First-principles study on superconductivity of P- and Cl-doped H$_3$S

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The recent reports on 203 K superconductivity in compressed hydrogen sulfide, H$_3$S, has attracted great interest in sulfur-hydrogen system under high pressure. Here, we investigated the superconductivity of P-doped and Cl-doped H$_3$S using the first-principles calculations based on the supercell method, which gives more reliable results on the superconductivity in doped systems than the calculations based on the virtual crystal approximation reported earlier. The superconducting critical temperature is increased from 189 to 212 K at 200 GPa in a cubic Im$ar{3}$m phase by the 6.25% P doping, whereas it is decreased to 161 K by the 6.25% Cl doping. Although the Cl doping weakens the superconductivity, it causes the Im$ar{3}$m phase to be stabilized in a lower pressure region than that in the non-doped H$_3$S.

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INTRODUCTION

Hydrogen sulfide (H$_2$S) shows a high-temperature superconductivity under high pressure, and the superconducting critical temperature ($T_c$) reaches the maximum of 203 K at pressure of 155 GPa, in which H$_2$S transforms into a stoichiometric compound with a chemical formula of H$_3$S via the intermediate compounds [1–8]. The mechanism of the high-$T_c$ superconductivity is considered to have origins of electron-phonon interaction because the isotope effect on the superconducting transition was experimentally observed [1], which supports Ashcroft’s prediction that metallic hydrides become high-$T_c$ conventional superconductors [3]. The conventional superconductors have an advantage that the $T_c$ can be predicted more quantitatively by the first-principles calculation than that in copper oxide superconductors and iron-based ones. Therefore, a cooperation between experimental measurements and first-principles calculations is effective for the exploration of novel superconducting hydrogen compounds.

Superconductivity has been observed experimentally in only a few hydrogen-containing compounds, namely silane (SiH$_4$) with a $T_c$ of 17 K at 96 GPa [10] and phosphine (PH$_3$) with a $T_c$ of 100 K at 207 GPa [11], in addition to H$_2$S. However, superconductivity is predicted in many other compounds using first-principles calculations (Table I). More information is summarized in Refs. [12, 25–28].

Intentional introduction of impurities into substances has been used as another approach for the exploration of high-$T_c$ superconducting materials. Ge et al. have investigated the effect of impurity doping on the superconductivity of H$_3$S using first-principles calculations based on the virtual crystal approximation (VCA) and predicted that the $T_c$ shows a further increase to 280 K at 250 GPa by 7.5% substitution of phosphorus (P) for S, i.e., hole doping [29]. The hole doping causes an increase in the density of states (DOS) at the Fermi level, which results in the enhancement of the $T_c$. At almost the same time, Fan et al. also reported the doping effect on the superconductivity of H$_3$S using VCA calculations [30]. Their calculations show an increase of $T_c$ from 185 to 197 K at 200 GPa by 15% P doping, which is due to the increase of electron-ion matrix elements.

In this paper, we report the results of the doping effect on the superconductivity of H$_3$S, obtained by first-principles calculations based on the supercell method, which gives more reliable results on the superconductivity in doped systems than the VCA method. Comparing the VCA results reported earlier [29, 30], we notice that the amount of the increase of $T_c$ is significantly different between them: 194 to 250 K in Ge’s calculations and 185 to 187 K in Fan’s calculations in 10% P-doped H$_3$S.

| P (GPa) | $T_c$ (K) | Reference |
|---------|---------|-----------|
| YH$_{10}$ | 400 | 303 | [12] |
| LaH$_{10}$ | 210 | 286 | [13] |
| MgH$_6$ | 300 | 271 | [14] |
| YH$_6$ | 120 | 264 | [15] |
| CaH$_6$ | 150 | 235 | [16] |
| SiH$_4$ | 202 | 166 | [17] |
| AsH$_4$ | 450 | 151 | [18] |
| AlH$_5$ | 250 | 146 | [19] |
| BiH$_3$ | 300 | 119 | [20] |
| SbH$_4$ | 150 | 118 | [21] |
| BiH$_6$ | 300 | 113 | [20] |
| SiH$_8$ | 250 | 107 | [22] |
| PbH$_8$ | 230 | 107 | [23] |
| ArH$_8$ | 1500 | 72 | [24] |

TABLE I: Example of superconducting hydrogen compounds.
at 200 GPa. Therefore, we verified the VCA results applying the supercell method to the $T_c$ calculations for P-doped and chlorine (Cl)-doped H$_3$S.

**METHODS**

We investigated the pressure dependence of superconductivity of H$_3$S at 6.25% and 12.5% doping of P (or Cl). First we prepared (A) a supercell consisting of $2 \times 2 \times 2$ primitive cells, including 8 formula units (f.u.) of H$_3$S, and (B) that consisting of $2 \times 2 \times 2$ conventional cells, including 16 f.u.. Next we created doped H$_3$S by substituting 12.5% of S atoms in the supercell A with P or Cl, i.e. H$_3$S$_{0.875}$P$_{0.125}$ and H$_3$S$_{0.875}$Cl$_{0.125}$, and 6.25% in the supercell B, i.e. H$_3$S$_{0.9375}$P$_{0.0625}$ and H$_3$S$_{0.9375}$Cl$_{0.0625}$. Then we performed structural optimization for the supercells in the pressure region of 100 to 250 GPa using the Parrinello-Rahman method without constraint of symmetry [31]. Comparing the optimized structures with that of the non-doped H$_3$S, we found that only H atoms are slightly moved from the starting positions in crystal coordinates by the optimization. The results at 200 GPa are listed in Table II and are illustrated in Fig. 1.

We performed first-principles calculations using the Quantum ESPRESSO code [32], in which the plane wave basis and pseudopotential methods are employed. We adopted the Vanderbilt type ultrasoft pseudopotential [33] and a generalized gradient approximation [34] of the Perdew-Burke-Ernzerhof type for the exchange correlation functional [34]. These pseudopotentials are available as H.pbe-van_bm.UPF, S.pbe-van_bm.UPF, P.pbe-van_akh.UPF, and Cl.pbe-n-van.UPF on Quantum ESPRESSO pseudopotential library [35]. The integration of reciprocal lattice space was performed using the Monkhorst-Pack grid [36]. The numbers of the grids are summarized in Table III. The energy cutoff of the wave function was set at 80 Ry.

For superconductivity, we calculated the dynamical matrix, phonon frequency, electronic phonon matrix, and Eliashberg function $\alpha^2F(\omega)$ using density functional perturbation theory [37]. The $T_c$ was calculated using the Allen-Dynes-modified McMillan formula [38, 39],

$$T_c = \frac{f_1 f_2 \omega_{\log}}{1.2} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right].$$

(1)

Here, $\lambda$ is the electron-phonon coupling constant, $\omega_{\log}$ is the logarithmic averaged phonon-frequency, $\mu^*$ is the screened Coulomb interaction constant, and $f_1$ and $f_2$ are correction factors for the system showing large $\lambda$. The value of $\mu^*$ is assumed to be 0.13, which has widely been used in metallic hydrides. The other parameters, $f_1$, $f_2$, $\lambda$, and $\omega_{\log}$ are defined as follows:

$$f_1 = \left\{1 + \frac{\lambda}{2.46(1+3.8\mu^*)}\right\}^{3/2},$$

(2)

$$f_2 = 1 + \frac{(\omega_f/\omega_{\log} - 1)\lambda^2}{\lambda^2 + 1.82(1+6.3\mu^*)(\omega_f/\omega_{\log})},$$

(3)

$$\lambda = \frac{2}{\int_0^\infty d\omega \alpha^2F(\omega)}$$

(4)

$$\omega_{\log} = \exp\left[\frac{2}{\lambda} \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} \log \omega\right],$$

(5)

where $\omega_f$ is defined as

$$\omega_f = \left[\frac{2}{\lambda} \int_0^\infty d\omega \alpha^2 F(\omega)\right]^{1/2}.\]$$

The calculated $T_c$ values were improved using the superconducting density functional theory [40] and the inclusion of anharmonic effect on phonon [41]. However, we discuss the superconductivity without these improvements to compare our results with the VCA results reported earlier [20, 30].

**FIG. 1:** Optimized structures of H$_3$S$_{0.875}$P$_{0.125}$ (upper) and H$_3$S$_{0.875}$Cl$_{0.125}$ (lower). A large gray (green) sphere at center, large yellow spheres, and small pink spheres represent P (Cl), S, and H atoms, respectively. Arrows indicate the displacements of the H atoms from the equilibrium positions in non-doped H$_3$S.


### TABLE II: Crystal coordinates before and after the structure optimizations for 12.5%-doped \(Im\bar{3}m\) H\(_3\)S at 200 GPa.

|                  | Before                   | After (P doping) | After (Cl doping) |
|------------------|--------------------------|------------------|-------------------|
| H1 12d           | 0.25 0.5 0.253           | no change       | no change         |
| H2 24h           | 0 0.25 0.25 0.24939      | 0 0.24939       | 0 0.24853 0.24853 |
| H3 12e           | -0.25 0 0 -0.24494       | 0 0 -0.26885    | 0 0               |
| S1 8c            | 0.25 0.25 0.25           | no change       | no change         |
| S2 6b            | 0 0.5 0.5 0              | no change       | no change         |
| P(Cl)1           | 2a 0 0 0                 | no change       | no change         |

### TABLE III: \(k\)-point and \(q\)-point grids used for the calculations.

| Doping amount | 0% | 6.25% | 12.5% |
|---------------|----|-------|-------|
| Electron      | 16 × 16 × 16 | 8 × 8 × 8 | 8 × 8 × 8 |
| Phonon        | 4 × 4 × 4    | 2 × 2 × 2  | 4 × 4 × 4  |
| Electron-phonon | 32 × 32 × 32 | 16 × 16 × 16 | 32 × 32 × 32 |

### RESULTS AND DISCUSSION

The x-ray diffraction measurements and the first-principles calculations including the anharmonic effect show that H\(_3\)S has a crystal structure with a space group of a hexagonal \(R\bar{3}m\) in the pressure region above 100 GPa and transforms into a cubic \(Im\bar{3}m\) structure at around 150 GPa \([4]\, [\underline{\underline{5}}]\) in which hydrogen atoms are moved from asymmetric to symmetric positions between the S atoms \([4]\). First we investigated this structural phase transition in the doped system. Figure 2 shows the enthalpies of \(R\bar{3}m\) relative to that of \(Im\bar{3}m\) for H\(_3\)S, H\(_3\)S\(_0.9375\)P\(_{0.0625}\), H\(_3\)S\(_{0.875}\)P\(_{0.125}\), H\(_3\)S\(_{0.9375}\)Cl\(_{0.0625}\), and H\(_3\)S\(_{0.875}\)Cl\(_{0.125}\). Non-doped H\(_3\)S continuously transforms from \(R\bar{3}m\) into \(Im\bar{3}m\) at 190 GPa, which is higher by about 40 GPa than the transition pressure observed experimentally but is almost consistent with that obtained using first-principles calculations without the anharmonic effect \([4]\). The transition pressure shows no change with P doping, whereas it shifts to lower pressure with the increase in Cl doping, \(i.e.,\) from 190 GPa for H\(_3\)S to 160 GPa for H\(_3\)S\(_{0.9375}\)Cl\(_{0.0625}\) and to 140 GPa for H\(_3\)S\(_{0.875}\)Cl\(_{0.125}\).

Figure 3 shows the pressure dependence of the \(T_c\) calculated by the Allen-Dynes formula for H\(_3\)S, H\(_3\)S\(_{0.9375}\)P\(_{0.0625}\), H\(_3\)S\(_{0.875}\)P\(_{0.125}\), H\(_3\)S\(_{0.9375}\)Cl\(_{0.0625}\), and H\(_3\)S\(_{0.875}\)Cl\(_{0.125}\). Unfortunately, no data of \(T_c\) for 6.25% doping was obtained in the \(R\bar{3}m\) phase owing to unexpected errors in the phonon calculations. The unexpected errors occur in subroutine which computes the matrices representing the small group of \(q\) on the pattern basis. Therefore, we consider that the errors are caused by not the phonon instability near the transition from \(R\bar{3}m\) into \(Im\bar{3}m\) but the symmetry of the structure. For the non-doped H\(_3\)S, \(T_c\) increases with pressurization in the \(R\bar{3}m\) phase, reaches the maximum at approximately 200 GPa where \(R\bar{3}m\) transforms into \(Im\bar{3}m\), and decreases with a further increase in pressure. Similar behavior is observed in 12.5% P-doped and Cl-doped samples. At 200 GPa, in the \(Im\bar{3}m\) phase, we found that \(T_c\) increases from 189 to 212 K at 6.25% P doping and decreases to 194 K at 12.5% doping (Table IV). In the case of Cl doping, \(T_c\) decreases to 161 K at 6.25% doping and to 136 K at 12.5% doping. These results suggest that at low levels of P doping, \(i.e.,\) low levels of hole doping, en-
hances the $T_c$ of H$_3$S. On the other hand, Cl doping, i.e., electron doping, decreases the $T_c$ but causes the Im3m phase to be stabilized in a lower pressure region compared to non-doped H$_3$S.

![Figure 3: Pressure dependence of $T_c$ for the doped H$_3$S. The transition pressures from R3m into Im3m are as follows: 190 GPa for H$_3$S, H$_3$S$_0$9.375P$_0$0.625, and H$_3$S$_0$8.75P$_0$1.25. 160 GPa for H$_3$S$_0$9.375Cl$_0$0.625, and 140 GPa for H$_3$S$_0$8.75Cl$_0$1.25.](image)

Table IV: Doping dependence of (a) $N(E_F)$, (b) $\lambda$, (c) $\omega_{\log}$, (d) $T_c$ calculated using the Allen-Dynes formula, and (e) $T_c$ calculated directly solving the isotropic Eliashberg equation [39] for Im3m H$_3$S.

| P(GPa) | Cl-12.5% | Cl-6.25% | non-doped | P-6.25% | P-12.5% |
|-------|----------|----------|-----------|---------|---------|
|       | $N(E_F)$ (states/eV/atom) |       |           |         |         |
| 100   | 0.112    | 0.120    | 0.123     |         |         |
| 150   | 0.106    | 0.121    | 0.129     |         |         |
| 200   | 0.105    | 0.114    | 0.128    | 0.137   | 0.132   |
| 250   | 0.105    | 0.115    | 0.131    | 0.137   | 0.130   |
|       | $\lambda$ |         |           |         |         |
| 100   | 1.85     | 1.70     | 1.89      |         |         |
| 150   | 2.18     | 2.22     | 2.22      |         |         |
| 200   | 1.32     | 1.52     | 1.94      | 2.32    | 2.22    |
| 250   | 1.14     | 1.23     | 1.58      | 1.60    | 1.53    |
|       | $\omega_{\log}$ (K) |       |           |         |         |
| 100   | 947      | 1050     | 895       |         |         |
| 150   | 851      | 1000     | 950       |         |         |
| 200   | 1380     | 1380     | 1230      | 1180    | 1110    |
| 250   | 1510     | 1610     | 1400      | 1530    | 1500    |
|       | $T_c$ (K) [Allen-Dynes formula] |       |           |         |         |
| 100   | 140      | 141      | 136       |         |         |
| 150   | 148      | 176      | 168       |         |         |
| 200   | 136      | 161      | 189      | 212     | 194     |
| 250   | 119      | 142      | 173      | 190     | 177     |
|       | $T_c$ (K) [Isotropic Eliashberg equation] |       |           |         |         |
| 100   | 187      | 190      | 174       |         |         |
| 150   | 198      | 215      | 225       |         |         |
| 200   | 179      | 199      | 225      | 268     | 249     |
| 250   | 161      | 182      | 248      | 251     | 229     |

Figure 4 shows the doping dependence of $T_c$, $\omega_{\log}$, $\lambda$, and $N(E_F)$ in the Im3m phase at 200 GPa normalized by the values of those of non-doped H$_3$S. The original values are listed in Table IV. The doping dependence of $T_c$ is explained by that of $N(E_F)$. As reported earlier [4, 30], Im3m H$_3$S shows a large peak in DOS around the Fermi level, i.e., 0 eV, which has been suggested as a reason for the high-$T_c$ observed in H$_3$S. However, strictly speaking, the peak maximum is located at $-0.2$ eV. Therefore, the Fermi level is shifted toward the peak maximum of DOS with hole doping, which causes a further increase of $N(E_F)$ with a low P doping of 6.25%. Fan et al. investigated DOS for non-doped H$_3$S, 15% P-doped H$_3$S, and 50% P-doped H$_3$S using the VCA calculations and found that these DOS plots have all very similar structure except for the position of the Fermi level (see Fig. 3 in Ref. [30]). They suggest that the simple level shift like a rigid band model is applicable to P-doped H$_3$S and the $N(E_F)$ maximum is obtained by the 15% doping, at which the Fermi level reaches the peak maximum of DOS. However, our supercell calculations show that the doping causes not only the Fermi level shift but also the peak broadening, and $N(E_F)$ decreases with further doping before the Fermi level reaches the peak maximum as observed at 12.5% P doping (see the lower panel of Fig. 3). Therefore, we suggest that the doping amount required for the $N(E_F)$ maximum is smaller than that predicted from the simple level shift and the Fan’s VCA calculations. In the case of electron doping, the Fermi level is shifted to higher energy compared to non-doped H$_3$S, which causes only a decrease of $N(E_F)$.

Here we compare our results obtained using the supercell method with those of the VCA method reported by Ge et al. [29] and by Fan et al. [30]. In Ge’s results, at 200 GPa, $T_c$ is increased from 197 to 240 K with 7.5% P doping, i.e., a rate of +5.73 K/%, and is decreased from 197 to 94 K with 12.5% Cl doping, i.e., -8.24 K/%. In Fan’s results, $T_c$ is increased from 185 to 190 K with 5% P doping, i.e., at a rate of +1 K/%. In contrast, in our supercell results, the rates are +3.68 K/% for P doping and -4.24 K/% for Cl doping, which suggests that our results are qualitatively consistent with the VCA results but the doping effect is less (more) remarkable than that predicted by Ge et al. (Fan et al.).

We discuss the reasons for the difference in the doping effects on the superconductivity between the VCA and our supercell results. The inset of Fig. 4 shows the normalized $T_c$, $\lambda$, and $N(E_F)$ values reported by Fan et al. The $\lambda$ value in our results is comparatively higher than that in Fan’s results for P doping. This difference is
considered to be caused by the difference of the phonon calculation method. They calculated the superconducting parameters for the doped system using the phonon frequency obtained from the calculated results for non-doped H₃S [4]. On the other hand, we directly calculated the phonon frequency using the supercell method. Consequently, larger λ and higher Tc were obtained in our calculations in comparison to Fan’s calculations. Figure 5 shows a comparison of the phonon DOS of Im₃m H₃S at 200 GPa among the present work and previous reports [4] [41]. Comparing our result at 12.5% P doping [Fig. 5(a)] with that of Ge’s [Fig. 5(b)], we found that the maximum of the phonon frequency in our phonon DOS is lower by about 20 THz. To judge the calculation accuracy, we also compared our phonon DOS with those of non-doped H₃S previously reported by Duan et al. [4] and Errea et al. [41]. Since the phonon DOS is shown as a projection on each atom in their papers, we extracted the data from those reports, obtained the total DOS by summing up the data, and plotted in Figs. 5 (c) and (d). Consequently, we found that our phonon DOS for the non-doped H₃S shows a good agreement with those reported earlier. The maximum of the phonon frequency is shifted by 5.7 THz towards higher frequency with P doping, whereas the phonon DOS is not expected to be drastically changed. Therefore, we conclude that our results on the phonon DOS and doping effect are more reliable than those calculated by Ge et al..

Finally we discuss on the feasibility of P-doped H₃S. We calculated the defect formation enthalpy Hf for H₃S₀.₉₃₇₅P₀.₆₂₅₅ and H₃S₀.₈₇₅P₀.₁₂₅₅ according to the following equation:

\[ H_f = H_{H_3S_{1-x}P_x} + xH_S - H_{H_3S} - xH_P \]  (7)

where \( H_{H_3S_{1-x}P_x} \) and \( H_{H_3S} \) represent the enthalpies of H₃S₁₋ₓPₓ \( (x = 0.0625, 0.125) \) and non-doped H₃S, respectively. \( H_S \) and \( H_P \) are the enthalpies per atom for S and P elements. Table V shows \( H_f \) per atom in temperature units. All the doped systems are thermodynamically unstable compared with non-doped H₃S, whereas the enthalpy differences show few hundreds kelvin, e.g. 167.3 K at 100 GPa for 6.25% P-doping. Very recently, Guigue et al. and Goncharov et al. directly synthesized pure H₃S from S and H₂ in laser-heated \( (< 1300 K) \) diamond anvil cells under high pressure [42, 43]. Therefore, we suggest that P-doped H₃S can be synthesized as metastable states by similar laser-heating experiments in the mixture of S, H₂, and a small amount of P.

SUMMARY

In this study, we investigated the doping effect on the superconductivity of Im₃m H₃S using first-principles cal-
TABLE V: Formation enthalpy of H$_3$S$_{1-x}$P$_x$. Abbreviations, rh, sc, and sh, represent a rhombohedral structure of $\beta$-Po type, a simple cubic structure, and a simple hexagonal structure, respectively.

| P (GPa) | structure | $x$ | $H_f$ (mRy/atom) | $T_c$ (K) |
|---------|-----------|-----|-----------------|----------|
| 100     | rh sc     | 0.0625 | 1.060           | 167.3    |
|         |           | 0.125  | 1.759           | 277.7    |
| 150     | rh sh     | 0.0625 | 1.367           | 215.9    |
|         |           | 0.125  | 2.297           | 362.7    |
| 200     | rh sh     | 0.0625 | 1.508           | 238.0    |
|         |           | 0.125  | 2.683           | 423.6    |
| 250     | rh sh     | 0.0625 | 1.523           | 240.5    |
|         |           | 0.125  | 2.831           | 447.0    |

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