High-$T_c$ superconductivity in H$_3$S: pressure effects on the superconducting critical temperature and Cooper pair distribution function

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Abstract

We use first-principles calculations to study the effects of pressure on the vibrational and superconducting properties of H$_3$S in the cubic $I\overline{m}3m$ phase for the pressure range where the superconducting critical temperature ($T_c$) was measured (155–225 GPa). The pressure effects were incorporated using the functional derivative method (FDM). In this paper we present for the first time the Cooper pair distribution functions $D_{cp}(\omega, T_c)$ for H$_3$S, which will allow us to identify the spectral regions where Cooper pair formation at temperature $T_c$ is more favorable. We analyze in detail the effects of pressure on the electron–phonon spectral density function $\alpha^2 F(\omega)$ and the phonon density of states and their relationship with $T_c$. The FDM manages to reproduce the trend of the pressure dependence of critical temperature, in good agreement with experimental data in the range of 155 to 190 GPa. $D_{cp}(\omega, T_c)$ suggests that the low-frequency vibration region is where Cooper pairs are possible, which means that S-vibrations have an important role in the superconductivity properties of H$_3$S.

Keywords: ab initio calculations, pressure effects, critical temperature, Cooper pairs

(Some figures may appear in colour only in the online journal)

Introduction

The effects of high pressures on the superconducting properties of sulfur hydrides have been an important topic of study and discussion in recent years, even more so when in 2015 one such hydride (H$_3$S) achieved the record experimental superconducting critical temperature ($T_c$) of 203 K at 155 GPa, as reported by Drozdov et al [1]. Experimentally, it was confirmed that the superconducting behavior of the H$_3$S originates from electron–phonon interactions [2]. In electron–phonon superconductors, pressure affects the vibration spectrum and electron–phonon interaction by shifting it to higher frequencies, which can enhance or lower the critical temperature depending on details of the system under study [3]. This has been evidenced by several experimental works [4–12]. In H$_3$S, $T_c$ decreases when the pressure is increased [1].

The relationship between $T_c$ and pressure in H$_3$S with the cubic $I\overline{m}3m$ structure has been explored theoretically in the framework of the Migdal–Eliashberg theory (MET) using different approximations; the Allen–Dynes equation [13], the Allen–Dynes-modified McMillan equation with self-consistent harmonic and anharmonic approximations (SSCHA) [14, 15], the isotropic Migdal–Eliashberg equations [13] for stable isotopes [16] and density functional theory for superconductors (SCDFT) [17], including screened Coulomb repulsion via the random-phase approximation (RPA) [18]. In some cases these theoretical results seem to reproduce the experimental ones; however, there is no consensus on the
method for estimating both the tendency and measured \( T_c \) values.

From electronic and vibrational spectral properties obtained by first-principles calculations for a superconductor material, and taking into account the nature of Cooper pairs, González-Pedreros et al [19] recently reported a novel method to determine the Cooper pair distribution function \( D_{cp}(\omega, T_c) \), which seeks to find the vibrational energy \( \omega \) regions where Cooper pair formation at temperature \( T_c \) is more favorable. The \( D_{cp}(\omega, T_c) \) function is given by

\[
D_{cp}(\omega, T_c) = \int_{\omega - \omega_s}^{\omega + \omega_s} \int_{-\omega_s}^{\omega_s} g_{cp}^{h}(\epsilon', \omega, T_c) g_{cp}^{s}(\epsilon, \omega, T_c) d\epsilon d\epsilon'.
\]  

Here, \( g_{cp}^{h}(\epsilon, \omega, T_c) \) is the probability at \( T_c \) that: (i) one electron is in energy state \( \epsilon \) and a second one is in energy state \( \epsilon' + \omega \); (ii) there are two empty electronic energy states \( \epsilon + \omega \) and \( \epsilon' \); (iii) two electrons are coupled to a phonon with energy \( \omega \); (iv) there is a vibrational energy state \( \omega \) and (v) an additional vibrational energy state \( \omega' \) and (vi) the electrons couple with a phonon, \( \alpha^2(\omega) \). The calculation contains the contribution of all the electrons in the energy interval \( \pm \omega_s \) around the Fermi level \( (E_F \pm \omega_s) \). For more details see [19].

In this paper, we report a theoretical study of the effects of pressure on the conventional superconductor \( H_3S \) by first-principles calculations for the pressure range where \( T_c \) was measured \((155–225 \text{ GPa})\). The effects of pressure on \( T_c \) are incorporated using the functional derivative method (FDM) [3]. \( D_{cp}(\omega, T_c) \) is determined following the procedure proposed by González-Pedreros et al [19]. Overall, our results agree very well with the experimental tendency and the calculated \( D_{cp}(\omega, T_c) \) allowed us to identify the vibrational energy intervals where Cooper pairs are possible for \( H_3S \).

**Method of calculation**

The lattice dynamics, phonon densities of states (PhDOS) and Eliashberg function \( ^2F(\omega) \) are calculated using the first-principle pseudopotential plane-wave method based on density functional theory and the density functional perturbation theory as implemented in the Quantum-Espresso package [20]. We used a 70 Ry cut-off for the plane-wave basis. To integrate over the Brillouin zone (BZ), we used the electronic integration a \( k \)-grid of \( 24 \times 24 \times 24 \) and to compute phonon frequencies a \( q \)-grid of \( 8 \times 8 \times 8 \), according to the Monkhorst–Pack scheme [21]. We adopted the Vanderbilt ultrasoft pseudopotential [22] and a generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof type (PBE) for the exchange–correlation energy functional [23]. In this work, the pressure effects were investigated in the range where the high \( T_c \) was measured \((155–225 \text{ GPa}) \) [1].

The stable structures of the \( Im3m \) \( H_3S \) for each pressure are obtained relaxing the internal and external degrees of freedom using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newtonian algorithm. This body-centered cubic structure, which reveals the superconducting phase in the pressure range \( 155–225 \text{ GPa} \), was confirmed by x-ray diffraction experiments \((150 \text{ GPa}) \) [24]. The Coulomb pseudopotential \( \mu^* \) at each pressure was calculated following the procedure suggested by Daams et al [25].

The effects of pressure on \( T_c \) were calculated by means of the FDM [3], based on ideas from Rainer and Bergman [26], calculating \( \Delta T_c \) from

\[
\Delta T_c = \int_0^\infty \frac{\delta T_c}{\delta \alpha^2 F(\omega)} \left|_{H_c} \right. \Delta \alpha^2 F(\omega),
\]

where \( \Delta \alpha^2 F(\omega) = \alpha^2 F(\omega, P_{i+1}) - \alpha^2 F(\omega, P_i) \). For more details see [3].

**Results and discussion**

The calculated lattice parameters as a function of pressure and their comparison with other theoretical predictions [16, 27, 28] are shown in figure 1. It is observed that our results agree well with previous theoretical reports. In general, these predictions have a difference of around 0.06 A from the experimental value at 150 GPa [24]. A fit of the Birch–Murnaghan equation (BME) [29] to our data points gives the zero-pressure bulk modulus \( B_0 = 85.76 \text{ GPa} \) and zero-pressure derivative of the bulk modulus \( B'_0 = 3.9 \), which are in good agreement with the values fitted to the experimental data reported by Errea et al [14].

The Eliashberg spectral function \( ^2F(\omega) \) and the PhDOS calculated at different pressures are shown in figure 2. We do not observe any imaginary frequency vibrations in our calculation, which confirms the dynamic stability of \( Im3m \) structure in this pressure range.
It is observed that pressure induces a progressive decrease of the area under the $\alpha^2 F(\omega)$ spectrum, mainly in the range of 10–90 meV, and an almost rigid displacement of the $\alpha^2 F(\omega)$ and PhDOS spectra toward higher frequencies (hardening), from frequencies greater than 75.4 meV. At 195 GPa the $\alpha^2 F(\omega)$ and PhDOS spectra show a significant decrease in their spectral contributions around 75.4 meV, which entails a gap ($\sim$16 meV) in both spectra at 225 GPa. This gap implies a reduction of the contribution of vibrational modes to the electron–phonon coupling constant ($\lambda$) and, therefore, of the effect on $T_c$.

The total shifting of the $\alpha^2 F(\omega)$ and PhDOS spectra induced by pressure (155–225 GPa) reaches $\sim$49 meV. However, this shifting at frequencies below 75 meV is no greater than $\sim$3.0 meV. The $\alpha^2 F(\omega)$ spectrum at 155 GPa reveals a small peak at 21.4 meV, which is not observed at higher pressures in either this or other works. Nevertheless, a similar peak can be observed in calculations using the stable S isotopes $^{33}$S and $^{34}$S at 155 GPa [16]. So, this peak seems to be related to a specific vibrational frequency of the S atom which disappears with increasing pressure. Although it does not show a great intensity, it is a particular behavior of the low-frequency vibration region at 155 GPa which ends up contributing to the high $T_c$. We do not find other theoretical results at 155 GPa that allow us to compare this behavior except for the one already mentioned.

On the other hand, it is observed that the increase in pressure induces a decrease in $\lambda$. It is important to note that a high value of $\lambda$ implies a high value of $T_c$.

Figure 3 shows the pressure dependence of measured $T_c$ [1] and the $T_c$ calculated in this work using the FDM and a comparison with previous theoretical reports [13–18]. Overall, the FDM manages to reproduce the trend established by the experimental results reported by Drozdov et al [1]. Our calculations show a $dT_c/dP = -1.0$ K GPa$^{-1}$ which is slightly greater than the experimental value ($dT_c/dP = -0.4$). The negative sign implies a reduction of the adequate physical conditions that induced a high $T_c$. The projected PhDOS reported in the literature for H$_3$S [15, 16, 27, 31] show that the low-frequency vibration region (below 70 meV) is due mainly to the vibrations of the S atom. According to this and our calculations, we suggest two possible conditions that reduce $T_c$: the decrease in the spectral contribution of electron–phonon coupling at low-frequency vibrational modes (S atoms) and a slight hardening of high-frequency vibration modes of H atoms. In relation to this, Amsler [31] and Flores-Livas et al [18] reported that when Se atoms are included in H$_3$S the contribution of S atoms to the PhDOS spectrum (in the low-frequency vibration region) decreases and consequently $T_c$ decreases. It is evident that S atoms play a relevant role in the high $T_c$ of H$_3$S.

Our $T_c$ values are in good agreement with experimental ones in the range of 155–190 GPa, lying within the 95% confidence band (155–175 GPa). For pressures greater than 190 GPa our results are outside the 95% band prediction. We suggest that the discrepancy at high pressures could be due to anharmonic and screened Coulomb repulsion effects not being included; their inclusion has produced acceptable $T_c$ values in other works [14, 15, 18]. Concerning other works, it...
is observed that the calculations reported by Szczęśniak et al [16], Flores-Livas et al [18] and Errea et al [15] show a $dT_c/dp \sim -0.4$, in excellent agreement with the experimental trend. However, some of their values are outside the experimental range. Errea et al propose that the inclusion of anharmonic effects is crucial for explaining the measured $T_c$.

However, the results reported by Nakanishi et al [13], which included these effects, did not reproduce the experimental trend. The $T_c(p)$ calculations using SCDFT reported by Akashi et al [17] show the greatest discrepancies with the experiment both in values and trends. However, Flores-Livas et al [18], using the same method but including screened Coulomb repulsion effects [15], obtained good results in the range 180–200 GPa.

We note that obtaining a good agreement for a specific value of $T_c$ does not necessarily imply an adequate reproduction of the experimentally observed tendency, as is the case with the results reported by Nakanishi et al [13]: using the Allen–Dynes equation they calculated a $T_c$ of 186 K at 200 GPa, in excellent agreement with the experiment, but their data reveal a positive $dT_c/dp$, in contradiction with the experimental behavior. They reported a $T_c$ value at 150 GPa that was 19 K below the experimental one.

An important number of theoretical calculations of $T_c$ at 200 GPa have been reported in the literature; values oscillate between 180 and 284 K [13, 15, 16, 18, 27, 32, 31, 33–37], some of them [13, 16, 18, 31, 34, 35] within the experimental range (160–192 K). In our case, the FDM determined a value (extrapolated) at 200 GPa of 155.4 K, which is 4.6 K below the experimental range.

In figure 4(a) the Cooper pair distribution functions $D_{cp}(\omega, T_c)$ of H$_3$S calculated at different pressures are presented. In general, it is observed that the system reveals the existence of possible Cooper pairs only in the frequency range from 10 to 80 meV, which is a surprising result since it significantly limits the analysis of the contribution of higher frequencies to the $\alpha^2F(\omega)$ and PhDOS spectrum in the interpretation of the physical mechanisms that induce the superconducting state and respective $T_c$. With respect to the effects of pressure, for frequencies higher than $\sim$44 meV $D_{cp}(\omega, T_c)$ shows a shift (not rigid) to the right and there is a progressive decrease of the area under the curve of the respective $D_{cp}(\omega, T_c)$ function.

As seen above in the PhDOS spectrum (see figure 2) the $D_{cp}(\omega, T_c)$ function makes an important contribution at 44.9 meV: due to the effects of pressure it is weakly displaced ($\sim$1 meV) towards higher energies. As in the $\alpha^2F(\omega)$ spectrum, only the $D_{cp}(\omega, T_c)$ calculated at 155 GPa reveals a peak at 21.4 meV. The contribution of this peak could be one of the differentiating factors that induces in H$_3$S the mechanisms to achieve the highest $T_c$. In the range 25–44 meV an increase in area under the curve is observed, as opposed to the decrease in $T_c$ with the increase in pressure.

In figure 4(b) details of the range 0–85 meV for the $\alpha^2F(\omega)$ and PhDOS spectra calculated at different pressures are shown. The $\alpha^2F(\omega)$ and PhDOS spectra both reveal a peak at 21.4 meV only at 155 GPa. It is evident that the pressure induces a considerable decrease of the area under the $\alpha^2F(\omega)$ spectrum with respect to that at 155 GPa. This decrease can be directly related to the decrease in $T_c$. At energies greater than 50 meV the PhDOS show a quasi-rigid shift to the right.

Electrons in a Cooper pair demand occupied and vacant states near the Fermi level and they move between these states by electron–phonon interaction. The energy proximity between $s$ and $p$ orbitals in H$_3$S [38] and their contribution to the Fermi level [16] are among the conditions that electrons require in a Cooper pair. $D_{cp}$ functions for H$_3$S show that the Cooper pair phonon energy lies in the 10–80 meV interval (the $D_{sp}$ region), and the main phonon energy contribution to Cooper pair formation is at $\omega_{sp}$ $\sim$ 44.9 meV at all pressures. According to pressure increases, the $\alpha^2F(\omega)$ spectrum (in the $D_{cp}$ region) decreases significantly in
intensity and moves to slightly higher frequencies, then the conditions for Cooper pair formation weaken and $T_c$ falls.

The projected PhDOS reported in [15, 16, 37] below 70 meV show the vibrational modes both of S and H atoms (see figure 4 in [16]). This suggests that $\text{H}_3\text{S}$ superconductivity is established by electrons of S $s$, S $p$ and H $s$ orbitals that interact with phonons in the $D_{cp}$ region, where S vibrations mainly contribute; however, H vibrations make an important contribution. The physical mechanism underlying the relationship between high-temperature superconductivity of $\text{H}_3\text{S}$ and pressure is metallization of covalent bonds [38]; however, when the pressure is increased electron–electron interactions become stronger, whereby $T_c$ decreases.

The electron–phonon coupling constant $\lambda$ as a function of pressure and $T_c$ as a function of $\lambda$ are presented in figure 5.

It is observed in figure 5(a) that an increase in pressure induces a non-linear decrease of $\lambda$, which is more significant in the pressure range 155–175 GPa where the decrease of the area under the $\alpha^2 F(\omega)$ spectrum at low frequencies (associated mainly with the S atom) is considerably greater (see figure 2). Flores-Livas et al. [18] and Nakanishi et al. [13] showed a similar tendency but $\lambda$ does not decrease as quickly with increasing pressure as in our case. The $\lambda$ values reported by Akashi et al. [17] show the opposite behavior to our results. In most cases, for $T_c(\lambda)$ we found that a strong $\lambda$ induces a high $T_c$ (figure 5(b)). A $\lambda$ value around 2.6 leads to a high $T_c$ for $\text{H}_3\text{S}$. The correlation between $T_c$ and $\lambda$ is in accordance with the Migdal–Eliashberg theory [39].

Conclusions

In this work, we present a theoretical study of the effects of pressure on high-$T_c$ superconductivity in the conventional superconductor $\text{H}_3\text{S}$ (lm$^{3m}$). The effects of pressure on $T_c$ were incorporated using the FDM. We present for the first time the Cooper pair distribution function, $D_{cp}(\omega, T_c)$, calculated for $\text{H}_3\text{S}$, following the procedure proposed by González-Pedreros et al. [19].

We found that pressure induces a decrease of the area under the $\alpha^2 F(\omega)$ spectrum, mainly in the range of 10 to 90 meV. From frequencies greater than 75.4 meV an almost rigid displacement of the $\alpha^2 F(\omega)$ spectrum and PhDOS toward higher frequencies is also observed. A small peak at 21.4 meV related to vibrational frequencies of S atom is only observed at 155 GPa, which generate a small contributions to reaching the high $T_c$ of 203 K. As a first idea, we suggest two possible conditions that reduce $T_c$ under the effects of pressure in $\text{H}_3\text{S}$: a decrease in the spectral contribution of electron–phonon coupling at low-frequency vibrational modes (S atoms) and slight hardening of the high-frequency vibration modes of H atoms. S atoms end up playing an important role in the high $T_c$ reached at 155 GPa in $\text{H}_3\text{S}$.

The FDM manages to reproduce the trend in $T_c(P)$ established by experimental results. Our $T_c$ calculations are in good agreement with experimental data in the range of 155–190 GPa. The discrepancy at high pressures (190–225 GPa) could be because anharmonic and screened Coulomb repulsion effects are not included (their inclusion has shown acceptable $T_c$ values in other works; this idea will be studied in our next research).

The $D_{cp}(\omega, T_c)$ values reveal that the 10–80 meV energy interval ($D_{cp}$ region) is where Cooper pairs are possible. According to pressure increases, the $\alpha^2 F(\omega)$ spectrum (in the $D_{cp}$ region) decreases significantly in intensity and moves to slightly higher frequencies, then the conditions for Cooper pair formation weaken and $T_c$ falls. We suggest that $\text{H}_3\text{S}$ superconductivity is established by electrons of S $s$, S $p$ and H $s$ orbitals that interact with phonons in the $D_{cp}$ region, where S vibrations make the major contribution, with some contribution from H vibrations.

Finally, the electron–phonon coupling constant $\lambda$ shows an important correlation with $T_c$ in accordance with the Migdal–Eliashberg theory.
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