Dissociation products and structures of solid $\text{H}_2\text{S}$ at strong compression

Yinwei Li, Lin Wang, Hanyu Liu, Yunwei Zhang, Jian Hao, Chris J. Pickard, Joseph R. Nelson, Richard J. Needs, Wentao Li, Yanwei Huang, Ion Errea, Matteo Calandra, Francesco Mauri, and Yanming Ma

Phys. Rev. B 93, 020103 — Published 11 January 2016
DOI: 10.1103/PhysRevB.93.020103
Dissociation products and structures of solid H$_2$S at strong compression


1 School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, China
2 Center for High Pressure Science and Technology Advanced Research, Shanghai, 201203, China
3 State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China
4 Geophysical Laboratory, Carnegie Institution of Washington, Washington D.C. 20015, USA
5 Department of Materials Science & Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom
6 Theory of Condensed Matter Group, Cavendish Laboratory, J J Thomson Avenue, Cambridge CB3 0HE, United Kingdom
7 Donostia International Physics Center (DIPC), Manuel de Lardizabal pasealekua 4, 20018 Donostia-San Sebastián, Basque Country, Spain
8 Fisika Aplikatua 1 Saila, EUITI Bilbao, University of the Basque Country (UPV/EHU), Rafael Moreno “Pitzitzoi” Pasealekua 3, 48013 Bilbao, Basque Country, Spain
9 IMPMC, UMR CNRS 7590, Sorbonne Universités - UPMC Univ. Paris 06, MNHN, IRD, 4 Place Jussieu, F-75005 Paris, France

Hydrogen sulfides have recently received a great deal of interest due to the record high superconducting temperatures of up to 203 K observed on strong compression of dihydrogen sulfide (H$_2$S). A joint theoretical and experimental study is presented in which decomposition products and structures of compressed H$_2$S are characterized, and their superconducting properties are calculated. In addition to the experimentally known H$_2$S and H$_3$S phases, our first-principles structure searches have identified several energetically competitive stoichiometries that have not been reported previously: H$_2$S$_3$, H$_2$S$_2$, HS$_2$, and H$_4$S$_3$. In particular, H$_2$S$_3$ is predicted to be thermodynamically stable within a large pressure range of 25–113 GPa. High-pressure X-ray diffraction measurements confirm the presence of H$_2$S and H$_3$S$_3$ through decomposition of H$_2$S that emerges at 27 GPa and coexists with residual H$_2$S$_2$, at least up to the highest pressure studied in our experiments of 140 GPa. Electron-phonon coupling calculations show that H$_2$S$_3$ has a small $T_c$ of below 2 K, and that H$_2$S$_2$ is mainly responsible for the observed superconductivity of samples prepared at low temperature (<100K).

PACS numbers: 62.50.-p, 61.50.Ah, 61.05.cp, 74.70.Ad

Superconductivity with a transition temperature $T_c$ of up to 203 K was observed recently in solid H$_2$S at Megabar pressures, which is the highest record among all known superconductors [1]. Ashcroft suggested that metallic hydrogen would be a superconductor at high pressures with a $T_c$ around room temperature [2], and subsequently predicted that hydrogen-rich metallic compounds might also be superconducting at high pressures [3]. Early theoretical studies focussed on high-pressure silicon and aluminum hydrides [4, 5], and a number of potential high-temperature superconductors have now been proposed in compressed hydrogen-rich compounds, with $T_c$s estimated in the range 40–250 K (e.g., GaH$_3$ [6, 7], SnH$_4$ [8], GeH$_4$ [9], NbH$_4$ [10], Si$_2$H$_6$ [11], SiH$_4$(H$_2$)$_2$ [12], CaH$_6$ [13], YH$_3$ [14], YH$_4$ and YH$_6$ [15]). Unfortunately, they have not been realized in practice, in part because of demanding experimental challenges. Very recent experimental studies have observed superconductivity in compressed phosphine (PH$_3$) with a $T_c$ above 100 K [16].

The high pressure phase diagram of H$_2$S has been studied extensively. H$_2$S is a sister molecule of H$_2$O, and is the only known stable compound in the H-S system at ambient pressure. High-pressure diamond anvil cell experiments led to the discovery of a metallic phase at about 96 GPa [17–28]. However, partial decomposition of H$_2$S and elemental sulfur was observed in Raman [27] and XRD studies [22] at room temperature above 27 GPa. H$_2$S had not been considered as a candidate for superconductivity because it was believed to dissociate into elemental sulfur and hydrogen under high pressures [29]. Recent first-principles structure searches predicted energetically stable metallic structures of H$_2$S above 110 GPa [30] and excluded dissociation into its elements. An estimated maximum $T_c$ for metallic H$_2$S of 80 K at 160 GPa was predicted [30]. Motivated by this study, Drozdov et al. [1] performed high-pressure experiments on solid H$_2$S looking for superconductivity and found an astonishing $T_c$ of 203 K at 155 GPa [1]. Interestingly, H$_2$S shows complex superconducting behavior at high pressures with the emergence of two different superconducting states. Samples prepared at low temperature (100 K) have a $T_c$ of ~30 K at 110 GPa at the onset of superconductivity, which increases rapidly to a maximum value of 150 K at 200 GPa, while samples at room temperature or above show a maximum $T_c$ of 203 K at 155 GPa.

Strobel et al. synthesized another H-S compound, H$_3$S, by compressing a mixture of H$_2$S and H$_2$ above 3.5 GPa [31]. The superconducting $T_c$ of H$_3$S at 200 GPa was...
recently predicted to be as high as 191–204 K [32], with H$_3$S in a cubic Im$\overline{3}$m structure. The same Im$\overline{3}$m structure was already predicted to occur for H$_2$O via the decomposition of water (H$_2$O) at terapascal pressures [33]. The agreement between experimental [1] and theoretical values of $T_c$ [32] led to the proposal by Drozdov et al. that H$_3$S could be formed by decomposition of H$_2$S and might be responsible for the observed superconductivity at 203 K [1]. This proposal was supported by first-principles density-functional-theory (DFT) studies which suggested that it is thermodynamically favorable for H$_2$S to decompose into H$_3$S + S [34–36] at pressures above 43 GPa [35]. However, there is a lack of experimental evidence to support the formation of H$_3$S, and the low $T_c$ superconducting phase has not been fully explored. There is an urgent need to characterize the decomposition products of compressed H$_2$S in an effort to build an understanding of the complex superconducting behavior exhibited by the H-S system.

Here we present a joint theoretical and experimental study of compressed H$_2$S which clarifies the possible decomposition products and their structures. First-principles DFT structure searches were used to predict several new stoichiometries (H$_2$S$_3$, H$_3$S$_2$, HS$_2$, and H$_4$S$_3$) and a new structure in H$_3$S not reported previously. High pressure X-ray diffraction (XRD) experiments demonstrate that above 27 GPa, H$_2$S partially decomposes into S + H$_3$S + H$_2$S$_2$. H$_3$S$_2$ emerges as the major component at around 66 GPa and coexists with a small fraction of H$_3$S and residual H$_2$S, at least up to the highest pressure studied experimentally of 140 GPa.

Extensive structure searches over 44 H-S stoichiometries at 25, 50, 100 and 150 GPa were performed using the CALYPSO [37, 38] and AIRSS [4, 39] methods, which have been successfully used to investigate structures of materials at high pressures [4, 13, 40–46]. The underlying structural relaxations were performed using the Vienna ab initio simulation package (VASP) [47] for CALYPSO and the CASTEP plane-wave code [48] for AIRSS. Electron-phonon coupling (EPC) calculations were performed with density functional perturbation theory using the Quantum-ESPRESSO package [49]. XRD data were collected at the 15U1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF) with a monochromatic beam of wavelength 0.6199 Å. The diffraction patterns were integrated with the FIT2D computer code [50] and fitted by Rietveld profile matching using the GSAS+EXPGUI programs [51, 52]. More information about the calculations and experiments is provided in the Supplemental Material [53].

Figure 1 shows convex hull diagrams at 25, 50, 100 and 150 GPa which summarize the results of the structure searches. The effects of including quantum zero-point vibrational motion are significant and they tend to increase with pressure. Our results suggest that up to six H-S compounds lie on the convex hull at some pressures and are therefore thermodynamically stable. Besides the experimentally known H$_2$S and H$_3$S compounds, we predict four additional stable compounds: H$_4$S$_3$, H$_3$S$_2$, H$_2$S$_3$, and HS$_2$. Note that H$_2$S is predicted to be stable only below 25 GPa, while H$_3$S is predicted to appear at all pressures considered. Enthalpy calculations show that H$_3$S becomes energetically more stable than H$_2$S+1/2H$_2$ at around 6 GPa (Supplemental Material, Fig. S1 [53]). The newly predicted H$_3$S$_2$, H$_2$S$_2$, and HS$_2$ phases have very narrow pressure ranges of stability and are unstable above 34 and 25 GPa, respectively (Supplemental Material, Fig. S3 [53]). We have therefore omitted further discussion of these two compounds. HS$_2$ is predicted to be energetically stable between 64 and 116 GPa on the basis of static-lattice enthalpy calculations. The stable pressure range was revised to be between 75 and 87 GPa when the zero-point vibrational enthalpy was included (Supplemental Material, Fig. S9 [53]). The corresponding crystallographic parameters and phonon dispersion curves are provided in the Supplemental Material [53].

For H$_4$S$_3$, besides the P1, Cccm, R3m and Im$\overline{3}$m structures of earlier studies [32], our searches predict a monoclinic C2/c structure (4 f.u./cell) that was not reported earlier. The C2/c structure consists of weakly bonded H$_2$S and H$_2$ molecules (Supplemental Material, Fig. S1b [53]), and is calculated to be more stable at pressures of 2–112 GPa than the Cccm structure proposed previously [32] (Supplemental Material, Fig. S1a [53]). Static-lattice enthalpy calculations give a zero-temperature phase sequence for H$_2$S of P1 → C2/c (2 GPa) → R3m (112 GPa) → Im$\overline{3}$m (180 GPa).

H$_4$S$_3$ adopts an orthorhombic P2$_1$2$_1$2$_1$ (4 f.u./cell) structure that consists of weakly bonded HS and H$_2$S molecules at 25 GPa (Fig. 2a). The H-S bond lengths

![FIG. 1: (Color online) Results from structure searching at 25 (a), 50 (b), 100 (c) and 150 GPa (d). Convex hulls are shown as continuous lines, with (red) and without (black) the inclusion of zero point vibrational enthalpy (ZPE).][1]
within the HS and H$_2$S molecules are 1.354 Å and 1.387-1.391 Å, respectively, which are significantly shorter than the H-S separation of 1.913-1.932 Å between molecules. With increasing pressure, the neighboring molecules bond with each other forming planar H-S-H-S zigzag chains and puckered H-S-H-S chains, respectively. P$_{2}1_{2}1_{2}$ transforms to a Pnma structure at 60 GPa (Fig. 2c). The convex hull data suggests two synthesis routes for H$_4$S$_3$: (i) decomposition of 8H$_2$S$ \rightarrow $ S + 4H$_2$S + H$_2$S$_3$ above 25 GPa; (ii) reaction of 4H$_2$S + 5S $ \rightarrow $ 3H$_2$S$_3$ in the pressure range of 25–113 GPa. Theoretically, it is found that H$_4$S$_3$ decomposes into H$_3$S + S above 113 GPa (Fig. 1d and Fig. 2d).

The H$_2$S samples were initially compressed to 10 GPa at low temperature (77 K) and then warmed to room temperature. Powder XRD patterns were then collected on increasing pressure from 10 to 140 GPa at room temperature, as shown in Fig. 3a. The XRD patterns collected at pressures up to 46 GPa are in excellent agreement with previous data [18–22], and the successive transitions of phase $I' \rightarrow$ phase IV $\rightarrow$ phase V are well reproduced. The XRD data at 10 GPa correspond to phase $I'$. Phase IV with additional peaks at around 12° and 15° (shown by arrows in Fig. 3a) was observed at 16 GPa. The diffraction peaks of phase IV weaken at pressures above 27 GPa, and a new diffraction profile observed at 46 GPa is responsible for phase V. The XRD data show that the IV$\rightarrow$V transition begins above 27 GPa, in excellent agreement with previous results [19, 22].

Previous high-pressure Raman [27] and XRD [22] studies have claimed that decomposition of H$_2$S occurs at room temperature above 27 GPa. Indeed, we found that H$_2$S partially decomposes in phase V. Unfortunately, we have not found it possible to resolve the decomposition products and their crystal structures from our current XRD data. Therefore we use the predicted structures and convex hull data to help in analysing the experimental data. At 50 GPa, our calculations suggest an energetically allowed dissociation path of 8H$_2$S$ \rightarrow $ S + 4H$_2$S + H$_2$S$_3$ (Fig. 1b). The XRD profile at 46 GPa was therefore fitted to a mixture of H$_2$S + S + H$_2$S + H$_2$S$_3$ by performing Rietveld refinements using the most energetically stable structures. Remarkably, we found that the XRD profile can be well indexed by a mixture of P-structured H$_2$S, I$_4$/acd-structured S, C$_2$/c-structured H$_2$S and P$_2$1$_2$1$_2$-structured H$_4$S$_3$, with phase fractions (ratios of numbers of unit cells) of 1147:85:31:1, as shown in Fig. 3b. The existence of a large proportion of H$_2$S demonstrates the partial decomposition. We also attempted other Rietveld refinements fitting the XRD patterns to pure H$_2$S, H$_2$S + S + H$_2$S or S + 4H$_2$S + H$_2$S$_3$, but all of these fits gave poorer results (Supplemental Material, Fig. S11 [53]). The calculated decomposition pressure (30 GPa) for 8H$_2$S$ \rightarrow $ S + 4H$_2$S + H$_2$S$_3$ (Supplemental Material, Fig. S17 [53]) is in excellent agreement with the value of 27 GPa observed in experiment [22].
With increasing pressure, more H$_2$S decomposes and its contribution to the XRD signal is reduced. The XRD pattern collected at 66 GPa shows entirely different features to that at 46 GPa. Rietveld refinement shows that a mixture of Pnma-structured H$_4$S$_3$, C2/c-structured H$_3$S, and Pmc2$_1$-structured H$_2$S with phase fractions 53:10:37 gives the best fit to the experimental data (Fig. 3c). The disappearance of elemental S and the reduction in the ratio of H$_2$S are understandable since a reaction of 4H$_2$S + 5S $\rightarrow$ 3H$_4$S$_3$ takes place as inferred from our convex hull calculations (Fig. 1b and 1c). The two shoulders on the main peak at 15° originate primarily from H$_3$S and H$_2$S. These shoulders weaken when the pressure is increased to 82 GPa and the XRD pattern can then be well indexed by Pnma-structured H$_4$S$_3$, C2/c-structured H$_3$S and Pmc2$_1$-structured H$_2$S with a major contribution (86%) from H$_4$S$_3$ (Fig. 4a). We also tried to refine the XRD profile at 82 GPa with the inclusion of HS$_3$, which is calculated to be stable in between 75 and 87 GPa. However, the inclusion of HS$_3$ results in a poorer fit with higher $R_p$ and $R_{wp}$ values (Supplemental Material, Fig. S13(a) [53]), which excludes HS$_3$ as a decomposition product. Our results demonstrate that H$_4$S$_3$ coexists with H$_3$S and H$_2$S at least up to 140 GPa, the highest pressure studied experimentally (Fig. 4b). At this pressure, a refinement based on Pnma-structured H$_4$S$_3$ and C2/c-structured H$_3$S leads to poorer fits with higher $R_p$ and $R_{wp}$ values (Supplemental Material, Fig. S14 [53]), which supports the existence of residual H$_2$S (about 1.6%).

H$_4$S$_3$ is predicted to become metallic at 102 GPa (Supplemental Material, Fig. S18 [53]). However, the calculated electron-phonon-coupling parameter ($\lambda = 0.42$) is very small at 140 GPa due to the low density of states at the Fermi level of 0.09 eV$^{-1}$/atom. As a result, the $T_c$ estimated from the Allen and Dynes modified McMillan equation [54] with $\mu^*$ of 0.16–0.13 is only 0.75–2.1 K at 140 GPa.

In Fig. 5, we compare the calculated $T_c$ values for H$_4$S$_3$, H$_2$S and H$_3$S to experimental data measured in compressed H$_2$S [1], where $T_c$ obtained for samples prepared at low and high temperatures are denoted by L-$T_c$ and H-$T_c$, respectively. On the one hand, the observed L-$T_c$ [1] at pressures below 160 GPa can only be quantitatively reproduced by H$_2$S, while the nature of the rapidly increasing L-$T_c$ above 160 GPa remains unclear because the calculated $T_c$ values of H$_2$S, H$_3$S, and H$_2$S are too high, too low, and tending to decrease, respectively. On the other hand, although the values of $T_c$ for Im3m structured H$_3$S calculated within the harmonic approximation are much higher than the observed H-$T_c$ [55], the inclusion of anharmonic effects reproduces the H-$T_c$ data above 180 GPa quite well [36]. However, at low pressures around 150 GPa, $T_c$ values [55] estimated for R3m-H$_3$S within the harmonic approximation are $\sim$45 K lower than the observed H-$T_c$. Meanwhile, the predicted $T_c$ for R3m-H$_3$S increases with pressure, in stark contrast to the experimental observation of a decrease in H-$T_c$. Further study is required to understand the steep $T_c$ increase of L-$T_c$ above 160 GPa and the high H-$T_c$ at around 150 GPa.

We find that kinetics plays an important role in determining the experimentally observed H-S structures. Theory suggests that H$_2$S and H$_4$S$_3$ decompose above 30...
and 113 GPa (Supplemental Material Fig. S17 and Fig. 2d), respectively. However, H$_2$S and H$_4$S$_3$ are observed to persist up to at least 140 GPa. Large kinetic barriers must therefore play a major role in suppressing decomposition at high pressures, as has been found in other materials [56–59].

In summary, first-principles structure searching calculations have been used to predict four new stable H-S compounds with stoichiometries H$_2$S$_2$, H$_2$S$_3$, HS$_2$ and H$_4$S$_3$ and a new C2/c structure of H$_2$S, enriching the phase diagram of H-S systems at high pressures. The formation of H$_2$S$_2$ and H$_2$S was confirmed by XRD experiments to occur through decomposition of compressed H$_2$S above 27 GPa resulting in the products S + H$_3$S + H$_4$S$_3$. H$_4$S$_3$ becomes a major component at around 66 GPa and is stable up to at least 140 GPa, with a small fraction of H$_2$S and residual H$_2$S. We have also examined potential superconductivity of metallic H$_4$S$_3$ via explicit calculations of electron-phonon coupling parameters and the superconducting T$_c$. Our work suggests that kinetically protected H$_2$S in samples prepared at low temperature is responsible for the observed superconductivity below 160 GPa.

After the submission of this work we became aware of an unpublished experimental study [60] by Einaga et al. supporting the formation of H$_2$S upon dissociation of H$_2$S, in agreement with our experimental results. However, their results suggested that H$_2$S is the major component with some unidentified phases. We attribute this discrepancy to the different experimental protocols used in the two experiments: in our experiments samples were compressed at ambient temperature above 10 GPa, whereas in Ref. 60 a temperature of 220 K was used. The unidentified minor phase in the data of Einaga et al. might be attributed to the H$_2$S$_3$ compound predicted here. It is possible that the use of different experimental protocols could give rise to similar dissociation products with different phase fractions, depending on the exact path followed.

Y. L. and J. H. acknowledge funding from the National Natural Science Foundation of China under Grant No. 11204111 and No. 11404148, the Natural Science Foundation of Jiangsu province under Grant No. BK20130223, and the PAPD of Jiangsu Higher Education Institutions. Y. Z. and Y. M. acknowledge funding from the National Natural Science Foundation of China under Grant Nos. 11274136 and 11534003, the 2012 Changjiang Scholars Program of China. R. J. N. acknowledges financial support from the Engineering and Physical Sciences Research Council (EPSRC) of the U.K. [EP/J017639/1]. Calculations were performed on the Cambridge High Performance Computing Service facility and the HECToR and Archer facilities of the U.K.’s national high-performance computing service (for which access was obtained via the UKCP consortium [EP/K013564/1]). J. R. N. acknowledges financial support from the Cambridge Commonwealth Trust. I. E. acknowledges financial support from the Spanish Ministry of Economy and Competitiveness (FIS2013-48286-C2-2-P). M. C. acknowledges support from the Graphene Flagship and Agence nationale de la recherche (ANR), Grant No. ANR-13-IS10-0003-01. Work at Carnegie was partially supported by EFree, an Energy Frontier Research Center funded by the DOE, Office of Science, Basic Energy Sciences under Award No. DE-SC-0001057 (salary support for H. L.). The infrastructure and facilities used at Carnegie were supported by NNSA Grant No. DE-NA-0002006, CDAC.

* Electronic address: mym@jlu.edu.cn