Enhanced superconductivity in C-S-H compounds at high pressure

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Recently, the superconducting transition temperature $T_c = 287$ K has been experimentally obtained in the material composed of carbon, sulfur, and hydrogen under the high pressure of 267 GPa. The material structure is unknown yet, where the carbon and sulfur were added at a molar ratio of 1:1. Here, fixing the molar ratio of C : S = 1:1, we studied several possible C-S-H structures, and found a new stable structure $C_2S_2H_4$ using the first-principles calculations. The $C_2S_2H_4$ shows an insulator-to-metal transition and the superconducting ground state at the pressure of 64 GPa, and its $T_c$ can reach 16.5 K at 300 GPa. In addition, we found another stable structure of $C_2S_3H_4$, whose $T_c$ is 47.4 K at 300 GPa. The calculations show that the added S atom in $C_2S_3H_4$ breaks part of C-H bonds in $C_2S_3H_4$, makes the vibration of H atom at a lower frequency, and thus enhances the electron-phonon coupling and $T_c$. Our results suggest that the molar ratio of C:S lower than 1:1 in the C-S-H systems may be favorable to enhance $T_c$. This can be useful to figure out the structure of the C-S-H material with room temperature $T_c$ in the recent experiment.

Room temperature superconductors have been the long-time dream of scientists because of the potential applications in the fields of information, detection, transportation, and power technology. Since the discovery of superconductivity in 1911 [1], great achievements have been made in theory and experiment. In 1957, Bardeen, Cooper and Schrieffer have proposed the BCS theory [2], which can well interpret many traditional superconductors. Following the BCS theory, it is highly expected that the metallic hydrogen may have high Debye temperature, strong electron-phonon coupling (EPC), and thus high $T_c$ [23–26]. In 1935, Wigner and Huntington proposed theoretically that hydrogen could be transformed into metal state under extreme conditions of high pressure [27]. In 2004, Ashcroft pointed out that high-temperature superconductors can be obtained by pressurizing hydrogen rich materials [28]. In 2014, $H_3S$ was predicted to become a hydride superconductor under high pressure [29, 30], and soon after a $T_c$ of 203 K at 90 GPa was obtained experimentally [31]. Higher $T_c$ was theoretically proposed in the P-, C- and Si-doped $H_3S$ [32, 33]. In recent years, many new hydrogen-rich materials with different structures were predicted, such as lanthanum, yttrium hydrides [34–36] and scandium hydrides [37]. The lanthanum hydride LaH$_{10}$ was synthesized and demonstrated to exhibit a $T_c$ of 250-260 K at 170-190 GPa [38–40]. Yttrium superhydride YH$_3$ with a $T_c$ of 262 K at 182 ± 8 GPa was also obtained [41]. In 2020, the room temperature superconductor with $T_c = 287$ K at 267 GPa has been experimentally obtained in the material composed of carbon, sulfur, and hydrogen [42]. In the experiment, the carbon and sulfur were added at a molar ratio of 1:1, but the material structure is unknown yet.

Following the BCS theory, it is highly expected that the metallic hydrogen may have high Debye temperature, strong electron-phonon coupling (EPC), and thus high $T_c$. In 1935, Wigner and Huntington proposed theoretically that hydrogen could be transformed into metal state under extreme conditions of high pressure. In 2004, Ashcroft pointed out that high-temperature superconductors can be obtained by pressurizing hydrogen rich materials. In 2014, $H_3S$ was predicted to become a hydride superconductor under high pressure, and soon after a $T_c$ of 203 K at 90 GPa was obtained experimentally. Higher $T_c$ was theoretically proposed in the P-, C- and Si-doped $H_3S$. In recent years, many new hydrogen-rich materials with different structures were predicted, such as lanthanum, yttrium hydrides [34–36] and scandium hydrides [37]. In 2014, $H_3S$ was predicted to become a hydride superconductor under high pressure [29, 30], and soon after a $T_c$ of 203 K at 90 GPa was obtained experimentally [31]. Higher $T_c$ was theoretically proposed in the P-, C- and Si-doped $H_3S$ [32, 33]. In recent years, many new hydrogen-rich materials with different structures were predicted, such as lanthanum, yttrium hydrides [34–36] and scandium hydrides [37].

In this Letter, by fixing the molar ratio of C : S = 1:1, we studied several possible C-S-H structures, and found a stable structure $C_2S_2H_4$ by first-principle calculations. A $T_c$ of 16.5 K at 300 GPa is predicted in $C_2S_2H_4$. In addition, a higher $T_c$ of 47.4 K at 300 GPa is obtained in another stable material $C_2S_3H_4$. The added S atom in $C_2S_3H_4$ makes the vibration of H atoms at a lower frequency, and thus enhances the electron-phonon coupling and $T_c$. Our results suggest that the molar ratio of C:S lower than 1:1 in the C-S-H systems may be favorable to enhance $T_c$.
FIG. 1. (a) The crystal structure and (b) Brillouin zone (BZ) of C$_2$S$_2$H$_4$. (c) The pressure dependence of lattice parameters in C$_2$S$_2$H$_4$ obtained by the DFT calculations, where the critical pressure of insulator to metal phase transition is 64 GPa.

In Fig. 2, we plot the electron band structures and projected density of states (PDOS) at two representative pressures of 45 and 300 GPa. We find that there is an energy gap of 0.283 eV in C$_2$S$_2$H$_4$ at 45 GPa, while it disappears at 300 GPa, which indicates the existence of the phase transition between insulator and metal as the change of pressure. In fact, we find that the critical pressure of insulator-metal phase transition is 64 GPa, as indicated in Fig. 1(c). In addition, it is noted that the DOS near Fermi level at 300 GPa mainly comes from the contribution of S atoms.

The metallicity of C$_2$S$_2$H$_4$ at 300 GPa allows to investigate its possible superconductivity. In Fig. 3(a) gives the phonon spectra along high-symmetry paths Γ-Z-D-B-Γ-A-E-Z-C$_2$-Y$_2$-Γ. There is no imaginary frequency mode in phonon spectra, indicating the dynamic stability of C$_2$S$_2$H$_4$. Meanwhile, the phonon density of states (PhDOS) in Fig. 3(a) shows that S atoms vibrate at low frequency from 10 to 20 THz, C atoms vibrate around 30 THz, and H atoms vibrate at relative high frequency. Based on Migdal-Eliashberg theory [43, 44], the Eliashberg spectral function $\alpha^2 F(\omega)$, and the cumulative frequency-dependent EPC $\lambda(\omega)$ of C$_2$S$_2$H$_4$ at 300 GPa are calculated as also given in Fig. 3(a). It is obvious that S atoms located at low frequency make more contributions to the EPC, while H atoms at high frequency have little contribution to EPC.

Based on the BCS theory with the McMillan-Allen-Dynes approach [45, 46] and taking a typical value of the effective screened Coulomb repulsion constant $\mu^* = 0.1$, we obtain the $T_c$ of C$_2$S$_2$H$_4$ at different pressures as plotted in Fig. 3(b). We find that with the increase of pres-
FIG. 3. (a) The phonon spectra, projected phonon density of states, Eliashberg spectral function $\alpha^2 F(\omega)$, and the cumulative frequency-dependent of EPC $\lambda(\omega)$ of C$_2$S$_2$H$_4$ at 300 GPa. (b) Pressure dependent $T_c$, where the critical pressure of insulator to metal (superconductor) phase transition is indicated.

TABLE I. The $T_c$ and total EPC $\lambda$ of C$_2$S$_2$H$_4$, C$_2$SCH$_4$, C$_2$SPH$_4$, C$_2$SFH$_4$, C$_2$S$_3$H$_4$ at 300 GPa.

|       | C$_2$S$_2$H$_4$ | C$_2$SCH$_4$ | C$_2$SPH$_4$ |
|-------|----------------|--------------|--------------|
| $T_c$ (K) | 16.475         | 8.532        | 0.155        |
| $\lambda$ | 0.5504         | 0.5130       | 0.2712       |

|       | C$_2$SFH$_4$ | C$_2$S$_3$H$_4$ |
|-------|--------------|-----------------|
| $T_c$ (K) | 3.613        | 47.439          |
| $\lambda$ | 0.3986       | 0.8646          |

sure, C$_2$S$_2$H$_4$ does not become superconducting until 64 GPa because of the insulator-to-metal phase transition, and the $T_c$ can reach 16.475 K at 300 GPa.

The temperature dependence of the electronic specific heat $C$ of C$_2$S$_2$H$_4$ at 300 GPa is presented in Fig. 4(a). It is seen that the specific heat $C(T)$ has distinct behaviors. When $T<50$ K, $C(T)$ is almost zero. At temperature region of 50 K$<T<300$ K, $C(T)\sim T^3$ (left upper inset), and at $T>300$K, $C(T)\sim T$. The result of $C(T)$ suggests that below 300 K, the normal state shows a non-Fermi liquid behavior [47].

To further verify this observation, we have also studied the temperature dependence of Lorenz number defined by $L = \kappa_e/\sigma T$, as given in Fig. 4(b), as well as the electrical $\sigma$ and thermal $\kappa_e$ conductivities over relaxation time $\tau$. It can be observed that at temperatures lower than 300 K, $L$ is not a constant, showing a dramatical violation of Wiedemann-Franz law [48], while at higher temperature it shows almost a constant, exhibiting a Fermi liquid behavior. Therefore, C$_2$S$_2$H$_4$ at 300 GPa shows a non-Fermi liquid behavior at temperatures below 300 K, implying that the interactions between electrons in the normal state play essential roles at low temperature.

Based on C$_2$S$_2$H$_4$, we have designed four new structures as shown in Fig. 5: (a) electron doping by replacing a S atom with a Cl atom; (b) hole doping by replacing a S atom with a P atom; (c) replacing a S atom with a light element F atom; (d) adding a S atom to the vertex of the primitive cell of C$_2$S$_2$H$_4$, where the added S atom is labeled as S$_1$ and the original S atoms are labeled...
C2SClH4 and C2S3H4. For C2S2H4 in Fig. 1, one C atom connects two S and two H atoms. Whereas, one C atom in C2S3H4 connects three S atoms and one H atom with another H atom originally connected to C atom isolated. The PhDOS in Fig. 5(e) shows that the isolated H atom contributes a new vibration peak within 25 and 30 THz, and the added S atom (S1) vibrates around 20 THz. The lowering vibration modes of S and H atoms greatly enhance the λ from 0.5504 of C2S2H4 to 0.8646 of C2S3H4, giving rise to a higher Tc of 47.439 K in C2S3H4. Our findings from C2S2H4 to C2S3H4 may provide a guide to find C-S-H superconductors with higher or even room temperature Tc experimentally in near future.

To conclude, we have searched for stable C-S-H structures with a C:S ratio of 1:1, and found a stable structure C2S2H4. The Tc at 300 GPa is calculated to be 16.475 K, which is mainly attributed to the low-frequency vibration of S atoms. With the applied pressure, an insulator-to-metal phase transition occurs, accompanied by the system into superconducting at 64 GPa. The electronic thermal conductivity and Lorentz number of C2S2H4 show a non-Fermi liquid behavior below 300K. In addition, we have designed four new stable structures on the basis of C2S2H4: C2SClH4, C2SPH4, C2SFH4, C2S3H4. Among them, C2S3H4 exhibits the highest Tc of 47.439 K. By analysis, we find that the added S atom in C2S3H4 changes the original bonding of C2S2H4, and contributes to new low-frequency vibration modes along with the isolated H atom. The molar ratio of C:S lower than 1:1 in the C-S-H systems may be favorable to enhance Tc, which will be useful not only to figure out the structure of the C-S-H material with room temperature Tc in the experiment, but also to find new superconductors with higher or even room temperature Tc in future.

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TABLE I lists the Tc and EPC λ of C2S2H4 and the other four new superconductors. It is noted that the λ of C2S2H4 is much higher than that of C2S3H4, and Tc of the former is about three times larger than that of the latter. To uncover possible mechanism to enhance Tc, we compared the crystal structure, PhDOS, and α²F(ω) of C2S2H4 as compared to C2S3H4.

FIG. 5. The crystal structures of (a) C2SClH4: replacing a S atom with a Cl atom, (b) C2SPH4: replacing a S atom with a P atom, (c) C2SFH4: replacing a S atom with a F atom, and (d) C2S3H4: adding a S atom to the vertex of C2S2H4. (e) The phonon spectra, projected phonon density of states, α²F(ω), and EPC λ(ω) of C2S3H4 at 300 GPa.

as S2. These four new structures are all demonstrated to be dynamically stable and exhibit superconductivity at 300 GPa (See details at Supplementary Information).

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