Debye temperature in highly compressed H\textsubscript{3}S and D\textsubscript{3}S

E. F. Talantsev\textsuperscript{1,2*}

1M.N. Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, 18, S. Kovalevskoy St., Ekaterinburg, 620108, Russia
2NANOTECH Centre, Ural Federal University, 19 Mira St., Ekaterinburg, 620002, Russia

*E-mail: evgeny.talantsev@imp.uran.ru

Abstract

If near-room-temperature (NRT) superconductivity in highly-compressed superhydrides/superdeuterides is originated from the electron-phonon coupling, then the superconducting transition temperature, $T_c$, and phonon spectrum characteristics (for instance, the Debye temperature, $T_\theta = \frac{\hbar}{k_B} \cdot \omega_D$, or logarithmic phonon temperature, $\omega_{ln} = \frac{\hbar}{k_B} \cdot \omega_{ln}$) should be linked through the electron-phonon coupling strength constant, $\lambda_{e-ph}$, which can be computed by first-principles calculations. Thus, by utilizing relations between $T_c$, $T_\theta$ or $\omega_{ln}$, and $\lambda_{e-ph}$ (proposed by Bardeen, Cooper and Schrieffer (1957 Phys Rev \textbf{108} 1175), McMillan (1968 Phys Rev \textbf{167} 331), Allen and Dynes (1975 Phys Rev B \textbf{12} 905)) it is possible to affirm/disprove the electron-phonon coupling mechanism in given superconductor. In this paper, we deduce $T_\theta$ for highly-compressed black phosphorous, boron, GeAs, SiH\textsubscript{4}, H\textsubscript{3}S and D\textsubscript{3}S by the fit of temperature-dependent resistivity data, $\rho(T)$, to Bloch-Grüneisen equation. We show that computed $\lambda_{e-ph}$ for highly-compressed black phosphorous, boron, GeAs, and SiH\textsubscript{4} are within weak-coupling limit of BCS theory. It is also found remarkable constancy of $T_\theta = 1531 \pm 70 \text{ K}$ for H\textsubscript{3}S at different ageing stages. Due to phonon spectra in H\textsubscript{3}S and D\textsubscript{3}S have identical shape, we show that these isotopic counterparts obey the relation of $T_{\theta,H3S}/T_{\theta,D3S} = T_{c,H3S}/T_{c,D3S} = \omega_{ln,H3S}/\omega_{ln,D3S}$. However, ratios of $T_{c,H3S}/T_{c,D3S} = \omega_{ln,H3S}/\omega_{ln,D3S} = 1.27$ are largely different from deduced $T_{\theta,H3S}/T_{\theta,D3S} = 1.65$. This
alludes that NRT superconductivity in H₃S-D₃S system is originated from more than one mechanism, where the electron-phonon coupling lifts $T_c$ in H₃S vs D₃S, but primary origin for NRT background of $T_c \sim 150$ K in both H₃S and D₃S remains to be discovered.

Debye temperature in highly compressed H₃S and D₃S

1. Introduction.

Demanded for several decades [1-4] near-room-temperature (NRT) superconductivity has been discovered by pioneer experimental work by Drozdov et al [5] who reported the superconducting transition temperature of $T_c = 203$ K in highly-compressed sulphur hydride, H₃S. To date, there is widely accepted point of view that the mechanism of NRT superconductivity in highly-compressed superhydrides/superdeuterides is the electron-phonon coupling [6-9]. If so, the superconducting transition temperature, $T_c$, and phonon spectrum characteristics (for instance, Debye frequency and Debye temperature, $\omega_D$ and $T_\theta$ respectively) should be linked through the electron-phonon coupling strength constant, $\lambda_{e-ph}$, introduced in Eliashberg theory [10]:

$$\lambda_{e-ph} = 2 \cdot \int_{0}^{\infty} \frac{\alpha^2(\omega) \cdot F(\omega)}{\omega} \cdot d\omega$$

(1)

where $\omega$ is the phonon frequency, $F(\omega)$ is the phonon density of states, and $\alpha^2(\omega) \cdot F(\omega)$ is the electron-phonon spectral function (more details can be found elsewhere [11,12]). In this phenomenology, all superconductors are characterized as having weak ($\lambda_{e-ph} \ll 1$), intermediate ($\lambda_{e-ph} \sim 1$), and strong ($\lambda_{e-ph} \gg 1$) coupling.

For weak-coupled superconductors, Bardeen, Cooper and Schrieffer [13] proposed an expression which links $T_c$, $T_\theta$ and $\lambda_{e-ph}$:

$$T_c = T_\theta \cdot e^{-\left(\frac{1}{\lambda_{e-ph} - \mu^*}\right)}$$

(2)
where $\mu^*$ is the Coulomb pseudopotential parameter, which is for a wide range of superconductors (including highly-compressed hydrides/deuterides) is assumed to be within a range of $\mu^* = 0.10$-0.17 [6].

Allen and Dynes [14,15] derived an asymptote for large $\lambda_{e-ph}$ values within the BCS theory [13]:

$$T_c = \frac{\lambda_{e-ph}}{2} \cdot T_\theta.$$  \hspace{1cm} (3)

From Eq. 3 it is clear that $T_c$ (within the BCS theory [13]) can be “arbitrarily large” [15], because high $T_0$ is not necessarily a requirement for high $T_c$.

McMillan [16] performed advanced analysis of the problem by utilizing the Eliashberg theory [10] and proposed the equation:

$$T_c = \left(\frac{1}{1.45}\right) \cdot T_\theta \cdot e^{-\frac{1.04(1+\lambda_{e-ph})}{\lambda_{e-ph}-\mu^*(1+0.62\lambda_{e-ph})}}$$  \hspace{1cm} (4)

which is highly accurate for a wide range of the coupling strength, $\mu^* \leq \lambda_{e-ph} \leq 1.5$ [14,15], and it is widely used to evaluate the $T_c$ in phonon mediated superconductors, including 2D superconductors [17].

It should be noted, that McMillan [16] introduce the multiplicative pre-factor of $\left(\frac{1}{1.45}\right) \cdot T_\theta$ in Eq. 4 based on experimental convenience to use the Debye temperature, $T_\theta$ (or, the Debye frequency, $\omega_D$), in comparison with more complicated functions which can be defined based on full $\alpha^2(\omega) \cdot F(\omega)$ phonon spectrum. And the reason for this was, that even for intrinsic uncompressed superconductors there are a very limited number of experimental techniques (for instance, the point-contact tunnelling spectroscopy) which can be used to measure full $\alpha^2(\omega) \cdot F(\omega)$ phonon spectrum. It should be stressed that none of these techniques have been ever applied for highly-compressed superconductors because of experimental challenges.
However, the Debye temperature, $T_\theta$, can be in “the safest” manner [18] deduced from the fit of experimental temperature dependent resistivity data, $\rho(T)$, to Bloch-Grüneisen (BG) equation [19,20]:

$$\rho(T) = \rho_0 + A \cdot \left(\frac{T}{T_\theta}\right)^5 \cdot \int_0^T \frac{T_\theta}{x^5} \frac{x^5}{(e^x-1)(1-e^{-x})} \cdot dx$$  \hspace{1cm} (5)

where, the first term is the residual resistivity due to the scattering of conduction charge carriers (holes) on the static defects of the crystalline lattice, while the second term describes the hole-phonon scattering, and $A$ and $T_\theta$ are free-fitting parameters.

Eqs. 4,5 are instructive tool to derive $\lambda_{e-ph}$ in intrinsic [21,22] and highly-compressed [23] superconductors, which works from weak to intermediate coupling strength of $\lambda_{e-ph} \lesssim 1$. In this paper, we further show that Eqs. 4,5 can be used to derive $\lambda_{e-ph}$ values in a variety of highly-compressed superconductors (i.e. black phosphorous [24,25], boron [26], GeAs [27], and silane [28]), which are in a good agreement with $\lambda_{e-ph}$ values reported by the first-principles calculations studies.

It should be noted, that one of the most widely used approximation of the Eliashberg theory [10] beyond Eq. 4 has been proposed by Allen and Dynes [14,15,18]:

$$T_c = \left(\frac{1}{1.20}\right) \cdot \frac{\hbar}{k_B} \cdot \omega_{ln} \cdot e^{-\left(\frac{1.04(1+\lambda_{e-ph})}{\lambda_{e-ph}-\mu^*\{1+0.62\lambda_{e-ph}\}}\right) \cdot f_1 \cdot f_2}$$ \hspace{1cm} (6)

where:

$$\omega_{ln} = \exp\left[\int_0^{\infty} \frac{\omega F(\omega) d\omega}{\int_0^{\infty} \frac{\omega F(\omega) d\omega}{\omega}}\right]$$ \hspace{1cm} (7)

$$f_1 = \left(1 + \left(\frac{\lambda_{e-ph}}{2.46(1+3.8\mu^*)}\right)^{3/2}\right)^{1/3}$$ \hspace{1cm} (8)

$$f_2 = 1 + \frac{\left(\frac{\omega_{ph}^{1/2}}{\omega_{ln}^{-1}}\right)^{\lambda_{e-ph}}}{\lambda_{e-ph}^2 + \left(1.82(1+6.3\mu^*)\left(\frac{\omega_{ph}^{1/2}}{\omega_{ln}^{-1}}\right)^{2}\right)}$$ \hspace{1cm} (9)

$$\langle \omega^2 \rangle^{1/2} = \frac{2}{\lambda_{e-ph}} \cdot \int_0^{\infty} \omega \cdot \omega^2 \cdot F(\omega) \cdot d\omega.$$ \hspace{1cm} (10)
where \(f_1\) and \(f_2\) are so-called the strong-coupling correction function and the shape correction function, respectively [15]. It should be stressed, that Eq. 6 is also an approximation of general Eliashberg theory [10], and Eq. 6 is not accurate approximation for some superconductors, which was discussed by Allen and Dynes [14,15,18].

Primary reason, why \(\left(\frac{1}{1.45}\right) \cdot T_\theta\) (in Eq. 4) was proposed to replace by \(\left(\frac{1}{1.20}\right) \cdot \omega_{tn}\) (in Eq. 6) is that the numerator \(\left(\frac{1}{1.45}\right)\) in Eq. 4 was deduced for niobium (the element with highest \(T_c\) and intermediate \(\lambda_{e-ph}\)). This numerator needs to be slightly adjusted from one material to another, while the pre-factor \(\left(\frac{1}{1.20}\right)\) in Eq. 5 is much less varied (however, this does not mean that it should not need to be adjusted). Allen and Dynes [15] explored the dependence of \(T_c\) vs \(\omega_{ln}\) for a wide range of theoretically possible values of \(0 \leq \lambda_{e-ph} \leq 10^6\), while the highest experimental \(\lambda_{e-ph}\) value at the time of their work was \(\lambda_{e-ph} = 2.59\) (this value is still one of the largest experimentally measured \(\lambda_{e-ph}\) to date).

Based on a fact that modern first-principles calculations techniques can compute \(\alpha^2(\omega) \cdot F(\omega)\) spectrum (and, thus, \(\lambda_{e-ph}\)) with a very high accuracy, Eq. 6 became a primary equation for the first-principles calculations studies for highly-compressed superhydrides/superdeuterides (extended reference list can be found elsewhere [6-9,29-32]). However, as we mentioned above, experimental measurements of \(\alpha^2(\omega) \cdot F(\omega)\) in highly-compressed superconductors are not performed to date and alternative experimental approaches need to be developed for NRT superconductors in term to reveal the nature of the pairing mechanism in this compound.

In this paper, we propose one of these approaches which consider the isotopic counterparts (designated by subscripts 1 and 2) of one chemical compound. We propose the exact relation between \(T_c\) and \(T_\theta\) which is independent from particular \(\alpha^2(\omega) \cdot F(\omega)\) spectrum. Truly, all first principles calculations studies show that the shape of \(\alpha^2(\omega) \cdot F(\omega)\)
spectra for isotopic counterparts of H\textsubscript{3}S-D\textsubscript{3}S and of LaH\textsubscript{10}-LaD\textsubscript{10} are practically undistinguishable, and thus, adjustable numerators of \(\left(\frac{1}{1.45}\right)\) in Eq. 4 and of \(\left(\frac{1}{1.20}\right)\) in Eq. 6 will be cancelled in the ratios:

\[
\frac{T_{c1}}{T_{c2}}_{\text{exp}} = \frac{\omega_{\ln1}}{\omega_{\ln2}}_{\text{first-principles calcs}} = \frac{T_{\theta1}}{T_{\theta2}}_{\text{exp } \rho(T)},
\]

where the subscript of \(\rho(T)\) on the right part designates that \(T_{0,1}\) and \(T_{0,2}\) are deduced by the fit of experimental \(\rho(T)\) data to Bloch-Grüneisen (BG) equation (Eq. 5).

Thus, surprisingly enough, the research task to reaffirm/disprove the electron-phonon coupling mechanism in highly compressed hydrides/deuterides is to compare experimentally observed \(\frac{T_{c1}}{T_{c2}}_{\text{exp}}\) and/or computed \(\frac{\omega_{\ln1}}{\omega_{\ln2}}_{\text{first-principles calcs}}\) (where the latter is, in fact, always calculated to match observed \(T_{c,1}\) and \(T_{c,2}\)) with deduced \(\frac{T_{\theta1}}{T_{\theta2}}_{\text{exp } \rho(T)}\).

By applying Eq. 11 to H\textsubscript{3}S-D\textsubscript{3}S system, we find that the ratio of \(\frac{T_{\theta,\text{H3S}}}{T_{\theta,\text{D3S}}}_{\text{exp } \rho(T)} \cong 1.65\) is remarkably different from \(\frac{T_{\theta,\text{H3S}}}{T_{\theta,\text{D3S}}}_{\text{exp } \rho(T)} \cong 1.28\).

From this we conclude that there are two distinctive mechanisms which cause the raise of NRT superconductivity in highly-compressed H\textsubscript{3}S-D\textsubscript{3}S system. One is the electron-phonon coupling which busts the observed \(T_c\) in H\textsubscript{3}S vs D\textsubscript{3}S, while the primary mechanism which is the origin for high background \(T_c \gtrsim 150\) \(K\) in both isotopic counterparts remains to be discovered. This means that, due to observed \(T_c\) in D\textsubscript{3}S is either not busted strongly, neither busted at all by the electron-phonon coupling, the research of D\textsubscript{3}S makes more fundamental interest in comparison with H\textsubscript{3}S.

In this regard, the sulphur tritiate, T\textsubscript{3}S, looks even more attractive to be studied, in comparison with H\textsubscript{3}S and D\textsubscript{3}S, in term to reveal fundamental mechanism of NRT superconductivity, because of, at least, three reasons:
1. The contribution of electron-phonon coupling on the superconducting state in T₃S should be even more suppressed in comparison with D₃S. Thus, unrevealed yet background mechanism which causes the raise NRT superconductivity in highly compressed super-hydrides/deuterides will be less distorted by the electron-phonon interaction.

2. Much greater chemical activity of tritium in comparison with hydrogen and deuterium, which originates from low-level $\beta$-radioactivity of the former, can be served as additional catalytic factor (in addition to primary laser heating) to form T₃S phase from T₂S gas in diamond-anvil cell.

3. Ground state upper critical field, $B_{c2}(0)$, in T₃S might be lower than ones in H₃S and D₃S. This makes it possible to measure temperature dependent $B_{c2}(T)$ for T₃S in a wider temperature range in comparison with H₃S and D₃S, and, thus, to perform deeper analysis of $B_{c2}(T)$.

Despite a fact that the cost of T₃S synthesis and studies will be much higher in comparison with ones for H₃S and D₃S, the former looks to be a key material to reveal the mechanism of NRT superconductivity.

2. Utilized models

In our previous works [33-35], we analysed temperature dependent self-field critical current densities, $J_c(sf,T)$, and the upper critical field, $B_{c2}(T)$, data in highly-compressed H₃S and showed that experiment supports the weak-coupling scenario in this superhydride. Kaplan and Imry [36] also showed that electron-phonon weak-coupling scenario is a valid theoretical model for compressed in H₃S. Thus, there is no a priory reason to reject the weak-coupling scenario from the consideration, and $\lambda_{e-ph}$ values derived by Eq. 2 will be designated as $\lambda_{e-ph,BSC}$. Deduced $\lambda_{e-ph}$ for strong-coupling scenario within BCS theory (Eq. 3) will be
designated as $\lambda_{e-ph,BS\text{c\,asym}}$, and coupling strength, $\lambda_{e-ph}$, computed by the first-principles calculations will be notated as $\lambda_{e-ph,fp\text{c}}$.

To turn now to strong-coupling scenario within the Eliashberg theory [10], we first should note that multiplicative shape correction function, $f_2$ (Eq. 8), has the term of $\left(\frac{\omega^2}{\omega_{ln}}\right)^{1/2}$ which was never been experimentally measured in highly-compressed hydrides/deuterides to date. From other hand, all materials considered by Allen and Dynes (Table 1 [15]) have $\lambda_{e-ph}$ values within a range of $0.69 \leq \lambda_{e-ph} \leq 2.59$, which covers the range of $\lambda_{e-ph}$ reported for highly-compressed superhydrides/superdeuterides by first principles calculations studies [6-9,29-32]. For all these materials multiplicative shape correction function, $f_2$, can be, with accuracy of several percent, approximated by a parabolic function. We demonstrate this in Fig. 1, where $f_2$ function (Eq. 8) is calculated for $\mu^* = 0.10, 0.15, 0.20$ for all materials considered by Allen and Dynes (Table 1 [15]). The upper $\mu^* = 0.20$ bound is intentionally taken larger in Fig. 1 than conventionally used upper bound of $\mu^* = 0.15$.

Thus, with an accuracy of several percent, multiplicative shape correction function $f_2$ (Eq. 7) can be replaced by the parabolic function:

$$f_2^* = 1 + (0.0241 - 0.0735 \cdot \mu^*) \cdot \lambda_{e-ph}^2.$$  \hspace{1cm} (12)

Numerators in Eq. 12 were deduced by the fit of tabulated $f_2$ values for all materials reported by Allen and Dynes (Table 1 [15]) for $\mu^* = 0.10, 0.12, 0.14, 0.16, 0.18, 0.20$.

As this was mentioned by Allen [18], the “safest procedure” to extract $T_0$ from experimental data is to fit $\rho(T)$ to Eq. 10 which we employ in this paper. The coupling constant deduced by the advanced McMillan Eq. 4:

$$T_c = \left(\frac{1}{1.45}\right) \cdot T_0 \cdot e^{-\left(\frac{1.04(1+\lambda_{e-ph,amMcM})}{\lambda_{e-ph}^2\cdot(1+0.62\lambda_{e-ph,amMcM})}\right)} f_1 \cdot f_2^*$$  \hspace{1cm} (13)

will be designated as $\lambda_{e-ph,amMcM}$ as noted.
Considering a fact that all first-principles calculations studies show that the shape of phonon spectra, $\alpha^2(\omega) \cdot F(\omega)$ and $\lambda_{e-ph,fp e}$ for H$_3$S and D$_3$S [37] are practically undistinguishable from each other, one can write:
\[
\frac{T_{c,H_3S}}{T_{c,D_3S}} = \frac{\omega_{ln,H_3S}}{\omega_{ln,D_3S}} \cdot f_{1,H_3S} f_{2,H_3S} = \frac{\omega_{ln,H_3S}}{\omega_{ln,D_3S}} \cdot f_{1,D_3S} f_{2,D_3S} = \frac{\omega_{ln,H_3S}}{\omega_{ln,D_3S}}
\]

\[
\frac{T_{c,H_3S}}{T_{c,D_3S}} = \frac{T_{\theta,H_3S}}{T_{\theta,D_3S}} \cdot f_{1,H_3S} f_{2,H_3S} = \frac{T_{\theta,H_3S}}{T_{\theta,D_3S}} \cdot f_{1,D_3S} f_{2,D_3S} = \frac{T_{\theta,H_3S}}{T_{\theta,D_3S}}
\]

\[
\frac{T_{c,H_3S}}{T_{c,D_3S}} \text{ exp} = \frac{\omega_{ln,H_3S}}{\omega_{ln,D_3S}} \cdot f_{1,H_3S} f_{2,H_3S} = \frac{T_{\theta,H_3S}}{T_{\theta,D_3S}} \text{ exp } \rho(T)
\]

because as we show in Fig. 3, \( f_2 \) function can be approximated by parabolic function \( f_2^* \) (Eq. 12).

Thus, major problem of the McMillan [16] approach (which is exact value for multiplicative numerator in Eq. 5), and of the Allen-Dynes approach [14,15,18] (which is experimentally unknown value of \( \omega_{ln} \) (Eq. 7)) are cancelled out for H_3S and D_3S counterparts (Eq. 16), and if the superconductivity in highly-compressed H_3S-D_3S mediates by the electron-phonon interaction, then three ratios: experimentally observed \( \frac{T_{c,H_3S}}{T_{c,D_3S}} \) computed \( \frac{\omega_{ln,H_3S}}{\omega_{ln,D_3S}} \) and derived \( \frac{T_{\theta,H_3S}}{T_{\theta,D_3S}} \) should be equal to each other. It should be noted, that if isotopic counterparts for some compounds have different \( \alpha^2(\omega) \cdot F(\omega) \) shape, then Eqs. 11,16 can be only approximately satisfied. However, taking in account that \( f_2 \) and \( f_2^* \) are very slow function of \( \lambda_{e-ph} \), Eqs. 11,16 can be still considered as the first order approximation.

We should stress that Eqs. 11,16 are free from the uncertainty related to the accuracy of multiplicative numerator of \( \left( \frac{1}{1.20} \right) \) in Eq. 6, proposed by Allen and Dynes as the first order approximation which compromised between the complexity and the accuracy for the model.
Because more thorough consideration requires the use of high-order momentums of normalized weight function:
\[
\langle \omega^n \rangle = \frac{\int_0^\infty \omega^{n-1} \omega^2 F(\omega) d\omega}{\int_0^\infty \omega^2 F(\omega) d\omega},
\]
and/or, its mean values:
\[
\overline{\omega^n} = \langle \omega^n \rangle^{1/n} = \left( \frac{\int_0^\infty \omega^{n-1} \omega^2 F(\omega) d\omega}{\int_0^\infty \omega F(\omega) d\omega} \right)^{1/n},
\]
which, however (from the author’s knowledge) these higher-orders momentums have been never implemented for the analysis.

To confirm that our approach (i.e., Eqs. 5, 13) is an instructive tool to analyse experimental data for highly-compressed superconductors, in Section 4.3 we perform the comparison of deduced parameters deduced by the \( R(T) \) analysis and by the upper critical field, \( B_{c2}(T) \), analysis for highly-compressed GeAs \((P = 15.3 \text{ GPa})\) recently reported by Liu et al [27].

To analyse \( B_{c2}(T) \) we use a model [35]:
\[
B_{c2}(T) = \frac{\phi_0}{2\pi\xi^2(0)} \left[ \left( \frac{1.77 - 0.43 \left( \frac{T}{T_c} \right)^2 + 0.07 \left( \frac{T}{T_c} \right)^3}{1.77} \right)^2 \cdot \frac{1}{\frac{1}{2k_B T} \int_0^\infty \frac{1}{\cosh^2 \left( \frac{\sqrt{\frac{\Delta^2 + \Delta(T)^2}{2k_B T}}}{2} \right)}} \right],
\]
where \( \phi_0 = 2.07 \cdot 10^{-15} \text{ Wb} \) is flux quantum, \( \xi(0) \) is the ground state coherence length, \( k_B \) is the Boltzmann constant, and temperature dependent amplitude of the energy gap, \( \Delta(T) \), is taken from Gross et al [38]:
\[
\Delta(T) = \Delta(0) \cdot \tanh \left( \frac{\pi k_B T c}{\Delta(0)} \cdot \sqrt{\frac{\eta \cdot \Delta C}{C}} \cdot \left( \frac{T_c}{T} - 1 \right) \right),
\]
where \( \Delta C/C \) is the relative jump in electronic specific heat at \( T_c \), and \( \eta = 2/3 \) for s-wave superconductors [38]. In result, four fundamental parameters of a superconductor, i.e. \( \xi(0), \Delta(0), \Delta C/C \) and \( T_c \), can be deduced by fitting experimental \( B_{c2}(T) \) data to Eq. 18. We need to
clarify that $\xi(0)$ determines the ground state $B_{c2}(0)$ amplitude, while $\Delta(0)$ and $\Delta C/C$ are deduced from the shape of $B_{c2}(T)$ curve (which is the part of Eq. 18 in square brackets). BCS weak coupling limits are:

$$\frac{2\Delta(0)}{k_B T_c} = 3.53,$$  \hfill (20)

$$\frac{\Delta C}{C} = 1.43,$$  \hfill (21)

and, thus, deduced values of $\frac{2\Delta(0)}{k_B T_c}$ and $\frac{\Delta C}{C}$ are independent quantities which can characterize the coupling strength in addition to $\lambda_{e-ph,BCS}$ and $\lambda_{e-ph,\alpha M\alpha M}$ values.

We should stress that Eqs. 18,19 are based on the assumption that the amplitude and the phase coherence have established in the material, and thus superconducting condensate has forms. This means that Eqs. 18,19 are applied for the state when:

$$\rho(T) = 0 \ \Omega \cdot m$$  \hfill (22)

In other words, Eq. 18 is applied when the London penetration depths, $\lambda(T)$, the superconducting coherence length, $\xi(T)$, and the Ginzburg-Landau parameter $\kappa(T) = \frac{\lambda(T)}{\xi(T)}$ have finite values:

$$\begin{cases} 
\lambda(T) \neq \infty \\
\xi(T) \neq \infty \\
\kappa(T) \text{ defined}
\end{cases} \hfill (23)$$

This means that experimental data which are valid to be fitted by Eq. 18 should be obey the $B_{c2}(T)$ definition based on Eq. 22 criterion. We note, that the upper critical field, $B_{c2}(T)$, is very often defined by 50% fraction of the normal state resistivity, $\rho_{\text{norm}}(T)$, criterion:

$$\rho(T) = 0.50 \cdot \rho_{\text{norm}}(T)$$  \hfill (24)

which, cannot be, rigorously speaking, be fitted by Eq. 18, except if the width of the superconducting transition, $\Delta T_c$ (which can be defined as the temperature range where 90% and 10% fractions of $\rho_{\text{norm}}(T)$ achieve), is very narrow, $\Delta T_c \ll T_c$. Truly, 50% drop in the
resistivity at some temperature \( T \) (we consider the case, when \( \rho(T) = 0 \, \Omega \cdot m \) achieves at lower \( T \)) indicates that there are large superconducting order parameter fluctuations (in space and time), at which, however, neither \( \lambda(T) \), nor \( \xi(T) \) are defined yet, because the phase coherence for the condensate has not been formed at this temperature. This issue is closely related to the definition of the superconducting transition temperature, \( T_c \), which we discuss in Section 3. We note, that \( B_{c2}(T) \) defined by Eq. 22, is also referred as the irreversibility field, \( B_{irr}(T) \), especially for cuprate superconductors.

Based on all above, the validity of electron-phonon mediated mechanism of superconductivity in highly-compressed superhydrides/superdeuterides can be, surprisingly enough, affirmed/disproved by the deducing the ratio of the Debye temperatures, \( \frac{T_{\Theta,H_3S}}{T_{\Theta,D_3S}} \), for isotopic counterparts, and compare this ratio with the ratio of experimentally observed

\[
\frac{T_{c,H_3S}}{T_{c,D_3S}}_{\text{exp}}
\]

We report on the result of these studies for \( H_3S-D_3S \) system, herein.

3. \( T_c \) definition

Due to primary focus of this paper is to compare experimentally observed and computed \( T_c \) values, there is a need to make strict definition for the superconducting transition temperature, which will be in use herein. In some papers, \( T_c \) is defined at temperature of the 95\%, 50\%, 10\%, or other fractions of the normal state resistivity, \( \rho_{\text{norm}}(T) \), while the most rigorous definition is at the zero resistivity point, \( \rho(T) = 0 \, \Omega \cdot m \) (Eq. 24).

The definition of \( T_c \) as the fraction of the \( \rho_{\text{norm}}(T) \) in highly-compressed hydrides/detereides is widely used, however, this definition unavoidably raises many problems. For instance, a drop in \( \rho(T) = 0.95 \cdot \rho_{\text{norm}}(T) \) at some temperature \( T \) cannot be a definitive confirmation for the superconducting state, before either \( \rho(T) = 0 \, \Omega \cdot m \), either Meissner-Ochsenfeld diamagnetic response can be detected in experiment. To demonstrate
this problem, in Fig. 2 we show $\rho(T)/\rho(T = 270 \text{ K})$ data for highly-compressed YH$_3$ ($P = 44$ GPa) reported by Matsuoka et al [39].

![Temperature dependent reduced resistivity $\rho(T)/\rho(T = 270 \text{ K})$ for highly compressed YH$_3$ (raw data reported by Matsuoka et al [39]) where $T_c$ is defined by $\rho(T)/\rho(T = 270 \text{ K}) = 0.95$ criterion.](image)

**Figure 2.** Temperature dependent reduced resistivity $\rho(T)/\rho(T = 270 \text{ K})$ for highly compressed YH$_3$ (raw data reported by Matsuoka et al [39]) where $T_c$ is defined by $\rho(T)/\rho(T = 270 \text{ K}) = 0.95$ criterion.

If one applies the criterion of $\rho(T)/\rho(T = 270 \text{ K}) = 0.95$, the superconducting transition temperature can be defined as high as $T_c = 170 \text{ K}$. This means, that if $T_c$ definition is based on any fraction of $\rho_{\text{norm}}(T)$, i.e., $\rho_{\text{norm}}(T) \neq 0 \Omega \cdot \text{m}$, the story of NRT superconductivity should be started in 2007, when Matsuoka et al [39] had reported their $\rho(T)$ dataset for highly compressed YH$_3$. We note, that recently NRT superconductivity with $T_c = 218$-$243 \text{ K}$ (defined by $\rho(T) = 0.99 \cdot \rho_{\text{norm}}(T)$ criterion) in yttrium hydrides compressed at $P = 165$-$237$ GPa has been reported by Troyan et al [31] and Kong et al [40]. Based on the criterion of $\rho(T) = 0.99 \cdot \rho_{\text{norm}}(T)$, the superconducting transition temperature in the yttrium hydride at $P = 44 \text{ GPa}$ [39], $T_c = 182 \text{ K}$, is not much different from recently reported values of $T_c = 218$-$243$ K [31,40]. We, however, should stress that as Troyan et al [31], as Kong et al [40] reported
experimental \( \rho(T) \) curves which have reached zero resistivity point, \( \rho(T) = 0 \ \Omega \cdot m \), within a narrow superconducting transition width, \( \Delta T_c \).

To further demonstrate that the definition of \( T_c \) is crucially important, we can refer recent report by Cao \textit{et al} [41] who discovered superconducting state in the magic-angle twisted bilayer graphene (MATBG) (i.e., 2D sheet where two single layers of graphene are rotated at Moiré superlattice angle, \( \theta \)). In Fig. 3 we show raw \( R(T) \) curve for MATBG sample with twisted angle of \( \theta = 1.05^\circ \) (raw data is from Ref. [41]). Three lines in the Fig. 3 indicate \( R(T)/R_{\text{norm}}(T) = 1.0; 0.90; 0.50 \) criteria and red data point indicate zero resistance state of \( R(T = 0.9 \text{ K}) \cong 0 \ \Omega \).

![Figure 3](image.png)

**Figure 3.** Temperature dependent resistivity \( R(T) \), \( R(T)/R_{\text{norm}}(T) = 1.0; 0.90; 0.50 \) lines and \( R(T = 0.9 \text{ K})/R_{\text{norm}}(T) = 0.0 \) data point are shown for MATBG (\( \theta = 1.05^\circ \)) (raw data reported by Cao \textit{et al} []).

Cao \textit{et al} [41] used \( T_c \) definition of \( R(T)/R_{\text{norm}}(T) = 0.5 \) and defined \( T_c \cong 1.7 \text{ K} \). This definition places MATBG in near proximity to the Bose-Einstein condensate materials (i.e., \(^4\text{He}, ^6\text{Li}, ^{40}\text{K}\) in the Uemura plot. And also, this was the primary reason to claim non-phonon mediated mechanism of superconductivity in MATBG. However, the analysis of the self-field critical current densities, \( J_c(\text{sf},T) \) [42], as well as \textit{ab initio} calculations [17], showed that
the superconductivity in MATBG is phonon mediated and $T_c$ should be defined by the temperature at which condensate phase coherence is established (i.e., by $R(T \cong 1.2 \text{ K}) \rightarrow 0 \ \Omega$ criterion). This $T_c$ definition places MATBG (in the Uemura plot) in the band where all cuprates, pnictides, fullerens, heavy fermions and highly-compressed hydries/deuterides are located [43,44].

However, for highly-compressed superconductors, the definition of $\rho(T=T_c) = 0 \ \Omega \cdot \text{m}$, unfortunately cannot be used either, because many $\rho(T)$ curves never reach $\rho(T) = 0 \ \Omega \cdot \text{m}$, due to experimental challenges (for instance, we can refer $\rho(T)$ data for highly-compressed boron [26] and lithium [45]). In some experiments, if even $\rho(T) = 0 \ \Omega \cdot \text{m}$ has been reached, the transition width are wide, $\Delta T_c \sim (0.3-0.5) \cdot T_c$.

Based on all above, it should be stressed that the comparison of computed (by the first-principles calculations) and experimentally measured $T_c$ values has, unfortunately, a very large uncertainty, which is based on the chosen criterion of $T_c$ definition. Due to $T_c$ is strongly linked to $\lambda_{e-ph}$, the robustness of computed $\lambda_{e-ph}$, $T_c$ and $\omega_{ln}$ values by the first-principles calculations is largely unknown. We demonstrate this issue by the analysis of experimental data for highly-compressed elemental boron (Sec. 4.2) and GeAs (Sec. 4.3).

In this paper, by compromising between all possible complications, we define $T_c$ by the criterion of $\rho(T) = 0 \ \Omega \cdot \text{m}$. If experimental $\rho(T)$ dataset does not reach zero resistivity point, $T_c$ will be defined either by the lowest experimentally available temperature, either (in a case, when $\rho(T)$ is flatten after the drop) by the temperature of the inflection point. For $T_c$ values defined by two latter criteria we report the ratio of $\rho(T)/\rho_{\text{norm}}(T)$, where $\rho_{\text{norm}}(T)$ is the extrapolative curve obtained by the $\rho(T)$ data fit to Bloch-Grüneisen equation (Eq. 5).
4. Results and Discussion

In this section we first show that the approach to use Eqs. 5,13 is a valid research tool to study highly-compressed superconductors. To demonstrate this, we perform $\rho(T)$ analysis and deduce $\lambda_{e-ph}$ values for highly-compressed black phosphorous ($P = 15$ GPa) [25] (Section 4.1), elemental boron ($P = 240$ GPa) [26] (Section 4.2), GeAs ($P = 15.3, 20.6$ and $24$ GPa) [27] (Sections 4.3), and silane ($P = 240$ GPa) [28] (Sections 4.4). Data for $\text{H}_2\text{S}$ and $\text{D}_2\text{S}$ are analysed in Section 4.5. The isotope effect in $\text{H}_2\text{S}-\text{D}_2\text{S}$ system is discussed in Section 4.6.

For the analysis we draw largely on experimental data reported by M. I. Eremets group (Max-Planck Institut für Chemie, Mainz, Germany).

4.1. Black phosphorous compressed at $P = 15$ GPa

Wittig and Matthias [24] discovered pressure-induced superconductivity in black phosphorous with $T_c = 4.7$ K ($P \sim 10$ GPa). Recent experimental studies [46,47] of highly-compressed black phosphorous start to confirm conceptual idea of Hirsch [48,49] that high-temperature superconductivity should be considered as an effect of the interaction between positively charge carriers (holes) and vibrations of positively charged lattice ions (phonons), which is fundamentally different from the idea of BCS theory which considers the interaction between negatively charged carriers (electrons) and vibrations of positively charged lattice ions (phonons). Experiments showed [46,47] that there is clear correlation between $T_c$ and the charge carriers sign in highly-compressed black phosphorous.

In Figure 3 we show raw experimental $\rho(T)$ data for highly-compressed black phosphorous ($P = 15$ GPa) reported by Shirotani et al [25] in their Figure 5. The $\rho(T)$ data fit to Eq. 5 is excellent and deduced $T_\theta$ and $\lambda_{e-ph}$ are presented in Table 1. To derive $\lambda_{e-ph}$ values we use conventional lower bound of $\mu^* = 0.10$ and the upper bound of $\mu^* = 0.17$ (for which the first-principles calculations results were reported by Li et al [47]).
Table 1. Deduced $T_0$ and calculated $\lambda_{e-ph}$ for highly-compressed black phosphorus at $P = 15$ GPa.

| $T_c$ (K) | $T_0$ (K) | $\lambda_{e-ph,BCS\ asymp}$ | Assumed $\mu^*$ | $\lambda_{e-ph,BCS}$ | $\lambda_{e-ph,aMcM}$ | $\lambda_{e-ph,fpc}$ [47] |
|-----------|-----------|-----------------------------|-----------------|----------------------|----------------------|------------------------|
| 6.7       | 563 ± 16  | 0.019 ± 0.001               | 0.10            | 0.314 ± 0.001        | 0.488 ± 0.003        | 0.628 ± 0.005          |
|           |           |                             | 0.17            | 0.384 ± 0.001        | 0.628 ± 0.005        | 0.627 - 0.673          |

**Figure 4.** Resistivity data, $\rho(T)$, and fit to BG model (Eq. 5) for highly-compressed black phosphorus (raw data is from Ref. 47). The fit quality is $R = 0.998$. 95% confidence bar is shown. Green balls indicate the bounds for which $\rho(T)$ data was used for the fit to Eq. 5. Cyan ball shows $T_c$ defined by $\rho(T)/\rho_{norm}(T) = 0.80$ criterion.

It can be seen (Table 1) that deduced $\lambda_{e-ph,BCS} = 0.31 - 0.38$ is within BCS weak coupling limit, which originates from low value for the ratio of $\frac{T_c}{T_0} \cong 0.009$ (it can be noted that weak-coupling aluminium has $\lambda_{e-ph,BCS} = 0.30 - 0.38$ [18]).

Thus, there is an uncertainty, why more complicated intermediate coupling strength scenario should be considered, if weak-coupling limit of BCS is well satisfied. However, due to Li et al [47] performed first-principles calculations and reported that highly-compressed black phosphorus has $\lambda_{e-ph,fpc} = 0.63 - 0.67$ ($\mu^* = 0.17$) we calculated $\lambda_{e-ph,aMcM} = 0.63$
(µ* = 0.17) by our Eq. 13, which appears to be in excellent agreement with the value reported by Li et al [47].

This result shows that calculated coupling strength λ_{e-ph} is actually dependent on the chosen model, rather than to be unique characteristic value for given superconductor. The only valid result, we can trust so far, that because of calculated λ_{e-ph, BCS assym} = 0.019 ≪ µ∗, then phonon-mediated Cooper pairs cannot exist in the assumption of strong-coupling scenario (which reflects a simple fact that there are no reasons to assume that λ_{e-ph} can be large, if the superconductor has Tc/T_θ ≃ 0.009).

4.2. Elemental boron compressed at P = 240 GPa

Eremets et al [26] discovered that elemental boron transforms into superconductor with T_c > 4 K at pressure of 160 GPa ≤ P ≤ 250 GPa. Ma et al [50] calculated λ_{e-ph, fpc} = 0.38 − 0.39 for µ* = 0.12 in the wide pressure range of 160 GPa ≤ P ≤ 273 GPa. Several years later, Sun et al [51] studied highly-compressed boron nanowires and reported T_c = 1.5 K at pressure of P = 84 GPa, and Shimizu et al [52] confirmed the superconducting state in bulk boron with T_c~3 K at pressure of P = 159±5 GPa.

Eremets et al [26] in their Figure 2 reported experimental resistance data, R(T), for the boron at different pressures, from which in Figure 4 we show R(T) at P = 240 GPa. It can be seen that R(T) = 0 Ω has not been achieved and thus we use a series of T_c definitions, R(T)/R_{norm}(T) = 0.95; 0.80; 0.67, where the latter is defined by the inflection point.

The R(T) data fit to Eq. 5 is excellent and deduced T_θ = 314 ± 2 K. In Table 2 we show deduced λ_{e-ph} values in the assumption of µ* = 0.12 (which is chosen to be the same with one used by Ma et al [50]).
Table 2. Deduced $T_0$ and calculated $\lambda_{e-ph}$ for highly-compressed boron at $P = 240$ GPa with assumed $\mu^* = 0.12$.

| $T_c$ (K) | $T_0$ (K) | $\lambda_{e-ph, asymp}$ | $\lambda_{e-ph, BCS}$ | $\lambda_{e-ph, aMCM}$ | $\lambda_{e-ph,fpc}$ [50] |
|-----------|-----------|------------------------|----------------------|----------------------|--------------------------|
| 10.1      | 314 ± 2   | 0.064                  | 0.411 ± 0.001        | 0.769 ± 0.002        |                          |
| 8.9       |           | 0.057                  | 0.401 ± 0.001        | 0.731 ± 0.002        | 0.39 (P = 215-279 GPa)   |
| 7.4       |           | 0.050                  | 0.387± 0.001         | 0.683 ± 0.002        |                          |

Figure 5. Resistance data, $R(T)$, and fit to BG model (Eq. 5) for highly-compressed elemental boron (raw data is from Ref. 26). The fit quality is $R = 0.9994$. 95% confidence bar is shown. Green balls indicate the bounds for which $\rho(T)$ data was used for the fit. Yellow ball shows $T_c$ defined by $R(T)/R_{norm}(T) = 0.95$ criterion; cyan ball shows $T_c$ defined by $R(T)/R_{norm}(T) = 0.80$ criterion; and red ball shows $T_c$ defined by $R(T)/R_{norm}(T) = 0.67$ criterion.

It should be stressed (Table 2), that $T_c$ values defined by three different criteria are varied by 36%, however this a large variation in $T_c$ corresponds to very small changes in $\lambda_{e-ph, BCS}$ (6%) and $\lambda_{e-ph, aMCM}$ (13%). Based on computed value of $\lambda_{e-ph,fpc} = 0.39$ [50] one can
conclude that highly-compressed elemental boron \((P = 240 \, \text{GPa})\) is a weak-coupling superconductor. This conclusion is also supported by low value for the ratio of \(\frac{T_{c,0.67 R_{\text{norm}}}}{T_{\theta}} = \frac{7.4 \, K}{314 \, K} \approx 0.024\), and \(\frac{T_{c,0.95 R_{\text{norm}}}}{T_{\theta}} = \frac{7.4 \, K}{314 \, K} \approx 0.032\).

However, there is a question, how the accuracy of first-principles calculations and numerators in Eqs. 4,6 can be evaluated, if the change in \(T_c\) by more than \(\frac{1}{3}\) corresponds to a minor change in computed \(\lambda_{e-ph}\). This means that numerators in Eqs. 4,6 (i.e. \(\frac{1}{1.45}\) and \(\frac{1}{1.20}\), correspondingly) practically do not make any effect on calculated \(T_c\) values.

### 4.3. Highly-compressed superconducting GeAs

Liu et al [27] reported that superconducting state can be induced in semiconducting compound of GeAs at pressures \(P \geq 10 \, \text{GPa}\). For GeAs subjected to pressure of \(P = 15.3 \, \text{GPa}\), Liu et al [27] reported \(R(T,B)\) curves (Fig. 4(a) [27]) from which \(B_{c2}(T)\) was deduced by the criterion of:

\[
R(T, B_{c2}(T)) = 0.01 \cdot R_{\text{norm}}(T = 9 \, \text{K})
\]  

(25)

Fit of \(B_{c2}(T)\) to Eq. 18 is shown in Fig. 6. Deduced parameters (within uncertainties) are very close to weak-coupling limits of BCS theory:

\[
\frac{2\Delta(0)}{k_B T_c} = 3.55 \pm 0.23
\]  

(26)

\[
\frac{\Delta C}{C} = 1.56 \pm 0.32
\]  

(27)

Raw \(R(T)\) curves (from Fig. 3(a) of Ref. 27) and data fits to BG equation for GeAs compressed at \(P = 15.3, 20.6, \text{ and } 24.0 \, \text{GPa}\) are shown in Fig. 7, where \(R(T)/R_{\text{norm}}(T) = 0.0\) points are taken from Fig. 3(b) [27], and \(R(T)/R_{\text{norm}}(T) = 0.95\) for Fig. 3(a) [27]. Deduced \(\lambda_{e-ph}\) values in assumption of \(\mu^* = 0.10\) (which is the same as one used by Liu et al [27]) are shown in Table 3.
It should be noted (Table 2), that at $P = 24$ GPa, $T_c$ values defined by $R(T)/R_{\text{norm}}(T) = 0.0$ and $R(T)/R_{\text{norm}}(T) = 0.95$ criteria are varied by nearly twice (i.e. 96%), however this large variation in $T_c$ corresponds to a small changes in $\lambda_{e-ph,\text{BCS}}$ (10%) and $\lambda_{e-ph,\text{aMCM}}$ (17%).

It can be seen also (Table 3), that calculated $\lambda_{e-ph,fpc} = 0.51$ (at $P = 24$ GPa) neither corresponds to the $T_c = 2.5$ K (defined by $R(T)/R_{\text{norm}}(T) = 0.0$ criterion), nor by $T_c = 4.9$ K (defined by $R(T)/R_{\text{norm}}(T) = 0.95$). Computed $\lambda_{e-ph,fpc} = 0.51$ corresponds to $T_c = 4.46$ K which means that the criterion for $T_c$ defined by $R(T)/R_{\text{norm}}(T) = 0.81$ criterion should be valid.

Similarly, at $P = 20.6$ GPa, computed $\lambda_{e-ph,fpc} = 0.51$ corresponds to $T_c = 4.54$ K which corresponds to $R(T)/R_{\text{norm}}(T) = 0.83$ criterion, which is also (despite its proximity to $R(T)/R_{\text{norm}}(T) = 0.81$ criterion deduced for GeAs compressed at $P = 24$ GPa) cannot be justified by any sensible background physics (at least, for the current status of the theory of superconductivity).

Figure 6. The fit to Eq. 18, the upper critical field, $B_{c2}(T)$, for GeAs compressed at pressure of $P = 15.3$ GPa (raw data is from Ref. 27), the fit quality is $R = 0.9998$, 95% confidence bar is shown.
Figure 7. $R(T)$ data and fits to BG model (Eq. 5) for highly-compressed GeAs (raw $R(T)$ data is from Ref. 27). 95% confidence bars are shown. Green balls indicate the bounds for which $\rho(T)$ data was used for the fit. (a) $P = 15.3$ GPa ($T_0 = 351 \pm 5$ K), fit quality $R = 0.9995$. (b) $P = 20.6$ GPa ($T_0 = 405 \pm 4$ K), fit quality $R = 0.9992$. (c) $P = 24.0$ GPa ($T_0 = 398 \pm 4$ K), fit quality $R = 0.9996$. Yellow balls show $T_c$ defined by $R(T)/R_{\text{norm}}(T) = 0.0$ criterion; cyan balls show $T_c$ defined by $R(T)/R_{\text{norm}}(T) = 0.95$ criterion;
However, one can see in Table 3, that deduced $\lambda_{e-ph, BCS} \approx 0.30 - 0.36$ (which are within BCS weak-coupling limit) are well matched $\frac{\Delta(0)}{k_B T_c} = 3.55 \pm 0.23$ and $\frac{\Delta_C}{\lambda} = 1.56 \pm 0.32$ values (which are also within BCS weak-coupling limits) deduced from the analysis of $Bc_2(T)$ data.

Table 3. Deduced $T_c$, $T_\theta$ and calculated $\lambda_{e-ph}$ for highly-compressed GeAs with assumed $\mu^* = 0.10$ [27].

| Pressure (GPa) | $T_\theta$ (K) | $T_c$ (K) | $\lambda_{e-ph, BCS}$ asymp | $\lambda_{e-ph, BCS}$ | $\lambda_{e-ph, aMCM}$ | $\lambda_{e-ph, fpc}$ [27] |
|---------------|---------------|-----------|-----------------------------|------------------------|------------------------|--------------------------|
| 15.3          | 351 ± 5       | 7.3       | $R(T)/R_{norm}(T) = 0.0$    | 0.041 ± 0.001          | 0.358 ± 0.001          | 0.612 ± 0.003           |
|               |               | 8.1       | $R(T)/R_{norm}(T) = 0.95$   | 0.042 ± 0.001          | 0.358 ± 0.001          | 0.634 ± 0.003           |
| 20.6          | 405 ± 4       | 3.95      | $R(T)/R_{norm}(T) = 0.0$    | 0.020 ± 0.001          | 0.316 ± 0.001          | 0.493 ± 0.001           |
|               |               | 6.3       | $R(T)/R_{norm}(T) = 0.95$   | 0.031 ± 0.001          | 0.340 ± 0.001          | 0.558 ± 0.001           |
| 24.0          | 398 ± 4       | 2.5       | $R(T)/R_{norm}(T) = 0.0$    | 0.13(4)                | 0.297 ± 0.001          | 0.446 ± 0.001           |
|               |               | 4.9       | $R(T)/R_{norm}(T) = 0.95$   | 0.025(4)               | 0.327 ± 0.001          | 0.523 ± 0.002           |

4.4. Silane compressed at $P = 192$ GPa

First principles calculations for highly compressed hydrogen-rich silane, SiH$_4$, have been performed by several authors, from which we can mention a report by Feng et al [53] who computed $T_\theta \approx 3,500 - 4,000$ $K$ and $T_c \approx 165$ $K$, and the report by Chen et al [54] who computed $T_c = 20 - 75$ $K$ for this hydrogen-rich material at pressure in the range of $70$ $GPa \leq P \leq 250$ $GPa$. 
Eremets et al. [28] discovered that SiH$_4$ exhibits low-temperature superconductivity with transition temperature in the range of $7 \, K \leq T_c \leq 17 \, K$ at pressure in the range of $60 \, GPa \leq P \leq 192 \, GPa$.

In Figure 8 we show raw $R(T)$ curve (from Fig. 2(b) of Ref. 28) and data fit to BG equation for SiH$_4$ compressed at $P = 192 \, GPa$. First of all, experimental data show that $T_\theta \cong 353 \pm 3 \, K$, which is by one order of magnitude lower than $T_\theta \cong 3,500 − 4,000 \, K$ computed by the first principles calculations [53].

To calculate $\lambda_{e-ph}$, we use $T_c = 7.7 \, K$ defined at the inflection point of temperature dependent resistance, $R(T=7.7 \, K)/R_{\text{norm}}(T) = 0.64$, and $T_c = 10.6 \, K$ defined by $R(T=10.6 \, K)/R_{\text{norm}}(T) = 0.95$ criterion. Computed values are in Table 4 for which $\mu^* = 0.10$ [55] and 0.12 [54] are used.

Taking in account that the ratio of \[ \frac{T_{c,0.64} R_{\text{norm}}}{T_\theta} = \frac{7.7 \, K}{353 \, K} \lesssim 0.022, \] there is no need to consider intermediate or strong coupling scenarios. This becomes even more evident if we take in account that first principles calculations compute $\lambda_{e-ph, fpc} = 0.8 − 0.9$ which leads to unrealistically high $T_c$ values of $T_c = 20 − 165 \, K$ [53,54].

| $T_\theta$ (K) | $T_c$ (K) | $\lambda_{e-ph,BCS\ asymp}$ | Assumed $\mu^*$ | $\lambda_{e-ph,BCS}$ | $\lambda_{e-ph,\alpha M\chi M}$ | $\lambda_{e-ph,fpc}$ |
|---------------|-----------|------------------|----------------|-----------------|----------------|----------------|
| 353 ± 3       | 7.7       | 0.044 ± 0.001    | 0.10 [55]     | 0.361 ± 0.001   | 0.622 ± 0.002 | 0.9 [55]     |
|               | 10.6      | 0.061 ± 0.001    | 0.10 [55]     | 0.386 ± 0.001   | 0.699 ± 0.002 | 0.9 [55]     |

Thus, we can make an intermediate conclusion that at least for the first discovered highly-compressed hydrogen-rich compound, SiH$_4$, first principles calculations based on electron-phonon coupling mechanism and full $\alpha^2(\omega) \cdot F(\omega)$ spectrum are not able to reproduce, even
approximately, observed in experiment \( T_c \) (with the difference as large, as 20 times). This conclusion is also applied for highly-compressed black phosphorus, boron and GeAs.

The simplest assumption we can make is that in highly-compressed superconductors \( T_c \) and \( T_\theta \) are independent from each other.

![Figure 8.](image)

**Figure 8.** \( R(T) \) data and fit to BG model (Eq. 5) for highly-compressed SiH\(_4\) \((P = 192 \text{ GPa})\). Raw \( R(T) \) data is from Ref. 28. 95% confidence bars are shown. Green balls indicate the bounds for which \( \rho(T) \) data was used for the fit. Fit quality \( R = 0.9994 \). Cyan ball shows \( T_c \) defined at the inflection point of \( R(T)/R_{\text{norm}}(T) = 0.64 \).

4.5. **Highly compressed H\(_3\)S**

Drozdov *et al* [5] reported milestone discovery of NRT superconductivity in highly-compressed laser annealed sulphur hydride, H\(_3\)S, exhibited \( T_c > 200 \text{ K} \) at megabar pressure. In this work, we analyse experimental \( R(T) \) data for one H\(_3\)S sample exhibiting four months ageing (at \( P = 155 \text{ GPa} \)) and one freshly prepared sample at \( P = 160 \text{ GPa} \). For both samples experimental \( R(T) \) curves were reported by Mozaffari *et al* [56].

The first H\(_3\)S sample was subjected to \( P = 155 \text{ GPa} \). \( R(T) \) curves measured at different ageing stages (within 4 months) show two superconducting transitions in the temperature
range of $192.5 \, K < T_c < 201 \, K$ (Fig. 9), however, all $R(T)$ curves for this sample reach zero resistance point, $R(T) = 0 \, \Omega$, at $T > 192.5 \, K$.

![Figure 9](image)

**Figure 9.** $R(T)$ data and fit to BG model (Eq. 5) for highly-compressed H$_3$S ($P = 155$ GPa) at different ageing stages. Raw $R(T)$ data is from Ref. 56. 95% confidence bars are shown. Green balls indicate the bounds for which $\rho(T)$ data was used for the fit. Cyan balls show $T_c$ defined by $R(T)/R_{\text{norm}}(T) = 0.0$ criterion. Yellow balls show $T_c$ defined by $R(T)/R_{\text{norm}}(T) = 0.95$ criterion. (a) Fit quality $R = 0.9998$. (b) Fit quality $R = 0.9995$. (c) Fit quality $R = 0.9971$. 

$T_\theta = 1,426 \pm 1 \, K$

$T_\theta = 1,561 \pm 2 \, K$

$T_\theta = 1,560 \pm 3 \, K$
The second sample subjected to pressure of $P = 160$ GPa has $R(T)$ curve which does not reach zero resistance point (Fig. 10) even at lowest available in experiment temperature of $T = 82.9$ K. For this sample, $T_c$ is defined by the inflection point of $R(T=158 \text{ K})/R_{\text{norm}}(T) = 0.08$, while $R(T=183 \text{ K})/R_{\text{norm}}(T) = 0.95$ (Fig. 10).

![Graph](image)

**Figure 10.** $R(T)$ data and fit to BG model (Eq. 5) for highly-compressed H$_3$S ($P = 160$ GPa). Raw $R(T)$ data is from Ref. 56. 95% confidence bars are shown. Green balls indicate the bounds for which $\rho(T)$ data was used for the fit. Cyan ball shows $T_c$ defined by the inflection point of $R(T)/R_{\text{norm}}(T) = 0.08$. Yellow ball shows $T_c$ defined by $R(T)/R_{\text{norm}}(T) = 0.95$ criterion. Fit quality $R = 0.997$.

Deduced $T_\theta$ and computed $\lambda_{e-ph}$ for both samples are shown in Table 5. First of all, we should mention remarkable constancy in deduced Debye temperature $T_\theta = 1531 \pm 70$ K for both samples and different ageing stages for the first sample, with standard deviation less than 2%.

It can be also seen in Table 5, that as $T_c$, as $\lambda_{e-ph}$ are varied in wide ranges covers values computed for harmonic and anharmonic models, when different criteria and coupling-strength models are applied, and thus there are no experimental evidences to make a conclusion which model is more preferable in comparison with others.
However, deduced from experiment the Debye temperature, $T_\theta$, is remaining to be constant for all samples. This result is in agreement with the report by Harshman and Fiory [57] who performed analyses of residual resistance ratios for H$_3$S and D$_3$S and found that $T_c$ values and the transition width of the transition in H$_3$S-D$_3$S system are related to the samples purity and atomic disorder, which overwhelming the influence on $T_c$ originated by other factors.

Table 5. Deduced $T_\theta$ and calculated $\lambda_{e-ph}$ for highly-compressed H$_3$S at $P = 155$ GPa (raw $R(T)$ curves were reported by Mozaffari et al [56]).

| Sample ID       | $T_\theta$ (K) | $T_c$ (K) | $\lambda_{e-ph,asymp}$ | Assumed $\mu^*$ | $\lambda_{e-ph,BCS}$ | $\lambda_{e-ph,AMCM}$ | $\lambda_{e-ph}$ (first-principles calculations) [37] |
|-----------------|----------------|-----------|-------------------------|-----------------|----------------------|------------------------|--------------------------------------------------|
| 07/2018 (P = 155 GPa) | 1426 ± 1 | 192.5 | 0.270 | 0.10 | 0.599 | 1.93 | 1.84 (anharmonic) 2.64 (harmonic) |
|                 |               | 197.0 | 0.276 | 0.10 | 0.605 | 1.98 |                      |
| 09/2018 (P = 155 GPa) | 1561 ± 2 | 195.5 | 0.251 | 0.10 | 0.582 | 1.78 |                      |
|                 |               | 200.7 | 0.257 | 0.10 | 0.588 | 1.83 |                      |
| 11/2018 (P = 155 GPa) | 1560 ± 3 | 195.5 | 0.251 | 0.10 | 0.582 | 1.78 |                      |
|                 |               | 200.8 | 0.257 | 0.10 | 0.588 | 1.83 |                      |
| 07/2018 (P = 160 GPa) | 1576 ± 11 | 158 | 0.201 | 0.10 | 0.535 | 1.44 |                      |
|                 |               | 183 | 0.232 | 0.10 | 0.564 | 1.65 |                      |

29
4.6. Highly compressed D$_3$S

Drozdov et al [5] in their Fig. 2(b) reported $R(T)$ dataset for highly-compressed D$_3$S ($P = 155$ GPa). $R(T)$ data fit to Eq. 5 is shown in Fig. 11. Reasonably large uncertainty in deduced $T_\theta = 982 \pm 127$ K is primarily related to narrow temperature range for which $R(T)$ data was measured. We should mention that sulphur deuteride at $P = 155$ GPa exhibits $R3m$ phase [58], which is different from $Im-3m$ phase of H$_3$S compound at the same pressure.

![Graph of R(T) data and fit to BG model](image)

**Figure 11.** $R(T)$ data and fit to BG model (Eq. 5) for highly-compressed D$_3$S in $R3m$ phase ($P = 155$ GPa). Raw $R(T)$ data is from Ref. 5. 95% confidence bars are shown. Green balls indicate the bounds for which $\rho(T)$ data was used for the fit. Cyan ball shows $T_c$ defined by $R(T)/R_{\text{norm}}(T) = 0.95$ criterion. Yellow ball shows $T_c$ defined by $R(T)/R_{\text{norm}}(T) = 0.07$ criterion. Fit quality $R = 0.978$.

In Figs. 12,13 we show $R(T)$ data fits for D$_3$S ($P = 173$ and 190 GPa, respectively) reported by Einaga et al [58] in their Fig. 3(b). Calculated $\lambda_{e-ph}$ for all three D$_3$S samples are in Table 7.

It should be noted that due to D$_3$S samples were subjected to a wide range of pressure, $P = 155 - 190$ GPa, at lowest pressure the compounds has $R3m$ phase symmetry, and for $P = 173$ and 190 GPa the compound has $Im-3m$ phase symmetry (which is exhibited at $P \geq 160$ GPa).

\[\text{T}_\theta = 982 \pm 127 \text{ K}\]
Based on this, we calculate average $T_\theta$ only for $Im\text{-}3m$ phase:

$$T_\theta = 930 \pm 92 \text{ K} \tag{28}$$

which has, nevertheless, a narrow uncertainty of 10%. However, due to its large uncertainty, the $T_\theta$ value for $R3m$ phase is also within this temperature range.
In overall, deduced $\lambda_{\text{e-ph}}$ (Table 6) for $Im$-$3m$ phase are equally well matched as harmonic, as anharmonic models, because the highest deduced $\lambda_{\text{e-ph}}$ value is agreed with the former, and the lowest $\lambda_{\text{e-ph}}$ value is agreed with the latter (the highest and the lowest $\lambda_{\text{e-ph}}$ values are marked in bold in Table 7).

Table 6. Deded $T_\theta$ and calculated $\lambda_{\text{e-ph}}$ for D$_3$S compressed at $P = 155, 173, \text{and } 190 \text{ GPa}$ (raw $R(T)$ curves were reported by Drozdov et al [5] and Einaga et al [58]).

| Pressure (GPa) | $T_\theta$ (K) | $T_c$ (K) | $\lambda_{\text{e-ph,asym}}$ | Assumed $\mu^*$ | $\lambda_{\text{e-ph,BCS}}$ | $\lambda_{\text{e-ph,AMCM}}$ | $\lambda_{\text{e-ph}}$ (first-principles calculations) |
|---------------|----------------|-----------|-----------------|---------------|----------------|----------------|--------------------------------|
| 155 (Drozdov et al [5]) | 982 ± 127 | 131 $R(T)/R_{\text{norm}}(T) = 0.07$ | 0.267 ± 0.031 | 0.10 | 0.597 ± 0.029 | 1.91 ± 0.23 | 1.87 (anharmonic) [37] |
| | | 147 $R(T)/R_{\text{norm}}(T) = 0.95$ | 0.299 ± 0.031 | 0.10 | 0.627 ± 0.032 | 2.17 ± 0.28 | |
| 173 (Einaga et al [58]) | 869 ± 4 | 138 $R(T)/R_{\text{norm}}(T) = 0.08$ | 0.318 ± 0.002 | 0.10 | 0.644 ± 0.002 | 2.33 ± 0.01 | 2.64 (harmonic) [37] |
| | | 155 $R(T)/R_{\text{norm}}(T) = 0.95$ | 0.357 ± 0.002 | 0.10 | 0.680 ± 0.002 | 2.68 ± 0.02 | |
| 190 (Einaga et al [58]) | 995 ± 8 | 138 $R(T)/R_{\text{norm}}(T) = 0.09$ | 0.275 ± 0.003 | 0.10 | 0.606 ± 0.002 | 1.99 ± 0.02 | |
| | | 144 $R(T)/R_{\text{norm}}(T) = 0.95$ | 0.290 ± 0.003 | 0.10 | 0.617 ± 0.002 | 2.09 ± 0.02 | |

It should be also noted, that, in overall, $\lambda_{\text{e-ph}}$ values deduced for D$_3$S are much much than $\lambda_{\text{e-ph}}$ deduced for H$_3$S, which is in remarkable contradiction with results of first-principles calculations, which showed that $\lambda_{\text{e-ph}}$ for both isotopic counterparts are indistinguishably close to each other [37]. More detailed discussion of the isotope effect in H$_3$S-D$_3$S system is given in next Section.
4.7. Isotope effect in H_{3}S-D_{3}S system

Now we turn to the discussion of the most crucial effect which can confirm or disprove the electron-phonon coupling mechanism in H_{3}S-D_{3}S system, which is the isotope effect. Due to all three available raw \( R(T) \) datasets for D_{3}S never reached \( R(T)/R_{\text{norm}}(T) = 0.0 \) state, we compare herein \( T_{c} \) data for H_{3}S and D_{3}S for \( R(T)/R_{\text{norm}}(T) = 0.95 \) criterion.

As we show above that if the superconductivity in two these isotope counterparts is belonging the electron-phonon coupling, then the Eq. 16 should be satisfied. By taking in account primary conclusion of first-principles calculations [37], that H_{3}S and D_{3}S are anharmonic electron-phonon superconductors:

\[
\left. \frac{\hbar \omega_{\text{ln},H_{3}S}}{\hbar \omega_{\text{ln},D_{3}S}} \right|_{f_{\text{pc,anharmonic}}} = \frac{92.86 \text{ meV}}{73.3 \text{ meV}} \left|_{f_{\text{pc,anharmonic}}} = 1.27 \right. \tag{29}
\]

The ratio in Eq. 29 should be compare with the ratio of average value for \( T_{c} \) for two isotopic counterparts in \( Im-3m \) crystallographic phase state (Tables 5 and 6):

\[
\frac{T_{c,H_{3}S}}{T_{c,D_{3}S}} \left|_{R(T)/R_{\text{norm}}(T) = 0.95} = \frac{195.4 \pm 8.4 \text{ K}}{149.5 \pm 7.8 \text{ K}} \right|_{R(T)/R_{\text{norm}}(T) = 0.95} = 1.31 \pm 0.05 \tag{30}
\]

which is in a good agreement with Eq. 29.

The ratio of the Debye temperatures for two isotopic counterparts in \( Im-3m \) crystallographic phase (Tables 5 and 6) is:

\[
\frac{T_{\theta,H_{3}S}}{T_{\theta,D_{3}S}} = \frac{1531 \pm 70 \text{ K}}{930 \pm 92 \text{ K}} = 1.65 \pm 0.17 \tag{31}
\]

5. Discussion

Taking in account that first-principles calculations is very accurate modern research tool, large disagreement of computed ratio of logarithmic phonon frequencies (Eq. 29) and experimentally observed ratio of critical temperatures (Eq. 30) with deduced ratio of Debye temperatures (Eq. 31) means that electron-phonon mechanism is irrelevant to observed NRT superconductivity, however it takes some effect of the second order for the magnitude of
observed $T_c$, because, quite likely that this mechanism is the origin for slightly higher transition temperature in H$_3$S in comparison with D$_3$S.

However, primary mechanism which is the background that both H$_3$S and D$_3$S are NRT superconductors is remains to be unknown. Alternative pairing mechanisms in superconductors are in discussion for several decades [59-62]. However, detail discussion of this most advanced way to treat NRT superconductivity is beyond the scope of this paper.

6. Conclusion

In this paper we deduce the Debye temperature, $T_\theta$, in highly-compressed black phosphorous, boron, GeAs, SiH$_4$, H$_3$S and D$_3$S by the fit of temperature-dependent resistivity data, $\rho(T)$, to Bloch-Grüneisen equation. We find that isotopic counterpart compounds (designated by subscripts 1 and 2) should obey the relation:

$$\frac{T_{c1}}{T_{c2}} = \frac{\omega_{ln1}}{\omega_{ln2}} = \frac{T_{\theta1}}{T_{\theta2}}$$

which can be considered as a new research tool to validate the electron-phonon mechanism of superconductivity in a variety of the materials. Application of Eq. 32 to H$_3$S-D$_3$S system leads us to a conclusion that NRT superconductivity in these compounds is originated from more than one mechanism.

Acknowledgement

Author thanks financial support provided by the state assignment of Minobrnauki of Russia (theme “Pressure” No. AAAA-A18-118020190104-3) and by Act 211 Government of the Russian Federation, contract No. 02.A03.21.0006.

References

[1] Ashcroft N W 1968 Metallic Hydrogen: A High-Temperature Superconductor Phys. Rev. Lett. 21, 1748
[2] Ginzburg V L 1969 Superfluidity and superconductivity in the universe J Stat Phys 1 3-24
[3] Eremets M I, Drozdov A P, Kong P P, Wang H 2019 Semimetallic molecular hydrogen at pressure above 350 GPa Nature Physics 15 1246-1249
[4] Ashcroft N W 2004 Hydrogen dominant metallic alloys: high temperature superconductors? Phys. Rev. Lett. 92 187002
[5] Drozdov A P, Eremets M I, Troyan I A, Ksenofontov V, Shylin S I 2015 Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system Nature 525 73-76
[6] Gor'kov L P and Kresin V Z 2018 Rev. Mod. Phys. 90 011001
[7] Zureka E and Bi T 2019 High-temperature superconductivity in alkaline and rare earth polyhydrides at high pressure: A theoretical perspective J. Chem. Phys. 150 050901
[8] Hamlin J J 2019 Nature 569 491
[9] Boeri L and Bachelet G B 2019 J. Phys.: Condens. Matter 31 234002
[10] Eliashberg G M 1960 Soviet Phys. JETP 11 696
[11] Carbotte J P 1990 Properties of boson-exchange superconductors Rev. Mod. Phys. 62 1027
[12] Marsiglio F 2020 Eliashberg theory: A short review Annals of Physics; in press https://doi.org/10.1016/j.aop.2020.168102
[13] Bardeen J, Cooper L N, and Schrieffer J R 1957 Phys. Rev. 108 1175
[14] Dynes R C 1972 McMillan's equation and the $T_c$ of superconductors Solid State Communications 10 615-618
[15] Allen P B and Dynes R C 1975 Transition temperature of strong-coupled superconductors reanalysed Phys. Rev. B 12 905-922
[16] McMillan W L 1968 Transition temperature of strong-coupled superconductors Phys. Rev. 167 331-344
[17] Lian B, Wang Z, and Bernevig B A 2019 Twisted bilayer graphene: A phonon-driven superconductor Phys Rev Lett 122 257002
[18] Allen P B, in Handbook of Superconductivity (edited by C. P. Poole, Jr.) (Academic Press, New York, 1999) Ch. 9, Sec. G, pp. 478-489
[19] Bloch F 1930 Zum elektrischen Widerstandsgesetz bei tiefen Temperaturen Z. Phys. 59 208-214
[20] Blatt F J 1968 Physics of Electronic Conduction in Solids (New York: McGraw-Hill) p. 185-190
[21] Shang T, et al 2019 Enhanced $T_c$ and multiband superconductivity in the fully-gapped ReBe$_2$ superconductor New J. Phys. 21 073034
[22] Barker J A T, et al 2018 Superconducting and normal-state properties of the noncentrosymmetric superconductor Re$_3$Ta Phys Rev B 98 104506
[23] Matsumoto R, et al 2019 Pressure-induced superconductivity in tin sulphide Phys Rev B 99 184502
[24] Wittig J and Matthias B T 1968 Superconducting phosphorus Science 160 994-995
[25] Shiratori I, et al 1994 Phase transitions and superconductivity of black phosphorus and phosphorus-arsenic alloys at low temperatures and high pressures Phys. Rev. B 50 16274-16278
[26] Eremets M I, Struzhkin V V, Mao H-K, Hemley R J 2001 Superconductivity in boron Science 293 272-274
[27] Liu L, Struzhkin V V, Ying J 2019 Pressure-induced superconductivity in GeAs Phys Rev B 100 214516
[28] Eremets M I, Trojan I A, Medvedev S A, Tse J S, Yao Y 2008 Superconductivity in hydrogen dominant materials: Silane Science 319 1506-1509
[29] Pickard C J, Errea I, and Eremets M I 2020 Annual Review of Condensed Matter Physics: in press (doi.org/10.1146/annurev-conmatphys-031218-013413) (2020).
[30] Flores-Livas J A, Boeri L, Sanna A, Profeta G, Arita R, Eremets M, 2019 arXiv:1905.06693v1 (2019).
[31] Troyan I A, et al 2019 Synthesis and superconductivity of yttrium hexahydride Im3m-YH6 arXiv:1908.01534
[32] Semenok D V, Kvashnin A G, Ivanova A G, Svitlyk V, Fominski V Y, Sadakov A V, Sobolevskiy O A, Pudalov V M, Troyan I A and Oganov A R 2019 Superconductivity at 161 K in thorium hydride ThH10: synthesis and properties Mater. Today (https://doi.org/10.1016/j.mattod.2019.10.005)
[33] Talantsev E F, Crump W P, Storey J G and Tallon J L 2017 Ann. Phys. 529 1600390
[34] Talantsev E F, Crump W P and Tallon J L 2017 Ann. Phys. 529 1700197
[35] Talantsev E F 2019 Modern Physics Letters B 33 1950195
[36] Kaplan D and Imry Y 2018 Proc. Nat. Acad. Sci. 115 5709
[37] Errea I, et al 2015 High-pressure hydrogen sulfide from first principles: A strongly anharmonic phonon-mediated superconductor Phys. Rev. Lett. 114 157004
[38] Gross F, et al 1986 Anomalous temperature dependence of the magnetic field penetration depth in superconducting UBe13 Zeitschrift für Physik B Condensed Matter 64 175-188.
[39] Matsuoka T, Kitayama T, Shimizu K, Nakamoto Y, Kagayama T, Aoki K, Ohishi Y, Takemura K 2007 Electrical properties of YH3 under high pressure J. Phys. Soc. Jpn. 76 (Suppl. A) 86-87
[40] Kong P P, et al 2019 Superconductivity up to 243 K in yttrium hydrides under high pressure arXiv:1909.10482v1
[41] Cao Y, et al. 2018 Unconventional superconductivity in magic-angle graphene superlattices Nature 556 43-50
[42] Talantsev E F, Mataira R C, Crump W P 2020 Classifying superconductivity in Moiré graphene superlattices Scientific Reports 10 212
[43] Talantsev E F and Mataira R C 2020 Classifying superconductivity in ThH-ThD superhydrides/superdeuterides Material Research Express 7 016003
[44] Talantsev E F 2020 Unconventional superconductivity in highly-compressed unannealed sulphur hydride Results in Physics 16 102993
[45] Shimizu K, Ishikawa T, Takao D, Yagi T and Amaya K 2002 Superconductivity in compressed lithium at 20 k Nature 419 597-599
[46] Guo J, et al 2017 Electron-hole balance and the anomalous pressure-dependent superconductivity in black phosphorus Phys Rev B 96 224513
[47] Li X, et al 2018 Pressure-induced phase transitions and superconductivity in a black phosphorus single crystal PNAS 115 9935-9940
[48] Hirsch J E, in “High Temperature Superconductors” X-th Winter Meeting on Low Temperature Physics, 16-18 January 1989, Cocoyoc, Morelos, Mexico, Eds Akachi T, Cogordan J A, Valladares A A, (World Scientific, Singapore, 1989), p. 43-48.
[49] Hirsch J E 2019 Superconducting materials: the whole story Journal of Superconductivity and Novel Magnetism (https://doi.org/10.1007/s10948-019-05284-5)
[50] Ma Y, Tse J S, Klug D D and Ahuja R 2004 Electron-phonon coupling of α-Ga boron Phys. Rev. B 70 214107
[51] Sun L, et al 2009 Pressure-induced superconducting state in crystalline boron nanowires Phys. Rev. B 79 140505(R)
[52] Shimizu K, et al 2010 Superconductivity in α-boron at Mbar pressure Physica C 470 S631–S632
[53] Feng J, et al 2006 Structures and potential superconductivity in SiH$_4$ at high pressure: En route to “metallic hydrogen” Phys. Rev. Lett. 96 017006
[54] Chen X-J, et al 2008 Pressure-induced metallization of silane PNAS 105 20-23
[55] Yao Y, Tse J S, Ma Y and Tanaka K 2007 Superconductivity in high-pressure SiH$_4$ EPL 78 37003
[56] Mozaffari S, et al 2019 Superconducting phase diagram of H$_3$S under high magnetic fields Nature Communications 10 2522
[57] Harshman D R and Fiory A T 2017 On the isotope effect in compressed superconducting H$_3$S and D$_3$S Supercond. Sci. Technol. 30 045011
[58] Einaga M, et al 2016 Crystal structure of the superconducting phase of sulfur hydride Nature Physics 12 835-838
[59] Matthias B T 1971 Anticorrelations in superconductivity Physica 55 69-72
[60] Hirsch J E 1997 Correlations between normal-state properties and superconductivity Phys. Rev. B 55, 9007 (1997)
[61] Monthoux P, Pines D and Lonzarich G G 2007 Superconductivity without phonons Nature 450 1177-1183
[62] Sachdev S 2012 What can gauge-gravity duality teach us about condensed matter physics? Annual Review of Condensed Matter Physics 3 9-33