScH<sub>n</sub>

The energetic stabilities of a variety of  $ScH_n$  (n = 4-8) compounds are evaluated through their formation enthalpies relative to the products of dissociation into scandium trihydride (ScH<sub>3</sub>) and solid hydrogen (H<sub>2</sub>) at 100, 200, 300, and 400 GPa, as depicted in Fig. 1. Moreover, the known structures for Fm-3m and P6<sub>3</sub>/mmc for ScH<sub>3</sub> [28] and P6<sub>3</sub>/m, C2/c and Cmca for H<sub>2</sub> [42] are considered depending on the applied pressures. The solid lines denote the convex hull that connects the lowest energy configurations at given compositions.

As shown in Fig. 1, the formation enthalpies of  $ScH_n$  are initially positive at 100 GPa but decrease rapidly to negative values as the pressure increases. At the higher pressure of 200 GPa, the formation enthalpies show that  $ScH_4$  and  $ScH_6$ become stable relative to  $ScH_3$  and solid  $H_2$ . At 300 GPa, in addition to these two species, another stable stoichiometry of  $ScH_8$  appears in the H-rich regime. The situation is preserved up to 400 GPa. Another interesting trend is that  $ScH_4$  has the highest formation enthalpy among these compounds at 100 GPa and becomes the most stable stoichiometry at 300 GPa.



FIG. 1. Formation enthalpies ( $\Delta$ H, with respect to ScH<sub>3</sub> and H<sub>2</sub>) of ScH<sub>n</sub> (n = 4-8). Data points located on the convex hull (solid lines) represent stable species against any type of decomposition.

Figure 2 displays the pressure-composition phase diagram of the predicted stable  $ScH_n$ . It can be seen that the stable conditions are 159 GPa for ScH<sub>4</sub>, 105 GPa for ScH<sub>6</sub>, and 300 GPa for ScH<sub>8</sub>. It is well known that quantum effects should be carefully considered when dealing with hydrogen atoms. The hydrogen zero-point energy (ZPE) has significantly revised the structural stability as in the case of solid hydrogen and hydrogen-rich materials. To gauge the effects on stability, we also calculated the ZPEs of ScH<sub>4</sub>, ScH<sub>6</sub>, and H<sub>2</sub> in the range of 100–170 GPa using the quasiharmonic approximation. When the ZPE corrections are included, the predicted pressures for the onset of stability are down to 138 GPa for ScH<sub>4</sub> but up to 109 GPa for ScH<sub>6</sub>, as shown in Fig. S1 of the Supplemental Material [43]. Since anharmonic effects become increasingly important at higher temperatures, we recomputed the free energy for  $ScH_n$  within the quasiharmonic approximation at 200 GPa, as shown in Fig. S2 of the Supplemental Material [43]. These calculations, however, showed only minor effects on the stabilities and the distances from the convex hull of ScH<sub>4</sub> and ScH<sub>6</sub> are only increased by a few meV per atom.



FIG. 2. Predicted pressure-composition phase diagram of the Sc-H system.



FIG. 3. Structures of stable Sc-H compounds at high pressures derived from the CALYPSO structure search: (a) and (c) ScH<sub>6</sub> in P6<sub>3</sub>/mmc and Im-3m structures; (b) ScH<sub>4</sub> in the I4/mmm structure; (d) ScH<sub>8</sub> in Immm structure.

The most H-rich stoichiometry under 200 GPa, namely ScH<sub>6</sub>, was predicted to crystallize in a hexagonal structure (space group P6<sub>3</sub>/mmc), consisting of H-sharing 12-fold ScH<sub>12</sub> octahedrons [Fig. 3(a)]. An unusual structural feature of this phase is that the short H-H contact (1.04 Å at 130 GPa) in the octahedron forms a quasimolecular H<sub>2</sub> unit. The electron localization function (ELF) between two H atoms within the H<sub>2</sub> unit is high (~0.87) [Figs. 4(c) and 4(d)], indicating a strong H-H covalent bond. The bader charge analysis shows



FIG. 4. ELF of ScH<sub>4</sub> in the I4/mmm structure at 200 GPa and ScH<sub>6</sub> in the P6<sub>3</sub>/mmc structure at 130 GPa. (a) and (c) Three-dimensional ELF of I4/mmm-ScH<sub>4</sub> and P6<sub>3</sub>/mmc-ScH<sub>6</sub> with isosurface value of 0.5 and 0.7, respectively. (b) and (d) (010) plane of I4/mmm-ScH<sub>4</sub> and P6<sub>3</sub>/mmc-ScH<sub>6</sub>.





FIG. 5. Electronic band structure and PDOS. (a)  $ScH_4$  in I4/mmm structure at 200 GPa. (b)  $ScH_6$  in  $P6_3$ /mmc structure at 130 GPa.

that the H atoms accept a charge of ~0.2*e* per H atom donated by Sc, which results in a longer H-H bond length than that of a free H<sub>2</sub> molecule (0.74 Å). These extra electrons reside in the H<sub>2</sub> antibonding orbital, and thus lengthen the intramolecular bond. The crystal orbital Hamiltonian population (COHP) plots, computed using the LOBSTER package [44], indicate H-H bonding and antibonding states just below the Fermi level (E<sub>f</sub>) in the structure [Fig. S2(a)] of the Supplemental Material [43]. This charge transfer is a prerequisite for forming quasimolecular H units in compressed hydrides, as reported for TeH<sub>4</sub> [45], SnH<sub>4</sub> [46,47], CaH<sub>6</sub> [12], GeH<sub>4</sub> [10]. No electron localization is found between H and Sc in the ELF, indicating the ionic nature of H-Sc bonding.

Upon compression, the P6<sub>3</sub>/mmc structure of ScH<sub>6</sub> transforms into a more energetically favored Im-3m structure at ~325 GPa [Fig. 3(c)]. This is a first-order phase transition, and it illustrates a body-centered cubic structure with hydrogen that forms unusual "sodalite" cages containing enclathrated Sc. This structure was also predicted for CaH<sub>6</sub> [12] and YH<sub>6</sub> [13], in which the quasimolecular H units are absent and they have higher superconducting  $T_c$  than any other hydrides.

The stable ScH<sub>4</sub> has a tetragonal structure (space group I4/mmm) with two formula units per unit cell [Fig. 3(b)]. We found that this structure is the same as tI10-Yh<sub>4</sub> [13] and tI10-CaH<sub>4</sub> [12]. The structure at 200 GPa consists of



FIG. 6. Phonon dispersions. (a) ScH<sub>4</sub> in the I4/mmm structure at 200 GPa. (b) ScH<sub>6</sub> in P6<sub>3</sub>/mmc structure at 130 GPa. (c) ScH<sub>6</sub> in Im-3m structure at 330 GPa. (d) ScH<sub>8</sub> in Immm structure at 300 GPa.

body-centered arranged Sc atom and two nonequivalent H1 and H2 atoms with H1-H2 and H2-H2 distances of 1.40 and 1.22 Å, respectively, which are similar to tI10-YH<sub>4</sub>. Valence electron localization was found between the two neighboring H2 atoms while absent between H1 and H2 atoms [Figs. 4(a) and 4(b)]. This indicates the presence of both molecular H<sub>2</sub> and monoatomic H in ScH<sub>4</sub>.

The next stoichiometry  $ScH_8$  has an Immm structure [Fig. 3(d)], where the coordination number of Sc increases to 28 with formation of H-sharing  $ScH_{28}$ . The structure of  $ScH_8$  at 300 GPa also consists of body-centered arranged Sc atom and two nonequivalent H1 and H2 atoms, but the distances between two H atoms are very short. The corresponding distances are only 0.96, 1.16, and 1.31 Å for H1-H1, H1-H2, and H2-H2, respectively. The COHP plots indicate H-H bonding states in the structure [Fig. S2(b)] of the Supplemental Material [43].

### B. Superconductivity of ScH<sub>n</sub>

The electronic properties, lattice dynamics of all the above stable Sc-H phases have been calculated. These four structures are found to be metals from the band structures and density of states (DOS) presented in Fig. 5 and Fig. S3 of the Supplemental Material [43]. In the energy region around ( $E_f$ ), the DOS of Sc is considerably higher than H in the structures

of I4/mmm-ScH<sub>4</sub> and P6<sub>3</sub>/mmc-ScH<sub>6</sub>, which suggests the dominance of Sc atom contribution to the bands at the  $E_f$ . The total DOS at  $E_f$  (N<sub>F</sub>) of I4/mmm-ScH<sub>4</sub> and P6<sub>3</sub>/mmc-ScH<sub>6</sub> are 0.503 and 0.42 eV<sup>-1</sup> per f.u., respectively. The high DOS at  $E_f$  is a typical feature favoring strong EPC, and thus high- $T_c$  superconductivity. Moreover, the  $E_f$  of I4/mmm-ScH<sub>4</sub> and P6<sub>3</sub>/mmc-ScH<sub>6</sub> fall on the shoulder of the density of states, while the record  $T_c$  in H<sub>3</sub>S [14] is explained to be due to the van Hove singularity close to the  $E_f$ . Therefore doping can be expected to raise N<sub>F</sub> and  $T_c$  values. Figure 6 shows the calculated phonon dispersions. The absence of any imaginary phonon modes prove the dynamical stability of these compounds at high pressure.

To investigate possible superconductivity, the EPC parameter  $\lambda$  and the Eliashberg phonon spectral function  $\alpha^2 F(\omega)$  have been calculated. The calculated EPC parameters  $\lambda$  for ScH<sub>4</sub> at 200 GPa and ScH<sub>6</sub> at 130 GPa are 0.99 and 1.39, respectively. Figure 7 shows the projected phonon DOS, Eliashberg EPC spectral function  $\alpha^2 F(\omega)$  and its integral  $\lambda(\omega)$  for ScH<sub>4</sub> and ScH<sub>6</sub>. For the I4/mmm-ScH<sub>4</sub> [Fig. 7(a)], the low-frequency translational vibrations from the heavy Sc atoms (below 15 THz) contribute 29% of the total  $\lambda$ . The high frequency stretching modes associated with the quasimolecular H<sub>2</sub> units (above 53 THz) contribute 8% to  $\lambda$ . The main contributor to the EPC (63% of  $\lambda$ ) originates from the H-Sc wagging



FIG. 7. Projected phonon density of states (PHDOS), Eliashberg spectral function  $\alpha^2 F(\omega)$  and EPC integration of  $\lambda(\omega)$ . (a) ScH<sub>4</sub> in the I4/mmm structure at 200 GPa. (b) ScH<sub>6</sub> in P6<sub>3</sub>/mmc structure at 130 GPa.

and H-Sc-H bending vibrations (30–53 THz). Similarly, for the P6<sub>3</sub>/mmc-ScH<sub>6</sub> [Fig. 7(b)], the Sc atoms contribute 29% of the total  $\lambda$ . The wagging, bending, and intermediatefrequency modes associated with hydrogen constitute the majority of  $\lambda$  contributions. Compared to some other high  $T_c$  superconducting hydrides, Sc contributes more to  $\lambda$  than other elements, such as Te [45], Y [13], and Ge [48], since Sc is lighter than these elements. This is a strong indication that ScH<sub>4</sub> and ScH<sub>6</sub> will have high superconducting  $T_c$ .

The superconducting  $T_c$  of the predicted stable H-rich compounds are evaluated through the Allen-Dynes [49] modified McMillan equation,

$$T_{c} = \frac{\omega_{\log}}{1.2} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^{*}(1+0.62\lambda)}\right],$$
 (1)

where  $\omega_{\log}$  is the logarithmic average frequency and  $\mu^*$  is the Coulomb pseudopotential. This equation has been found to be highly accurate for materials with  $\lambda < 1.5$ . The  $\omega_{\log}$  are calculated directly from the phonon spectrum, and  $\mu^*$  is often taken as 0.1 for most metals. With these values, the resultant  $T_c$ are calculated to be 119 and 98 K for ScH<sub>6</sub> at 130 GPa and ScH<sub>4</sub> at 200 GPa, respectively. The highest  $T_c$  of ScH<sub>6</sub> is attributed to its strong EPC ( $\lambda = 1.39$ ) and very high  $\omega_{\log}(1162.6 \text{ K})$ .

We also investigated the pressure dependence of the critical transition temperature (Fig. 8). The results show two opposite trends in different phases. The values of  $T_c$  for ScH<sub>4</sub> and ScH<sub>6</sub> decrease with pressure, while ScH<sub>8</sub> shows an increase, even surpasses the Im-3m- ScH<sub>6</sub> at about 350 GPa.

## **IV. CONCLUSION**

In summary, we have employed the evolutionary algorithm CALYPSO in combination with first-principles calculations to



FIG. 8. Superconducting  $T_c$  at different pressures of four phases.

investigate the high pressure crystal structures of the Sc-H system. Three stable stoichiometries:  $ScH_4$ ,  $ScH_6$ , and  $ScH_8$  were identified. Although Sc is isoelectronic with Y, we observe different stoichiometries and stable structures of compressed scandium hydrides compared with yttrium hydrides.

The band structures of the stable phases reveal that they are indeed metallic phases. We also found that these three stoichiometries all have high superconducting  $T_c$ , especially the ScH<sub>6</sub>, with predicted  $T_c$  of up to 129 K at 130 GPa. Moreover, scandium hydrides are good candidates for high  $T_c$  superconductors. We expect that the present theoretical investigation of stable scandium hydrides and their superconducting properties will stimulate future experimental studies on the synthesis of scandium hydrides to probe their high  $T_c$  superconductivity at high pressures.

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