A Little Bit of Carbon Can do a Lot for Superconductivity in H₃S

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Abstract

Recently, room temperature superconductivity was measured in a carbonaceous sulfur hydride material whose identity remains unknown. Herein, first-principles calculations are performed to provide a chemical basis for structural candidates derived by doping H₃S with low levels of carbon. Pressure stabilizes unusual bonding configurations about the carbon atoms, which can be six-fold coordinated as CH₆ entities within the cubic H₃S framework, or four-fold coordinated as methane intercalated into the H-S lattice, with or without an additional hydrogen in the framework. The doping breaks degenerate bands, lowering the density of states at the Fermi level (N_F), and localizing electrons in C-H bonds. Low levels of CH₄ doping do not increase N_F to values as high as those calculated for Im3m-H₃S, but they yield a larger logarithmic average phonon frequency, and an electron-phonon coupling parameter comparable to that of R3m-H₃S. The implications of carbon doping on the superconducting properties are discussed.

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Introduction

The decades old quest for a room-temperature superconductor has recently come to fruition. Inspired by Ashcroft’s predictions that hydrogen-rich compounds metallized under pressure could be phonon-mediated high-temperature superconductors, synergy between experiment and theory has led to remarkable progress. A superconducting critical temperature, $T_c$, of 203 K near 150 GPa was reported for $\text{H}_3\text{S}_6$, followed by a $T_c$ of 260 K near 200 GPa in $\text{LaH}_{10}$. Recently, a carbonaceous sulfur hydride superconductor with a measured $T_c$ of 288 K at 267 GPa was discovered, but many questions remain unanswered about this material. Perhaps the most pressing of these questions is: “What is the composition and structure of the phase, or phases, responsible for the remarkably high $T_c$?” Recent x-ray diffraction (XRD) studies suggest the material is derived from the $\text{Al}_2\text{Cu}$ structure type up to 180 GPa, but its evolution upon further compression where the $T_c$ is highest has not yet been determined experimentally. The reported $T_c$ versus pressure shows evidence for a transition near 200 GPa, although the scatter in the data are consistent with a continuous change in $T_c$. On the other hand, the XRD results suggest that this change in $T_c$ could arise from the collapse of the observed lower symmetry orthorhombic to higher symmetry superconducting phases.

To understand the nature of carbonaceous sulfur hydride, it is useful to review the work leading to the discovery of the initial high-$T_c$ $\text{H}_3\text{S}$ superconductor. Synthesis of novel (H$_2$S)$_2$H$_2$ van der Waals compounds at pressures up to 40 GPa inspired the computational search for additional H-S phases that might be stable and potentially superconducting at megabar pressures. An $\text{Im}\bar{3}m$ symmetry $\text{H}_3\text{S}$ phase, which can be described as a body centered cubic sulfur lattice with H atoms lying midway between adjacent S atoms ($T_c=191-204$ K at 200 GPa), was predicted to be stable above 180 GPa. An analogous lower-symmetry $\text{R}3\text{m}$ phase with asymmetric H-S bonds was preferred at pressures down to 110 GPa ($T_c=155-166$ K at 130 GPa). Experiments on the H-S system confirmed the maximum $T_c$ (203 K) near the expected pressures (155 GPa), leading to the proposal that the synthesized structure was the predicted $\text{Im}\bar{3}m$ phase. Subsequently XRD measurements largely confirmed the predicted cubic structure. However, the synthesis conditions were found to dictate the product that formed, and $T_c$s as low as 33 K were measured. Thus, reproducing the synthesis of the cubic phase proved difficult, and more recently altogether new structures have been reported.

These observations suggest that a number of $\text{H}_x\text{S}_y$ superconductors can be made. Indeed, additional peaks observed in XRD measurements have been assigned to possible secondary phases. Various stoichiometries including $\text{H}_2\text{S}$, $\text{HS}_2$, $\text{H}_4\text{S}_3$, and $\text{H}_5\text{S}_2$ have been proposed for materials with lower $T_c$s. Exotic Magnéli phases with $\text{H}_2\text{S}_{1-x}$ ($2/3 < x < 3/4$) compositions characterized by alternating $\text{H}_2\text{S}$ and $\text{H}_3\text{S}$ regions with a long modulation whose ratio can be varied to tune the $T_c$ have also been proposed. First-principles calculations suggested that $\text{H}_2\text{S}$ self-ionizes under pressure forming a $\text{(SH}^-)(\text{H}_3\text{S})^+$ perovskite-type structure that may undergo further deformations to a complex modulated phase. A $Z = 24$ $\text{R}3\text{m}$ symmetry phase whose density of states (DOS) at the Fermi level ($E_F$) was predicted to be lower than that of $\text{R}3\text{m}$ and $\text{Im}\bar{3}m$ $\text{H}_3\text{S}$ was computed to be more stable than these two phases between 110-165 GPa. The role
of quantum nuclear and anharmonic effects on the $R3m \rightarrow Im\bar{3}m$ transition and $T_c$ has been investigated\textsuperscript{30,31}, as has the response of the Fermi surface to uniaxial strain\textsuperscript{32}.

Turning to the C-S-H ternary, initial crystal structure prediction calculations conducted prior to the discovery of the carbonaceous sulfur hydride superconductor considered stoichiometric $C_xS_yH_z$ compositions with relatively high carbon dopings\textsuperscript{33,34}. These studies identified metastable CSH\textsubscript{7} structures that were based on the intercalation of methane into an H\textsubscript{3}S framework, with maximum $T_c$s estimated to be 194 K at 150 GPa\textsuperscript{33} and 181 K at 100 GPa\textsuperscript{34}. However, the measured structural parameters, $P-V$ equations of state\textsuperscript{11}, and the variation of $T_c$ versus pressure\textsuperscript{9} do not match those calculated for these hydride perovskite-like materials. First-principles calculations employing the virtual crystal approximation (VCA) predicted that remarkably low-level hole-doping resulting from the incorporation of carbon in the parent H\textsubscript{3}S phase (i.e. C\textsubscript{0.038}S\textsubscript{0.962}H\textsubscript{3}) could increase the $T_c$ up to 288 K\textsuperscript{35,36}. It was argued that doping tunes the position of $E_F$, moving it closer to the maximum in the DOS that arises from the presence of two van Hove singularities (vHs). Because vHs increase the number of states that can participate in the electron-phonon-coupling (EPC) mechanism, this effect is known in general to enhance the total coupling strength, $\lambda$, and in turn the $T_c$ in conventional superconductors. The role that the vHs play in increasing the $T_c$ in H\textsubscript{3}S has been studied in detail\textsuperscript{37–40}.

Despite the striking success of the VCA model in reproducing theoretically the very high $T_c$ measured for the C-S-H superconductor\textsuperscript{35}, this approach does not take into account the effect of the doping on the local structure and electronic properties, and its limitations have been discussed\textsuperscript{41,42}. To overcome these limitations we systematically study the role of doping on the thermodynamic and dynamic stability, electronic structure, and geometric properties of phases with doping levels as low as 1.85%. Three types of substitutions are considered involving S replaced by C, together with different numbers of hydrogens, yielding either six-fold or four-fold coordinate carbon atoms. We find that CH\textsubscript{6} and CH\textsubscript{4} form stable configurations within the dense solid in phases that are dynamically stable at the pressures studied experimentally. Moreover, doping decreases the DOS at $E_F$ because it breaks degeneracies and localizes electrons in C-H bonds. Our results illustrate that the rigid band model does not reliably predict the superconducting properties of the doped phases. Finally, the descriptors associated with superconductivity, such as the DOS at $E_F$ and the logarithmic average phonon frequency are used to identify the C-S-H phase likely to possess the highest $T_c$.

Results and Discussion

Octahedrally Coordinated Carbon in $C_xS_{1-x}H_3$ Phases

To investigate how different levels of doping affect the kinetic and thermodynamic stability, electronic structure, and superconducting properties of H\textsubscript{3}S, we constructed supercells of the $Im\bar{3}m$ structure where one of the sulfur atoms was replaced by carbon. Calculations were carried out at 270 GPa with $C_xS_{1-x}H_3$ stoichiometries and two different types of coordination environments around the dopant atom were considered. In the first the carbon atom was octahedrally coordinated by six hydrogen atoms, and in the second two of these
Figure 1: (a) Optimized geometry and (b,c) electron localization function (ELF) contour plot of C_{0.0625}S_{0.9375}H_{3} (O_{h}-CS_{15}H_{48}, space group Pm\bar{3}m), where the carbon atom is octahedrally coordinated by hydrogen atoms at 270 GPa. The plane of the contour passes through (b) CH_{6} and (c) H_{3}S, and the range of the isovalue is from 0.5 (blue/cold) to 1.0 (red/warm). The atoms through which the plane passes are labelled. (d) The following electron density difference: \( \rho(CH_{6}) + \rho(S_{15}H_{48}) - \rho(CS_{15}H_{48}) \) where red denotes a loss of charge and green a gain of charge (isovalue=0.005). Sulfur/carbon/hydrogen atoms are yellow/black/white and select geometric parameters are provided.

C-H bonds broke resulting in a quasi-tetrahedral CH_{4} molecule. A detailed analysis was carried out on the C_{0.0625}S_{0.9375}H_{3} (CS_{15}H_{48}) stoichiometry at 270 GPa because both geometries were dynamically stable at this pressure (Figure S2d, S10c), and because this unit cell size pushes the limits of the phonon and EPC calculations.

The calculated C-H distance in the octahedrally coordinated phase, which we refer to as O_{h}-CS_{15}H_{48} (Figure 1a), measures 1.17 \( \AA \). The negative of the crystal orbital Hamilton population integrated to the Fermi level (-iCOHP), which can be used to quantify the bond strength, is calculated to be 5.11 eV for this bond. The distance between the hydrogen atom bonded to carbon and its nearest neighbor sulfur (1.71 \( \AA \)), is significantly larger than the H-S distance found in Im\bar{3}m H_{3}S at this pressure (1.45 \( \AA \)). The weakening of the CH-S bond upon doping is evident in the -iCOHP, which decreases from 3.74 eV/bond (in H_{3}S) to 2.00 eV/bond. Despite the non-negligible -iCOHPs between the hydrogen atoms bonded to carbon and the nearest neighbor sulfur atoms, the ELF (Figure 1b,c) does not show any evidence of covalent CH-S bond formation. The integrated crystal orbital bond index
(iCOBI), which is a quantification of the extent of covalent bond formation \[^{43}\] is calculated to be 0.34 for each S-H bond in H\(_3\)S, indicating a bond order of roughly 1/3. Substituting C in an octahedral coordination environment leaves the S-H iCOBI essentially unchanged for bonds distant from the C substitution site, but for CH-S bonds the iCOBI drops to 0.21, showing the weakening of this bond. Practically no antibonding states are filled in the S-H interaction with H coordinating C (Figure S6), but the increased S-H distance leads to an overall decrease in the magnitude of the iCOBI. The C-H bonds in the octahedral CH\(_6\) motif possess the largest iCOBI in the system, 0.51. Subtracting the charge density of the CS\(_{15}\)H\(_{48}\) structure from a sum of the density arising from the neutral CH\(_6\) molecule and the neutral H-S framework (Figure [I]) illustrates that charge is transferred from the CH\(_6\) unit into the nearest neighbor sulfur lone pairs, which can also be seen in the ELF plot (Figure [I]). A Bader analysis, which typically underestimates the formal charge, yields a +0.25 charge on CH\(_6\), indicating that charge redistribution is associated with stabilization of this configuration in the dense structure.

An analysis using the reversed approximation Molecular Orbital (raMO) method, which uses linear combinations of the occupied crystal orbitals of the system to reproduce target orbitals, revealed substantial bonding interactions within the CH\(_6\) cluster. The reproduced s orbital on the hydrogen atom in this motif contained electron density with p-orbital symmetry on the neighboring C atom, indicative of sp bonding. Similarly, the reproduced s orbital on C strongly interacted with the surrounding H atoms, which is evident in its anisotropy as comparison to the more isotropic sulfur s orbital reproductions (Figure S7).

Theoretical considerations have been key in designing ways to stabilize four-coordinate carbon in novel bonding configurations such as planar tetracoordinate carbon \[^{44};^{45}\]. While a wide variety of molecular compounds containing coordination numbers surpassing four, such as carbocations, carboranes, organometallics, and carbon clusters, are also known \[^{46};^{47}\], octahedrally coordinated carbon is quite unusual. Examples include elemental carbon, which has been predicted to become six-fold coordination at terapascal pressures \[^{48};^{49}\], and high pressure Si-C compounds such as rock-salt SiC\(_{15}\)H\(_{48}\), and two predicted Si\(_3\)C phases \[^{52}\]. More relevant to the C-S-H system are carbon atoms bonded to more than four hydrogen atoms such as the nonclassical carbocation, C\(_s\)-CH\(_2^+\). It can be viewed as a proton inserted into one of the \(\sigma\) C-H bonds within methane, forming a three-center two-electron (3c-2e) bond between one carbon and two hydrogen atoms \[^{53}\]. \textit{Ab initio} calculations for the isolated molecule have shown that the minimum energy configuration for the di-carbocation, CH\(_2^+\), possesses \(C_{2v}\) symmetry with two long 3c-2e and two short classic 2c-2e bonds, rather than the \(O_h\) symmetry CH\(_2^+\) geometry \[^{54};^{55}\]. Following one of the triply degenerate imaginary normal modes, which can be described as a wagging motion along the three sets of H-C-H 180° angles in the octahedron, leads to the \(C_{2v}\) minimum. Turning now to hypercoordinated carbon atom in the \(O_h\)-CS\(_{15}\)H\(_{48}\) model structure, explicit calculation of the phonons at the \(\Gamma\) point reveals that in the solid state the frequency of this same triply degenerate mode is real (calculated frequency of 1712 cm\(^{-1}\)), and the vibration is coupled with the motions of the hydrogens in the H\(_3\)S lattice. Thus, the stabilization of the octahedral molecular complex is facilitated by weak interactions with the host lattice. Notably, the calculated C-H bond length in CH\(_2^+\) obtained at the HF/6-311+G(2d,p) level of theory, is nearly identical to that of
That the carbon weakly interacts with the host lattice is supported by calculations where the carbon (or sulfur) is replaced with neon. The optimized $O_h$-$NeS_{15}H_{48}$ structure is dynamically stable at these pressures, with a calculated Ne-H distance of 1.37 Å (Figure S30).

**Quasi-Tetrahedrally Coordinated Carbon in C$_x$S$_{1-x}$H$_3$ Phases**

When placed in a cube a tetrahedral methane molecule can retain its symmetry only if its hydrogens point toward four corners of the cube. In the phases studied here such an orientation introduces unfavorable steric interactions, and a lower enthalpy can be obtained when the hydrogens point towards four cube faces instead. Because of this the four coordinate CH$_4$ species within the phase we refer to as $T_d$-$CS_{15}H_{48}$ actually possesses $C_2v$ symmetry. As illustrated in Figure 2a, at 270 GPa its two C-H bond lengths are nearly identical with calculated -iCOHPs of 6.34 and 6.30 eV/bond. The H-S distances between two of the hydrogens bonded to carbon elongate to 1.73 Å, and a further two to 1.91 Å. At the same time two of the S-H bonds contract relative to those within $Im\bar{3}m$ H$_3$S (1.34 Å). The encapsulated methane molecule possesses H-C-H angles that deviate from the ideal tetrahedral angle (100°, 103° and 140°), and its Bader charge, -0.09, is suggestive of electron donation from the H-S lattice. Plots of the ELF (Figure 2b) clearly illustrate the C-H bond, but do not show any evidence of covalent bond formation between CH$_4$ and the H-S framework. Thus, two H-S and four C-H bonds per unit cell in $T_d$-$CS_{15}H_{48}$ become classical 2c-2e bonds, no longer participating in delocalized multi-centered bonding as they would within H$_3$S.

![Figure 2](image.png)

**Figure 2:** (a) Optimized geometry and (b) electron localization function (ELF; isovalue=0.8) of the CH$_4$-based C$_{0.0625}S_{0.9375}$H$_3$ ($T_d$-$CS_{15}H_{48}$, space group $Amm2$) in which the carbon atom is quasi-tetrahedrally coordinated by hydrogen atoms at 270 GPa. Sulfur/carbon/hydrogen atoms are yellow/black/white and select geometric parameters are provided.
Properties of the S $\rightarrow$ C Doped Phases at 270 GPa

Our calculations find the DOS at the Fermi level, $N_F$, in H$_3$S to be 0.050 states eV$^{-1}$Å$^{-3}$ at 270 GPa. Moving $E_F$ down in energy by 0.17 eV, which can be achieved by doping with $\sim$5.7% C, yields the highest possible value of 0.055 states eV$^{-1}$Å$^{-3}$. Given a reference material whose superconducting critical temperature, $T_c^0$, is known, the approximate Bardeen-Cooper-Schrieffer formula can be employed to estimate the $T_c$ of a similar material via the formula $T_c = 1.13\Theta_D(T_c^0/1.13\Theta_D^0)^{N_F^0/N_F}$, where $\Theta_D$ is the Debye temperature and $N_F$ is given per unit volume. Using the measured value of $T_c^0 = 170$ K at 270 GPa for Im$\bar{3}$m H$_3$S, this simple model predicts the $T_c$ to increase to 208 K for $\sim$5.7% C doping, which is somewhat lower than the results obtained using the VCA at the same pressure and doping level.

To study the effect of doping on the electronic structure, we performed a single point calculation on an unrelaxed $2 \times 2 \times 2$ supercell of Im$\bar{3}$m H$_3$S where a single sulfur atom was replaced by carbon. In contrast to the VCA model predictions we found that $N_F$ decreases to 0.048 states eV$^{-1}$Å$^{-3}$. Structural relaxation to the $O_h$- and $T_d$-CS$_{15}$H$_{48}$ phases further lowers $N_F$ to 0.040 and 0.033 states eV$^{-1}$Å$^{-3}$, respectively, as illustrated in Figure 3. This initially counter-intuitive behavior of $N_F$ can be understood by considering the following: replacing sulfur by carbon followed by structural relaxation decreases the number of degenerate bands near $E_F$ because some of the metallic electrons that were delocalized in the H$_3$S framework now become localized in covalent C-H bonds. Whereas 14 bands (some of which are degenerate) cross $E_F - 0.17$ eV in Im$\bar{3}$m H$_3$S at 270 GPa, only 11 bands intersect with the Fermi level within both $O_h$- and $T_d$-CS$_{15}$H$_{48}$ (Figure 3a-3c).

![Figure 3: Band structure at 270 GPa for (a) Im$\bar{3}$m H$_3$S in a $2 \times 2 \times 2$ supercell of the standard conventional lattice, (b) Pm$\bar{3}$m $O_h$-CS$_{15}$H$_{48}$, and (c) Amm2 $T_d$-CS$_{15}$H$_{48}$. To compare the band structures of the three phases, which all possess different space-groups, simple cubic symmetry is assumed and the high symmetry special points used are $\Gamma$ (0,0,0), $X$ (0.5,0,0), $M$ (0.5,0.5,0) and $R$ (0.5,0.5,0.5). (d) Densities of states of these phases where CH$_6$ denotes CS$_{15}$H$_{48}$ with hexacoordinate carbon and CH$_4$ with tetracoordinate carbon. The black horizontal dashed line denotes $E_F$ and the red dashed line $E_F - 0.17$ eV, which corresponds to the top of the peak in the DOS in Im$\bar{3}$m H$_3$S.](image-url)
We also investigated how the vibrational properties of $Im\bar{3}m$ H$_3$S are affected by carbon doping. The Debye temperature of the phase in which carbon is four-coordinate is larger than that containing six-coordinated carbon, which is higher than that of pure H$_3$S (Figure S24). The frequencies of the asymmetric H-C-H stretching modes of $T_d$-CS$_{15}$H$_{48}$ were calculated to be 3125 and 3286 cm$^{-1}$, whereas the symmetric ones occurred at 3140 and 3173 cm$^{-1}$. $O_h$-CS$_{15}$H$_{48}$ possessed a single C-H stretching mode at 2358 cm$^{-1}$. Because the quasi-molecular CH$_4$ species has stronger and shorter C-H bonds as compared to the octahedrally coordinated carbon, these vibrations are found at higher frequencies.

$C_xS_{1-x}H_3$ Phases as a Function of Doping and Pressure

We now consider the dynamic stability of the C$_x$S$_{1-x}$H$_3$ stoichiometries as a function of doping at 270 GPa, beginning with phases where carbon is octahedrally coordinated. Both the H-S and H-C bond lengths in the 50% doped dynamically unstable CSH$_6$ structure measured 1.37 Å. A majority of the phonon modes that were imaginary at some point within the Brillouin Zone (BZ) turned out to be related to the motions of the hydrogen atoms bonded to carbon. Decreasing the doping level to 25% allowed the C-H and S-H bonds to assume different values (1.08 Å and 1.41-1.44 Å, respectively). As a result, some of the imaginary modes in the 50% doped structure become real, specifically the asymmetric and symmetric H-C-H stretching modes found near ∼2700 and 2500 cm$^{-1}$, respectively. Lowering the doping level left a single imaginary phonon mode throughout the whole BZ. This mode arose from the movement of a hydrogen atom sandwiched between two carbons that led to the lengthening of one, and contraction of another C-H bond that measured 1.43 Å in the optimized geometry. The other C-H bond in this structure measured 1.13 Å. Thus, the structural instability is a result of the too-long C-H bonds that arise because of the constraints imposed by the doping level and S-H lattice.

The $O_h$-CS$_{15}$H$_{48}$ phase possesses the stoichiometry with the lowest percentage doping that is a local minimum at 270 GPa. Phonon calculations showed this structure becomes dynamically unstable below 255 GPa (Figure S4). Visualization of one of the triply degenerate imaginary modes at Γ revealed that it can be described as a lengthening/contraction of the CH-S distance, which measured 1.73 Å in the optimized structure, with the other two modes corresponding to the same vibration but along the other crystallographic axes. Upon decreasing pressure from 270 to 240 GPa the C-H bond length increased minimally ($\Delta d = 0.005$ Å, -ΔiCOHP = 0.02 eV/bond), whereas the increase in the CH-S distance was an order of magnitude larger ($\Delta d = 0.03$ Å, -ΔiCOHP = 0.10 eV/bond). These results suggest that the instability that emerges near 255 GPa is primarily a result of decreased S-H interaction at lower pressures.

We also consider $O_h$-CS$_{53}$H$_{162}$, which corresponds to 1.85% doping, with calculated C-H bond lengths of 1.16 Å and S-H bonds ranging from 1.43-1.48 Å. Unsurprisingly, its DOS at $E_F$ of 0.0484 states eV$^{-1}$Å$^{-3}$ and Debye temperature of 1375 K approach the values obtained for $Im\bar{3}m$ H$_3$S. Phonon calculations revealed that this phase was dynamically stable at 270 GPa, and it could be stabilized to lower pressures than $O_h$-CS$_{15}$H$_{48}$, becoming unstable at approximately 160 GPa. The structures that possess four-coordinated carbon atoms are found to be dynamically stable at 270 GPa when the doping level was less
than 25% (CS$_3$H$_{12}$, CS$_7$H$_{24}$, CS$_{15}$H$_{48}$ and CS$_{53}$H$_{162}$). CS$_3$H$_{12}$ was unstable by 140 GPa and visualization of the largest magnitude imaginary mode found at the $R$ point illustrated that it corresponded to a symmetric/asymmetric H-S-H stretch. CS$_{15}$H$_{48}$ and CS$_{15}$H$_{48}$ became dynamically unstable near 250 GPa via a softening of the longitudinal acoustic mode at an off Γ point, and $T_d$-CS$_{53}$H$_{162}$ was stable (unstable) at 200 (160) GPa.

**C$_x$S$_{1-x}$H$_{3+x}$ Phases: Doping H$_3$S via Substituting SH$_3$ by CH$_4$**

Instead of replacing a fraction of the S atoms by C atoms, another way to dope H$_3$S would be to replace some of the SH$_3$ units by CH$_4$ in a large supercell. Indeed, XRD and equation of state analysis show that the precursor phases of the C-S-H superconductor are (H$_2$S)$_2$H$_2$ and (CH$_4$)$_2$H$_2$ van der Waals compounds that have identical volumes at the synthesis pressure, thereby allowing readily mixed (H$_2$S,CH$_4$)$_2$H$_2$ alloys. This leads to the possibility that CH$_4$ molecules persist in the structure well into the superconducting H$_3$S-based phase or phases with H$_2$ taken up in the structure. First-principles calculations have previously been employed to investigate the properties of metastable phases that correspond to 50% SH$_3$ → CH$_4$ substitution, wherein methane molecules were intercalated in an H$_3$S framework. Lower dopings could be derived from the $T_d$-C$_x$S$_{1-x}$H$_{3}$ phases discussed above by adding a single hydrogen atom to the S-H lattice. Unlike structures in which C replaced S, all of the CH$_4$ dopings we considered (25, 12.5, 6.25 and 1.85% C) were found to be dynamically stable at 270 GPa and remained so on decompression to at least 140 GPa (Figures S17, S19-S22).

The optimized geometry obtained by taking a sixteen formula unit supercell and replacing one SH$_3$ by CH$_4$, corresponding to a stoichiometry of CS$_{15}$H$_{49}$, is illustrated in Figure S16c. The Bader charge on the $C_{3v}$ symmetry methane molecule was nearly the same as in $T_d$-CS$_{15}$H$_{48}$, −0.10, but the bonds were somewhat shorter and stronger (1.03 Å and 6.92 eV/bond ($\times$ 1), 1.04 Å and 6.98 eV/bond ($\times$ 3)) and the angles were closer to those of a perfect tetrahedron (105°, 113°). The DOS at $E_F$ of CS$_{15}$H$_{49}$ (0.034 states eV$^{-1}$Å$^{-3}$) is quite comparable to that of $T_d$-CS$_{15}$H$_{48}$, but its Debye temperature is significantly higher (1825 K, Figure S24), suggesting that its $T_c$ may be higher as well.

**Thermodynamic Properties and Equation of States**

The relative enthalpies of the doped structures from H$_3$S, as well as carbon in the diamond phase and the $C2/c$ phase of molecular H$_2$ (Figure[4]) illustrate that doping is thermodynamically unfavorable within the pressure range considered, consistent with previous studies of carbon doped SH$_3$ phases. For a given number of C+S atoms the phase where CH$_4$ replaced H$_3$S was always the most stable, followed by phases where a tetrahedrally coordinated C replaced an S atom, and lastly those where C was octahedrally coordinated. Exploratory calculations suggested that it was not enthalpically favorable to add another hydrogen to the SH$_3$ → CH$_4$ doped phases by forming another S-H bond (e.g. $\Delta H$ for the reaction CS$_3$H$_{13}$ + $\frac{1}{2}$H$_2$ → CS$_3$H$_{14}$ was +17.8 meV/atom).

The enthalpies of the phases with the lowest levels of doping were within < 2 meV/atom of each other, and they were the closest to the threshold for thermodynamic stability, with
Figure 4: $\Delta H$ as a function of pressure for the following reaction: $\text{C} + x(\text{H}_3\text{S}) + \left(\frac{y-3x}{2}\right)\text{H}_2 \rightarrow \text{CS}_x\text{H}_y$ in meV/atom using the diamond phase of carbon$^{57}$, $C2/c$ phase of $\text{H}_2$$^{58}$ and $Im\overline{3}m$ phase of $\text{H}_3\text{S}$$^{14}$ as a reference. The open (closed) circles correspond to structures that were found to be dynamically unstable (stable).

$\Delta H$ for the formation of $\text{CS}_{53}\text{H}_{163}$ being 0.14 and 6.82 meV/atom at 140 and 270 GPa, respectively. At 270 GPa the zero-point-energy disfavored the doped species where carbon was tetrahedrally coordinated (Table S2) but this had less of an effect on the octahedrally coordinated systems, such that for $\text{S} \rightarrow \text{C}$ replacements, the structures in which $\text{C}$ was six coordinate became slightly preferred. Even though the carbon doped phases are not thermodynamically stable, their enthalpies of formation are generally within the $\sim 70$ meV/atom threshold corresponding to the 90th percentile of DFT-calculated metastability for inorganic crystalline materials at 1 atm$^{59}$.

### Superconducting Properties

In addition to the phonon band structures and phonon densities of states, we calculated the Eliashberg spectral function, $\alpha^2 F(\omega)$, and the EPC integral, $\lambda(\omega)$, for the model structures considered here (Figure S1d, S7a, and S16a). Initially, $O_h$-$\text{CS}_{15}\text{H}_{48}$ was singled out for analysis because its high $N_F$ relative to other carbon-doped phases suggests it may have the highest $T_c$. Calculations for structures with lower carbon concentrations are currently computationally unfeasible because of their large supercells. Since $T_c$ is usually highest near the onset of dynamic instability the calculation was performed at 255 GPa (Figure S27). The estimated EPC (Table 1) was a modest $\lambda = 1.09$, with 27% arising from the low frequency modes associated with the motions of the sulfur atoms ($<700 \text{ cm}^{-1}$), and 72.5% resulting from motions predominantly due to the hydrogen atoms bonded to sulfur, with a minor contribution from the hydrogens bonded to carbon ($700-2200 \text{ cm}^{-1}$). Numerical solution of the Eliashberg equations using a typical value of the Coulomb pseudopotential, $\mu^* = 0.1$, resulted in a $T_c$ of 136 K at 255 GPa.

The $T_c$ computed for $O_h$-$\text{CS}_{15}\text{H}_{48}$ is over 100 K lower than the maximum measured for
Table 1: Debye temperature (Θ\(_D\)), density of states at the Fermi level (\(N_F\), in states/eV/Å\(^3\)), logarithmic average of phonon frequencies (\(\omega_{\ln}\)), electron-phonon coupling constant (\(\lambda\)), and superconducting critical temperature (\(T_c\)) obtained via numerical solution of the Eliashberg equations using \(\mu^* = 0.1\) at 270 GPa. The pressure range where dynamic stability was confirmed in this study (phonon calculations were carried out between 140-270 GPa) is also provided.

| Structure       | \(\Theta_D\) (K) | \(N_F\)   | \(\omega_{\ln}\) (K) | \(\lambda\) | \(T_c\) (K) | \(P_{\text{stab}}\) (GPa) |
|-----------------|------------------|-----------|-----------------------|-------------|-------------|--------------------------|
| \(Im3m\) H\(_3\)S | 1314             | 0.0502    | 1603                  | 1.25        | 174         | N/A                      |
| \(R3m\) H\(_3\)S | 1340             | 0.0440    | 1615                  | 0.95        | 140         | N/A                      |
| \(^a\)O\(_h\)-CS\(_{15}\)H\(_{48}\) | 1449             | 0.0401    |                       |             |             | 260-270                  |
| \(O_h\)-CS\(_{53}\)H\(_{162}\) | 1375             | 0.0484    |                       |             |             | 200-270                  |
| \(T_d\)-CS\(_3\)H\(_{12}\) | 1813             | 0.0281    | 1370                  | 0.85        | 80          | 180-270                  |
| \(T_d\)-CS\(_7\)H\(_{24}\) | 1875             | 0.0395    |                       |             |             | 270                      |
| \(T_d\)-CS\(_{15}\)H\(_{48}\) | 1639             | 0.0325    |                       |             |             | 270                      |
| \(T_d\)-CS\(_{53}\)H\(_{162}\) | 1774             | 0.0460    |                       |             |             | 260-270                  |
| \(Cmcm\) CSH\(_7\) | 1781             | 0.0256    |                       |             |             | 140-270                  |
| \(R3m\) CSH\(_7\) | 1851             | 0.0275    |                       |             |             | 140-270                  |
| CS\(_3\)H\(_{13}\) | 1821             | 0.0245    | 1704                  | 1.01        | 142         | 140-270                  |
| CS\(_7\)H\(_{25}\) | 1868             | 0.0313    |                       |             |             | 140-270                  |
| CS\(_{15}\)H\(_{49}\) | 1825             | 0.0343    |                       |             |             | 140-270                  |
| \(^b\)CS\(_{53}\)H\(_{163}\) | 1818             | 0.0434    |                       |             |             | 140-270                  |

\(^a\) The computed values for this phase at 255 GPa are: \(\Theta_D = 1490\) K, \(N_F = 1414\) K, \(\lambda = 1.09\), \(T_c = 136\) K (numerically solving Eliashberg equations).

\(^b\) Assuming \(\omega_{\ln} = 1704\) K and \(\lambda = 2.5\) yields \(T_c = 280\) K (calculated using the Allen-Dynes modified McMillan equation – see text).

The computed values for this phase at 255 GPa are: \(\Theta_D = 1490\) K, \(N_F = 1414\) K, \(\lambda = 1.09\), \(T_c = 136\) K (numerically solving Eliashberg equations).

We now examine whether tetrahedral coordination of the carbon atoms can enhance \(T_c\). Unfortunately, because the symmetries of \(T_d\)-CS\(_{15}\)H\(_{48}\) and CS\(_{15}\)H\(_{49}\) are lower than that of \(O_h\)-CS\(_{15}\)H\(_{48}\) calculating their \(T_c\)s was prohibitively expensive. Therefore, 25% doped systems were considered instead. Despite the fact that the estimated Debye temperature for \(T_d\)-CS\(_{15}\)H\(_{48}\) was higher than that of H\(_3\)S, \(\omega_{\ln}\) was lower, mirroring the findings for \(O_h\)-CS\(_{15}\)H\(_{48}\). In addition, the EPC was lower, consistent with the much smaller \(N_F\), resulting in a \(T_c\) of 80 K. Even though decreasing the doping increases \(N_F\), once again it is unlikely that compounds belonging to this family of structures could be superconducting at temperatures higher than those found for H\(_3\)S. However, adding one more hydrogen atom per unit cell to members of this family leads to a remarkable improvement. Both \(\omega_{\ln}\) and \(\lambda\) of CS\(_3\)H\(_{13}\)
are higher than that of $T_d$-CS$_3$H$_{12}$, yielding a $T_c$ of 142 K at 270 GPa. Thus, a little bit of carbon does a lot for superconductivity in H$_3$S, and the way in which it is altered (whether it be an increase or decrease) is intimately related to the local bonding configuration around carbon.

To better understand how adding a single hydrogen atom can dramatically increase $T_c$ by 60 K, we compare $\lambda(\omega)$ and $\omega_{ln}(\omega)$ of these two model structures (Figure S24). At $\sim 1550$ cm$^{-1}$ their $\omega_{ln}(\omega)$ are almost identical. At higher frequencies $\omega_{ln}(\omega)$ for CS$_3$H$_{13}$ increases much faster until a near plateau region is attained at 2220 cm$^{-1}$ (1670 K). In $T_d$-CS$_3$H$_{12}$, on the other hand, $\omega_{ln}(\omega)$ reaches 1309 K at 2450 cm$^{-1}$. Beyond $\sim 2500$ cm$^{-1}$, the flat high-frequency bands contribute less than 40 K to $\omega_{ln}(\omega)$ for both structures. Therefore, the main difference in the total $\omega_{ln}$ for the two phases arises from modes in the 1550-2500 cm$^{-1}$ frequency range. From the projected phonon density of states (Figure S10a and S17a) modes associated with motions of the H atoms in the H-S lattice (H1) primarily comprise this region, with some contribution from H atoms in the CH$_4$ molecule (H2). At $\sim 1410$ cm$^{-1}$ $\lambda(\omega)$ was almost the same for the two structures ($\sim 0.45$). At higher frequencies the $\lambda(\omega)$ for CS$_3$H$_{13}$ increases much faster until 2220 cm$^{-1}$ where it reaches a value of 1.00, while for $T_d$-CS$_3$H$_{12}$ $\lambda(\omega)$ reaches 0.83 at 2450 cm$^{-1}$. Beyond $\sim 2500$ cm$^{-1}$, the high-frequency flat bands contribute less than 0.005 towards $\lambda$ for both structures.

Additional insight into the types of motions that result in a larger $\lambda$ within CS$_3$H$_{13}$ can be obtained by visualizing selected vibrational modes that have a notable $\lambda_{qv}$, e.g., modes about halfway along the $Y \rightarrow Z$ (1412 cm$^{-1}$) and $Z \rightarrow L$ (1361 cm$^{-1}$) paths, which have very large contributions (Figure 5). Both of these involve H2 vibrations between neighboring S atoms, leading to a snakelike undulation of the H1/H2 chains. The addition of the extra S-bonded H atom expands the S-H lattice in the $ab$ plane, leaving looser contacts between the S and H atoms (1.44 Å and 1.43 Å as opposed to 1.41-1.43 Å in $T_d$-CS$_3$H$_{12}$), thereby softening the phonon frequencies. The $c$ axis is largely unchanged by the addition of an extra H, but the H-S distances that are relatively even in CS$_3$H$_{12}$ (1.43-1.44 Å) become disproportionate in CS$_3$H$_{13}$ to 1.41 and 1.46 Å. Within the methane fragments, two H1 atoms possessed mirrored circular motions that were part of the undulating H chains.

Although decreasing the doping does not appreciably change the Debye temperature, it increases the $N_F$ substantially such that at 1.85% doping the value is almost double that of the 25% doped phase. Assuming that $\omega_{ln}$ for CS$_{53}$H$_{163}$ is close to that for CS$_3$H$_{13}$ a $T_c$ of 280 K could be obtained using the Allen-Dynes modified McMillan equation for $\lambda \sim 2.5$. Since this approximate equation is known to underestimate $T_c$ for systems where $\lambda \geq 1.5$, within the Eliashberg formalism somewhat smaller $\lambda$ values would yield a similar result. Therefore, it is plausible that the $\lambda$ of CS$_{53}$H$_{163}$ could fall within this range given its high $N_F$. For comparison, at 200 GPa $Im\bar{3}m$ H$_3$S is computed to have a similar $\lambda$ (2.19), but its $\omega_{ln}$ (1335 K) is significantly smaller, yielding an estimated $T_c$ of 191-204 K. Moreover, its DOS at $E_F$, 0.041 states/eV Å$^3$, is comparable to that obtained for CS$_{53}$H$_{163}$. It is beyond the scope of this study to explicitly calculate the $T_c$ of C$_x$S$_{1-x}$H$_{3+x}$ phases over a broad range of doping levels (e.g., 1.85-12.5%). We note that unlike the other families of structures studied to date, structures belonging to this family were found to be dynamically stable across a broad pressure range (at least 140-270 GPa).

In summary, our detailed computations have shown that doping H$_3$S by 1.85-25% of
carbon at 270 GPa leads to a plethora of metastable phases where carbon can be either six-coordinated or four-coordinated to hydrogen. In the first case we see the remarkable emergence of an \(O_h\) symmetry \(\text{CH}_6\) motif reminiscent of a di-carbocation, but stabilized in the solid state under pressure via weak interactions by the negatively charged environment of the surrounding host \(\text{H}_3\text{S}\)-like lattice. The second case is an example of methane intercalated within an \(\text{H}_3\text{S}\)-like framework. These doping schemes split degenerate bands thereby decreasing \(N_F\), and localizing electrons in covalent C-H bonds whose signatures are far removed from the Fermi energy.

Both \(\omega_{ln}\) and \(\lambda\) of \(O_h\)-CS\(_{15}\)H\(_{48}\) and \(T_d\)-CS\(_3\)H\(_{12}\) were smaller than the values computed for \(Im3m\) \(\text{H}_3\text{S}\), as was the resulting \(T_c\). Remarkably, adding a single hydrogen atom to \(T_d\)-CS\(_3\)H\(_{12}\) increased \(T_c\) by 60 K. The larger \(\lambda\) and \(\omega_{ln}\) of the resulting CS\(_3\)H\(_{13}\) phase could be traced back to the emergence of soft phonon modes, a consequence of the weaker and longer S-H bonds in the host lattice caused by the insertion of the extra S-bonded hydrogen atom. At 270 GPa the \(T_c\) of CS\(_3\)H\(_{13}\) was about the same as that of \(R3m\) \(\text{H}_3\text{S}\) despite its much lower DOS at \(E_F\). Decreasing the doping level in this family of structures, derived from \(\text{H}_3\text{S}\) by low-level incorporation of CH\(_4\), is likely to increase \(T_c\) further. We hope that the present results will stimulate further theoretical studies, large supercell calculations of the superconducting properties of these structures, as well as additional experiments in search of still higher \(T_c\)s and phases that may be stable over a broader range of conditions.
Methods

Electronic Structure Calculations

Geometry optimizations and electronic structure calculations were performed using density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional as implemented in the Vienna Ab initio Simulation Package (VASP) 5.4.1. The valence electrons (H 1s, S 3s23p4, and C 2s2p2) were treated explicitly using plane wave basis sets with a cutoff energy of 800 eV (as previously employed by Cui et al.), while the core states were treated with the projector-augmented wave (PAW) method. The reciprocal space was sampled using a Γ-centered Monkhorst-Pack scheme, and the number of divisions along each reciprocal lattice vector was chosen such that the product of this number with the real lattice constant was 70 Å for the density of states (DOS) calculations, and 50 Å otherwise. The crystal orbital Hamilton populations (COHPs), the negative of the COHPs integrated to the Fermi level (-iCOHPs), and the crystal orbital bond index (COBI) were calculated using the LOBSTER package (v2.2.1 for -iCOHP and v4.1.0 for COBI), and the results used to analyze the bonding. The dynamic stability of the phases was investigated via phonon calculations performed using the finite difference scheme as implemented in the PHONOPY software package. For the DFT-raMO procedure, single point calculations were carried out in VASP with coarse k-point grids sampling the full Brillouin zone with dimensions equal to the supercell used in the raMO analysis, corresponding to 3×3×3 for Cs15H48 and 5×5×5 for H3S.

Superconducting Properties

Phonon calculations were performed using the Quantum Espresso (QE) package program to obtain the dynamical matrix and the electron-phonon coupling (EPC) parameters. The pseudopotentials were obtained from the PSlibrary using H 1s, S 3s23p4, and C 2s2p2 valence electrons and the PBE exchange-correlation functional. Plane-wave basis set cutoff energies were set to 80 Ry for all systems. We employed a Γ-centered Monkhorst-Pack Brillouin zone sampling scheme, along with Methfessel-Paxton smearing with a broadening width of 0.02 Ry. Density functional perturbation theory (DFPT) as implemented in QE was employed for the phonon calculations. The EPC matrix elements were calculated using the k and q-meshes, and Gaussian broadenings listed in Table S1. The EPC parameter (λ) converges to within 0.05 for differences of the Gaussian broadening that are less than 0.02 Ry. The critical superconducting temperature, \( T_c \), has been estimated using the Allen-Dynes modified McMillan equation, where \( \omega_{\text{ln}} \) is the logarithmic average frequency, and \( \mu^* \) was set to 0.1. The \( T_c \) were also obtained by solving the Eliashberg equations numerically based on the spectral function, \( \alpha^2 F(\omega) \), obtained from the QE calculations.
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**Data availability**

The data supporting this publication are available from the authors upon reasonable request.
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Author contributions

R.J.H. and E.Z. conceived the project. X.W., T.B., K.P.H., and A.L. carried out the DFT calculations. All authors were involved in data analysis and results discussions. X.W., E.Z. and R.J.H. wrote the manuscript, with contributions from K.P.H.

Additional information

Supplementary Information accompanies this paper at https://doi.org/xxx/aaa-bbb.ccc

Competing interests

The authors declare that no competing interests.