The superconducting transition temperatures of C-S-H based on inter-sublattice S–H₄-tetrahedron electronic interactions†

Dale R. Harshman¹,a) and Anthony T. Fiory ²

¹ Department of Physics, The College of William and Mary, Williamsburg, Virginia 23187, USA
² Bell Labs Retired, Summit, New Jersey 07901, USA

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ABSTRACT

Significant characteristics of the superconducting transitions reported for carbonaceous sulfur hydride [Snider et al., Nature 585, 373 (2020)] are the exceptionally abrupt onset temperatures and their marked increase toward room temperature at high pressure. Theoretical and experimental studies addressing the superconducting composition and structure have thus far returned mixed results. One possibility, consistent with the experimentally suggested stoichiometry of CSHₓ, is the theoretically-discovered compressed 4̅43m CSH₇ structure [Sun et al., Phys. Rev. B 101, 174102 (2020)], which comprises a sublattice similar to Im3m H₃S with CH₄ intercalates. Positing an electronic genesis of the superconductivity, a model is presented in analogy with earlier work on superconductivity in Im3m H₃S, in which pairing is induced via purely electronic Coulomb interactions across the mean distance ζ between the S and H₄ tetrahedra enclosing C. Theoretical superconducting transition temperatures for 4̅43m CSH₇ are derived as $T_{C0} = (2/3)^{1/2} \sigma^{1/2} \beta/a\zeta$, where $\beta = 1247.4$ Å²K is a universal constant, $\sigma$ is the participating charge fraction, and $a$ is the lattice parameter. Analysis suggests persistent bulk superconductivity with a pressure-dependent $\sigma$, increasing from $\sigma = 3.5$, determined previously for Im3m H₃S, to $\sigma = 7.5$ at high pressure owing to additionally participating C-H bond electrons. With $a$ and $\zeta$ determined by theoretical structure, $T_{C0} = 283.6 \pm 3.5$ K is predicted at $267 \pm 10$ GPa, in excellent agreement (within uncertainty) with the corresponding experimental $T_C = 287.7 \pm 1.2$ K. Pressure-induced variations in $\sigma$ combined with experimental uncertainties in pressure yield overall average $(T_C - T_{C0}) = (-0.8 \pm 3.5)$ K.

Keywords: Carbonaceous sulfur hydride, transition temperature, electronic Coulomb mediation

a) Author to whom correspondence should be addressed: drh@physikon.net

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II. INTRODUCTION

Superconductivity is reported in carbonaceous sulfur hydride (C-S-H) over a broad pressure range, with maximum $T_C = 287.7 \pm 1.2$ K at pressure $P = 267 \pm 10$ GPa, exceeding the previous high-$T_C$ record of ($Fm\overline{3}m$) LaH$_{10}$ and approaching the room-temperature regime. Pressure dependence in $T_C$ also suggests a possible evolution in superconductive dominance between differing superconducting phases. Of particular note are the anomalously narrow transition widths $\Delta T_C$ in resistance and magnetic susceptibility, indicative of a continuum of superconducting states. A narrow $\Delta T_C$ also persists in high magnetic field, which may be evidence of strong pinning or trapping of magnetic fluxons. Although alternative explanations were offered for the anomalous behavior observed, strong-coupled bulk superconductivity is assumed for the present work.

While the precise composition and structure of C-S-H are not determined in the original work, unity ratio of elemental C to S and Raman analysis of non-metallic precursor crystals have suggested CSH stoichiometry and possibly H$_2$-containing compounds such as (CH$_4$)$_x$(H$_2$S)$_{2-x}$H$_2$. Analysis of single-crystal x-ray diffraction of a sample with similar preparation ($T_C$ unreported) has determined an orthorhombic system and ruled out $I4/mcm$ symmetry. For C-S-H synthesized from sulfur and methane precursors and followed by laser annealing, x-ray and Raman analyses find formation of an orthorhombic $Pnma$ structure, which has fostered the suggestion that a stable sulfur-based cage structure is a host of superconductivity analogous to $I\overline{4}3m$ H$_3$S.

Several theoretical treatments have considered thermodynamically stable forms of carbon-doped H$_3$S. However, accurate calculations of electron-phonon interactions predict values of $T_C$ that fall significantly below experiment, indicating a theoretical breakdown suggestive of a novel mechanism for the superconductivity in C-S-H. Alternatively, there are several theoretical compressed phases of CSH, which include metastable structures of low formation enthalpy ($\sim$0 meV). Discovered computationally, $I\overline{4}3m$ CSH comprises a host H-S-H chain framework similar to $Im\overline{3}m$ H$_3$S, but with enclosed intercalated CH$_4$ molecules, while orthorhombic $Pnma$ CSH has 2D characteristics with layers in the $bc$ plane. Electron-phonon calculations predict relatively low $T_C$ of 181 K at 100 GPa for $I\overline{4}3m$ CSH, and $T_C$ of 157 – 170 K at 150 GPa for $Pnma$ CSH, diminishing at higher pressure in each case. Host-guest hydride structures are also explored theoretically in a recent phonon-based study of high-pressure phases of CS$_2$H$_{10}$, in which both the $Cmc2_1$ and $P3m1$ phases have CH$_4$ molecules inserted into the $Im\overline{3}m$-H$_3$S and $R3m$-H$_3$S sublattices, respectively; results indicate a detrimental effect of intercalated CH$_4$ on superconductivity, in contrast to experiment.

Following the stoichiometry suggested by experiment, superconductivity with highest $T_C$ is assumed to occur in a nominally CSH material. Rationalized by structural study, as well as by findings of quantitative agreement with experiment, analysis is centered on the theoretical $I\overline{4}3m$ CSH structure, comprising a cubic unit cell containing eight (H$_2$S)(CH$_4$) formula units. In lieu of electron-phonon coupling, which systematically disagrees with experiment, a purely electronic mechanism, in
analogy with that described for $Im\bar{3}m$ H$_3$S,\textsuperscript{17} is considered to be the origin of the extraordinarily high values of $T_C$, in which pairing is mediated via electronic interactions between charges of the H-S-H network and those of intercalated CH$_4$. Originally introduced for layered structures in Ref. 18 and subsequently extended to 3D systems including the superhydrides $Im\bar{3}m$ H$_3$S and $Fm\bar{3}m$ LaH$_{10}$,\textsuperscript{17,19} the model treats superconductive pairing as arising from electronic interactions between two charge reservoirs, denoted type I (superconducting) and type II (mediating), with a calculated transition temperature defined as $T_{C0} \propto (e^2/\zeta)(\sigma/A)^{1/2}$. Here, $\sigma$ is the charge fraction in each reservoir, being equal at optimal $T_{C0}$, $\zeta$ is the distance separating the reservoirs, and $A$ is the type I area.\textsuperscript{18} Structural analogy between $I\bar{4}3m$ CSH$_7$ and $Im\bar{3}m$ H$_3$S logically suggests that the superconducting condensate in C-S-H resides in the extended H-S-H host sublattice network (see Ref. 17), while the CH$_4$ molecules form the secondary sublattice, thus establishing the charge reservoirs as types I and II, respectively. Determining the charge fraction $\sigma = 15/2 = 7.5$ from the maximum participating valence electrons of C, S, and H, divided equally between the two charge reservoirs, and $\zeta$ from the average distance between an S site in the H-S-H host sublattice and the nearest points on the eight neighboring H$_4$-tetrahedra of the CH$_4$ intercalants, the maximum transition temperature is calculated to be $T_{C0} = 283.6 \pm 3.5$ K for $I\bar{4}3m$ CSH$_7$ at 267 \pm 10 GPa, which agrees remarkably well with experiment. The narrow $\Delta T_C$ maintained over wide pressure range and the concomitant behavior of $T_c(P)$ [see Figs. 1(a) and 1(c) of Ref. 1, respectively] indicate not only a broad continuum in charge equilibrium, but also a strong pressure-dependent participating charge fraction $\sigma(P)$ varying in the range $3.5 \leq \sigma \leq 7.5$ attributable to electron localization effects. Since $\sigma = 3.5$ for $Im\bar{3}m$ H$_3$S,\textsuperscript{19} essentially all of the pressure variation in $\sigma(P)$ can be attributed to the CH$_4$ electrons.

In this work, notation $T_c$ refers to experimental data and $T_{C0}$ designates the results of the theoretical calculations. Section II presents the theoretical model for electronic mediated superconductivity in $I\bar{4}3m$ CSH$_7$, with determination of maximum $T_{C0}$, and analysis of $\sigma(P)$ and $T_{C0}(P)$ assuming pressure-dependent dispersion of the C-H bonds. In Sec. III important features of the experimental data of Ref. 1 are analyzed, seemingly conflicting x-ray data are addressed, and supporting evidence for non-phononic superconductivity in the superhydrides, along with a comparison with other optimally-compressed high-$T_c$ materials, are provided. Summary and concluding remarks are given in Sec. IV. An Appendix is included describing the methodology of extracting the pressure dependence of the structural parameters for $I\bar{4}3m$ CSH$_7$ and associated errors.

II. THEORETICAL MODEL

The inter-reservoir electronic interaction model for high-$T_c$ superconductivity has enjoyed significant success in accurately predicting the transition temperatures of numerous materials optimized to yield maximal $T_c$, including most recently $Im\bar{3}m$ H$_3$S and $Fm\bar{3}m$ LaH$_{10}$.\textsuperscript{17,19} The calculated transition temperature is given generally by the algebraic relation,

$$T_{C0} = k_B^{-1} \Lambda \left( \sigma \eta / A \right)^{1/2} \frac{e^2}{\zeta},$$

where $\Lambda$ ($= 0.007465$ Å) is a universal constant, $\sigma$ is the participating charge fraction per formula unit (f.u.) from the valence electrons of constituent atoms (e.g., C, S, and H), $A$ is the surface area per f.u. of the (type I) charge reservoir hosting the superconducting condensate, $\eta$ (equal to unity for $I\bar{4}3m$ CSH$_7$) is the number of type II layers (see, e.g., Ref. 18 for the definition of type II layers and $\eta$), and $\zeta$ is the mean distance between the interacting species in the two reservoirs.

The theoretical compound $I\bar{4}3m$ CSH$_7$ of Ref. 14, comprising an H$_3$S-like host sublattice containing
intercalated CH$_4$, is found through analysis presented herein to be demonstrably applicable to the compressed C-S-H studied in Ref. 1. Drawing on the structural correspondence with the dual-sublattice structure of $Im\bar{3}m$ H$_3$S, the H$_3$S-like framework is modeled as type I, making the CH$_4$ intercalates type II. Analogous to interaction distances determined for compounds comprising polyhedral structures, e.g., in $Fm\bar{3}m$ LaH$_{10}$ and Cs$_5$C$_{60}$, $\zeta$ for $I\bar{4}3m$ CSH$_7$ is the mean nearest distance between an S (type I) site and the eight neighboring H$_4$-tetrahedra of the CH$_4$ (type II) intercalate. Area $A$ in Eq. (1) is formulated similarly as for $Im\bar{3}m$ H$_3$S by taking the surface area of the cube enclosing one f.u.,$^{17}$ yielding $A = (3/2)a^2$ in terms of cubic lattice parameter $a$, given eight f.u. per unit cell.

Expressing theoretical $T_{C0}$ by defining the factor $\beta \equiv k_B^{-1}e^2\Lambda$ (=1247.2 K–Å$^2$) provides a compact representation of Eq. (1), convenient for drawing comparisons to experiment. Thus, in terms of $\sigma$, $\zeta$, and $a$, Eq. (1) is evaluated for $I\bar{4}3m$ CSH$_7$ as,

$$T_{C0} = (2/3)^{1/2}\sigma^{1/2}\beta/a\zeta. \quad (2)$$

The charge fraction $\sigma$ in Eq. (2) is determined theoretically by the participating valence electrons of the constituent atoms in one f.u., a number that is divided by 2 for sharing between the type I and II reservoirs (a factor denoted $\gamma = 1/2$).$^{18}$ The value $\sigma = 3.5$ was previously determined for $Im\bar{3}m$ H$_3$S from analysis of calculations for hydrogen- and sulfur-projected density of states, showing a total of 7 participating electrons from S $3p^4$ and $3 \times$ H $1s^1$ and non-participating electrons from core-like S $3s^2$.$^{17,19}$ Since the S-projected density of states for $I\bar{4}3m$ CSH$_7$ quantitatively resembles that of $Im\bar{3}m$ H$_3$S, at least within several eV of the Fermi level,$^{14}$ the participating valence electrons for $I\bar{4}3m$ CSH$_7$ is a maximum of 15, as counted from C $2s^22p^2$, S $3p^4$, and $7 \times$ H $1s^1$, predicting a charge fraction elevated to a maximum of $\sigma = 15/2 = 7.5$.

In view of experimental indications of optimization occurring over a wide pressure range, values of $\sigma$ in Eq. (2) are hence modeled with a fixed number from H$_3$S, augmented by a pressure-dependent number of participating CH$_4$ electrons. Since experiment points to equivalence between measured $T_C$ and theoretical $T_{C0}$ at various pressures, experimental determinations of charge fractions, denoted as $\sigma^{(X)}$, are derived from experiment according Eq. (2) by assuming theoretical determinations of $a$ and $\zeta$. Sections II A and II B describe further the calculations of $a$ and $\zeta$ from theoretical pressure dependence in lattice spacings for $I\bar{4}3m$ CSH$_7$,$^{14}$ the model introduced for the pressure dependence in $\sigma$, results for $\sigma^{(X)}$ derived from experimental $T_C$, and overall comparisons between theoretical $T_{C0}$ and experimental $T_C$ as functions of pressure.

### A. Calculation of $T_{C0}$ at 267 GPa

According to the theoretical structure of $I\bar{4}3m$ CSH$_7$ at $P = 100$ GPa,$^{14}$ the H$_4$-tetrahedra, comprising Wyckoff positions H(8c) and H(24g), have an apex or a face nearest to S(2a) sites and edges nearest to S(6b) sites. The cubic unit cell per f.u. is illustrated in Fig. 1, where cube corners represent S sites and an enclosed tetrahedron represents H$_4$. Nearest distances between a cube corner and sites on the tetrahedron surface are indicated as $\zeta_1$ and $\zeta_2$ for an apex and a face center, respectively, and $\zeta_3$ and $\zeta_4$ for the two three-fold symmetric edge centers. Using theoretical structural parameters,$^{14}$ the calculated distances, in terms of lattice parameter $a$, are $\zeta_1 = 0.2950a$, $\zeta_2 = 0.3458a$, $\zeta_3 = 0.3343a$, and $\zeta_4 = 0.2901a$. Averaging the eight distances determines $\zeta = 0.3142a$. The area $A = (3/2)a^2$ is the surface area of the cube of edge length $a/2$, which contains the volume of one f.u. In order to predict $a$ and $\zeta$ at higher pressures, theoretical pressure dependences of volume per f.u. ($V = a^3/8$) and the S-H distance $r_0 \equiv \zeta_1$ given in Ref. 14 are assumed and extrapolated to experimental values of
pressure, as described in the Appendix. Values of \( V \), \( a \) and \( \zeta \) calculated at experimental pressures \( P \) are given in Table I, with uncertainties from extrapolating theoretical pressure dependences given in parentheses.

Assuming the maximum value \( \sigma = 15/2 = 7.5 \) for CSH\(_7\) occurs at \( P = 267 \pm 10 \) GPa, corresponding to maximum observed \( T_C (= 287.7 \pm 1.2 \) K), and with \( a = 5.663 \pm 0.027 \) Å and \( \zeta = 1.737 \pm 0.009 \) Å (determined by theoretical extrapolation and pressure uncertainty), one finds from Eq. (2) the result \( T_{C0} = 283.6 \pm 3.5 \) K which, given the uncertainties, is in good agreement with experiment. Assuming the full complement of 6 electrons from sulfur would give 301.9 K. By averaging the three peak transition temperatures, to better account for the large uncertainties in pressure, a comparison between experiment and theory can be made showing remarkable equivalence with \( T_{C0} = 283.6 \pm 3.9 \) K and \( T_C = 283.6 \pm 3.2 \) K.

**B. Pressure dependence**

Based on the abrupt superconductive transitions observed for C-S-H over a broad range of applied pressures,\(^1\) bulk superconductivity is evidently maintained throughout. The transitions are quantified herein by defining the width \( \Delta T_C \) as the difference between onset \( T_C \) and the transition midpoint; results for \( \Delta T_C \) so obtained are listed in Table I, along with the values of \( P \), uncertainty \( \Delta P \), and \( T_C \), determined from Fig. 1(c) in Ref. 1. Assuming that the \( I43m \) CSH\(_7\) structure is preserved, where \( a \) and \( \zeta \) vary smoothly with pressure, the precipitous decrease in \( T_C \) with decreasing pressure below the maximum value at 267 GPa must, therefore, be attributable to a decrease in the participating charge fraction and retained equilibrium between the two charge reservoirs. Consequently, the theoretical \( T_{C0} \) function of Eq. (2) would be applicable to the experimental results for \( T_C \) at various pressures, obtaining an experiment-based solution for \( \sigma \) as,

\[
\sigma^{(X)} = (3/2)[a \zeta T_C / \beta]^2,
\]

where pressure-dependent \( a \) and \( \zeta \) are calculated from \( I43m \) CSH\(_7\) structure. Results for \( \sigma^{(X)} \) calculated according to Eq. (3) are plotted as a function of experimental pressure in Fig. 2, demonstrating that strong pressure dependence in \( T_C \) is traceable to similar behavior in \( \sigma^{(X)} \). Owing to experimental uncertainties in measurements of pressure \( \Delta P \), shown as horizontal error bars, uncertainties propagate into the calculations of \( \sigma^{(X)} \). Such uncertainties are determined from the theoretical pressure dependences in \( a \) and \( \zeta \) as

\[
\delta \sigma^{(X)} = (3/2) (T_C / \beta)^2 \left[ \partial (a^2 \zeta^2) / \partial P \right] \Delta P,
\]
and are plotted as vertical error bars in Fig. 2.

Theoretically, the participating charge fraction $\sigma$ equals one-half (from $\gamma = 1/2$) of the number of the participating valence electrons of the constituent atoms in the f.u. The likely origin of the unusually strong pressure dependence in $\sigma$ is the presence of CH$_4$, given that such behavior is not observed in H$_3$S absent carbon.\textsuperscript{21} The following two-component expression is introduced to model the pressure dependence,

$$\sigma(P) = (1/2) (n_S + 3n_H) + (1/2) \left[ 4n_H\left(1 - \exp[-(P/P_1)^{q_1}\right]] + n_C\left(1 - \exp[-(P/P_2)^{q_2}\right]) \right],$$

(5)

where the numbers of participating electrons are determined as $n_S = 4$ (sulfur), $n_H = 1$ (hydrogen), and $n_C = 4$ (carbon). The first term is the contribution from the 7 electrons in the H$_3$S component and is presumed to be independent of pressure and the same as in H$_3$S.\textsuperscript{19} The second term models electrons contributed from CH$_4$, which are assumed to be non-participating at low pressure owing to localized electron density, e.g., as indicated for $P = 100$ GPa in Fig. S7(a) in the supplementary material in Ref. 14; electron transfer from CH$_4$ to H$_3$S with increasing pressure is shown in Fig. S4 in the supplementary material of Ref. 14. Factors $[1 - \exp(-(P/P_1)^{q_1})]$ model the participation of CH$_4$-associated electrons, nearly zero at low pressure and approaching unity high pressures where the valence electrons become increasingly delocalized owing to reduced interatomic spacings. Such factors model the pressure dependence in analogy to the probabilities of electron tunneling through potential barriers that diminish dramatically at high pressure and are represented by power-law functions with large exponents. The parameters $P_1$, $P_2$, $q_1$, and $q_2$ are determined empirically from experimental data for $T_C$ vs. $P$ and theoretical pressure dependence of $a$ and $\zeta$. The continuous curve in Fig. 2 is a fit of Eq. (5) to the data, with fitted parameters, $P_1 = 233(7)$ GPa, $P_2 = 249(3)$ GPa, $q_1 = 10(3)$, and $q_2 = 38(14)$. The dashed horizontal lines at 3.5, 5.5, and 7.5 correspond to charge fractions for H$_3$S (7/2), H$_3$S + H$_4$ (11/2), and H$_3$S + CH$_4$ (15/2), respectively. The two dotted curves delimit uncertainties in $\sigma(P)$ originating from the experimental uncertainties in pressure and correspond to calculations of $\sigma(P \pm \Delta P)$.

According to Eq. (2), the fitted model function $\sigma(P)$ in Eq. (5) thus generates a prediction for the pressure dependence of $T_{C0}$ as,

$$T_{C0}(P) = [2\sigma(P)/3]^{1/2} / a\zeta.$$

(6)

Figure 3 shows $T_{C0}(P)$ as the solid blue curve, together with experimental data (symbols) for $T_C$ vs. $P$ from Table I (experimental data from Ref. 1). The two dotted curves denote uncertainties calculated from
TABLE I. Experimental applied pressure $P$, uncertainty $\Delta P$, measured transition temperature $T_C$, and transition width $\Delta T_C$ are given for C-S-H from data in Ref. 1. Theoretical values (uncertainties) for volume per f.u. $V$, lattice parameter $a$, and interaction distance $\zeta$ are listed for $I\bar{4}3m$ CSH, at same values of $P$, from theory of Ref. 14.

| $P$ (GPa) | $\Delta P$ (GPa) | $T_C$ (K) | $\Delta T_C$ (K) | $V$ (Å$^3$) | $a$ (Å) | $\zeta$ (Å) |
|-----------|-----------------|----------|--------------------|-----------|--------|---------|
| 271       | 11              | 280.0    | 9.6                | 22.58(14) | 5.653(11) | 1.733(4) |
| 267       | 10              | 287.7    | 0.5                | 22.71(14) | 5.663(11) | 1.737(4) |
| 258       | 10              | 276.0    | 0.4                | 23.01(14) | 5.688(11) | 1.745(4) |
| 258       | 10              | 283.1    | 1.2                | 23.01(14) | 5.688(11) | 1.745(4) |
| 253       | 10              | 267.0    | 2.1                | 23.18(14) | 5.702(11) | 1.750(4) |
| 251       | 10              | 274.1    | 5.5                | 23.24(14) | 5.708(11) | 1.752(4) |
| 250       | 10              | 254.9    | 2.1                | 23.28(14) | 5.711(11) | 1.753(4) |
| 243       | 10              | 241.0    | 0.3                | 23.52(14) | 5.730(11) | 1.760(4) |
| 241       | 10              | 238.9    |                    | 23.59(14) | 5.736(11) | 1.761(4) |
| 233       | 9               | 234.0    | 7.8                | 23.88(14) | 5.759(11) | 1.769(4) |
| 233       | 9               | 214.1    |                    | 23.88(14) | 5.759(11) | 1.769(4) |
| 224       | 9               | 199.9    |                    | 24.20(14) | 5.785(11) | 1.779(4) |
| 220       | 9               | 207.9    | 1.3                | 24.35(14) | 5.797(11) | 1.783(4) |
| 212       | 8               | 206.9    |                    | 24.65(14) | 5.821(11) | 1.791(4) |
| 211       | 8               | 195.0    |                    | 24.69(14) | 5.824(11) | 1.792(4) |
| 210       | 8               | 189.9    | 0.6                | 24.73(14) | 5.827(11) | 1.793(4) |
| 202       | 8               | 191.9    |                    | 25.04(14) | 5.851(11) | 1.802(4) |
| 200       | 8               | 187.9    |                    | 25.12(14) | 5.857(11) | 1.804(4) |
| 189       | 8               | 197.9    |                    | 25.55(14) | 5.891(11) | 1.817(4) |
| 185       | 7               | 180.0    |                    | 25.71(15) | 5.903(11) | 1.821(4) |
| 182       | 7               | 191.1    |                    | 25.83(15) | 5.912(11) | 1.825(4) |
| 181       | 7               | 178.0    |                    | 25.87(15) | 5.915(11) | 1.826(4) |
| 178       | 7               | 184.4    |                    | 25.99(15) | 5.925(11) | 1.829(4) |
| 175       | 7               | 171.0    |                    | 26.12(15) | 5.934(11) | 1.833(4) |
| 174       | 7               | 180.9    | 0.2                | 26.16(15) | 5.937(11) | 1.834(4) |
| 166       | 7               | 172.0    |                    | 26.49(15) | 5.962(11) | 1.844(4) |
| 160       | 6               | 169.9    |                    | 26.74(15) | 5.981(11) | 1.851(4) |
| 157       | 6               | 166.0    |                    | 26.86(15) | 5.990(11) | 1.855(4) |
| 148       | 6               | 164.5    |                    | 27.24(15) | 6.018(11) | 1.866(4) |
| 138       | 6               | 146.8    |                    | 27.67(15) | 6.049(11) | 1.879(4) |

$T_{C0}(P \pm \Delta P)$. Taking the pressure uncertainties into account, data and theory differ by an average ($T_C - T_{C0}$) = (-0.8 \pm 3.5) \, K; the root-mean-square difference between the symbols and solid curve in Fig. 3 is otherwise 7.3 K.

III. DISCUSSION

The proposed structure of the C-S-H superconducting system is rather unique, comprising intercalated CH$_4$ molecules within an H$_3$S-like sublattice. What is even more interesting, from the perspective of the present work, is the sharp superconducting transition widths reported over a broad pressure range, indicative of a persisting charge balance between the two charge reservoirs throughout the pressure range. Taking the data as a whole at face value, the analysis of $T_C(P)$ indicates that at the lowest pressure, only the H$_3$S charges are involved in the superconductivity, with the number of participating charges increasing with pressure to include those of the CH$_4$ molecules. All three of these features make C-S-H a very special system.

Experimental data for C-S-H indicate limitations on the superconducting states. At the highest experimental pressure of 271 GPa, $T_C$ is less than the maximum observed at 267 GPa and also less than theoretical $T_{C0}$ (Fig. 3), suggesting a form for $T_C(P)$ “approaching a dome shape” and a peak or maximum value of $T_C$.\textsuperscript{1} Together with the concomitant increase in $\Delta T_C$ by over an order of magnitude (Table I), maximum $T_C$ is evidently limited to pressures near 270 GPa. Note that larger values of $\Delta T_C$ occur at 233 GPa and a few other intermediate pressures. A lower bound in pressure is also indicated in Fig. 3, where data for $T_C$ (symbols) also fall systematically and progressively below the theoretical $T_{C0}$ (continuous curve) at pressures below about 175 GPa, which is particularly pronounced at the lowest reported pressure of 138 GPa. This may be due to a further reduction in participating charge (presumably from the H$_3$S sublattice), or a consequence of differing crystal structure, given that orthorhombic symmetry is found by x-ray diffraction at pressures limited to below 178 GPa.\textsuperscript{9}
X-ray refinement of the \textit{Pnma} structure at 143 GPa finds a sulfur arrangement with S-S distances of 2.401(7) to 3.004(6) Å,\textsuperscript{10} which may be compared to theoretical S-S distance \(a/2 = 3.017\) Å, as determined from calculations of \(\overline{I}43m\) CSH\(_7\) at this same pressure.\textsuperscript{14} Thus, the framework of S atoms in the theoretical \(\overline{I}43m\) CSH\(_7\) work bears close quantitative consistency with x-ray refinement data on C-S-H material, with caveats being the unresolved positions of light atoms H and C in an orthorhombic cell.\textsuperscript{10} Theoretical compounds comprising intercalated CH\(_4\) structures\textsuperscript{13-16} also logically follow from the preferred syntheses reported for using methane as a precursor and the evident difficulties with elemental carbon.\textsuperscript{10} Alternative theoretical structures containing H\(_2\) tend to have lower theoretical phonon-mediated \(T_C\), owing to the molecular characteristics of H\(_2\);\textsuperscript{14} moreover, the reduced availability of participating electronic charges resulting from H\(_2\) inclusions is also unfavorable for a wholly electronic mediation. By analogy in the case of CSH\(_7\), the presence of CH\(_4\) units in the form of localized molecules is similarly detrimental to not only phonon-mediated superconductivity,\textsuperscript{16} but also to the electronic mechanism should the electrons be non-participating.

The inability of electron-phonon theory to calculate adequately high values of \(T_C\) for candidate compounds, which include C-doped H\(_3\)S,\textsuperscript{10,11,13,14,22,23} suggests that phonon interactions are unlikely to be the primary pairing mechanism. Independently, evidence for unconventional superconductivity in C-S-H is also proposed through analysis of temperature dependence in normal-state resistance,\textsuperscript{24} similar to conclusions drawn for H\(_3\)S and LaH\(_{10}\).\textsuperscript{25}

In identifying the pairing mechanism, a mass isotope effect may be considered within the context of observations from H-D isotopic substitutions in related (H/D)\(_3\)S materials. Recent results report a mass isotope effect coefficient \(\alpha \approx 0.22\) in \(T_C\) from resistance measurements for H\(_3\)S and D\(_3\)S taken at nearly the same pressure, 155 and 157 GPa, respectively.\textsuperscript{26} This result for \(\alpha\) affirms the reanalysis\textsuperscript{27} presented for earlier data,\textsuperscript{20,28} noting that the correction for the H-D isotopic shift in the pressure dependence of \(T_C\) yields \(\alpha = 0.13 \pm 0.11\).\textsuperscript{27} Given the added possibility of a sympathetic response of the lattice to an otherwise wholly electronic mechanism,\textsuperscript{17,20} the experimental \(\alpha\) appears to fall well short of estimates for electron-phonon coupling.\textsuperscript{26} Interpreting apparent shifts in \(T_C\) also evidently entails taking into account mass isotope effects associated with the quantum nature of hydrogen bonding and structure.\textsuperscript{29} Given the narrow superconducting transitions observed for C-S-H over a broad pressure range, and the absence of a phonon-based explanation of the elevated \(T_C\), a companion study of C-S-D, assuming that high-\(T_C\) C-S-D can be

![Graph](image)

**FIG. 4.** Measured \(T_C\) vs. calculated \(T_{C0}\) for compressed high-\(T_C\) superconductors; \(\overline{I}43m\) CSH\(_7\) (267 GPa), \(Fm\overline{3}m\) LaH\(_{10}\) (169 and 192 GPa),\textsuperscript{19} \(Im\overline{3}m\) H\(_3\)S (155 GPa),\textsuperscript{17} HgBa\(_2\)Ca\(_2\)Cu\(_2\)O\(_{8+\delta}\) (25 GPa),\textsuperscript{18} YBa\(_2\)Cu\(_3\)O\(_y\) (12 GPa),\textsuperscript{18} A15 Cs\(_2\)S\(_6\) (0.93 GPa),\textsuperscript{20} FeSe\(_{0.977}\) (7.5 GPa),\textsuperscript{31} Fe\(_{1.03}\)Se\(_{0.57}\)Te\(_{0.43}\) (2.3 GPa) and C/C (twisted bilayer graphene device D2, 1.33 GPa).\textsuperscript{32} The solid line represents Eq. (1), highlighting the equality between \(T_C\) and \(T_{C0}\).
similarly synthesized, would greatly benefit the further understanding of these materials.

The model genesis of the superconductivity in C-S-H comprises electronic interactions localized in real space, as depicted in Fig. 1, replicating earlier findings for H$_2$S, LaH$_{10}$, and Cs$_3$C$_{60}$. Calculations of $T_{C0}$ therefore apply to C-doped H$_2$S materials, presuming that $\zeta$ and $A$ are similar to those calculated for the CSH$_7$ model and coupling among localized C-containing structures sufficiently sustains bulk superconductivity.

In Fig. 4, the measured maximum $T_C$ for C-S-H from Ref. 1 is plotted against calculated $T_{C0}$ for $I43m$ CSH$_7$ at $P = 267$ GPa, and compared to $T_C$ vs. $T_{C0}$ for several other optimally-compressed high-$T_C$ superconductors at the pressures indicated. The solid line represents Eq. (1) and highlights the equality between measurements of $T_C$ and calculations of $T_{C0}$, with remarkable concurrence between theory and experiment exhibited over a range in $T_C$ covering nearly 300 K. A key takeaway from Fig. 4 is the common genesis of the superconductive state in both the new high-$T_C$ hydrides and the earlier cuprate-based and other high-$T_C$ materials. Since the universal constant $\Lambda$ in Eq. (1) approximates twice the reduced Compton wavelength ($\Lambda = 1.933(6)\hbar/mc$), the involvement of Compton scattering in purely electronic high-$T_C$ pairing is considered plausible (see, e.g., Ref. 17).

The seminal work presented in Ref. 18 reports remarkable compliance with the methodology of 31 different superconductors from several superconducting families. Subsequent research increased this number, as reported in Ref. 17 in the case of H$_2$S, Ref. 19 in the case of the hydrogen clathrates, and Ref. 20 for Cs$_3$C$_{60}$. Excluding C-S-H, this approach has been validated with statistical accuracy of $\pm 1.30$ K (or $\pm 4\%$) in $T_{C0}$ for 55 different materials from 11 disparate superconducting families. These comprise the above-mentioned 3D compounds, layered cuprates, ruthenates, ruthenocuprates, iron pnictides, BEDT-based [bis(ethylenedithio)tetrathiafulvalene] organics, iron chalcogenides, intercalated group-4 metal nitride halides, and gated twisted bilayer graphene, with measured $T_{C0}$ values ranging from $\sim 2$ to 260 K.

**IV. CONCLUSION**

Accepting an electronic genesis of the superconductivity in carbonaceous sulfur hydride (C-S-H), having a maximum superconductive transition $T_C = 287.7 \pm 1.2$ K at pressure $P = 267 \pm 10$ GPa, a model is presented in which pairing is induced via Coulomb interactions between electronic charges occupying two sublattices, the H-S-H host network (type I, superconducting) and the CH$_4$ intercalate (type II, mediating). Assuming the computationally derived structure, $I43m$ CSH$_7$, extrapolating $a$ and $\zeta$ to 267 GPa, and setting $\sigma = 7.5$ (the maximum participating charge fraction), Eq. (2) yields $T_{C0} = 283.6 \pm 3.5$ K, which is in good agreement with experiment. Averaging the three peak transition temperatures, a remarkable equivalence between experiment and theory is found with $\langle T_C \rangle = 283.6 \pm 3.9$ K and $\langle T_{C0} \rangle = 283.6 \pm 3.2$ K.

Most curious, however, is the anomalously narrow transition widths $\Delta T_C$ observed for C-S-H over a wide pressure range, indicating that charge equilibration between the two charge reservoirs is maintained throughout. This revelation, coupled with the behavior of $T_C(P)$ shown in Fig. 1(c) of Ref. 1, necessitates a pressure-dependent $\sigma$ ranging between 3.5 and 7.5, with essentially all of the variation in $\sigma$ originating from CH$_4$ electrons via pressure-induced dispersion of the C–H bonds. Functional forms for $\sigma(P)$ and $T_{C0}(P)$, assuming tunneling behavior of the CH$_4$ electrons, are derived and shown to compare well with experimental $T_C(P)$. Combined with experimental uncertainties in pressure, variations in $\sigma$ yield overall differences averaging $(T_C - T_{C0}) = (\sim 0.8 \pm 3.5)$ K.
AUTHOR DECLARATIONS
Conflict of Interest
The authors declare that they have no conflict of interest.

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DATA AVAILABILITY
The data that support the findings of this study are available within the article.

APPENDIX: PRESSURE DEPENDENCE OF STRUCTURAL PARAMETERS
Calculations for $\bar{I}43m$ CSH$_7$ at pressures up to 200 GPa are presented in Ref. 14, yielding pressure dependences of volume per H$_3$S host lattice ($V$) in Fig. S9 and various S-H spacings in Fig. S8 in the supplementary material. Pressure dependences in $a$ and $\zeta$ are determined by modeling these results.

Transcribed calculations of $V$ vs. pressure $P$ are shown as symbols in Fig. 5(a). The pressure dependence is fitted to a model emulation of the equation of state, $V(P) = [c_0 + c_1 P + c_2 \exp(-c_3 P)]^{-1}$, with parameters $c_0 = 0.0268(2)$ Å$^{-3}$, $c_1 = 6.44(8) \times 10^{-5}$ Å$^{-3}$ GPa$^{-1}$, $c_2 = -0.0080(1)$ Å$^{-3}$, and $c_3 = 0.0210(7)$ GPa$^{-1}$ with root-mean-square fitting error of 0.016 Å$^3$, and is shown by the solid curve in Fig. 5(a). Evaluations of $V(P)$ and lattice parameters $a = (8V)^{1/3}$, along with the fitting uncertainties, are given for the various experimental pressures in Table I.

Transcribed calculations for the S-H distance $r_0$ (illustrated as $\zeta_1$ in Fig. 1), divided by $a$ and normalized to $r_0/a$ at pressure $P_{100} = 100$ GPa, are shown as symbols in Fig. 5(b). The red curve is the fitted model function $[r_0/a](P) = b_1 + b_2 \exp(-b_3 P)$ with parameters $b_1 = 0.9745(8)$, $b_2 = 0.0720(6)$, and $b_3 = 0.0104(3)$ GPa$^{-1}$ with root mean square fitting error of $3.1 \times 10^{-4}$. Pressure dependence in $\zeta$ is scaled to calculations at $P = P_{100}$ as $\zeta(P) = (\zeta/a)|_{P=100} a [r_0/a](P)$, noting that $r_0/a$ decreases by only 2.1 % from 100 to 271 GPa. Pressure dependent $\zeta$ values are given in Table I.

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