The thermodynamic properties of the high-pressure superconducting state in the hydrogen-rich compounds

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I. INTRODUCTION

The superconducting state in the hydrogen-rich compounds can be characterized by a very high value of the critical temperature \( T_c \) at 150 GPa has the highest critical temperature among the examined hydrogen-rich compounds. For this reason, the relevant thermodynamic parameters of the superconducting state in CaH\(_6\) have been determined; a wide range of the Coulomb pseudopotential has been assumed: \( \mu^* \in (0.1,0.3) \). It has been found that: (i) The critical temperature \( (T_C) \) changes in the range from 243 K to 180 K. (ii) The values of the ratio of the energy gap to the critical temperature \( (R_{\Delta} \equiv 2\Delta(0)/k_B T_C) \) can be found in the range from 5.42 to 5.02. (iii) The ratio of the specific heat jump \( (\Delta C(T_C)) \) to the value of the specific heat in the normal state \( (C^N(T_C)) \), which has been represented by the symbol \( R_C \), takes the values from 3.30 to 3.18. (iv) The ratio \( R_{\mu} \equiv T_C C^N(T_C)/H^2_C(0) \), where \( H_C(0) \) denotes the critical thermodynamic field, changes from 0.122 to 0.125. The above results mean that even for the strong electron depairing correlations the superconducting state in CaH\(_6\) is characterized by a very high value of \( T_c \), and the remaining thermodynamic parameters significantly deviate from the predictions of the BCS theory. The study has brought out the expressions that correctly predict the values of the thermodynamic parameters for the superconducting state in CaH\(_6\) and for the compounds: SiH\(_4\)(H\(_2\))\(_2\), Si\(_2\)H\(_6\), B\(_2\)H\(_6\), SiH\(_4\), GeH\(_4\), and PtH. Next, in the whole family of the hydrogen-rich compounds, the possible ranges of the values have been determined for \( T_c, R_{\Delta}, R_C, \) and \( R_{\mu} \). It has been found that the maximum value of the critical temperature can be equal to 764 K, which very well correlates with \( T_c \) for metallic hydrogen \( (p = 2\ \text{TPa}) \). Other parameters \( (R_{\Delta}, R_C, \) and \( R_{\mu} \) should not deviate from the predictions of the BCS theory more than the analogous parameters for CaH\(_6\).

The above result is connected with the existence of the strong-coupling and retardation effects.

For higher pressures - in the range from 500 GPa to 3.5 TPa - the metallic phase of the atomic hydrogen is formed \([13, 19, 20, 21, 22]\). It has been found that the highest value of the critical temperature can be predicted for \( p \approx 2\ \text{TPa} \), where \( T_c \) is of the order of 600-700 K \([19, 23]\). In addition, the other thermodynamic parameters differ very significantly from the predictions of the BCS theory \([24]\). In particular, the ratio of the energy gap to the critical temperature assumes values comparable to the values observed in the high-temperature superconductors (cuprates) \([22, 23, 26]\).

In the case of the hydrogen-rich compounds the metalization can occur as early as in the interval of the pressures from 50 GPa to 60 GPa \( (\text{e.g. SiH}_4) [6, 7] \). Additionally, for SiH\(_4\) the existence of the superconducting state with the critical temperature of 17 K has been found experimentally \( (p = 96\ \text{GPa} \) and 120 GPa) \([7]\). Most probably, much higher values of the critical temperature can be observed in the compounds of the type: SiH\(_4\)(H\(_2\))\(_2\), Si\(_2\)H\(_6\), B\(_2\)H\(_6\), GeH\(_4\), and PtH \([3, 27, 28, 29, 30]\).

It should be noted that in the pure elements under the influence of the high pressure the superconducting state...
with the relatively high critical temperature is also induced at this point. The experimental results obtained for lithium and calcium are worth mentioning. In the case of lithium, the maximum value of the critical temperature is equal to 14 K for \( p = 30.2 \text{ GPa} \) [31]; whereas calcium is characterized by the superconducting state of the highest critical temperature among the pure elements \( (T_C = 25 \text{ K} \text{ for } 161 \text{ GPa}) \) [32]. Additionally, in 2011, it was suggested that \( T_C \text{ (Ca)} \) can be equal to 29 K \( (p = 216 \text{ GPa}) \) [33]. However, this result has been challenged in the paper [34].

Let us note that the thermodynamic properties of the superconducting state of lithium and calcium differ significantly from the expectations of the BCS theory [35, 36, 37, 38, 39, 40]. It is also important to describe their properties, it is necessary to assume anomalously high values of the Coulomb pseudopotential \( (\mu^*) \). This proves the existence of the strong electron deparing correlations in the examined elements \((\mu^*^{(Li)}_{p=22.6 \text{ GPa}} = 0.22, \mu^*^{(Ca)}_{p=29.7 \text{ GPa}} = 0.36, \text{ and } \mu^*^{(Ca)}_{p=161 \text{ GPa}} = 0.24) \) [35, 40].

Recently, the branch literature has suggested that the critical temperature of the superconducting state can reach a very high value in the CaH₆ compound \( (p = 150 \text{ GPa}) \) [41]. As a result of the conducted analysis, the authors of the work [41] have found that \( T_C \) can be found in the range from 235 K to 220 K for the Coulomb pseudopotential from 0.1 to 0.13. Such unusually high values of the critical temperature suggest the existence of the superconducting state with strongly anomalous thermodynamic properties. However, it is unclear whether the value of the critical temperature for CaH₆ will not to significantly decrease when too large values of \( \mu^* \) are assumed. This possibility cannot be excluded \( \text{ a priori } \) taking into account the results obtained for the superconducting state in calcium [35, 41].

Due to extremely interesting results obtained in the publication [41], we have determined the values of all relevant thermodynamic parameters characterizing the superconducting state in CaH₆. We have taken into consideration a wide range of the Coulomb pseudopotential: \( \mu^* \in (0.1, 0.3) \). The results have been then generalized, so as to be able to characterize the superconducting state in the entire group of the hydrogen-rich compounds.

### II. THE FORMALISM

The thermodynamic properties of the superconducting state in CaH₆ have been determined with the help of the Eliashberg equations in the mixed representation [42]:

\[
\phi(\omega + i\delta) = \frac{\pi}{\beta} \sum_{m=-M}^{M} \left[ \lambda(\omega - i\omega_m) - \mu^*\theta(\omega_c - |\omega_m|) \right] \frac{\phi_m}{\sqrt{\omega_m^2 + \phi_m^2}} \right]
\]

\[
+ i\pi \int_0^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' - \omega) \right] \frac{\phi(\omega - \omega' + i\delta)}{\sqrt{(\omega - \omega')^2 Z^2(\omega - \omega' + i\delta) - \phi^2(\omega - \omega' + i\delta)}}
\]

\[
+ i\pi \int_0^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' + \omega) \right] \frac{\phi(\omega + \omega' + i\delta)}{\sqrt{(\omega + \omega')^2 Z^2(\omega + \omega' + i\delta) - \phi^2(\omega + \omega' + i\delta)}}
\]

and

\[
Z(\omega + i\delta) = 1 + \frac{\pi}{\omega \beta} \sum_{m=-M}^{M} \lambda(\omega - i\omega_m) \frac{\omega_m Z_m}{\sqrt{\omega_m^2 + \phi_m^2}} \right]
\]

\[
+ i\pi \int_0^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' - \omega) \right] \frac{(\omega - \omega') Z(\omega - \omega' + i\delta)}{\sqrt{(\omega - \omega')^2 Z^2(\omega - \omega' + i\delta) - \phi^2(\omega - \omega' + i\delta)}}
\]

\[
+ i\pi \int_0^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' + \omega) \right] \frac{(\omega + \omega') Z(\omega + \omega' + i\delta)}{\sqrt{(\omega + \omega')^2 Z^2(\omega + \omega' + i\delta) - \phi^2(\omega + \omega' + i\delta)}}
\]

where the symbols \( \phi(\omega) \) \( (\phi_m \equiv \phi(i\omega_m)) \) and \( Z(\omega) \) \( (Z_m \equiv Z(i\omega_m)) \) denote the order parameter function and the wave function renormalization factor on the real \( (\text{imaginary } i \equiv \sqrt{-1}) \) axis, respectively. The Matsub-
ara frequency is represented by the formula: $\omega_m \equiv (\pi/\beta) \left(2m - 1\right)$, where $\beta \equiv (k_B T)^{-1}$; $k_B$ is the Boltzmann constant. The order parameter is defined by the ratio: $\Delta \equiv \phi/Z$.

The pairing kernel for the electron-phonon interaction has the form: $\lambda(z) \equiv 2 \int_0^\Omega_{\text{max}} d\Omega z^{\frac{1}{2}} \Omega^{-1} \Omega^{2} F(\Omega)$. The Eliashberg function ($\alpha^2 F(\Omega)$) for CaH$_6$ has been determined in the paper \cite{41}. The value of the maximum phonon frequency ($\Omega_{\text{max}}$) is equal to 244.7 meV.

Let us notice that knowing the Eliashberg function allows us to calculate the electron-phonon coupling constant $\lambda \equiv 2 \int_0^\Omega_{\text{max}} d\Omega \alpha^2 F(\Omega)$. In the case of CaH$_6$, we have the value $\lambda \approx 2.69$. From the physical point of view, the above result means that in CaH$_6$ a very strong coupling exists between the electrons and the crystal lattice vibrations.

The quantity $\theta$ in Eq. (1) denotes the Heaviside unit function; $\omega_c$ is the cut-off frequency ($\omega_c = 3\Omega_{\text{max}}$).

The symbols $N(\omega)$ and $f(\omega)$ represent the functions of Bose-Einstein and Fermi-Dirac, respectively.

The order parameter function and the wave function renormalization factor on the imaginary axis have been calculated using the equations \cite{43, 44, 45, 46}:

$$\phi_n = \frac{\pi}{\beta} \sum_{m=-M}^{M} \frac{\lambda(\omega_n - \omega_m - \mu^* \theta(\omega_c - \omega_m))}{\sqrt{\omega_m^2 \phi_m^2 + \phi_m^2}} \phi_m, \quad (3)$$

$$Z_n = 1 + \frac{1}{\omega_n^2} \sum_{m=-M}^{M} \frac{\lambda(\omega_n - \omega_m)}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}} \omega_m Z_m, \quad (4)$$

where $M = 1100$.

We can notice that the Eliashberg equations have been numerically solved with the use of the methods presented in the papers: \cite{47, 48, 49, 50}. The stable solutions have been obtained in the temperature range from $T_0 = 10$ K to $T_C$.

### III. THE CRITICAL TEMPERATURE FOR CaH$_6$

In the first step, we have determined the dependence of the critical temperature on the Coulomb pseudopotential ($\mu^* \in \left(0.1, 0.3\right)$). It has been found that the value of the critical temperature varies in the range from 243 K to 180 K (see Fig. 1). The obtained result means that even in the case of the strong electron depairing correlations the value of the critical temperature in CaH$_6$ is very high.

In addition, the classical analytical formulas (the Allen-Dynes or McMillan expression \cite{51, 52}) significantly underestimate the critical temperature, especially for the high values of the Coulomb pseudopotential (see also Fig. 1). A relatively good agreement between the analytical and numerical results can be obtained only for $\mu^* \sim 0.1$ using the Allen-Dynes approach.

Due to the problem mentioned above, a new expression of the critical temperature has been tested. The examined formula has been recently postulated by ourselves for the SiH$_4$ (H$_2$)$_2$ compound ($p = 250$ GPa) \cite{53}:

$$k_B T_C = f_1 f_2 \omega_{\text{ln}} \exp \left[\frac{-1.125 \left(1 + \lambda\right)}{\lambda - \mu^*}\right], \quad (5)$$

where the functions $f_1$ and $f_2$ are defined by \cite{51}: $f_1 \equiv \left[1 + \left(\frac{\lambda}{\Lambda_2}\right)^2\right]^{\frac{1}{2}}$ and $f_2 \equiv 1 + \left(\frac{\omega_{\text{ln}} - 1}{\Lambda_1 + \Lambda_2}\right)^2$. The second moment of the normalized weight function ($\omega_2$) and the logarithmic frequency ($\omega_{\text{ln}}$) can be calculated using the following expressions: $\omega_2 \equiv \frac{2}{\Lambda} \int_0^{\Omega_{\text{max}}} d\Omega \alpha^2 F(\Omega) \Omega$ and $\omega_{\text{ln}} \equiv \exp \left[\frac{2}{\Lambda} \int_0^{\Omega_{\text{max}}} d\Omega \alpha^2 F(\Omega) \ln (\Omega)\right]$.

In the case of CaH$_6$, we have achieved the following results: $\sqrt{\omega_2} = 104$ meV and $\omega_{\text{ln}} = 88.8$ meV.

The functions $\Lambda_1$ and $\Lambda_2$ have the form: $\Lambda_1 = 2 - 0.14 \mu^*$, $\Lambda_2 = (0.27 + 10 \mu^*) \left(\sqrt{\omega_2}/\omega_{\text{ln}}\right)$.

On the basis of the results presented in Fig. 1, it can be easily noticed that the modified Allen-Dynes formula properly reproduces the numerical results.

Referring to the results included in the paper \cite{41}, it has been stated that the values of the critical temperature presented there are undervalued in comparison to the values of $T_C$ obtained with the presented method. For instance, in the work \cite{41} the following has been obtained: $T_C (\mu^* = 0.1) = 235$ K and $T_C (\mu^* = 0.3) = 152$ K, while the result of our approach are: $T_C (\mu^* = 0.1) = 243$ K and $T_C (\mu^* = 0.3) = 180$ K. The indicated differences in the predictions of the critical temperature probably result from the approximations used for the determination of $T_C$ in the paper \cite{41}.

![FIG. 1: The effect of the influence of the Coulomb pseudopotential on the critical temperature.](image-url)
IV. THE RANGE OF THE CRITICAL TEMPERATURE IN THE HYDROGEN-RICH COMPOUNDS

In the paragraph, we have estimated the maximum value of the critical temperature for the hydrogen-rich compounds, which can be obtained assuming the reasonable value of the coupling constant and the Coulomb pseudopotential. In particular: \( \lambda \in (1, 3) \) and \( \mu^* \in (0.1, 0.3) \).

The critical temperature has been calculated using the formula (5). The first step was to verify whether under consideration one can obtain sufficiently accurate \( T_C \) values compared to the values determined with the use of the Eliashberg equations. Beside \( \text{CaH}_6 \), the hydrogenated compounds characterized by a very high critical temperature have been chosen: \( \text{SiH}_4 \), \( \text{SiH}_6 \), \( \text{B}_2\text{H}_6 \), \( \text{SiH}_4 \), \( \text{GeH}_4 \) and \( \text{PtH} \). The results have been shown in Fig. 2. It is easy to notice that the formula (5) reproduces results obtained by solving the Eliashberg equations with a very good accuracy.

At this point it should be again clearly underlined that the classical Allen-Dynes or McMillan formula should not be used, because the mentioned formulas significantly lower \( T_C \).

The obtained results suggest that for the reasonable values of the input parameters, the maximum critical temperature in the hydrogenated compounds may be equal to 764 K. This result coincides with the estimation of the maximum critical temperature for the metallic atomic hydrogen (\( p = 2 \text{ TPa} \)). Bearing in mind the fact that the hydrogen-rich compounds are used for the chemical pre-compression of hydrogen, there is a real chance of obtaining the superconducting state at the room temperature and at the pressure, which is much lower when compared to the pressure required for metallic hydrogen.

Finally, we have found that the formula (5) works very-well also for pure metallic hydrogen. We have illustrated this fact in the Appendix A.

V. THE ORDER PARAMETER FOR \( \text{CaH}_6 \)

In Fig. 3 the form of the order parameter on the imaginary axis for \( \text{CaH}_6 \) compound has been presented. The selected values of the temperature and the Coulomb pseudopotential have been taken into account. It can be observed that with the increase of the \( m \) parameter, the values of the function \( \Delta_m \) are yielding to a strong decrease and then become saturated. Based on the presented data, it has been found that the increase in the

\[
\lambda = 2\Omega_1/\Omega_2, \quad \omega_{in} = \Omega_2, \quad \text{and} \quad \omega_2 = \Omega_2^2. \quad \text{Considering the above results, the expression for the critical temperature can be rewritten as:}
\]

\[
k_B T_C = \frac{\Omega_2}{1.37} \left[ 1 + \left( \frac{2\Omega_1}{\Lambda_1\Omega_2} \right)^{3/2} \right]^{1/3} \exp \left[ \frac{1.125 (\Omega_2 + 2\Omega_1)}{\mu^*\Omega_2 - 2\Omega_1} \right]. \quad (7)
\]
Coulomb pseudopotential also causes the decrease of the order parameter.

The temperature dependence on the order parameter can be represented by plotting the form of the function $\Delta_{m=1} (T)$. Note, that from the physical point of view, the quantity $2\Delta_{m=1} (T)$ reproduces the value of the energy gap at the Fermi level with the good approximation. The obtained results have been presented in Fig. 4.

The physical value of the order parameter has been calculated using the formula below:

$$\Delta (T) = \text{Re}[\Delta (\omega = \Delta (T))].$$

(8)

In particular, for $T = T_0$ it has been obtained: $\Delta (T_0) \equiv \Delta (0) \in (56.6, 39.0)$ meV, for the range of the values $\mu^*$ from 0.1 to 0.3. On that basis, the dimensionless ratio $R_{\Delta} = 2\Delta (0)/k_BT_C$ has been determined. The result has the form: $R_{\Delta} \in (5.42, 5.02)$.

It should be noted that the values of the parameter $R_{\Delta}$ very significantly exceed the value predicted by the BCS theory ($R_{\Delta} = 3.53$).

The above result is related to the existence of the strong-coupling and retardation effects in CaH$_4$. In the simplest case, it can be characterized by the ratio: $k_BT_C/\omega_n$. In the case of the BCS theory 0 value is obtained. For CaH$_4$, the examined ratio varies in the range from 0.156 to 0.098 ($\mu^* \in (0.1, 0.3)$).
It is easy to notice that the values of the parameter $R_\Delta$ require a number of complicated and time-consuming calculations. For this reason, the appropriate formula has been given below. It allows us to estimate the parameter $R_\Delta$ with a good approximation, depending on the assumed value of $\mu^*$:

$$\frac{R_\Delta}{[R_\Delta]_{BCS}} = 1 + 3.2 \left( \frac{k_B T_C}{\alpha \omega_n} \right)^2 \ln \left( \frac{\alpha \omega_n}{k_B T_C} \right), \quad (9)$$

where $\alpha = 0.517$. In the case of CaH$_6$, the differences between the numerical and the analytical results do not exceed 2%.

VI. THE RANGE OF THE PARAMETER $R_\Delta$ IN THE HYDROGEN-RICH COMPOUNDS

The correctness of the formula (9) for CaH$_6$ suggests its applicability for the other hydrogenated compounds. This hypothesis has been verified for those systems, for which accurate numerical data can be found in the literature. The results have been summarized in Fig. 8.

Based on Fig. 8 it can be easily seen that the expression (9) correctly predicts the dependence of $R_\Delta$ on $\mu^*$ for the analyzed group of the systems.

Generalizing the obtained result allowed the determination of the possible range of the $R_\Delta$ parameter in the entire group of the hydrogenated compounds. For this purpose the formula (9) and the Eliashberg function defined by the expression (10) have been used. The results have been summarized in Fig. 9.

It has been found that the maximum value of the pa-
The lines have been obtained using the formula (9).

\[ \frac{\Delta F}{\rho (0)} = - \frac{2 \pi}{\beta} \sum_{n=1}^{M} \left( \sqrt{\omega_n^2 + \Delta_n^2} - |\omega_n| \right) \]

(10)

where \( \rho (0) \) denotes the value of the density of states at the Fermi level; \( Z_n^S \) and \( Z_n^N \) denote the wave function renormalization factors for the superconducting (\( S \)) and the normal (\( N \)) state, respectively.

VII. THE THERMODYNAMIC CRITICAL FIELD AND THE SPECIFIC HEAT FOR \( \text{CaH}_6 \)

The thermodynamic critical field and the specific heat should be calculated using the formula for the free energy difference between the superconducting and the normal state [61]:

\[ \frac{H_C}{\sqrt{\rho (0)}} = \sqrt{-8 \pi \left[ \Delta F/\rho (0) \right]} \]

(11)

Also Fig. [10] shows the obtained data. The destructive influence of the depairing electron correlations on the value of the thermodynamic critical field can be characterized by the ratio: \([H_C (0)]_{\mu^* = 0.3} / [H_C (0)]_{\mu^* = 0.1} = 0.73\), where it has been assumed that: \( H_C (0) \equiv H_C (T_0) \).

The difference in the specific heat between the superconducting and the normal state \( (\Delta C \equiv C^S - C^N) \) should be calculated with the use of the following formula:

\[ \frac{\Delta C (T)}{k_B \rho (0)} = - \frac{1}{\beta} \frac{d^2 [\Delta F/\rho (0)]}{d (k_B T)^2} \]

(12)
The specific heat of the normal state can be most conveniently estimated using the formula: 
\[ \frac{C^N(T)}{k_B \rho(0)} = \frac{2}{3} \beta \]
where the Sommerfeld constant is given by: \( \gamma = \frac{3}{2} \pi^2 (1 + \lambda) \).

Fig. 11 represents the dependence of the specific heat in the superconducting and the normal state as a function of the temperature for the selected values of the Coulomb pseudopotential. The characteristic jump at the critical temperature has been marked with the vertical line. The impact of the Coulomb pseudopotential on the value of the jump determines the ratio: 
\[ \frac{[\Delta C (T_C)]_{\mu^* = 0.3}}{[\Delta C (T_C)]_{\mu^* = 0.1}} = 0.72. \]

TABLE I: The dependence of the parameters \( R_H \) and \( R_C \) on the value of the Coulomb pseudopotential.

| \( \mu^* \) | \( R_H \) | \( R_C \) |
|-----------|---------|---------|
| 0.1       | 0.122   | 3.30    |
| 0.2       | 0.123   | 3.21    |
| 0.3       | 0.125   | 3.18    |

FIG. 12: The dependence of the parameters \( R_H \) and \( R_C \) on the value of the Coulomb pseudopotential for CaH\(_6\). The filled circles represent the numerical results. The lines have been obtained with the help of the expressions (14) and (15).

VIII. THE RANGE OF THE PARAMETERS \( R_H \) AND \( R_C \) IN THE HYDROGEN-RICH COMPOUNDS

In the presented paragraph, we have estimated the range of the values \( R_H \) and \( R_C \) for the hydrogenated compounds. For this purpose, the analytical formulas have been proposed, which have been derived based on the numerical results obtained for CaH\(_6\). In particular, they take the following form:

\[ \frac{R_H}{[R_H]_{BCS}} = 1 - 1.5 \left( \frac{k_B T_C}{\omega_{\text{in}}} \right)^2 \ln \left( \frac{c \omega_{\text{in}}}{k_B T_C} \right), \quad (14) \]

and

\[ \frac{R_C}{[R_C]_{BCS}} = 1 + 7 \left( \frac{k_B T_C}{c \omega_{\text{in}}} \right)^2 \ln \left( \frac{c \omega_{\text{in}}}{k_B T_C} \right), \quad (15) \]

where: \( b = 0.345 \) and \( c = 0.388 \). The numerical and the analytical results have been presented together in Fig. 12. The presented data demonstrate the correctness of the expressions (14) and (15).

In the next step, the results have been generalized taking into account the Eliashberg function. Assuming reasonable ranges of the values for the input parameters (\( \lambda \in (1, 3) \) and \( \mu^* \in (0.1, 0.3) \)), it has been found that the lowest value of the parameter \( R_H \) is equal to 0.122, whereas the highest value of \( R_C \) equals 3.30 (see also Fig. 13). From the physical point of view, the presented estimations mean that the values of \( R_H \) and \( R_C \) obtained for
FIG. 13: The ratios $R_H$ and $R_C$ as functions of $\mu^*$ and $\Omega_1$ for the selected values of $\Omega_2$. The intervals of the values $\Omega_1$ have been selected in such a way that for the assumed $\Omega_2$ the maximum value of the electron-phonon coupling constant would be equal to 3.

FIG. 14: The wave function renormalization factor on the imaginary axis for the selected values of the temperature and the Coulomb pseudopotential.

the CaH$_6$ compound determine the maximum derogation of the expectations of the BCS theory in the group of the hydrogen-rich compounds.

**IX. THE ELECTRON EFFECTIVE MASS IN THE CaH$_6$ COMPOUND**

The strong electron-phonon interaction, responsible for the formation of the superconducting state in the CaH$_6$ compound, contributes to the significant renormalization of the electron mass. In the framework of Eliashberg formalism this effect has been determined by the wave function renormalization factor.

Fig. 14 presents the form of the function $Z_m$ on the imaginary axis for the selected values of the temperature and the Coulomb pseudopotential. It can be noticed that with $m$ increasing, the values of $Z_m$ strongly decrease and then become saturated. The growth of the temperature causes successively quicker saturation of the wave function renormalization factor, such that for $T = T_C$ only a few dozens of the initial values make the significant contribution to the Eliashberg equation.

The influence of the Coulomb pseudopotential on the wave function renormalization factor can be investigated in the most convenient way by analyzing the behavior of $Z_{m=1}$. Based on Fig. 15 it can be easily observed that with the increase of $\mu^*$, the value of the wave function renormalization factor increases only slightly.

In the Eliashberg formalism, the quantity $Z_{m=1}$ plays an important role, because it determines the effective electron mass with a good approximation: $m^*_e \simeq Z_{m=1}m_e$, where $m_e$ denotes the electron band mass. Analyzing the courses presented in Fig. 15 it can be concluded that the effective mass of the electron is high in the entire area of the existence of the superconducting state. The parameter $m^*_e$ only slightly increases with the growth of the temperature and reaches the maximum at the critical temperature. If $T = T_C$, the parameter $m^*_e$ does not depend on the assumed value of the Coulomb pseudopotential and can be calculated analytically: $m^*_e = (1 + \lambda) m_e$. The obtained result is $m^*_e = 3.69m_e$. An identical result has been also obtained by the numerical means, which proves the high accuracy of the computer calculations.
The exact value of the parameter \( m^*_c \) should be estimated on the basis of the formula: \( m^*_c = \text{Re} \{ Z(0) \} m_c \), where \( Z(0) \) denotes the value of the wave function renormalization factor on the real axis for \( \omega = 0 \). On the basis of Eqs. (1) and (2), it has been found that the exact maximum effective mass equals 3.74\( m_c \).

X. SUMMARY

In the paper, all the relevant thermodynamic parameters of the superconducting state in the CaH\(_6\) compound have been determined \((p = 150\) GPa\).

It has been found that for the range of the Coulomb pseudopotential from 0.1 to 0.3, the critical temperature changes from 243 K to 180 K.

Then, the values of the order parameter have been estimated. We have shown that the dimensionless ratio \( R_\Delta \) very significantly differs from the prediction of the classical BCS theory. In particular, \( R_\Delta \in (5.42, 5.02) \).

Also, the parameters associated with the thermodynamic critical field and the specific heat cannot be correctly estimated in the framework of the BCS model: \( R_H \in (0.122, 0.125) \) and \( R_C \in (3.30, 3.18) \).

The results obtained for CaH\(_6\) compound have been then generalized in such a way that it would be possible to estimate the values of the thermodynamic parameters in the group of the hydrogen-rich compounds.

It has been shown that for the reasonable values of the input parameters, the maximum value of the critical temperature is equal to 764 K. The obtained data correlates well with the maximum value of \( T_C \), estimated for metallic atomic hydrogen \((p = 2\) TPa) \cite{19,23}. Thus, from the physical point of view, the achieved result means that in the group of the hydrogenated compounds the systems may exist which are characterized by the critical temperature comparable to the room temperature at the relatively low pressure.

According to the remaining thermodynamic parameters \((R_\Delta, R_H, \text{and } R_C)\), it has been stated that their values in the group of the hydrogen-rich compounds should not deviate from the predictions of the BCS theory more than the analogous parameters in CaH\(_6\).

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Appendix A: The value of the critical temperature for the metallic hydrogen

In the Appendix we have calculated the critical temperature for metallic hydrogen by using the formula \( \beta \). We have considered the selected values of the pressure. The results from Tab. \( \beta \) have proved the validity of the presented analytical approach.

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TABLE II: The critical temperature for the metallic hydrogen.

| $p$ (GPa) | $\lambda$ | $\omega_0$ (meV) | $\sqrt{\omega^2}$ (meV) | $\mu^*$ | $T_C$ (Eliashberg) | $T_C$ (Eq. (5)) | Ref. |
|-----------|-----------|-----------------|-----------------|--------|-------------------|-----------------|------|
| 347       | 0.93      | 141.99          | 199.01          | 0.08 – 0.15 | 120 – 90          | 113 – 85        | [14] |
| 428       | 1.20      | 141.95          | 207.48          | 0.08 – 0.15 | 179 – 141         | 176 – 140       | [63] |
| 480       | 2.21      | 153.77          | 195.99          | 0.1 – 0.3  | –                 | 304 – 255       | [18] |
| 539       | 2.04      | 166.71          | 208.00          | 0.1 – 0.3  | 360               | 307 – 252       | [24] |
| 608       | 1.91      | 174.25          | 217.84          | 0.1 – 0.3  | –                 | 302 – 242       | [18] |
| 802       | 1.70      | 184.86          | 237.82          | 0.1 – 0.3  | 332 – 259         | 285 – 218       | [62] |
| 2000      | 7.32      | 89.20           | 161.07          | 0.1 – 0.5  | 631 – 413         | 719 – 506       | [23] |