Route to high-$T_c$ superconductivity via CH$_4$-intercalated H$_3$S hydride perovskites

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Phys. Rev. B 101, 134504 — Published 9 April 2020

DOI: 10.1103/PhysRevB.101.134504
New route to high-$T_c$ superconductivity via CH$_4$ intercalated H$_3$S

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(Dated: February 19, 2020)

While exploring potential superconductors in the C-S-H ternary system using first-principles crystal structure prediction methods, we uncovered a new class of hydrides based on the intercalation of methane into an H$_3$S framework. These intriguing H$_3$S-CH$_4$ structures emerge as metastable at $\sim$100 GPa. Electron-phonon coupling calculations indicate that phases with the CSH$_7$ stoichiometry are potential superconductors with $T_c$ values of 100 K and 190 K at 100 GPa and 150 GPa, respectively. The results are expected to guide the experimental search for new high-$T_c$ superconductors, including those stable at lower pressures than previously documented superconducting hydrides such as H$_3$S and LaH$_{10}$.

The pursuit of high-$T_c$ and even room-temperature superconductivity has been a grand challenge in physics since the 1911 discovery of superconductivity [1]. Bardeen–Cooper–Schrieffer (BCS) theory [2] can well describe the mechanism for conventional superconductors, opening the door for the discovery and design of high-$T_c$ materials. Ashcroft [3] proposed that compressed hydrides are good candidates for high-$T_c$ superconductors due to chemical ‘pre-compression’ effects. Subsequent theoretical studies provided explicit predictions of these phenomena, and have led to the discovery of very high temperature superconductivity, first in H$_3$S ($T_c$ of 203 K) [4] and more recently in LaH$_{10}$ ($T_c$ up to 260 K) [5–7]. These experimental results confirmed theoretical predictions for both the structures and basic mechanism of superconductivity [8–11], thereby marking a new era for both superconductivity and ‘materials by design’ [5, 12–14].

Compared to binary hydrides, exploration of high-$T_c$ superconductors in ternary hydrides greatly enlarges the configurational space and opens up new chemistry and physics that could in principle enhance both $T_c$ and stability, including at modest pressures. This additional elemental degree of freedom in compressed ternary hydride systems has led to new predicted high-$T_c$ superconductors such as CaYH$_{12}$ ($T_c$ = 258 K at 200 GPa) [15], LiPH$_6$ ($T_c$ = 150–167 K at 200 GPa) [16], and most remarkably Li$_2$MgH$_{16}$ ($T_c$ = 473 K at 250 GPa) [17]. On the other hand, existing experimental studies have uncovered only relatively low $T_c$ materials such as in BaReH$_6$ ($T_c$ = 7 K) [18] and Li$_3$MoH$_{11}$ ($T_c$ = 6.5 K) [19]. Returning to sulfur-containing systems, carbon disulfide (CS$_2$) has been shown to transform to a metal at 50 GPa, and a superconductor with a $T_c$ of $\sim$6 K at 60-170 GPa [20]. Several ternary hydrides based on the H$_3$S structure are predicted to exhibit high-$T_c$ behavior, including H$_6$SSe (i.e., SH$_3$-SeH$_3$, with an estimated $T_c$ of 195 K at 200 GPa) [21], Y(La)SH$_6$ [SH$_3$-Y(La)H$_3$, $T_c$ = 95 K and 35 K at 210 GPa and 300 GPa, respectively] [22], and even the noble gas Xe with H$_3$S (H$_3$SXe, $T_c$ = 89 K at 240 GPa) [23]. Moreover, several superconductors have also been reported in ternary F-S-H, Y-S-H and B-S-H compounds [24–26].

There is also general interest in carbon-containing high-$T_c$ superconductors. Dense carbides that are isostructural with hydrides have been predicted to exhibit high $T_c$ behavior and to be stable on decompression owing to their rigid carbon $sp^3$ frameworks [27]. Various hydrocarbons (e.g., CH$_3$, C$_2$H$_4$ and C$_2$H$_6$) are stable in different molecular phases to megabar pressures [28–30]. CH$_4$ and Mg are predicted to form CH$_3$Mg, a potential superconductor with a $T_c$ of 84–121 K at 75 to 120 GPa [31]. The related compound CH$_4$K has a predicted $T_c$ of about 12 K at 80 GPa [32]. These results encouraged us to theoretically search for high-$T_c$ superconductors in the C-S-H ternary system. As shown in detail below, metastable $Cm$ and $R3m$ symmetry phases were found, and electron-phonon coupling calculations revealed that both are potential superconductors with $T_c$s of 97–108 K at 130 GPa and 181–194 K at 150 GPa, respectively as estimated by solving the Eliashberg equations numerically using the typical choice of the Coulomb potential, $\mu^*$ = 0.10–0.13.

We began by identifying stable structures in the C-S-H system, focusing on C$_x$S$_y$H$_z$ (x = 1–2; y =1-2; z = 1-8) compositions at megabar pressures (100–200 GPa), using heuristic algorithms based on particle swarm optimization [33–35] and evolutionary algorithms [36] in combination with first-principles theory (computational details are provided in the Supporting Information, SI [37]). The CSH$_7$ stoichiometry emerged as being particularly stable relative to the elements in the pressure range considered. The enthalpies of formation from the elemental phases for CSH$_7$ were -83, -72, -61, and -25 meV/atom at 100, 130, 150 and 200 GPa, respectively. Interestingly, the structures of CSH$_7$, shown in Fig. S1 of the SI, are composed of CH$_4$ molecules intercalated within
different, but related, H$_3$S networks. At 100 GPa, the H$_3$S sublattice is characterized by SH$_6$ layers. Upon compression (~130 GPa), the $R3m$ phase shown in Fig. 1 becomes enthalpically favored, with CH$_4$ molecules intercalated into the cubic H$_2$S framework formed by two neighboring SH$_5$ layers that are linked via shared H atoms.

Although the enthalpies of formation of the CSH$_7$ phases are negative with respect to the elemental phases, these species do not lie on the 3D convex hull. In fact, they are metastable with respect to CH$_4$ + H$_3$S (and CH$_4$ + H$_2$S + 1/2H$_2$), but stable relative to H$_2$S + C + 5/2H$_2$ below 188 GPa. The zero-point energy (ZPE) uncorrected enthalpy of $R3m$ is 33 meV/atom above the convex hull at 130 GPa. As shown in Table S1 of the SI, inclusion of the ZPE or finite temperature effects does not stabilize the ternary phase. It should however be noted that a number of compressed hydrides found to be metastable via first-principles calculations have been synthesized in the laboratory. Examples include a Ca$_3$H$_5$ phase, which was calculated to be 20 meV/atom above the convex hull [38], and hydrides of phosphorus, which are at least 30 meV/atom above the convex hull [39–41]. Moreover, these phases could potentially be stabilized by anharmonic or nuclear quantum effects as found for LaH$_{10}$ [42]. Therefore, it is expected that the CSH$_7$ phases could be realized experimentally, especially if they are calculated to be dynamically stable.

The relative enthalpies of the CSH$_7$ phases between 100 to 300 GPa are shown in Fig. S2. The $Cm$ phase is calculated to transform to $R3m$ at 130 GPa, followed by a transition to $Amm2$ symmetry at 250 GPa. Phonon calculations reveal that $Cm$ is dynamically stable from 100 to 110 GPa, whereas $R3m$ is dynamically stable from 130 to 300 GPa, and $Amm2$ is not dynamically stable at the current level of approximation at 250 and 300 GPa (Fig. S3). Molecular dynamics simulations (Fig. S4), on the other hand, suggest that $Cm$, $R3m$ and $Amm2$ are stable at 130, 150, and 250 GPa at 300 K, respectively.

The three predicted 0 K structures of CSH$_7$ and cubic $Im3m$ H$_3$S are shown in Fig. 1 and Fig. S1. In pure H$_3$S, the S atoms form a bcc lattice with each S atom octahedrally coordinated by H atoms (Fig. 1a). The CSH$_7$ phases are based on the H$_3$S structure with the central SH$_6$ unit replaced by a CH$_4$ molecule, and a distortion of the cubic framework. In the $Cm$ phase (Fig. S1a), the cubic H$_3$S lattice is replaced by two layers of SH$_5$. The H-S distance between neighboring SH$_5$ layers is too long (1.906 Å) to form an H-S covalent bond. On compression the $Cm$ phase transforms to $R3m$ at 130 GPa (Fig. 1b). In this structure, the H$_3$S framework is retained but with a slight rhombohedral distortion such that the $a$, $b$, and $c$ unit cell vectors are equal in length, but the $\alpha$, $\beta$, and $\gamma$ angles measure 89.4° (instead of 90°). The rotation barrier of the CH$_4$ unit in $R3m$-CSH$_7$ was estimated to be <1 meV/atom at 150 GPa (Fig. S5), suggesting the molecule may rotate freely. At 250 GPa the $Amm2$ phase, with a slightly distorted SH$_3$ lattice, becomes enthalpically favored (Fig. S1b).

In order to explore the bonding in the CSH$_7$ phases, their electronic localization functions (ELFs) were plotted (Fig. S6). The ELF is useful for visualizing covalent bonds and lone pairs; it maps values in the range from 0 to 1, where 1 corresponds to perfect localization of the valence electrons indicative of a strong covalent bond. The ELF values for the S-H and C-H bonds are close to 0.9, indicating their strong covalent character. The $Cm$ structure is characterized by 5 S-H bonds (bond lengths of 1.38 to 1.55 Å) and one lone electron pair (Figs. S6a and b). Similar to free methane, the CH$_4$ units contain 4 strong covalent C-H bonds, as shown in the 3D ELF plots. In the $R3m$ structure, the cubic H$_3$S framework is clearly evident.

The calculated pressure-volume equation of states (EOS) of
FIG. 3. Calculated (a) band structure, total DOS, and site-projected DOS near the Fermi level, and (b) phonon dispersion curves, PH-DOS projected on the C, S and H atoms, Eliashberg spectral function, $\alpha^2 F(\omega)$, and $\lambda(\omega) = \int_0^{\omega_0} d\omega'2\pi n^2 F(\omega')/(\omega')^\gamma$ for CSH$_7$ ($R3m$ structure) at 150 GPa. Red solid circles represent the phonon line width with the radius proportional to the respective coupling strength.

CSH$_7$ and assemblages consisting of CH$_4$ and H$_2$S, as well as C+4S+7H$_2$, are shown in Fig. 2. The sum of the volume of the predicted CH$_4$ ($Cmca$) [43] and H$_2$S ($R3m$ and $I1m3m$) [9] phases is also plotted for comparison. The evolution of the volume under pressure of CSH$_7$ falls between the experimental and theoretical data obtained for CH$_4$+H$_2$S. As shown in Fig. S7, the $PV$ contribution to the enthalpy favors the assemblages over CSH$_7$ within this pressure range. The pressure dependence of select S-H distances are plotted in Fig. S8. Under pressure the S1-H and S2-H bonds in the $Cm$ phase approach each other, and the S3-H distance decreases, as the phase undergoes pressure induced bond equalization. Because the CH$_4$ molecule breaks the symmetry, the S-H1 and S-H2 bonds in the $R3m$ phase differ slightly. Both S-H bonds in $R3m$-CSH$_7$ are slightly shorter than those calculated for $I1m3m$ H$_2$S, whose highest $T_c$, 203 K, was measured at 155 GPa [4]. If the S-H distance, which can be modulated by the identity of the intercalant molecule as well as the pressure, is an important factor in determining the $T_c$, it is expected that the maximum value for CSH$_7$ would be at smaller pressures, near the $R3m$ to $Cm$ structural instability.

The band structures and partial densities of states (DOS) for CSH$_7$ of $R3m$ and $Cm$ were calculated to further explore their electronic properties (Fig. 3a and Fig. S9a). Both exhibit metallic features, wherein the states near the Fermi level are mainly from the contribution of the H$_2$S framework, with negligible character from the CH$_4$ molecules. The significant overlap of states with H and S character indicates strong H-S hybridization under pressure, which has been demonstrated to play a key role in driving the high-$T_c$ superconductivity of cubic H$_2$S [12].

Fig. 3b and Fig. S9b show the phonon dispersions, projected phonon density of states (PHDOS), Eliashberg spectral function, $\alpha^2 F(\omega)$, and electron-phonon coupling integral, $\lambda(\omega)$, for $R3m$ and $Cm$ CSH$_7$, respectively. A notable feature of the CH$_4$ intercalation in the structures is the separation of the vibrational modes into three well distinct regions: the lower frequencies (below 20 THz) are associated with the heavier S, and C atoms, and modes including some of the CH$_4$ hydrogens; the intermediate frequencies (between 30 and 63 THz) are derived from combinations of H-wagging, bending, and stretching modes; and the higher frequencies ($\sim$100 THz, 3300 cm$^{-1}$) primarily from the C-H stretching modes of the molecular CH$_4$ units, close to the asymmetric stretching modes of free CH$_4$ ($\sim$97 THz, 3200 cm$^{-1}$).

The superconducting properties of the CSH$_7$ phases were estimated by the Allen-Dynes modified McMillan equation [49], using typical values of the Coulomb pseudopotential, $\mu^* = 0.13$-0.1. As shown in Table 1, below 250 GPa $\lambda$ was calculated to be appreciable for both phases. At 100 GPa $\lambda$ was 1.2 and $\omega_{\log}$ was 1091 K for the $Cm$ phase, yielding a $T_c$ of 86-98 K. For $R3m$ at 150 GPa, $\lambda$ was 2.47, which is twice the value found for $Cm$ and comparable to that calculated for cubic H$_2$S at 200 GPa (\lambda$=2.19$) [9], resulting in a $T_c$ of 143-152 K. The logarithmic average phonon frequency of $R3m$ CSH$_7$ at 150 GPa is somewhat lower than that of $I1m3m$ H$_2$S at 200 GPa [9], 925 K vs. 1335 K, which is the reason for the slightly lower $T_c$ of the ternary. The increase in $\lambda$ for $R3m$ as compared to $Cm$ is not unreasonable in view of the differences in their phonon band structures. In $R3m$, there are two obvious Kohn anomalies and softened modes at 18-32 THz located along the F-$\Gamma$, and $\Gamma$-Z high symmetry lines, which contribute a significant amount ($\sim$36%) to $\lambda$. In addition, $\lambda$ of

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pressure (GPa)</th>
<th>$\lambda$</th>
<th>$\omega_{\log}$ (K)</th>
<th>ADM</th>
<th>Eliashberg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Cm$</td>
<td>100</td>
<td>1.20</td>
<td>1091 (86)</td>
<td>108 (97)</td>
<td></td>
</tr>
<tr>
<td>$R3m$</td>
<td>150</td>
<td>2.47</td>
<td>925 (143)</td>
<td>194 (141)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.35</td>
<td>1379 (128)</td>
<td>158 (144)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.88</td>
<td>1738 (95)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.82</td>
<td>1730 (85)</td>
<td>-</td>
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</tr>
</tbody>
</table>
\[ R3m \] was found to decrease with increasing pressure, which was not offset by the increase in \( \omega_{\text{ph}} \) so that \( T_c \) decreased from 150 to 300 GPa. The maximum \( T_c \) for \( R3m \) therefore occurs at a slightly lower pressure than for \( H_2S \). For strongly coupled superconductors (\( \lambda > 1.5 \)), Eliashberg theory [50] gives a better estimate of \( T_c \), and therefore we also numerically solved the Eliashberg equations for select pressures, as shown in Table I and Fig. 4. As expected, the estimated \( T_c \) values were higher, 181–194 K and 141–158 K for \( R3m \) at 150 GPa and 200 GPa.

In summary, we have explored the stability and electronic properties of \( C_{\text{3}}S_{\text{y}}H_{\text{2}} \) ternary compounds at high pressure. Stoichiometric \( CSH_7 \) was found to be dynamically stable above 100 GPa, and two phases with \( Cm \) and \( R3m \) space group symmetries were found. Interestingly, these structures are characterized by \( CH_4 \) intercalated into a distorted \( H_2S \) framework, which could represent a new class of high-temperature superconductors. Electron-phonon coupling calculations indicate that \( CSH_7 \) phases are promising conventional superconductors with \( T_c \) estimated to be as high as \( \sim 200 \) K. The results are expected to stimulate the search for other high-\( T_c \) \( H_2S \) intercalation compounds and more chemically complex hydride superconductors, especially in carbon-bearing systems. Just like pressure, the size of the intercalant molecule can be used to modulate the H-S framework, and thereby to tune its properties, such as \( T_c \). Additional theoretical studies would be useful to examine the effects of quantum and anharmonic dynamics on the calculated critical temperatures and stability of this class of materials, as well as mechanisms for enhancing their phase stabilities at lower pressures.

W.C., J.S. and Y.L. acknowledge funding from the National Natural Science Foundation of China under Grant Nos. 11804128, 11804129 and 11722433. Y.L. acknowledges funding Qing Lan Project of Jiangsu Province. W.C. and J.S. acknowledge the Project Funded by Jiangsu Normal University under Grant No. 18XLRS004 and No. 18XLRS003.

R.J.H. acknowledges support from the U.S. National Science Foundation (DMR-1809783). T.B. acknowledges the NSF (DMR-1827815) for financial support. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Fusion Energy Sciences under Award Number DE-SC0020340 to R.J.H. and E.Z. Calculations were performed using the High Performance Computing Center of the School of Physics and Electronic Engineering of Jiangsu Normal University, and the Center for Computational Research at SUNY Buffalo.

W.C. and T.B. contributed equally to this work.

FIG. 4. Calculated anisotropic superconducting gap of \( CSH_7 (R3m \) structure) at (a) 150 GPa, and (b) 200 GPa.


[37] See Supplemental Material at [URL will be inserted by publisher], which includes Refs. [51–61]. It contains more detailed computational methods, explicit structural information of the identified stable CSH$_7$ compounds, the structures of Cm and Amn2, as well as additional results on the phase stabilities, zero-point energy effect, the ELF plot, the electron-phonon coupling feature, superconducting properties, etc.


