Abstract: \( \text{H}_2\text{S} \) is converted under ultrahigh pressure (> 110 GPa) to a metallic phase with \( T_c \) of ~200 K. It has been proposed that the superconducting phase is body-centered cubic \( \text{H}_2\text{S} \) \( (\text{Im} \bar{3}m, \ a = 3.089 \ \text{Å}) \) resulting from a decomposition reaction \( 3\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{S} + \text{S} \). The analogy of \( \text{H}_2\text{S} \) and \( \text{H}_2\text{O} \) leads us to a very different conclusion. The well-known dissociation of water into \( \text{H}_2\text{O}^+ \) and \( \text{OH}^- \) increases by orders of magnitude under pressure. An equivalent behavior of \( \text{H}_2\text{S} \) is anticipated under pressure with the dissociation, \( 2\text{H}_2\text{S} \rightarrow \text{H}_3\text{S}^+ + \text{SH}^- \) forming a perovskite structure \((\text{SH})(\text{H}_3\text{S}^+)\), which consists of corner-sharing \( \text{SH}_6 \) octahedra with \( \text{SH}^- \) at each \( \text{A}\)-site (i.e., the center of each \( \text{S}_8 \) cube). Our DFT calculations show that the perovskite structure \((\text{SH})(\text{H}_3\text{S}^+)\) is thermodynamically more stable than the \( \text{Im} \bar{3}m \) structure of \( \text{H}_2\text{S} \); and suggest that the \( \text{A}\)-site \( \text{H} \) atoms are most likely fluxional even at \( T_c \).

For the phase of \( \text{H}_2\text{S} \) under a pressure larger than 110 GPa high temperature superconductivity has been reported\(^1\) with \( T_c \) of ~200 K. The decomposition of \( \text{H}_2\text{S} \) into \( \text{SH} + \text{S} \) under such conditions has been deduced from synchrotron x-ray diffraction (XRD) experiments.\(^2,3,4\) The obtained XRD patterns can be indexed based on a mixture of two phases, namely, the bcc \( \text{Im} \bar{3}m \) structure ascribed to \( \text{H}_2\text{S} \) with cell parameter \( a = 3.089 \ \text{Å} \) and the \( \beta\)-Po structure of sulfur.\(^1,5\) Another XRD study under high pressure reported a more complex decomposition mixture that includes \( \text{H}_2\text{S} \) and \( \text{H}_3\text{S} \) phases.\(^6\) DFT calculations confirmed the proposed \( \text{Im} \bar{3}m \) structure of \( \text{H}_2\text{S} \) as the lowest energy one.\(^2,7,8,9,10,11\)

The \( \text{Im} \bar{3}m \) structure of \( \text{H}_2\text{S} \) \( (a = 3.089 \ \text{Å}) \) consists of two interpenetrating \( \text{SH}_3 \) perovskite sublattices (Figure 1a)) with a \( \text{H}--\text{H} \) contact distance of ~1.5 Å, which is very short compared with the van der Waals radii sum of 2.4 Å but very long compared with the \( \text{H}--\text{H} \) single-bond distance 0.74 Å in \( \text{H}_2\text{O} \). The decomposition, \( 3\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{S} + \text{S} \), implies that the XRD intensities of \( \text{H}_3\text{S} \) and sulfur with \( \beta\)-Po structure should have a 2:1 ratio. However, the comparison of the simulated XRD patterns with the observed ones taken from the literature in Figure S1 of the supporting information (SI) shows that the amounts of \( \text{S} \) in the samples vary and are always substantially smaller or hardly detectable than the expected one. Except for some spurious reflections the XRD patterns belong to a bcc lattice of sulfur atoms, but are not adequate enough to refine and assign the hydrogen atom positions with the Rietveld method. The bcc pattern is plotted in red color in Figure S1. The diagram in green color corresponds to sulfur with \( \beta\)-Po structure that should form in the decomposition reaction \( 3\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{S} + \text{S} \), however, sulfur does not show up except for one weak reflection at \( 2\theta = 12^\circ \). Thus the formation of \( \text{H}_2\text{S} \) itself is questionable. The above-mentioned inconsistencies together with the apparent analogies between \( \text{H}_2\text{S} \) and \( \text{H}_2\text{O} \) were our motivation to reinvestigate the structure of the superconducting phase obtained from \( \text{H}_2\text{S} \) under ultrahigh pressure.

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At ambient conditions H2O dissociates into H2O’ and OH- to the extent given by [H2O’](OH-) = 10^-14, which increases by orders of magnitude under high pressure.\textsuperscript{[2, 12]} For H2S an analogous dissociation process for H2S into H+S’ and SH’ under ultrahigh pressure can be expected, consistent with earlier ab initio calculations.\textsuperscript{[13]} A perovskite structure (SH’)(H3S’) with nominal composition H2S and disordered SH units at each A-site (i.e., the center of each S8 cube) appears in reasonable agreement with the observed cubic lattice constant, see Figure 1 b). On the basis of DFT calculations,\textsuperscript{[14,15,16]} we show that the perovskite (SH’)(H3S’) is thermodynamically more favorable than H2S. In view of the expected dynamic motions of hydrogen, one can imagine that the functionalities of the S atoms on the A and B sites of the perovskite ABO3 can easily be interchanged, according to (SH’)(H3S’) ⇔ (H3S’)(SH’). In addition, our calculations reveal that at every A-site of a perovskite (SH’)(H3S’) the S–H bonds orient preferentially toward any one of the six faces of the S8 cube, as shown in Figures 1 c) and d). In case of all A-site S–H bonds pointing in one direction, the optimization of the crystal structure of (SH’)(H3S’) results in an arrangement of four H atoms of the H3S’ sublattice with short H···H contacts. These H atoms are displaced away from the H atom of the S–H bond (Figure 1 c) for the cif files of this P4mm structure, see SI). Alternatively, neighboring S–H units can be arranged orthogonal to each other (Fig 1d). There exists an infinite number of ways of arranging adjacent S–H bonds with 90° angles. Examples of some planar patterns of orthogonal S–H–S bonds are illustrated in Figure S2. They have small but significant energy differences, and the geometry optimization for (SH’)(H3S’) with a staggered pattern of zigzag chains (Figure 2) leads to an Imma (SG = 46) structure in which the H–S bonds of 1.492 and 1.597 Å alternate. This structure is the most stable one among the optimized structures with the planar patterns of Figure S2, see Table S1 (for the cif files of the optimized Cmmm, Cmc21 and Imma structures). It is important to emphasize that these structure optimizations rely on a static picture whereas in reality the hydrogen atoms are highly mobile and tunnel from side to side and carry out a hopping motion through the bcc sulfur lattice. Such a mobile configurational change may even lead to a plastic-like behavior, which would result in similar conclusions as derived here.\textsuperscript{[17]}

**Figure 2.** Schematic representation of a plane of orthogonally arranged S–H···S bridges made up of the A-site S–H bonds forming zigzag chains in (SH’)(H3S’). Blue circles represent the H atoms, orange circles S atoms.

We then estimate the relative stabilities of the H2S (Im3m) and (SH’)(H3S’) structures. Since the compositions of the two phases are not identical, we first examine the enthalpy change ∆H of the hypothetical reaction,

\[
2 \text{H}_2\text{S} (\text{Im3m}, a = 3.089 \text{ Å}) \rightarrow (\text{SH})\text{(H3S')} + \text{H}_2
\]

The calculations show that ∆H = -122.5, -170.9 and -194.3 meV, for the Cmmm, Cmc21, and Imma structures of (SH)(H3S’), respectively, i.e., the (SH)(H3S’) phase is energetically more stable than the H2S structure (Im3m). In terms of the free energy ∆G = ∆H + ∆S, the (SH)(H3S’) phase is even more favored. Because there are three possible orthogonal arrangements of S–H···S bridges at any given A-site, fluxional behavior of the A-site H atoms as mentioned above will lead to a configuration entropy gain ∆S = Rln3 = 2.18 cal/mol/deg. At 200 K this contributes -T∆S = -18.9 meV to the free energy, so that the Cmmm, Cmc21 and Imma structures of (SH)(H3S’) are more likely than the H2S structure (Im3m) by ∆G = -140.4, -189.8 and -213.2 meV, respectively.

The calculated electronic structure of (SH)(H3S’) with zigzag chains of S–H bonds (Figure 2) is presented in Figure 3. The occupied S 3p states of the B-site sulfur atoms (i.e., the atoms of the perovskite framework) lie lower in energy than those of the A-site sulfur atoms, which dominate the states at the Fermi level. The electronic structure description (SH)(H3S’) is consistent with the formal charges. The flat band part along the Γ-X direction observed at the Fermi level resembles closely the corresponding band structure of the superconductor MgB2.\textsuperscript{[18][19]} for which a multigap superconductivity has been proposed. The Fermi surface exhibits cube-like features (see Figure S3 of the SI).

**Figure 3.** The electronic structure calculated for the ultrahigh pressure phase of H2S with the perovskite structure (SH)(H3S’) containing zigzag chains of SH’ units (SG = Imma), s. Figure 2. a) The band dispersion relations with fat-bands representations, where the 3p states of the A-site S atoms are represented in green, those of the B-site S atoms in red, and the s/p states of the H atoms in blue. b) The PDOS plot for the 3p states of the A-site S atoms (green), that of the B-site S atoms (red), and the s/p states of the H atoms (blue).

The remarkably high Tc’s in the 80–200 K range for the proposed H2S under high pressure have been explained on the basis of the strong-coupling theory of superconductivity,\textsuperscript{[7,8]} with the electron-phonon coupling increasing strongly with increasing pressure where more than 90 % of the coupling arises from H vibrations.\textsuperscript{[9,10, 20]} This is supported by the observation of a substantial isotope effect upon deuteration. However, the Tc of the deuterated sample D2S is reduced to ~90 K at the highest pressure corresponding to an isotope exponent a ≈ 1, and this exponent varies with pressure.\textsuperscript{[21]} Recently, Bianconi and Jahlborg,\textsuperscript{[22]} showed that these observations are not explained by the single gap superconductivity theory of Eliashberg\textsuperscript{[23]} and Allen-Dynes,\textsuperscript{[24]} and pointed out the need to consider a multigap superconductivity theory.
In summary, concerning the high-Tc superconducting phase of H2S under high pressure, our work presents a picture different from the currently adopted one. Namely, H2S does not decompose into H3S and S, but dissociates under the formation of a perovskite type structure (SH)(H3S+). Furthermore, our work suggests that the A-site H atoms are most likely fluxional even at Tc.

Experimental Section

We carried out non-spin-polarized DFT calculations employing the projector augmented wave method encoded in the Vienna ab initio simulation package[14-16] and the generalized gradient approximation of Perdew, Burke and Ernzerhof for the exchange-correlation functionals. The plane wave cutoff energy of 1200 eV and the threshold of self-consistent-field energy convergence of 10^-8 eV were used. The Brillouin zone was sampled by a set of 12 x 12 x 12 k-points.

Acknowledgements

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Keywords: H2S superconductor · H2S perovskite · ionization under pressure · electronic structure

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Supporting Information

for

Structure and composition of the 200 K-superconducting phase of H₂S under ultrahigh pressure: the perovskite (SH⁻)(H₃S⁺)

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Figure 1. Experimental XRD patterns for D$_2$S at different pressures (taken from ref. S1) together with the calculated XRD patterns for the Im$ar{3}$m structure of D$_3$S (red curve) and β-Po elemental sulfur (green curve) at 180 GPa (taken from ref. S2, S3).
References

S1. Einaga, M., Sakata, M., Ishikawa, T., Shimizu, K., Eremets, M.I., Drozdov, A.P., Troyan, I.A., Hirao, N., Ohishi, Y. Crystal Structure of 200 K-Superconducting Phase of Sulfur Hydride System arXiv: 1509.03156v1.

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Fig. S2. Three patterns of orthogonally-arranged S–H...S bridges made up of the A-site S–H bonds. (a) Isolated squares. (b) Meander chains. (c) Zigzag chains. The black circles represent the H atoms of the perovskite-framework, and the blue circles those of the A-site S–H bonds.
The relative energies per formula unit (FU), $\Delta E$ (meV/FU), of the $(SH^-)(H_3S^+)$ structures with the three different arrangements of the A-site S–H...S bridges depicted in Fig. S2 as well as the P4mm structure of $(SH^-)(H_3S^+)$ shown in Fig. 1c are listed in Table S1. Also summarized in this table are the S–H bond lengths (Å) of the S–H...S bonds between A-site S atoms and the short H···H contacts (Å) between the A-site H and the B-site H atoms in the perovskite structures $(SH^-)(H_3S^+)$. The stabilities of the four structures increase in the order, P4mm < Cmmm < Cmc2₁ < Ima2. Table S1 shows that the Ima2 structure with zigzag chain patterns of the S–H...S bridges is the most stable one, but the Cmc2₁ structure with meander chains is only slightly less stable than the Ima2 structure (by 23.4 meV/FU). Thermodynamically, these two structures are nearly equally probable around 200 – 300 K, given the associated thermal energies $RT = 17.2 – 25.8$ meV.

![Table S1](image-url)

| Structure | P4mm SG = 99 | Cmmm SG = 65 | Cmc2₁ SG = 36 | Ima2 SG = 46 |
|-----------|--------------|--------------|---------------|--------------|
| Structural features | no orthogonal S–H...S | isolated squares | ribbon chains | zigzag chains |
| $\Delta E$ (meV/FU) | 383.0 | 71.8 | 23.4 | 0.0 |
| S–H–S | 1.338/1.751 | 1.545/1.544 | 1.498/1.591 1.541/1.548 | 1.492/1.597 |
| H···H contacts | 1.592 (×4) | 1.548 (×2) 1.547 (×2) 1.542 1.541 | 1.677 1.645 1.552 1.546 | 1.678 (×2) 1.645 (×2) |
[4] The cif files for the optimized structures of (SH⁻)(SH₃⁺).

(a) P4mm structure

```
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_cell_angle_beta                       90
_cell_angle_gamma                      90
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_symmetry_Int_Tables_number            1

_loop_
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  'x, y, z'

_loop_
_atom_site_label
_atom_site_occupancy
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_adp_type
_atom_site_B_iso_or_equiv
_atom_site_type_symbol
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S2  1.0  0.000000  0.000000  0.500000  Biso  1.000000 S
S3  1.0  0.000000  0.500000  0.000000  Biso  1.000000 S
S4  1.0  0.000000  0.500000  0.500000  Biso  1.000000 S
S5  1.0  0.500000  0.000000  0.000000  Biso  1.000000 S
S6  1.0  0.500000  0.000000  0.500000  Biso  1.000000 S
S7  1.0  0.500000  0.500000  0.000000  Biso  1.000000 S
S8  1.0  0.500000  0.500000  0.500000  Biso  1.000000 S
```
|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| S9 | 1.0 | 0.250000 | 0.250000 | 0.250000 | Biso | 1.000000 | S |
| S10 | 1.0 | 0.250000 | 0.250000 | 0.750000 | Biso | 1.000000 | S |
| S11 | 1.0 | 0.250000 | 0.750000 | 0.250000 | Biso | 1.000000 | S |
| S12 | 1.0 | 0.250000 | 0.750000 | 0.750000 | Biso | 1.000000 | S |
| S13 | 1.0 | 0.750000 | 0.250000 | 0.250000 | Biso | 1.000000 | S |
| S14 | 1.0 | 0.750000 | 0.250000 | 0.750000 | Biso | 1.000000 | S |
| S15 | 1.0 | 0.750000 | 0.750000 | 0.250000 | Biso | 1.000000 | S |
| S16 | 1.0 | 0.750000 | 0.750000 | 0.750000 | Biso | 1.000000 | S |
| H1  | 1.0 | 0.230390 | 0.000000 | 0.000000 | Biso | 1.000000 | H |
| H2  | 1.0 | 0.230390 | 0.000000 | 0.500000 | Biso | 1.000000 | H |
| H3  | 1.0 | 0.230390 | 0.500000 | 0.000000 | Biso | 1.000000 | H |
| H4  | 1.0 | 0.230390 | 0.500000 | 0.500000 | Biso | 1.000000 | H |
| H5  | 1.0 | 0.730390 | 0.000000 | 0.000000 | Biso | 1.000000 | H |
| H6  | 1.0 | 0.730390 | 0.000000 | 0.500000 | Biso | 1.000000 | H |
| H7  | 1.0 | 0.730390 | 0.500000 | 0.000000 | Biso | 1.000000 | H |
| H8  | 1.0 | 0.730390 | 0.500000 | 0.500000 | Biso | 1.000000 | H |
| H9  | 1.0 | 0.029044 | 0.250000 | 0.000000 | Biso | 1.000000 | H |
| H10 | 1.0 | 0.029044 | 0.250000 | 0.500000 | Biso | 1.000000 | H |
| H11 | 1.0 | 0.029044 | 0.750000 | 0.000000 | Biso | 1.000000 | H |
| H12 | 1.0 | 0.029044 | 0.750000 | 0.500000 | Biso | 1.000000 | H |
| H13 | 1.0 | 0.529044 | 0.250000 | 0.000000 | Biso | 1.000000 | H |
| H14 | 1.0 | 0.529044 | 0.250000 | 0.500000 | Biso | 1.000000 | H |
| H15 | 1.0 | 0.529044 | 0.750000 | 0.000000 | Biso | 1.000000 | H |
| H16 | 1.0 | 0.529044 | 0.750000 | 0.500000 | Biso | 1.000000 | H |
| H17 | 1.0 | 0.029044 | 0.000000 | 0.250000 | Biso | 1.000000 | H |
| H18 | 1.0 | 0.029044 | 0.000000 | 0.750000 | Biso | 1.000000 | H |
| H19 | 1.0 | 0.029044 | 0.500000 | 0.250000 | Biso | 1.000000 | H |
| H20 | 1.0 | 0.029044 | 0.500000 | 0.750000 | Biso | 1.000000 | H |
| H21 | 1.0 | 0.529044 | 0.000000 | 0.250000 | Biso | 1.000000 | H |
| H22 | 1.0 | 0.529044 | 0.000000 | 0.750000 | Biso | 1.000000 | H |
| H23 | 1.0 | 0.529044 | 0.500000 | 0.250000 | Biso | 1.000000 | H |
| H24 | 1.0 | 0.529044 | 0.500000 | 0.750000 | Biso | 1.000000 | H |
| H25 | 1.0 | 0.466592 | 0.250000 | 0.250000 | Biso | 1.000000 | H |
| H26 | 1.0 | 0.466592 | 0.250000 | 0.750000 | Biso | 1.000000 | H |
| H27 | 1.0 | 0.466592 | 0.750000 | 0.250000 | Biso | 1.000000 | H |
| H28 | 1.0 | 0.466592 | 0.750000 | 0.750000 | Biso | 1.000000 | H |
| H29 | 1.0 | 0.966592 | 0.250000 | 0.250000 | Biso | 1.000000 | H |
| H30 | 1.0 | 0.966592 | 0.250000 | 0.750000 | Biso | 1.000000 | H |
| H31 | 1.0 | 0.966592 | 0.750000 | 0.250000 | Biso | 1.000000 | H |
| H32 | 1.0 | 0.966592 | 0.750000 | 0.750000 | Biso | 1.000000 | H |
(b) Cmmm structure

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_cell_length_b                         6.17800
_cell_length_c                         6.17800
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_cell_angle_beta                       90
_cell_angle_gamma                      90
_symmetry_space_group_name_H-M         'P 1'
_symmetry_Int_Tables_number            1

loop_
_symmetry_equiv_pos_as_xyz
'x, y, z'

loop_
_atom_site_label
_atom_site_occupancy
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_adp_type
_atom_site_B_iso_or_equiv
_atom_site_type_symbol
S1 1.0 0.000000 0.000000 0.000000 Biso 1.000000 S
S2 1.0 0.000000 0.000000 0.500000 Biso 1.000000 S
S3 1.0 0.000000 0.500000 0.000000 Biso 1.000000 S
S4 1.0 0.000000 0.500000 0.500000 Biso 1.000000 S
S5 1.0 0.500000 0.000000 0.000000 Biso 1.000000 S
S6 1.0 0.500000 0.000000 0.500000 Biso 1.000000 S
S7 1.0 0.500000 0.500000 0.000000 Biso 1.000000 S
S8 1.0 0.500000 0.500000 0.500000 Biso 1.000000 S
S9 1.0 0.250000 0.250000 0.250000 Biso 1.000000 S
S10 1.0 0.250000 0.250000 0.750000 Biso 1.000000 S
S11 1.0 0.250000 0.750000 0.250000 Biso 1.000000 S
S12 1.0 0.250000 0.750000 0.750000 Biso 1.000000 S
|   |    |    |    |    |    |
|---|----|----|----|----|----|
|S13| 1.0| 0.750000| 0.250000| 0.250000| Biso 1.000000 S|
|S14| 1.0| 0.750000| 0.250000| 0.750000| Biso 1.000000 S|
|S15| 1.0| 0.750000| 0.750000| 0.250000| Biso 1.000000 S|
|S16| 1.0| 0.750000| 0.750000| 0.750000| Biso 1.000000 S|
|H1 | 1.0| 0.250000| 0.000000| 0.000000| Biso 1.000000 H|
|H2 | 1.0| 0.250000| 0.000000| 0.500000| Biso 1.000000 H|
|H3 | 1.0| 0.250000| 0.500000| 0.000000| Biso 1.000000 H|
|H4 | 1.0| 0.250000| 0.500000| 0.500000| Biso 1.000000 H|
|H5 | 1.0| 0.750000| 0.000000| 0.000000| Biso 1.000000 H|
|H6 | 1.0| 0.750000| 0.000000| 0.500000| Biso 1.000000 H|
|H7 | 1.0| 0.750000| 0.500000| 0.000000| Biso 1.000000 H|
|H8 | 1.0| 0.750000| 0.500000| 0.500000| Biso 1.000000 H|
|H9 | 1.0| 0.000000| 0.250000| 0.000000| Biso 1.000000 H|
|H10| 1.0| 0.000000| 0.250000| 0.500000| Biso 1.000000 H|
|H11| 1.0| 0.000000| 0.750000| 0.000000| Biso 1.000000 H|
|H12| 1.0| 0.000000| 0.750000| 0.500000| Biso 1.000000 H|
|H13| 1.0| 0.500000| 0.250000| 0.000000| Biso 1.000000 H|
|H14| 1.0| 0.500000| 0.250000| 0.500000| Biso 1.000000 H|
|H15| 1.0| 0.500000| 0.750000| 0.000000| Biso 1.000000 H|
|H16| 1.0| 0.500000| 0.750000| 0.500000| Biso 1.000000 H|
|H17| 1.0| 0.999907| 0.020674| 0.253947| Biso 1.000000 H|
|H18| 1.0| 0.000093| 0.020674| 0.746053| Biso 1.000000 H|
|H19| 1.0| 0.999907| 0.479326| 0.253947| Biso 1.000000 H|
|H20| 1.0| 0.000093| 0.479326| 0.746053| Biso 1.000000 H|
|H21| 1.0| 0.499907| 0.979326| 0.253947| Biso 1.000000 H|
|H22| 1.0| 0.500093| 0.979326| 0.746053| Biso 1.000000 H|
|H23| 1.0| 0.499907| 0.520674| 0.253947| Biso 1.000000 H|
|H24| 1.0| 0.500093| 0.520674| 0.746053| Biso 1.000000 H|
|H25| 1.0| 0.499953| 0.250000| 0.250586| Biso 1.000000 H|
|H26| 1.0| 0.249649| 0.250000| 0.999894| Biso 1.000000 H|
|H27| 1.0| 0.250351| 0.750000| 0.000106| Biso 1.000000 H|
|H28| 1.0| 0.000047| 0.750000| 0.749414| Biso 1.000000 H|
|H29| 1.0| 0.750351| 0.250000| 0.000106| Biso 1.000000 H|
|H30| 1.0| 0.500047| 0.250000| 0.749414| Biso 1.000000 H|
|H31| 1.0| 0.999953| 0.750000| 0.250586| Biso 1.000000 H|
|H32| 1.0| 0.749649| 0.750000| 0.999894| Biso 1.000000 H|
(c) Cmc2\_1 structure

#CRYSTAL DATA

data_VESTA_phase_1

_pd_phase_name          '…S H              '
cell_length_a          6.17800
cell_length_b          6.17800
cell_length_c          6.17800
cell_angle_alpha       90
cell_angle_beta        90
cell_angle_gamma       90
_symmetry_space_group_name_H-M   'P 1'
symmetry_Int_Tables_number  1

loop_
symmetry_equiv_pos_as_xyz
    'x, y, z'

loop_
    atom_site_label
    atom_site_occupancy
    atom_site_fract_x
    atom_site_fract_y
    atom_site_fract_z
    atom_site_type_symbol
    atom_site_B_iso_or_equiv
    atom_site_type_symbol
S1  1.0  0.000000  0.000000  0.000000  Biso  1.000000 S
S2  1.0  0.000000  0.000000  0.500000  Biso  1.000000 S
S3  1.0  0.000000  0.500000  0.000000  Biso  1.000000 S
S4  1.0  0.000000  0.500000  0.500000  Biso  1.000000 S
S5  1.0  0.500000  0.000000  0.000000  Biso  1.000000 S
S6  1.0  0.500000  0.000000  0.500000  Biso  1.000000 S
S7  1.0  0.500000  0.500000  0.000000  Biso  1.000000 S
S8  1.0  0.500000  0.500000  0.500000  Biso  1.000000 S
S9  1.0  0.250000  0.250000  0.250000  Biso  1.000000 S
S10  1.0  0.250000  0.250000  0.750000  Biso  1.000000 S
S11  1.0  0.250000  0.750000  0.250000  Biso  1.000000 S
S12  1.0  0.250000  0.750000  0.750000  Biso  1.000000 S
|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| S13 | 1.0 | 0.750000 | 0.250000 | 0.250000 | Biso | 1.000000 | S |
| S14 | 1.0 | 0.750000 | 0.250000 | 0.750000 | Biso | 1.000000 | S |
| S15 | 1.0 | 0.750000 | 0.750000 | 0.250000 | Biso | 1.000000 | S |
| S16 | 1.0 | 0.750000 | 0.750000 | 0.750000 | Biso | 1.000000 | S |
| H1  | 1.0 | 0.258747 | 0.020725 | 0.009549 | Biso | 1.000000 | H |
| H2  | 1.0 | 0.241253 | 0.979275 | 0.509549 | Biso | 1.000000 | H |
| H3  | 1.0 | 0.258747 | 0.479275 | 0.009549 | Biso | 1.000000 | H |
| H4  | 1.0 | 0.241253 | 0.520725 | 0.509549 | Biso | 1.000000 | H |
| H5  | 1.0 | 0.758747 | 0.979275 | 0.009549 | Biso | 1.000000 | H |
| H6  | 1.0 | 0.741253 | 0.020725 | 0.509549 | Biso | 1.000000 | H |
| H7  | 1.0 | 0.758747 | 0.520725 | 0.009549 | Biso | 1.000000 | H |
| H8  | 1.0 | 0.741253 | 0.479275 | 0.509549 | Biso | 1.000000 | H |
| H9  | 1.0 | 0.018889 | 0.250000 | 0.004028 | Biso | 1.000000 | H |
| H10 | 1.0 | 0.981111 | 0.250000 | 0.504028 | Biso | 1.000000 | H |
| H11 | 1.0 | 0.981358 | 0.750000 | 0.998506 | Biso | 1.000000 | H |
| H12 | 1.0 | 0.018642 | 0.750000 | 0.498506 | Biso | 1.000000 | H |
| H13 | 1.0 | 0.481358 | 0.250000 | 0.998506 | Biso | 1.000000 | H |
| H14 | 1.0 | 0.518642 | 0.250000 | 0.498506 | Biso | 1.000000 | H |
| H15 | 1.0 | 0.518889 | 0.750000 | 0.004028 | Biso | 1.000000 | H |
| H16 | 1.0 | 0.481111 | 0.750000 | 0.504028 | Biso | 1.000000 | H |
| H17 | 1.0 | 0.003818 | 0.978667 | 0.230822 | Biso | 1.000000 | H |
| H18 | 1.0 | 0.996182 | 0.978667 | 0.730822 | Biso | 1.000000 | H |
| H19 | 1.0 | 0.003818 | 0.521333 | 0.230822 | Biso | 1.000000 | H |
| H20 | 1.0 | 0.996182 | 0.521333 | 0.730822 | Biso | 1.000000 | H |
| H21 | 1.0 | 0.503818 | 0.021333 | 0.230822 | Biso | 1.000000 | H |
| H22 | 1.0 | 0.496182 | 0.021333 | 0.730822 | Biso | 1.000000 | H |
| H23 | 1.0 | 0.503818 | 0.478667 | 0.230822 | Biso | 1.000000 | H |
| H24 | 1.0 | 0.496182 | 0.478667 | 0.730822 | Biso | 1.000000 | H |
| H25 | 1.0 | 0.252509 | 0.250000 | 0.507519 | Biso | 1.000000 | H |
| H26 | 1.0 | 0.000519 | 0.250000 | 0.753488 | Biso | 1.000000 | H |
| H27 | 1.0 | 0.499481 | 0.750000 | 0.253488 | Biso | 1.000000 | H |
| H28 | 1.0 | 0.247491 | 0.750000 | 0.007519 | Biso | 1.000000 | H |
| H29 | 1.0 | 0.999481 | 0.250000 | 0.253488 | Biso | 1.000000 | H |
| H30 | 1.0 | 0.747491 | 0.250000 | 0.007519 | Biso | 1.000000 | H |
| H31 | 1.0 | 0.752509 | 0.750000 | 0.507519 | Biso | 1.000000 | H |
| H32 | 1.0 | 0.500519 | 0.750000 | 0.753488 | Biso | 1.000000 | H |
(d) Ima2 structure

#======================================================================
# CRYSTAL DATA
#======================================================================

data_VESTA_phase_1

_pd_phase_name                         'f__________________________________ S    H                            '
_cell_length_a                         6.17800
_cell_length_b                         6.17800
_cell_length_c                         6.17800
_cell_angle_alpha                      90
_cell_angle_beta                       90
_cell_angle_gamma                      90
_symmetry_space_group_name_H-M         'P 1'
_symmetry_Int_Tables_number            1

loop_
_symmetry_equiv_pos_as_xyz
'x, y, z'

loop_
_atom_site_label
_atom_site_occupancy
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_type_symbol
_atom_site_B_iso_or_equiv
_atom_site_type_symbol
S1    1.0     0.000000     0.000000     0.000000     Biso  1.000000 S
S2    1.0     0.000000     0.000000     0.500000     Biso  1.000000 S
S3    1.0     0.000000     0.500000     0.000000     Biso  1.000000 S
S4    1.0     0.000000     0.500000     0.500000     Biso  1.000000 S
S5    1.0     0.500000     0.000000     0.000000     Biso  1.000000 S
S6    1.0     0.500000     0.000000     0.500000     Biso  1.000000 S
S7    1.0     0.500000     0.500000     0.000000     Biso  1.000000 S
S8    1.0     0.500000     0.500000     0.500000     Biso  1.000000 S
S9    1.0     0.250000     0.250000     0.250000     Biso  1.000000 S
S10   1.0     0.250000     0.250000     0.750000     Biso  1.000000 S
S11   1.0     0.250000     0.750000     0.250000     Biso  1.000000 S
S12   1.0     0.250000     0.750000     0.750000     Biso  1.000000 S
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| S13 | 1.0 | 0.750000 | 0.250000 | 0.250000 | Biso | 1.000000 S |
| S14 | 1.0 | 0.750000 | 0.250000 | 0.750000 | Biso | 1.000000 S |
| S15 | 1.0 | 0.750000 | 0.750000 | 0.250000 | Biso | 1.000000 S |
| S16 | 1.0 | 0.750000 | 0.750000 | 0.750000 | Biso | 1.000000 S |
| H1  | 1.0 | 0.267044 | 0.021028 | 0.007515 | Biso | 1.000000 H |
| H2  | 1.0 | 0.267044 | 0.978972 | 0.507515 | Biso | 1.000000 H |
| H3  | 1.0 | 0.267044 | 0.478972 | 0.007515 | Biso | 1.000000 H |
| H4  | 1.0 | 0.267044 | 0.521028 | 0.507515 | Biso | 1.000000 H |
| H5  | 1.0 | 0.767044 | 0.978972 | 0.007515 | Biso | 1.000000 H |
| H6  | 1.0 | 0.767044 | 0.021028 | 0.507515 | Biso | 1.000000 H |
| H7  | 1.0 | 0.767044 | 0.521028 | 0.007515 | Biso | 1.000000 H |
| H8  | 1.0 | 0.767044 | 0.478972 | 0.507515 | Biso | 1.000000 H |
| H9  | 1.0 | 0.019347 | 0.250000 | 0.016936 | Biso | 1.000000 H |
| H10 | 1.0 | 0.983064 | 0.250000 | 0.480653 | Biso | 1.000000 H |
| H11 | 1.0 | 0.983064 | 0.750000 | 0.980653 | Biso | 1.000000 H |
| H12 | 1.0 | 0.019347 | 0.750000 | 0.516936 | Biso | 1.000000 H |
| H13 | 1.0 | 0.483064 | 0.250000 | 0.980653 | Biso | 1.000000 H |
| H14 | 1.0 | 0.519347 | 0.250000 | 0.516936 | Biso | 1.000000 H |
| H15 | 1.0 | 0.519347 | 0.750000 | 0.016936 | Biso | 1.000000 H |
| H16 | 1.0 | 0.483064 | 0.750000 | 0.480653 | Biso | 1.000000 H |
| H17 | 1.0 | 0.992485 | 0.021028 | 0.232956 | Biso | 1.000000 H |
| H18 | 1.0 | 0.992485 | 0.978972 | 0.732956 | Biso | 1.000000 H |
| H19 | 1.0 | 0.992485 | 0.478972 | 0.232956 | Biso | 1.000000 H |
| H20 | 1.0 | 0.992485 | 0.521028 | 0.732956 | Biso | 1.000000 H |
| H21 | 1.0 | 0.492485 | 0.978972 | 0.232956 | Biso | 1.000000 H |
| H22 | 1.0 | 0.492485 | 0.021028 | 0.732956 | Biso | 1.000000 H |
| H23 | 1.0 | 0.492485 | 0.521028 | 0.232956 | Biso | 1.000000 H |
| H24 | 1.0 | 0.492485 | 0.478972 | 0.732956 | Biso | 1.000000 H |
| H25 | 1.0 | 0.247908 | 0.250000 | 0.508488 | Biso | 1.000000 H |
| H26 | 1.0 | 0.991512 | 0.250000 | 0.752092 | Biso | 1.000000 H |
| H27 | 1.0 | 0.991512 | 0.750000 | 0.252092 | Biso | 1.000000 H |
| H28 | 1.0 | 0.247908 | 0.750000 | 0.008488 | Biso | 1.000000 H |
| H29 | 1.0 | 0.491512 | 0.250000 | 0.252092 | Biso | 1.000000 H |
| H30 | 1.0 | 0.747908 | 0.250000 | 0.008488 | Biso | 1.000000 H |
| H31 | 1.0 | 0.747908 | 0.750000 | 0.508488 | Biso | 1.000000 H |
| H32 | 1.0 | 0.491512 | 0.750000 | 0.752092 | Biso | 1.000000 H |
[5] Fermi surface of the Ima2 structure of (SH\textsuperscript{-})(H\textsubscript{3}S\textsuperscript{+})
In our estimation of $\Delta H_1$ for the reaction,
$$2\text{H}_3\text{S} \rightarrow (\text{SH})(\text{H}_3\text{S}^+) + \text{H}_2,$$
we made an inadvertent error of using half the energy of $\text{H}_2$ instead of the full energy. For the $P4mm$, $Cmmm$, $Cmc21$ and $Ima2$ structures of $(\text{SH})(\text{H}_3\text{S}^+$), the correct $\Delta H_1$ values are -3.200, -3.511, -3.559 and -3.582 eV, respectively. Thus, at 200 K, the correct $\Delta G_1$ values are -3.219, -3.529, -3.578 and -3.601 eV, respectively. These estimates are valid at ambient pressure because we employed the energy of $\text{H}_2$ calculated for its structure at ambient pressure.

To estimate the $\Delta H_1$ values at ultrahigh pressure $P$, it is necessary to consider the VP term, where $V$ is the cell volume. In our calculations, the $Im\overline{3}m$ structure of $\text{H}_3\text{S}$ and the structures of $(\text{SH})(\text{H}_3\text{S}^+)$ have the same cell volume, so their relative energies are not affected by the VP term. However, one needs to consider the VP term for $\text{H}_2$. Under ultrahigh pressure, it is most likely that $\text{H}_2$ dissociates into $\text{H}$ atoms, and the latter are present on the surface or at the interstitial sites of the Re metal (i.e., the gasket material for the high-pressure cell) forming Re-H bonds. Then, the VP term for "$\text{H}_2$" vanishes. It is reasonable to assume that the loss of H-H bonding is compensated by the Re-H bonding. Then, to a first approximation, our estimates of $\Delta H_1$ at ambient pressure are also reasonable at ultrahigh pressure.

For the following reaction,
$$1.5(\text{SH})(\text{H}_3\text{S}^+) \rightarrow 2\text{H}_3\text{S} + \text{S},$$
where S refers to the $\beta$-Po structure of elemental sulfur, our calculations show that the enthalpy changes $\Delta H_2$ under the pressure of 160 GPa, for the $P4mm$, $Cmmm$, $Cmc21$ and $Ima2$ structures of $(\text{SH})(\text{H}_3\text{S}^+)$ are -3.630, -3.163, -3.091 and -3.056 eV, respectively. The activation energies of both reactions, Eq. 1 and Eq. 2, cannot be both small. Otherwise, all $\text{H}_2\text{S}$ under ultrahigh pressure would be converted to elemental $\text{S}$ in disagreement with experiment. Due to the possible catalytic effect of the Re metal surface, Eq. 1 is more likely to have a low activation than does Eq. 2.

We thank Dr. Igor Mazin and Dr. Noam Bernstein for alerting us to recheck our calculations.