Influence of bonding on superconductivity in high-pressure hydrides

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The recent reports on high-temperature superconductivity above 190 K in hydrogen sulfide at 200 GPa pressure, exceeding all previously discovered superconductors, has greatly invigorated interest in dense hydrogen-rich solids. Here, we investigate a possible way to optimize the critical temperature in these compounds by using first-principles linear-response calculations. We construct hypothetical alchemical atoms to smoothly interpolate between elements of the chalcogen group and study their bonding and superconducting properties. Our results show that the already remarkable critical temperatures of H₃S could be improved even further by increasing the ionic character of the relevant bonds, i.e., partially replacing sulfur with more electronegative elements.

The recent experimental report of superconductivity with a critical temperature (Tc) exceeding 190 K in dense hydrogen sulfide [1] could be one of the most important discoveries in the field of superconductivity, if confirmed. Although x-ray scattering data are lacking due to the extreme pressures involved (p ~ 200 GPa), there is a widespread consensus that the superconducting samples are composed of a sulfur-trihydride (H₃S) bcc phase predicted by Duan et al. [2]. Theoretical studies [3–9] and isotope effect measurements [10] unambiguously indicate that, unlike the high-Tc iron pnictides and cuprates, H₃S is a conventional BCS [11] superconductor.

Phonon-mediated superconductors are accurately described by the Migdal-Eliashberg theory [12, 13]: their Tc is well approximated by the Allen-Dynes formula [14],

\[ T_c = \frac{\omega_{\ln}}{1.2} \exp \left( \frac{-1.04 (1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right), \]

where \( \lambda \) is the electron-phonon (e-p) coupling constant, \( \omega_{\ln} \) is the logarithmic average of phonon frequencies, and \( \mu^* \) is the Coulomb pseudopotential. Thus, Migdal-Eliashberg theory indicates a clear path to optimize Tc, i.e., looking for materials with high characteristic phonon frequencies (\( \omega_{\ln} \)) and strong e-p coupling constants \( \lambda \).

In a seminal paper that is now almost 50 years old, Ashcroft noticed that these conditions could be realized in ultra-dense metallic hydrogen [15], yet only the recent progress in experimental techniques for high-pressure research and improved methods for crystal-structure prediction have made this hypothesis viable [16]. In the last few years, there has been significant interest in the superconducting behavior of hydrogen-rich solids at high pressures [17–24]. These compounds display a fascinating variety of crystal structures, as some contain molecular hydrogen, in others the H-H bond is broken, and hydrogen forms direct bonds with the other atoms. The predicted Tc’s close to ambient pressures are just a few K, while for pressures above 150 GPa they range from 64 to 235 K.

Among these compounds, H₃S has been predicted to exhibit one of the highest Tc’s. Reference [8] underlined that the mechanism boosting its Tc is essentially the same one that occurs in magnesium diboride (MgB₂), which broke the record of critical temperatures for conventional superconductors in 2001 [25–27]. In MgB₂, the presence of electronic bands with a strong covalent character at the Fermi level leads to e-p matrix elements much larger than those found in other conventional superconductors. The experience with this material has shown that, besides the well-known strategy of carrier doping, a very promising route to increase Tc is to act on the bonding properties of the materials, directly influencing the e-p matrix elements. Within the range of MgB₂-like materials, the highest critical temperature was predicted for hole-doped LiBC, whose stiff ionic bonds are even more favorable for superconductivity [28].

H₃S is very similar to MgB₂ as it also exhibits strong covalent bonds giving rise to large electron-phonon couplings [4, 5] and strong anharmonic effects [6, 29–31], and although its critical temperature is already spectacularly high, there is no reason to expect that it cannot be increased any further.

The aim of this Rapid Communication is to explore whether the superconducting properties of H₃S can be further enhanced by increasing (or decreasing) the covalent character of the sulfur-hydrogen bond. We perform a systematic study of the electron-phonon properties of several H₃X compounds in the bcc high-pressure structure of H₂S, using linear-response calculations [32]. The X atom is either one of the first four atoms of the chalcogen group (O, S, Se, Te), or a hypothetical alchemical mixture of neighboring chalcogens (i.e., O and S, S and Se, and so on) [33–34]. This approximation allows us to study the influence of covalency and atomic size on the bonding, dynamical stability, and electron-phonon coupling of the H₃X structure in a controlled way, without introducing spurious effects related to doping. We will also introduce quantities to measure the bonding characteristics of dense hydrogen-rich compounds that will be useful in the search for new high-Tc materials with high-throughput methods [35]. In order to minimize the number of external parameters, we work at a fixed pres-
Figure 1 shows the $Im\bar{3}m$ bcc structure of the H$_3$X compounds at high pressures: The X atoms (green) occupy the 2$a$ Wyckoff position and form a bcc lattice, while the hydrogen atoms (H, blue) occupy the 6$b$ Wyckoff positions in between. Each H forms two short and four long bonds with its X neighbors in the (100), (110) and (110) directions. When the electronegativity of the X atom is slightly larger than that of H (2.1), as in S (2.4) and Se (2.5), the charge accumulates around the center of the short X-H-X bonds, giving them a strongly ionic character. The red, H-centered ellipsoids in Fig. 1(a) delimit regions in which the charge density of H$_3$Se is higher than that of hypothetical Se and H$_3$ solids in the same crystal structure. A contour plot of the same quantity in the basal plane is plotted in Fig. 1(b). As the X-H-X bonds acquire an increasing ionic character by increasing the electronegativity of X, the maximum of the charge density distribution moves from the vicinity of hydrogen to that of the X atom; this is seen in the contour plot for H$_3$O, shown in Fig. 1(c).

We will now discuss in detail how and why the electronic and vibrational properties of these two compounds differ. We start from Fig. 2(a), where we show the electronic structure of the two compounds. The band structure of H$_3$Se (solid black) is in nice agreement with previous calculations and, as discussed by several authors, very similar to the one of H$_3$S [6] [6] [8]. Se- and H-derived electronic states are strongly hybridized, especially in the vicinity of the Fermi energy. This leads to several avoided crossings and eventually to a strong van-Hove singularity. The remarkable difference in the electronic structure of the two compounds is due to the large electronegativity of O, which increases the hybridization between O and H states and leads to even larger avoided crossings. As a consequence, the van Hove singularity close to $E_F$ splits in two peaks, which move apart as well.

Figure 3 shows the corresponding vibrational properties: Phonon dispersions are plotted in Figs. 3(a) and 3(c), while Figs. 3(b) and 3(d) show the partial phonon density of states (DOS) and the $e$-$p$ spectral function $\alpha^2 F(\omega)$:

$$\alpha^2 F(\omega) = \frac{1}{N_{E_F}} \sum_{kq,\nu} |g_{k,k+q,\nu}|^2 \delta(\epsilon_k) \delta(\epsilon_{k+q}) \delta(\omega - \omega_{q,\nu})$$

(2)

where $N_{E_F}$ is the DOS at the Fermi level, $\omega_{q,\nu}$ is the phonon frequency of mode $\nu$ at wavevector $q$, and $|g_{k,k+q,\nu}|$ is the electron-phonon matrix element [28], between two electronic states with momenta $k$ and $k+q$ at the Fermi level. The dotted line shows the $\omega$-dependent $e$-$p$ coupling parameter $\lambda(\omega) = 2 \int_0^\infty d\Omega \omega^2 F(\Omega)$; $\lambda(\infty)$ gives the total $e$-$p$ coupling parameter already discussed in Eq. (1).

In H$_3$Se [Fig. 3(a)] the acoustic modes extend up to an energy of about 50 meV. The first six optical branches are separated by a gap of around 25 meV from the acoustic ones and have a bandwidth of $\sim$100 meV. Separated again by an energy gap of 25 meV are the last three optical branches. These three modes have a mainly bond-stretching character, according to the definition of Ref. [6]. In turn, the middle six phonon branches have a mostly bond-bending oscillatory character. The acoustic modes contribute $\sim 1/3$ to the total value of $\lambda$. The $\alpha^2 F(\omega)$ of the bond-stretching modes is distinctly different from the shape of the phonon DOS and adds about 1/4 to the total $\lambda$. For H$_3$Se, we obtain $\omega_{\text{in}} = 84$ meV.
and $\lambda = 1.35$, leading to a $T_c = 100$ K for $\mu^* = 0.1$.

The superconducting properties improve for the smaller-Z chalcogens, which have smaller atomic masses, decreasing ionic radii, and increasing electronegativities. In agreement with previous calculations, we find that the $T_c$ of H$_3$S is distinctly larger than that of H$_3$Se (for H$_3$S we get $\omega_{\text{in}} = 97$ meV, $\lambda = 1.83$, and $T_c = 151$ K for $\mu^* = 0.1$) [39]. In addition, we find that a further improvement of the superconducting properties occurs in the oxygen-rich part of our alchemical phase diagram, where the X-H-X bond becomes more and more ionic, before the dynamical stability of the lattice breaks down eventually for oxygen contents larger than 50%. Indeed, H$_3$O should crystallize in the Im$3m$ structure only above 11000 GPa [40, 41].

Figure 3(c) shows the electron-phonon properties of the last stable compound, i.e., H$_3$O$_{0.5}$S$_{0.5}$. The acoustic branches extend up to $\sim$70 meV and contribute again about 1/3 to the total $\lambda = 1.95$. The optical modes are located in the energy window from 80 to 245 meV. Bond-stretching modes are mainly responsible for the peaks in $\alpha^2 F(\omega)$ centered at 110, 150, and 175 meV. Integrating $\alpha^2 F(\omega)$ for H$_3$O$_{0.5}$S$_{0.5}$, we obtain $\omega_{\text{in}} = 100$ meV and $T_c = 164$ K for $\mu^* = 0.1$.

We have so far discussed only specific choices of X. To comprehend how individual differences in bonding properties, dynamical stability, and electron-phonon coupling translate into actual trends in an alchemical phase diagram, we present in Fig. 4 an overview of representative quantities as a function of a continuous variable $\beta$ that ranges from zero (oxygen) to three (tellurium); non-integer values represent alchemical pseudatoms.

Figure 4(a) shows in black the optimized lattice constant, which increases smoothly with $\beta$ from $a = 2.62$ to 3.33 Å. In red, we plot a compact measure of the charge localization along the short bond direction, i.e., the fraction $\rho_X/\rho_{\text{tot}}$ of total charge which is localized around the X atom [42]. This quantity increases as $\beta \to 0$, as the maximum of the charge distribution shifts smoothly from the H to the X atom. In Fig. 4(b) we show the frequency evolution of the triply degenerate optical phonon branches at the $\Gamma$ point – see Fig. 2. All branches have a (partially) H bond-stretching and bond-bending character and evolve smoothly with $\beta$. While the green and red branches have $T_{1\text{v}}$ symmetry, the black one is of $T_{2\text{g}}$ symmetry. For high O and Te contents, the lowest branch displays imaginary frequencies, indicating a dynamical instability of the structure [40, 43]. In O-rich compounds, another instability occurs earlier near the $P$ point. The gray-shaded areas in the figure indicate parts of the $\beta$ phase diagram where the H$_3$X structure is dynamically unstable.

In Fig. 4(c), we plot in red the value of the electronic DOS at the Fermi level $N_{E_F}$; it is essentially constant for S$\to$Se$\to$Te ($\beta > 1$), and decreases sharply for $\beta \to 0$, due to the increased O-H hybridization – see Fig. 2. On the other hand, $\lambda$ is almost monotonously increasing for decreasing $\beta$; $\omega_{\text{in}}$ [Fig. 3(e)] exhibits a similar behavior, i.e., it remains nearly constant between O and S, and bends downwards for Se and Te. A large value of $\omega_{\text{in}}$ for small $\beta$ is not in contradiction with the incipient lattice instability, since, as mentioned earlier, the phonon modes which undergo softening carry only a small fraction of the total $e-p$ coupling [26, 27, 44]. The combined effect of $\omega_{\text{in}}$ and $\lambda$ thus results in a net monotonous increase of $T_c$, from 83 K on the Te-rich side to 164 K on the O-rich side, as shown as the red dashed line in Fig. 4(c) [45].

Figure 4(c) also shows that the behavior of $\lambda$ does not correlate with $N_{E_F}$, especially for $\beta \to 0$. Instead, the average $e-p$ coupling matrix element $\lambda/N_{E_F}$, plotted in Fig. 4(d), increases by $\sim 50\%$ when going from H$_3$Se to H$_3$O. To rule out that this increase is not just a lattice-constant (pressure) effect, we additionally performed $e-p$ calculations for H$_3$S at the same lattice constant as H$_3$O$_{0.5}$S$_{0.5}$, i.e., at a pressure of 265 GPa: The results, shown as isolated triangles and stars in Figs. 4(c) and 4(d) are in line with those of the other chalcogen hydrides ($\lambda = 1.70$, $\omega_{\text{in}} = 103$ meV, and $T_c = 152$ K). The behavior of $\lambda/N_{E_F}$ strongly resembles that of $\rho_X/\rho_{\text{tot}}$,
plotted in the same panel as the red lines. This is a clear indication that increasing the ionic character of the X-H-X bond can be beneficial for superconductivity. Although the increase in $T_c$ is not as spectacular as in LiBC compared to MgB$_2$ [28], our findings indicate increased ionicity as a clear path that experimentalists could follow to optimize $T_c$ in high-pressure hydrides.

In summary, we have studied a possible route to optimize the critical temperature in recently discovered high-$T_c$ superconducting hydrides using first-principles linear-response calculations. We constructed hypothetical alchemical atoms, which smoothly interpolate atoms of the chalcogen group, and studied their phonon and electron-phonon coupling properties. The effect of alchemical doping is qualitatively very different from charge doping or pressure, as it allows one to tune the bonding properties of a material, crucially affecting the e-p matrix elements. We observed the existence of a “sweet spot” for electron-phonon superconductivity in H$_3$O$_{0.5}$S$_{0.5}$, for which the bond is ionic enough to profit from increased electron-phonon coupling, but not so strongly as to lead to a structural instability.

This implies that, although H$_3$S is already almost optimal for electron-phonon coupling superconductivity, its critical temperature could be improved further making the X-H-X bond more ionic, i.e., partially replacing sulfur with more electronegative atoms, such as oxygen or members of the halogen group. Together with the compact measure we provided to characterize the bonding situation, our results highlight promising paths in the search for new conventional high-$T_c$ superconductors with high-throughput methods [35].

Note added. Recently, we became aware of a similar investigation [50].

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[1] A. P. Drozdov, M. I. Eremets, and I. A. Troyan, arXiv:1412.0460.
[2] D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, and T. Cui, Sci. Rep. 4 (2014).
[3] Y. Li, J. Hao, H. Liu, Y. Li, and Y. Ma, The Journal of Chemical Physics 140, 174712 (2014).
[4] D. A. Papaconstantopoulos, B. M. Klein, M. J. Mehl, and W. E. Pickett, Phys. Rev. B 91, 184511 (2015).
[5] J. A. Flores-Livas, A. Sanna, and E. K. U. Gross, arXiv:1501.06536.
and a tetrahedron method. Phonon properties were calculated on a 8\textsuperscript{4} Monkhorst-Pack \textit{q}-point grid and interpolated with a real space Fourier procedure. We counterchecked our results, whenever possible, with \textsc{wien2k} and \textsc{quantum espresso}.

[33] The \textit{alchemical} mixing of pseudopotentials is equivalent to the virtual crystal approximation if two atoms are neighbors in the periodic table. $V_{\text{VCA}} = \gamma V_{X_1} + (1 - \gamma) V_{X_2}$, $\gamma \in [0, 1]$, and analogously for the mass.

[34] Previous studies on the thermodynamic stability in chalcogen hydrides exist – see Refs. [2]–[6] [8] [43] [49].

[35] S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, and O. Levy, \textit{Nat Mater} \textbf{12}, 191 (2013).

[36] The lattice constant given by Ref. [2] results in a pressure of 190 GPa in our calculations, which we have kept constant for all compounds.

[37] We also performed rigid-band calculations (not shown) for H\textsubscript{2}S to investigate charge doping effects. These calculations, however, revealed that $\lambda$ and $T_c$ cannot be significantly increased with charge doping.

[38] P. B. Allen, \textit{Phys. Rev. B} \textbf{6}, 2577 (1972).

[39] We want to remark that the $\lambda$ values we obtain are systematically lower than in other works, which use different codes. Reference [5], for example, computed $\lambda = 2.41$ and $\omega_\text{in} = 109$ meV for H\textsubscript{2}S, which are substantially larger than ours. Apart from numerical differences due to the different method for $k$-space integration, there is a significant difference in the dispersion of the lower bond-stretching modes, which in our calculations are much harder than in Ref. [5]. Errea et al. [5] point out a strong phonon anharmonicity in H\textsubscript{2}S, thus even small differences in the computational details used for linear-response calculations may result in discernible deviations in the estimates obtained with the harmonic approximation. In fact, our phonon dispersion, and $\lambda$ and $\omega_\text{in}$ values, are much closer to the values reported in Ref. [5].

[40] M. Benoit, M. Bernasconi, P. Focher, and M. Parrinello, \textit{Phys. Rev. Lett.} \textbf{76}, 2934 (1996).

[41] S. Zhang, H. F. Wilson, K. P. Driver, and B. Militzer, \textit{Phys. Rev. B} \textbf{87}, 024112 (2013).

[42] What is computed in practice is the percentage of charge contained outside the volume in which 90% of the total charge of a hypothetical H\textsubscript{3} solid in the same unit cell would be found.

[43] X. Zhong, H. Wang, J. Zhang, H. Liu, S. Zhang, H.-F. Song, G. Yang, L. Zhang, and Y. Ma, \textit{arXiv}:1503.00396.

[44] Y. Yao, J. S. Tse, K. Tanaka, F. Marsiglio, and Y. Ma, \textit{Phys. Rev. B} \textbf{79}, 054524 (2009).

[45] As $\beta$ further approaches the transition point, $\omega_\text{in}$ is expected to decrease rapidly, limiting the maximum $T_c$ achievable.

[46] The \textsc{abinit} code is a common project of the Université Catholique de Louvain and other contributors, “http://www.abinit.org”.

[47] N. Troullier and J. L. Martins, \textit{Phys. Rev. B} \textbf{43}, 1993 (1991).

[48] J. P. Perdew, K. Burke, and M. Ernzerhof, \textit{Phys. Rev. Lett.} \textbf{77}, 3865 (1996).

[49] S. Zhang, Y. Wang, J. Zhang, H. Liu, X. Zhong, H.-F. Song, G. Yang, L. Zhang, and Y. Ma, \textit{arXiv}:1502.02607.

[50] Y. Ge, F. Zhang, and Y. Yao, \textit{arXiv}:1507.08525.