Cubic H$_3$S around 200 GPa: an atomic hydrogen superconductor stabilized by sulfur

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The multiple scattering-based theory of Gaspari and Gyorffy for the electron-ion matrix element in close packed metals is applied to Im$ar{3}$m H$_3$S, which has been predicted by Duan et al. and Bernstein et al to be the stable phase at this stoichiometry around 190 GPa, thus is the leading candidate to be the phase observed to superconduct at 190K by Drozdov, Eremets, and Troyan. The nearly perfect separation of vibrational modes into those of S and of H character provides a simplification that enables identification of contributions of the two atoms separately. The picture that arises is basically that of superconducting atomic H stabilized by strong covalent mixing with S and d character. The reported isotope shift is much larger than the theoretical one, suggesting there is large anharmonicity in the H vibrations. Given the relative unimportance of sulfur, hydrides of lighter atoms at similarly high pressures may also lead to high temperature superconductivity.

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The report by Drozdov, Eremets, and Troyan (DET) of superconductivity up to $T_c$=190 K in H$_3$S compressed to the 200 GPa regime has reigned excitement in the possibility of achieving room temperature superconductivity. This report builds on previous success of pressure enhancement of $T_c$ in a variety of types of materials: from 134 K to 164 K in the cuprate Hg$_2$2223$^{14}$ from zero to 20-25 K in the simple metals Li, Ca, and Y$^{15}$ and from zero to 14K in the insulator silicon$^{16}$. An anticipated major factor is the increase in the phonon energy scale with compression, since it sets the temperature scale for $T_c$, as pointed out early on$^{14}$ and reviewed more recently$^{17}$ by Ashcroft in predicting possible room temperature superconductivity in metallic hydrogen.

The newly reported high values of $T_c$ appear to confirm theoretical predictions that predated the experiment. Applying particle swarm crystal structure search techniques founded on density functional theory, Li et al. predicted$^{14}$ candidate stable crystal structures of H$_3$S up to 220 GPa. These predictions were followed by linear response calculations of the phonon spectrum $\omega_Q$, electron-phonon matrix elements, and finally the Eliashberg spectral function $\alpha^2 F(\omega)$, from which $T_c$ can be calculated, depending only mildly on the presumed value of the retarded Coulomb repulsion $\mu^*$ = 0.10-0.13. For pressures of 140-180 GPa, they obtained an electron-phonon coupling strength $\lambda$=1.0-1.2, an Allen-Dynes characteristic frequency $\omega_{\text{log}}$$\sim$1000K, and $T_c$ of 40K at 140 GPa and peaking at 80 K at 160 GPa. While 80K is well short of the reported $T_c$=190K, the result is convincing that very high $T_c$ is predicted in H$_3$S at high pressure.

The sister stoichiometry H$_2$S has been explored in very similar fashion by Duan et al$^{18}$ Predicting structures to more than 200 GPa, their linear response results for Im$ar{3}$m H$_2$S led to very large calculated values of electron-phonon coupling strength $\lambda$=2.0-2.2, frequency scales $\omega_{\text{log}}$$\sim$1300K, and values of $T_c$ up to 200K. In the calculations of Li et al. and Duan et al., the high values of $\omega_{\text{log}}$ are expected from the anticipated increase of force constants as volume is decreased. The large values of $\lambda$, a factor of two or more over most other very good superconductors (including MgB$_2$), imply that the electronic matrix elements are substantially larger than in nearly all known conventional superconductors.

In this report we use Gaspari-Gyorffy (GG) theory$^{17}$ to provide insight into why electron-ion matrix elements vary, and evidently increase strongly, with pressure. Such understanding is necessary not only to interpret the results described above, but also to provide essential clues how to increase matrix elements, and $\lambda$, at lower or possibly ambient pressure. Ironically, shortly after the formulation of this theory, two of the present authors applied it to predict $T_c$$\sim$250K in metallic hydrogen at a few Mbar pressure$^{16}$.

GG theory$^{17}$ builds on the earlier observation of Hopfield$^{19}$ that electron scattering off (moving) ions has strong local character. First, metallic screening means the Thomas-Fermi screening length is short, of the order of 1 Å, and very weakly dependent on carrier density (more correctly, the Fermi level density of states [DOS] $N(E_F)$). GG employed a multiple scattering Green’s function formalism that facilitated three simplifications. The first is that the potential is spherical (very good approximation) and is negligible beyond the atomic sphere; the second is that the linear change in potential of a displaced ion can be approximated by a rigid shift of the...
atomic potential. Thirdly, the direction dependence of the wavefunction coefficients is averaged out, thereby neglecting any special influence of Fermi surface shape. The H$_3$S Fermi surface is large and multisheeted, minimizing the likelihood of Fermi surface effects. It is possible that these approximations may improve with reduction in volume, in any case these approximations should not degrade as the system become denser. The bands shown in Fig. 1 demonstrating the two interlaced ReO$_3$ sublattices. Large sphere is S, small sphere is H.

The coupling strength $\lambda$, and the frequency weighting spectrum $g(\omega)$ normalized to unity, are given in Eliashberg theory by

$$\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega; \quad g(\omega) = \frac{2\alpha^2 F(\omega)}{\lambda \omega},$$

where $\alpha^2 F$ is the Eliashberg electron-phonon spectral function that governs many superconducting properties. The calculations by Li et al. for H$_2$S and Duan et al. for H$_3$S demonstrate that the lower range of phonon frequencies (the acoustic modes) have negligible H character, while the optic modes above the gap at 20-25 THz have negligible S character, making it an ideal platform for applying the GG expression to the atoms separately.

Thus $\lambda = 3\lambda_H + \lambda_S$, where the latter arise from the integral over the low frequency S modes, the former from the nine higher frequency H branches. In this case the GG expression, given originally for an elemental solid, can be applied to the S and H spheres separately. Each atomic ($j$) coupling constant $\lambda_j$ is given by the integral over the appropriate frequency region, leading to

$$\lambda_j = \frac{N(E_F) \langle \bar{I}_j^2 \rangle}{M_j\omega_j^2} = \frac{\eta_j}{M_j\omega_j^2}.$$  

(2)

The averaged matrix elements $\langle \bar{I}_j^2 \rangle$ obtained from GG theory are discussed below.

The separation of mode character also allows a simple estimate of the total frequency moments that enter the Allen-Dynes (AD) equation for $T_c$, through the weight function

$$g(\omega) = \left[ \lambda_S g_S(\omega) + 3\lambda_H g_H(\omega) \right] / (\lambda_S + 3\lambda_H),$$

(3)

where the partial $g_j$ functions, defined analogously to that of AD (Eq. 1) are separately normalized to unity.

Both H$_2$S and H$_3$S having been shown to have strong electron-phonon coupling at high pressure. Bernstein et al. have provided convincing evidence that H$_2$S is unstable to decomposition into bcc H$_3$S and sulfur, and that competing stoichiometries are unlikely. This result confirms the suggestion of DET, who reported sulfur formation in their samples. Because of this evidence on the most likely superconducting phase, we focus on $Im3m$ H$_3$S with its simple bcc structure based in two interlaced ReO$_3$ structure sublattices. From $\alpha^2 F$ of Duan et al., we simplify with a constant $\alpha^2 F_j$ (constant for each atom species $j$) with frequency ranges (in kelvin) of [430,820] for S and [1250,2500] for H. Results are insensitive to these limits, depending mostly on the mean frequencies and the separation of $\lambda$ into S and H contributions. The resulting frequency moments $\omega_{log_1}, \omega_1,$ and $\omega_2$ and associated data, for insight into separate S and H contribution,
for use in the AD equation and to compare with results below from GG theory, are presented in Table I.

With \( \mu^* = 0.15 \), \( T_c = 234 \) K results; the difference from the value quoted by Duan et al. might be due to neglect of the strong coupling factor \( f_1 = 1.13 \) factor in the AD equation, which amounts to a 26 K increase, or partially to our constant \( \alpha^2 F \) modeling. Neglecting the contribution from the S modes, \( \lambda \) is decreased from 2.2 to 1.5 but \( \omega_{\log} \) increases from 1500 K to 1770 K, and \( T_c \) decreases by only 19 K to 215 K. The sulfur contribution to \( T_c \) is 8%\(^{\circ}\); \( \text{H}_3\text{S} \) is basically an atomic hydrogen high temperature superconductor. Bernstein et al. also suggested that S vibrations are not essential for the high \( T_c \) (though in practice there is no clear method of effecting such a tradeoff).

The second moment frequency at 200 GPa of S is \( \omega_2^S = 615 \) K, while that of H is \( \omega_2^H = 1840 \) K, thus with the atomic masses of 32 and 1 a.m.u respectively, the denominator \( M \omega_2^S \) is 32/9 = 3.5 larger for S. The consequence is that a given contribution to \( \eta_S \), is 3.5 \times 3 \approx 10 \) times more effective in increasing \( \lambda \) than the same contribution to \( \eta_S \) (though in practice there is no clear method of effecting such a tradeoff).

In terms of the phase shifts \( \delta_{\ell,j} \) for the \( j \)-th atom for orbital channel \( \ell \), the square electron-ion matrix element averaged of the Fermi surface can be written in the simple form as

\[
\langle I_j^2 \rangle = \frac{E_F}{\pi^2 N(E_F)} \frac{1}{N(E_F)} \sum_{\ell=0}^{2} 2(\ell + 1) \sin^2(\delta_{\ell} - \delta_{\ell+1}) \nu_\ell \nu_{\ell+1}\langle 4 \rangle
\]

where \( \nu_\ell = N_\ell(E_F)/N^{(1)}_\ell \) is the ratio of the \( \ell \)-th partial DOS to the \( N^{(1)} \), the single scatterer DOS, for the given atomic potential in a homogeneous system. Energy cannot affect the result, \( \langle I_j^2 \rangle \) is independent of \( N(E_F) \) since it can equally well be expressed in terms of the fractions \( N_\ell(E_F)/N(E_F) \) which usually do not reflect the van Hove singularities of either one. The calculated DOS at 210 GPa is shown in Fig. 2. The Fermi level falls at the peak of a sharp and narrow peak; calculations at other volumes indicate this is a persistent occurrence. \( \langle I_j^2 \rangle \) will tend to be maximized in the cases where “neighboring” channels \( \ell, \ell + 1 \) have a large difference in phase shifts but as similar as possible ratios \( \nu_{\ell} \). From the GG expression, for each atom \( \eta_j = N(E_F) \langle I_j^2 \rangle \), and the latter factor involves the \( \sin^2(\delta_{\ell} - \delta_{\ell+1}) \) factor and products of PDOS ratios \( \nu_\ell \nu_{\ell+1} \). \( M_j \omega_j^2 \) can be expressed in terms of the force constants, independent of \( M_j \), so that any isotope effect different from \( M^{-1/2} \) will arise from factors beyond \( \lambda \) (primarily anharmonicity). The calculations have been carried out with two all-electron linearized augmented plane wave (LAPW) codes, one developed at NRL and also ELK. The sphere radii were 1.8 a.u. and 1.0 a.u. for S and H respectively, except for the smallest volume where the S radius was reduced because the sum of the radii must be no more than \( a/2 \).

The band structure consists of nearly filled bands, leaving some holes at \( \Gamma \) and electrons around \( \text{N} \). In addition, a fifth broad band is roughly half filled. The DOS is noteworthy: free electron like over 20 eV of the valence band before strong structure arises in a \( \pm 7 \) eV range centered at \( E_F \), which lies very close (slightly above) the strong and nearly constant \( \text{H} \) peak in the DOS. This peak at \( E_F \) persists for all pressures from \( P = 0 \) to 300 GPa and even above, almost as if \( E_F \) were pinned at this peak, while other features of the DOS evolve.

Table I shows the Fermi level values of total and angular momentum components of the electronic densities of states across a wide range of volumes. Even though \( 1m\overline{3}m \) \( \text{H}_3\text{S} \) may not be stable at lower pressures, we provide results for the large range \( P = 0-210 \) GPa to observe the effect of interatomic distance on the electronic structure and coupling. While the total \( N(E_F) \) shows a weak non-monotonic variation, the \( \ell \)-components have a stronger lattice constant(pressure) dependence. As expected the sulfur 3\( p \)-like states are the dominant component but a strong participation of 3\( d \) character especially at high pressures is present, hybridizing with the also strong and nearly constant H 1s contribution. Now we discuss the electronic factor \( \eta_j \). It should be kept in mind that the relative importance for \( T_c \) of H versus S modes is not simply \( \lambda_j \), but more like \( \lambda_j \omega_{2,j} \) which is a factor of ten greater for 3\( H \) than for S). For hydrogen, which dominates the contribution to \( T_c \) only the \( s - p \) channel is relevant at all pressures. The phase

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**TABLE I:** Electron-phonon coupling data for \( \text{H}_3\text{S} \), obtained from modeling the results of Duan et al. with a constant \( \alpha^2 F \) model. Frequencies are in Kelvin.

|                  | S   | H   | Total |
|------------------|-----|-----|-------|
| \( \omega_{\log} \) | 595 | 1770| 1500  |
| \( \omega_2 \)   | 605 | 1800| 1530  |
| \( M \omega_2^S \) (eV/\( \text{\AA}^2 \)) | 9.3 | 2.6 | –     |
| \( \eta \) (eV/\( \text{\AA}^2 \)) | 4.7 | 1.48| –     |
| \( \lambda \)    | 0.5 | 1.7/3| 2.2   |

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\[ \langle I_j^2 \rangle = \frac{E_F}{\pi^2 N(E_F)} \frac{1}{N(E_F)} \sum_{\ell=0}^{2} 2(\ell + 1) \sin^2(\delta_{\ell} - \delta_{\ell+1}) \nu_\ell \nu_{\ell+1}\langle 4 \rangle \]
shift factor $\sin^2(\delta_s - \delta_p)$ decreases with pressure. Fig. 3 illustrates the factor of two increase in $\eta_H$ from P=100 GPa to 300 GPa. This dramatic increase results from an even larger increase in the PDOS product $\nu^{H}_{d} \nu^{H}_{p}$, reflecting transfer of 1s character to 2p character. In the spherical harmonic expansion of the atomic wavefunctions this ‘2p’ character represent the expansion of tails of the orbitals on neighboring atoms that gives rise to the increased H-S hybridization under pressure.

As noted above from our analysis of the results of Duan et al., the sulfur contribution is less important. As for H, the increase in $\eta$ occurs in spite of a decrease in the $\sin^2(\delta_p - \delta_d)$ factor, by 30% from P=100 to P=300 GPa. Over this pressure range, the PDOS ratio product $\nu^{S}_{d} \nu^{S}_{p}$ increases by 75%, giving a net $\eta$ increase by more than 50%. In addition, the S s–p and even d–f channels begin to contribute, reaching 20% of the total of $<I^2>$. Due to this, the PDOS ratio product $\nu^{S}_{d} \nu^{S}_{p}$ increases by 75%, giving a net $\eta$ increase by more than 50%. In addition, the S s–p and even d–f channels begin to contribute, reaching 20% of the total of $<I^2>$ at 300 GPa. Thus the increase is a composite effect of increase of both $d$ and $s$ character of S, which is reflected also in the growing phase shifts of these channels. These transfers of atomic character under pressure are consistent with general expectations of the evolution of atomic character under reduction of volume. Interpolating to 200 GPa to obtain $\eta_S=5.84$ eV/Å$^2$, $\eta_H=1.71$ eV/Å$^2$, and using the frequency moments from Table 1, we obtain $\lambda=2.6$, thus $T_c \sim 250^\circ K$ depending somewhat on the chosen value of $\mu^*=-0.10$-$0.13$. This value is very consistent with the value of $T_c$ (above) obtained from our modeling of the Duan data. Though the numbers might vary for other low-Z hydrides (H$_2$P, H$_2$B, ...) the lack of any special role of S in these results suggests there should also be a strong increase in $T_c$ with pressure in other low-Z element hydrides.

A question of great interest is whether $T_c$ increases further at higher pressure. The data presented in Table I provides the pressure dependence of the important quantities entering $\eta_S$ and $\eta_H$. This data demonstrates that the strongest contributions arise for sulfur from the pd channel and for hydrogen from the sp channel. Note that for H one should multiply by three to account for the three H atoms in the unit cell.

Since $\lambda_H$ dominates the sulfur contribution, we can focus on the H contribution alone. The pressure variation of the $M\omega^2$ denominators is challenging to approximate without full calculations of the spectrum and $\alpha^2 F$. We have chosen to model the variation of the H spectrum by assuming the three 3-fold $\Gamma$ point modes are representative. The lower two of these modes are IR-active involving H-S bond stretch and bond bending modes, the hardest frequency is a silent mode with quadrapolar H motion with respect to S. From calculations of these $\Gamma$ frequencies in the 240-270 GPa range using the ELK code we find a positive but modest pressure increase $d\log \omega_H/dP=5\times10^{-3}$ GPa$^{-1}$. From Fig. 3 we obtain $d\log \eta_H/dP=3.5\times10^{-3}$ GPa$^{-1}$, thus $\lambda$ decreases with pressure as $d\lambda_H/dP\sim1.5\times10^{-2}$ K/GPa.

The total pressure derivative contains other contributions from

$$
\frac{d\log T_c}{dP} = \frac{d\log \omega_{\log}}{dP} + \frac{d\log f_1}{dP} + \frac{d\log E(\lambda)}{dP}
$$

(5)

where $f_1$ is the strong coupling correction and $E(\lambda)$ is the exponential term in the Allen-Dynes equation. The first term is positive but doesn’t compensate for the decrease of $\lambda_H$ under pressure, and the net result is a predicted decrease in $T_c$ starting at some point above 240 GPa. This result agrees in sign with Duan et al., who quoted a small negative value of $dT_c/dP=-0.12$ K/GPa from direct calculation.

To summarize: The report by DET of $T_c$ up to 190 K in H$_n$S samples has breathed new life into the 50 year...
old expectation of high $T_c$ in atomic H systems. Both Li et al. and Duan et al. had found that Eliashberg theory and linear response results for electron-phonon coupling account for $T_c$ in the 80-200 K range for H$_2$S and H$_3$S at high pressure, and the analysis of Bernstein et al make Im$s$Im H$_2$S the primary candidate to be this record-high temperature superconductor. In this paper we have established that the coupling of H vibrations increases strongly for pressures up to and even beyond 210 GPA, and that 90+% of the coupling arises from H vibrations in this hydride that is stabilized by hybridization with S. This picture is analogous to the finding of the essential contribution of H in the superconductor PdH at high pressure, and the analysis of Bernstein et al make Im$s$Im H$_2$S the primary candidate to be this record-high temperature superconductor. In this paper we have established that the coupling of H vibrations increases strongly for pressures up to and even beyond 210 GPA, and that 90+% of the coupling arises from H vibrations in this hydride that is stabilized by hybridization with S. This picture is analogous to the finding of the essential contribution of H in the superconductor PdH at high pressure, and the analysis of Bernstein et al make Im$s$Im H$_2$S the primary candidate to be this record-high temperature superconductor. In this paper we have established that the coupling of H vibrations increases strongly for pressures up to and even beyond 210 GPA, and that 90+% of the coupling arises from H vibrations in this hydride that is stabilized by hybridization with S. This picture is analogous to the finding of the essential contribution of H in the superconductor PdH at high pressure, and the analysis of Bernstein et al make Im$s$Im H$_2$S the primary candidate to be this record-high temperature superconductor.

TABLE III: Pressure variation of the Hopfield parameter $\eta$ (eV/Å$^2$) and electron-ion squared matrix element $<I^2>$ (eV$^2$/Å$^2$), both decomposed into the three channels $sp, pd$, and $df$ for S, and the H $sp$ channel (given for a single atom).

| P (GPa) | $\eta_{sp}$ | $S_{I_{sp}}$ | $\eta_{pd}$ | $S_{I_{pd}}$ | $\eta_{df}$ | $S_{I_{df}}$ | $H_{I_{sp}}$ | $H_{I_{pd}}$ |
|---------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 5.6     | 210         | 6.68        | 2.66        | 5.12        | 20.1        | 0.31        | 1.21        | 1.80        | 7.06        |
| 5.8     | 142         | 0.39        | 1.65        | 4.45        | 18.9        | 0.21        | 0.89        | 1.43        | 6.06        |
| 6.0     | 92          | 0.24        | 1.00        | 4.14        | 17.4        | 0.15        | 0.63        | 1.24        | 5.21        |
| 6.2     | 57          | 0.19        | 0.78        | 4.13        | 17.5        | 0.13        | 0.57        | 1.02        | 4.34        |
| 6.4     | 31          | 0.08        | 0.33        | 3.52        | 14.1        | 0.08        | 0.31        | 0.96        | 3.87        |
| 6.6     | 13          | 0.05        | 0.18        | 3.37        | 12.7        | 0.06        | 0.21        | 0.87        | 3.31        |
| 6.8     | 0           | 0.02        | 0.09        | 3.12        | 11.2        | 0.04        | 0.14        | 0.79        | 2.83        |

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and D. J. Singh was used with Hedin-Lundqvist exchange-correlation. DOS results were generated from 285 k points in the irreducible Brillouin zone with the tetrahedron method. Total energies were fit to the Birch equation to obtain the P(V) equation of state.

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