Computational discovery of a dynamically stable cubic SH$_3$-like high-temperature superconductor at 100 GPa via CH$_4$ intercalation

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The 203 K superconductivity of SH$_3$ stimulates enormous interest in searching for high-temperature superconductors in compressed hydrides. While several hydrides show high-temperature superconductivity (>180 K) at extremely high pressure, it is highly desired to design hydrides that can achieve similar superconductivity at relatively lower pressure. In this work we identify a cubic structure in ternary CSH$_7$ that can be viewed as methane (CH$_4$) molecules inserted into the SH$_3$ host lattice as a guest. Ionic bonding in this special host-guest arrangement acts as a chemical precompression for SH$_3$, leading to a much lower predicted dynamically stable pressure of 100 GPa for CSH$_7$ than that of SH$_3$ at 170 GPa. Given the superhigh superconductivity of the parent SH$_3$ sublattice, we performed electron-phonon coupling calculations to estimate the $T_c$ of CSH$_7$ at high pressure, which could reach 181 K at 100 GPa. Our results may shed light on the design principle for other multinary host-guest high-temperature superconducting hydrides with low stable pressure.

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I. INTRODUCTION

Seeking of the room-temperature superconductor is one of the most significant challenges in condensed matter physics. As the lightest element, metallic hydrogen should have the highest vibrational frequency and strong electron-phonon interaction. Thus it is the most likely to become a room-temperature superconductor based on BCS theory [1,2]. Although various theoretical calculations predicted metallic hydrogen to show high superconducting temperature $T_c$ ranging from 100 to 760 K [3–5], the metallization of hydrogen has never been fully confirmed by experiments up to 495 GPa [6,7].

Alternatively, metallic hydrides with high hydrogen content were proposed to be another way to approach high-temperature superconductivity at relatively lower pressure [8,9]. In hydrides, interaction between the nonhydrogen atoms and a hydrogen sublattice acts as a chemical precompression (e.g., SiH$_4$ [9] and LiH$_6$ [10]) making the hydrogen sublattice metallic at pressures much lower than that of solid hydrogen. To this end, many attempts have been made to search high-temperature superconducting hydrides (HTSH) in the past two decades [11–13]. However, not until 2014, the first HTSH SH$_3$ was discovered with a $T_c$ of 203 K at 150 GPa [14–16], which further stimulates the research interests. As a result, including CaH$_6$ [17], YH$_6$ [18–22], YH$_9$ [19,20,22], LaH$_{10}$ [19,20,23,24], CaYH$_{12}$ [25,26], Li$_2$MgH$_{16}$ [27], and other hydrides [11–13], a number of HTSH have been identified, where LaH$_{10}$ shows the highest $T_c$ ever measured of 250–260 K at 170–180 GPa [19,20,23,24]. In addition, advanced materials informatics and machine learning approaches have also been used to predict novel HTSH, and several hydrides with $T_c$ values of about 100 K have been proposed (KScH$_{12}$, GaAsH$_6$, RbH$_{12}$, and CsH$_7$ showing $T_c$ of 122, 98, 115, and 90 K, respectively) [28,29].

Out of all the proposed HTSH, SH$_3$ is very special as it is the only covalent prototype with a $T_c$ higher than 200 K. It crystallizes in a cubic structure (space group: 229, Im$ar{3}$m), where two body-centered cubic [SH$_3$] sublattices interpenetrate with each other [16]. This covalent three-dimensional (3D) network of H only appears in SH$_3$ [15,16] and SeH$_3$ [30,31] for binary hydrides. Due to its uniqueness, many efforts have been devoted to optimizing the superconducting performance of SH$_3$ by substitution or doping [32–43]. For instance, 2.5% of P (S$_0.975$P$_{0.025}$H$_3$) can push the $T_c$ to 280 K at 250 GPa [33]. On another hand, Se substitution [37,39] or replacing partial SH$_6$ octahedron with Xe atoms [36] not only lowers the $T_c$ but also increases the superconducting pressure. While SH$_3$ and some of its derivatives are indeed high-temperature superconductors, the high superconducting pressure is the main obstacle for the practical application of these HTSH. It is an urgent need to design HTSH with similar $T_c$ but much lower superconducting pressure.

Recently, Snider et al. experimentally observed an insulator-metal transition in C-S-H compounds at above

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55 GPa, and discussed these compounds as potential superconductors with high transition temperatures at the APS March Meeting in 2019 [44]. Notably, the detailed composition and structure of C-S-H compounds are not determined. Therefore, investigation of the C-S-H system’s structural evolution is necessary to provide useful complementary information to experimental observation. Here the high-pressure ternary phase diagram of the C-S-H system at 100 GPa is constructed through extensive structural searches via the swarm intelligence-based CALYPSO method [45–47]. In particular, a unique host-guest CSH7 compound has been predicted, where C and H form methane molecules CH4 and insert them into the [SH3] sublattice. Importantly, CSH7 is dynamical stable at pressures as low as 100 GPa. Analysis suggests this might originate from the precompression as the ionic interaction between CH4 and [SH3] sublattice is enhanced when pressure increases. Subsequent electron-phonon coupling calculations indicate this phase is likely to be a high-temperature superconductor with a Tc of 181 K at 100 GPa. Our results indicate that the interaction in the host-guest hydride CSH7 greatly reduces the stable pressure of the [SH3] host lattice, which may act as useful guidance to lower the stable pressure of more high-temperature superconducting hydrides.

II. COMPUTATIONAL DETAILS

Universal variable-composition structure searches for CxSxHy (x = 1 − 4, y = 1 − 4, z = 1 − 36) were performed at 100 GPa with the CALYPSO structure prediction method [45–47], which requires only chemical compositions for given compounds to predict stable or metastable structures at a given pressure, using simulation cells that consist of a maximal number of 50 atoms. To ensure the highest prediction efficiency, the particle swarm optimization (PSO) technology combined with the symmetry constraints on structural generation was used to generate the child structures following the current optimal structure. In total, 330 different compositions, where nearly 400 structures for each stoichiometry have been studied. For 87 compositions with a formation enthalpy (compared to the most competing elements, binaries and ternaries) lower than 100 meV/atom, further fixed-composition structural predictions were conducted until they reached the convergence after we generated 3000 structures per stoichiometry.

The underlying structural relaxation was carried out within the framework of density functional theory as implemented in the Vienna ab initio simulation package (VASP) [48]. The electron-ion interaction was described by projector-augmented-wave (PAW) potentials [49] with the 2s2p2, 3s3p, and 1s1 configurations treated as valence electrons for C, S, and H, respectively. The generalized gradient approximation (GGA) [50] in the scheme of Perdew-Burke-Ernzerhof (PBE) [51] was chosen for the exchange-correlation functional, and kinetic cutoff energy of 800 eV and Monkhorst-Pack k meshes with grid spacing of 0.20 Å−1 were then adopted to ensure a satisfactory degree of convergence was achieved. Iterative relaxation of atomic positions was stopped when the forces generally acting on the atoms were found to be smaller than 0.01 eV/Å. With this criterion, the change in total energy between successive steps was less than 0.01 meV/cell. The electron localization function (ELF) [52] was used to describe and visualize chemical bonds in molecules and solids. Mulliken population charges [53] were calculated using CASTEP code [54].

Phonon calculations were carried out by using the supercell approach [55] as implemented in the PHONOPY [56], which showed a good agreement with those computed using the Quantum-ESPRESSO [57] and the computational settings described below. Lattice-dynamical and superconducting properties were estimated using density functional perturbation theory (DFPT) [58], performed with the Quantum-ESPRESSO code. Ultrasoft pseudopotentials [59] were used with a kinetic energy cutoff of 100 Ry and the charge density is integrated on a Γ-centered 12 × 12 × 12 k-point mesh. A Methfessel-Paxon first-order smearing of 0.02 Ry was applied. The first-order potential perturbation and dynamical matrices were calculated using DFPT on an irreducible 3 × 3 × 3 Γ-centered q-point mesh.

Electron-phonon couplings (EPC) constant λ, ωbg, and Tc are solved using the ELK code [60]. Tc are estimated using both the standard Allen-Dynes modified McMillan equation [61] and the Migdal-Eliashberg theory [62–64], and the latter approach gives us the superconducting gap as a function of temperature. The highest temperature for which the superconducting gap value is nonzero defines the critical temperature Tc.

III. RESULTS AND DISCUSSION

Based on the results from the variable-composition structure searches, we constructed the ternary phase diagram of C-S-H as presented in Fig. 1(a). With the higher H content, the compound is found to be more stable, but none of the ternary C-S-H compounds are thermodynamically stable, indicating the ternaries tend to decompose into elements and binaries under certain conditions [16,65–68]. In previous high-throughput material discovery studies, the convention for the threshold between semistable (likely to be synthesized) and unstable (unlikely to be synthesized) compounds is 50 meV/atom [69]. The same convention was adopted in this work. Therefore, metastable ternary C-S-H compounds cannot be precluded. Some possible formation routes to C-S-H ternaries are provided in Table S1 [70] as a candidate reference for experimental synthesis.

Analysis shows there are 44 ternaries with formation enthalpy lower than 50 meV/atom (see the structural parameters of these compounds in Table S3). In these compounds, C atoms always form CH4 molecules with H atoms. Meanwhile, the coordination number of S is varied from 2 to 6, resulting in different S-H sublattices with distinctive structural features. As the coordination number increases, the S-H sublattice evolves from zero-dimensional (0D) SH2 molecules, to onedimensional (1D) S-H chains, then to two-dimensional (2D) S-H planes, and finally become three-dimensional (3D) S-H covalent networks [as shown in Figs. 1(b) and S1]. Except for CH4 and the S-H sublattice, we also find the existence of H2-like molecules with a bond length of about 0.75 Å in some C-S-H ternaries.

Previous studies have shown that hydrides containing 3D covalent networks may have relatively high Tc [11–13]. Thus,
FIG. 1. (a) Calculated stability of the C-S-H system at 100 GPa. Colored squares denote metastable phases with different formation enthalpies. Purple circles indicate stable phases. (b) Bonding behavior and band gap of C-S-H ternary compounds with formation enthalpies below 50 meV/atom at 100 GPa. Colored triangles, squares, pentagons, and hexagons represent different configurations of the S-H sublattice, respectively. Compounds in red or blue are metallic or nonmetallic.

CSH$_7$, CS$_2$H$_{20}$, and CS$_3$H$_{24}$ with 3D [SH$_3$], [S$_2$H$_4$], and [S$_3$H$_6$] covalent networks [Figs. 2(a), S2, and S3] caught our attention. At 100 GPa, CSH$_7$ crystallizes in a highly symmetrical body-centered cubic structure (space group: $I\bar{4}3m$). CSH$_7$ only consists of two parts, CH$_4$ molecules and the [SH$_3$] sublattice with six-coordinated S, where the latter is identical to the [SH$_3$] sublattice in $Im\bar{3}m$-SH$_3$ [15,16] except for the symmetric S-H bonds. Interestingly, each methane molecule

![Image](image1.png)

FIG. 2. Conventional cells of (a) $I\bar{4}3m$-CSH$_7$, (b) $Im\bar{3}m$-SH$_3$, and (c) $Pm\bar{3}m$-XeSH$_3$. The large, medium, and small spheres represent the Xe, S, and H atoms, respectively, and the translucent regular tetrahedrons represent the CH$_4$ molecules. Purple lattices represent the [SH$_3$] host lattice in a unit. (d) ELF in (1 1 0) direction for $I\bar{4}3m$-CSH$_7$ (left panel) at 100 GPa, $Im\bar{3}m$-SH$_3$ (middle panel) at 200 GPa, and $Pm\bar{3}m$-XeSH$_3$ (right panel) at 100 GPa. Black dotted lines represent the ionic bonds between the host [SH$_3$] lattice and the guest CH$_4$ molecules in $I\bar{4}3m$-CSH$_7$. 

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sits in the center of the interstitial space in CSH$_7$. Therefore, it can be viewed as a host-guest structure. Small charge transfer from [SH$_3$] host to CH$_4$ guest was observed as derived from Mulliken population analyses [53] (Fig. S4), which generates negatively charged CH$_4$ molecules and positively charged [SH$_3$] framework. An ionic bond between these two oppositely charged ions is represented with the black dotted line in Fig. 2(a). This charge transfer increases with pressure, indicating an enhanced ionic interaction between host and guest sublattices.

Alternatively, S atoms in CS$_2$H$_{20}$ and CS$_3$H$_{24}$ form covalent bond with four nearby H atoms, resulting in an [S$_2$H$_4$] and [S$_3$H$_6$] 3D covalent network, respectively, by sharing H atoms. Besides CH$_4$, H$_2$ molecules are also found within the 3D covalent networks. Consequently, in a similar manner to CSH$_7$, CS$_2$H$_{20}$ and CS$_3$H$_{24}$ can be regarded as CH$_4$[S$_2$H$_4$](H$_2$)$_6$ and CH$_4$[S$_3$H$_6$](H$_2$)$_7$, respectively. Although the 3D covalent network itself may correspond to high superconductivity, H$_2$ molecules are not conducive and hydrides with H$_2$ usually show low superconducting temperature [11,12,17,20,27]. The calculation of the electronic band structures confirms that CS$_2$H$_{20}$ and CS$_3$H$_{24}$ with H$_2$ molecules exhibit nonmetallic characteristics with large band gaps of 1.65 and 1.55 eV at 100 GPa, respectively [as shown in Fig. 1(b)]. We then focus our investigation on CSH$_7$.

Lattice dynamics simulation shows that CSH$_7$ and SH$_3$ will theoretically lose their dynamically stability at pressures of <100 and <170 GPa, respectively (Figs. S5 and S6). As both CSH$_7$ and SH$_3$ are mainly consisting of an [SH$_3$] sublattice, this indicates the intercalation of CH$_4$ molecules might stabilize an [SH$_3$] sublattice at a much lower pressure than that of two self-nesting [SH$_3$][SH$_3$] sublattices. We have to mention that previous work has also reported on the intercalation of Xe into an [SH$_3$] sublattice [Pm$3m$-XeSH$_3$, Fig. 2(c)] [36]. However, XeSH$_3$ only becomes stable at pressures higher than 240 GPa.

To explore why CSH$_7$, SH$_3$, and XeSH$_3$ have the same S-H framework but with different stable pressures, we analyzed the interaction between atoms via the electron localization function (ELF) [52]. At high pressure it is clear that the ELF value between S and H atoms is larger than 0.75 in all three [SH$_3$] sublattices confirming their covalent nature [Figs. 2(d)–2(f)]. The ELF is around 0.3 between CH$_4$ and [SH$_3$] lattice in CSH$_7$, which is a typical value for ionic bonds [dashed lines in Fig. 2(d)]. In contrast, the ELF is close to 0 between the two sublattices in SH$_3$ and XeSH$_3$, implying a weak chemical interaction. Analysis of electron charge density [Fig. S7(a)] further confirms the different host-guest interactions among these three compounds as it shows similar behavior to the ELF. Noteworthy, at lower pressure, such as 0 GPa, the ELF turns to be close to 0 between CH$_4$ and [SH$_3$] lattice in CSH$_7$ [Fig. S7(c)], indicating a weakened host-guest interaction. This interaction exists between one of the H atoms of the CH$_4$ molecule and the apex or body-center S atom of the [SH$_3$] lattice, that is, the host-guest interaction is anisotropic. Though weakened at lower pressure, chemical interaction between CH$_4$ and [SH$_3$] greatly affects the [SH$_3$] lattice due to its anisotropic character. For instance, H atoms are all symmetrically located between every two S atoms in SH$_3$ and XeSH$_3$ and the S-H bond length is uniformly distributed. While some H atoms were driven away from their symmetric positions to asymmetric ones in CSH$_7$ due to the anisotropic interaction, resulting in three different S-H bond lengths ($r_1$, $r_2$, and $r_3$) in Fig. 2(a), especially at 0 GPa (Fig. S8). Upon compression, combined with the pressure-enhancing host-guest ionic interaction, the length of S-H bonds in CSH$_7$ reduces faster than that in the other two compounds (Fig. S8), thus, the volume of [SH$_3$] sublattice in CSH$_7$ also shrinks faster and becomes the smallest one when pressure is higher than 56 GPa (Fig. S9). A smaller volume means a smaller PV term under high pressure which in turn means a lower enthalpy. Thus, the predicted different dynamical stable pressure of CSH$_7$, SH$_3$, and XeSH$_3$ might be accounting for the different interaction behaviors, and introducing of the host-guest ionic interactions could be a way to precompress the host hydrides to lower its stable pressure.

Next, we compared the electronic band structures and projected density of states (PDOS) of CSH$_7$ at 120 GPa and (b) $Im3m$-SH$_3$ at 200 GPa.

FIG. 3. Electronic band structure (left panel) and projected density of states (right panel) of (a) $I\bar{A}3m$-CSH$_7$ at 120 GPa and (b) $Im3m$-SH$_3$ at 200 GPa.

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The flat band–steep band scenario, which has been suggested to be a favorable condition for the occurrence of superconductivity [71]. Therefore, CSH₇ has a large possibility to be superconductive. Moreover, for the reason that $N(E_F)$ of CSH₇ is comparable to that of SH₃, CSH₇ is expected to be a high-temperature superconductor similar to SH₃.

We further investigated the pressure-dependent superconducting properties of CSH₇, in comparison with SH₃ and XeSH₃ (Fig. 4). $T_c$ of SH₃ has been experimentally observed [15] while half-filled squares, circles, and stars indicate theoretical results of $I43m$-CSH₇ in this work, $Im3m$-SH₃ reported by Huang et al. [72], and $Pm3m$-XeSH₃ reported by Li et al. [36], respectively.

FIG. 4. Pressure dependence of $T_c$ in sulfur hydride. Filled circles show experimental results reported by Drozdov et al. [15] while half-filled squares, circles, and stars indicate theoretical results of $I43m$-CSH₇ in this work, $Im3m$-SH₃ reported by Huang et al. [72], and $Pm3m$-XeSH₃ reported by Li et al. [36], respectively.

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IV. CONCLUSION

In summary, we have extensively explored the phase diagram of the C-S-H system at 100 GPa. A unique $I43m$-CSH₇ host-guest hydride with CH₄ guest molecules and [SH₃] host lattice has been identified. CSH₇ is dynamically stable at 100 GPa where the pressure is much lower than that of $Im3m$-SH₃ (170 GPa) with similar [SH₃] sublattices. Analysis shows ionic interactions between host and guest lattices may induce chemical precompression and, thus, lower the stable pressure. Calculations suggest CSH₇ is also a high-temperature superconductor with $T_c$ up to 181 K at 100 GPa, where the [SH₃] host lattice mainly contributes to the superconductivity. Our current results show it is possible to reduce the dynamical stable pressure of high superconducting SH₃ with the intercalation of interacting guest molecules, and may also shed light on the high-pressure experimental findings.

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