

Refined phase diagram of the H-S system with high- T_c superconductivity

Ivan Kruglov,^{1,2,*} Ryosuke Akashi,³ Seiji Yoshikawa,³ Artem R. Oganov,^{4,5,1,2} and M. Mahdi Davari Esfahani⁵

¹*Dukhov Research Institute of Automatics (VNIIA), Moscow 127055, Russian Federation*

²*Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region 141700, Russian Federation*

³*Department of Physics, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

⁴*Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, Moscow 143026, Russian Federation*

⁵*Department of Geosciences, State University of New York, Stony Brook, New York 11794-2100, USA*

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Recently, hydrogen sulfide has attracted enormous attention due to the record high-temperature superconductivity of H_3S with $T_c = 203$ K at a pressure of 155 GPa. In addition to H_3S , there are many theoretically and experimentally confirmed compositions and crystal structures forming under high pressure. Here, using the *ab initio* variable-composition evolutionary algorithm USPEX, we performed a comprehensive search for new phases in the H-S system and built a refined composition-pressure phase diagram. For H_5S_2 , a new stable semiconducting $P2_1$ phase was found. We predicted a new sulfur-rich stable HS_2 phase and metastable compound H_5S_8 and calculated their T_c using superconducting density functional theory (11 K at 100 GPa and 9.2 K at 80 GPa, respectively). Our results show that among stable phases only H_3S is a high- T_c superconductor, and highlight that compositional descriptors alone are insufficient for indicating superconductivity, and crystal structure plays an essential role.

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I. INTRODUCTION

The search for superconductors with a high transition temperature to the superconducting state (T_c) and the explanation of the phenomenon of high-temperature superconductivity (HTSC) are among the most interesting problems in modern physics. A theory which explains the nature and behavior of all HTSC is still lacking, but according to Bardeen-Cooper-Schrieffer (BCS) theory, a superconductor will have a high T_c , if the following three conditions are satisfied: the presence of high-frequency phonons, strong electron-phonon coupling, and a high density of states at the Fermi level. Metallic hydrogen meets all three conditions, but requires extremely high pressures for synthesis [1]. So, logically, the search was extended to covalent compounds containing hydrogen and other elements. Hydrogen sulfide stands out among the rest. The H-S phase diagram was investigated [2] using the evolutionary code USPEX [3–5], and trigonal $R3m$ and cubic $Im\bar{3}m$ phases of H_3S were predicted at high pressures (above 120 GPa). For the cubic phase T_c was estimated to be in the range 191–204 K at 200 GPa. Soon thereafter an independent experimental work appeared [6], which confirmed the existence of a superconducting phase with a record T_c equaling 203 K at 155 GPa. The experimental superconducting phase was found to be identical to the previously predicted bcc H_3S phase [7]. The causes of its high T_c were discussed in Refs. [8–19].

Duan *et al.* [20] originally suggested H_3S to be the only stable H-S compound at pressures in the range 37–300 GPa, yet H_3S_2 , H_2S_3 , H_4S_3 , HS_2 , and HS compositions were later found to be stable. Theoretically and experimentally, it was shown that at pressures below 35 GPa, H_2S_3 and H_3S_2 have stability fields, and H_4S_3 is stable from 25 to 113 GPa [21]. The T_c of all these predicted phases does not exceed 10 K. Metastable Magneli-like phases consisting of H_2S and H_3S

motifs [22], including the intermediate H_5S_2 , were proposed to explain the linear dependence of T_c on pressure at low temperatures [23]. HS_2 has been proposed to be stable above 110 GPa. At pressures above 200 GPa, theoretically it was shown that HS is near stability and HS_2 is thermodynamically stable [17].

As it follows from the above, the composition-pressure phase diagram of the H-S system is complex and controversial, yet knowledge of the phase diagram is essential for designing optimal synthetic strategies. Our goal is to build a complete phase diagram, and, if new stable phases are found, explore their superconductivity. Indeed, employing a structure-search algorithm in combination with first-principles calculations, we found various new stable and low-enthalpy metastable phases in the sulfur-rich regime. Our findings provide insights into the possible reaction paths in the H-S system under pressure.

II. METHOD

We carried out extensive searches for stable H-S compounds using the evolutionary algorithm USPEX [3–5]. Variable-composition calculations were done at pressures from 0 to 200 GPa with steps of 30 GPa. In each evolutionary search, there were 120 random structures in the first generation, and the next generations (100 structures) consisted of 20% random structures and 80% made by heredity, soft-mutation, and transmutation operators. The calculation stopped after 100 generations. After each calculation the most stable structures (near and on the convex hull) were taken for further analysis. For compositions where the stable phase was predicted to have $P1$ symmetry, we performed additional calculations using USPEX with fixed composition. As a result, we found 15 potentially stable structures. All these new candidates plus the previously known structures were relaxed with high precision at a series of pressures in the range 0–200 GPa. At each pressure the convex hull diagram was built, where the enthalpy

*ivan.kruglov@phystech.edu

of formation (normalized per atom):

$$\Delta H(\text{H}_x\text{S}_y) = \frac{1}{x+y} [H(\text{H}_x\text{S}_y) - yH(\text{S}) - xH(\text{H})] \quad (1)$$

is plotted vs composition $y/(x+y)$.

A phase is deemed thermodynamically stable if its enthalpy is lower than the enthalpies of all possible isochemical states (or mixtures of phases)—thus, all stable phases form a convex hull. The structures of H and S at different pressures were taken from Refs. [24–27]. If at a certain pressure H_xS_y is on the convex hull, then we say that it is stable at that pressure. In order to ascertain the phase boundaries, enthalpies were calculated with a 1 GPa step, and linearly interpolated in between.

Structure relaxations and total energy calculations were performed using density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) [28] within the generalized gradient approximation of Perdew-Burke-Ernzerhof [29]. The projector augmented wave (PAW) [30] method was employed to describe the core electrons and their effect on valence electrons. We used a plane-wave energy cutoff of 600 eV and a Γ -centered k -point mesh with a resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$.

The values of T_c for some newly found structures were calculated with the first-principles scheme based on density functional theory for superconductors (SCDFT) [31,32]. The effects of phonon-mediated pairing, phonon-induced electron mass renormalization, and pair-breaking Coulomb repulsion were included within the level of the Migdal-Eliashberg theory [33–36], and a dynamical correction to the Coulomb interaction (the plasmon effect) was also considered [37–39]. For this purpose, the electron, phonon, and electron-phonon coupling properties were re-

calculated with the plane-wave pseudopotential method as implemented in the QUANTUM ESPRESSO package [40,41]. More details are given in the Supplemental Material [42].

III. RESULTS AND DISCUSSION

Using the methodology described above, the phase diagram of the H-S system was calculated (Fig. 1). We found new stable crystal structures for H_3S_2 and HS_2 compositions, and their stability regions are shown on the phase diagram (Fig. 1). We also estimated that account for zero-point energy can shift the stability ranges by 1–2 GPa. Figure 1 also shows the values of T_c for different hydrides, where the gray color means that this phase is not a superconductor or its superconducting properties are unexplored due to the high computational cost required, and red color encodes highest-temperature superconductivity with T_c of 203 K.

At 0 GPa the only stable compound is H_2S . We studied both previously known stable structures (e.g., see Ref. [43]) and the new ones [44]. Following Ref. [44], the stable at 0 GPa phase III of H_2S (space group $Pbcm$) transforms at 12 GPa into the $P2_12_12_1$ phase, and then into Pc at 28 GPa. In Ref. [44], no structural information was given—however, we found this structure in our searches and provide it in Table II in the Supplemental Material [42]. Consistent with Ref. [44], we find the transition from phase III ($Pbcm$) to $P2_12_12_1$ at 12 GPa and from $P2_12_12_1$ to Pc at 25 GPa (Fig. S6 in the Supplemental Material [42]). Starting from 3 GPa, the previously known $C2/c$ phase of H_3S [21] becomes stable. At 112 GPa, the $C2/c$ phase transforms into $R3m$, and at 158 GPa the next phase transition occurs, from $R3m$ to $Im\bar{3}m$. A Magnéli-like H_5S_2 phase has been predicted to be stable from 112 to 122 GPa [23]. Among the Magnéli-like phases with a periodicity

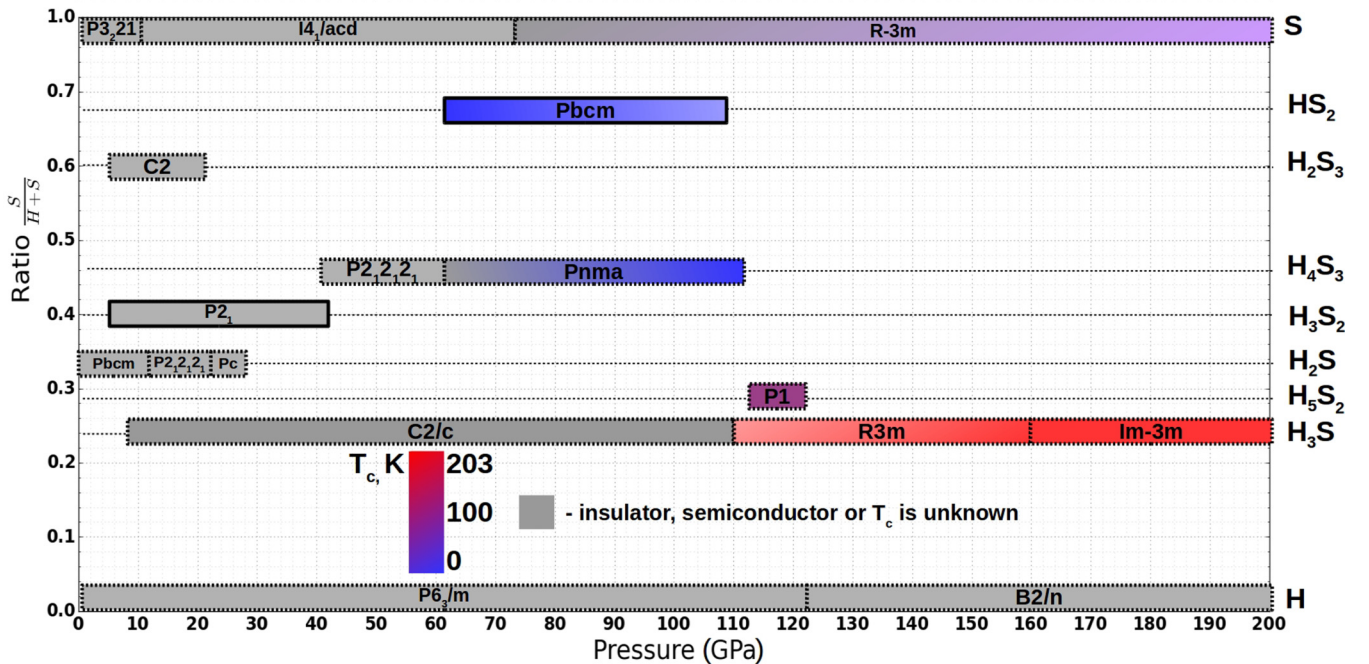


FIG. 1. Composition-pressure phase diagram of the H-S system. Solid and dashed lines indicate new structures (predicted here by USPEX) and previously known crystal structures, respectively.

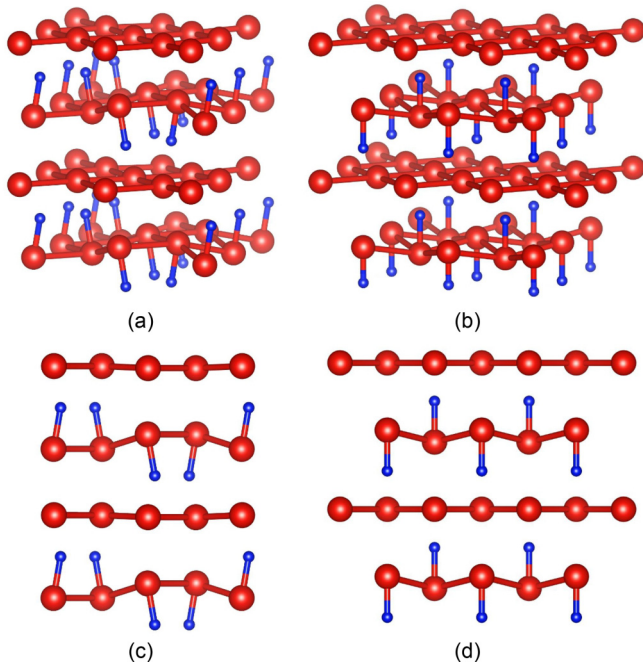


FIG. 2. (a) and (c) Crystal structure of our *Pbcm* phase of HS_2 . (b) and (d) Crystal structure of the previously predicted *P4/nmm* phase of HS_2 .

up to four in the notation in Ref. [22], we confirmed the stability of H_5S_2 against decomposition to H_3S and S (Fig. S5 in the Supplemental Material [42]), which is consistent with Ref. [23]. Some Magnéli-like phases such as H_7S_3 have also been confirmed to have a closely competing stability (with an enthalpy higher by ~ 1 meV/atom than the mixture $\text{H}_5\text{S}_2 + \text{S}$).

Besides H_2S and H_3S compositions, with increased pressure up to 5 GPa, there appear *C2* H_2S_3 [21] and *P2*₁ H_3S_2 predicted by us on the phase diagram. The newly predicted *P2*₁

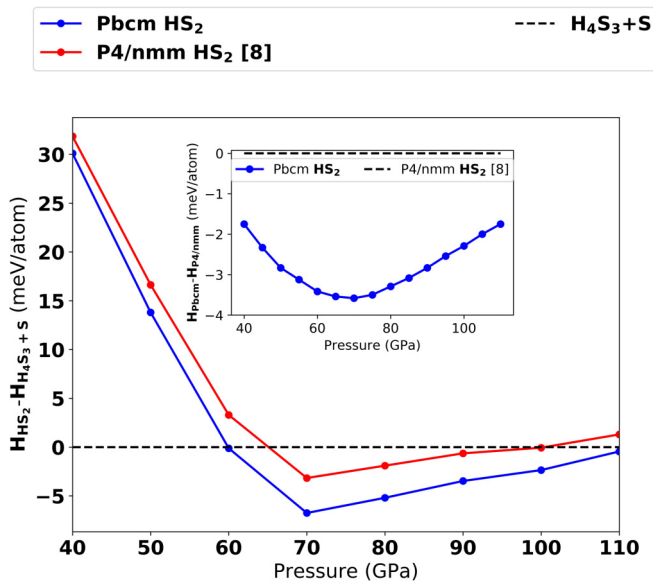


FIG. 3. Enthalpy of decomposition of the predicted and previously known HS_2 structures into H_4S_3 and S .

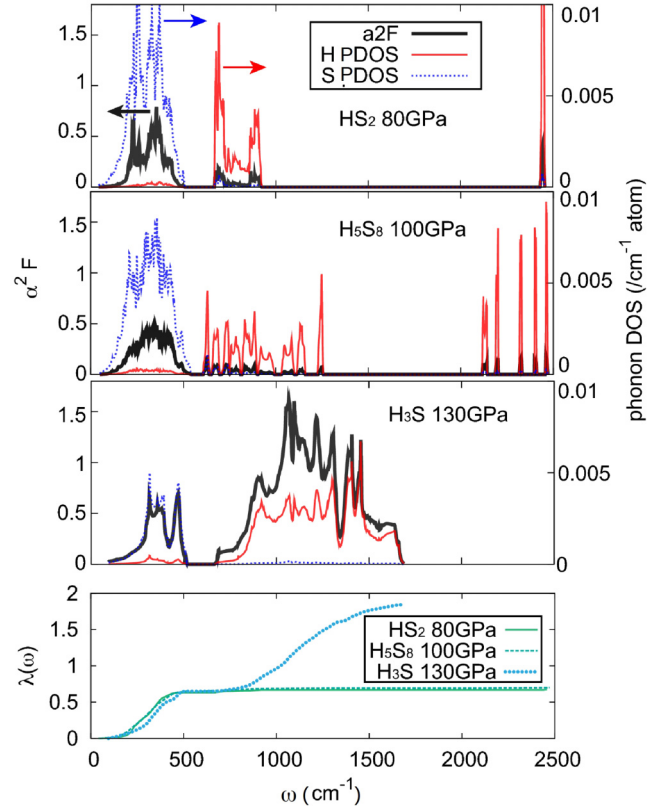


FIG. 4. Comparison of the Eliashberg spectral function $\alpha^2 F(\omega)$, phonon density of states, and integrated $\lambda(\omega)$ for HS_2 , H_5S_8 , and H_3S . Data for H_3S are taken from Ref. [18].

phase of H_3S_2 is more stable than *P1* previously proposed in Ref. [21]. The new structure consists of the same building blocks as the *P1* H_3S_2 structure, H_2S and H_2S_2 , but their orientation is different (Fig. S1 in the Supplemental Material [42]). The enthalpy difference is shown in Fig. S2 in the Supplemental Material [42].

The previously predicted stable *P2*₁*2*₁*2*₁ H_4S_3 (which at 60 GPa transforms into *Pnma* [21]) and the newly predicted *Pbcm* HS_2 appear at pressures above 40 and 60 GPa, respectively. H_4S_3 is stable up to 113 GPa and HS_2 is stable up to 108 GPa. We compared the crystal structure of our (*Pbcm*) phase of HS_2 with the previously predicted *P4/nmm* structure [Figs. 2(a)–2(d)]. Both HS_2 structures contain alternating planar sulfur layers and corrugated HS layers [see Figs. 2(a)–2(d)]. In both previously known and new structures the S-H bond length is equal to 1.33–1.34 Å, and the distance from hydrogen to the closest sulfur in the next layer is 2.04 Å in the *P4/nmm* and 2.14 Å in the *Pbcm* phase (at 80 GPa). The difference between the structures is that H-S bonds in the *Pbcm* phase are differently oriented: AABBA instead of ABABAB. This affects corrugation of sulfur atoms in the HS-layer. *Pbcm* HS_2 is always more stable than the previously predicted *P4/nmm* structure (Fig. 3). Both structures of HS_2 are consistent with experimental data reported in Ref. [45].

In addition to stable phases, we found a new low-enthalpy metastable phase with a previously unseen composition H_5S_8 . Its enthalpy is higher by less than 10 meV/atom than the enthalpy of the $\text{H}_4\text{S}_3 + \text{HS}_2$ mixture at pressures from 50

to 110 GPa (Fig. S4 in the Supplemental Material [42]). Its structure consists of parallel buckled sulfur layers, with some S atoms attached to one H atom (Fig. S3 in the Supplemental Material [42]). The distance between the closest H and S atoms from different layers at 100 GPa is 2.17 Å, and a S-H bond in the layer varies from 1.34 to 1.40 Å. Taking into account our phase diagram, the decomposition path of H₂S can be built: H₂S → (28 GPa) H₃S + H₃S₂ → (42 GPa) H₃S + H₄S₃ → (112 GPa) H₃S + H₅S₈ → H₃S + S.

We studied the superconducting properties of the newly predicted H₅S₈ and HS₂ phases. Superconductivity of the material is mainly determined by the spectral function $\alpha^2 F(\omega)$ and, consequently, the electron-phonon coupling coefficient λ . We calculated $\alpha^2 F(\omega)$ and integrated $\lambda(\omega)$ of H₅S₈ and HS₂ at 80 and 100 GPa, respectively, and compared them with R3m H₃S at 130 GPa (Fig. 4). Plots for H₅S₈ and HS₂ show that the main contribution in $\alpha^2 F(\omega)$ is given by the vibrations of sulfur atoms, while in H₃S the vibrations of hydrogen atoms play the dominant role for superconductivity. Using SCDFT we calculated the T_c of the new phases. For H₅S₈ at 100 GPa, it is equal to 11 K with McMillan parameters $\lambda = 0.70$, $\omega_{\log} = 444$ K, and $\mu^* = 0.15$. For HS₂ at 80 GPa, T_c is equal to 9.3 K with parameters $\lambda = 0.67$, $\omega_{\log} = 438$ K, and $\mu^* = 0.139$ (μ^* was derived so that the McMillan equation

reproduces SCDFT T_c). These T_c values are close to the experimental values for compressed pure sulfur [6,46].

IV. CONCLUSIONS

Using the variable-composition evolutionary algorithm US-PEX to predict stable compounds and their crystal structures, we found new H₃S₂, HS₂, and H₅S₈ phases. We showed that the newly predicted H₃S₂ and HS₂ are more stable than the previously predicted ones. Taking into consideration all the known and predicted phases, we built a refined phase diagram of H-S, at pressures from 0 to 200 GPa. Using the SCDFT method we calculated T_c for new HS₂ and H₅S₈. According to our results, superconductivity of these phases is mostly due to electron coupling with the vibrations of sulfur atoms. The values of T_c are 11 and 9.3 K for H₅S₈ at 100 GPa and HS₂ at 80 GPa, respectively.

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