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High-pressure superconducting state in hydrogen

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ABSTRACT

The paper determines the thermodynamic parameters of the superconducting state in the metallic atomic hydrogen under the pressure at 1 TPa, 1.5 TPa, and 2.5 TPa. The calculations were conducted in the framework of the Eliashberg formalism. It has been shown that the critical temperature is very high (in the range from 301.2 K to 437.3 K), as well as high are the values of the electron effective mass (from $3.43m_e$ to $6.88m_e$), where m_e denotes the electron band mass. The ratio of the low-temperature energy gap to the critical temperature explicitly violates the predictions of the BCS theory: $2\Delta(0)/k_B T_C \in \langle 4.84, 5.85\rangle$. Additionally, the free energy difference between the superconducting and normal state, the thermodynamic critical field, and the specific heat of the superconducting state have been determined. Due to the significant strong-coupling and retardation effects those quantities cannot be correctly described in the framework of the BCS theory.

1. Introduction

The superconducting state with the possibly high value of the critical temperature (T_C) is one of the most important goals of the solid state physics.

Initially the greatest hopes were related to the group of the superconductors discovered in 1986 by Bednorz and Müller (the so-called cuprates) [1,2]. Unfortunately, the years of study within the family of the compounds under consideration allowed to obtain the maximum value of T_C equal only to 135 K ($HgBa_2Ca_2Cu_3O_{8+y}$) [3]. However, the critical temperature could still be slightly increased up to $T_C = 164$ K, when increasing the external pressure (p) up to the value of about 31 GPa [4], or up to 153 K for $p = 15$ GPa, which is suggested in the paper [5].

Let us notice that the new families of the superconductors discovered in the later years (the fulleride, the iron-based, and the MgB_2-based compounds [6–8]) have been characterized by the significantly lower values of the critical temperature than cuprates.

Alongside the mainstream of the research, also the search for the high-temperature superconducting state in the more exotic physical systems was conducted. The most promising direction is connected with the superconducting state inducing in the metallic hydrogen (Ashcroft in 1968 [9]).

The predicted high value of the critical temperature for the superconducting state in hydrogen is related to the following facts: (i) the large value of the Debye frequency resulting from the small mass of the atomic nucleus (single proton) and (ii) lack of the electrons on the inner shells, which should result in the strong coupling of the electron-phonon type [10,11].

Unfortunately, the theoretical predictions has not been able to be confirmed experimentally to the present day, which results from the very high value of the pressure of hydrogen metallization ($p_m \sim 400$ GP) [12]. However, recent experimental data obtained for the compounds H_2S and H_3S ($[T_C]_{max} \sim 200$ K [13,14]), where the chemical pre-compression lowers the value of p_m [15], indirectly confirms the results of the theoretical considerations for hydrogen [16]. The additional information about the hydrogen sulfide the reader can find in the papers [17–19].

Referring specifically to the theoretical results obtained for the superconducting state in hydrogen, the attention has to be paid to the fact that the value of T_C is high in the whole range of the pressure from about 400 GPa to 3.5 TPa (the pressure near the core of the planet of the Jovian-type [20]). In particular, for the molecular phase of hydrogen ($p \in \langle 400, 500\rangle$ GPa), the critical temperature grows rapidly from about 80 K to 350 K [21–25]. Above 500 GPa, the value of T_C stabilizes in the range from ~300 K to ~470 K, whereas for 2 TPa, the maximum of the critical temperature able to reach even the value of 630 K is predicted [10,11].

The thermodynamics of the superconducting state in hydrogen has been studied for the few selected pressures [11,23,25]. The obtained results suggest that, due to the significant strong-coupling

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and retardation effects, the description with the use of the BCS theory [27,26] is not sufficient and the Eliashberg method should be used instead [28].

The thermodynamic parameters of the superconducting state in hydrogen for the pressure at 1 TPa, 1.5 TPa, and 2.5 TPa have been determined in the present work. The calculated values of the coupling constant (λ) and the logarithmic frequency ($\omega_{\ln}$) in the considered case prove that the parameter determining the magnitude of the strong-coupling and retardation effects ($r = k_B T_C/\omega_{\ln}$) significantly deviates from the limit value of BCS: $[r]_{\rm BCS} = 0$ (see Table 1). For this reason, the thermodynamics of the superconducting state was described with the help of the Eliashberg equations [28].

2. The formalism

The Eliashberg equations on the imaginary axis ($i = \sqrt{-1}$) take the following form:

$$\phi_m = \frac{\pi}{\beta} \sum_{n=-M}^{M} \frac{\lambda\left(i\omega_m - i\omega_n\right) - \mu^\star \theta\left(\omega_c - |\omega_n|\right)}{\sqrt{\omega_n^2 Z_n^2 + \phi_n^2}} \phi_n, \tag{1}$$

$$Z_m = 1 + \frac{1}{\omega_m} \frac{\pi}{\beta} \sum_{n=-M}^{M} \frac{\lambda\left(i\omega_m - i\omega_n\right)}{\sqrt{\omega_n^2 Z_n^2 + \phi_n^2}} \omega_n Z_n. \tag{2}$$

The order parameter is defined by the ratio: $\Delta_m = \phi_m/Z_m$, where $\phi_m = \phi\left(i\omega_m\right)$ represents the order parameter function and $Z_m = Z\left(i\omega_m\right)$ is the wave function renormalization factor. The m-th Matsubara frequency is given by: $\omega_m = \left(\pi/\beta\right)\left(2m - 1\right)$, where: $\beta = \left(k_B T\right)^{-1}$. The pairing kernel is given with the following formula: $\lambda(z) = 2\int_0^{\Omega_{\max}} d\Omega \frac{\Omega}{\Omega^2 - z^2} \alpha^2 F(\Omega)$, where $\alpha^2 F\left(\Omega\right)$ is the Eliashberg function. The Eliashberg functions were calculated in the paper [29] for the cases under consideration. The values of the maximum phonon frequency ($\Omega_{\max}$) are collected in Table 1.

The depairing correlations were modelled parametrically with the help of the Coulomb pseudopotential: $\mu^\star \in \{0.1, 0.2, 0.3\}$. θ denotes the Heaviside function, ω_c represents the cut-off frequency: $\omega_c = 5\Omega_{\max}$.

Table 1
The selected parameters of the high-pressure superconducting state in hydrogen.

Quantity	Unit	$\mu^\star$	1 TPa	1.5 TPa	2.5 TPa
λ			5.88	4.71	2.43
$\omega_{\ln}$	meV		50.1	43.18	147.22
r		0.1	0.802	0.827	0.256
		0.2	0.679	0.690	0.210
		0.3	0.606	0.601	0.180
$\Omega_{\max}$	meV		479.40	544.55	650.47
T_C	K	0.1	466.1	414.1	437.3
		0.2	395.1	345.7	359.3
		0.3	352.1	301.2	308.0
$\Delta(0)$	meV	0.1	106.06	89.03	89.80
		0.2	89.73	73.42	72.37
		0.3	78.93	63.37	61.24
$H_C(0)/\sqrt{\rho(0)}$	meV	0.1	612.16	489.6	476.7
		0.2	533.98	416.8	392.6
		0.3	480.06	364.0	336.8
$\Delta C\left(T_C\right)/k_B\rho(0)$	meV	0.1	2871.3	2065.35	1879.4
		0.2	2677.67	1584.87	1505.9
		0.3	3265.82	1652.47	1262.8

The Eliashberg equations were solved for $M = 1100$, which ensured the stability of the functions ϕ_m and Z_m for the temperatures larger than, or equal to $T_0 = 50\, rmK$. The numerical modules described and tested in the papers: [23,25,30–34] were used.

In order to accurately determine the value of the energy gap and the electron effective mass, the solutions of the Eliashberg equations from the imaginary axis should be analytically extended on the real axis ($\phi_m \to \phi(\omega)$ and $Z_m \to Z(\omega)$). The following equations were used for this purpose:

$$\begin{aligned}\phi(\omega + i\delta) = {} & \frac{\pi}{\beta} \sum_{m=-M}^{M} \left[\lambda(\omega - i\omega_m) - \mu^\star \theta(\omega_c - |\omega_m|)\right] \frac{\phi_m}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}} \\ & + i\pi \int_0^{+\infty} d\omega' \alpha^2 F(\omega') \\ & \left[[N(\omega') + f(\omega' - \omega)] \frac{\phi(\omega - \omega' + i\delta)}{\sqrt{(\omega - \omega')^2 Z^2\left(\omega - \omega' + i\delta\right) - \phi^2\left(\omega - \omega' + i\delta\right)}} \right] \\ & + i\pi \int_0^{+\infty} d\omega' \alpha^2 F(\omega') \\ & \left[[N(\omega') + f(\omega' + \omega)] \frac{\phi(\omega + \omega' + i\delta)}{\sqrt{(\omega + \omega')^2 Z^2\left(\omega + \omega' + i\delta\right) - \phi^2\left(\omega + \omega' + i\delta\right)}} \right],\end{aligned} \tag{3}$$

and

$$\begin{aligned}Z(\omega + i\delta) = {} & 1 + \frac{i}{\omega} \frac{\pi}{\beta} \sum_{m=-M}^{M} \lambda(\omega - i\omega_m) \frac{\omega_m Z_m}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}} \\ & + \frac{i\pi}{\omega} \int_0^{+\infty} d\omega' \alpha^2 F(\omega') \\ & \left[[N(\omega') + f(\omega' - \omega)] \frac{(\omega - \omega') Z(\omega - \omega' + i\delta)}{\sqrt{(\omega - \omega')^2 Z^2\left(\omega - \omega' + i\delta\right) - \phi^2\left(\omega - \omega' + i\delta\right)}} \right] \\ & + \frac{i\pi}{\omega} \int_0^{+\infty} d\omega' \alpha^2 F(\omega') \\ & \left[[N(\omega') + f(\omega' + \omega)] \frac{(\omega + \omega') Z(\omega + \omega' + i\delta)}{\sqrt{(\omega + \omega')^2 Z^2\left(\omega + \omega' + i\delta\right) - \phi^2\left(\omega + \omega' + i\delta\right)}} \right].\end{aligned} \tag{4}$$

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

2.1. The obtained results

Fig. 1 presents the form of the order parameter on the real axis for the lowest temperature analysed in the paper. It can be easily noticed that the non-zero values are taken only by the real part of the order parameter in the range of the low frequencies. Physically it means no damping effects, which is tantamount to the forever living Cooper pairs [35]. Additionally, clearly noticeable is the destructive impact of the increase in the value of the Coulomb pseudopotential on the superconducting state.

The open dependence of the order parameter on the temperature is depicted in Fig. 2. It has been found that the values of the function $\Delta(\omega)$ on the complex plane construct the characteristic deformed spirals, whose size clearly decreases with the increasing temperature.

The physical value of the order parameter for the given temperature has been calculated on the basis of the formula:

$$\Delta(T) = {\rm Re}\left[\Delta\left(\omega = \Delta(T)\right)\right]. \tag{5}$$

The obtained results are plotted in Fig. 3. It can be clearly seen that, irrespective of the assumed magnitude of the depairing electron correlations, the order parameter for $T = T_0$ and the critical temperature take the high values. In particular, T_C changes in the range from about 300 K to 470 K, whereas $\Delta(0) = \Delta\left(T_0\right)$ lies in the range from about 61 meV to 106 meV (see also Table 1). Let us also notice that due to the strong-coupling and retardation effects, the ratio of the energy gap to the critical temperature clearly