Quantifying the Nonadiabaticity Strength Constant in Recently Discovered Highly Compressed Superconductors

Evgeny F. Talantsev

1 M. N. Miheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, 18, S. Kovalevskoy St., 620018 Ekaterinburg, Russia; evgeny.talantsev@imp.uran.ru; Tel.: +7-912-676-0374
2 NANOTECH Centre, Ural Federal University, 19 Mira St., 620002 Ekaterinburg, Russia

Abstract: Superconductivity in highly pressurized hydrides has become the primary direction for the exploration of the fundamental upper limit of the superconducting transition temperature, $T_c$, after Drozdov et al. (Nature 2015, 525, 73) discovered a superconducting state with $T_c = 203\,\degree K$ in highly compressed sulfur hydride. To date, several dozen high-temperature superconducting polyhydrides have been discovered and, in addition, it was recently reported that highly compressed titanium and scandium exhibit record-high $T_c$ (up to 36 K). This exceeded the $T_c = 9.2\,\degree K$ value of niobium many times over, which was the record-high $T_c$ ambient pressure metallic superconductor. Here, we analyzed the experimental data for the recently discovered high-pressure superconductors (which exhibit high transition temperatures within their classes): elemental titanium (Zhang et al., Nature Communications 2022; Liu et al., Phys. Rev. B 2022), TaH$_3$ (He et al., Chinese Phys. Lett. 2023), LaBeH$_4$ (Song et al., Phys. Rev. Lett. 2023), black phosphorous (Li et al., Proc. Natl. Acad. Sci. 2018; Jin et al., arXiv 2023), and violet (Wu et al., arXiv 2023) phosphorous to reveal the nonadiabaticity strength constant $\delta T_F^2$ (where $\theta_D$ is the Debye temperature, and $T_F$ the Fermi temperature) in these superconductors. The analysis showed that the $\delta$-phase of titanium and black phosphorous exhibits $T_F^2$ scores that are nearly identical to those associated with A15 superconductors, while the studied hydrides and violet phosphorous exhibit constants in the same ballpark as those of $H_3S$ and $LaH_{10}$.

Keywords: hydrogen-rich superconductors; highly compressed superconductors; electron–phonon coupling constant; Debye temperature; nonadiabaticity

1. Introduction

The discovery of near-room-temperature superconductivity in highly compressed sulfur hydride by Drozdov et al. [1] presented a new era in superconductivity. This research field represents one of the most fascinating scientific and technological explorations in modern condensed-matter physics. In this area of research, advanced first-principles calculations [2–11] are essential parts of the experimental quest for the discovery of new hydrides phases [12–21], and both of these directions drive the development of new experimental techniques with which to study highly pressurized materials [22–31].

From 2015 until now, several dozen high-temperature superconducting polyhydride phases have been discovered and studied [1,12–21,24,32–45]. At the same time, high-pressure studies of superconductivity and high-pressure material synthesis [46–48] in non-hydrides (including cuprates [49–52]) have also progressed [53–62], including the observation of $T_c > 26\,\degree K$ in highly compressed elemental titanium [63,64] and scandium [65,66], and the discovery that $T_{onset} \approx 78\,\degree K$ [67,68] and $T_{zero} \approx 45\,\degree K$ [69] in $La_2Ni_3O_7$.

First-principles calculations [12–21,70–79] are essential tools in the quest for room-temperature superconductivity (they were used [76] to explain the experimental results [80] for one of the most difficult-to-explain hydride cases, $AlH_3$), and the primary calculated parameter in these calculations is the transition temperature, $T_c$. In addition, another difficult-to-explain hydride should be mentioned, which is $LiPdH_x$ [46]. This hydride...
was synthesized at high pressure in a bulk form [46]; however, as was predicted by the first-principles calculations, the high transition temperature [81] was not confirmed by the experiment [46].

Thus, the experiment [1,3,25] remains the final criterion. Therefore, the confirmation of the predicted $T_c$ in order to determine the other fundamental ground-state parameters, including the upper critical field, $B_{c2}(0)$; the lower critical field, $B_{c1}(0)$ [12,22]; the self-field critical current density, $J_c(s_f, T)$ [24,82–84]; the London penetration depth, $\lambda(0)$ [22,23,85,86]; the superconducting energy gap amplitude, $\Delta(0)$ [87–89]; and gap symmetry [90,91] is the task of the experiment and the data analysis.

Another complication in understanding the superconductivity of highly-pressurized materials is the phenomenon of nonadiabaticity, which originates from the fact that the Migdal–Eliashberg theory of the electron–phonon-mediated superconductivity [92,93] is based on the primary assumption/postulate that the superconductor obeys the inequality:

$$T_\theta \ll T_F$$

(1)

where $T_\theta$ is the Debye temperature and $T_F$ is the Fermi temperature. In other words, Equation (1) implies that the superconductor exhibits fast electric charge carriers and slow ions. This assumption simplifies the theoretical model of electron–phonon-mediated superconductivity; however, Equation (1) is not satisfied for many unconventional superconductors [94–102] (which was first pointed out by Pietronero and co-workers [103–106]) and many highly compressed superconductors [91,101,107–109].

While the theoretical aspects of the nonadiabatic effects can be found elsewhere [11,94,100,103–107], in practice, the strength of the nonadiabatic effects can be quantified via the $T_\theta/T_F$ ratio [101,102], for which, in Ref. [101], three characteristic ranges were proposed:

$$\begin{cases} 
T_\theta/T_F < 0.025 & \rightarrow \text{adiabatic superconductor;} \\
0.025 \lesssim T_\theta/T_F \lesssim 0.4 & \rightarrow \text{moderately strong nonadiabatic superconductor;} \\
0.4 < T_\theta/T_F & \rightarrow \text{nonadiabatic superconductor.}
\end{cases}$$

(2)

It was found in Ref. [101], and confirmed in Ref. [91], that superconductors with $T_c > 10$ K (from a dataset of 46 superconductors from all major superconductor families) exhibit the $T_\theta/T_F$ ratio in the range $0.025 \lesssim T_\theta/T_F \lesssim 0.4$.

This is an interesting and theoretically unexplained empirical observation.

In this study, we further extended the empirical $T_\theta/T_F$ database by deriving several fundamental parameters:

1. the Debye temperature, $T_\theta$;
2. the electron–phonon coupling constant, $\lambda_{e-ph}$;
3. the ground-state coherence length, $\xi(0)$;
4. the Fermi temperature, $T_F$;
5. the nonadiabaticity strength constant, $T_\theta/T_F$;
6. and the ratio, $T_c/T_F$;

for five recently discovered highly compressed superconductors for which the reported raw experimental data are enough to deduce the above-mentioned parameters. These superconductors represent materials with high or record-high $T_c$ in their families:

1. elemental titanium, $\delta-Ti$ [63,64];
2. $TaH_3$ [21];
3. $LaBeH_8$ [110];
4. black phosphorous [111–114];
5. violet phosphorous [62].
In the result, we derived the nonadiabaticity strength constant, $T_0/T_F$, for these superconductors. Derived $T_0/T_F$ values confirmed the previously reported empirical observation [91,101] that the superconductors with $T_c > 10$ K obey the condition $0.025 \lesssim T_0/T_F \lesssim 0.4$.

2. Utilized Models and Data Analysis Tools

2.1. Debye Temperature

Within electron–phonon phenomenology, the Debye temperature, $T_\theta$, is a fundamental parameter that determines the superconducting transition temperature, $T_c$ [93,115–119]. $T_\theta$ can be deduced as a free-fitting parameter from a fit of temperature-dependent resistance, $R(T)$, to the Bloch–Grüneisen (BG) equation [120–123]:

$$R(T) = \frac{1}{R_{\text{sat}}} + \frac{1}{R_0 + A \left( \frac{T}{T_\theta} \right)^{3/2} \int_0^{T_\theta/T_0} \frac{dx}{(e^{-x} - 1)(1 - e^{-x})}}$$  (3)

where $R_{\text{sat}}$, $R_0$, $T_\theta$, and $A$ are free-fitting parameters.

2.2. The Electron–Phonon Coupling Constant

From the deduced $T_\theta$, the electron–phonon coupling constant, $\lambda_{e-\text{ph}}$, can be calculated as the root of advanced McMillan equation [116–119]:

$$T_c = \left( \frac{1}{1.45} \right) \times T_\theta \times e^{-\left( \frac{1.04(1 + \lambda_{e-\text{ph}})}{\lambda_{e-\text{ph}} - \phi(1 + 3.8\mu^*)} \right)} \times f_1 \times f_2$$  (4)

where

$$f_1 = \left( 1 + \left( \frac{\lambda_{e-\text{ph}}}{2.46(1 + 3.8\mu^*)} \right)^{3/2} \right)^{1/3}$$  (5)

$$f_2 = 1 + (0.0241 - 0.0735 \times \mu^*) \times \lambda_{e-\text{ph}}^2$$  (6)

where $\mu^*$ is the Coulomb pseudopotential parameter, which we assumed to be $\mu^* = 0.13$ (which is the typical value utilized in the first-principles calculation for many electron–phonon-mediated superconductors [63,124]). In Equations (4)–(6), we defined the $T_c$ by a strict resistance criterion of $R(T)/R_{\text{norm}} \to 0$, where $R_{\text{norm}}$ is the sample resistance at the onset of the transition.

2.3. Ground-State Coherence Length

We used a model proposed by Baumgartner et al. [125–127] to fit the upper critical field dataset, $B_{c2}(T)$, and determine the ground-state coherence length $\xi(0)$:

$$B_{c2}(T) = \frac{1}{\phi_0} \times \frac{\phi_0}{\sqrt{\pi^2}e^2(0)} \times \left( 1 - \frac{L}{T} \right) - 0.153 \times \left( 1 - \frac{L}{T} \right)^2 - 0.152 \times \left( 1 - \frac{L}{T} \right)^4$$  (7)

where $\phi_0 = \frac{h}{2e}$ is the superconducting flux quantum, $h = 6.626 \times 10^{-34}$ J · s is Planck constant, $e = 1.602 \times 10^{-19}$ C, and $\xi(0)$ and $T_c \equiv T_c(B = 0)$ are free fitting parameters.

2.4. The Fermi Temperature

The Fermi temperature, $T_F$, can be calculated by using a simple expression of the free-electron model [128,129]:

$$T_F = \frac{\epsilon_F}{k_B} = \frac{\left( \frac{3\pi^2 \hbar^3}{2m_e} \right)^{3/2}}{2m_e \left( 1 + \lambda_{e-\text{ph}} \right) k_B}$$  (8)
where $m_e = 9.109 \times 10^{-31} \text{ kg}$ is bare electron mass, $\hbar = 1.055 \times 10^{-34} \text{ J} \cdot \text{s}$ is reduced Planck constant, $k_B = 1.381 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$ is Boltzmann constant, and $n$ is the charge carrier density per volume ($\text{m}^{-3}$). Equation (8) can be used if the Hall resistance experiments are performed, and the charge carrier density, $n$, is established.

If Hall resistance measurements do not perform, then $T_F$ can be calculated using the equation [58,59]:

$$T_F = \frac{\pi^2 m_e}{8k_B} \times \left(1 + \lambda_{e-ph}\right) \times \zeta^2(0) \times \left(\frac{ak_BT_c}{\hbar}\right)^2$$

(9)

where $\alpha = \frac{2\Delta(0)}{k_BT_c}$ is the gap-to-transition temperature ratio. This parameter is the only unknown parameter in Equation (9).

2.5. The Gap-to-Transition Temperature Ratio

To calculate the Fermi temperature using Equation (9), there is a need to know $\alpha = \frac{2\Delta(0)}{k_BT_c}$. To determine $\alpha = \frac{2\Delta(0)}{k_BT_c}$, we utilized the following approach. Carbotte [124] collected various parameters for 32 electron–phonon-mediated superconductors that exhibit $0.43 \leq \lambda_{e-ph} \leq 3.0$ and $3.53 \leq \frac{2\Delta(0)}{k_BT_c} \leq 5.19$. In Figure 1, we presented the dataset reported by Carbotte in Table IV [124]. The dependence $\frac{2\Delta(0)}{k_BT_c}$ vs. $\lambda_{e-ph}$ can be approximated using a linear function (Figure 1) [130]:

$$\frac{2\Delta(0)}{k_BT_c} = C + D \times \lambda_{e-ph},$$

(10)

where $C = 3.26 \pm 0.06$, and $D = 0.74 \pm 0.04$.

![Figure 1](image-url)

**Figure 1.** The gap-to-transition temperature ratio, $\frac{2\Delta(0)}{k_BT_c}$, vs. the electron–phonon coupling constant, $\lambda_{e-ph}$, dataset reported by Carbotte in Table IV of Ref. [124]. A linear fit is shown by the pink line. Positions for some representative superconductors and superconductors studied in this report (where bP stands for black phosphorus and vP stands for violet phosphorus) are shown. The pink shadow area indicates 95% confidence bands for the linear fit.

Insofar as $\lambda_{e-ph}$ is known, the $\frac{2\Delta(0)}{k_BT_c}$ ratio can be estimated from Equation (10).
3. Results

3.1. Highly Compressed Titanium

Zhang et al. [63] and Liu et al. [64] reported record-high $T_c$ in the $\delta - Ti$ phase compressed at megabar pressures. In Figure 2, we show the fit of the $R(T)$ dataset measured by Zhang et al. [63] for the $\omega - Ti$ phase compressed at $P = 18 \text{GPa}$ to Equation (3).

![Figure 2](image_url)

**Figure 2.** Temperature-dependent resistance data, $R(T)$, for compressed titanium ($\omega - Ti$-phase at $P = 18 \text{GPa}$) and data fit to Equation (3) (raw data reported by Zhang et al. [63]). Green balls indicate the bounds for which $R(T)$ data were used for the fit to Equation (3). (a) Fit to Debye model: $p = 5$ (fixed), $T_0 = (361 \pm 1) \text{K}$, $T_{c,0.25} = 2.1 \text{K}$, $\lambda_{e-ph} = 0.49$, fit quality is 0.99988. (b) Fit to Equation (3): $p = 3.15 \pm 0.03$, $T_0 = (421 \pm 2) \text{K}$, $T_{c,0.25} = 2.1 \text{K}$, fit quality is 0.99999. The pink shadow areas in both panels show 95% confidence bands.

The deduced Debye temperature (Figure 2a) for $\omega - Ti$-phase ($P = 18 \text{GPa}$) is $T_0 = 361 \pm 1 \text{K}$. This value is within the ballpark value for uncompressed titanium, which exhibits a $\alpha - Ti$ phase [131].

To calculate the electron–phonon coupling strength constant, $\lambda_{e-ph}$, using Equations (4)–(6), we defined the superconducting transition temperature, $T_c = 2.1 \text{K}$, with the $R(T)$ data to $0.25$ criterion. This criterion was chosen based on the lowest temperature at which experimental $R(T)$ data measuring at $P = 18 \text{GPa}$ were reported by Zhang et al. [63]. The deduced value $\lambda_{e-ph} = 0.49$ is very close to the $\lambda_{e-ph} = 0.43$ of pure elemental aluminum (Figure 1, and Ref. [124]).

We also confirmed the power-law exponent $n = 3.1$ (reported by Zhang et al. [63]) for the temperature-dependent $R(T)$. Zhang et al. [63] extracted this power-law exponent from the simple power-law fit of $R(T)$ at the temperature range of $3 \text{K} \leq T \leq 70 \text{K}$:

$$R(T) = R_0 + X \times T^n,$$

(11)

where $R_0$, $X$, and $n$ are free-fitting parameters. As we showed earlier [132], Equation (11) does not always return correct $n$-values. The reliable approach is to fit the $R(T)$ data to Equation (3), where $p$ is a free-fitting parameter. For the given case, our fit to Equation (3) (Figure 2b) returns the same power-law exponent, $p = 3.15 \pm 0.03$, as the one reported by Zhang et al. [63].

In Figure 3, we show $R(T)$ data measured by Zhang et al. [63] and Liu et al. [64] and the results of data fitting to Equations (3)–(7) for the $\delta - Ti$ phase compressed at $P = 154 \text{GPa}$ (Figure 3a), $P = 180 \text{GPa}$ (Figure 3b), $P = 183 \text{GPa}$ (Figure 3c), and $P = 245 \text{GPa}$ (Figure 3d).
Liu et al. [64] reported $\lambda_{e-ph}$ and logarithmic frequency $\omega_{\log}$ for highly compressed titanium over a wide range of applied pressure calculated using first-principles calculations. In Figure 4, we present a comparison of the deduced $\lambda_{e-ph}$ and $T_\theta$ values from the experiment and show the calculation results [64]. To compare $\omega_{\log}$ (calculated using first-principles calculations) and $T_\theta$ deduced from the experiment, we used the theoretical expression proposed by Semenok [133]:

$$\frac{1}{0.827} \times \frac{\hbar}{k_B} \times \omega_{\log} \cong T_\theta. \quad (12)$$

In Figure 4c, we also show $T_F$ values calculated using Equation (8), where we used derived $\lambda_{e-ph}$ and bulk density of charge carriers in compressed titanium, $n$, measured by Zhang et al. [63]. Zhang et al. [63] reported the $R(T)$ and $n$ measured at different pressures. For $T_F$, calculations we assumed the following approximations: $n(P = 18 \ GPa) = n(P = 31 \ GPa) = 1.72 \times 10^{28} \ m^{-3}$; $n(P = 154 \ GPa) = 2.39 \times 10^{28} \ m^{-3}$; and $n(P = 180 \ GPa) = n(P = 183 \ GPa) = n(P = 177 \ GPa) = 1.70 \times 10^{28} \ m^{-3}$.

The evolution of the adiabaticity strength constant $T_\theta / T_F$ vs. pressure is shown in Figure 4c.

Figure 4 shows a very good agreement between values calculated using first-principles calculations and extracted from experiment $\lambda_{e-ph}$ and characteristic phonon temperatures, $T_\theta$ and $\frac{1}{0.827} \times \frac{\hbar}{k_B} \times \omega_{\log}$, at low and high applied pressures. More experimental data are required to perform detailed comparison.
The derived $T_F$, $\lambda_{e-ph}$, and $\frac{T_0}{T_F}$, values for highly compressed titanium are shown in Figures 5–7, together with values for the main superconducting families. It should be noted that other global scaling laws utilize different variables [83,134–140].

It is interesting to mention that $\delta - Ti$ is located close to A15 superconductors in all these plots (Figures 5–7). This proximity can be interpreted as a reflection that the highest performance of the electron–phonon-mediated superconductivity is achieved for these materials.

Figure 4. Evolution of (a) the electron–phonon coupling constant $\lambda_{e-ph}$; (b) characteristic phonon temperatures $T_0$ and $\frac{1}{12\pi^2} \times \frac{\hbar}{k_B} \times \omega_{\log}^{0.827}$; and (c) Fermi temperature, $T_F$, calculated using Equation (8) and the used of carrier density reported by Zhang et al. [63] and deduced $\lambda_{e-ph}$ (in Panel (a)) and the nonadiabaticity strength constant, $\frac{T_0}{T_F}$, for highly compressed titanium.
Figure 5. Uemura plot, where highly compressed Ti, TaH$_3$, LaBeH$_6$, black, and violet phosphorous (BP and VP, respectively) are shown together with several families of superconductors: metals, iron-based superconductors, diborides, cuprates, Laves phases, hydrides, and others. References for original data can be found in Refs. [91,101,141,142].

Figure 6. The nonadiabaticity strength constant $\frac{T_f}{T_c}$ vs. $\lambda_{e-ph}$, where several families of superconductors and highly compressed Ti, TaH$_3$, LaBeH$_6$, black, and violet phosphorous are shown. References for original data can be found in Refs. [91,101,141,142].
Figure 7. The nonadiabaticity strength constant \( \frac{T_F}{T_T} \) vs. \( T_T \) for several families of superconductors and highly compressed \( Ti, TaH_3, LaBeH_6 \), black, and violet phosphorous are shown. References for original data can be found in Refs. [91,101,141,142].

3.2. Highly Compressed I-43d-Phase of TaH_3

Recently, He et al. [21] reported on the observation of high-temperature superconductivity in the highly compressed \( I-43d \)-phase of \( TaH_3 \). In Figure 8, we show the fit of the \( R(T) \) dataset (measured by He et al. [21]) for the tantalum hydride compressed at \( P = 197 \text{ GPa} \).

We deduced \( \lambda_{e-ph} = 1.53 \) (Figure 8) by using Equations (4)–(6). The deduced value was within the ballpark value for other highly compressed hydride superconductors [3,119].

He et al. [21] did not report the result of the Hall coefficient measurements. Based on this, we determined the Fermi temperature using Equation (9). To do this, we deduced the \( B_{c2}(T) \) dataset from \( R(T,B) \) curves reported by He et al. [21] in their Figure 2a [21]. We
defined the $B_c^2(T)$ using the criterion of $\frac{R(T)}{K_{norm}} = 0.02$. Obtained $B_c^2(T)$ data and the data fit are shown in Figure 8b. Deduced $\xi(0) = (5.45 \pm 0.10) \text{ nm}$.

To calculate the Fermi temperature in the $I-43d$-phase of TaH$_3$ at $P = 197 \text{ GPa}$, we substituted derived $\lambda_{e-ph} = 1.53$ and $\xi(0) = 5.45 \text{ nm}$ in Equation (9), where $\alpha = \frac{2\lambda(0)}{\xi^2} = 4.39$ was obtained by substituting $\lambda_{e-ph} = 1.53$ in Equation (10) (Figure 1).

In the result, we determined the following fundamental parameters of the $I-43d$-phase of TaH$_3$ ($P = 197 \text{ GPa}$):

1. the Debye temperature, $T_\Theta = 263 \text{ K}$;
2. the electron–phonon coupling constant, $\lambda_{e-ph} = 1.53 \pm 0.13$;
3. the ground-state coherence length, $\xi(0) = (1.53 \pm 0.13) \text{ nm}$;
4. the Fermi temperature, $T_F = (1324 \pm 74) \text{ K}$;
5. $\frac{T_F}{T_\Theta} = 0.019 \pm 0.01$, which implies that this phase falls in the unconventional superconductors band in the Uemura plot;
6. the nonadiabaticity strength constant, $\frac{T_F}{T_\Theta} = 0.20 \pm 0.01$.

In Figures 5–7, one can see the position of the $I-43d$-phase of TaH$_3$ at $P = 197 \text{ GPa}$. The position of this hydride in Figures 5–7 confirmed that the TaH$_3$ is typical superhydride, exhibiting a similar strength of nonadiabatic effects to H$_3$S and LaH$_{10}$.

### 3.3. Highly Compressed $Fm\bar{3}m$-Phase of LaBeH$_8$

Recently, Song et al. [110] reported on the observation of high-temperature superconductivity in highly compressed LaBeH$_8$. The crystalline structure of this superhydride at $P = 120 \text{ GPa}$ was identified as $Fm\bar{3}m$. This crystalline structure was predicted by Zhang et al. [143]. Figure 9a shows the fit of the $(T)$ dataset (measured by Song et al. [110]) in the LaBeH$_8$ compressed at $P = 120 \text{ GPa}$.

![Figure 9](image_url)

**Figure 9.** Analyzed experimental data for $Fm\bar{3}m$-phase of LaBeH$_8$ at $P = 120 \text{ GPa}$ (raw data reported by Song et al. [110]). (a) Temperature-dependent resistance data, $R(T)$, and data fit to Equation (3). Green balls indicate the bounds for which $R(T)$ data were used for the fit to Equation (3). Deduced $T_\Theta = (752 \pm 6) \text{ K}, T_c = 68.8 \text{ K}, \lambda_{e-ph} = 1.46$, fit quality is 0.9990. (b) The upper critical field data, $B_c^2(T)$, and data fit to Equation (7). Definition $B_c^2(T)$ criterion of $\frac{R(T)}{K_{norm}} = 0.25$ was used. Deduced parameters are: $\xi(0) = 2.8 \text{ nm}, T_c = 68.8 \text{ K}$. Fit quality is 0.9995. The pink areas in both panels show 95% confidence bands.

The $B_c^2(T)$ dataset was extracted from $R(T,B)$ curves reported by Song et al. [110] in their Figure 3a [110]. For the $B_c^2(T)$ definition, we utilized the criterion of $\frac{R(T)}{K_{norm}} = 0.25$. The obtained $B_c^2(T)$ data and the data fit are shown in Figure 9b. Deduced $\xi(0) = 2.8 \text{ nm}$.

Examining the results of the performed study, we determined that the $Fm\bar{3}m$-phase of LaBeH$_8$ at $P = 120 \text{ GPa}$ exhibits the following parameters:

1. the Debye temperature, $T_\Theta = (752 \pm 6) \text{ K}$;
2. the electron–phonon coupling constant, $\lambda_{e-ph} = 1.46$;
3. the ground-state coherence length, $\xi(0) = (2.80 \pm 0.02) \text{ nm}$;
(4) the Fermi temperature, \( T_F = 2413 \text{ K} \);
(5) \( \frac{T_D}{T_F} = 0.029 \), which implies that this phase falls in the unconventional superconductors band in the Uemura plot;
(6) the nonadiabaticity strength constant, \( \frac{T_\theta}{T_F} = 0.31 \pm 0.01 \).

3.4. Highly Compressed Black Phosphorous

The impact of high pressure on the superconducting parameters of black phosphorous has been studied over several decades [111–114]. Recent detailed studies in this field have been reported by Guo et al. [112], Li et al. [111], and Jin et al. [114].

To show the reliability of high-pressure studies of superconductors (which was recently questioned by non-experts in the field [144,145]), in Figure 10, we show raw \( R(T) \) datasets measured at \( P = 15 \text{ GPa} \) from the two independent research groups of Shirotani et al. [113] and Li et al. [111]. It should be stressed that these reports have been published within a timeframe of 24 years.

![Figure 10](image)

**Figure 10.** Analysis of experimental \( \rho(T) \) datasets for black phosphorous compressed at \( P = 15 \text{ GPa} \) reported by (a) Shirotani et al. [113] and by (b) Li et al. [111]. Green balls indicate the bounds for which \( \rho(T) \) data were used for the fit to Equation (3). Deduced parameters are: (a) \( T_\theta = (563 \pm 16) \text{ K} \), \( \lambda_{\text{e-ph}} = 5.3 \text{ K} \), \( \lambda_{\text{e-ph}} = 0.546 \), fit quality is 0.9983; (b) \( T_\theta = (611 \pm 2) \text{ K} \), \( \lambda_{\text{e-ph}} = 5.9 \text{ K} \), \( \lambda_{\text{e-ph}} = 0.549 \), fit quality is 0.9998. The pink shadow areas in both panels 95% confidence bands.

The agreement between deduced \( \lambda_{\text{e-ph}} \) (Figure 10) from two datasets [111,113] is remarkable. It should be noted that the approach used for our analysis (Figure 10) was developed to analyze data measured in highly compressed near-room-temperature superconductors [119]. This feature implies that several concerns expressed by non-experts in the field [144–147] with regard to highly compressed near-room-temperature hydride superconductors do not have any scientific background.

Figure 11 shows \( B_{c2}(T) \) datasets extracted from raw \( R(T, B) \) datasets measured at very close pressures, with values of \( P = 15.9 \text{ GPa} \) [112] (panel a) and \( P = 15 \text{ GPa} \) [111] (panel b). These two datasets were reported by two independent groups. For the \( B_{c2}(T) \) definition, we utilized the same strict criterion of \( \frac{R(T)}{R_{\text{norm}}} = 0.01 \) for both \( R(T, B) \) datasets in Figure 11.

The average deduced parameters for black phosphorous \( P = 15 \text{ GPa} \), which we derived from experimental data analysis reported by three different research groups, are as follows:

1. the Debye temperature, \( T_D = 587 \text{ K} \);
2. the electron–phonon coupling constant, \( \lambda_{\text{e-ph}} = 0.548 \);
3. the ground-state coherence length, \( \xi(0) = 77 \text{ nm} \);
4. the Fermi temperature, \( T_F = 5200 \text{ K} \);
5. \( \frac{T_D}{T_F} = 0.001 \), which implies that black phosphorus falls in the conventional superconductors band in the Uemura plot;
6. the nonadiabaticity strength constant, \( \frac{T_\theta}{T_F} = 0.11 \).
The deduced parameters show that the black phosphorus at $P = 15$ GPa exhibits low-strength nonadiabatic effects.

![Graph](image-url)

**Figure 11.** Analysis of experimental $B_2(T)$ datasets for black phosphorus compressed at (a) $P = 15$ GPa reported by Li et al. [111], and (b) $P = 15.9$ GPa reported by Guo et al. [112]. Deduced parameters are: (a) $\xi(0) = (67 \pm 1) \text{ nm}$, $T_c = 5.5 \pm 0.1 \text{ K}$, fit quality is 0.9965; (b) $\xi(0) = (86 \pm 1) \text{ nm}$, $T_c = 5.5 \pm 0.1 \text{ K}$, fit quality is 0.9981. Pink shadow areas in both panels show 95% confidence bands are shown.

### 3.5. Highly Compressed Violet Phosphorous

Recently, Wu et al. [62] reported on the observation of the superconducting state in compressed violet phosphorus (vP). This material exhibits $T_c > 5 \text{ K}$ at high pressure in the range of $3.6 \text{ GPa} \leq P \leq 40.2 \text{ GPa}$. In Figure 12a, we showed the $R(T)$ dataset (measured by Wu et al. [62]) and fitted data to Equation (3).

![Graph](image-url)

**Figure 12.** Analysis of experimental data for violet phosphorus compressed at (a) $P = 40.2$ GPa and (b) $P = 34.8$ GPa. Raw data reported by Wu et al. [62]. (a) Temperature-dependent resistance data, $R(T)$, and data fit to Equation (3). Green balls indicate the bounds for which $R(T)$ data were used for the fit to Equation (3). Deduced $T_\theta = (655 \pm 4) \text{ K}$, $T_{c,0.01} = 9.4 \text{ K}$, $\lambda_{e-ph} = 0.607$, fit quality is 0.9991. (b) The upper critical field data, $B_2(T)$, and data fit to Equation (13). Definition $B_2(T)$ criterion of $\frac{R(T)}{R_{trans}} = 0.14$ was used. The deduced parameters are: $\xi(0)_{band1} = (50 \pm 1) \text{ nm}$, $T_{c,band1} = (9.0 \pm 0.2) \text{ K}$, $\xi(0)_{band2} = (53 \pm 2) \text{ nm}$, $T_{c,band2} = (4.0 \pm 0.1) \text{ K}$. Fit quality is 0.9977. The pink areas in both panels show 95% confidence bands.

The $B_2(T)$ dataset was extracted from the only $R(T,B)$ dataset reported by Wu et al. [62] for material compressed at $P = 34.8$ GPa [62]. The $B_2(T)$ was defined by the criterion of $\frac{R(T)}{R_{trans}} = 0.14$. The deduced $B_2(T)$ dataset is shown in Figure 12b. Equation (7) does not fit the $B_2(T)$ data well because the $B_2(T)$ goes up at $T \lesssim 4 \text{ K}$. We think this means a second band opens up, so we used a two-band model to fit the data [141,148]:

\[\xi(0) = 67 \pm 1 \text{ nm}, \quad T_c = 5.5 \pm 0.1 \text{ K}, \quad \text{fit quality is 0.9965}; \quad \xi(0) = 86 \pm 1 \text{ nm}, \quad T_c = 5.5 \pm 0.1 \text{ K}, \quad \text{fit quality is 0.9981}.\]
\[ B_{c2,\text{total}}(T) = B_{c2,\text{band1}}(T) + B_{c2,\text{band2}}(T), \]

where \( B_{c2,\text{band1}}(T) \) and \( B_{c2,\text{band2}}(T) \) exhibit their independent transition temperature and the coherence length. We list deduced values in the figure caption to Figure 12. However, for further analysis, we used \( T_c = T_{c,\text{band1}} = 9.0 \, K \), and \( \xi(0)_{\text{total}} = (36 \pm 1) \, \text{nm} \).

In the result, we derived the following parameters for violet phosphorus compressed at \( P \sim 40 \, \text{GPa} \):

1. The Debye temperature, \( T_D = (665 \pm 4) \, K \);
2. The electron–phonon coupling constant, \( \lambda_{e-ph} = 0.607 \);
3. The ground-state coherence length, \( \xi(0) = (36 \pm 1) \, \text{nm} \);
4. The Fermi temperature, \( T_F = 3240 \, K \);
5. \( \frac{T_c}{T_F} = 0.003 \), which implies that this phase falls near the conventional superconductors band in the Uemura plot;
6. The nonadiabaticity strength constant, \( \frac{T_c}{T_F} = 0.21 \).

We concluded, that nonadiabatic effects in violet phosphorus compressed at \( P \sim 40 \, \text{GPa} \) are like those in \( H_3S \) and \( LaH_{10} \) near-room-temperature superconductors.

4. Discussion

As we mentioned, above superconductors can be classified by the ratio of maximum phonon energy, \( \hbar \omega_D \) (where \( \omega_D \) is Debye frequency) to the charge carrier energy at the Fermi level, \( \frac{\hbar \omega_D}{k_B T_D} \). For practical use, it is more convenient to replace the \( \hbar \omega_D \) with \( k_B T_D \), where \( T_D \) is the Debye temperature.

Thus, in the adiabatic regime, \( \frac{\hbar \omega_D}{k_B T_D} = \frac{T_D}{T_F} \lesssim 10^{-3} \), superconductors have fast charge carriers and slow phonons. This condition is satisfied for pure metals and some superconducting alloys (Figures 5–7).

However, as can be seen in Figures 6 and 7, more than \( \frac{3}{2} \) of superconductors (including important for practical use \( Nb_3Sn \), \( MgB_2 \), pnictides, cuprates, and record-high \( T_c \) near-room-temperature superconducting hydrides) have the ratio in a different range [91,101]:

\[
0.025 \leq \frac{\hbar \omega_D}{k_B T_F} \leq 0.4, \tag{14}
\]

Our experimental data search [70,80] revealed that only six superconductors exhibit (Figures 6 and 7):

\[
\frac{\hbar \omega_D}{k_B T_F} > 0.4. \tag{15}
\]

These materials are [91,101]: \( Nb_{0.75}Mo_{0.25}B_2 \) and \( Nb_{0.5}Os_{0.5} \), which are highly compressed metalized oxygen; magic-angle twisted bilayer graphene \( SrTiO_3 \); and highly compressed metalized ionic salt, \( Csl \). It should be stressed that all these superconductors exhibit low transition temperatures, \( T_c \lesssim 8 \, K \).

The five recently discovered superconductors (Sections 3.1–3.5) studied in this report confirmed the validity of Equation (14). And, thus, perhaps a deep physical origin related to the strength of the nonadiabaticity \( \frac{\hbar \omega_D}{k_B T_F} = \frac{T_D}{T_F} \) within the range indicated in Equation (14) can be revealed.

Nonadiabatic effects are crucial in reducing the superconducting transition temperature to well below the value predicted by classical (BCS-Eliashberg) theories of electron–phonon-mediated superconductivity [93,115]. This understanding was first reported by Pietronero and co-workers [103–105,107]. It can be seen in Figure 7 that materials with the highest strength of nonadiabaticity \( \frac{T_D}{T_F} \) (for instance, \( SrTiO_3 \) and magic-angle twisted bilayer graphene) exhibit the superconducting transition temperature \( T_c \lesssim 1 \, K \), while all materials with \( T_c \gtrsim 35 \, K \) exhibit \( \frac{T_D}{T_F} \) within a range indicated by Equation (14).
5. Conclusions

In this work, we analyzed experimental data for five new highly compressed superconductors: $\delta$–Ti [63,64], TaH$_5$ [21], LaBeH$_8$ [110], black phosphorous [111–113], and violet phosphorous [62]. We established several superconducting parameters for these superconductors, including the strength of nonadiabaticity: $\frac{h\omega_p}{k_B T_F} = \frac{f_a}{f_F}$.

**Funding:** This research was funded by the Ministry of Science and Higher Education of the Russian Federation, grant number No. 12202100032-5 (theme “Pressure”). The research funding from the Ministry of Science and Higher Education of the Russian Federation (Urals Federal University Program of Development within the Priority-2030 Program) is gratefully acknowledged.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The author declares no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

**References**


9. Du, M.; Song, H.; Zhang, Z.; Duan, D.; Cui, T. Room-Temperature Superconductivity in Yb/Lu Substituted Clathrate Hydrides under Moderate Pressure. *Research* 2022, 9784309. [CrossRef]


Symmetry 2023, 15, 1632


Symmetry 2023, 15, 1632


64. Liu, X.; Jiang, P.; Wang, Y.; Li, M.; Li, N.; Zhang, Q.; Wang, Y.; Li, Y.-L.; Yang, W. Tc up to 23.6 K and Robust Superconductivity in the Transition Metal $\delta$-Ti Phase at Megabar Pressure. Phys. Rev. B 2022, 105, 224511. [CrossRef]


82. Talantsev, E.F.; Tallon, J.L. Universal Self-Field Critical Current for Thin-Film Superconductors. Nat. Commun. 2015, 6, 7820. [CrossRef]
89. Khasanov, R. Perspective on Muon-Spin Rotation/Relaxation under Hydrostatic Pressure. J. Appl. Phys. 2022, 132, 190903. [CrossRef]
91. Talantsev, E.F. D-Wave Superconducting Gap Symmetry as a Model for Nb1−xMo2B (x = 0.25; 1.0) and WB2 Diborides. Symmetry 2023, 15, 812. [CrossRef]
100. Szczesniak, D. Scalability of Non-Adiabatic Effects in Lithium-Decorated Graphene Superconductor. Europhys. Lett. 2023, 142, 36002. [CrossRef]
101. Talantsev, E.F. Quantifying Nonadiabaticity in Major Families of Superconductors. Nanomaterials 2022, 13, 71. [CrossRef]
106. Grimaldi, C.; Cappelluti, E.; Pietronero, L. Isotope Effect on m * in High-Tc Materials Due to the Breakdown of Migdal’s Theorem. Europhys. Lett. 1998, 42, 667–672. [CrossRef]
130. Talantsev, E.F. The Compliance of the Upper Critical Field in Magic-Angle Multilayer Graphene with the Pauli Limit. Materials 2022, 16, 256. [CrossRef]
133. Semenok, D. Computational Design of New Superconducting Materials and Their Targeted Experimental Synthesis. Ph.D. Thesis, Skolkovo Institute of Science and Technology, Moscow, Russia, 2022. [CrossRef]


Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.