Properties of the superconducting state in molecular metallic hydrogen under pressure at 347 GPa

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I. INTRODUCTION

The influence of the pressure \( p \) on thermodynamic properties of the superconducting state is one of more interesting issues in the solid state physics.

In the case of simple-metal superconductors with the electron-phonon pairing mechanism for a long time there was conviction, that the increase of the pressure leads to the decrease of the critical temperature \( T_C \) and the remaining thermodynamic parameters do not demonstrate interesting properties [1]. The change took place in the last years when in some of the classical materials the pressure-induced superconducting state of relatively high critical temperature was discovered, for example: in lithium \( T_C \) max \( \simeq 14 \text{ K} \) for \( p \simeq 30 \text{ GPa} \) and in calcium, where \( T_C \) max \( \simeq 25 \text{ K} \) for \( p \simeq 160 \text{ GPa} \) [2, 3].

The obtained results are keeping an eye on the metallic hydrogen again, where the existence of the pressure-induced superconducting state with the very high value of the critical temperature (comparable with the value of the room temperature) was expected [4]. From the theoretical point of view the following facts enable to make the above assumption true [5]: (i) high value of the phonon frequency caused by a small mass of atomic nuclei building the crystal lattice (single proton), (ii) large value of the electron-phonon coupling related to the lack of the inner electronic shells and (iii) low value of the Coulomb pseudopotential (at least in the range of pressures up to 500 GPa [6, 7]).

Since the time of publishing the Ashcroft’s work it is stated that the value of \( T_C \) for metallic hydrogen is located in the range from 80 K to 300 K for selected pressures lesser than 500 GPa [8, 9, 10]. Under the extremely high pressure \( p = 2000 \text{ GPa} \) the metallic state of the hydrogen may transit itself into the superconducting state in the range of the temperatures from 413 K to 631 K [5, 7]. Let us note that in this case the thermodynamic properties of the superconducting state strongly deviate from the predictions of the BCS theory [10].

In the range of the “low” pressures (up to 500 GPa) the thermodynamic properties outside the critical temperature were not studied. For that reason we will calculate the selected thermodynamic parameters of the superconducting state in the molecular metallic hydrogen for the exemplary pressure of 347 GPa. In particular, in the framework of the Eliashberg approach [11], we will determine the value of the critical temperature as a function of the Coulomb pseudopotential. Next, we will exactly calculate the order parameter \( \Delta (T) \) and the wave function renormalization factor. On the basis of obtained results the ratio \( 2\Delta (0)/k_B T_C \) as a function of the Coulomb pseudopotential and the maximum value of the electron effective mass will be determined. Additionally, in the paper, the relationship between the structure of the electron-phonon coupling and the form of the solutions to the Eliashberg equations along the real axis will be discussed.

II. THE ELIASHBERG EQUATIONS

The Eliashberg equations can be determined on the real axis, imaginary axis or in the mixed representation (simultaneously on the real and imaginary axis). Each of the mentioned approaches have the unique advantages, but also come with the characteristic mathematical problems. The exact solution of the Eliashberg equations on the real axis composes an extremely difficult mathematical problem [12]. From the other side, the Eliashberg equations on the imaginary axis can be solved in a simpler way [13]. However, in this case in order to interpret physically the obtained results (e.g. to calculate the value of the energy gap near the temperature of zero Kelvin)
the achieved solutions should be analytically continued on the real axis. Unfortunately, the procedure of the analytical continuation is complicated and it demands very high precision during the numerical calculations. It is worth mentioning, that the results obtained in a such way are stable only in the range of the low frequencies.

The Eliashberg equations in the mixed representation are proclaimed to be a reasonable compromise between the two previously mentioned approaches. Firstly, they can be exactly solved in the much simpler way than equations on the real axis. Secondly, the obtained results are stable even for the very large values of the frequency. In the case of molecular metallic hydrogen it is an important matter, because the maximum phonon frequency ($\Omega_{\text{max}}$) is equal to 477 meV.

The Eliashberg equations in the mixed representation can be written in the form:

\begin{equation}
\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 (i\omega_m)}{\sqrt{\omega_m^2 Z^2 (i\omega_m) + \phi^2 (i\omega_m)}}
\end{equation}

\begin{equation}
+ \frac{i\pi}{\omega} \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') Z^2 (\omega - \omega' + i\delta) - \phi^2 (\omega - \omega' + i\delta)}}
\end{equation}

\begin{equation}
+ \frac{i\pi}{\omega} \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') Z^2 (\omega + \omega' + i\delta) - \phi^2 (\omega + \omega' + i\delta)}}
\end{equation}

\begin{equation}
+ \frac{i\pi}{\omega} \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') Z^2 (\omega + \omega' + i\delta) - \phi^2 (\omega + \omega' + i\delta)}}
\end{equation}

\begin{equation}
\end{equation}
The shape correction function \( f \) respectively to the classical Allen-Dynes expression and the McMillan formula \( f = f_1 = f_2 = 1 \) \([16], [17] \).

The parameter \( \mu \) determines correctly the critical temperature. The solid line has been obtained using the modified Allen-Dynes formula. Empty squares and triangles refer to the classical Allen-Dynes expression and 120 values of \( T_C \) obtained with an use of the Eliashberg equations. In the considered case, the modified Allen-Dynes formula takes the form:

\[
k_B T_C = f_1 f_2 \frac{\omega_{ln}}{1.2} \exp \left[ -1.04 \frac{(1 + \lambda)}{\lambda - \mu^* (1 + 0.62 \lambda)} \right],
\]

where the strong-coupling correction function \( f_1 \) and the shape correction function \( f_2 \) are given by:

\[
f_1 \equiv \left[ 1 + \left( \frac{\lambda}{\Lambda_1} \right)^2 \right]^{1/2},
\]

and

\[
f_2 \equiv 1 + \frac{(\omega_{2}^2 - 1)}{\lambda^2 + \Lambda_2^2} \lambda^2.
\]

The new functions \( \Lambda_1 \) and \( \Lambda_2 \) can be written as follows:

\[
\Lambda_1 \equiv 4.11 (1 - 4.61 \mu^*) \tag{7}
\]

and

\[
\Lambda_2 \equiv 13.57 (1 - 4.79 \mu^*) \left( \frac{\sqrt{\omega_2}}{\omega_{ln}} \right). \tag{8}
\]

The parameter \( \omega_2 \) denotes the second moment of the normalized weight function and should be calculated on the basis of the formula:

\[
\omega_2 \equiv 2 \frac{\lambda}{\Lambda} \int_0^{\Omega_{\max}} d\Omega \frac{\alpha^2 F(\Omega)}{\Omega} \ln(\Omega). \tag{9}
\]

The quantity \( \omega_{ln} \) is called the logarithmic phonon frequency and \( \lambda \) is the electron-phonon coupling constant:

\[
\omega_{ln} \equiv \exp \left[ \frac{2}{\lambda} \int_0^{\Omega_{\max}} d\Omega \frac{\alpha^2 F(\Omega)}{\Omega} \ln(\Omega) \right], \tag{10}
\]

\[
\lambda \equiv 2 \int_0^{\Omega_{\max}} d\Omega \frac{\alpha^2 F(\Omega)}{\Omega}. \tag{11}
\]

In the case of molecular metallic hydrogen \( (p = 347 \text{ GPa}) \) the following results were achieved: \( \sqrt{\omega_2} = 199 \text{ meV}, \omega_{ln} = 142 \text{ meV} \) and \( \lambda = 0.927 \).

Below, we draw the reader’s attention to the fact, that the new parameterization of \( \Lambda_1 \) and \( \Lambda_2 \) very relevantly affects the dependence of the functions \( f_1 \) and \( f_2 \) on the value of the Coulomb pseudopotential. Namely, it comes to: \( f_1 > f_2 \approx 1 \). Additionally, the values of \( f_1 \) grow together with the growth of the pseudopotential. The above result means that \( T_C \) very significantly depends on the strong-coupling effects modeled by the function \( f_1 \); while the shape correction function weakly affects the critical temperature.

When coming back to the data presented in Fig. 1 it can be easily noticed, that in the considered range of the Coulomb pseudopotential’s values the critical temperature decreases from 120 K to 90 K. The achieved result clearly states that, even for the relatively large \( \mu^* \), the critical temperature takes very high value.

### B. The order parameter function

The Eliashberg equations were solved for the range of temperature from 23.2 K to \( T_C \). As an example, the dependence of the real and imaginary part of the order parameter on the frequency in Fig. 2 was presented. For the low values of \( \omega \) the non-zero is only the real part of the order parameter. Next, we observe the characteristic sequence of the local maximums (minimums) and the points of the fold both for \( \text{Re} \{\Delta(\omega)\} \) and \( \text{Im} \{\Delta(\omega)\} \). Additionally, in Fig. 2 the Eliashberg function is shown; in order of the better representation its values were multiplied by 15. When comparing the shapes of \( \text{Re} \{\Delta(\omega)\} \) and \( \text{Im} \{\Delta(\omega)\} \) with the form of the Eliashberg function the correlation between the characteristic points of the considered functions can be easily noticed. Let us mark the fact, that from the physical point of view, the existence of the peak in the Eliashberg function determines the area of \( \omega \) in which the electron-phonon interaction is exceptionally strong. Thus, the distribution of the characteristic points of the real and imaginary part of the order parameter is inseparably connected with the specific structure of the electron-phonon interaction.
In a global way the dependence of $\Delta(\omega)$ on the temperature was presented in Fig. 3 (A). It can be clearly seen that on the complex plane the values of $\Delta(\omega)$ form the characteristic "ear". The obtained result allows to characterize the effective potential of the electron-electron interaction, which is connected with the real part of the order parameter [18]. In particular, let us notice that only in the range of frequencies from zero to the frequency slightly lesser than $\Omega_{\text{max}}$, the effective electron-electron interaction is attractive ($\text{Re}[\Delta(\omega)] > 0$); the achieved conclusion is true for any considered value of $\mu^*$. Below, the values of the ratio $R_1 \equiv 2\Delta(0)/k_BT_C$ for $\mu^* \in (0.08, 0.15)$ are determined; the symbol $\Delta(0)$ denotes the order parameter near the temperature of zero Kelvin. Let us notice, that in the framework of the weak-coupling approach (the BCS model) the parameter $R_1$ takes the constant value equal to 3.53. In the case when $\lambda > 0.2$ its exact value can be calculated only with the help of the Eliashberg equations. In particular, $\Delta(T)$ is calculated on the basis of $\text{Re}[\Delta(\omega)]$ with an use of the expression:

$$\Delta(T) = \text{Re} [\Delta(\omega = \Delta(T))].$$ \hspace{1cm} (12)

In Fig. 3 (B) the dependence of the order parameter on $T$ is plotted. Due to the fast saturation of the function $\Delta(T)$ in the area of the lower temperatures, for $\Delta(0)$ one can assume the value of $\Delta(T = 23.2K)$. The final results are presented in Fig. 4, where the function $R_1(\mu^*)$ is shown. It is easy to notice, that the values of the ratio $R_1$ are higher than $[R_1]_{\text{BCS}}$ and only slightly decreasing with the growth of the Coulomb pseudopotential (from 3.98 to 3.84). The determined dependency of $R_1$ on $\mu^*$ is connected with the strong, but comparable, influence of the electronic depairing correlations on $T_C$ and $\Delta(0)$; see Fig. 4 and the inset in Fig. 4.

C. The electron effective mass

In Fig. 4 the wave function renormalization factor is plotted. Similarly as for the order parameter, in the low-frequencies region the non-zero is only the real part of $Z(\omega)$. For higher frequencies, we can observe the complicated dependence of $\text{Re}[Z]$ and $\text{Im}[Z]$ on $\omega$, which is plainly correlated with the form of the Eliashberg function. However, it should be noticed, that in the opposition to the order parameter, the function $Z(\omega)$ is significantly weaker dependent on the temperature (see Fig. 4).

In the framework of the Eliashberg theory the wave
function renormalization factor plays a very significant role, because with the help of it one can calculate the ratio of the electron effective mass \(m_e^*\) to the bare electron mass \(m_e\):

\[
\frac{m_e^*}{m_e} = \text{Re}[Z(0)].
\]

In order to precisely track the values of the electron effective mass in the superconducting area the dependence of \(m_e^*/m_e\) on the temperature is plotted in the inset of Fig. 6. For the molecular metallic hydrogen the value of the electron effective mass is pretty high and takes its maximum equal to 1.96 for \(T = T_C\). Let us notice that in this case \(m_e^*\) is independent of \(\mu^*\).

IV. SUMMARY

In this paper the thermodynamic properties of the superconducting state induced in molecular metallic hydrogen \((p = 347\ \text{GPa})\) were studied. In order to do that, the Eliashberg equations in the mixed representation were exactly solved. The obtained results enabled to determine the dependence of the order parameter and the wave function renormalization factor in the wide range of the frequency. It has been stated, that for \(\omega \in (0, \Omega_{\text{max}})\) the existence of the characteristic points of the function \(\Delta(\omega)\) and \(Z(\omega)\) is strictly correlated with the structure of the electron-phonon coupling modeled by the Eliashberg function. Additionally, in the range of frequencies from zero to the frequency slightly lesser than \(\Omega_{\text{max}}\), the effective electron-electron interaction is attractive (\(\text{Re}[\Delta(\omega)] > 0\)).

When basing on the exact solutions of the Eliashberg equations it has been shown, that the value of the critical temperature decreases slower with the growth of the Coulomb pseudopotential, than it is predicted by the classical Allen-Dynes formula. In particular, \(T_C\) changes from 120 K to 90 K for \(\mu^* \in (0.08, 0.15)\). Next, the dependence of the dimensionless ratio \(R_1\) on \(\mu^*\) was determined. It has been proven that the parameter \(R_1\) weakly depends on the value of the Coulomb pseudopotential and \(|R_1|_{\text{max}} = 3.98\) for \(\mu^* = 0.08\). In the last step, the value of the electron effective mass in the superconducting area was calculated. On the base of the obtained results it has been shown, that \(m_e^*/m_e\) for \(T = T_C\) is

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