

The metallization and superconductivity of dense hydrogen sulfide

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Hydrogen sulfide (H_2S) is a prototype molecular system and a sister molecule of water (H_2O). The phase diagram of solid H_2S at high pressures remains largely unexplored arising from the challenges in dealing with the pressure-induced weakening of S–H bond and larger atomic core difference between H and S. Metallization is yet achieved for H_2O , but it was observed for H_2S above 96 GPa. However, the metallic structure of H_2S remains elusive, greatly impeding the understanding of its metallicity and the potential superconductivity. We have performed an extensive structural study on solid H_2S at pressure ranges of 10–200 GPa through an unbiased structure prediction method based on particle swarm optimization algorithm. Besides the findings of candidate structures for nonmetallic phases IV and V, we are able to establish stable metallic structures violating an earlier proposal of elemental decomposition into sulfur and hydrogen [R. Rousseau, M. Boero, M. Bernasconi, M. Parrinello, and K. Terakura, Phys. Rev. Lett. **85**, 1254 (2000)]. Our study unravels a superconductive potential of metallic H_2S with an estimated maximal transition temperature of ~80 K at 160 GPa, higher than those predicted for most archetypal hydrogen-containing compounds (e.g., SiH₄, GeH₄, etc.). © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4874158]

I. INTRODUCTION

Information on the structures of hydrogen-containing molecular systems at high pressures is central to many problems in physics, chemistry, and allied sciences.¹ Due to the alteration of interatomic interactions and the redistribution of electron density, a variety of fascinating physical phenomena have been observed or predicted for hydrogencontaining molecular compounds under pressure. Among these phenomena, the ubiquitous presence of a superconducting state in various high-pressure phases is attractive, since a large number of hydrogen-containing compounds (e.g., SiH_4 ,²⁻⁴ SnH_4 ,^{5,6} GeH_4 ,⁷ $SiH_4(H_2)_2$,⁸ etc.) have been predicted (or even observed²) to be superconductive at pressures (90-250 GPa) accessible to current experiments. Interestingly, many hydrogen-containing compounds were predicted to possess very high superconducting transition temperatures (T_c) , e.g., 64 K in GeH₄ (220 GPa),⁷ 80 K in SnH₄ $(120 \text{ GPa})^{6}$ and striking $\sim 100 \text{ K}$ in SiH₄(H₂)₂ (250 GPa).⁸

 H_2S is an analog of water (H_2O) at the molecular level. However, the phase diagram of solid H_2S at high pressures up to 100 GPa⁹⁻¹² is fundamentally different from that of H_2O . At ambient pressure, H_2S crystallizes in three typically molecular solids (phases I–III, dependent upon temperature^{13,14}). Upon compression, H_2S transforms into three high-pressure phases (phases IV, V, and VI⁹⁻¹²). Due to the extremely weak X-ray scattering of hydrogen, the crystal structures of these high-pressure phases are under intensive debate.¹⁵⁻²⁰ Experimentally, tetragonal I41/acd and monoclinic Pc structures have been suggested for phase IV by Fujihisa et al.¹⁵ and Endo et al.,¹⁶ respectively. Theoretically, ab initio molecular dynamics (MD) simulations¹⁷⁻¹⁹ at low temperatures (100-300 K) have proposed three candidate structures for phase IV: partially rotational disordered tetragonal P4₂/ncm (T = 300 K),¹⁷ orthorhombic Pbca,¹⁸ and Ibca (T = 100 K).¹⁹ Pressurizing from an initial configuration of the P42/ncm structure, MD simulations²⁰ at room temperature predicted two orthorhombic structures with symmetries of Pmn21 and $Cmc2_1$ as candidates for phases V and VI, respectively. The large structure diversity proposed for solid H₂S posts great challenges in understanding of its high-pressure phase diagram. Further investigation on the high-pressure structures of H₂S is greatly demanded.

The most fascinating topic about H_2S is its metallization at moderate pressure (~96 GPa). This is in contrast to the situation in H_2O , where decomposition into H_2O_2 and a hydrogen-rich $H_{2+\delta}O$ ($\delta \ge 1/8$) compound at terapascal pressure regions²¹ was predicted before the metallization. Optical experiments¹¹ showed that the color of H_2S changes from thin yellow to black at ~27 GPa, indicating a large decrease of the band gap. An infrared spectral study¹² demonstrated that H_2S eventually turns into a metal at ~96 GPa. It is essential to uncover the metallic structure in order to understand the metallicity of H_2S and its potential superconductivity. To note, the metallization has been interpreted as the metallization of elemental sulfur rather than the

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compound, since H_2S was predicted to decompose into sulfur and hydrogen under the metallic pressure.²⁰ We show in this work by first-principles structure predictions that H_2S is thermodynamically stable against this decomposition at least up to 200 GPa. Intriguingly, the metallization of H_2S is predicted to occur at ~130 GPa with the band gap closure.

II. COMPUTATIONAL METHODS

Structure predictions for H₂S were performed through the swarm intelligence CALYPSO structure prediction method^{22,23} as implemented in the CALYPSO code.²³ This approach has been benchmarked on a variety of known systems²³ and has made several successful predictions of high pressure structures of, for example, Li,²⁴ Bi₂Te₃,²⁵ and W-B system.²⁶ The underlying *ab initio* structure relaxations were performed using density functional theory within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation as implemented in the Vienna ab initio simulation package (VASP).²⁷ The all-electron projector augmented wave $(PAW)^{28}$ method was adopted with the PAW potentials taken from the VASP library. The HSE06^{29,30} hybrid functional reproduces well the band gap³¹ of semiconductors, thus the HSE06 hybrid functional was applied to revise the band gaps of those semiconducting phases of H2S calculated by the PBE functional. For the structure searches, an energy cutoff of 700 eV and Monkhorst-Pack Brillouin zone sampling grid with the resolution of $2\pi \times 0.05$ Å⁻¹ was used. The obtained structures were re-optimized more accurately with grids denser than $2\pi \times 0.03$ Å⁻¹ and energy cutoff of 1000 eV, resulting in total energy convergence better than 1 meV/atom. Phonon dispersion and electron-phonon coupling (EPC) calculations were performed with density functional perturbation theory using the Quantum-ESPRESSO package³² with a kinetic energy cutoff of 90 Ry. $4 \times 4 \times 3$ and $6 \times 6 \times 2$ *q*-meshes in the first Brillouin zones were used in the EPC calculations for the P-1 and Cmca structures, respectively. A same force convergence threshold (1 meV/Å) for structural optimizations was applied to avoid any unnecessary error caused by the use of two different codes.

III. RESULTS AND DISCUSSION

We performed variable-cell structure predictions with simulation cells containing 1, 2, 4, 6, and 8 H₂S formula units (f.u.) at pressures of 10–200 GPa. Previous study⁹ has pointed out that the high temperature phases I and II are orientationally disordered while the low temperature phase III is ordered. Since our structure searches were performed at zero temperature and high pressures, therefore, the orientationally disordered nature of H₂S is not reflected in our structure searches. Interestingly, within the whole pressure range studied, we did not find any previously proposed structures, but instead five completely new low-enthalpy structures with space groups of P2/c, Pc, Pmc2₁, P-1, and Cmca (Fig. 1 and Ref. 33 for detailed structure information) were uncovered. Phonon dispersion calculations of these structures do not give any imaginary frequencies and therefore have verified their dynamical stabilities.³³ The enthalpies of these new structures together with the ambient phase III¹⁴ and the previously proposed structures with respect to the Ibca structure were plotted as a function of pressure in Fig. 2(a). According



FIG. 1. The energetically favorable structures predicted by CALYPSO structure searching for H_2S : (a) molecular P2/c structure, (b) molecular Pc structure, (c) polymeric Pmc2₁ structure, (d) polymeric P-1 structure, and (e) atomic Cmca structure. Arrows in (b) illustrate the displacements of H atoms under pressure. The inset figures in (d) and (e) represent the bonding situation of each S atom. (f) and (g) show the valence electron localization function (ELF)³⁹ in the (110) plane of the P-1 (90 GPa) structure and (100) plane of the Cmca (160 GPa) structure, respectively.



FIG. 2. (a) Enthalpy curves of various structures with respect to the previously predicted Ibca structure.¹⁹ The results of some previously proposed structures are not shown since their enthalpies are extremely high, out of comparison range in the figure. The enthalpies of $S + H_2$ with respect to the Ibca structure were also plotted to examine the thermodynamical stability of H₂S at high pressure, where the structures of phases I_s^{40} III,⁴¹ IV,⁴² and V⁴² for S and P6₃/m and C2/c structures for H₂⁴³ were adopted, respectively. Inset in (a) is an enlarged view of the phase transition sequence in pressure range 10–70 GPa. (b) and (c) are the electronic band structures and projected density of states (PDOS in unit of eV^{-1} per f.u.) for P-1 structure at 130 GPa and Cmca structure at 160 GPa, respectively.

to our results, the zero-temperature high pressure phase diagram should be revised, since our predicted structures are energetically more stable than all earlier structures at the entire pressure ranges studied. We found that the ambient-pressure phase III transforms to the P2/c structure at 8.7 GPa and then to the Pc structure at 29 GPa. Both P2/c and Pc structures consist of four H₂S molecules per unit cell, forming van der Waals molecular solids (Figs. 1(a) and 1(b), Ref. 33). The averaged intra-molecular S–H bond lengths are 1.353 Å at 14 GPa and 1.385 Å at 30 GPa for the P2/c and Pc structures, respectively, slightly longer than that (1.336 Å) in a gas H₂S molecule.

With increasing pressure, the polymerization of H_2S takes place with the evolution of the Pc structure. As shown in Fig. 1(b), half of hydrogen atoms move toward to the midpoint of two neighboring S atoms. Consequently, one-dimensional chains of edge-sharing SH₃ tetrahedrons (each S forms three covalent bonds with H atoms) are formed and the Pc structure eventually transforms to the $Pmc2_1$ structure at ~65 GPa without the major modification of the S sublattice (Fig. 1(c)). The polymerization behavior of H₂S is rather unique and is in clear contrast to the hydrogen bond symmetrization in H₂O taking place above 60 GPa,^{14,34} where each oxygen atom forms four covalent bonds with H atoms. The polymerization mechanism predicted here differs from the earlier proposal,¹² in which H atoms were squeezed out of the hydrogen-bond axes into interstitial spaces forming various S-S bonds.

We have simulated the X-ray diffraction (XRD) patterns of the predicted P2/c, Pc and Pmc21 structures and compared with the experimental data.^{11,15} Note that the similar S sublattices in Pc and Pmc21 structures give nearly identical XRD patterns. The available experimental XRD data for phases IV and V of H₂S are generally low in quality, consisting of several main broad peaks.^{11,15} As shown in Fig. 3, the P2/c structure is able to reproduce the main peaks of phase IV^{15} below $2\theta = 20^{\circ}$, as well as the weak peaks around 25° and 28°. However, the simulated weak peaks of the P2/c structure around 22° , 23.5° , and 27° are not visible in experiment. It is known that XRD peak with extremely weak intensity may not be properly detected in real experiment. Therefore, we propose that the P2/c structure is a good candidate for phase IV. For phase V, the three peak groups between 14° and 18° in experiment¹¹ can be seen in the simulated pattern of the Pc (Pmc2₁) structure but with a shift of position. However, the rest of the XRD pattern of the Pc $(Pmc2_1)$ structure fits poorly with experiment.¹¹ Especially, the weak peak observed around 12° is not visible in the simulated pattern. It is possible that phase V possesses larger unit cell and lower symmetry than that of $Pm (Pmc2_1)$. Therefore, the final determination of the structure for phase V need further study.

Upon further compression, the $Pmc2_1$ structure transforms to the P-1 structure at 80 GPa (Fig. 2(a)). The P-1 structure is intriguing with various S–S bonds, forming dumbbell-like H_3S-SH_3 units. It is worth noting that



FIG. 3. The simulated XRD patterns of the predicted P2/c, Pc, and Pmc2₁ structures along with the experimental data for (a) phase IV^{15} at 14 GPa and (b) phase V^{11} at 42.6 GPa. Vertical bars indicate the calculated positions of the diffraction peaks.

the H_3S-SH_3 units connect each other through planar symmetric hydrogen bonds via H2 and H3 atoms (Fig. 1(d)), forming edge-shared planar S_6H_4 quasi-rectangles (Fig. 1(f)). Two inner H1 atoms per S_6H_4 quasi-rectangle do not form bond within the layer (Fig. 1(f)) but bond with S atoms in the adjacent layers. Therefore, the P-1 structure is a typical threedimensional structure.

The P-1 structure is thermodynamically stable up to 160 GPa, above which the Cmca structure (Fig. 1(e)) takes over. The Cmca structure is similar to the P-1 structure in a manner that Cmca structure is also composed of S_6H_4 quasirectangles and its interlayers are bridged through S-H1 bonds. However, different from the one directional arrangement in the P-1 structure, the S_6H_4 quasi-rectangles in the Cmca structure distribute in two orientations, as shown in Figs. 1(f) and 1(g). Interestingly, each S atom in the Cmca structure bonds with two H1 atoms in adjacent two layers, resulting in fivefold coordination of S atom. More intriguingly, all H atoms in the Cmca structure bond with two S atoms. Therefore, the Cmca phase of H_2S can be regarded as an "atomic crystal."

The enthalpies of the decomposition $(S + H_2)$ relative to that of the Ibca structure as a function of pressure have also plotted in Fig. 2(a) to examine the phase stability of H₂S under pressure. By assuming the earlier Cmc2₁ structure, our calculations show that $S + H_2$ becomes energetically stable than the Cmc2₁ structure at 80 GPa, in excellent agreement with the previously proposed decomposition of H₂S beyond 80 GPa.²⁰ However, with the findings of our new structures, the Cmc2₁ structure is never thermodynamically stable and the proposed decomposition scenario²⁰ should be ruled out. It is well-known that the zero-point energy (ZPE) may play an important role in determining the phase stability of hydrogencontaining compounds. Our calculations show that the inclusion of ZPE does not change the phase sequence as depicted in Fig. 2(a). For example, the ZPE effects do not modify the decomposition enthalpy since the ZPE difference between H₂S and $(S + H_2)$ is estimated to be 6 meV/f.u. at 160 GPa, hardly comparable to their enthalpy difference (249 meV/f.u.) at the same pressure. Further, a rather small change (18 meV/f.u. at 160 GPa) of the decomposition enthalpy was estimated when including the vibrational motion up to 1000 K, indicating that H₂S is thermodynamically stable against decomposition at least up to 1000 K.

The electronic band structures³³ of H₂S have been calculated at selected pressures with PBE functional and the band gaps of those insulating/semiconducting phases were then revised by performing HSE06 functional^{29,30} calculations. Results show that H₂S is an insulator with a large indirect band gap of ~5.5 eV at 0.3 GPa, slightly larger than that (4.8 eV) observed in experiment.³⁴ With increasing pressure, the band gap decreases gradually to \sim 3.75 eV at 15 GPa in the P2/c structure and is further reduced to \sim 1.6 eV at 40 GPa in the Pc structure and only 0.27 eV at 120 GPa in the P-1 structure.³³ Band structure and projected density of states (DOS) at 130 GPa (Fig. 2(b)) reveal that the P-1 structure has transformed to a metal with relatively large DOS at Fermi level ($N_{\rm F}$, 0.33 eV⁻¹ per f.u.). The metallization pressure predicted here is slightly higher than that (96 GPa) observed in experiment.¹² The $N_{\rm F}$ value has a dramatic increase at the transition to the Cmca phase $(0.51 \text{ eV}^{-1} \text{ per f.u. at } 160 \text{ GPa})$ and then decreases slightly with pressure (the inset in Fig. 5(a)). The strong S-H hybridization can be derived from the significant overlap of Sand H-DOS both in the P-1 and Cmca structures. Band structures for both the P-1 and Cmca structures feature "flat bandsteep band" character,³⁵ which may suggest their superconductive potentials.



FIG. 4. (a) and (b) represent phonon dispersions, partial phonon density of states (PHDOS) for P-1 at 130 GPa and Cmca at 160 GPa, respectively. Red dashed lines in left panel of (a) show the softening phonon modes in the P-1 phase when pressure is increased up to 150 GPa.

Figure 4 presents the phonon band dispersions and partial phonon density of states of the P-1 and Cmca structures at selected pressures. As expected, the low frequencies (<15 THz) are dominated by the vibrations of S atoms, whereas the high end of the spectrum is due to the H atoms. Under pressure, we find interesting features in our computed phonon dispersion curves. For the P-1 structure, most phonons harden with pressure; however, the phonon modes around Γ and Z points at ~20 THz and along the F-Q direction at ~50 THz soften with pressure (Fig. 4(a)). Subsequent analysis shows that these phonon softenings play a crucial role in enhancing the electron-phonon coupling of P-1 phase under pressure. For the Cmca structure, all phonon modes harden up with pressure.

The Eliashberg spectral function $\alpha^2 F(\omega)$,³⁶ logarithmic average frequency ω_{log} and electron-phonon coupling parameter λ for the P-1 and *Cmca* structures were explicitly calculated to explore the potential superconductivity of H₂S (Fig. 5). The superconducting T_c was estimated by using the Allen and Dynes modified McMillan equation³⁷ with a typical choice of $\mu^* = 0.13$.^{20,38} It is found that once H₂S is metalized, it has a high potential to be superconductive. The calculated T_c increases nearly linearly with pressure in the P-1 structure from 33 K at 130 GPa to 60 K at 158 GPa (main panel of Fig. 5(a)). Intriguingly, T_c increases abruptly up to 82 K at the transition to the Cmca structure and then decreases monotonically to 68 K at 180 GPa. From Fig. 5(b), we found that the low frequency S vibrations in the P-1 structure contribute to 47% of the total λ , while the remaining 53% is from the H vibrations. As the pressure increases to 150 GPa, three distinct peaks of spectral functions at 15, 20, and 46 THz appear in the P-1 structure (Fig. 5(b)), arising from pressure-induced phonon softening. These phonon softenings lead to a pronounced increase of λ from 0.77 at 130 GPa to 0.97 at 150 GPa. The substantial increase of T_c in the Cmca phase mainly arises from the sharply elevated N_F , while the phonon hardening gives rise to the decreased λ and thus a lowering of T_c .

In a survey of the literature, we find that superconductivity is generally predicted in hydrogen-containing compounds with stoichiometry AH or AH_x ($x \ge 3$). H₂S is peculiar since it is the first AH_2 -type example having the potential to be superconductive. The estimated maximal T_c of 82 K in H₂S is rather high, even higher than those predicted for most archetypal hydrogen-containing compounds, such as SiH₄, GeH₄, YH₃, and ScH₃, etc.

Our current work has shown that the precise determination of structure is crucially important to understand the physical properties of materials. Indeed, as we have shown here, earlier decomposition picture of H_2S was fundamentally revised with the newly predicted structures. Although the final determination of the crystal structures of compounds must be based on X-ray or neutron diffraction experiments, we believe that CALYPSO can provide important guidance to experiments. For example, using CALYPSO, we predicted two



FIG. 5. (a) Pressure dependence of T_c within P-1 and Cmca phases. Insets in (a) show the evolutions of the N_F (left panel) and the logarithmic average phonon frequency (ω_{log}) and λ (right panel) with pressure. (b) and (c) show the spectral functions $\alpha^2 F(\omega)/\omega$ and electron-phonon coupling integration of $\lambda(\omega)$ at selected pressures for P-1 and Cmca structures, respectively. Shaded regions in (b) show the significant contribution of three strong peaks of $\alpha^2 F(\omega)/\omega$ to λ .

energetically stable superconducting structures of H_2S , which can simulate future experiments. Especially, the molecular dissociation of H_2S observed in experiment¹² has been well described with the structures predicted by CALYPSO. The S–H bond breaking, proton motion, and eventual formation of S–S bonds have been clearly demonstrated with the structure evolution of H_2S . The results presented here highly indicate that CALYPSO is a very promising and powerful tool to predict the solid structures of molecules, such as H_2O , NH_3 , etc.

IV. CONCLUSION

In summary, we have performed extensively firstprinciples structure searching calculations on H_2S in a large pressure regime of 10–200 GPa. Five high-pressure phases were predicted and are found to be energetically more stable than all earlier structures at certain pressure ranges, leading to a fundamental modification of the entire zero-temperature high-pressure phase diagram of H_2S . Our results have led us to predict that H_2S is thermodynamically stable with respect to elemental decomposition into sulfur and hydrogen at least up to 200 GPa. This result stands in sharp contrast with earlier proposal on compositional instability of H_2S and revises our understanding on the observed metallicity of H_2S . Moreover, our electron-phonon coupling calculations have proposed high superconductive potential of the metallic H_2S . Our work will stimulate the future high-pressure experiments on the structural and conductivity measurements.

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