Usage Report for Fiscal Year 2019

Project Title:

Prediction of Crystal Structure and Properties

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1. Background and purpose of the project, relationship of the project with other projects

Seeking of the room–temperature superconductor is one of the most significant challenges in condensed matter physics. As the lightest element, metallic hydrogen should have the highest vibrational frequency and strong electron–phonon interaction. Thus, it is most likely to be a room–temperature superconductor based on BCS theory. Although various theoretical calculations predicted metallic hydrogen shows high superconducting temperature T_c ranging from 100 K to 760 K, the metallization of hydrogen has never been fully confirmed by experiments up to 495 GPa.

Alternatively, metallic hydrides with high hydrogen content were proposed to be another way to approach high–temperature superconductivity at relative lower pressure. In hydrides, the interaction between the non–hydrogen atoms and hydrogen sub–lattice acts as chemical pre–compression (e.g., SiH_4 and LiH_6) making hydrogen sub–lattice to be metallic at pressures much lower than that of solid hydrogen. To this end, many attempts have been made to search high–temperature superconducting hydrides (HTSH) in the past two decades. However, not until 2014, the first HTSH SH_3 was discovered with a T_c of 203 K at 150 GPa, which further stimulate the research interests. As a result, including CaH_6, YH_6, YH_9, LaH_{10}, $CaYH_{12}$, Li_2MgH_{16} and other hydrides, a number of HTSH have been identified, where LaH_{10} shows the highest T_c ever measured of 250–260 K at 170–180 GPa.

In 2014, solid H_2S was predicted to possess high superconductivity above 100 GPa. Subsequent experimental work found two superconducting states with T_c of 30–150 and 203 K. Superconductivity at 203 K was explained by cubic H_3S arising from the decomposition of H_2S under high pressure. Similar structure was also found in H_3Se. Clathrate hydride was also could be a prototype structure as a perfect candidate for high-temperature superconductors, namely CaH_6 with a T_c of 235 K at 150 GPa, and was later found to be ubiquitous in alkaline-earth, rare earth hydrides, and actinide hydrides. Recently, clathrate LaH_{10} also suggested to become a superconductor with T_c ~ 280 K at a pressure above 200 GPa. Encouagingly, two subsequent experiments confirmed this prediction and measured high superconductivities of T_c = 260 and 250 K at high pressures of 180 and 170 GPa, respectively, setting a new record of the highest T_c value up to now, and the hydrogen clathrate cage was found play an important role in determining such high superconductivity, resulting in a flurry of searching for new clathrate hydrides under pressure. Encouraged by this work, tremendous superhydrides (MH_x, $x > 6$) with atomic-like clathrate hydrogen cage have been synthesized in the experiment. Moreover, several phase were observed with high superconductors with T_c of 100-200 K. Very recently, our theoretical work predicted a metastable ternary compound in Li-Mg-H system (Li_2MgH_{16}) with high superconductivity at 250 GPa.

Out of all the proposed HTSH, SH_3 is very special as it is the only covalent prototype with a T_c higher than 200 K. It crystallizes in a cubic structure (space group: 229, $Im\text{–}3m$), where two body–centered cubic [SH_3] sublattices interpenetrating with each other. This covalent three–dimensional (3D) network of H only appears in SH_3 and SeH_3 for binary hydrides. Due to its uniqueness, many efforts have been devoted to optimizing the superconducting performance of SH_3 by substitution or doping. For instance, 2.5 % of P ($S_{0.975}P_{0.025}H_3$) can push the T_c to 280 K at 250 GPa. On another hand, Se substitution or replacing partial SH_6 octahedron with Xe atoms not only lower the T_c but also increases the superconducting pressure. While SH_3 and some of its derivatives are indeed high–temperature superconductors, the high superconducting pressure is the main obstacle for the practical application of these HTSH. It is an urgent need to design HTSH with similar T_c but much lower superconducting pressure.

Recently, Snider *et al.* reported the experimental realization of C–S–H ternary hydrides at high pressures. Notably, the superconducting pressure of C–S–H ternary is much lower than that in sulfur hydrides. But the detailed composition and structure of C–S–H compounds are not determined. Therefore, investigation of C–S–H system's structural evolution is necessary to provide useful complementary information to experimental observation. Here, the high–pressure ternary phase diagram of the C–S–H system at 100 GPa is constructed through extensive structure searches via the swarm intelligence–based CALYPSO method. In particular, a unique host–guest CSH_7 compound has been predicted, where C and H form methane molecules CH_4 and insert into the [SH_3] sublattice. Importantly, CSH_7 is dynamical stable at pressure as low as 100 GPa. Analysis suggests this might originate from the pre–compression as the ionic interaction between CH_4 and [SH_3] sublattice is enhanced when pressure increases. The subsequent electron–phonon coupling calculations indicate this phase is likely to be a high–temperature superconductor with a T_c of 181 K at 100 GPa. Our results indicate that the interaction in the host–guest hydride CSH_7 greatly reduces the stability pressure of [SH_3] host lattice, which may act as useful guidance to lower the stabilization pressure of more high–temperature superconducting hydrides.

2. Specific usage status of the system and calculation method

During the fiscal year 2019, we have used about 80% of the total allocated CPU hours and, the rest 20% will be used up at the end of this financial year. Universal variable–composition structure searches for $C_xS_yH_z$ (x = 1 ~ 4, y = 1 ~ 4, z = 1 ~ 36) was performed at 100 GPa with CALYPSO structure prediction method, which requires only chemical compositions for a given compounds to predict stable or metastable structures at given pressure, using simulation cells that consists of maximal number of 50 atoms. In total, 330 different compositions, where nearly 400 structures for each stoichiometry, have been studied. For 87 compositions with a formation enthalpy (comparing to the most competing elements, binaries, and ternaries) lower than 100 meV/atom, further fixed–composition structural predictions were conducted until reach the convergence after we generated 3,000 structures per stoichiometry. The total energy calculations and local structural relaxations were carried out using the density functional theory as implemented in the VASP code. To estimate the superconducting transition temperature (T_c), we calculated the electron–phonon coupling properties using the Quantum ESPRESSO code.

3. Result

Based on the results from the variable–composition structure searches, we constructed the ternary phase diagram of C–S–H as presented in Fig. 1a. Although the more H content the more stable of the compound, none of the ternary C–S–H compounds is thermodynamically stable, indicating the ternaries tend to decompose into elements and binaries. Noteworthy, according to the inorganic crystal structure database, 20 % of experimentally synthesized materials are metastable, some of which even have high positive formation enthalpies larger than 50 meV/atom. Therefore, the metastable ternary C–S–H compounds cannot be precluded and might be accounting for the experimental observations.

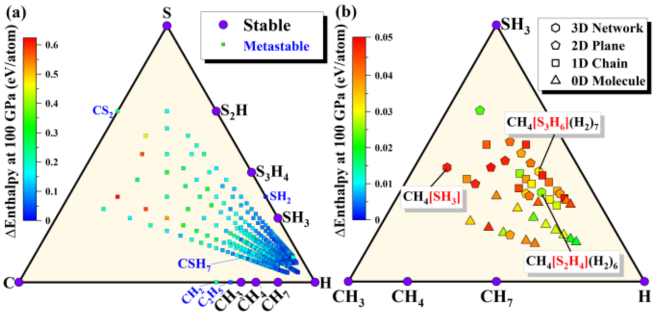

Fig. 1. (a) Calculated stability of C–S–H system at 100 GPa. Colored squares denote metastable phases with different formation enthalpies. Blue circles indicate stable phases. (b) Bonding behavior of C–S–H ternary compounds with formation enthalpies below 50 meV/atom at 100 GPa. Triangle, square, pentagon, and hexagon represents different configurations of the S–H sublattice, respectively.

Analysis shows there are 44 ternaries with formation elthalpy lower than 50 meV/atom. In these compounds, C atom always forms CH_4 molecule with H atoms. Meanwhile, the coordination number of S is varied from 2 to 6, resulting in different S–H sublattices with distinctive structural features. As the coordination number increases, the S–H sublattice evolves from zero–dimensional (0D) SH_2 molecules, to one–dimensional (1D) S–H chains, then to two–dimensional (2D) S–H planes, and finally become three–dimensional (3D) S–H covalent networks (as shown in Fig. 1b). Except for CH_4 and S–H sublattice, we also find the existence of H_2–like molecules with a bond–length of ~0.75 Å space in some C–S–H ternaries.

Previous studies have shown that hydrides containing 3D covalent networks may have relatively high T_c. Thus, CSH_7, CS_2H_{20} and CS_3H_{24} with 3D $[SH_3]$, $[S_2H_4]$ and $[S_3H_6]$ covalent networks (Figs. 2a) caught our attention. At 100 GPa, CSH_7 crystallizes in a highly symmetrical body–centered cubic structure (space group: *I*–43*m*). CSH_7 only consists of two parts, the CH_4 molecules and the $[SH_3]$ sublattice with six–coordinated S, where the latter is identical to the $[SH_3]$ sublattice in *Im*–3*m*–SH_3 except for the symmetric S–H bonds. Interestingly, each methane molecule sits in the center of the interstitial spaces in CSH_7. Therefore, it can be viewed as a host–guest structure. Small charge transfer from CH_4 guest to $[SH_3]$ host was observed as derived from Mulliken population analyses. This charge transfer increases with pressure, indicating an enhancing ionic interaction between host and guest sublattices.

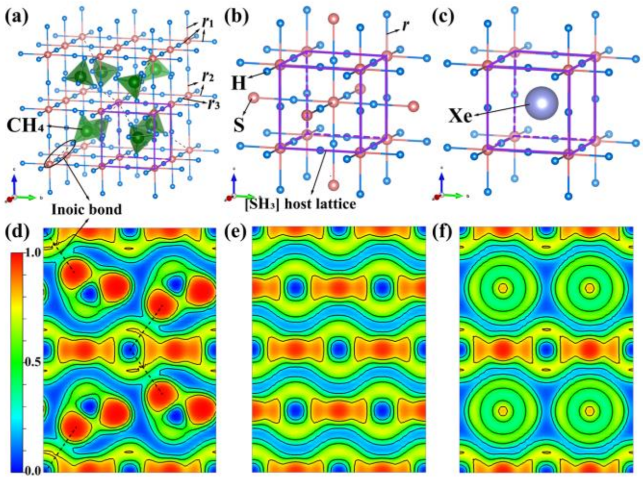

Fig. 2. (a) Conventional cells of (a) *I–43m*–CSH_7, (b) *Im*–3*m*–SH_3, and (c) *Pm*–3*m*–$XeSH_3$. The large, medium and small spheres represent the Xe, S and H atoms, respectively, and the translucent regular tetrahedrons represent the CH_4 molecules. Purple lattices represent the $[SH_3]$ host lattice in a unit. (d) ELF in (1 1 0) sections for *I–43m*–CSH_7 (left panel) at 100 GPa, *Im*–3*m*–SH_3 (middle panel) at 200 GPa, and *Pm*–3*m*–$XeSH_3$ (right panel) at 100 GPa. Black dotted lines repersent the ionic bonds between the host $[SH_3]$ lattice and the guest CH_4 moleculars in *I–43m*–CSH_7.

Alternatively, S atoms in CS_2H_{20} and CS_3H_{24} form covalent bond with four nearby H atoms, resulting in $[S_2H_4]$ and $[S_3H_6]$ 3D covalent network, respectively, by sharing H atoms. Besides CH_4, H_2 molecules are also found within the 3D covalent networks. Consequently, in a similar manner to CSH_7, CS_2H_{20} and CS_3H_{24} can be regarded as $CH_4[S_2H_4](H_2)_6$ and $CH_4[S_3H_6](H_2)_7$, respectively. Although the 3D covalent network itself may correspond to high superconductivity, H_2 molecules are not conducive and hydrides with H_2 usually show low superconducting temperature. We then focus our investigation on CSH_7.

Lattice dynamics simulations suggest CSH_7 and SH_3 become dynamical stable at 100 and 170 GPa, respectively, due to the absence of any imaginary frequency of the phonon spectra. As both CSH_7 and SH_3 are mainly consist of $[SH_3]$ sublattice, this indicates the intercalation of CH_4 molecules can stabilize $[SH_3]$ sublattice at a much lower pressure than that of two self–nesting $[SH_3][SH_3]$ sublattices. We have to mention that previous work has also reported the intercalation of Xe into $[SH_3]$ sublattice (*Pm*–3*m*–$XeSH_3$, Fig. 2c). However, $XeSH_3$ only becomes stable at pressure higher than 240 GPa. Since CSH_7, SH_3, and $XeSH_3$ all have the same S–H framework, we analyzed the interaction within the crystal cell via electron localization function (ELF) as shown in Fig. 2d–2f. The ELF is around 0.3 between CH_4 and $[SH_3]$ lattice in CSH_7, which is a typical value for ionic bonds (dashed lines in Fig. 2d). On another hand, the ELF is close to 0 between the two sublattices in SH_3 and $XeSH_3$, implying a weak chemical interaction. Thus, the predicted different dynamical stable pressures of CSH_7, SH_3, and $XeSH_3$ might be accounting for the different interaction behaviors and initial volumes. Moreover, introducing of the host–guest ionic interactions could be a way to per–compress the host hydrides to lower its stable pressure.

Next, we compared the electronic band structures and projected density of states (PDOS) of CSH_7 at 120 GPa with that of SH_3 at 200 GPa (Fig. 3). Both of CSH_7 and SH_3 show “flat band–steep band” characteristic around the E_f, resulting in a high DOS peak around the Fermi level. The $N(E_f)$ of CSH_7 is comparable to that of SH_3. Thus, CSH_7 is expected to be a high–temperature superconductor similar to SH_3.

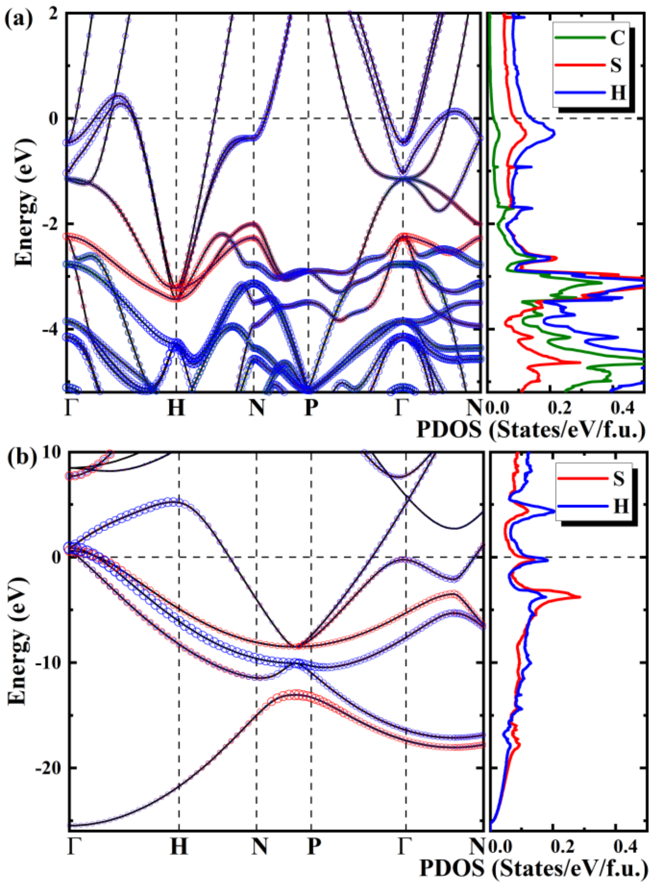

Fig. 3. Electronic band structure (left panel) and projected density of states (right panel) of (a) *I–43m*–CSH_7 at 120 GPa and (b) *Im*–3*m*–SH_3 at 200 GPa.

We further investigated the pressure–dependent superconducting properties of CSH_7, in comparison with SH_3 and $XeSH_3$ (Fig. 4). T_c of SH_3 has been experimentally observed and theoretically calculated to be up to 203 K at 155 GPa and 190 K at 200 GPa, respectively, while superconducting temperature of $XeSH_3$ was predicted to be just 89 K at 240 GPa. For CSH_7, λ is calculated to be 1.84 at 120 GPa. This value is a little bit higher than that of 1.73 for SH_3 at 200 GPa. For both CSH_7 and SH_3, H–derived wagging and bending modes (500 ~ 1300 cm^{-1}) contribute the most (68 % and 83 %, respectively) of the total λ, while S–derived acoustic mode (0 ~ 300 cm^{-1}) contribute the rest (32 % and 17 %, respectively). High–frequency vibrations (3200 ~ 3500 cm^{-1}) are not observed in SH_3 due to the absence of the CH_4 molecules. Since the Eliashberg equation gives a better description of systems with strong electron–phonon coupling ($\lambda > 1.5$), T_c of CSH_7 is evaluated through the direct numerical solution of the Eliashberg equation. The superconducting temperatures of CSH_7 is estimated to be 181, 173, and 132 K at 100, 120, and 150 GPa, respectively, using typical Coulomb pseudopotential parameter μ^* = 0.1 (Fig. 4). The slightly lowered T_c may correspond to the presence of CH_4 molecules that suppresses the electron density of states at the Fermi surface and enhances the Coulomb shielding effect within the crystal lattice

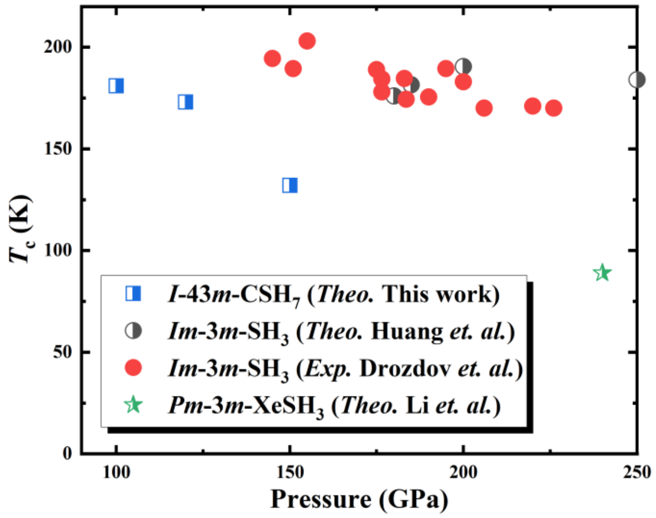

Fig. 4. Pressure dependence of T_c in sulfur hydride. Filled circles show experimental results reported by Drozdov *et. al.* while half–filled squares, circles and stars indicate theoretical results of *I–43m*–CSH_7 in this work, *Im*–3*m*–SH_3 reported by Huang *et. al.*, and *Pm*–3*m*–$XeSH_3$ reported by Li *et. al.*, respectively.

4． Conclusion

In summary, we have extensively explored the phase diagram of C–S–H system at 100 GPa. A unique *I*–43*m*–CSH_7 host–guest hydride with CH_4 guest molecules and SH_3 host lattice has been identified. CSH_7 is dynamical stable at 100 GPa that the pressure is much lower than that of *Im*–3*m*–SH_3 (170 GPa) with similar [SH_3] sublattices. Analysis shows ionic interactions between host and guest lattices may induce chemical pre–compression and, thus, lower the stale pressure. Calculations suggest CSH_7 is also a high–temperature superconductor with T_c up to 181 K at 120 GPa, where the [SH_3] host lattice mainly contributes to the superconductivity. Our current results show it is possible to reduce the dynamical stable pressure of high superconducting SH_3 with the intercalation of interacting guest molecules, and may also shed light on the high–pressure experimental findings.

5． Schedule and prospect for the future

I have been a HOKUSAI general user and wish to continue using the system. During the last fiscal year 2019, I have submitted one paper on the high–pressure behaviors of various C–S–H compounds. For the next fiscal year 2020, we plan to continue using HOKUSAI supercomputer to study the Li–RE–H (RE = Sc, Y, and La) at pressures through CALYPSO code, and research superconducting properties of stable phases. We expect high standard publications can be eventually achieved.

Fiscal Year 2019 List of Publications Resulting from the Use of the supercomputer

1. Ying Sun, Yifan Tian, Bowen Jiang, Xue Li, Hefei Li, Toshiaki Iitaka, Xin Zhong, and Yu Xie, **Computational Discovery of Dynamically Stable Cubic SH_3-like High-Temperature Superconductor at 100 GPa via CH_4 Intercalation**, *Phys. Rev. B*, submitted (2020).