Absence of conventional room temperature superconductivity at high pressure in carbon doped H$_2$S

Tianchun Wang,$^{1, *}$ Motoaki Hirayama,$^{1, 2}$ Takuya Nomoto,$^1$
Takashi Koretsune,$^3$ Ryotaro Arita,$^{1, 2}$ and José A. Flores-Livas$^{4, 2, 4}$

$^1$Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan
$^2$RIKEN Center for Emergent Matter Science, 2-1 Hirosawa, Wako, 351-0198, Japan
$^3$Department of Physics, Tohoku University, 6-3 Aza-Aoba, Sendai, 980-8578 Japan
$^4$Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 5, I-00185 Roma, Italy

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In this work, we show that the same theoretical tools that successfully explain other hydrides systems under pressure seem to be at odds with the recently claimed conventional room temperature superconductivity of the carbonaceous sulfur hydride. We support our conclusions with I) the absence of a dominant low-enthalpy stoichiometry and crystal structure in the ternary phase diagram. II) Only the thermodynamics of C-doping phases appears to be marginally competing in enthalpy against H$_3$S. III) Accurate results of the transition temperature given by ab initio Migdal-Eliashberg calculations differ by more than 110 K to recently theoretical claims explaining the high-temperature superconductivity in carbonaceous-hydrogen sulfide. A novel mechanism of superconductivity or a breakdown of current theories in this system is possibly behind the disagreement.

Over the last decade, pressurized hydride compounds have led the path to many important landmarks in superconductivity. Notable cases include silane in 2008 [1], H$_3$S in 2014 [2, 3] which has triggered most of the field, and the confirmation of high-$T_c$ in LaH$_{10}$ by independent teams in 2019 [4–6]. This unfolding success of important breakthroughs is largely due to the symbiosis of theory, computation, and experimental sciences, which has accelerated the discovery by pointing to niches of interesting systems [7–11].

Recently, Snider et al. [12] achieved a decades-old quest; they reported solid evidence of the first room-temperature superconductor (RTS) made of carbon-sulfur-hydrogen. Although the report set a landmark in the annals of science, there are still many open questions surrounding this important discovery. For instance, the exact stoichiometry of the claimed carbonaceous hydrogen sulfide that exhibits RTS is still elusive. Moreover, there is a debate with confronted arguments on the possibility of unusual superconducting features in all superhydrides at odds with the Bardeen-Cooper-Schrieffer theory [13–15]. It includes the sharp drop of electric resistivity at $T_c$ and its dependence on a magnetic field [13, 16, 17]. It is worth noticing that the room-temperature superconductor reported at 287.7 K at 267 GPa, has not been confirmed by magnetic susceptibility measurements [12]. But, amidst such unsolved puzzles, perhaps the most intriguing question is: what is the crystalline structure of the RTS?

Certainly, it is difficult to measure the crystalline structure of a tiny sample under extremely high pressure, additionally complicated by the small scattering ratio of low-Z hydrogen. Hence, to clarify the mechanism of superconductivity and electronic and phonon properties, it is highly desirable to know the crystalline structure from the theoretical side. So far, there have been two works on crystal structure prediction for C-S-H ternary systems [18, 19]. In these works, plausible structures were explored under high-pressure $p = 100$ GPa [18] and 100-200 GPa [19], which reported many structure candidates for high-$T_c$ superconductivity, including CSH$_T$. However, these candidates are not thermodynamically stable, and also, the pressure explored is much lower than $p \sim 270$ GPa, at which the RTS was reported.

In this Letter, we shed light on different open issues of the RTS. Resorting to structure prediction, we enlarged the chemical composition search and estimated C-S-H ternary systems’ formation enthalpy at 250 GPa. We also analyzed the doped phases, from their thermodynamic stability to superconducting properties and found flagrant differences compared to recent theoretical reports on C-doped H$_3$S [20, 21]. On the transition temperatures obtained within virtual crystal approximation (VCA) and McMillan-Allen-Dynes (MAD) theory, presumably, an electronic smearing parameter holds to overestimate $T_c$’s theoretical value. In contrast, we found more than 110 K difference in $T_c$ between experimental and the converged ab initio values. Our theoretical results show that the room-temperature superconductor cannot be explained by conventional superconductivity of carbon-doped H$_3$S phases nor other stoichiometries explored so far.

Due to the prohibited computational overhead of calculating a huge number of available compositions in the ternary system, we focus our strategy on exploring only representative sections of the compositional landscape in detail. Fig. 1 shows the C-S-H ternary convex hull for selected compositions at 250 GPa (see details in Ref. [22]). We find CSH$_7$ (enthalpy of formation $\sim$0 meV) and the absence of a dominant (low enthalpy) phase, which is in agreement with previous works [18, 19]. In our searches, we observed that different sections of the compositional
Figure 1. C-S-H convex hull of the formation enthalpy calculated for selected stoichiometries at 250 GPa. Elemental phases and other low-lying enthalpy compositions are coloured in yellow, in red, unstable, and from blue to dark-blue, chemical compositions with negative formation enthalpy. At this pressure, the lowest enthalpy phase is H$_3$S (130 meV), followed by doped phases. However, already at 3.7% of C incorporation, the enthalpy difference between the parental phase and the dope one changes by 25 meV or $\sim$290 K. Representative low-enthalpy structures of selected compositions are displayed outside the ternary hull. Intriguingly, in all the different regions studied in the phase diagram, the motifs with the lowest enthalpy correspond to molecular parts, either H$_x$C and H$_x$S, but nothing points towards a fused, covalently bonded C-S-H compound.

space were governed by anticipated trends.

The high content of carbon and hydrogen (top left areas of the Gibbs triangle) will form CH$_2$ and CH$_4$. Increasing hydrogen content (H$_5$–16) in these areas will then produce phase separation to H$_2$ and CH$_x$, which are compositions with formation enthalpy well above 100 meV/atom (not shown). Moving to the middle section of the triangle, for C and S on 1:1 ratio with increasing H; H$_3$, H$_4$, H$_5$ and H$_6$; these stoichiometries are highly energetic and unlikely to occur. In these phases, decompositions to H$_2$, H$_3$S or CH$_x$ are seen.

CSH$_7$ and CSH$_{10}$ are interesting compositions that become metastable due to their conformation and "poor" metallicity. These compositions are formed by H$_3$S and CH$_x$ units with weak Van der Walls interaction [18] between them (detrimental to high-$T_c$ phonon-superconductivity). Increasing the hydrogen above H$_{10}$ in the ternary compounds, C-H binaries or S-H binaries also result in phase separation. Most of the found phases present simple patterns, and these can be classified almost as amorphous phases. Coming back to the ratio of C$_{0.25}$S$_{0.75}$, the same pattern emerges, shown in the plotted figure (C$_{0.25}$S$_{0.75}$H$_3$; the characteristic cubic arrangement of sulfur-hydrogen with distinctive layers and enclosed CH$_4$ units (a poor metal). Moving to C$_{0.5}$S and lower hydrogen (below H$_2$) content seems odd for high-$T_c$ superconductivity since decreasing the hydrogen content reduces the chances of finding key ingredients: metallic phases with light atomic mass. Explorations below the CSH$_7$ range with C points towards the C-C formation of stable covalent bonds; however, these are semiconducting phases. In sulfur-rich areas, S-S metallic phases are found. However, these are unlikely to be responsible for the RTS.

The region close to the lowest enthalpy (H$_3$S) phase is the most relevant in the compositional space. The varying C doping into the matrix of H$_3$S (C-substitution in S sites) is the most reasonable solution from the thermodynamical point of view: we report that enthalpy decreases from -2 meV/atom at 25%C to -50 for 12.5%C, to -77 meV/atom for 8.3%C, to -95 meV/atom for 5.5%C, and finally to -105 meV/atom for 3.7%C, and so on until reaching the H$_3$S with enthalpy of -130 meV/atom (clearly the dominant composition). Judging by the convex hull of stability, C-doping offers a possible structure model to explain the RTS, which is not new for other systems (see Ref. [7] for a review). Nevertheless, introducing carbon into the H$_3$S lattice comes at a price: it plays a
Figure 2. Calculated doping-superconductivity-pressure phase diagrams using two protocols: the left panel shows $T_c$ with a non-converged parameter (see text) and the right panel with the controlled and converged protocol. The abscissa in both panels displays pressure in the range where the RTS was reported. The ordinate represents the carbon doping as simulated by the VCA and the colour bar shows the estimated $T_c$ given by the MAD-formula. The Coulomb parameter $\mu^*$ is set to 0.1. Maximum and minimum $T_c$'s for each panel are shown. Beyond the technical validity of the VCA, it is clear that independently of doping and pressure, an RTS is absent for the converged case.

detrimental role to single-phase stability (at 3.7% of C
doping level, the enthalpy difference between the parental
phase and the doped one changes by 25 meV or $\sim$ 290 K),
and excessive doping could also worsen the pristine elec-
tronic structure of H$_3$S.

It has been reported that, at least in the other two
major systems (H$_3$S and LaH$_{10}$), the highly symmetric
arrangements of atoms in hydrides under pressure dis-
play a van Hove singularity (VHS) near the Fermi level
($E_F$) [7, 23]. In the case of H$_3$S (close to the C-S-H case),
the VHS peak resides slightly lower than $E_F$ [24]. From
the electronic point of view, it is favourable for super-
conductivity to attempt electron doping. Recent studies
based on the McMillan-Allen-Dynes (MAD) [25, 26] for-

mula have shown exceptionally that $T_c$ of C$_x$S$_{1-x}$H$_3$ can
be as high as room-temperature when $x$ is $\sim$0.05 [20, 21].
However, it is also well documented that the MAD for-

mula is not a good approximation when the electron-
phonon coupling is strong [27] or when the density of
states (DOS) has a significant energy dependence around
the VHS (as for electron doping) [27].

Let us first examine the effects of carrier doping onto
the possible explanation of the RTS. Fig. 2 confronts two
phase diagrams of doping-pressure-$T_c$: the left one repro-
duces satisfactorily the one presented by Ge et al. [20].
The right panel (this work) shows quite the opposite
phase diagram, with much lower $T_c$ values. Notice-
able, when calculating the Eliashberg function $\alpha^2F(\omega)$,
a sensitive parameter is the broadening width $\delta$ of the
smearing for the double-delta integral. The left dia-
gram in Fig. 2 is the result using the broadening width
$\delta = 0.002$ Ry, and the right one is the result produced
by $\delta = 0.014$ Ry. Since the results have significant de-
pendence on the broadening width $\delta$, to reach con-
vergence, we choose the value of $\delta$ so that it can reproduce
$N(0)$, where $N(0)$ is the DOS at the Fermi level given
by the tetrahedron method [28] using a sufficiently dense
mesh [29]. We ascribe the difference between the plots
from a lack of convergence in the article by Ge et al. [20];
$T_c$ is overestimated, especially with the MAD formula
when too narrow smearing is used for the integral of the
electron-phonon line width in the momentum space. The
right panel summarizes $T_c$ using a protocol and carefully
tested electronic parameters [30] that reproduce theoret-
cal values for H$_3$S [31] and LaH$_{10}$ [6].

Besides the discussions above, another shortcoming of
the MAD-formula is the Coulomb interaction, which is
introduced phenomenologically by a pseudo Coulomb pa-
rameter, $\mu^*$, with a value set around 0.1. However, there
is no reason why these values should be transferred at
high pressure. In our case, the Migdal-Eliashberg (ME)
calculation used the Coulomb interaction kernel, in which
we solved the gap equation directly to get rid of $\mu^*$. Thus,
the ME calculation is more robust and straight-
forward, without any empirical parameters involved [30].
Using accurate first-principles Migdal-Eliashberg calcu-
lations [30, 31] (see details in [32]), for which the doping
effects are described by the VCA, we found that $T_c$ of
the doped phases of H$_3$S are hardly enhanced by $\sim$20 K and decreases as a function of pressure (red line shown in Fig. 3). This tendency is also observed in H$_3$S [33–36] and LaH$_{10}$ [6].

In addition to the shortcomings of the MAD formula used in Fig. 2, another concern is the validity of VCA when mixing atomic potentials for non-neighbouring species. The theoretical accuracy of VCA to estimate doping phase diagrams of hydrides under pressure is beyond the scope of this work. However, we would like to briefly discuss and compare the VCA and the supercell calculation, a more conventional scheme to treat the doping effects, phonon density of states, and a thorough investigation of different doping models and how the electronic singularity is altered by carbon.

Finally, we reach two contradicting points: on the one hand, doping appears to be the most likely explanation for the RTS. However, a low degree of doping does not alter the electronic structure, and $T_c$ is close to the reported $T_c$ of H$_3$S, as shown in Fig. 2. And on the other hand, large doping alters the so-called fine-tuning [12] of the VHS drastically.

In summary, from the thermodynamic perspective, substituting carbon in sulfur sites or interstitial space increases the formation enthalpy (it becomes less stable). Introducing carbon in the $Im3m$ phase of H$_3$S plays against high-$T_c$, changes the shape of DOS, decouples phonons, slightly modify the lattice and factors down $T_c$. Perhaps the current level of theory is insufficient to reconcile the scenario with the present experimental results. We conclude by asserting that in previous systems (H$_3$S [36] and LaH$_{10}$ [6]), remarkable compatibility between theoretical and experimental sides in $T_c$ and phase diagram is found; for the carbonaceous-sulfur hydride, this might not be the case.

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* tianchun.wang@riken.jp
† jose.flores@uniroma1.it

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