Carbon-Doped Sulfur Hydrides as a Room-Temperature Superconductor at 270 GPa

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Superconductivity is the property of the complete absence of electrical resistance at temperatures below a critical transition temperature (T_c). For conventional superconductors, the electron–phonon coupling mediates the formation of a Cooper pair of electrons with opposite spins, as described in the Bardeen–Cooper–Schrieffer (BCS) theory. However, the highest transition temperature attained by any conventional superconductors so far is $T_c = 39$ K in MgB_2. In the past five years, exciting high-T_c superconducting materials have been discovered. In particular, the first experimental synthesis of H_3S gave an unprecedentedly high $T_c = 203$ K at a pressure of $P \approx 150$ GPa (Ref. 1). Most recently, a room-temperature superconductor has been experimentally realized in a carbonaceous sulfur hydride (CSH) system,[2] which demonstrated $T_c = 287.7\pm1.2$ K at 267±10 GPa. This experimental finding has excited the condensed-matter and high-pressure physics communities to understand this "puzzling" ternary CSH system since recent studies[3,4] prior to the experiment[2] did not predict room-temperature T_c behavior.

We used the evolutionary structure searching code USPEX combined with the density-functional-theory code VASP to determine the possible stoichiometry and stable crystal structures, in a wide pressure range from 20 to 300 GPa, for various combinations of $C_iS_jH_k$ using the electronic formation enthalpy ΔH (eV/atom) < 0 as the criterion. These results showed a general trend: CSH compounds composed of one CH_4 "guest" molecule and integer numbers of H_3S "host" molecules tend to have lower formation enthalpy. This energetics observation prompted us to look into the binary components of C_iH_k, S_jH_k, and C_iS_j. These binary searches resulted in the following conclusion: the basic unit of H_3S in its *Im-3m* cubic structure gives the lowest formation enthalpy of $\Delta H_{H_3S} \approx -0.125$ eV/atom among all such binary compounds. From a thermodynamic stability point of view, these results unambiguously suggest that a higher H_3S concentration in a ternary CSH compound should drive the system to lower formation enthalpy (more stable). This led us to explore the energetics and stability of carbon doping in H_3S systems.

To examine the formation enthalpy of carbon-doped H_3S systems, we varied the ratio of carbon to sulfur in a "supercell" composed of an integral number of H_3S units in its *R3m* or *Im-3m* structure, i.e., taking systems like $C_1S_{15}H_{48}$ and $C_1S_{17}H_{54}$ as examples. We then calculated the total formation enthalpy (including the zero point energy of ions: ΔE_{ZPE}) for these energetically optimized CSH compounds in the pressure range of 80 to 300 GPa. The H_3S system has the lowest formation enthalpy for all the structures examined in this pressure range. Carbon-doped sulfur hydrides, varying from $C_1S_{35}H_{108}$ to $C_1S_{19}H_{30}$, are energetically second to the pure H_3S system within an ~50-meV difference of ΔH_{total}. Nevertheless, these carbon-doped sulfur hydrides are both thermodynamically and dynamically stable since they all have $\Delta H_{total} < 0$ and no imaginary components in their phonon spectra. At low pressures (<80 GPa), the CSH system takes the most-stable stoichiometry of $C_2S_2H_{10}$, composed of one C_2H_6 (ethane) molecule linked by hydrogen bonding with two H_2S molecules in P_1 symmetry.

To examine if these identified carbon-doped sulfur hydrides exhibit any high-temperature superconductivity, we employed the Allen–Dynes–McMillian equation implemented in the density functional theory code *Quantum Espresso* to estimate the T_c for compounds varying from $C_1S_9H_{30}$ to $C_1S_{35}H_{108}$ in the pressure range of 150 to 300 GPa, with the virtual crystal approximation. The T_c results from these calculations for $C_1S_{15}H_{48}$ and $C_1S_{17}H_{54}$, as shown in Fig. 1(b) as a function of pressure, showed good agreement with experiment and a room-temperature T_c = 280±10 K at ~270 GPa. Figure 1(c) plots the estimated maximum T_c variation as a function of carbon-doping level, corresponding to the stable CSH compounds ranging from $C_1S_9H_{30}$ to $C_1S_{35}H_{108}$ at 270 GPa. A peak of T_c ~ 290 K appears at an *optimal* carbon-doping level of ~5.56% (corresponding to $C_1S_{17}H_{54}$). In the CSH experiment[2] there was no intentional control of the carbon-doping level. Therefore, the experimentally synthesized CSH samples

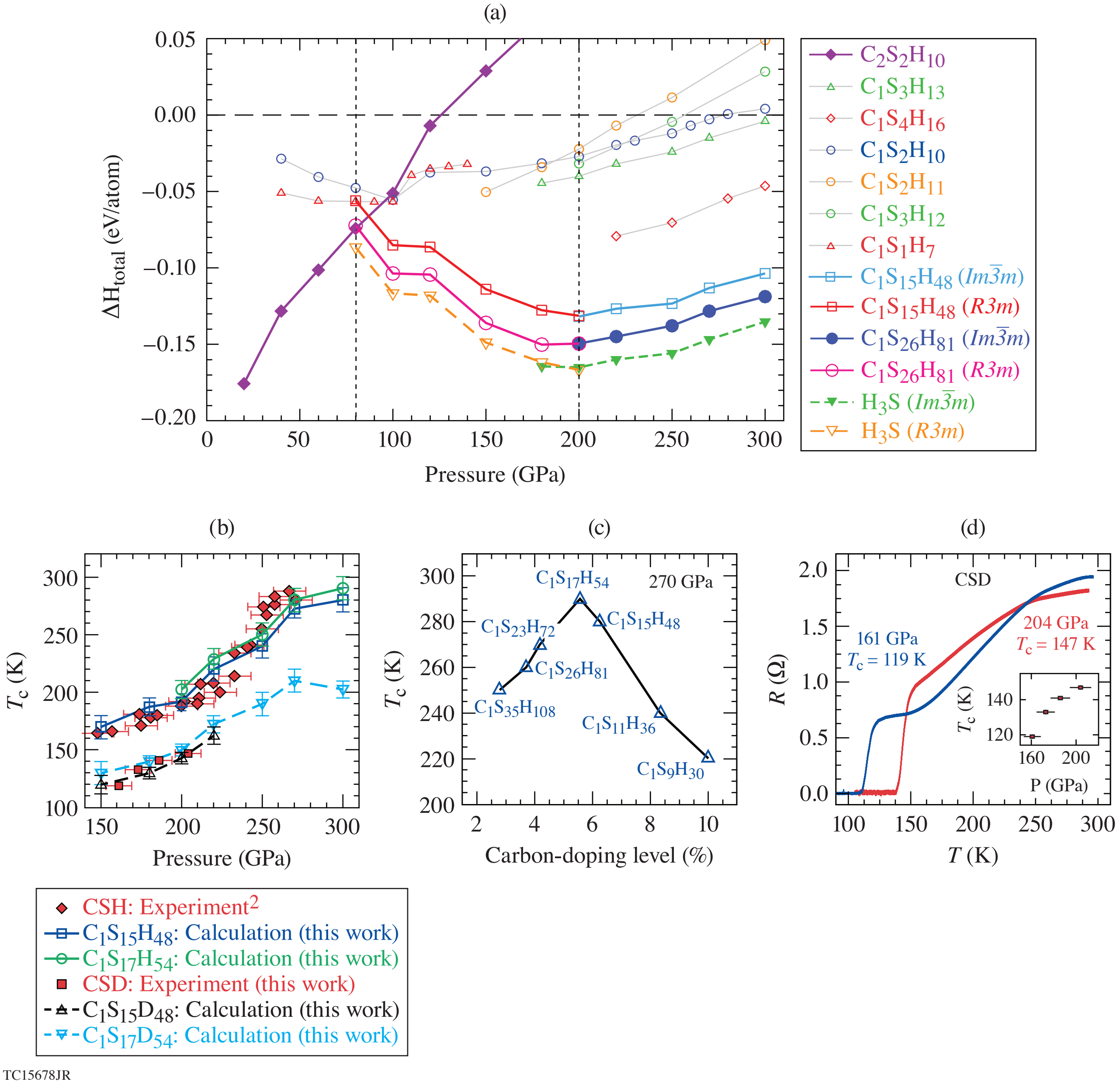

Figure 1

(a) The Convex Hull Analysis of CSH compounds: the total formation enthalpy versus pressure for different CSH compounds in the pressure range of 20 to 300 GPa. (b) The calculated superconducting transition temperature T_c versus pressure for compounds $C_1S_{15}H_{48}/C_1S_{17}H_{54}$ and $C_1S_{15}D_{48}/C_1S_{17}D_{54}$ compared to both the CSH experiment[2] and the new CSD (carbon sulfur deuterium) experiment. (c) The maximum T_c as a function of carbon doping level in different CSH compounds at the same pressure of 270 GPa. (d) The measured temperature-dependent electrical resistance of carbonaceous sulfur deuteride at high pressures, showing the superconducting transitions as high as 147 K at 204 GPa, the highest pressure measured in this experimental run. Inset: The pressure dependence of the T_c as determined by the sharp drop in electrical resistance, showing the increase in T_c with pressure.

in the diamond-anvil cell might contain around 5%–6% carbon doping that should dominantly contribute to the measured zero resistance. The new CSD experimental results in Fig. 1(d) show good agreement between CSD experiments and calculations for $C_1S_{15}H_{48}$ and $C_1S_{17}D_{54}$, and demonstrate a pronounced shift of T_c from an isotopic substitution. The substitution of deuterium lowers T_c, indicating phonon-assisted superconductivity. This is a result of carbon doping contributing more to the higher-frequency phonon mode due to its strong covalent bonding to hydrogen atoms. This leads to a significant enhancement of the logarithmic averaged phonon frequency, changing from $\omega_{\ln} \sim 1010$ K at 200 GPa to $\omega_{\ln} \sim 1550$ K at 270 GPa, with the transition temperature T_c being saturated at above ~270 GPa. For $C_1S_{17}D_{54}$, the logarithmic averaged phonon frequency $\omega_{\ln}$ is overall lower than that of $C_1S_{17}H_{54}$ at the same pressure due to the heavier deuterium mass. This suggests that the synthesized carbonaceous sulfur hydride superconducts via an electron–phonon mechanism consistent with the BCS theory of conventional superconductors.

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