Strong-Coupling Description of the High-Temperature Superconductivity in the Molecular Hydrogen

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The detailed study of the selected thermodynamic properties of the superconducting phase in the molecular hydrogen under the pressure at 428 GPa has been presented. For the increasing value of the Coulomb pseudopotential \( \mu^* \in (0.08, 0.15) \), the following results have been obtained: (i) the critical temperature decreases from 179 K to 141 K, (ii) the ratio \( R_1 \equiv 2 \Delta (0)/k_BT_C \) differs noticeably from the BCS value: \( R_1 \in (4.71, 3.60) \); (iii) the electron effective mass is large and grows slightly together with the temperature \( (m_e/m_\text{max} = 2.2 \) for \( T = T_C \).

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1. Introduction

At low temperature, hydrogen exhibits the nontrivial structural behavior under the pressure \( p \) [1, 2]. Below 110 GPa the hexagonal-closed-packed lattice with freely rotating molecules is stable (phase I). At higher pressures, up to 150 GPa, the broken symmetry phase has been observed (phase II). In the pressure range of 150–350 GPa the so-called phase III exists. The experimental measurements have proved, that the all listed phases do not demonstrate the metallic properties. In the pressure range from \( \approx 400 \) GPa to \( \approx 500 \) GPa, the theoretical studies predict the existence of the molecular metallic phase (the \( Cmca \) crystal structure) [3–5]. Above \( \approx 500 \) GPa, the molecular metallic phase transforms to the Cs-IV monatomic phase [3–6]. This phase is stable at least up to 802 GPa [7]. For the extremely high value of the pressure (2000 GPa) Maksimov and Savrasov have proposed the simple \( fcc \) structure [8].

The molecular and monatomic metallic form of the hydrogen can be the superconductor with the high critical temperature \( T_C \) [9]. In particular, the calculated values of the critical temperature have been presented in the Table. We notice that \( T_C \) has usually been obtained by using the McMillan formula [14], which represents the weak coupling limit of the more elaborate Eliashberg approach [15]. However, in the case of the metallic hydrogen the electron-phonon interaction is strong, hence the McMillan expression is inappropriate.

For this reason, we have calculated the critical temperature with the help of the Eliashberg equations. We have considered the case \( p = 428 \) GPa (the value of \( p \) close to the metallization pressure). Additionally, we have studied precisely the properties of the order parameter and the electron effective mass.

In the paper we have taken into consideration the Eliashberg set in the mixed representation [16]. This approach allows one to obtain the stable solutions on the real axis, since the analysis does not involve any principal-part integrals with singular integrands.

<table>
<thead>
<tr>
<th>( p ) [GPa]</th>
<th>( T_C ) [K]</th>
<th>( \mu^* )</th>
<th>Structure</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>130–230</td>
<td>0.1</td>
<td>( sh, dh ), ( 9R^3 )</td>
<td>[10]</td>
</tr>
<tr>
<td>414</td>
<td>84</td>
<td>–</td>
<td>( Cmca )</td>
<td>[11]</td>
</tr>
<tr>
<td>428</td>
<td>162 ( a^* )</td>
<td>0.1</td>
<td>( Cmca )</td>
<td>[12]</td>
</tr>
<tr>
<td>450</td>
<td>242 ( b^* )</td>
<td>–</td>
<td>( Cmca )</td>
<td>[11]</td>
</tr>
<tr>
<td>480</td>
<td>281 ( 266 ) ( b^* )</td>
<td>0.1 (0.13)</td>
<td>( Cs-IV )</td>
<td>[7]</td>
</tr>
<tr>
<td>539</td>
<td>291 ( 272 ) ( a^* )</td>
<td>0.1 (0.13)</td>
<td>( Cs-IV )</td>
<td>[7]</td>
</tr>
<tr>
<td>608</td>
<td>291 ( 271 ) ( a^* )</td>
<td>0.1 (0.13)</td>
<td>( Cs-IV )</td>
<td>[7]</td>
</tr>
<tr>
<td>802</td>
<td>282 ( 260 ) ( a^* )</td>
<td>0.1 (0.13)</td>
<td>( Cs-IV )</td>
<td>[7]</td>
</tr>
<tr>
<td>2000</td>
<td>\approx 600</td>
<td>–</td>
<td>( fcc )</td>
<td>[8]</td>
</tr>
<tr>
<td>3000 ( b^* )</td>
<td>( 633, 413 ) ( d^* )</td>
<td>(0.1, 0.5)</td>
<td>( fcc )</td>
<td>[13]</td>
</tr>
</tbody>
</table>

\( a^* \) The McMillan formula [14]. \( b^* \) Probably unstable. \( c^* \) The three-band model. \( d^* \) The exact solution of the Eliashberg equations [15].

2. The Eliashberg equations

The Eliashberg equations in the mixed representation have been written in the following form [16]:

\[
\phi(\omega) = \frac{\pi}{3} \sum_{m=-M}^{M} \frac{\lambda(\omega - i\omega_m) - \mu^* (\omega_m)}{\sqrt{\omega_m^2 + \phi_m^2}} \phi_m \\
+ i\pi \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left( N(\omega') + f(\omega' - \omega) \right) \\
	imes K(\omega, -\omega') \phi(\omega - \omega') \\
+ i\pi \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left( N(\omega') + f(\omega' + \omega) \right) \\
	imes K(\omega, \omega') \phi(\omega + \omega'),
\]

and

\[ C_m \sim \langle \omega > \omega < \rangle \]
The Eliashberg equations have been solved for 1601 Matsubara frequencies \((M = 800)\) by using the numerical method presented in the papers [17]. In the considered case, the functions \(\phi(\omega)\) and \(Z(\omega)\) are stable for \(T \geq 11.6\) K.

3. Results

In Fig. 1 we have presented the dependence of the critical temperature on the value of the Coulomb pseudopotential. The exact numerical solutions of the Eliashberg equations have been represented by the black circles. The dashed and dotted lines represent the calculation of the critical temperature by using Allen–Dynes formula [18] and the McMillan expression respectively. It is easy to see, that McMillan formula lowers much \(T_C\) in the whole range of the Coulomb pseudopotential’s values, whereas the Allen–Dynes expression predicts correctly the critical temperature only for very low values of \(\mu^*\). For this reason we have modified the classical Allen–Dynes expression in order to obtain the analytical formula, which reproduces the Eliashberg results exactly (the solid line in Fig. 1). In particular, we have fitted the selected parameters in the Allen–Dynes expression \((A_1\) and \(A_2\)) with the help of 250 numerical values of \(T_C(\mu^*)\). The final result takes the form:

\[
k_B T_C = f_1/2 \omega_{\text{in}}^{1.2} \exp\left(-1.04 \left(1 + \lambda \right) \frac{\mu^*}{\lambda} \right),
\]

where:

\[
f_1 \equiv \left(1 + \left(\frac{\lambda}{A_1}\right)^{1/2}\right)^{1/2}
\]
from the BCS prediction; $[R_1]_{\text{BCS}} = 3.53$ [19]. Additionally, in the inset in Fig. 4 we have shown the dependence of $\Delta(0)$ on $\mu^*$. 

$$f_2 \equiv 1 + \frac{\sqrt{\omega_0^2 - 1}}{\lambda^2} \lambda^2. \quad (8)$$

Additionally:

$$A_1 \equiv 3.64 - 12.92 \mu^*$$

and

$$A_2 \equiv \frac{\omega_0}{\omega_{in}} (1.39 - 59.74 \mu^*). \quad (9)$$

The parameters $\lambda$, $\sqrt{\omega_0}$ and $\omega_{in}$ are equal to: 1.2 meV, 207.5 meV and 141.9 meV, respectively.

In Fig. 2 we have shown the order parameter on the real axis for the selected states, and $\mu^* = 0.1$; the Eliashberg function is also plotted. On the basis of the presented results one can state, that both the real and imaginary part of the function $\Delta(\omega)$ is plainly correlated with the shape of the electron–phonon interaction. This effect is especially clearly visible for the low values of the temperature. The full form of the order parameter on the complex plane has been presented in Fig. 3a. We have stated, that the $\Delta(\omega)$ values form the distorted spirals which shrink with the growth of the temperature. Basing on Fig. 3a it is also possible to notice, that the effective electron–electron interaction is attractive ($\text{Re}(\Delta(\omega)) > 0$) in the range of the frequencies from zero to $\approx 0.9\Omega_{\text{max}}$.

Taking into consideration the equation: $\Delta(T) = \text{Re}(\Delta(\omega = \Delta(T)))$ we have calculated the dependence of the order parameter on the temperature (see Fig. 3b).

Next, the value of the ratio $R_1 \equiv \frac{2\Delta(0)}{k_BT_C}$ can be obtained, where $\Delta(0)$ denotes the value of the order parameter close to the zero temperature and $\Delta(0) \simeq \Delta(T = 11.6K)$. In Fig. 4 we have presented the possible values of $R_1$ for $\mu^* \in (0.08, 0.15)$. It is easy to see that in the whole range of the considered values of the Coulomb pseudopotential, the ratio $R_1$ differs essentially
Fig. 6. The wave function renormalization factor on the complex plane ($\mu^* = 0.1$). The lines with symbols represent the solutions for $\omega \in (0, \Omega_{\text{max}})$, whereas the regular lines correspond to the solutions for $\omega \in (\Omega_{\text{max}}, \omega)$. The inset shows the ratio $m^*_e/m_e$ as a function of the temperature.

sent in the Fig's. 6 inset. According to the presented data, it is easy to spot, that $m^*_e$ is high in the full range of the considered temperatures and $[m^*_e/m_e]_{\text{max}} = 2.2$ for $T = T_C$. We notice that at the critical temperature, the electron effective mass is independent of $\mu^*$ and $[m^*_e/m_e]_{\text{max}} = 1 + \lambda$.

4. Summary

We have calculated the selected thermodynamic properties of the superconducting state in the molecular hydrogen ($p = 428$ GPa). The numerical analysis has been conducted in the framework of the one-band Eliashberg formalism for the wide range of the Coulomb pseudopotential’s values: $\mu^* \in (0.08, 0.2)$. We have proved, that the critical temperature is high even for large values of $\mu^*$ ($[T_C]_{\text{min}} = 141$ K). Next, it has been shown, that the superconducting phase is characterized by high value of the dimensionless ratio $R_1$, which differs from the BCS result; $R_1 \in (4.71, 3.60)$. Finally, we have observed that the electron-phonon interaction strongly enhances the effective electron mass for the temperatures from zero to $T_C$. In particular, the maximum of $m^*_e$ is equal to 2.2$m_e$ for $T = T_C$. In the future we will analyze the superconducting state in the molecular hydrogen in the framework of the three-gap Eliashberg model. It will be done in order to discuss the effect of the multi-band anisotropy [11].

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References