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# Pressure-induced metallization of dense $(\text{H}_2\text{S})_2\text{H}_2$ with high- $T_c$ superconductivity

SUBJECT AREAS:

THEORY AND  
COMPUTATION

CONDENSED-MATTER PHYSICS

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The high pressure structures, metallization, and superconductivity of recently synthesized  $\text{H}_2$ -containing compounds  $(\text{H}_2\text{S})_2\text{H}_2$  are elucidated by *ab initio* calculations. The ordered crystal structure with *P1* symmetry is determined, supported by the good agreement between theoretical and experimental X-ray diffraction data, equation of states, and Raman spectra. The *Ccm* structure is favorable with partial hydrogen bond symmetrization above 37 GPa. Upon further compression,  $\text{H}_2$  molecules disappear and two intriguing metallic structures with *R3m* and *Im-3m* symmetries are reconstructive above 111 and 180 GPa, respectively. The predicted metallization pressure is 111 GPa, which is approximately one-third of the currently suggested metallization pressure of bulk molecular hydrogen. Application of the Allen-Dynes-modified McMillan equation for the *Im-3m* structure yields high  $T_c$  values of 191 K to 204 K at 200 GPa, which is among the highest values reported for  $\text{H}_2$ -rich van der Waals compounds and  $\text{MH}_3$  type hydride thus far.

Closed shell systems (e.g.,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$ ,  $\text{NH}_3\text{BH}_3$ , Ar, Kr, and Xe) can absorb additional  $\text{H}_2$  molecules under high pressure conditions, forming a series of new  $\text{H}_2$ -containing stoichiometric compounds, such as  $\text{H}_2\text{O}(\text{H}_2)$ <sup>1</sup>,  $(\text{H}_2\text{S})_2\text{H}_2$ <sup>2</sup>,  $\text{CH}_4(\text{H}_2)$ <sup>3</sup>,  $\text{SiH}_4(\text{H}_2)$ <sup>4,5</sup>,  $\text{GeH}_4(\text{H}_2)$ <sup>6</sup>,  $\text{NH}_3\text{BH}_3(\text{H}_2)_x$ <sup>7,8</sup>,  $\text{Ar}(\text{H}_2)$ <sup>9</sup>,  $\text{Kr}(\text{H}_2)$ <sup>10</sup>, and  $\text{Xe}(\text{H}_2)$ <sup>11</sup>. Given their high amount of hydrogen, these compounds are potential energy storage materials and high-temperature superconductors. For example,  $\text{CH}_4(\text{H}_2)_4$  with 33.4 wt% high hydrogen content is a potentially high hydrogen storage material<sup>12</sup>. Metallic hydrogen is one of the most important physical problems in high-pressure research, which is believed to be a room-temperature superconductor<sup>13,14</sup>. However, the metallization of hydrogen is still under debate in laboratories<sup>15,16</sup>. Hydrogen-rich compounds, such as  $\text{GaH}_3$ <sup>17</sup>,  $\text{GeH}_3$ <sup>18</sup>,  $\text{Si}_2\text{H}_6$ <sup>19,20</sup>,  $\text{SiH}_4$ <sup>21-24</sup>,  $\text{GeH}_4$ <sup>25</sup>,  $\text{KH}_6$ <sup>26</sup>,  $\text{CaH}_6$ <sup>27</sup>,  $\text{SiH}_4(\text{H}_2)$ <sup>28</sup>, and  $\text{GeH}_4(\text{H}_2)$ <sup>29</sup> are extensively explored as alternatives because their metallization can occur at relatively lower pressures through chemical pre-compressions, which present high temperature superconductivity.  $\text{H}_2$ -containing compounds  $\text{SiH}_4(\text{H}_2)_2$  and  $\text{GeH}_4(\text{H}_2)_2$  have been predicted to have high  $T_c$  values of 98 K to 107 K at 250 GPa and 76 K to 90 K at 250 GPa (with the Coulomb parameter  $\mu^* = 0.1-0.13$ ), respectively<sup>28,29</sup>. For the  $\text{MH}_3$  ( $M = \text{Ga}, \text{Ge}, \text{Si}$ ) type hydride,  $T_c$  is estimated theoretically to be 76 K to 86 K ( $\mu^* = 0.1-0.13$ ) at 160 GPa<sup>17</sup>, 140 K ( $\mu^* = 0.13$ ) at 180 GPa<sup>18</sup>, and 139 K to 153 K ( $\mu^* = 0.1-0.13$ ) at 275 GPa<sup>19</sup>, respectively. Theoretical predictions also revealed that the  $T_c$  of sodalite-like  $\text{CaH}_6$  at 150 GPa reached 220 K to 235 K ( $\mu^* = 0.1-0.13$ )<sup>27</sup>. Considering that  $\text{H}_2$  is the most abundant substance in the universe, the behavior of  $\text{H}_2$ -containing compounds over a broad P-T range is important for planetary sciences.

Recently, Strobel *et al.* reported that mixing hydrogen sulfide ( $\text{H}_2\text{S}$ ) and hydrogen ( $\text{H}_2$ ) can form a stoichiometric compound  $(\text{H}_2\text{S})_2\text{H}_2$  near 3.5 GPa, which is characteristic of a rotationally disordered structure<sup>2</sup>. X-ray diffraction (XRD) results have indicated that this structure belongs to the tetragonal space group *I4/mcm*. The experimental Raman data indicated that an ordering process occurred with structural transformation above 17 GPa. A candidate structure with space group *I222* was proposed by *ab initio* density functional theory (DFT) calculations through structural optimizations. However, obtaining the most stable structure only by structural relaxation is difficult because of potential energy barrier. Another unexpected structure can possibly become stable instead.

We have taken a new route in this study using the recently fast-developed evolutionary algorithm Universal Structure Predictor: Evolutionary Xtallography (USPEX)<sup>30-32</sup> to explore the high-pressure ordered crystal structures of  $(\text{H}_2\text{S})_2\text{H}_2$ . We found that a triclinic (*P1*) structure is energetically favorable. Motivated by the metallization and potential high-temperature superconductivity in  $(\text{H}_2\text{S})_2\text{H}_2$ , higher pressure structures have been



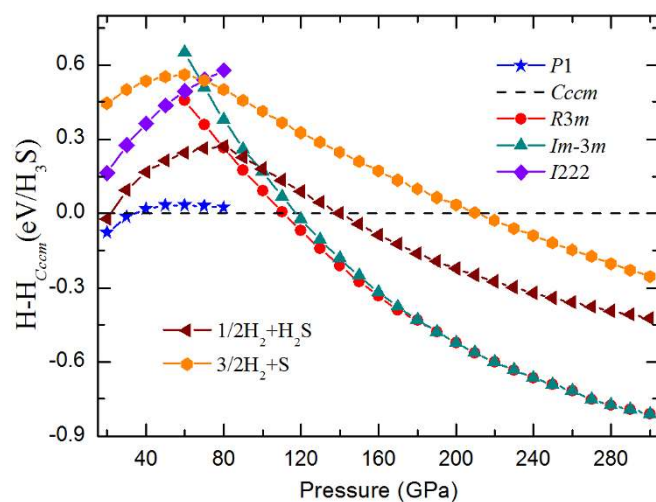
extensively explored. Our calculations reveal a metallization pressure of 111 GPa and a high  $T_c$  of 200 K at 200 GPa. The lower metallization pressure is within the reach of current diamond–anvil techniques, which will inevitably stimulate extensive experiments.

## Results

Variable-cell structure prediction simulations with 1 to 4, 6, and 8  $\text{H}_3\text{S}$  formula units per cell (f.u./cell) at pressures between 20 and 300 GPa were performed. A group of new structures was uncovered under high pressure—triclinic  $P1$  (8 f.u./cell), orthorhombic  $Ccmm$  (16 f.u./cell), trigonal  $R3m$  (3 f.u./cell), and cubic  $Im-3m$  (2 f.u./cell) as shown in Fig. 1. The lattice parameters of these structures at different pressures are also listed in Table S1 of the supplementary information.

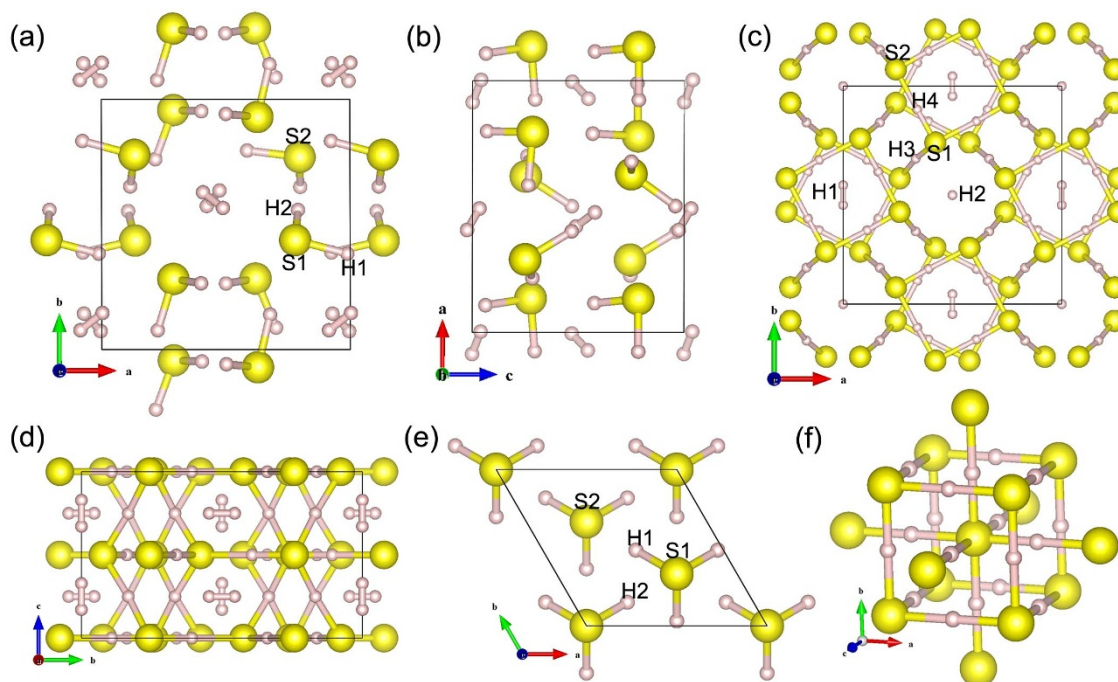
Enthalpy difference curves (relative to the  $Ccmm$  structure) for different structures are presented in Fig. 2.  $P1$  is the most stable structure below 37 GPa, which has lower energy than that of the proposed experimental  $I222$  structure<sup>2</sup>. This  $P1$  structure consists of an ordered H-bonded  $\text{H}_2\text{S}$  network and two anti-parallel hydrogen molecules occupying the interstitial sites. One molecule lies at  $z = 0$ , whereas the other lies at the  $z = 1/2$  plane (Figs. 1a and 1b). The  $Ccmm$  structure is energetically stable between 37 and 111 GPa. Unlike the  $P1$  structure, partial hydrogen bond symmetrization is formed in the  $Ccmm$  structure. This structure consists of 3D  $\text{H}_2\text{S}$  networks that trap two different types of hydrogen molecules in channels: one type is arranged such that the head-tail hydrogen molecule ( $\text{H}_2\text{--H}_2$ ) alignment follows the  $c$ -axis, whereas the other type is characterized by parallel hydrogen molecule ( $\text{H}_1\text{--H}_1$ ) configuration pointing to the  $b$ -axis (Figs. 1c and 1d). The absence of any imaginary frequency also confirms the dynamic stability of the  $P1$  and  $Ccmm$  phases (see supplementary Fig. S1).

The lattice angles  $\alpha = 90.12^\circ$ ,  $\beta = 89.85^\circ$ , and  $\gamma = 90.15^\circ$  is approximately equal to  $90^\circ$  for the  $P1$  structure at 20 GPa (see supplementary Table S1), which can thus be viewed as a slightly distorted orthorhombic lattice. This condition can explain the experimental suggestion of an orthorhombic structure. We compared the XRD patterns of the  $P1$  structure with that of the experimental pattern in

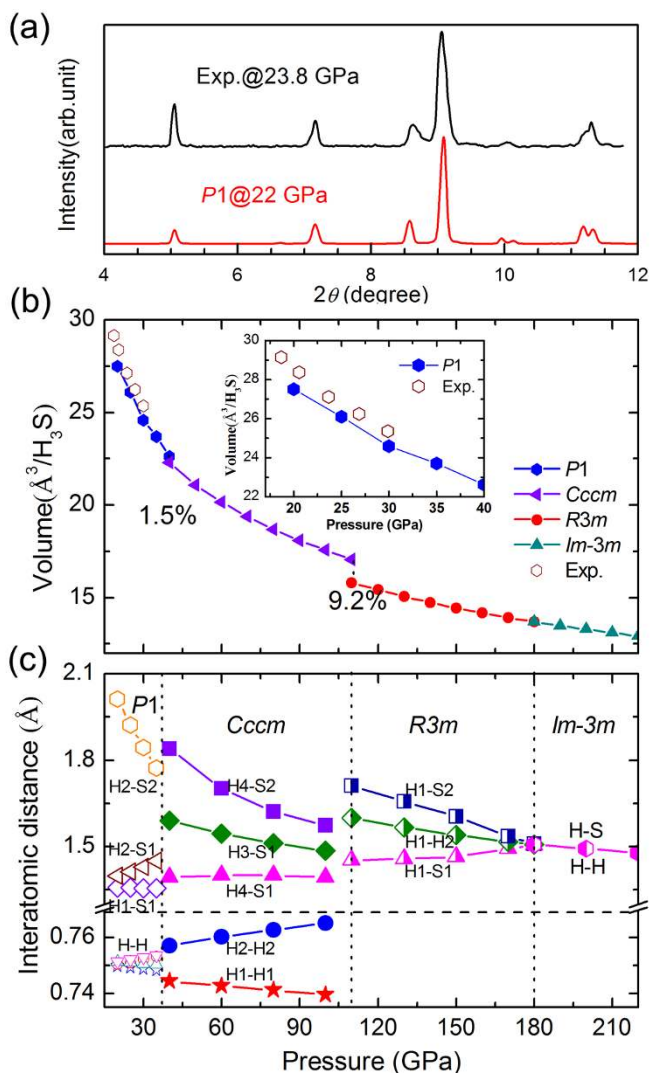


**Figure 2** | Calculated enthalpies per  $\text{H}_3\text{S}$  unit as the function of pressure. Calculated enthalpy curves for various structures relative to our predicted  $Ccmm$  structure as a function of pressure. The decomposition enthalpies into  $\text{S} + 3/2\text{H}_2$  and  $\text{H}_2\text{S} + 1/2\text{H}_2$  are also plotted.

Fig. 3a. A theoretical pattern was obtained with the same X-ray wavelength of  $0.39796 \text{ \AA}$  as the experimental one. The simulated XRD patterns for the  $P1$  structures agree well with those for the experiment data<sup>2</sup>. The calculated equation of states (EOS) for the  $P1$  structure was also compared with experimental one in Fig. 3b. Good agreement between the theoretical and experimental results provides another support for the validity of the  $P1$  structure. Given that hydrogen atoms are undetectable by XRD patterns, the Raman spectrum of  $P1$  is presented for comparison with the experimental results (see supplementary Fig. S2). Two  $\text{H}_2$  vibron-peaks are well reproduced, and the two low-frequency features agree qualitatively between theory and experiment. This Raman result, together with the XRD and EOS evidence, support our predicted  $P1$  structure in  $(\text{H}_2\text{S})_2\text{H}_2$ .



**Figure 1** | High-pressure crystal structures of  $(\text{H}_2\text{S})_2\text{H}_2$ . (a)  $P1$  structure normal to the (001) plane, (b)  $P1$  structure normal to the (010) plane, (c)  $Ccmm$  structure normal to the (001) plane, (d)  $Ccmm$  structure normal to the (100) plane, (e)  $R3m$ , and (f)  $Im-3m$ . Large spheres represent S and small spheres denote H atoms, respectively.



**Figure 3** | Calculated XRD and EOS compared with experiment data. (a) The simulated XRD patterns and (b) calculated EOS for the P1 structures compared with experiment data (ref. 2). (c) Various interatomic distances of P1, *Cccm*, *R3m*, and *Im-3m* structures with pressure.

The *Cccm* structure transforms to a denser *R3m* structure above 111 GPa with a volume collapse of 9.2% on further compression (Fig. 3b). The *R3m* structure shows a disappearing  $H_2$  molecule and forms a pyramidal  $H_3S$  molecular unit as depicted in Fig. 1e. A high-symmetry *Im-3m* structure becomes favorable above 180 GPa. This structure is characterized by two S atoms located at a simple body centered cubic lattice and H atom located symmetrically between the S atoms (Fig. 1f). The hydrogen bond symmetrization completed in the *R3m*→*Im-3m* transition is observed. The coordination number of the S atom increased from three to six with the formation of hydrogen-shared  $SH_6$ .

The decomposition enthalpies into S +  $H_2$  and  $H_2S$  +  $H_2$  are examined to check the phase stability of  $(H_2S)_2H_2$  under pressure (Fig. 2). The structures of  $P6_3m$ ,  $C2/c$ , and  $Cmca$  for  $H_2^{33}$ ,  $I4_1/acd^{34}$ , and  $\beta$ -Po<sup>35</sup> for S,  $P2/c$ ,  $Pc$ ,  $Pmc2_1$ ,  $P-1$ , and  $Cmca$  for  $H_2S^{36}$  in their corresponding stable pressures are adopted. The most stable phases of  $(H_2S)_2H_2$  have lower enthalpy than S +  $H_2$  and  $H_2S$  +  $H_2$  over the pressure range of 20 GPa to 300 GPa. Thus, the  $(H_2S)_2H_2$  crystal remains stable against decomposition in our studied pressure range. The calculated pressure–volume data of  $(H_2S)_2H_2$  is also shown in Fig. 3b. The volume collapses with 1.5% for P1 to *Cccm* transition and 9.2% for *Cccm* to *R3m* transition, suggesting a first-order phase

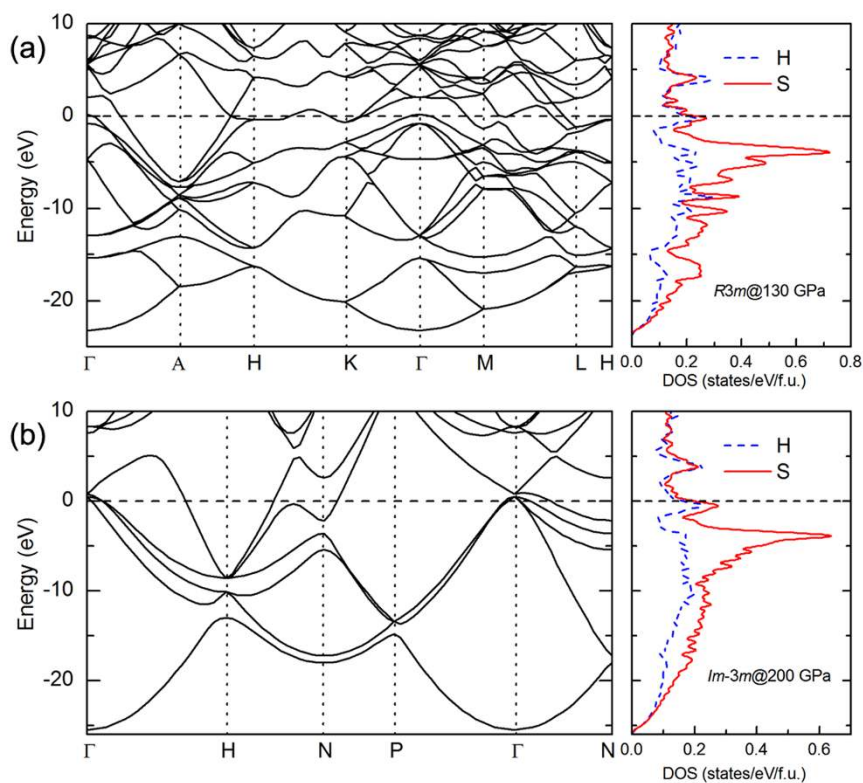
transition character, whereas the volume change is continuous for *R3m* to *Im-3m* transition, supporting a second-order nature.

The pressure dependence of the nearest intramolecular and intermolecular bond distances are plotted in Fig. 3c to understand the molecular interactions observed in  $(H_2S)_2H_2$ . Four types of intramolecular H–H bond lengths are nearly equal with distances of approximately 0.75 Å and slightly longer than that 0.74 Å in solid  $H_2$  at 20 GPa, indicating a weak interaction between  $H_2S$  and  $H_2$ . The two H–H bond lengths increased, whereas the other two decreased with increasing pressure, consistent with the observed redshift and blueshift of H–H Raman vibrons<sup>2</sup>, respectively. The hydrogen bond ( $H_2\cdots S_2$ ) is also relatively weak with distance of 2.01 Å at 20 GPa. The strength of the hydrogen bond gradually increases with increasing pressure and significantly elongates one of the H2–S1 covalent bonds for a single molecule. The length of the H3–S1 bond (symmetrization hydrogen bond) is 1.59 Å, the H4–S1 covalent bond is 1.39 Å, and the H4 $\cdots$ S2 bond is 1.84 Å in the *Cccm* structure at 40 GPa, indicating a strong hydrogen bond. The length of the strong hydrogen bond decreases, whereas the length of the H4–S1 bond slightly increases with increasing pressure. Notably, the length of the H1–H1 bond decreases to 0.744 Å, whereas the length of the H2–H2 bond increases to 0.757 Å at 110 GPa (Fig. 3d), indicating a slightly increased interaction between S and H2 under pressure. The *R3m* structure is reconstructive with the disappearing  $H_2$  molecule and forms new H–S bonds at 111 GPa. Thus, a large kinetic barrier is formed for the transformation from *Cccm* to *R3m*. The length of the H1–S1 bond increases with increasing pressure, whereas the length of the hydrogen bond (H1 $\cdots$ S2) decreases. Thus, the hydrogen bond symmetrized completely accompanied by the *R3m*→*Im-3m* phase transition at a pressure of 180 GPa. The nearest H–H distance at 110 GPa in the *R3m* structures is 1.599 Å, much longer than the H–H bond length of  $\sim 1.2$  Å in  $CaH_6$  which is characteristic of a weak covalent bond<sup>27</sup>. The H–H distance decreases slowly and becomes 1.433 Å at 300 GPa with increasing pressure, indicating that H and H atoms do not present any bond.

The electronic band structure and projected density of states (DOS) for all  $(H_2S)_2H_2$  structures were also explored. The P1 structure is an insulator with an indirect band gap of 3.34 eV at 20 GPa (see supplementary Fig. S3). The bands are flat, indicating that the P1 structure is a typical molecular crystal. The band gap for the *Cccm* structure decreases with increasing pressure and closes at approximately 110 GPa. Given the deficiency of DFT associated with generalized gradient approximation (GGA), the calculated band gaps are likely to be underestimated. Therefore, the *Cccm* structure should be an insulator in its stable pressure range. Notably, both the *R3m* and *Im-3m* structures are good metals with a large DOS at the Fermi level, as shown in Fig. 4. The projected DOS clearly indicates strong hybridizations of S and H orbitals. Energy band structures near the Fermi level for both *R3m* and *Im-3m* are characterized as “flat band-steep band”, indicating that they may be good superconductors<sup>37</sup>. The predicted metallization pressure of 111 GPa is significantly lower than the currently suggested pressure for the metallization of bulk molecular hydrogen<sup>38</sup>.

The calculated phonon dispersion curves and projected phonon DOS for *R3m* and *Im-3m* structures are presented in Fig. 5. The absence of any imaginary frequency indicates their dynamical stability. The low-frequency bands come mainly from the vibrations of the S atom, whereas higher-frequency modes are mostly related to the H atoms. The electron phonon coupling (EPC)  $\lambda$ , logarithmic average phonon frequency  $\omega_{log}$ , and the Eliashberg phonon spectral function  $\alpha^2F(\omega)$ <sup>39</sup> are investigated to explore the possible superconductivity of  $(H_2S)_2H_2$ . The resulting  $\lambda$  of *R3m* is 2.07 at 130 GPa, indicating a fairly strong EPC; the  $\omega_{log}$  calculated from the phonon spectrum is 1125.1 K. The calculated  $\lambda$  of *Im-3m* is 2.19 at 200 GPa, whereas the  $\omega_{log}$  is 1334.6 K. Using the calculated  $\omega_{log}$  and commonly accepted values of the Coulomb pseudopotential  $\mu^*$  (0.1–





**Figure 4 | Electronic band structure and density of states (DOS).** Electronic band structure and atom-projected DOS for (a) *R3m* at 130 GPa and (b) *Im-3m* at 200 GPa along the selected high symmetry lines, where the dotted lines at zero indicate the Fermi level.

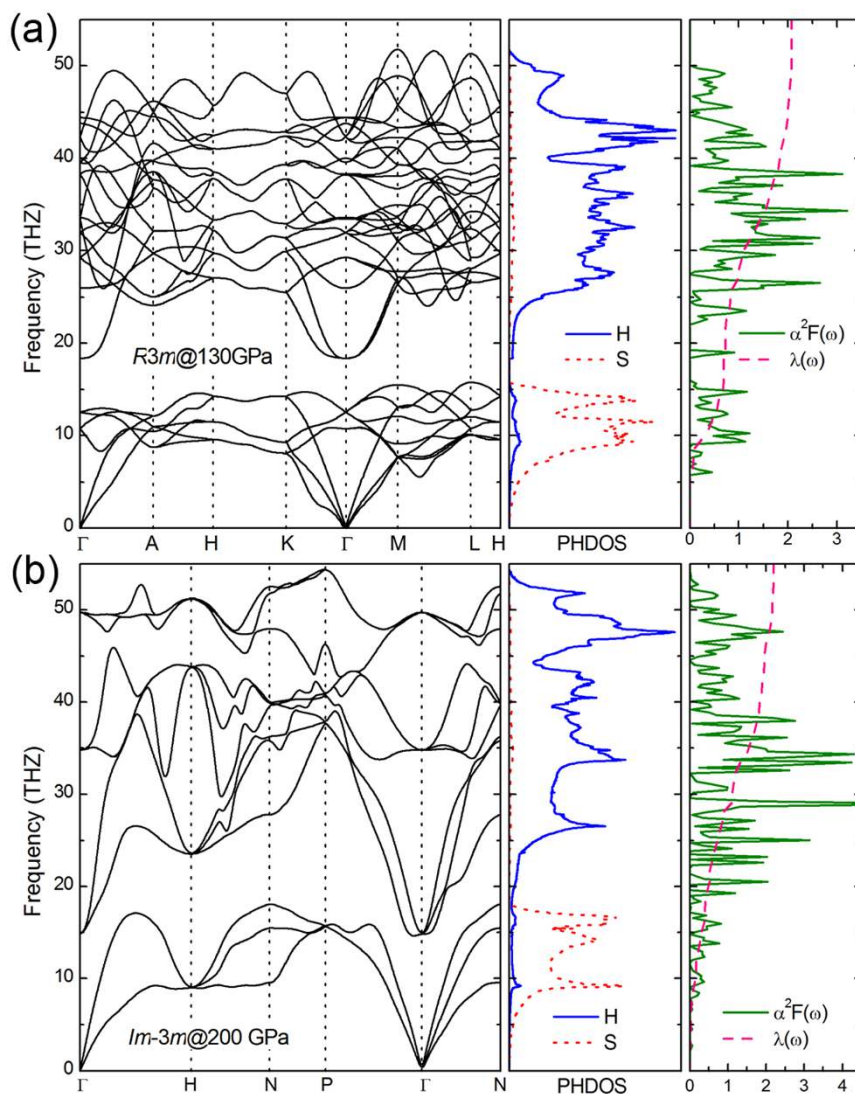
0.13)<sup>40</sup> from the Allen-Dynes-modified McMillan equation<sup>41</sup>, the superconducting transition temperature  $T_c$  for *R3m* was obtained in the range of 155 K to 166 K at 130 GPa. Similarly, the calculated  $T_c$  for the *Im-3m* structure at 200 GPa reaches high values of 191 K to 204 K.  $T_c$  decreases nearly linearly with pressure (184 K at 250 GPa and 179 K at 300 GPa for  $\mu^* = 0.13$ ) at an approximate rate ( $dT_c/dP$ ) of  $-0.12$  K/GPa for the *Im-3m* structure.

## Discussion

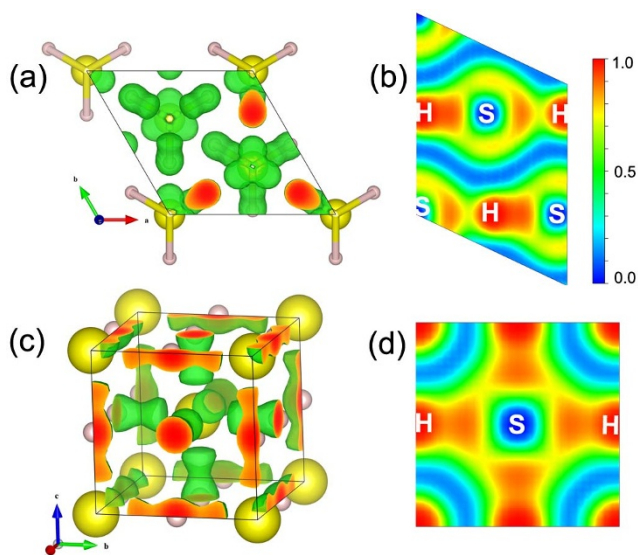
Motivated by the metallization and potential high-temperature superconductivity in hydrogen-rich materials of  $(\text{H}_2\text{S})_2\text{H}_2$  or  $\text{H}_3\text{S}$ , high-pressure structures at a wide pressure range of 20 GPa to 300 GPa were extensively explored. Four order structures under high pressure have been predicted: *P1* (stable below 37 GPa), *Cccm* (stable at 37 GPa–111 GPa), *R3m* (stable at 111 GPa–180 GPa), and *Im-3m* (stable above 180 GPa). The *R3m* and *Im-3m* structures are good metals above 111 GPa. The estimated  $T_c$  of the *Im-3m* phase at 200 GPa is 191 K–204 K, which are among the highest values reported for  $\text{H}_2$ -rich van der Waals compounds<sup>28,29</sup> and  $\text{MH}_3$  ( $M = \text{Ga}, \text{Ge}, \text{Si}$ )-type hydride<sup>17–19</sup> thus far. In a survey of literature, many similarities in structures, metallization, and superconductivity for the  $\text{MH}_3$ <sup>17–19</sup> are observed. They all have a high-symmetry cubic structure under high pressure, with high superconducting transition temperature. The lowest  $T_c$  value is 86 K for  $\text{GaH}_3$ . They are also good metals at an experimentally accessible pressure, with the highest metallization pressure at 190 GPa for  $\text{Si}_2\text{H}_6$ . Although the crystal structure-predicting methods implemented by USPEX code are efficient for global structural convergence, it is limited by the sizes of the simulation cell employed. Given that the number of energy minima on the potential-energy surface grows exponentially with increasing cell size, making an extensive structural search is impossible. Thus, we cannot rule out the possibility that the actual high-pressure phase of  $(\text{H}_2\text{S})_2\text{H}_2$  with larger unit cells may exist.

Notably, no  $\text{H}_2$  molecules were observed in the *R3m* and *Im-3m* structures. However,  $\text{H}_2$  molecules still exist up to 300 GPa for other  $\text{H}_2$ -containing compounds<sup>28,29,42</sup>, such as  $\text{SiH}_4(\text{H}_2)_2$ ,  $\text{GeH}_4(\text{H}_2)_2$ , and  $\text{Ar}(\text{H}_2)_2$ , although the intramolecular H–H bond was stretched under high pressure. We calculated the electron localization function (ELF) to understand the bonding nature in the *R3m* and *Im-3m* structure (Fig. 6). The ELF value for the S–H bonds is close to 1.0, which suggests a strong polar covalent bond. The ELF value between the nearest H–H is very low, indicating the absence of covalent bond characteristics between hydrogen atoms. This scenario is different from  $\text{MH}_3$  ( $M = \text{Ga}, \text{Ge}, \text{Si}$ )<sup>17–19</sup>, where the charge transfer from M to H atoms forms a strong ionic character. We propose a possible formation process of covalent bond in the *R3m* structure as follows: the  $\text{H}_2$  molecules dissociated to hydrogen atoms under high pressure, and the hydrogen atoms then cooperated with sulfur atoms to form a strong polar covalent bond. This strong bond makes the H and S atoms tightly bound to form a dense  $\text{H}_3\text{S}$  structure, yielding the reduction of its volume.

The predicted high  $T_c$  for  $(\text{H}_2\text{S})_2\text{H}_2$  or  $\text{H}_3\text{S}$  in the order of  $\sim 200$  K is very encouraging, which prompted us to study the underlying superconducting mechanism. The corresponding Eliashberg spectral function  $\alpha^2F(\omega)$  and integrated  $\lambda$  as a function of the frequency for the *R3m* at 130 GPa and *Im-3m* at 200 GPa are presented in Fig. 5. S vibrations in the frequency region below 15 THz contribute approximately 33.1% in total  $\lambda$  for the *R3m* structure, whereas H vibrations above 18 THz contribute 66.9% of  $\lambda$ . The low-frequency S vibrations ( $< 18$  THz) and high-frequency H vibrational mode ( $> 20$  THz) contribute 18.4% and 82.6% to the EPC, respectively, for the *Im-3m* structure. This result highlights that the H atoms play a significant role in superconductivity, although the S vibrations at low frequencies are also contributors. This physical mechanism is similar to  $\text{GaH}_3$ <sup>18</sup> and  $\text{GeH}_4(\text{H}_2)_2$ <sup>29</sup>, but different from  $\text{SiH}_4(\text{H}_2)_2$ <sup>28</sup> where the strong interactions between  $\text{H}_2$  and  $\text{SiH}_4$  molecules vibrations dominate the superconductivity.



**Figure 5 | Phonon properties and Eliashberg spectral function.** Phonon dispersion curves, phonon density of states (PHDOS) projected on S and H atoms, and Eliashberg spectral function  $\alpha^2 F(\omega)$  together with the electron-phonon integral  $\lambda(\omega)$  for (a) *R3m* at 130 GPa and (b) *Im-3m* at 200 GPa.



**Figure 6 | Calculated ELF of  $(\text{H}_2\text{S})_2\text{H}_2$ .** The calculated ELF of (a) *R3m* with isosurface value of 0.73, (b) *R3m* for the (011) plane, (c) *Im-3m* with isosurface value of 0.73, (d) *Im-3m* for (100) plane.

Notably, the calculated metallization pressure of  $(\text{H}_2\text{S})_2\text{H}_2$  (111 GPa) is within the diamond anvil cell capability. The DFT calculation is well known to underestimate the band gap because of its systematic defects for treating the excited states. Thus, the actual metallization pressure for  $(\text{H}_2\text{S})_2\text{H}_2$  is likely higher than the DFT estimated values in this study. Nevertheless, the calculated metallization pressure for  $(\text{H}_2\text{S})_2\text{H}_2$  is approximately one-third of the suggested pressure for the metallization of solid hydrogen<sup>38</sup>. The estimated maximal  $T_c$  of 200 K in  $(\text{H}_2\text{S})_2\text{H}_2$  is higher than those predicted for most hydrogen-containing compounds, such as  $\text{SnH}_4(\text{H}_2)_2$ <sup>28</sup>,  $\text{GeH}_4(\text{H}_2)_2$ <sup>29</sup>, and  $\text{MH}_3$  ( $M = \text{Ga}, \text{Ge}, \text{Si}$ )<sup>17-19</sup>. Our findings represent a significant step toward the understanding of the high pressure behavior of metallic hydrogen and hydrogen-rich hydrides, which can stimulate future high-pressure experiments on structural and conductivity measurements.

## Methods

The high-pressure crystal structure of  $(\text{H}_2\text{S})_2\text{H}_2$  were explored by merging the evolutionary algorithm and *ab initio* total-energy calculations, as implemented in the USPEX code<sup>30-32</sup>. Structures (population size: 10–60 structures, increasing with system size) were produced randomly in the first generation. The subsequent generation is created from 60% of the lowest-enthalpy structures of the preceding generation. New structures are created by heredity (60%), permutation (10%), and lattice mutation (30%) operations. The best structure of each generation is also carried over to the next generation. The calculation stops when the best structure does not change for more than 20 generations.



The underlying structure relaxations are performed using density functional theory within the Perdew-Burke-Ernzerhof parameterization of the GGA<sup>43</sup>, as implemented in the Vienna *ab initio* simulation package VASP code<sup>44</sup>. The all-electron projector augmented wave method<sup>45</sup> is adopted with the core radii of 0.8 a.u. for H (1s<sup>2</sup>) and 1.5 a.u. for S (3s<sup>2</sup>3p<sup>4</sup>). Brillouin zone (BZ) sampling using a grid of spacing of  $2\pi \times 0.05 \text{ \AA}^{-1}$  and a plane-wave basis set cutoff of 500 eV are sufficient for the initial search over structures. However, we recalculated the enthalpy curves with higher accuracy using the energy cutoff 800 eV and k-point mesh of  $2\pi \times 0.03 \text{ \AA}^{-1}$ . These values were selected to ensure that the total energy are well converged to be better than 1 meV/atom.

Lattice dynamics and superconducting properties were calculated using density functional perturbation theory<sup>46</sup> and the plane-wave pseudopotential method with Vanderbilt-type ultrasoft potentials<sup>47</sup>, as implemented in the QUANTUM-ESPRESSO code<sup>48</sup>. Convergence tests provide a suitable value of 80 Ry kinetic energy cutoff. The q-point mesh in the first BZ of  $3 \times 3 \times 5$  for R3m and  $8 \times 8 \times 8$  for Im-3m structures are used in the interpolation of the force constants for the phonon dispersion curve calculations. A denser k-point mesh  $16 \times 16 \times 24$  for R3m and  $32 \times 32 \times 32$  for Im-3m structures are adopted to ensure k-point sampling convergence with a Gaussians width of 0.03 Ry, which approximates the zero width limits in the calculation of EPC parameter  $\lambda$ .

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T.C. and D.F.D. designed research. D.F.D. and Y.X.L. performed research. D.F.D., F.B.T., D.L., Z.H.Z., H.Y.Y., X.L.H., B.B.L. and W.J.T. analyzed the data. D.F.D. and T.C. wrote the paper.

## Additional information

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