Structural Diversity and Superconductivity in S-P-H Ternary Hydrides Under Pressure

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Abstract

Evolutionary structure searches revealed a plethora of stable and low-enthalpy metastable phases in the S-P-H ternary phase diagram under pressure. A wide variety of crystalline structure types were uncovered ranging from those possessing one-dimensional chains, two-dimensional sheets based on S-H or S-P-H square lattices as well as S-H or P-H honeycombs, and cage-like structures. Some of the cage-like structures could be derived from doping the high-pressure high-temperature superconducting $Im\bar{3}m$ H$_3$S phase with phosphorous. Most of the discovered compounds were metallic, however those derived from $Im\bar{3}m$ H$_3$S lattices with low levels of P-doping were predicted to possess the highest superconducting critical temperatures ($T_c$s). The propensity for phosphorous to assume octahedral coordination, as well as the similar radii of sulfur and phosphorous are key to maintaining a high density of states at the Fermi level in $Im\bar{3}m$ S$_{0.875}$P$_{0.125}$H$_3$, whose $T_c$ was estimated to be similar to that of H$_3$S at 200 GPa.
Introduction

The recent successes in the search for materials with ever-higher superconducting critical temperatures ($T_c$s) can be traced back to ideas planted by the late Neil Ashcroft. Building on his earlier prediction of phonon-mediated high-temperature superconductivity in metallic hydrogen, in 2004 Ashcroft elegantly showed how chemical doping may be employed to decrease the pressure required to reach a metallic and superconducting state. This proposal ultimately led to the experimental discovery of superconductivity in $\text{H}_3\text{S}$, $\text{LaH}_{10}$, $\text{YH}_6$, $\text{YH}_9$ and room temperature superconductivity in an unknown C-S-H phase.

Because of the experimental difficulties inherent in high pressure research, theoretical calculations have been integral in suggesting targets for synthesis and for interpreting experimental measurements. Advances in ab initio crystal structure prediction techniques and computational methods to approximate $T_c$ have enabled the in silico search for superconductivity in high pressure hydrides. By now, the phase diagrams of most binary hydrides have been explored computationally. Ternary hydrides are the next frontier, however the combinatorial possibilities, potential for large unit cells, and role of metastability results in many challenges.

One way that new ternary superconductors could potentially be made is by combining two binary hydrides that are thought to be good superconductors. For example, the extraordinary $T_c$ values predicted for $\text{CaH}_6$ and measured for $\text{SH}_3$ inspired the computational search for superconductivity in $\text{Ca}_x\text{S}_y\text{H}_z$ phases. A $P\bar{6}m2$ CaSH$_3$ compound built from CaH$_2$ layers separated by honeycomb H-S layers was predicted to have a $T_c$ reaching 100 K at 128 GPa. Inspired by the prediction of high $T_c$ in metal superhydrides with clathrate cages, the (La/Y)H$_{10}$ and (La/Y)H$_6$ ternaries were synthesized, and their maximum measured $T_c$s were 253 and 237 K, respectively.

Another strategy that could be used to find promising ternary superconductors is to begin with a binary phase known to have a large $T_c$ and dope it with a third (or fourth) element. The doping could potentially increase $T_c$ (c.f. Li$_2$MgH$_{16}$ versus MgH$_{16}$) or extend the region of phase stability to lower pressures (c.f. LaBH$_8$ or LaBeH$_8$ versus LaH$_{10}$).

It has been proposed that doping can be employed to tune the position of the Fermi level
($E_F$) so that it lies on a maximum in the density of states (DOS) thereby increasing the electron phonon coupling parameter, $\lambda$, and concomitantly the $T_c$. This mechanism ought to be particularly useful for enhancing the $T_c$ in H$_3$S, whose $E_F$ is just shy of the top of a peak caused by the presence of two van Hove singularities (vHs) that straddle $E_F$. Computations using the virtual crystal approximation (VCA), which creates alchemical atoms whose properties vary smoothly upon doping, have explored the effect of doping on the $T_c$ of H$_3$S. Heil and Boeri found that $T_c$ could be enhanced by replacing sulfur by more electronegative elements such as oxygen or halogen atoms, whereas Ge et al. and Hu et al. concluded that $T_c$s above the freezing point of water could be obtained by low dopings of phosphorous, silicon, and most recently carbon. However, other VCA-based studies found that partial substitution of sulfur with another $p$-block element did not enhance $T_c$ significantly, or not at all.

The VCA model is advantageous since it enables the study of low doping levels that can only be modelled by large unit cells whose $T_c$s cannot be computed from first principles because of the immense expense. At the same time, the VCA assumes the band structure will not be perturbed by doping, and only the position of $E_F$ will change (rigid band model). Recent theoretical studies have called this assumption into question. For example, calculations on C$_x$S$_{1-x}$H$_3$ and C$_x$S$_{1-x}$H$_{3+x}$ supercells with doping levels ranging from 1.85-25% illustrated that incorporation of carbon into the H-S lattice decreases the number of bands at $E_F$ by breaking degeneracies and localizing electrons in covalent C-H bonds. Calculations on phases where half of the SH$_3$ units were substituted by methane resulting in a CSH$_7$ stoichiometry, yielded maximal $T_c$s of 181 K at 100 GPa and 194 K at 150 GPa. Theory has shown that Se and Cl dopings do not raise the superconducting critical temperature of H$_3$S. And, phosphorous dopings have been shown to both increase and decrease its $T_c$. For example, a 6.25% phosphorus doping resulted in a $T_c$ of 212 K or 262 K at 200 GPa, a 12.5% phosphorus doped structure was predicted to possess a $T_c$ of 194 K at 200 GPa or 190 K at 155 GPa, and a 50.0% phosphorus doped structure yielded a $T_c$ of 89 K at 200 GPa or 157 K at 155 GPa. Another drawback of both the VCA and the supercell models with S→P substitutions is that they did not explore the potential energy...
landscape for the compositions considered, and the S-P-H ratios were fixed. Moreover, the studies carried out with both methods employed structures derived from $Im\bar{3}m$ or $R3m$ H$_3$S cells, which may not form in experiment, especially if other novel S-P-H ternary phases are thermodynamically preferred.\cite{12}

To overcome these limitations, herein we perform a thorough theoretical study that employs crystal structure prediction techniques to identify the most stable ternary phases for a wide $S_xP_yH_z$ composition range. The electronic structure including the density of states, electron localization functions, electronic and phonon band structures are analyzed. Four different families of structures including those comprised of cages, two dimensional sheets with hexagonal or other motifs, and one-dimensional molecular chains are found. Unlike our previous results on carbon doping of H$_3$S, here we find at least one system where phosphorous doping does not decrease the DOS at $E_F$. This $Im\bar{3}m$ S$_7$PH$_{24}$ compound is estimated to have a $T_c$ comparable to its parent $Im\bar{3}m$ H$_3$S structure at 200 GPa. We hope our study can guide the experimental discovery and characterization of new ternary superconducting S-P-H compounds under pressure.

**Computational Details**

Crystal structure prediction (CSP) searches were performed to find stable and low enthalpy metastable phases with $SPH_n$ ($n = 1 – 6$), $S_xPH$ and $SP_yH$ ($x, y = 2, 3$) stochiometries, as well as those corresponding to phosphorus doped H$_3$S phases at 100, 150 and 200 GPa using 1-4 formula units in the simulation cell. The stoichiometries of the doped phases we considered were $S_xP_{1-x}H_3$ ($x = 0.125, 0.2, 0.25, 0.33, 0.4, 0.6, 0.67, 0.75, 0.8$), which were modelled by $S_7PH_{24}$, $S_4PH_{15}$, $S_3PH_{12}$, $S_2PH_9$, $S_3P_2H_{15}$, $S_2P_3H_{15}$, $SP_2H_9$, $SP_3H_{12}$, and $SP_4H_{15}$ cells, respectively. These were chosen based on a similar study for $S_xSe_{1-x}H_3$ systems.\cite{38} In this case the EA searches were seeded with doped supercells from the previously reported $Im\bar{3}m$ H$_3$S and $R3m$ H$_3$S structures.\cite{19} The CSP searches were performed using the open-source evolutionary algorithm (EA) XTALOPT\cite{44,45,47} version 12.\cite{5} The initial generation consisted of random symmetric structures that were created by
the RANDSPG algorithm,⁴⁸ and the minimum interatomic distance between S-S, S-H, S-P, H-H, H-P, and P-P atoms were constrained to 0.88, 0.71, 0.93, 0.53, 0.76 and 0.98 Å using a uniform scaling factor of 0.5 multiplied by tabulated covalent radii. Duplicate structures were identified via the XTALCOMP algorithm⁴⁹ and discarded from the breeding pool. The lowest enthalpy structures in each EA run were relaxed from 100 to 200 GPa and their relative enthalpies and equations of states are given in the Supplementary Information Figs. S1-6.

Geometry optimizations and electronic structure calculations including band structures, the densities of states (DOS), electron localization functions (ELFs), and Bader charges were carried out using density functional theory (DFT) as implemented in the Vienna ab-initio Simulation Package (VASP) version 5.4.1,⁵⁰,⁵¹ with the gradient-corrected exchange and correlation functional of Perdew-Burke-Ernzerhof (PBE).⁵² The crystal orbital Hamilton population (COHP) and the negative of the COHP integrated to the Fermi level (-iCOHP) was calculated using the LOBSTER package to analyze the bonding of selected phases.⁵³

The projector augmented wave (PAW) method⁵⁴ was employed, and the S 3s²3p⁴, P 3s²3p³ and H 1s⁴ electrons were treated explicitly in all of the calculations. The plane-wave basis set energy cutoffs were 350-400 eV in the EA searches and 700 eV in precise geometry optimizations. The \( k \)-point meshes were generated using the \( \Gamma \)-centered Monkhorst-Pack scheme, while the number of divisions along each reciprocal lattice vector was selected so that the product of this number with the real lattice constant was 30 Å in the EA searches and 50 Å for precise geometry optimizations.

Phonon calculations were carried out via the supercell approach using the VASP package coupled to the PHONOPY code.⁵⁵ The electron-phonon coupling (EPC) calculations were carried out using the Quantum Espresso (QE) program.⁵⁶ The S 3s²3p⁴, P 3s²3p³ and H 1s⁴ pseudopotentials were obtained from the PSlibrary, and generated by the method of Trouiller-Martins.⁵⁷ The plane-wave basis set energy cutoffs were chosen to be 60 Ry. The Brillouin zone sampling scheme of Methfessel-Paxton⁵¹ was applied. The EPC parameter, \( \lambda \), was calculated using a set of Gaussian broadenings with an increment of 0.005 Ry from 0.0 to 0.500 Ry. The broadening for which \( \lambda \) was converged to within 0.05 Ry is provided in Table S5, along with the \( k \) and \( q \) grids that were deemed...
to be converged. The $T_c$ was estimated using the Allen-Dynes modified McMillan equation$^{62}$ with a renormalized Coulomb potential, $\mu^*$, of 0.1. For phases with $\lambda$ greater than 1.3 more accurate estimates of the $T_c$ were also calculated by numerically solving the Eliashberg equations.$^{63}$

**Results and Discussion**

The enthalpies of formation, $\Delta H_F$, of the most stable S-P-H ternary phases found in our EA searches for a given stoichiometry at 100, 150 and 200 GPa were calculated and employed to construct the convex hull. If the $\Delta H_F$ of a structure falls on the convex hull, it is a thermodynamically stable phase. However, previous theoretical and experimental work on binary hydrides has illustrated that synthesizability is not only determined by the $\Delta H_F$ estimated within the static lattice approximation. It turns out that the synthesis pathway, which includes the choice of the precursors and annealing schemes, is also key in determining the products that are formed. For example, despite the fact that Ca$_2$H$_5$ lies 20 meV/atom above the convex hull, this binary hydride has been synthesized.$^{77}$ Moreover, even though DFT calculations predict that hydrides of phosphorous are not thermodynamically stable under pressure,$^{78-80}$ a superconducting PH$_n$ phase$^{81}$ and a van der Waals (PH$_3$)$_2$H$_2$ crystalline compound$^{82}$ have been synthesized. Moreover, a number of H$_x$S$_y$ superconductors have been made,$^{83}$ and various stoichiometries including H$_3$S,$^{19,84}$ H$_2$S,$^{85,86}$ HS$_2$,$^{75}$ H$_4$S$_3$,$^{73}$ H$_5$S$_2$,$^{87}$ exotic Magnéli phases,$^{88}$ and self-ionized (SH$^-$)(H$_3$S)$^+$ perovskites$^{89}$ that may have long modulations$^{90,91}$ have been proposed. Because metastable binary S-H and P-H phases have been synthesized, herein we have chosen to analyze structures that fall on the convex hull (Fig. 1), as well as several metastable phases with unique structural characteristics that are within the realm of synthesizability.

At 100 GPa both S$_2$PH$_9$, which can be considered a P-doped H$_3$S phase with a S$_{0.67}$P$_{0.33}$H$_3$ composition, and S$_3$PH lie on the hull. In addition to S$_3$PH, S$_2$PH also comprises the 150 GPa hull, whereas only SPH falls on the hull at 200 GPa. Notably, most of the compositions studied were within the 70 meV/atom threshold corresponding to the 90th percentile of DFT-calculated
Figure 1: Distance from the convex hull of the S-P-H phases considered with respect to elemental S, P, and $\frac{1}{2} H_2$ as computed with the PBE functional at 100, 150, and 200 GPa. The thermodynamically stable phases are shown in black while the metastable phases are represented by different colors based on their distance from the hull. The phases with positive enthalpies are shown with a half-filled shape. The phases containing special geometrical motifs such as cage-like structures, 2D hexagonal or other sheets, and 1D chains are labelled as stars, pentagons, triangles, and squares, respectively. $\Delta H_F$ was calculated using the enthalpies of the experimentally or theoretically known structures: simple cubic (sc, 100 GPa) $^{64-66}$ and simple hexagonal (sh, 150–200 GPa) $^{66}$ for P; $P6_3/m$ (100 GPa) $^{67}$ and $C2/c$ (150–200 GPa) $^{67}$ for H; $\beta$-Po $^{68}$ for S (100–200 GPa) since the crystal structure of S above 83 GPa is still disputed, $^{65,71}$ $C2/c$ (200 GPa) for $S_3P$, $^{72}$ $C2/m$ (100–150 GPa) and $P3m1$ (200 GPa) for $S_2P$, $^{72}$ $P2_1/m$ (150 GPa) for SP $^{72}$ $C2/m$-I (100 GPa) and $C2/m$-II (150 GPa) for SP $^{72}$, $C2/m$ (100 GPa) for $SP_3$, $^{72}$ $C2/c$ (100 GPa), $R3m$ (150 GPa), and $Im\overline{3}m$ (200 GPa) for $H_3S_3$ $^{71,72}$ $Pbcm$ (100 GPa) and $C2c$ (150–200 GPa) for $HS_2$ $^{74,75}$ $Pnma$ (100 GPa) for $H_4S_3$ $^{75}$ $C2/m$ (100 GPa) for $H_3S_9$. $^{76}$
metastability for inorganic crystalline materials at 1 atm, but the $\Delta H_F$ for three phosphorus-rich compounds, $\text{SP}_2\text{H}_9$ ($\text{S}_{0.33}\text{P}_{0.67}\text{H}_3$), $\text{SP}_3\text{H}_{12}$ ($\text{S}_{0.25}\text{P}_{0.75}\text{H}_3$) and $\text{SP}_4\text{H}_{15}$ ($\text{S}_{0.2}\text{P}_{0.8}\text{H}_3$), were positive with respect to the elemental phases at all pressures. $\text{SP}_5\text{H}$ was also unstable with respect to $\text{H}_2$, $\text{P}$ and $\text{S}$ at 200 GPa. The structural parameters and the distance from the convex hull for all $\text{S-P-H}$ ternary phases considered are provided in Table S6-8 and S2, respectively.

Because the enthalpy of formation of the binary hydrides of phosphorous is positive above 40 GPa, none of the previously predicted phases are plotted on Fig. [1]. For the hydrides of sulfur the $C2/c \text{H}_3\text{S}, \text{Pnma} \text{H}_4\text{S}_3$, $\text{Pbcm} \text{HS}_2$ and $C2/m \text{H}_3\text{S}_2$ phases were employed to construct the 100 GPa hull, while $R3m$ and $Im\overline{3}m \text{H}_3\text{S}$ phases were used to build the 150 and 200 GPa hulls, respectively. For the $\text{P-S}$ phases we employed structures previously identified via crystal structure prediction. $C2/m \text{SP}_3$, $C2/m-\text{I SP}_2$ and $C2/m \text{S}_2\text{P}$ lay on the 100 GPa hull; $C2/m-\text{II SP}_2$, $P2_1/m \text{SP}$ and $C2/m \text{S}_2\text{P}$ lay on the hull at 150 GPa; $P\overline{3}m1 \text{S}_2\text{P}$ and $C2/c \text{S}_3\text{P}$ lay on the hull at 200 GPa.

In our work we found stable and metastable ternary $\text{S-P-H}$ species with a variety of distinct structural motifs including: (i) cage-like geometries, e.g. $\text{S}_7\text{PH}_{24}$ ($\text{S}_{0.875}\text{P}_{0.125}\text{H}_3$), $\text{S}_4\text{PH}_{15}$ ($\text{S}_{0.8}\text{P}_{0.2}\text{H}_3$), $\text{S}_3\text{PH}_{12}$ ($\text{S}_{0.75}\text{P}_{0.25}\text{H}_3$), $\text{S}_3\text{P}_2\text{H}_{15}$ ($\text{S}_{0.6}\text{P}_{0.4}\text{H}_3$), $\text{SPH}_6$ ($\text{S}_{0.5}\text{P}_{0.5}\text{H}_3$) and $\text{SPH}_2$; (ii) two-dimensional hexagonal sheets, e.g. $\text{S}_2\text{PH}$ and $\text{SP}_2\text{H}$; (iii) other types of two-dimensional sheets, e.g. $P\overline{1} \text{SP}_2\text{H}_0$ ($\text{S}_{0.33}\text{P}_{0.67}\text{H}_3$) and $\text{SP}_3\text{H}_{12}$ ($\text{S}_{0.25}\text{P}_{0.75}\text{H}_3$); and (iv) one-dimensional chains, e.g. $\text{SPH}_5$, $\text{S}_2\text{P}_3\text{H}_{15}$ ($\text{S}_{0.4}\text{P}_{0.6}\text{H}_3$) and $\text{SP}_4\text{H}_{15}$ ($\text{S}_{0.2}\text{P}_{0.8}\text{H}_3$). We also studied other thermodynamically stable phases (e.g. $\text{S}_3\text{PH}$ and $\text{S}_2\text{PH}_0$ ($\text{S}_{0.67}\text{P}_{0.33}\text{H}_3$)), and other superconducting phases (e.g. $\text{SPH}_3$ and $\text{SPH}_4$). The structural peculiarities of many of these are described in the following sections to showcase the rich potential energy landscape and geometrical complexity that is possible. However, for brevity we do not discuss dynamically stable phases that either did not possess any distinct structural motifs, or those that are only slight variations of presented phases. Information on some of these, e.g. $\text{SPH}_n$ ($n = 3 - 5$) and $\text{SP}_4\text{H}_{15}$ ($\text{S}_{0.2}\text{P}_{0.8}\text{H}_3$), can be found in Fig. S42.

To gauge the stability of the P doped phases, we considered the enthalpy of the reaction $\text{H}_3\text{S} + x\text{P} \rightarrow \text{H}_3\text{S}_{1-x}\text{P}_x + x\text{S}$ (Table [1]). Our results for $\text{S}_{0.875}\text{P}_{0.125}\text{H}_3$ ($\text{S}_7\text{PH}_{24}$) were similar to those
Table 1: \(\Delta H\) (meV/atom) for the reaction \(\text{H}_3\text{S} + x\text{P} \rightarrow \text{H}_3\text{S}_{1-x}\text{P}_x + x\text{S}\) for different doping levels, \(x\), at various pressures.

| \(P/x\) | 12.5\(^a\) | 20\(^a\) | 25\(^a\) | 33\(^b\) | 40\(^a\) | 50\(^a\) | 60\(^c\) | 67\(^c\) | 75\(^c\) | 80\(^d\) |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 100     | 34.3 (23.9\(^e\)) | 41.5 | 87.4 | 48.1 | N/A | 82.1 | 133.0 | 119.4 | 139.1 | 79.8 |
| 150     | 26.6 (31.2\(^e\)) | 43.4 | 96.4 | 47.4 | 57.2 | 93.7 | 136.3 | 120.2 | 147.0 | 79.5 |
| 200     | 40.0 (36.5/37.0\(^f\)) | 55.3 | 116.2 | 66.1 | 100.7 | 123.1 | 149.7 | 142.7 | 175.6 | 107.1 |

\(^a\) Illustrated in Fig. 2
\(^b\) Illustrated in Fig. 6
\(^c\) Illustrated in Fig. 5
\(^d\) Illustrated in Fig. S42
\(^e\) Ref. 40
\(^f\) Ref. 41

calculated for the same stoichiometry by Nakanishi and co-workers.\(^{40}\) The relatively small positive \(\Delta H\) values suggest that this phase could potentially be synthesized, especially if configurational entropy is able to overcome the enthalpic penalty, as is the case for numerous multicomponent systems.\(^{23}\) Generally speaking, as the doping level increases, the ternaries become progressively destabilized with the sulfur-rich and phosphorous-rich phases possessing \(\Delta H\) values ranging from 26.6-116.2 meV/atom and 79.8-175.6 meV/atom, respectively. \(\text{S}_x\text{PH}_{9} (\text{S}_{0.67}\text{P}_{0.33}\text{H}_3)\), and \(\text{S}_3\text{P}_2\text{H}_{15} (\text{S}_{0.6}\text{P}_{0.4}\text{H}_3)\), whose structural peculiarities will be discussed below, did not follow this trend.

### Cage Like Structures

The discovery of record breaking \(T_c\) in \(\text{H}_3\text{S}\) is a milestone in the search for room-temperature superconducting materials. Theoretical calculations predicted that \(\text{Im}\overline{3}m\) \(\text{H}_3\text{S}\) is the most stable phase at 200 GPa with a \(T_c\) of 191-204 K,\(^{19}\) in-line with independent experiments that measured a \(T_c\) of 203 K when hydrogen sulfide was compressed to 155 GPa.\(^{3}\) The S atoms in \(\text{Im}\overline{3}m\) \(\text{H}_3\text{S}\), which are separated symmetrically by hydrogen atoms, form a bcc lattice. Another structurally related \(\text{H}_3\text{S}\) phase with \(R\overline{3}m\) symmetry, which contains a pyramidal \(\text{H}_3\text{S}\) unit with a calculated \(T_c\) of 155-166 K at 130 GPa, was also proposed.\(^{19}\) Therefore, we seeded all of our \(\text{S}_x\text{P}_{1-x}\text{H}_3\) EA searches with supercells of both \(\text{Im}\overline{3}m\) and \(R\overline{3}m\) \(\text{H}_3\text{S}\) where some of the sulfur atoms were replaced by phosphorous atoms. Several cage-like structures including \(\text{S}_7\text{PH}_{24} (\text{S}_{0.875}\text{P}_{0.125}\text{H}_3)\),
Figure 2: Illustrations of predicted S-P-H phases with cage-like structures: (a) Cm $\text{S}_7\text{PH}_{24}$ ($\text{S}_{0.875}\text{P}_{0.125}\text{H}_3$) at 150 GPa, (b) $I4/m$ $\text{S}_4\text{PH}_{15}$ at 200 GPa, (c) $Immm$ $\text{S}_3\text{PH}_{12}$ at 200 GPa, (d) $P1$ $\text{S}_3\text{P}_2\text{H}_{15}$ at 150 GPa, (e) $Amm2$ $\text{SPH}_6$ at 150 GPa, and (f) $Pm\overline{3}m$ $\text{SPH}_2$ at 200 GPa. S/P/H atoms are colored yellow/orange/white.
S₄PH₁₅ (S₀.₈P₀.₂H₃), S₃PH₁₂ (S₀.₇₅P₀.₂₅H₃), S₃P₂H₁₅ (S₀.₆P₀.₄H₃), SPH₆ (S₀.₅P₀.₅H₃) and SPH₂, which resembled Im₃m and R₃m H₃S, were found and are discussed below (see Fig. 2).

A Cm S₇PH₂₄ (S₀.₈₇₅P₀.₁₂₅H₃) structure with 1 formula unit in the primitive cell was found via CSP, and it also possessed the lowest enthalpy at 100 GPa. This phase lay only 24.5 and 12.2 meV/atom above the convex hull at 100 and 150 GPa, respectively. It could be viewed as a distorted version of the R₃m cell considered by Nakanishi, and the distortion stabilized the structure by 14.9 and 7.0 meV/atom at 100 and 150 GPa, respectively. By 200 GPa the high-symmetry Im₃m phase became preferred, and it lay 23.6 meV/atom above the convex hull. The Cm phase contained SH₃ and SH₄ structural motifs, along with PH₆ units whose geometry deviated ever-so-slightly from ideal octahedral coordination. In the higher pressure Im₃m phase these motifs were forced close enough to each other so they formed multi-centered bonds where every S and P atom was octahedrally coordinated with SH-P and PH-S distances of 1.462 and 1.522 Å, respectively, at 200 GPa. The HS-H distances in this phase were the same as within Im₃m H₃S at the same pressure, 1.492 Å. The Bader charge on the PH₆ unit within S₇PH₂₄ was calculated to be -0.09 e at 150 GPa and 0.03 e at 200 GPa.

Our calculations show that the peak in the DOS of H₃S lies 0.28 eV below E_F at 200 GPa. Assuming a rigid band model, this peak could be accessed by ~12% P doping, which corresponds well to the S₀.₈₇₅P₀.₁₂₅H₃ stoichiometry (Fig. 3). In contrast to our results on H₃S with low levels of S→C and SH₃→CH₄ replacements, the DOS at E_F (g(E)/Å³) within Im₃m S₇PH₂₄ is about the same as that of the undoped binary. A Bader analysis, which typically underestimates the formal charge, suggested a charge of +0.25 on CH₆, whereas PH₆ is nearly neutral. Moreover, a plot of the electron localization function (ELF) is indicative of the formation of mult centered P-H-S bonds, whereas the ELF plot for O₆-CS₁₅H₄₈ suggested the presence of strong C-H bonds, with the positively charged CH₆ motif weakly interacting with the nearby sulfur atoms. The different behavior of P versus C doping can be traced back to their elemental properties. The atomic radius of phosphorus (98 pm) is slightly larger than that of sulfur (87 pm), but the radius of carbon is markedly smaller (67 pm). Moreover, whereas the electronegativity of sulfur and carbon is about
the same, phosphorous is somewhat less adept at attracting electrons. As a result, low levels of P-doping have a markedly different effect on the electronic structure of H₃S as compared to small amounts of C-doping. This finding suggests that choosing the right element for chemical substitution is key towards designing a material with an electronic structure that is particularly conducive towards superconductivity.

Figure 3: (a) Im\bar{3}m S₇PH₂₄ (S₀.₈₇₅P₀.₁₂₅H₃) at 150 GPa. (b) The Electron Localization Function (ELF) contour plotted in a plane that bisects the S-H-P contacts. (c) The density of states (DOS) plot near the Fermi (E_F) level of Im\bar{3}m H₃S (black) and Im\bar{3}m S₇PH₂₄ (red) at 200 GPa. The value of the DOS at E_F is 0.043 and 0.045 states eV⁻¹Å⁻³ (0.063 and 0.067 states eV⁻¹/valence electron), respectively.

To further interrogate the bonding in the P-doped structure the negative of the crystal orbital Hamilton population integrated to the Fermi level (-iCOHP) was calculated. In Cm S₇PH₂₄ at 150 GPa five of the P-H bonds were stronger than the S-H bonds (4.18-4.23 eV/bond versus 1.97-2.12 eV/bond) and one bond was about the same strength (3.44 versus 3.13 eV/bond). Higher pressures promote multi-centered bonding so that in Im\bar{3}m S₇PH₂₄ at 200 GPa the PH-S and SH-P -iCOHPs were almost equivalent (3.22 versus 3.74 eV/bond), and quite comparable to the bond strength within undoped Im\bar{3}m H₃S at this pressure (3.67 eV/atom). Again, this differs markedly from our previous results, which showed that carbon doping decreased the CH-S bond strength to 2.00 eV/bond. Because P-doping does not perturb the structure nor the electronic structure of the H₃S lattice to the same degree as C-doping, it does not decrease the metallicity of H₃S significantly, or at all, and the electrons remain delocalized throughout the S-P-H lattice at 200 GPa. In contrast
to our previous findings on S→C substitutions in an octahedral coordination environment,[25] which decreased the $T_c$ from 174 to 130 K at 270 GPa, we would therefore expect the $T_c$ of $Im3m$ $S_7PH_{24}$ to be closer to that of $Im3m$ $H_3S$ at 200 GPa, and perhaps even to surpass it. This hypothesis will be tested below.

$S_4PH_{15}$ ($S_{0.8}P_{0.2}H_3$) possessed the second highest S-concentration of the doped $S_{1-x}P_xH_3$ phases that were considered. $P1$, $I4$, and $I4/m$ symmetry structures were the most stable at 100, 150, and 200 GPa, respectively, and they lay only 25.7, 20.2, and 29.0 meV/atom above the convex hull at these pressures. $P1$ $S_4PH_{15}$ contains four $H_2$, one $PS_2H_2$ and one $(SH_2)_2$H unit in the primitive cell. We do not show it in Fig. 2 since it is not a cage-like structure, and it is semiconducting at 100 GPa. The $I4$ and $I4/m$ symmetry phases are related to each other, and both can be considered as cage-like structures similar to $Cm$ $S_7PH_{24}$. At 150 GPa the H-S distances measured 1.415-1.667 Å, shortening slightly to 1.412-1.590 Å at 200 GPa (c.f. 1.492 Å in $Im3m$ $H_3S$ at 200 GPa). The ideal octahedral geometry about the P atom was somewhat distorted in the $I4/m$ phase with four P-H bonds measuring 1.427 Å, and the remaining two measuring 1.483 Å. Lowering the pressure induces further distortions from the ideal octahedral coordination environment in both the H-P-H angles (89.9-90.1°) and P-H distances (1.437/1.485/1.580 Å).

For the $S_3PH_{12}$ ($S_{0.75}P_{0.25}H_3$) stoichiometry, two metastable cage-like structures with $Imm2$ (100-190 GPa) and $Imm$ (200 GPa) symmetries were found with a distance of 28.4, 18.5, 33.2 meV/atom above the convex hull at 100, 150, and 200 GPa, respectively. The $Imm$ phase was also identified at 200 GPa by Tsuppayakorn-aek et al.,[43] but the $Imm2$ was not reported before. At 150 GPa the S-H distances ranged from 1.386-1.711 Å, and increasing pressure decreased this range (1.422-1.613 Å at 200 GPa). The geometry about the P atom deviated somewhat from that of a perfect octahedron with four short and two long P-H distances (1.417 and 1.483 Å at 200 GPa, and 1.422 Å, 1.476 and 1.588 Å at 150 GPa). The DOS at $E_F$ of these two metallic phases was somewhat lower than for 12.5% doping.

Several other dynamically stable cage-like structures with larger P-dopings were also found: $P1$ $S_3P_2H_{15}$ (stable between 150-200 GPa), $Amm2$ $SPH_6$ (stable between 100-200 GPa), and
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$Pm\bar{3}m$ SPH$_2$ (stable at 200 GPa). Their distance from the convex hull was typically somewhat larger than that of the aforementioned phases (Table S2), but still within the realm of synthesizability. Therefore, their structural peculiarities and electronic structures are also briefly described. Whereas, $P1$ S$_3$P$_2$H$_{15}$ can still be viewed as a perturbation of a doped H$_3$S parent, larger phosphorous content has a profound impact on the geometries of the most stable structural alternatives. For a 1:1 chalcogen to pnictogen ratio CSP identified an $Amm2$ SPH$_6$ phase that was built from a 2D square S-H net where the sulfur atoms lay on the corners, and the hydrogen atoms bisected the edges. A layer of PH$_4$ units separated the layers, with the phosphorous atoms forming additional bonds to two sulfur atoms, one in each of the adjacent layers, thereby attaining quasi-octahedral coordination. This phase possessed the lowest enthalpy between 100-200 GPa, and it was 28 meV/atom more stable than the $Imma$ SPH$_6$ structure proposed by Tsuppayakorn-aek and co-workers. It is instructive to compare the geometry of $Amm2$ SPH$_6$ with CSH$_7$, since the two systems have the same valence electron counts. The family of dynamically stable CSH$_7$ structures could also be described as being built from 2D S-H square nets separated by CH$_4$ molecules. But, the smaller radius of carbon relative to phosphorous facilitated the bonding of two adjacent S-H layers via the extra hydrogen atom per formula unit, thereby forming an SH$_3$ cage within which methane was intercalated.

Finally, a $Pm\bar{3}m$ SPH$_2$ structure whose unit cell contained a phosphorous atom at the center and faces of the cube, and sulfur atoms at the cube edges and vertices was identified at 200 GPa. The phosphorus atom at the center of the cube was coordinated to eight hydrogen atoms at a distance of 1.593 Å. At lower pressures the most stable EA structures consisted of SP layers terminated and separated by atomic or molecular hydrogen, similar to some of the PH$_n$ phases previously proposed between 40-100 GPa.

$Im\bar{3}m$ H$_3$S is a highly symmetric structure where each H-S distance measures 1.492 Å at 200 GPa because of bond symmetrization that occurs under increasing pressure. At relatively low levels of S → P substitutions the doped structures retain the same basic lattice, with slight distortions that can be traced back to the atomic size and electronegativity differences between
the two \( p \)-group elements. With the exception of 12.5\% doping, the DOS at \( E_F \) of all of the
aforementioned cage-like structures was found to be smaller than that of the \( \text{H}_3\text{S} \) parent. Below
we will see how chemical substitution affects the propensity for superconductivity of these \( \text{S-P-H} \)
phases.

**Structures with 2D Hexagonal Sheets**

![Illustrations of predicted S-P-H phases that contained hexagonal H-S and/or P-H sheets: (a) \( R3m \) \( S_2\text{PH} \) at 200 GPa, (b) \( \text{Cmc}_2 \) \( \text{SP}_2\text{H} \) at 150 GPa, and (c) \( P6_3mc \) \( \text{SP}_2\text{H} \) at 200 GPa. S/P/H atoms are colored yellow/orange/white.](image)

Stoichiometries that differed from those that could be derived by doping \( \text{H}_3\text{S} \) with phosphorous
were also explored via evolutionary crystal structure searches. Previous theoretical studies pin-
pointed a unique \( P\bar{6}m2 \) \( \text{CaSH}_3 \) phase consisting of alternating \( \text{CaH}_2 \) and honeycomb H-S sheets
that possessed two vHs bracketing \( E_F \) thereby increasing the number of states that can participate
in the pairing mechanism, and concomitantly the \( T_c \) of this phase.\(^{20}\) This structure was metastable
down to 128 GPa, where its \( T_c \) was estimated to be as high as 100 K. Analogous layered structures
were identified in this study (Fig. 4), but they could be comprised of either H-P or H-S honeycomb
sheets, and some contained both.
For example, $R3m$ $S_2PH$ could be described as a layered structure comprised of H-S and H-P hexagonal nets that were separated from each other by a layer of sulfur atoms (located on top of the centers of the hexagons), or by three S-P-S layers. This structure was just 2.7 meV/atom shy of the 200 GPa convex hull. Whereas the S-H honeycomb nets did not bond with atoms in the adjacent CaH$_2$ layers in $P6m2$ CaSH$_3$, here covalent bonds are formed between the main group elements in the honeycomb sheets and the sulfur atoms in the next layer. Both the H-S and H-P bond lengths in the hexagonal sheets present in $R3m$ $S_2PH$ (1.650 and 1.658 Å) were longer than the one found in $P6m2$ CaSH$_3$ (1.605 Å) at 200 GPa. At lower pressures the most stable phases with this stoichiometry did not contain these types of hexagonal layer motifs.

Finally, two different SP$_2$H structures, both comprised of 2D hexagonal P-H sheets that were separated by a layer of sulfur and a layer of phosphorous atoms lying above or below the hexagonal holes, were found. The main difference between these two phases is that the $Cmc2_1$ structure, stable between 110-170 GPa, possessed two distinct P-H distances (1.643/1.730 Å), whereas all of the P-H distances were equalized in the higher pressure $P6_3/mc$ phase (1.660 Å). These systems lay 22.4 and 54.8 meV/atom above the convex hull at 150 and 200 GPa, respectively.

**Structures with 2D Sheets and/or 1D Molecular Chains**

In addition to the previously discussed cage-like structures and 2D hexagonal sheets, several metastable phases that contained 2D sheets and/or 1D molecular chains were found in our evolutionary searches. Some examples, illustrated in Fig. 5, include SP$_2$H$_9$ and S$_2$P$_3$H$_{15}$ (at 150 and 200 GPa), which contained both 1D molecular chains and 2D sheets, SP$_3$H$_{12}$, which possessed 2D sheets and S$_2$P$_3$H$_{15}$ (at 100 GPa), comprised of 1D molecular chains. Other systems not discussed here (Fig. S42), such as SPH$_5$ and SP$_4$H$_{15}$, only contained 1D molecular chains.

Though phases with the SP$_2$H$_9$ stoichiometry were enthalpically unstable with respect to elemental H$_2$, S and P, their $\Delta H_F$ was still within the threshold proposed to gauge the synthesizability of a metastable material at 1 atm. At 100 and 150 GPa the most stable SP$_2$H$_9$ geometry adopted a $P\overline{1}$ symmetry structure that contained 2D H-S square nets, where the sulfur atoms comprised the
edges and the hydrogen atoms the vertices, extending along the c-axis. These sheets were separated from one another by a layer of H₃P-PH₃ molecular motifs that were linked to each other via an extra hydrogen atom bonded to two phosphorous atoms from adjacent units thereby forming a 1D chain analogous to a nanothread. The bond length between phosphorous and a bridging hydrogen atom was longer than between phosphorous and a terminal hydrogen atom (1.51-1.54 Å vs. 1.36-1.40 Å at 150 GPa). At 200 GPa the preferred SP₂H₉ structure did not possess any distinguishing features, so it is not discussed here.

Like SP₂H₉, the most stable SP₃H₁₂ phases were within the realm of synthesizability even though their enthalpies of formation were positive. At 200 GPa the enthalpy of the most stable structure found at 200 GPa, *Cm* SP₃H₁₂, was 33 meV/atom lower than that of a previously pro-

![Figure 5: Illustrations of predicted S-P-H phases that contained 2D sheets and/or 1D “nanothreads”: (a) *P*-1 SP₂H₉ at 150 GPa, (b) *C*₂ SP₃H₁₂ at 100 GPa, (c) *P*-I S₂P₃H₁₅ at 100 GPa, (d) *P*-II S₂P₃H₁₅ at 150 and 200 GPa. S/P/H atoms are colored yellow/orange/white.](image)
posed phase with this stoichiometry, \textit{Immm} SP$_3$H$_{12}$ at 200 GPa.\cite{13} However, neither it nor the 
\textit{Cc} phase found at lower pressures possessed characteristic structural motifs. Therefore, here we
describe the \textit{C2} phase, which was the ground state structure at 100 GPa. \textit{C2} SP$_2$H$_9$ possessed 2D
square nets similar to those found within the previously described \textit{P\overline{1}} SP$_2$H$_9$ phase, except some
of the sulfur atoms were replaced by phosphorous. These layers were separated by PH$_4$ motifs that
were within bonding distance to the \textit{p}-block elements above or below them in the 2D nets.

The most stable S$_2$P$_3$H$_{15}$ phase found at 100 GPa can be described as an S-P-H nanothread
where each phosphorus atom is octahedrally coordinated to four hydrogen atoms that lie in the
same plane and two SH motifs, or to one SH motif and one hydrogen atom. The sulfur atoms
in these SH motifs and the hydrogen atoms are bonded to a nearby PH$_4$ unit. Higher pressures
push adjacent nanothreads close enough to form S-H-S bonds along the \(a\) axis resulting in a 2D
S-H square net that is characteristic of many of these compounds by 150 GPa. Another difference
between the preferred S$_2$P$_3$H$_{15}$ structures at 150 and 200 GPa is that the hydrogen atom that bridges
two phosphorous atoms in the lower pressure phase migrates to the 2D S-H net upon compression.

\textbf{Phases on the Hull}

Our calculations revealed four thermodynamically stable species that lay on the convex hull; these
are illustrated in Fig. 6. A \textit{Cmcm} symmetry SPH phase that was 5.8 meV/atom above the hull at
150 GPa and lay on the hull at 200 GPa possessed. It can be considered as a distorted ZrBeSi-type
lattice (e.g. BaAgAs\cite{96}) with the P and H atoms on the Be and Si sites, but the P and H atoms
did not form the hexagonal sheets since the P-H distance (1.459/1.728 Å) were too long. At lower
pressures a \textit{P2\textsubscript{1}}/\textit{m} symmetry structure, which is not discussed here because it did not present any
distinguishing characteristics, was the most stable SPH stoichiometry phase.

S$_2$PH$_9$ was the only thermodynamically stable system with a S$_x$P$_{1-x}$H$_3$ stoichiometry (\(x = 0.67\)). It lay on the 100 GPa convex hull, but was 18.6/56.9 meV/atom above the hull at 150/200 GPa.
At 100 GPa the preferred structure possessed \textit{C2/m} symmetry, and it could be derived from adding
hydrogen to the most stable S$_2$P phase found at this pressure.\cite{22} A 1D chain of vertex sharing S-
Figure 6: Illustrations of predicted S-P-H phases that lay on the convex hull: (a) $Cmcm$ SPH at 200 GPa (Some P-H are connected by dash lines for better eye-view) , (b) $C2/m$ $S_2PH_9$ at 100 GPa, (c) $C2/m$ $S_3PH$ at 150 GPa, (d) $C2/m$-II $S_2PH$ at 150 GPa. S/P/H atoms are colored yellow/orange/white.
P-S-P rhombii comprised this phase. The phosphorous atoms, which belonged to two rhombii, were octahedrally coordinated to four sulfur atoms and two hydrogen atoms. Each sulfur atom was bonded to a hydrogen atom, which was further bonded to a sulfur atom in an adjacent 1D chain, and H₂ molecules were interspersed between the chains. A $C2/m$ symmetry $S_3PH$ phase lay on the 100 and 150 GPa convex hulls, but it was 25.4 meV/atom above the 200 GPa hull. It could be viewed as a distorted cubic network where phosphorous or sulfur atoms were found on the vertices of the cubes. All of the phosphorus atoms were octahedrally coordinated by bonds to sulfur atoms. Many sulfur atoms were octahedrally coordinated as well, and those that weren’t were bonded to hydrogen atoms that were shared between two sulfur atoms. Finally, $C2/m$-II $S_2PH$ was also thermodynamically stable at 150 GPa. It resembled $S_3PH$, except the octahedrally coordinated phosphorous atoms were bonded to both P and S, some of the sides of the distorted cubes were more like parallelograms, and the hydrogen atoms were only bonded to a single sulfur atom. Both $S_2PH$ and $S_3PH$ could be derived from the most stable high pressure $S_2P$ and $S_3P$ phases that were predicted in previous reports.\textsuperscript{72}

**Electronic Structure and Superconducting Properties**

The PBE electronic band structures and DOS plots of both thermodynamically and dynamically stable S-P-H phases (Figs. S8-26) showed that most were metallic except for $P\bar{1}$ $SPH_1$ at 100 GPa, $Pm$ $SPH_2$ at 100-150 GPa, $P1$ $S_4PH_{15}$ ($S_{0.8}P_{0.2}H_3$) at 100 GPa, $C2/m$ $S_2PH_9$ ($S_{0.67}P_{0.33}H_3$) at 100-200 GPa and $P\bar{1}$ $S_2P_3H_{15}$ ($S_{0.4}P_{0.6}H_3$) at 100 GPa. In general the DOS at the Fermi level in the $SPH_n$ ($n = 1-2$) phases was dominated by the phosphorous and sulfur p states in nearly equivalent proportions. In most of the phases with a larger hydrogen content such as $SPH_n$ ($n = 3-6$) all three atom types contributed nearly equally to the DOS at $E_F$, and the most abundant p block element possessed the largest amount of character at $E_F$ in $S_xP_yH$ ($x, y = 2, 3$) phases. For the cage-like doped systems illustrated in Fig.\textsuperscript{2} the states at $E_F$ were primarily characterized by sulfur and hydrogen character, whereas those with 2D or 1D motifs (i.e. those in Fig.\textsuperscript{5}) possessed more hydrogenic character.
A large DOS at $E_F$ is a prerequisite for high $T_c$, in particular if it results from states related to hydrogen. Another descriptor that can be associated with high temperature conventional superconductors is an increased Debye frequency, which is a consequence of the vibrations of atoms with light masses. Therefore, these quantities were calculated for the metallic S-P-H phases found in our work (Table S3-4) and used to screen for the most likely structures to have a high $T_c$. If the DOS per valence electron at $E_F$ was calculated to be $\gtrsim 0.035$ states/eV and the Debye frequency was $\gtrsim 750$ cm$^{-1}$, electron phonon coupling (EPC) calculations were performed to probe the superconducting properties of the phase. In addition, EPC calculations were carried out for SPH, SP$_2$H, S$_2$PH, S$_3$PH, SPH$_2$ and SPH$_3$ though they did not meet these criteria because their superconducting characteristics could be compared to those previously computed for S-P phases.

Table 2 lists the electron phonon coupling parameter, $\lambda$, and logarithmic average of phonon frequencies ($\omega_{\log}$) for the considered phases, as well as their $T_c$s as estimated via the Allen-Dynes modified McMillan equation. Comparison of our results with the $T_c$s previously computed$^{[22]}$ for SP, SP$_2$, and PS$_2$ (1.5-4.3 K) shows that addition of a single hydrogen atom can raise $T_c$ by an order of magnitude (cf. 17-21 K for SPH and SP$_2$H) primarily because of an increase in $\lambda$. Adding one or two more hydrogen atoms, e.g. to form SPH$_2$ or SPH$_3$, does not impact $T_c$ by much, but the $T_c$ of $P2_1/m$ SPH$_4$ (Fig. S42) was estimated to be significantly larger, 64 K at 200 GPa.

Generally speaking, phases that were constructed by doping $I\bar{m}3m$ H$_3$S with phosphorous, e.g. those with $S_{1-x}P_xH_3$ stoichiometries, were the best superconductors. The $T_c$ of the most stable 12.5% doped structure at 150 GPa was estimated to be 117 K, which is lower than previous reports for this stoichiometry at the same pressure (168 K$^{[40]}$ and 190 K$^{[42]}$). However, the structures considered in prior studies were not found using crystal structure prediction techniques and were at least 7 meV/atom less stable than the phase found here at 150 GPa. The $I4/m$ symmetry 20% doped structure possessed the second highest $T_c$ of any phase we considered (136 K at 200 GPa), decreasing slightly at lower pressures (114 K at 150 GPa within the $I4$ spacegroup). Because the modified McMillan equation is known to underestimate $T_c$ for systems with large EPC values, we also numerically solved the Eliashberg equations for both the 12.5% and 20% dopings. However,
A comparison of our calculated $T_c$ for $\text{Im\breve{3}}m$ $\text{H}_3\text{S}$ at 200 GPa with experiment ($\sim$175-190 K) shows that when $\mu^*$ is chosen to be 0.1, the modified McMillan equation gives values that better agree with those that were measured.

Increasing the doping to 25% decreases $T_c$ to 28/93 K at 150/200 GPa. The drop in $T_c$ with an increase in doping correlates with the decreased DOS at $E_F$, which is maximal for 12.5% doping. Previously, Durajski and Szczęśniak used the supercell approach to propose a 50% doped structure with a $T_c$ of 157 K at 155 GPa, while Tsuppayakornaek et al. used crystal structure prediction to find an SPH$_6$ phase with an estimated $T_c$ of 89 K at 200 GPa. The most stable structure XTALOPT found with this stoichiometry was 70.2 meV/atom lower than the one generated via the supercell approach at 150 GPa, and 28 meV/atom lower than Tsuppayakornaek’s structure at 200 GPa. However, the DOS at $E_F$ of our predicted SPH$_6$ phase was so low that an EPC calculation was not considered. Even though the stoichiometry of $Pm\text{SP}_2\text{H}_9$ is compatible with that of a P-doped $\text{H}_3\text{S}$ structure, the large concentration of phosphorous has a dramatic impact on the geometry of this phase (Fig. S42), which did not show any distinct structural features. Nonetheless, it’s estimated $T_c$, 66 K at 200 GPa, was comparably high.

The superconducting critical temperatures of all of the phases discussed so far are lower than that of the parent $\text{Im\breve{3}}m$ $\text{H}_3\text{S}$ structure. However, as illustrated in Fig. 3 at 200 GPa the DOS at $E_F$ of the $\text{Im\breve{3}}m$ $S_7\text{PH}_{24}$ phase is slightly higher than that of the undoped structure. Like sulfur, many textbook examples highlight the propensity of phosphorous to assume hypervalent coordination environments so the phase is stable to lower pressures than octahedrally coordinated carbon in $O_{h-}\text{CS}_{15}\text{H}_{48}$. Moreover, unlike in the carbon doped phase the hydrogen atoms retain their multi-centered coordination so the metallicity is not decreased.

Previous studies have computed the $T_c$ of $\text{Im\breve{3}}m$ $S_7\text{PH}_{24}$ and arrived at different conclusions. Durajski and Szczęśniak concluded that $S\rightarrow P$ replacement cannot raise the $T_c$ of $\text{H}_3\text{S}$, finding a maximum $T_c$ of 190 K at 155 GPa using the Eliashberg formualism and $\mu^* = 0.15$, but lower level dopings were not considered. At about the same time, Nakanishi and co-workers found that 12.5% doping increases the $T_c$ of $\text{H}_3\text{S}$ at 200 GPa from 189 to 194 K using the Allen-Dynes
Table 2: Electron-phonon coupling parameter (λ), logarithmic average of phonon frequencies (ω_{log}), and estimated superconducting critical temperature (T_c) for a given pressure of various S-P-H phases. The calculations employed the Allen-Dynes modified McMillan equation with a renormalized Coulomb potential, µ^* = 0.1. Values in parentheses were calculated via numerical solution of the Eliashberg equations.

| System | Pressure | λ  | ω_{log} (K) | T_c (K) |
|--------|----------|----|-------------|---------|
| P2/m SP | 100 | 0.46 | 522.4 | 4.3 |
| C2/m SP | 150 | 0.38 | 506.8 | 1.5 |
| C2/m PS | 100 | 0.45 | 453.3 | 1.7 |
| P3m1 PS | 200 | 0.37 | 611.0 | 1.5 |
| R3m H3S | 130 | 2.07 | 1125.1 | 166 |
| IImcm H3S | 200 | 1.94 | 1337.0 | 188.5 (249.2) |
| Cmcm SPH | 200 | 0.66 | 724.9 | 21.9 |
| CmS2 | 150 | 0.64 | 588.8 | 16.5 |
| CmS2 | 150 | 0.70 | 594.3 | 21.0 |
| CmS2 | 150 | 0.53 | 562.7 | 8.7 |
| P2/m SPH | 150 | 0.57 | 853.3 | 17.0 |
| P2/m SPH | 200 | 0.88 | 1124.5 | 63.7 |
| CmS7PH24 (S0.875P0.125H3) | 100 | 1.06 | 782.4 | 59.4 |
| CmS7PH24 (S0.875P0.125H3) | 150 | 1.42 | 1081.2 | 116.8 (147.6) |
| IIm3m S7PH24 (S0.875P0.125H3) | 200 | 2.21 | 1188.1 | 182.5 (257.5) |
| I4 S1PH15 (S0.8P0.2H3) | 150 | 1.47 | 1020.5 | 113.9 (145.9) |
| I4/m S1PH15 (S0.8P0.2H3) | 200 | 1.42 | 1259.2 | 135.9 (171.6) |
| Imm2 S3PH12 (S0.75P0.25H3) | 150 | 0.64 | 1153.0 | 27.3 |
| Imm3m S3PH12 (S0.75P0.25H3) | 200 | 1.08 | 1187.5 | 92.6 |
| Pm SP2H9 (S0.33P0.67H3) | 200 | 0.99 | 951.2 | 65.5 |

a Calculated in Ref.\textsuperscript{[24]} b Calculated in Ref.\textsuperscript{[19]}

modified McMillan equation with strong coupling and shape factors, and from 225 to 249 K using the isotropic Eliashberg equation with µ^* = 0.13. Even higher T_c's (212 and 268 K via the Allen-Dynes and Eliashberg methods, respectively) were computed for 6.5% doping levels. Most recently, Guan and colleagues reported that 12.5% phosphorous content barely changes the T_c of H3S at 200 GPa. A decreased doping of 6.5%, on the other hand, increased the T_c of at 200 GPa from 214 to 231 K using the Allen-Dynes modified McMillan equation with strong coupling and shape factors, and from 238 to 262 K via Migdal-Eliashberg theory with µ^* = 0.1.

Our results echo those of Guan and co-workers: at 200 GPa the estimated T_c of IIm3m S7PH24 differs by 6-8 K from the value predicted for IIm3m H3S, which is within our calculation error.
Therefore, we conclude that the 12.5% doping of H$_3$S by phosphorous does not change $T_c$ by much. While Guan and Nakanishi both found that 6.25% doping increased the $T_c$ relative to that of Im$\bar{3}$m H$_3$S slightly, this system was not considered here because its DOS at $E_F$ was calculated to be lower than that of Im$\bar{3}$m S$_7$PH$_{24}$ at 200 GPa (Fig. S7).

**Conclusions**

The exciting discovery of novel hydride-based superconductors with record breaking superconducting critical temperatures, $T_c$s, has fueled the search for evermore complex systems. One way to design new superconducting materials is by doping known structures in the hopes of finding a material with a higher $T_c$, or a lower stabilization pressure. Previous studies have consider the effect of phosphorous doping on the $T_c$ of Im$\bar{3}$m H$_3$S, however they were performed either using the virtual crystal approximation or they only considered phases derived from S→P replacement within the Im$\bar{3}$m H$_3$S parent.

To overcome these limitations we have employed crystal structure prediction techniques to explore a wide S$_x$P$_y$H$_z$ composition range. The convex hull was mapped out under pressure and found to consist of $C_{mcm}$ SPH (200 GPa), $C2/m$ S$_2$PH$_9$ (100 GPa), $C2/m$ S$_3$PH (100, 150 GPa) and $C2/m$-II S$_2$PH (150 GPa). Of these phases, the ones whose $T_c$s were calculated ranged from 9-22 K. In addition, a wide variety of potentially synthesizable compounds were predicted containing unique structural motifs such as one-dimensional nanothreads, two-dimensional square nets or honeycomb sheets, as well as cages. From the cages, those with the highest $T_c$s corresponded to low dopings of Im$\bar{3}$m H$_3$S with phosphorous. The propensity for phosphorous to participate in hypervalent bonds coupled to its similar-to-sulfur-size were key to retaining a high density of states at the Fermi level in Im$\bar{3}$m S$_7$PH$_{24}$ (S$_{0.875}$P$_{0.125}$H$_3$), whose $T_c$ was predicted to be 183 K at 200 GPa. We hope this study inspires the eventual synthesis of these compounds, and the exploration of their physical and chemical behavior.
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Supporting Information: The Supporting Information is available free of charge upon request.
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