

X-ray Diffraction and Equation of State of the C-S-H Room-Temperature Superconductor

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X-ray diffraction indicates that the structure of the recently discovered carbonaceous sulfur hydride (C-S-H) room temperature superconductor is derived from previously established van der Waals compounds found in the H₂S-H₂ and CH₄-H₂ systems. Crystals of the superconducting phase were produced by a photochemical synthesis technique leading to the superconducting critical temperature T_c of 288 K at 267 GPa. X-ray diffraction patterns measured from 124 to 178 GPa, within the pressure range of the superconducting phase, are consistent with an orthorhombic structure derived from the Al₂Cu-type determined for (H₂S)₂H₂ and (CH₄)₂H₂ that differs from those predicted and observed for the S-H system to these pressures. The formation and stability of the C-S-H compound can be understood in terms of the close similarity in effective volumes of the H₂S and CH₄ components, and denser carbon-bearing S-H phases may form at higher pressures. The results are crucial for understanding the very high superconducting T_c found in the C-S-H system at megabar pressures.

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I. INTRODUCTION

The seminal prediction that chemical doping could lower the transition pressure of atomic-metallic and superconducting hydrogen¹ inspired the exploration of the high-pressure behavior of simple molecules mixed with hydrogen under pressure.²⁻⁴ Later theoretical calculations predicted new classes of novel hydrogen-rich solids exhibiting very high T_c behavior when such molecular mixtures are subjected to megabar pressures.⁵⁻⁹ Resulting experimental efforts in the last few years have led to the discovery of T_c above 203 K in H_3S ,¹⁰ up to 260 K LaH_{10} ,¹¹⁻¹⁴ and later, similar values for Y-H hydrides.¹⁵⁻¹⁷ These studies include other low-Z materials such as possible carbon-bearing high T_c hydrides in view of their possible stability at lower, and even ambient, pressures¹⁸ as well as predicted incorporation of other components within these structures to form very high T_c chemically doped¹⁹⁻²¹ or stoichiometric perovskite-like structures.²²⁻²⁴

Recently, high temperature superconductivity with a critical temperature of 288 K at 267 GPa has been reported in the C-S-H system.²⁵ Information on the low-pressure precursor phases were obtained from Raman spectroscopy together with theoretical calculations. The Raman data revealed the formation of C-H bonding as well as phase transitions at 15 GPa and 37 GPa, but spectra were not measurable above 60 GPa when the samples became opaque. The formation of C-H bonding prior to the darkening of the phase that becomes superconducting, leading to the expectation of carbon uptake, persists into the superconducting phase.²⁵ However, no diffraction or direct information on the structure of the material in the superconducting state was reported. Subsequent electron-phonon calculations indicated that incorporation of a small amount (*i.e.*, 4 atom %) in the structure could produce the very high T_c by hole-doping of H_3S .^{20, 21}

Here we report measurements of x-ray diffraction and the P - V equation of state (EOS) of the very high T_c superconducting material reported in Ref. ²⁵. X-ray diffraction indicates that the structure is derived from previously established van der Waals compounds found in the CH_4 - H_2 ³ and H_2S - H_2 ⁴ systems but has a lower symmetry over the measured range. The structure differs in detail from those found and predicted for phases in the S-H system. The results provide a mechanism for incorporation of carbon in molecular hydrogen sulfide structures starting at low pressures and are consistent with the hole-doping model for the room-temperature superconductivity proposed for the C-S-H system at megabar pressures.

II. METHODS

The samples were prepared using the diamond-anvil cell (DAC) techniques described previously.²⁵ Specifically, The superconductor was synthesized via a photochemical process with 532 nm laser of 10-25 mW at 3.9 GPa for 10 to 25 minutes, and the very high T_c superconductivity was verified in all other runs. The material examined by x-ray diffraction was synthesized by using exactly the same technique (runs #21 and #22).²⁵ Raman spectra at 4 GPa for the sample discussed below here (run #22, Fig. S1) matched the others reported in Ref. ²⁵. The spectra have features found in earlier studies of the CH_4 - H_2 and H_2S - H_2 systems.

X-ray diffraction patterns were collected at the IDB station of HPCAT (Sector 16, Advanced Photon Source) using an incident wavelength of 0.4066 Å, and at the IDD station of GSECARS (Sector 13, APS) with an incident wavelength of 0.2952 Å. The principal results reported here are for run 22. Because the DACs used were designed for observations of superconductivity,²⁵ the opening angle of the cells for diffraction was 30°, which limited the reciprocal space that was accessible and precluded full crystal structure refinement to determine atomic positions. Complete areal x-ray diffraction maps of the sample were measured at 124 GPa,

and diffraction patterns were measured at selected pressures up to 178 GPa. The pressure was determined from diffraction of the Re gasket near the sample. A membrane drive was used to increase the pressure in the DACs. The x-ray diffraction images were collected using Pilatus detectors and integrated using the DIOPTAS software,²⁶ and the Rietica LHPM Rietveld program was used to analyze integrated powder diffraction patterns.²⁷

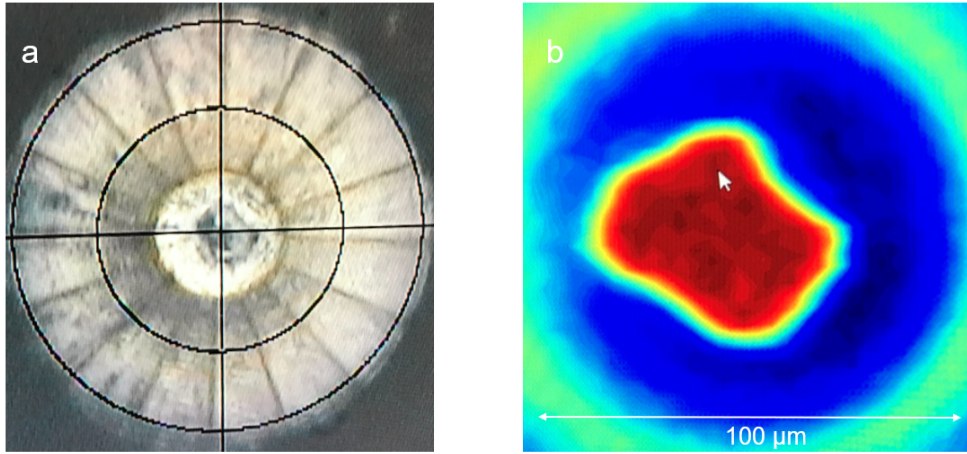


Figure 1. Images of the sample in a diamond anvil cell at 124(2) GPa (run 22 from Ref. ²⁵). (a) Combined transmission/reflection photomicrograph showing the optically dark superconducting C-S-H sample at the center of the cross-hairs within the sample chamber (grey region); the white area is the highly reflecting Re gasket on the 100- μ m culet of the beveled diamond anvil. (b) X-ray transmission image of a magnified view of the sample chamber (red) showing the C-S-H sample and the diamond culet (blue).

III. RESULTS

Images of the sample at 124 GPa prepared by the procedures described above are shown in Fig. 1. The x-ray and optical imaging show the size of sample to be around 40 μ m. X-ray diffraction mapping was performed on a 7 μ m \times 7 μ m grid in the vicinity of the sample (Fig. S2). Diffraction of the sample in the region surrounding the optically dark area matches high-pressure x-ray patterns reported for disordered H carbon²⁸ and, at the sample edges, Re and Re-H gasket material, which was also used for pressure calibration. At the start of the x-ray experiments, the initial pressure of 122 GPa measured by diffraction from Re peaks at both GSECARS and HPCAT data agreed with the pressure determined from diamond anvil Raman edge measurements.²⁵ Numerous experiments show that the optically dark region is the superconducting sample at this pressure.²⁵ X-ray diffraction reveals the dark region to be largely single-crystalline, as indicated by the angular relationships found among the principal reflections. The possibility of contributions from multiple single crystals does not affect the conclusions since we rely principally on the d -spacing values for the analysis, *e.g.*, to constrain the unit-cell symmetry and equation of state.

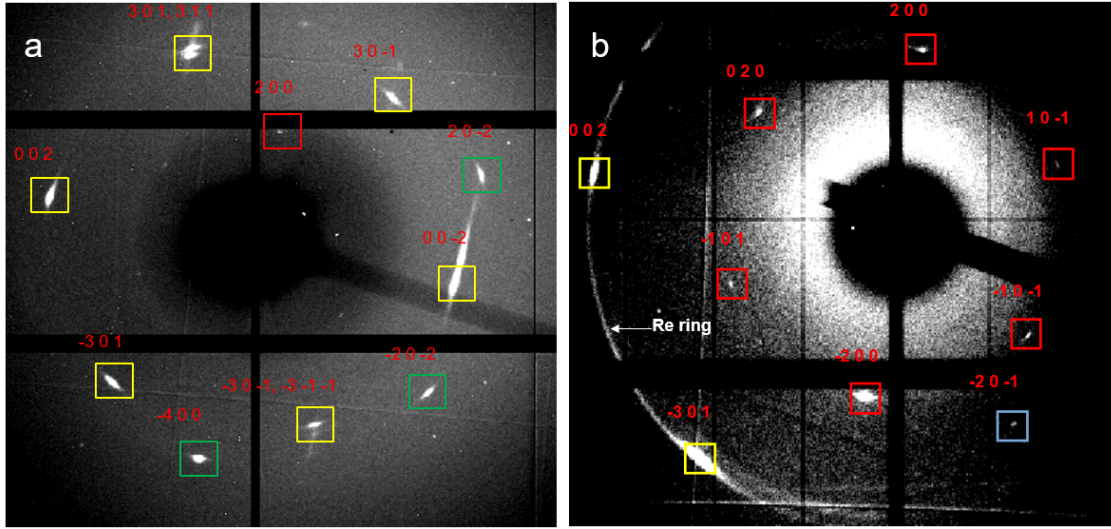


Figure 2. Single-crystal diffraction images of the C-S-H sample at 124(2) GPa. (a) Image obtained at GSECARS showing symmetry equivalent reflections corresponding to (200), (002)/(102) and (022) planes labeled with red, yellow and green boxes, respectively. The streak near the 00-2 reflection is due to disorder. (b) Image obtained at HPCAT showing symmetry equivalent reflections corresponding to (200)/(020), (201) and (002) planes labeled with red, blue and yellow boxes, respectively. The ring appearing on the left side of the image is polycrystalline diffraction from the Re gasket. The black circles in the center of both images are shadows of the x-ray beam stop, and the black crosses arise from the detector. Images as a function of pressure are provided in the Supplementary Material.

Examples of diffraction images are shown in Fig. 2. For each of the images, we obtained d -spacings by averaging the values of symmetry equivalent peaks (Fig. 3). The prominent reflections could be identified as belonging to planes (110), (002), (121) and (112) (GSECARS) and (110), (002), and (111) (HPCAT) of a cell that is close to tetragonal. However, the (110) reflections for both gave two different populations of d -spacings indicating a weak orthorhombic distortion that can be interpreted as a 110_t splitting into $200/020_o$, with twice the unit cell volume. Moreover, the observation of the 111_t ($= 201_o$) reflections at all pressures rules out the $I4/mcm$ and $Cccm$ space groups that had been observed or predicted for structures in the binary systems of $\text{CH}_4\text{-H}_2$ and $\text{H}_2\text{S-H}_2$.^{3, 4, 7, 29-32} X-ray diffraction mapping of the sample showed no symmetry lowering due to possible pressure gradients. The lattice parameters obtained, for example at 124(2) GPa, give $a = 7.76(2)$ Å, $b = 7.70(2)$ Å, $c = 4.48(2)$ Å and $V = 16.73(3)$ Å³/S, with a smooth evolution with pressure (Fig. 4). The data indicate a nearly constant c/a (and c/b), both 0.82(2), with respect to a tetragonal cell over the measured pressure range (for example, $\sqrt{2}(c/a)_o \rightarrow (c/a)_t$ and $\sqrt{2}(c/b)_o \rightarrow (c/b)_t$), which is essentially the same as that found for $I4/mcm$ $\text{CH}_4\text{-H}_2$ ³ and $\text{H}_2\text{S-H}_2$ ⁴ near 5 GPa.

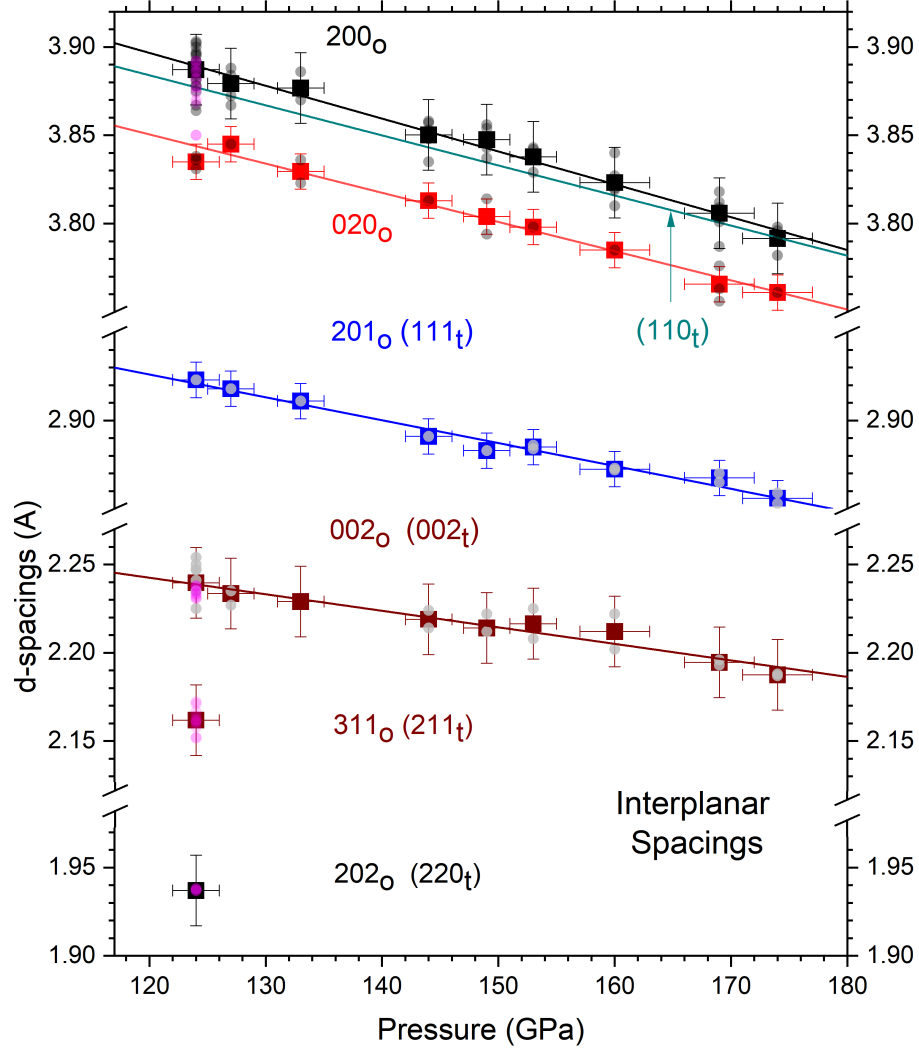


Figure 3. Pressure dependence of d -spacings determined from integration of single-crystal reflections. The solid squares correspond to the average of the d -spacing values measured by single-crystal diffraction, which are shown by transparent grey circles (HPCAT) and transparent pink circles (GSECARS). The solid lines are fits through the data points assuming an orthorhombic structure, i.e., $(hkl)_o$; the fit of the data assuming a tetragonal structure is also shown for 110_t . In this setting, 201_o and 002_o correspond to 111_t and 002_t , respectively. The uncertainties in the d -spacings for the averaged 200_o data points correspond to 2σ in the measured distribution of the d -spacings, whereas those for 020_o and 201_o are estimated from the observed spread in the data.

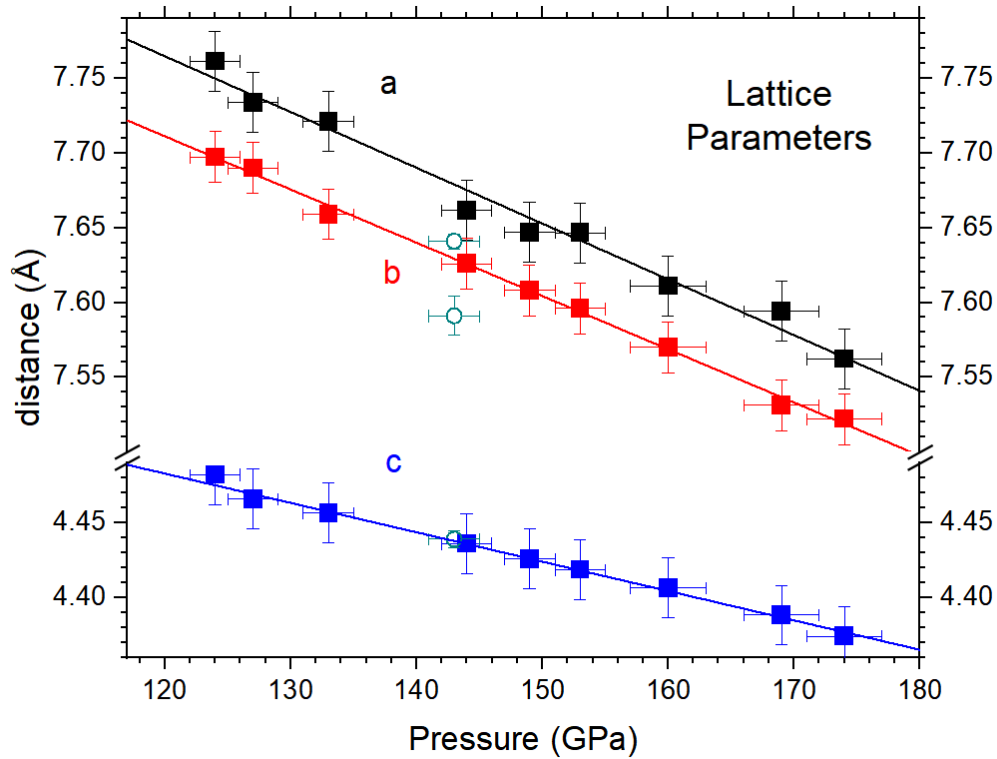


Figure 4. Pressure dependence of the lattice parameters determined from d -spacing values obtained in the orthorhombic crystal system. Solid squares are lattice parameters from the average of the d -spacing data at a given pressure. Open circles are lattice parameters of a structure reported after laser heating a C-S-H sample at 143 GPa.³³

Figure 5 shows the P - V relations obtained from diffraction data as a function of pressure from 124 to 178 GPa. We also compare the measured volumes reported for the C-S-H material by Bykova et al.³³ and those reported for S-H phases.^{29-32, 34, 35} The difference between the EOS obtained here for C-S-H and that reported for H_3S ³⁴ is about $1.4 \text{ \AA}^3 / \text{S, C}$ across the indicated pressure range. The room-temperature compression data reported for a C-S-H sample of Bykova et al.³³ and for $(H_2S)_2H_2$ by Guigue et al.²⁹ differ from that found here. The molecular volumes of $Cccm$ $(H_2S)_2H_2$ identified by Pace et. al.³¹ are close to those measured here for the C-S-H sample. The nearly constant difference between the volumes for C-S-H and H_3S over the measured pressure range contrasts with the trend reported for room-temperature compression of a C-S-H sample by Bykova et al.³³ On the other hand, the P - V point for that sample after laser heating to form an orthorhombic structure is closer to the EOS measured here.

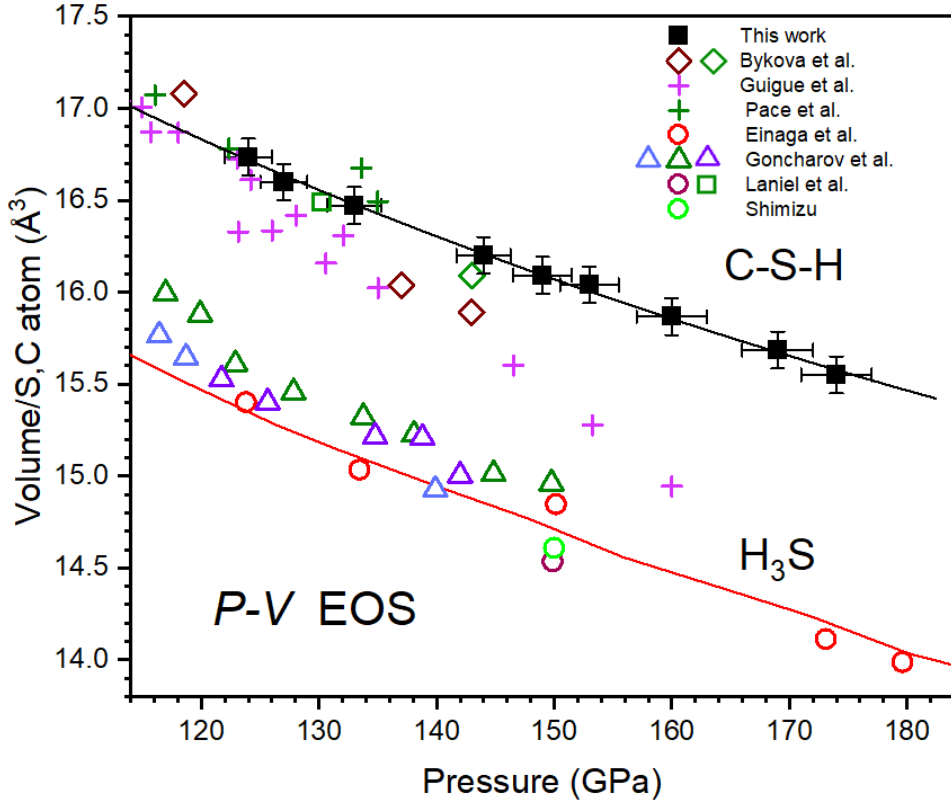


Figure 5. Pressure-volume (P - V) relations measured for C-S-H compared to data from experiments on H₃S composition samples. Filled squares are from the orthorhombic structure obtained in the present work, and the black line is an EOS fit. The volume and pressure uncertainties were determined from analysis of the d -spacings (Fig. 3) and the Re x-ray diffraction peaks. Open diamonds correspond to the C-S-H data of Bykova et al.,³³ where the brown diamond is that of the tetragonal structure (identified as $I4/mcm$) after lower pressure synthesis and room-temperature compression, and the green diamond that of the orthorhombic structure (identified as $Pnma$) produced after laser heating of that sample. Open circles correspond to the proposed structures of H₃S composition by Einaga et al.³⁴ (two highest data points are for D_3S), Shimizu,³⁵ and Laniel et al.³²; open triangles, Goncharov et al.,³⁰ crosses, $Cccm$ phase of Guigue et al.²⁹ and Pace et al.³¹ The red line is the EOS fit from Einaga et al.³⁴ The green square corresponds to the $I4/mcm$ structure reported by Laniel et al.³² after laser heating sulfur-paraffin mixtures under pressure.

The P - V EOS relations for phases in the C-S-H system over an extended pressure range are presented in Fig. 6. The results show that our measurements of the compression of the C-S-H superconductor can be viewed as an extension of the EOS of (H₂S)₂H₂ and (CH₄)₂H₂, which have essentially identical volumes in their $I4/mcm$ structures at synthesis pressures near 5 GPa. The atomic ratios for such Al₂Cu-related structures range from 1.13:1 to 1.61:1.³ Experimentally constrained EOS curves for H₂S,³⁶ CH₄,³⁷ C (diamond),³⁸ and H₂³⁹ phases are also shown in Fig. 6. CH₄ and H₂S have similar molecular volumes over a wide range of pressures, consistent with the similarity in molar volumes of (CH₄)₂H₂ and (H₂S)₂H₂ van der Waals compounds. The EOS measurements and analyses indicate that the effective molecular volumes of H₂S and CH₄ are comparable over a broad range of pressures (Fig. 6). For example, at 124 GPa, effective volumes are both around 14 Å³ / molecule. The H₂ volume decreases from roughly 13 Å³ at the room-temperature freezing pressure of 5.4 GPa to 4.3 Å³ at the pressures studied here.³⁹ We also compare the volumes of the CH₄ + H₃S molecular^{29, 34, 40} and the C + S + 7H elemental^{39, 41, 42} assemblages.

The volume for CSH_7 ($\text{H}_3\text{S}-\text{CH}_4$ perovskite) is lower than that of H_3S , consistent with the smaller volume of methane, and is metastable with respect to decomposition to CH_4 and H_3S as described in Ref. ²²

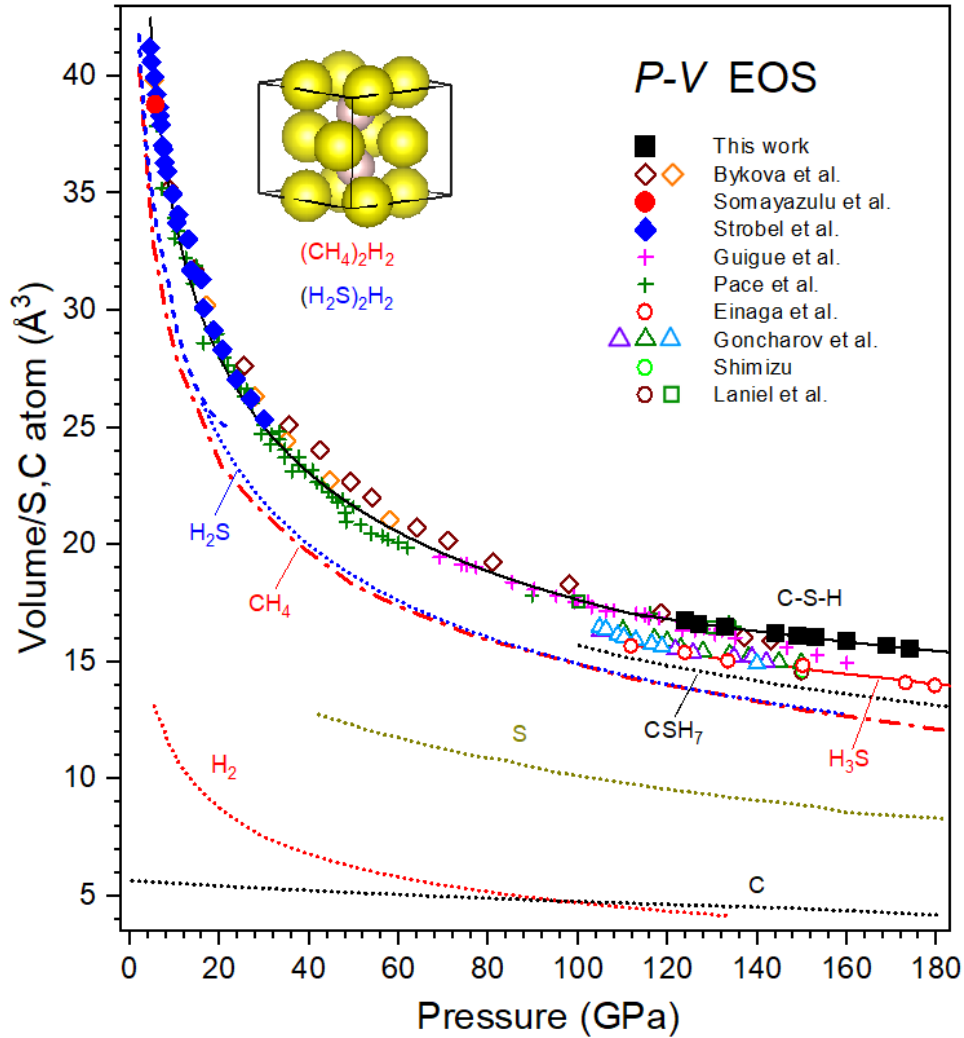


Figure 6. Extended P - V EOS comparison of phases and phase components in the C-S-H system. The references for data points for the C-S-H and S-H compounds are given in the caption to Fig. 5. The data point for $\text{CH}_4\text{-H}_2$ is from Somayazulu et al.³ The black line is a continuation to low pressures of the EOS fit of the C-S-H points. The yellow spheres in the structure model drawing correspond to H_2S and CH_4 , whereas the pink spheres represent rotationally disordered (or $J = 0$) H_2 molecules. The hydrogen positions are not determined in these x-ray diffraction experiments. Hydrogen bonding between H_2S , including pressure-induced symmetric hydrogen bonding under pressure, is expected.⁴ The EOS of H_2S ,³⁶ CH_4 ,³⁷ H_2 ($\text{\AA}^3/\text{molecule}$),³⁹ C (diamond),³⁸ and S^{42} phases are shown. For H_2S , the EOS for the data reported in Ref. ³⁶ as well as a fit to data below 20 GPa and extrapolated to higher pressures are shown (see also Ref. ³²). The CH_4 curve is a theoretical EOS³⁷ that agrees with experimental data over a wide range of compression,^{40, 43} and the diamond result³⁸ is consistent with earlier data.⁴¹ The calculated static lattice EOS for CSH_7 perovskite²² is also compared. The calculated P - V curves for the competitive low-enthalpy structures considered in that study are within 0.5% of each other.

IV. DISCUSSION

We now comment on the implications of the above x-ray diffraction and EOS data for the structure, chemical interactions, and very high- T_c superconductivity documented in the recent studies of the C-S-H system under pressure. The structure is derived from the high-symmetry $I4/mcm$ structure observed for the two van der Waals compounds. The stoichiometry may thus be written $[(CH_4)_2H_2]_x[(H_2S)_2H_2]_y$; although x and y cannot be determined from the x-ray diffraction data, $y \gg x$ is suggested by the similarity in initial T_c of C-S-H and H_3S . On the other hand, the structure of the material over the pressure range studied has a lower symmetry than that theoretically predicted or found in the pure H_2S or CH_4 compounds. The similarity in size between CH_4 and H_2S allows for facile mixing of molecules to form pseudo-ternary H_2S - CH_4 - H_2 van der Waals compounds during photochemically-induced synthesis of the precursor phase (or phases) to the superconductor. The constant volume difference of about $1.4 \text{ \AA}^3 / \text{S,C}$ for the C-S-H and H_3S EOS suggest that H_2 in the parent $I4/mcm$ structure is retained in the structure at these pressures. The difference in volume between H_3S and C-S-H could also arise from the incorporation of additional C or H in the S-H structure. It is possible that at higher pressures, residual molecular components in the structure such as H_2 undergo pressure-induced dissociation and the structure collapses to form a denser framework with an EOS similar to that shown for $Im\bar{3}m$ H_3S .

Density-functional theory calculations have predicted the stability of hydride perovskite or intercalation H_3S - CH_4 compounds with a ground state orthorhombic ($Pnma$) and cubic ($I4\bar{3}m$) structures that are nearly degenerate at these pressures.^{22, 23} The predicted orthorhombic phase differs from that observed experimentally and has a higher density (Fig. 6). However, much less incorporation of CH_4 in the H_3S than previously considered is possible in such perovskite-like structures. This could give rise to stoichiometric $H_3S(CH_4)_n$ compounds corresponding to Magneli phases; alternatively, alloys having a broad range of compositions and hydrogen content are possible, both of which would provide another mechanism for the incorporation of carbon in the hydrogen sulfide. Density functional theory calculations assuming BCS/Eliashberg model electron-phonon coupling and using the virtual crystal approximation (VCA) predict that the high T_c observed in the C-S-H structure can arise from hole-doping of carbon in H_3S .^{20, 21} The parent cubic ($Im\bar{3}m$) phase of H_3S was assumed as a model structure in these calculations. We point out that the apparent increase in T_c near 200 GPa suggested a transition at that pressure.²⁵ However, given the scatter in the data, the results are also consistent with a continuous increase in T_c with pressure from 120 GPa to 267 GPa, a result that is also consistent with the theoretical calculations.^{20, 21}

Bykova et al.³³ reported that the tetragonal $I4/mcm$ structure for one of their C-S-H samples transformed to an orthorhombic structure upon laser heating near 143 GPa. As described above, the volume and lattice parameters are close to the trend found here for the C-S-H sample synthesized photochemically at low pressures. Synthesis of high-pressure superconducting phases in the S-H system in general is path dependent,¹⁰ and this is likely to be especially true for synthesis of high-quality crystals of the C-S-H superconductor, which is facilitated by laser irradiation at specific pressures (see Ref. ²⁵). In high-pressure x-ray crystallographic studies of hydrogen sulfide in which samples are synthesized using a carbon-bearing hydrogen source,³² it would be difficult to rule out low levels of carbon incorporation predicted to significantly enhance T_c if there is random substitution of C for S; for example, 4% carbon doping is predicted to increase T_c by up to ~ 90 K,^{20, 21} Variable carbon content in the phases is likely to arise from differences in sample preparation. Although nearly 1:1 molar ratios of C and S were used in the synthesis of the present

samples,¹⁷ the composition of the CH₄-H₂S-H₂ van der Waals compound or alloy that is a precursor to the superconducting phase is not known. Indeed, variations in the alloying in the initial CH₄-H₂S-H₂ mixture are likely to give rise to slight differences in the reported low-pressure Raman spectra.^{25, 33} The methods used in the preparation of the samples studied here produced the very high T_c superconductor; although not directly measured, at the maximum pressures of the diffraction study the T_c is estimated to be 180 K.²⁵

In conclusion, high-pressure x-ray diffraction measurements indicate that the structure of the high T_c superconductor formed in the C-S-H system up to 178 GPa is derived from structures found at lower pressure in the H₂S-H₂⁴ and CH₄-H₂³ van der Waals compounds. The mechanism of formation and stability of the material can be understood in terms of the pressure dependence of the effective volumes of CH₄, H₂S, H₃S, and H₂. Although more detailed structural information is possible from dedicated single-crystal diffraction with broad reciprocal space coverage, the present measurements on C-S-H samples synthesized for observations of superconductivity establish the overall unit cell symmetry and compressional behavior of the material. As such, the results provide crucial constraints for theoretical studies of the detailed mechanism of the observed room-temperature superconductivity. The incorporation of carbon in hydrogen sulfide is broadly consistent with hole-doping of H₃S by carbon predicted theoretically, but further studies are required for definitive tests. The bonding, coordination, and amount of carbon as a dopant could be determined by x-ray Raman measurements.⁴⁴ At higher pressures, the material may evolve toward denser framework structures, ideally examined using combined measurements of transport and structural properties. Alternative synthesis routes and chemical stabilization of the superconductor at lower pressures should also be explored.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Supplementary Material

Supplementary Material contains Raman spectra, additional x-ray diffraction images, and x-ray mapping information.

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