High-Pressure Hydrogen Sulfide from First Principles: A Strongly Anharmonic Phonon-Mediated Superconductor

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We use first-principles calculations to study structural, vibrational, and superconducting properties of H2S at pressures \( P \geq 200 \) GPa. The inclusion of zero-point energy leads to two different possible dissociations of H2S, namely \( 3\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{S} + \text{S} \) and \( 5\text{H}_2\text{S} \rightarrow 3\text{H}_2\text{S} + \text{HS}_2 \), where both \( \text{H}_2\text{S} \) and \( \text{HS}_2 \) are metallic. For \( \text{H}_2\text{S} \), we perform nonperturbative calculations of anharmonic effects within the self-consistent harmonic approximation and show that the harmonic approximation strongly overestimates the electron-phonon interaction (\( \lambda \approx 2.64 \) at 200 GPa) and \( T_c \). Anharmonicity hardens H–S bond-stretching modes and softens H–S bond-bending modes. As a result, the electron-phonon coupling is suppressed by 30% (\( \lambda \approx 1.84 \) at 200 GPa). Moreover, while at the harmonic level \( T_c \) decreases with increasing pressure, the inclusion of anharmonicity leads to a \( T_c \) that is almost independent of pressure. High-pressure hydrogen sulfide is a strongly anharmonic superconductor.

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Cuprates [1] have for many years held the world record for the highest superconducting critical temperature \( (T_c = 133 \text{ K}) \) [2]. However, despite almost 30 years of intensive research, the physical mechanism responsible for such a high \( T_c \) is still elusive, although the general consensus is that it is highly nonconventional. The measurements by Drozdov et al. [3] which suggest a 190 K superconducting phase in hydrogen sulfide under high pressure (200 GPa), could break the cuprates record, if confirmed.

The claim that hydrogen at high pressure could be superconducting is not new [4] and it was recently supported by first-principles calculations based on the harmonic approximation applied to dense hydrogen [5–8] and several hydrides [9–15]. More recently, two theoretical papers predicted the occurrence of high-\( T_c \) superconductivity in high-pressure sulfur hydrides [16,17]. However, as shown in Refs. [18,19], anharmonicity can be crucial in these systems. For example, in PdH, the electron-phonon coupling \( \lambda \) parameter is found to be 1.55 at the harmonic level, while a proper inclusion of anharmonic effects leads to \( \lambda = 0.40 \) [18], in better agreement with experiments. Thus, in hydrogen-based compounds, the phonon spectra are strongly affected by anharmonic effects.

Given the sensitivity of superconductivity to the physical and electronic structures, it is extremely important to identify the correct crystal structures (see, for example, the early discussion of superconductivity in silane in Ref. [15], and one of the first applications of first-principles structure prediction in Ref. [20]). Several first-principles calculations [16,17,21–23] suggested that decomposition of the \( \text{H}_2\text{S} \) sample occurs within the diamond-anvil cell at high pressures. The high-\( T_c \) superconducting material is therefore very unlikely to be \( \text{H}_2\text{S} \), while \( \text{H}_2\text{S} \) is the obvious candidate for the H-rich decomposition product.

Here we study the structural, vibrational, and superconducting properties of \( \text{H}_2\text{S} \) above 200 GPa, where the highest \( T_c \) occurs. We show that the inclusion of zero-point motion in the convex hull at 200 and 250 GPa stabilizes two metallic structures, \( \text{H}_2\text{S} \) and \( \text{HS}_2 \). Finally, we show that, contrary to suggestions in previous work [16,21], the harmonic approximation does not explain the measured \( T_c \) in \( \text{H}_2\text{S} \), and the inclusion of anharmonic effects is crucial.

As decomposition of \( \text{H}_2\text{S} \) has been demonstrated in the experiments of Ref. [3], it is crucial to develop an understanding of the different H–S compounds that might be stable in the pressure range of interest. We therefore perform a search over 44 H:S stoichiometries, determining the stoichiometries at which stable structures exist, and the associated crystal structures. These searches were performed with the \textit{ab initio} random structure searching...
energetically allowed decomposition is at 200 GPa, without zero-point energy (ZPE), the only possible at 200 GPa, namely $\text{HS} \rightarrow 2\text{H}_3\text{S} + \text{S}_2$. When ZPE is included, a second decomposition becomes possible at 200 GPa, namely $5\text{H}_2\text{S} \rightarrow 3\text{H}_3\text{S} + \text{HS}_2$, where $\text{HS}_2$ crystallizes in a structure of space group $\text{Im} \bar{3} \text{m}$, as shown in Ref. [16]. When ZPE is included, a second decomposition becomes possible at 200 GPa, namely $5\text{H}_2\text{S} \rightarrow 3\text{H}_3\text{S} + \text{HS}_2$, where $\text{HS}_2$ crystallizes in a structure of space group $\text{C} 2/c$ with 12 atoms/cell. At 250 GPa and above, the latter decomposition is allowed even without ZPE, and the $\text{C} 2/c\text{HS}_2$ structure undergoes a phase transition to a more stable $\text{C} 2/m$ structure with 6 atoms/cell. Each of the $\text{HS}_2$ structures is metallic. Finally, at 300 GPa, a metallic HS phase with $\text{C} 2/m$ space group becomes stable [30]. Detailed information on the crystal structures is provided in the Supplemental Material [30].

Having determined the most stable crystal structures at high pressure, we turn to the study of vibrational properties [35,36]. As summarized in Table I, the superconducting $T_c$ values obtained within the harmonic approximation for the $\text{C} 2/c\text{HS}_2$, $\text{C} 2/m\text{HS}_2$, and $\text{C} 2/m\text{HS}$ phases are in the range of 15 to 35 K (see Supplemental Material [30] for phonon spectra and details of the calculations), far from the observed extraordinary values. The measured $T_c$’s could not have occurred in any of these phases. Thus, we focus on the $\text{Im} \bar{3} \text{m}$ $\text{H}_3\text{S}$ structure. In this structure, each H atom is twofold coordinated and has 6 neighbors, 2 of which are S atoms while the other 4 are H atoms. The H vibrations can then be decomposed into $\text{H}–\text{S}$ bond-stretching modes ($\text{H}_||$), in which an H atom moves toward one of the two S atoms, and bond-bending modes ($\text{H}_\perp$), in which one H atom moves in the direction perpendicular to the $\text{H}–\text{S}$ bond (see FIG. 2 (color online). Phonon dispersion, phonon density of states projected onto selected atoms and directions, and the Eliashberg function of $\text{H}_3\text{S}$ in the harmonic approximation (top) and with the inclusion of anharmonic effects (bottom) for $\text{H}_3\text{S}$ at 200 GPa. $\text{H}_\perp$ and $\text{H}_||$ label displacements of an H atom in the directions perpendicular or parallel to a $\text{H}–\text{S}$ bond. The magnitude of the phonon linewidth is indicated by the size of the red error bars.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$P$ (GPa)</th>
<th>$\lambda$ (meV) $\omega_{\text{log}}$</th>
<th>$T_c^{0.10}$ (K)</th>
<th>$T_c^{0.16}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C} 2/c\text{HS}_2$</td>
<td>200</td>
<td>0.86</td>
<td>56.7</td>
<td>35.3</td>
</tr>
<tr>
<td>$\text{C} 2/m\text{HS}_2$</td>
<td>250</td>
<td>0.75</td>
<td>53.8</td>
<td>25.1</td>
</tr>
<tr>
<td>$\text{C} 2/m\text{HS}$</td>
<td>300</td>
<td>0.78</td>
<td>74.3</td>
<td>38.0</td>
</tr>
</tbody>
</table>

FIG. 1 (color online). Results of structure searching at 200 and 250 GPa. Convex hulls are shown as continuous lines, with and without the inclusion of zero-point energy (ZPE).
Fig. 1 in the Supplemental Material [30]). The harmonic phonon spectrum of H$_2$S at 200 GPa [39] is shown in Fig. 2 and overall shows a clear separation into H modes at high energy and S modes below 75 meV. To gain more insight, we use Wannier interpolation [40,41] of the electron-phonon matrix elements and evaluate the electron-phonon contribution to the phonon linewidth as [42]

$$\gamma_{\mathbf{q}w} = \frac{4\pi\omega_{\mathbf{q}w}}{N_k} \sum_{k,n,m} |g_{nm}^+(\mathbf{k}, \mathbf{k} + \mathbf{q})|^2 \delta(\epsilon_{kn}) \delta(\epsilon_{k+\mathbf{q}m}).$$  (1)

Here, $\omega_{\mathbf{q}w}$ are the phonon frequencies, $N_k$ the number of electron-momentum points in the grid, $g_{nm}^+(\mathbf{k}, \mathbf{k} + \mathbf{q}) = \langle \mathbf{k}n|V_{\text{KS}}|\mathbf{k} + \mathbf{q}m \rangle$ is the electron-phonon matrix element, $V_{\text{KS}}$ is the Kohn-Sham potential, and $u_{\mathbf{q}w}$ is a phonon displacement. The Kohn-Sham energy and eigenfunctions are labeled $\epsilon_{kn}$ and $|\mathbf{k}n\rangle$. The electron-phonon coupling at a given phonon-momentum $\mathbf{q}$ for a phonon mode $\nu$ can be obtained [42] from the phonon linewidth as $\lambda_{\mathbf{q}w} = \gamma_{\mathbf{q}w}/(2\pi\omega_{\mathbf{q}w}N(0))$.

As shown in Fig. 2, at the harmonic level, the phonon linewidths of the H vibrations are fairly uniform throughout the spectrum. The contribution of each mode to the average electron-phonon interaction, $\lambda = \sum_i \lambda_{\mathbf{q}w}/N_q$, can be obtained from the isotropic Eliashberg function,

$$\alpha^2 F(\omega) = \frac{1}{2N_q} \sum_{\mathbf{q}w} \lambda_{\mathbf{q}w} \omega_{\mathbf{q}w} \delta(\omega - \omega_{\mathbf{q}w}).$$  (2)

where $N_q$ is the number of phonon-momentum points in the grid. $\lambda(\omega) = \int_0^\infty [\alpha^2 F(\omega')/\omega']d\omega'$ and then $\lambda$ is obtained (see Table II). (see Table II), which is larger than that obtained in Refs. [16,21] with a much coarser sampling of the BZ, but consistent with the result in Ref. [22]. This huge value of $\lambda$ comprises substantial contributions from many H vibrational modes. The situation is therefore very different from MgB$_2$ in which a single mode dominates $\lambda$.

Given the low mass of H and the consequent large phonon displacements, we investigate the occurrence of anharmonic effects using the stochastic self-consistent harmonic approximation (SSCHA) developed by some of us [18,19,43]. As shown in Fig. 2 (bottom), the anharmonic correction leads to nontrivial changes in the harmonic spectrum. While it is very clear that all H bond-stretching modes are hardened, the effect on H bond-bending modes is less straightforward. By computing the average phonon frequency as of H$_2$ and of H$_3$ modes, we find that $\bar{\omega}_{\parallel}^{\text{anh}} \approx 158.1$ meV and $\bar{\omega}_{\perp}^{\text{anh}} \approx 203.3$ meV, while for bond-bending modes $\bar{\omega}_{\parallel}^{\text{anh}} \approx 157.0$ meV and $\bar{\omega}_{\perp}^{\text{anh}} \approx 147.9$ meV. Thus bond-stretching modes are hardened, while bond-bending modes are softened.

It is important to remark that the large and most dispersive mode along PT is strongly hardened at the anharmonic level and undergoes a nontrivial change in polarization, as can be seen from the large effect of anharmonicity on the phonon linewidth $\gamma_{\mathbf{q}w}$ in Fig. 2. It is worthwhile recalling that the phonon linewidth depends on the phonon eigenvector but not on the phonon energy. This effect demonstrates the need to calculate not only the phonon frequencies at the anharmonic level, but also the phonon polarizations.

The anharmonic electron-phonon interaction is $\lambda = 1.84$, which is 30% smaller than the harmonic result. This reduction is mostly explained by the hardening of the H$_3$ modes. In contrast to the harmonic case, which shows uniform coupling over all modes, the anharmonic Eliashberg function has two main peaks, a broad peak in the 40–75 meV region, and a second one in the 175–200 meV region. Their contributions to $\lambda$ are 0.59 and 0.77, respectively, accounting for $\approx 73\%$ of the total $\lambda$. We note, however, that the logarithmic average of the phonon frequencies $\omega_{\text{log}}$ is only weakly enhanced by anharmonicity (see Table II).

The superconducting critical temperature can be obtained either from the McMillan equation or the isotropic Migdal-Eliashberg approach. However, it is well known [44] that the use of the McMillan equation for such values of $\lambda$ leads to a substantial underestimation of $T_c$. We solved the isotropic Eliashberg equations (see the Supplemental Material [30]) and found, contrary to claims in previous publications [16,21], that calculations based on the harmonic phonon spectrum do not explain the measured $T_c$ as, even using large values of $\mu^*$ [45,46], $T_c$ is substantially overestimated (i.e., $T_c = 250$ K for $\mu^* = 0.16$ [30]). When the anharmonic phonon spectrum and electron-phonon coupling are used, the Migdal-Eliashberg equations account for the experimental $T_c$ when the value $\mu^* = 0.16$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda^{\text{bar}}$</th>
<th>$\omega_{\parallel}^{\text{bar}}$</th>
<th>$\lambda^{\text{anh}}$</th>
<th>$\omega_{\parallel}^{\text{anh}}$</th>
<th>$T_c^{\text{M.E.,har}}$</th>
<th>$T_c^{\text{M.E.,anh}}$</th>
<th>$T_c$ (expt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S (200 GPa)</td>
<td>2.64</td>
<td>90.4</td>
<td>1.84</td>
<td>92.86</td>
<td>250</td>
<td>194.0</td>
<td>190</td>
</tr>
<tr>
<td>H$_2$S (250 GPa)</td>
<td>1.96</td>
<td>109.1</td>
<td>1.71</td>
<td>101.3</td>
<td>226</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>D$_3$S (200 GPa)</td>
<td>2.64</td>
<td>68.5</td>
<td>1.87</td>
<td>73.3</td>
<td>183</td>
<td>152.0</td>
<td>90</td>
</tr>
</tbody>
</table>
is used, as shown in Table II. The superconducting gap at zero temperature is $\Delta \approx 36.5$ meV. By using the smaller value of $\mu' = 0.1$, we obtain $T_c = 222$ K and $\Delta \approx 43$ meV.

Interestingly, the large anharmonic effects lead to very different variations in $T_c$ with pressure. By performing the harmonic electron-phonon calculation for the $\text{Im} \bar{\delta}m$ structure at 250 GPa and using the Migdal-Eliashberg equations with $\mu' = 0.16$ we found $T_c = 226$ K, decreasing with increasing pressure. However, at the anharmonic level, we find $T_c = 190$ K, essentially independent of pressure in the region 200–250 GPa.

Finally, we consider the extent to which the occurrence of large anharmonic effects can explain the isotope shift in D\text{ }2\text{ }S. At 164 GPa, $T_c(D_2S) = 90$ K, leading to an isotope coefficient $\alpha \approx 1.07$, which is substantially enhanced from the canonical BCS value of $\alpha \approx 0.5$. Assuming a similar decomposition of D\text{ }2\text{ }S into D\text{ }3\text{ }S and S at high pressures, we calculate the anharmonic phonon spectrum (see the Supplemental Material [30]) and electron-phonon coupling in D\text{ }2\text{ }S at 200 GPa. We find at the anharmonic level that the electron-phonon coupling is essentially unaffected, while $\omega_{\text{log}}$ is softened from 92.9 meV to 73.3 meV, leading to an isotope coefficient of $\alpha = 0.35$, which is strongly reduced from the BCS value. Thus, contrary to the claim made in Ref. [47], anharmonicity reduces $\alpha$. As long as the same crystal structure for H\text{ }2\text{ }S and D\text{ }2\text{ }S is considered, as predicted by our calculation, the theoretical isotope coefficient remains inconsistent with the value of $\alpha \approx 1.07$ found in experiments. This disagreement could be reconciled if in experiment kinetics stabilize different structures for hydrides and deuterides at a given pressure. More experimental data are necessary to clarify this issue.

We have studied the structural, vibrational, and superconducting properties of high-pressure H\text{ }2\text{ }S. We have included zero-point motion when comparing the stabilities of different H-S phases, which has been neglected in other publications so far. This is important because zero-point motion stabilizes a new phase at $P \geq 200$ GPa. In particular, we found that decomposition of HS\text{ }2\text{ } into metallic phases can occur following two main paths, namely $3\text{H}_2\text{S} \rightarrow 2\text{H}_3\text{S} + S$ and $5\text{H}_2\text{S} \rightarrow 3\text{H}_3\text{S} + \text{HS}_2$. We have performed a detailed study of the vibrational properties of high-pressure H\text{ }2\text{ }S and D\text{ }2\text{ }S, finding that the phonon spectra are strongly affected by anharmonic effects. Anharmonicity hardens H–S bond-stretching modes and softens H–S bond-bending modes. Moreover, anharmonicity leads to a reduction in the electron-phonon coupling by $\approx 30\%$ and to an approximately constant $T_c$ in the range 200–250 GPa. Our work demonstrates that the superconducting properties of high-pressure H\text{ }2\text{ }S can only be properly described by including both nuclear quantum effects and anharmonicity.

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Our superconductivity results were obtained from first-principles DFT linear-response calculations as implemented in the QUANTUM-ESPRESSO [35] package. We used ultrasoft pseudopotentials, a generalized gradient approximation [38], a plane-wave cutoff energy of 60 Ry on the kinetic energy and 600 Ry on the charge density. The charge density and dynamical matrices were calculated using a $3\times3$ Monkhorst-Pack shifted electron-momentum grid and a Hermitian-Gaussian smearing of 0.03 Ry. The average electron-phonon coupling was obtained using Wannier interpolation [40]. We used a $3\times3$ electron-momentum grid randomly shifted from the origin and a $3\times3$ Monkhorst-Pack shifted phonon-momentum grid with a smearing of 0.03 eV. The phonon linewidth at a given phonon momentum was calculated using a $50 \times 50 \times 50$ electron-momentum mesh (randomly shifted from the origin).

[39] The pressure computed here is without inclusion of ZPE. Neglecting ZPE underestimates the pressure of $\approx 12$ GPa for $H_2S$ and 6 GPa for $D_2S$ for a volume of 89.9822 (a.u.)$^3$. See the Supplemental Material [30] for more details.
[43] The SSCHA calculations were performed using a $3 \times 3 \times 3$ supercell for both $H_2S$ and $D_2S$ at 0 K, yielding dynamical matrices on a commensurate $3 \times 3 \times 3$ $q$-point grid. An additional calculation at 200 K confirmed that temperatures within the range of the predicted superconductivity do not affect the phonon spectra. The difference between the harmonic and anharmonic dynamical matrices in the $3 \times 3 \times 3$ phonon-momentum grid was interpolated to a $6 \times 6 \times 6$ grid. Adding the harmonic matrices to the result, the anharmonic dynamical matrices were obtained in a $6 \times 6 \times 6$ grid. These dynamical matrices were used for the anharmonic electron-phonon coupling calculation.