Quantum hydrogen-bond symmetrization in the superconducting hydrogen sulfide system

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Hydrogen compounds are peculiar in that the quantum nature of the proton can crucially affect their structural and physical properties. A remarkable example is the high-pressure phases [1, 2] of H2O, where quantum proton fluctuations favor symmetrization of the H bond and lower by 30 GPa the boundary between asymmetric and symmetric structures [3]. Here we show that an analogous quantum symmetrization occurs in the recently discovered [4] sulfur hydride superconductor with a record superconducting critical temperature \( T_c = 203 \) K at 155 GPa. Superconductivity occurs via formation of a structure of stoichiometry H3S with S atoms arranged on a body-centered-cubic (bcc) lattice [5–9]. If the H atoms are treated as classical particles, then for \( P \gtrsim 175 \) GPa they are predicted to sit midway between two S atoms in a structure with \( \text{Im}3m \) symmetry. At lower pressures the H atoms move to an off-center position forming a short H–S covalent bond and a longer \( \text{H} \cdots \text{S} \) hydrogen bond in a structure with \( R3m \) symmetry [5–9]. X-ray diffraction experiments confirmed the H3S stoichiometry and the S lattice sites, but were unable to discriminate between the two phases [10]. Our present \textit{ab initio} density-functional theory (DFT) calculations show that quantum nuclear motion lowers the symmetrization pressure by 72 GPa for H3S and by 60 GPa for D3S. Consequently, we predict that the \( \text{Im}3m \) phase dominates the pressure range within which a high \( T_c \) was measured. The observed pressure-dependence of \( T_c \) is closely reproduced in our calculations for the \( \text{Im}3m \) phase, but not for the \( R3m \) phase. Thus, the quantum nature of the proton fundamentally changes the superconducting phase diagram of H3S.

The discovery of high-temperature superconductivity in compressed hydrogen sulfide [4] has generated intense interest over the last year, and has led to a number of theoretical studies aimed at understanding the phase diagram of the H–S system as well as the origin of the astonishingly high \( T_c \) observed [5–9, 12–18]. The overall consensus is that H2S, the only stable compound formed by hydrogen and sulfur at ambient conditions, is metastable at high pressures and its decomposition gives rise to several H-S compounds. High-\( T_c \) superconductivity is believed to occur in a structure of H3S stoichiometry, and is considered to be conventional in nature, i.e., mediated by electron-phonon interactions [4, 5, 7, 9, 12–17]. Alternatives to conventional superconductivity have also been...

![Crystal structures of the competing phases. Crystal structure in the conventional bcc cell of the R3m and Im3m phases. In the R3m structure the H–S covalent bond of length \( d_1 \) is marked with a solid line and the longer H–S hydrogen bond of length \( d_2 \) with a dotted line. In the Im3m phase \( d_1 = d_2 \). In the Im3m structure we mark the lattice parameter \( a \).](image-url)
FIG. 2. Energetics. $E_{\text{BO}}$, $E_{\text{vib}}$, and $E = E_{\text{vib}} + E_{\text{BO}}$ curves are shown as a function of the reaction coordinate $Q$ that transforms the $Im3m$ structure ($Q = 0$) into the $R\bar{3}m$ structure ($Q = 1$), as well as the relative coordinate $x$ that measures the off-centering of the H atoms, defined as $x = (d_2 - a/2)/a$, where $d_2$ is the length of the hydrogen bond and $a$ the lattice parameter (see Fig. 1). The left-hand axes show the energy scale for $E_{\text{vib}}$ and $E$, and the right-hand axes show the scale for $E_{\text{BO}}$. Crystal symmetry implies that $E(Q) = E(-Q)$, so that the curves can be fitted to polynomials with only even terms. This guarantees that the transition is second-order according to Landau theory [11]. Results are presented for two different volumes of the primitive bcc lattice; $V = 97.85 \text{a}_0^3$ corresponds to approximately 150 GPa and $V = 102.11 \text{a}_0^3$ to 130 GPa. The pressure associated with each volume depends on both the isotope and $Q$ (see Extended Data for the equations of states). Black circles represent calculated $E_{\text{vib}}$ points and the black dashed line the fitted $E_{\text{vib}}(Q)$ curve (see Methods). The $E(Q)$ curve is obtained by addition of the fitted $E_{\text{vib}}$ and $E_{\text{BO}}$ curves.

FIG. 3. Second-order phase transition. (a) For each volume we plot the relative coordinate $x$ that yields the minimum total energy, $x$ measures the off-centering of the H atoms (see caption of Fig. 2). The results are shown in the classical nuclei limit, as well as in the quantum case both for H$_2$S and D$_2$S. The volume at which $x$ departs from zero marks the second-order phase transition from the $Im3m$ phase to $R\bar{3}m$ phase. Transition pressures are also indicated, which include the effects of vibrational energies. (b) Phase diagram for the second-order phase transition as a function of pressure. As shown in Ref. 8, below 112 GPa H$_2$S adopts a very different $C2/c$ phase. We mark the expected emergence of this phase by a box.

structure has a negligible effect on the energy difference between the $R\bar{3}m$ and $Im3m$ structures. Consequently, we assume a cubic lattice for both phases in the following.

The bond-symmetrizing second-order transition from $R\bar{3}m$ to $Im3m$ occurs at 175 GPa according to our static lattice calculations. At this pressure, our harmonic phonon calculations show that a Γ-point optical phonon of the high-symmetry $Im3m$ phase becomes imaginary, implying that $Im3m$ is at a saddle point of the BOES between 112 and 175 GPa, while the $R\bar{3}m$ phase lies at the minimum. Crystal symmetry guarantees that the transition is of second-order type (see Extended Data for a symmetry analysis). As occurs in the high-pressure ice X phase [3, 19, 20] and other hydrogenated compounds [21], the quantum nature of the proton can radically alter the pressure at which the second-order phase transition occurs and, in the present case, can strongly affect the stability of the $R\bar{3}m$ phase below 175 GPa. Determining the stability ranges of these phases therefore requires the inclusion of vibrational zero-point energy (ZPE) alongside the static BOES energy. However, the presence of imaginary phonon frequencies hinders calculations of discussed [18]. According to structural predictions [5–9], H$_2$S adopts a rhombohedral $R\bar{3}m$ form between approximately 112 and 175 GPa, and a cubic $Im3m$ at higher pressures. As shown in Fig. 1, the $R\bar{3}m$ phase is characterized by covalently bonded SH$_3$ units with a covalent H–S bond of length $d_1$. Each of these H atoms is bonded to the next S atom by a hydrogen H···S bond of length $d_2$. The $Im3m$ phase, in contrast, has full cubic symmetry, with $d_1 = d_2$ so that each H atom resides midway between the two S atoms, as shown in Fig. 1. The $R\bar{3}m$ structure is nevertheless very close to cubic symmetry, for example, the DFT-relaxed $R\bar{3}m$ structure, which represents the minimum of the Born-Oppenheimer energy surface (BOES), has a rhombohedral angle of 109.49° at ~150 GPa, compared to 109.47° for a perfect bcc lattice. We have verified that imposing a cubic angle on the $R\bar{3}m$
The ZPE, since the quasi-harmonic approximation breaks down, and anharmonicity becomes a crucial ingredient.

To elucidate the role of anharmonicity and quantum effects in the pressure range in which the record $T_c$ was observed, we make use of the stochastic self-consistent harmonic approximation (SSCHA) [22, 23]. The variational SSCHA method was devised for calculating the free energy and phonon spectra while fully incorporating quantum and anharmonic effects, and it is therefore perfectly suited for our purpose. All of the calculations presented here are performed at 0 K. Primitive cells for the $R3m$ and $Im3m$ structures contain 4 atoms (1 S atom and 3 H atoms), and therefore a particular nuclear configuration can be described by a 12-dimensional vector $\mathbf{R}$ containing the atomic coordinates. In the classical limit the ZPE is neglected and the energy of a nuclear configuration $\mathbf{R}$ is given by the DFT Born-Oppenheimer energy $E_{\text{BO}}(\mathbf{R})$. In the SSCHA, the ZPE is accounted for by approximating the nuclear wave-function by a Gaussian centered on a centroid coordinate $\mathbf{R}_c$, which denotes the average and most probable position of the nuclei. For a given $\mathbf{R}_c$, the width of the Gaussian is obtained by a variational minimization of the expectation value of the sum of the nuclear potential and kinetic energies. In the following analysis it is convenient to split the SSCHA total energy $E(\mathbf{R}_c)$ into static and anharmonic-vibrational-

ZPE contributions: $E(\mathbf{R}_c) = E_{\text{BO}}(\mathbf{R}_c) + E_{\text{vib}}(\mathbf{R}_c)$.

We study the energy landscape $E(\mathbf{R}_c)$ along the line defined by $\mathbf{R}_c(Q) = \mathbf{R}_{Im3m} + Q(\mathbf{R}_{R3m} - \mathbf{R}_{Im3m})$, where $\mathbf{R}_{Im3m}$ and $\mathbf{R}_{R3m}$ are, respectively, the coordinates corresponding to the saddle point and minimum of the BOES, representing the two different symmetries. Here, $Q$ is a real number describing the reaction coordinate, so that at $Q = 0$ the centroids are located at the atomic positions of $Im3m$, and at $Q = 1$ at the atomic positions of $R3m$. Hence, $Q$ measures the off-centering of the hydrogen nuclear wave-function and can be associated with the relative coordinate $x = (d_2 - a/2)/(a/2)$ that quantifies the length of the H⋯S hydrogen bond with respect to the symmetric position ($a$ is the lattice parameter). We analyze the curve $E(\mathbf{R}_c(Q)) = E(Q)$ for a fixed primitive bcc unit cell. As shown in Fig. 2(a) for a cell volume of 97.85$\text{a}_0^3$, the $E_{\text{BO}}(Q)$ curve has a shallow double-well structure favoring the $R3m$ structure by only 5.6 meV/H$_3$S. However, after adding the $E_{\text{vib}}(Q)$ energy calculated with the SSCHA, the full $E(Q)$ curve shows a clear minimum at $Q = 0$, which favors the $Im3m$ structure. At a larger volume of 102.11 $\text{a}_0^3$, which corresponds to a pressure of around 130 GPa, the minimum of $E(Q)$ is also at $Q = 0$, despite the fact that the one-dimensional Born-Oppenheimer well in $E_{\text{BO}}(Q)$ becomes deeper, as shown in Fig. 2(c). Repeating these calcula-

![Graph](image-url)
tions for D₃S, we find that the Im̅3m structure is the most favorable once the ZPE has been included. We therefore conclude that the quantum nature of the nuclei symmetrizes the hydrogen bond and leads to a proton wave-function centered at the atomic positions of Im̅3m for both H₃S and D₃S. To eliminate the possibility that the energy minimum occurs beyond the Rₐ(Q) line studied, we performed an unconstrained SSCHA minimization, optimizing both the width of the Gaussians and the Rₐ centroid positions. The results of this minimization show again that, within stochastic error, the centroid position obtained corresponds to the Im̅3m structure, in which the H-S covalent and H···S hydrogen bond distances equalize, leading to symmetric hydrogen bonds.

The difference between the vibrational energies of R3m and Im̅3m as a function of the x coordinate is weakly dependent on volume. This allows us to interpolate E(x) in a wide volume range and estimate the pressure at which the proton wave-function shifts away from the centered position. Our calculations show that this symmetry breaking occurs at 103 GPa in H₃S and 115 GPa in D₃S (see Fig. 3). The higher transition pressure in D₃S is due to weaker quantum effects. This isotope effect is similar to the one observed in the ice VII/ice X transition [24]. Considering that below 112 GPa the R3m phase is expected to transform into a very different C2/c phase consisting of isolated H₂S and H₂ molecules with H₃S stoichiometry [8], R3m-H₃S might not be formed. However, D₃S may adopt the R3m structure at pressures below the transition to the Im̅3m phase.

The quantum proton symmetrization has an enormous impact on the phonon spectra of H₃S. As mentioned earlier, and shown in Fig. 4, the phonon spectra of Im̅3m-H₃S have several imaginary modes in the harmonic approximation below 175 GPa. The corresponding anharmonic SSCHA phonon spectra for Im̅3m-H₃S show well-behaved phonon dispersion relations with positive frequencies in the pressure range of interest (Fig. 4). This is analogous to ice X, which has only real positive phonon frequencies once the classical limit predicts symmetrization of the hydrogen bond [25-28]. The anharmonic renormalization of the phonon energies is huge, especially for the H-S bond-stretching modes in which H atoms move towards the neighboring S atoms, which are precisely those modes which drive the second-order phase transition between the Im̅3m and R3m phases. Therefore, the proximity to the second-order quantum phase transition is the origin of the strong anharmonicity.

While the bond symmetrization in ice X occurs in an insulating system, H₃S is metallic and the symmetrization strongly affects the superconductivity. Indeed, the calculated electron-phonon coupling and superconducting Tₗ lend further support to the suggestion that Im̅3m-H₃S yields the record Tₗ. We use Wannier interpolated electron-phonon matrix elements in our calculations [29] and estimate Tₗ solving the isotropic Migdal-Eliashberg equations. The phonon frequencies and polarizations that enter the electron-phonon calculations are calculated using the SSCHA. Thus, in the present treatment we neglect non-linear corrections of the electron-phonon vertices and non-adiabatic effects that could arise from the small mass of H. The results obtained for the Im̅3m structure using anharmonic phonon frequencies agree well with experimental measurements of Tₗ for H₃S and D₃S and correctly capture the observed increase in Tₗ with decreasing pressure. We also find an isotope coefficient α = −(lnTₗ(D₃S) − lnTₗ(H₃S))/ln2 for H→D substitution of α = 0.35 at 210 GPa and α = 0.40 at 155 GPa in good agreement with experiment (see Fig. 4(c)). The electron-phonon coupling constant λ, which scales with the phonon frequencies as ∝ 1/ω², is enhanced with decreasing pressure due to the overall softening of the phonon modes. This explains the smooth decrease of Tₗ with increasing pressure. Between approximately 130 and 150 GPa the increase in λ is compensated by the decrease in the average phonon frequency and Tₗ saturates. We also present SSCHA calculations for the R3m structure keeping the centroids at the Q = 1 position. We find a rapid drop in Tₗ with decreasing pressure as in previous harmonics calculations [13]. Therefore, the observed high-Tₗ superconductivity cannot be explained by H₃S in the R3m phase, although the sudden drop in Tₗ measured for D₃S below 150 GPa [4] could be an indication of the symmetry breaking that we predicted at 115 GPa. Indeed, the predicted transition pressure depends on the choice of the exchange correlation functional (see Methods). Even if our choice of the PBE exchange-correlation functional [30] appears appropriate, based on agreement between the experimentally observed equation of state [10] and DFT calculations, we cannot exclude a small error in the transition pressure. However, the isotropic shift of the transition pressure is independent of the functional. Thus, if the drop in Tₗ observed experimentally in D₃S is due to the transition from R3m to Im̅3m, we predict that a similar drop also occurs in H₃S but is shifted to lower pressures by about 12 GPa. Considering that the Im̅3m phase has no Raman active modes, if the drop in Tₗ in D₃S coincides with the second-order phase transition, we predict that Raman peaks from the R3m phase would emerge at that pressure.

The recent experiment by Drozdov et al. [4] suggests that room-temperature superconductivity is reachable in other hydrogen-rich compounds. Our results show that in such hydrogen-rich materials with prospects for high Tₗ superconductivity the quantum motion of the proton induces non-trivial effects that strongly affect the thermodynamical stability, the hydrogen chemical bonding, and the electron-phonon coupling strength.

Online Content See Methods and Extended Data items in the online version of the paper for a symmetry analysis of the phase transition, calculations with different exchange-correlation functionals, the equations...
of state, harmonic and anharmonic phonon spectra of $Im3m$-$D_6S$, anharmonic phonon spectra of the $R3m$ phase, and superconducting properties of both the $Im3m$ and $R3m$ structures.


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**Author Contributions** I.E., M.C., and F.M. performed the anharmonic and superconducting calculations. All authors contributed to the design of the research project and to the writing of the manuscript.

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METHODS

Calculation Details  Supercell calculations for the SSCHA [22, 23] and linear response calculations [31] were performed within DFT and the generalized gradient approximation functional [30] as implemented in the QUANTUM ESPRESSO [32] code. We used ultrasoft pseudopotentials [33], a plane-wave cutoff energy of 60 Ry for the kinetic energy and 600 Ry for the charge density. The charge density and dynamical matrices were calculated using a 32×32×32 Monkhorst-Pack shifted electron-momentum grid for the unit cell calculations. This mesh was adjusted accordingly in the supercell calculations. The electron-phonon coupling was calculated by using electron and phonon momentum grids composed of up to 42×42×42 randomly displaced points in the Brillouin zone. The isotropic Migdal-Eliashberg equations were solved using 512 Matsubara frequencies and \( \mu^* = 0.16 \).

The SSCHA calculations were performed using a 3×3×3 supercell for both H\(_2\)S and D\(_2\)S in the Im3m phase, yielding dynamical matrices on a commensurate 3×3×3 q-point grid. The difference between the harmonic and anharmonic dynamical matrices in the 3×3×3 phonon momentum grid was interpolated to a 6×6×6 grid. Adding the harmonic matrices to the result, the anharmonic dynamical matrices were obtained on a 6×6×6 grid. These dynamical matrices were used for the anharmonic electron-phonon coupling calculation. The SSCHA calculations for \( Q = 1 \) were performed with a 2×2×2 supercell. For consistency, the vibrational energies presented in Fig. 2 were also calculated using a 2×2×2 supercell. The electron-phonon calculations for \( Q = 1 \) were, however, performed with the SSCHA dynamical matrices interpolated to a 6×6×6 grid from the 2×2×2 mesh.

The \( E_{\text{vib}}(Q) \) curves in Fig. 2 were obtained as follows. \( E_{\text{vib}} \) was calculated for \( Q = 0 \) and \( Q = 1 \) with the SSCHA. With the SSCHA calculation at \( Q = 1 \), we extracted \( \frac{dE_{\text{vib}}}{dQ}(Q = 1) \) with no further computational effort. Considering that the derivative of the curve at \( Q = 0 \) vanishes by symmetry, we can obtain straightforwardly a potential of the form \( E_{\text{vib}}(Q) = A + BQ^2 + CQ^4 \). The \( E_{\text{vib}} \) fit curves presented in Fig. 2 were obtained in this way. The extra point obtained at \( Q = 0.5 \) for H\(_2\)S at \( V = 97.85a_0^3 \) (see Fig. 2(a)) confirmed the validity of the fitting procedure. The \( E_{\text{BO}}(Q) \) BOES energies were calculated for many \( Q \) points yielding an accurate fitting curve. Fig. 3 was obtained using a polynomial interpolation of the BOES in the volume range and adding the \( E_{\text{vib}}^{3m} = E_{\text{vib}}^{\text{Im}3m}(x) \) curves that are practically independent of volume.

Symmetry analysis of the second-order phase transition The bond-symmetrization transition from R3m to Im3m is a second-order transition and is driven by the softening of an optical mode at \( \Gamma \). The mode driving the transition belongs to the irreducible representation \( T_{1u} \), also denoted as \( \Gamma_4^- \), whose dimension is 3 [34, 35]. This irreducible representation is compatible with a group-subgroup relation between the Im3m and R3m space groups. As the mode driving the transition is at the \( \Gamma \) point, the transition occurs without increasing the unit cell size, which contains four atoms in the primitive cell of the bcc lattice of the Im3m structure as well as in the rhombohedral lattice of the R3m phase.

In a transition from the m\(_3m\) (\( O_h \)) point group to the 3m (\( C_{3v} \)), the most general free energy expansion only contains even terms of the order parameters [36]. Therefore, according to Landau theory [11], the transition must be of second-order. Our reaction coordinate \( Q \) used to describe the second-order transition is a simplified order parameter. The fact that \( E(Q) = E(-Q) \) confirms that the transition is of second-order.

Equations of state In Extended Data Fig. 1 we present the equation of state both for the Im3m and R3m phases. The pressure is calculated both with and without the vibrational contribution to the energy, for H\(_2\)S and D\(_2\)S. The latter curves are used to include the vibrational effects on the calculated pressures. The vibrational energy calculated includes anharmonicity in all cases as calculated by the SSCHA. The vibrational energy has a small contribution to the calculated pressure, which varies slightly with the isotopic mass. The \( P(V) \) curve can be efficiently fitted to the third-order Birch-Murnaghan equation. The parameters of the fit are given in Extended Data Table I.

Dependence on the exchange-correlation functional  All calculations presented in the manuscript are calculated within the generalized gradient approximation (GGA) under the PBE parametrization [30]. However, we have performed additional calculations within the local density approximation (LDA) [37] and the BLYP [38, 39] parametrization of the GGA. The second order phase transition at the static level from Im3m to R3m, which occurs at 175 GPa within PBE, is reduced to 145 GPa in the LDA and increased to 257 GPa with the BLYP parametrization. In Extended Data Fig. 2 we compare the relative coordinate \( x = (d_2-a/2)/(a/2) \) as a function of volume, where \( d_2 \) is the length of the hydrogen bond and \( a \) is the lattice parameter. The \( x \) coordinate is obtained both with the static BOES energy \( E_{\text{BO}} \) as well as with the total energy \( E = E_{\text{BO}} + E_{\text{vib}} \). The vibrational energy is however assumed to be independent of the functional, and the value obtained with PBE is used for estimating \( E_{\text{vib}} \) for both LDA and BLYP. We believe this is justified because the differences between the vibrational energies of Im3m and R3m calculated within the SSCHA and using PBE are very weakly volume dependent as shown in Extended Data Fig. 4. At the static level, the LDA symmetrizes the structure at a pressure 30 GPa below PBE, while BLYP symmetrizes...
it at a pressure 82 GPa above PBE. When including the
vibrational contribution as described above, the transition
between \textit{Im}$\overline{3}$m and \textit{R}$\overline{3}$m occurs at 170 GPa for H$_3$S
and 185 GPa for D$_3$S within BLYP. The shift of the transi-
tion pressure induced by the zero-point energy and its
isotope dependence is similar for PBE and BLYP. The
fully symmetric \textit{Im}$\overline{3}$m H$_3$S structure is always favored
within the LDA for H$_3$S over the pressure range studied,
and it only becomes unfavorable below 89 GPa for D$_3$S.

Although the choice of exchange-correlation functional
adds some uncertainty to the predicted transition pres-
sure, we believe PBE is the most appropriate choice. This
statement is based on the fact that PBE best reproduces
the experimental equation of state results of Einaga et
al. [33]. BLYP overestimates the volume, especially when
the vibrational contribution is considered (see Extended
Data Fig. 3). Indeed, it is well known that BLYP vastly
overestimates the equilibrium volumes in metals [40] and,
therefore, it is not the best choice for H$_3$S. On the con-
try, when including the vibrational contribution to the
pressure, which is calculated in all cases using the PBE
functional, the PBE equation of state is in rather good
agreement with experimental results [10] and certainly
performs better than LDA and BLYP.

Phonons of \textit{Im}$\overline{3}$m-D$_3$S In Extended Data Fig. 5 we
show the harmonic and anharmonic phonon spectra of
D$_3$S in the \textit{Im}$\overline{3}$m phase at two different pressures.

Anharmonic phonon dispersion in the \textit{R}$\overline{3}$m
phase In Extended Data Fig. 6 we show the SSCHA
phonon spectra calculated for the \textit{R}$\overline{3}$m phase at two dif-
ferent pressures. Here the centroid position of the SS-
CHA is placed at the minimum of the BOES, which is
not a minimum of the total energy as discussed in the
manuscript. The Raman active modes of the \textit{R}$\overline{3}$m phase
are listed in Extended Data Table II.

Superconducting properties In Extended Data
Table III we summarize the calculated values of the
electron-phonon coupling constant $\lambda$, logarithmic fre-
quency average $\omega_{\log}$, and superconducting $T_c$.

In Extended Data Fig. 7 we show the Eliashberg func-
tion $\alpha^2F(\omega)$ and integrated electron-phonon coupling
constant $\lambda(\omega)$ of the \textit{Im}$\overline{3}$m phase at two different pres-
sures calculated using the SSCHA phonons. The $\alpha^2F(\omega)$
in the anharmonic case for the \textit{R}$\overline{3}$m structure is given in
Extended Data Fig. 6.

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(2008).
Extended Data Table I. Birch-Murnaghan fit to the equation of state. Parameters of the $P(V) = \frac{3}{2}B_0 \left[ (V_0/V)^{7/3} - (V_0/V)^{5/3} \right] \left[ 1 + \frac{3}{8}(B_0' - 4)(V_0/V)^{2/3} - 1 \right]$ fit to the equation of state for Im$3m$ with classical nuclei, and with vibrational contributions for both H$_3$S and D$_3$S.

<table>
<thead>
<tr>
<th></th>
<th>$B_0$ (GPa)</th>
<th>$V_0 (a_0^3)$</th>
<th>$B'_0$</th>
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<tr>
<td>Classical nuclei</td>
<td>129.8</td>
<td>158.4</td>
<td>3.6</td>
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<tr>
<td>H$_3$S</td>
<td>86.63</td>
<td>176.4</td>
<td>3.9</td>
</tr>
<tr>
<td>D$_3$S</td>
<td>87.81</td>
<td>174.8</td>
<td>3.9</td>
</tr>
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</table>

Extended Data Figure 1. Equations of state. Pressure as a function of volume calculated from the static energy $E_{BO}$ that represents the classical nuclei limit as well as including the vibrational contribution within the SSCHA for both H$_3$S and D$_3$S.
Extended Data Figure 2. **Bond symmetrization within LDA and BLYP.** For each volume the relative coordinate \( x = (d_2 - a/2)/(a/2) \), where \( d_2 \) is the length of the hydrogen bond and \( a \) is the lattice parameter, obtained at the energy minimum is marked. When \( x = 0 \) the covalent and hydrogen bond have the same length and the structure is fully symmetric. The energy is calculated at the static level without any vibrational contribution as derived from the BOES, and including the quantum anharmonic vibrational contribution both for H\(_3\)S and D\(_3\)S. The pressure below which the cubic structure distorts is given in each case.

Extended Data Figure 3. **Functional dependence of the equation of state.** The equation of state is calculated with different exchange correlation functionals with and without the vibrational contribution to the pressure. At each volume the pressure of the structure with minimum energy is given, which depends on whether or not the vibrational contribution is included (see Extended Data Fig. 2). The results are compared with the two curves obtained experimentally [10].
Extended Data Figure 4. **Vibrational energy.** SSCHA anharmonic vibrational energy calculated as a function of the relative coordinate $x = (d_2 - a/2)/(a/2)$ for different volumes.

Extended Data Figure 5. **Phonons of Im$\bar{3}m$-$D_3S$.** Comparison between the harmonic and anharmonic phonons of $Im\bar{3}m$ at two different pressures for $D_3S$. 
Extended Data Figure 6. **Anharmonic phonons of R3m-H₃S at two different pressures.** The Eliashberg functions $\alpha^2 F(\omega)$ are also shown.

Extended Data Table II. **Raman and infrared active modes.** Phonon modes at the $\Gamma$ point for the Im$\bar{3}$m and R3m phases at different pressures calculated including anharmonicity within the SSCHA. The results for R3m are obtained keeping the centroid position at the minimum of the BOES. Raman (R) and Infrared (I) activity is indicated for each mode.

<table>
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<th>Im$\bar{3}$m</th>
<th>Mode Degeneracy</th>
<th>R or I active?</th>
<th>$\omega$ (meV)</th>
<th>$H_3S$</th>
<th>$D_3S$</th>
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<td>157 GPa</td>
<td>133 GPa</td>
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<tr>
<td>$T_{1u}$</td>
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<table>
<thead>
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<th>$\omega$ (meV)</th>
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<tr>
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Extended Data Figure 7. **Superconducting properties of Im$\bar{3}$m-H₃S.** Anharmonic Eliashberg function $\alpha^2 F(\omega)$ and integrated electron-phonon coupling constant $\lambda(\omega)$ of the Im$\bar{3}$m phase at two different pressures.
Extended Data Table III. **Superconducting parameters.** Calculated $\lambda$, $\omega_{log}$ and $T_c$. The pressure given includes the vibrational contribution.

<table>
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<th>Compound</th>
<th>P (GPa)</th>
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<th>$\omega_{log}$ (meV)</th>
<th>$T_c$ (K)</th>
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