On the high-pressure superconducting phase in platinum hydride

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Abstract
Motivated by the ambiguous experimental data for the superconducting phase in silane (SiH₄), which may originate from platinum hydride (PtH), we provide a theoretical study of the superconducting state in the latter alloy. The quantitative estimates of the thermodynamics of PtH at 100 GPa are given for a wide range of Coulomb pseudopotential values (μ*) within the Eliashberg formalism. The obtained critical temperature value (Tₘₐₓ = 12.94, 20.01°C) for μ* ∈ (0.05, 0.15) agrees well with the experimental Tₘₐₓ for SiH₄, which may be ascribed to PtH. Moreover, the calculated characteristic thermodynamic ratios exceed the predictions of the Bardeen–Cooper–Schrieffer theory, implying the occurrence of strong-coupling and retardation effects in PtH. We note that our results may be of high relevance for future theoretical and experimental studies on hydrides.

Keywords: superconductors, thermodynamic properties, high-pressure effects

(Some figures may appear in colour only in the online journal)

1. Introduction

Recent experimental results on the superconducting phase in H₂S hydride at high pressure [1], which report record high critical temperature value (Tₘₐₓ ~ 190 K), may become another breakthrough in the research on room-temperature superconductivity. In addition to the exceptional thermodynamic properties of the H₂S alloy [2–4], the discussed material is considered to be a phonon-mediated superconductor. The latter fact is of great importance, since it is possible to describe the electron-phonon superconductors within the well-established Bardeen–Cooper–Schrieffer (BCS) theory [5, 6] and its derivatives, such as the strong-coupling Eliashberg formalism [7].

In this spirit, hydride materials, whose concept stems from themilestone works by Ashcroft [8, 9], are currently one of the most promising candidates for future high-temperature superconductors [10] in addition to cuprates [11, 12]. Among the family of hydrogen-based materials, the high-pressure superconducting phase has been experimentally observed only in the mentioned earlier H₂S alloy and likely in the platinum hydride material (PtH). Please note, however, that these are not yet fully confirmed results.

From the scientific point of view, the irrefutable testimonies for the existence of the superconducting phase in the PtH and H₂S alloys are equally important for pushing forward research in the discussed domain. However, in the case of PtH the already available results are not so clear and direct as for the H₂S hydride.

In particular, in 2008 Eremets et al conducted the high-pressure experiment for silane (SiH₄) and stated that the induction of the superconducting state in this material is possible [13]. However, further investigations of the results obtained by Eremets et al questioned to some extent the outcome of this work. Degtyareva et al claimed in their paper [14] that, in the discussed experiment, silane can decompose, and the released hydrogen may react with the surrounding metals, in particular with platinum. This statement was motivated by the x-ray diffraction data, which matches PtH instead of the SiH₄ alloy, suggesting that the observed superconducting state may originate from the first mentioned material. Further theoretical studies confirmed that such a
scenario is highly possible [15–18]. However, all cited theoretical papers presented approximate estimations of the critical temperature by using the McMillan formula [19] and did not provide the discussion of other crucial thermodynamic properties. In this context, the discussed problem of the existence of the superconducting state in PtH is still an open and emerging question.

To address the issues raised in the previous paragraph, we present complementary and comprehensive theoretical analysis of all of the most important thermodynamic properties of the PtH superconductor at the pressure of $p = 100$ GPa. This pressure value is chosen to match the conditions at which the highest value of the critical temperature has been obtained in the experiment of Eremets et al [13]. In particular, our calculations are conducted within the relatively high electron-phonon constant for the PtH hydride ($\lambda = 0.84$, as predicted by Kim et al [18]).

The present paper is organized as follows. In the first section we briefly discuss the technical aspects of the Eliashberg formalism and applied numerical procedures. Next we present our numerical results obtained on the imaginary axis as well as in the mixed representation of the Eliashberg equations. Our paper ends with some pertinent conclusions.

2. Theoretical model

The theoretical analysis presented in this paper is based on the isotropic Eliashberg equations, which are solved, at the imaginary axis and in the mixed representation, by using the iterative method applied in [20] and [21]. The isotropic character of the Fermi surface is imposed by the Eliashberg spectral function ($\alpha^2 F(\Omega)$), which models the electron-phonon interactions and was taken from [18]. We note that in order to assure the consistency of our calculations with the experimental conditions in [13], the chosen $\alpha^2 F(\Omega)$ function corresponds to the pressure value of 100 GPa and the hcp structure of the space group P63.

Due to the uncertain experimental data, we consider three distinct values of the coulomb pseudopotential ($\mu^*$), which models the depairing electron correlations and allows us to sample the superconducting phase of PtH. In particular, $\mu^* = (0.05, 0.1, 0.15)$ and matches the general estimations suggested by Ashcroft for the hydride superconductors in [8]. Furthermore, the wide range of the $\mu^*$ values allows us to appropriately examine the convergence of our results and the experimental data of Eremets et al [13], as well as investigate the influence of the $\mu^*$ value on the superconducting properties of PtH.

The precision of our numerical analysis is controlled by assuming a sufficiently high numerical for the Matsubara frequencies: $\omega_m \equiv \frac{\pi}{\beta} (2m - 1)$, where $\beta \equiv 1/k_BT$ is the so-called inverse temperature, and $k_B$ stands for the Boltzmann constant. Our calculations are then conducted for the 2201 Matsubara frequencies, allowing us to estimate quantitatively the superconducting properties of the PtH for temperatures $T \geq T_B \equiv 3$ K. Finally, the cut-off frequency is set to be $\omega_c = 10 \Omega_{\text{max}}$, where $\Omega_{\text{max}}$ is the maximum phonon frequency equal to 193.25 meV.

3. Numerical results and discussion

In the first step we analyze the temperature dependence of the order parameter ($\Delta_m$) by conducting our numerical calculations on the imaginary axis. The obtained results are presented, for all considered $\mu^*$ values and selected temperatures, in figures 1(a)–(c) as a function of $m$. The physically reasonable gradual decrease of the $\Delta_m$ value with increasing $\mu^*$ and $T$ can be observed. Moreover, together with increasing $m$, we notice saturation of the obtained solutions in all cases. It is a testimonial for the precision of our calculations and the quantitative character of the obtained results.

The value of the critical temperature is determined on the basis of the condition: $\Delta_{m=1}(T_c) = 0$, where $\Delta_{m=1}$ denotes the maximum value of the order parameter. Supplementary functional dependence of the $\Delta_{m=1}$ function on the temperature for the selected values of $\mu^*$ is depicted in figure 1(d). In particular, calculated $T_c$ amounts 20.01 K, 15.78 K, and 12.94 K for $\mu^*$ equal 0.05, 0.1, and 0.15, respectively.

We note that the experimental value of $T_c$ obtained by Eremets et al [13] is $\sim 17$ K for $p \approx 100$ GPa. In what follows, it matches our predictions, falling in to the physically feasible region of $\mu^* \in (0.05, 0.1)$.

The results obtained on the imaginary axis and presented in figures 1(a)–(d) provide information on another measurable
observable, namely, the effective electron mass \( m_e^\ast \). Specifically, the value of the \( m_e^\ast \) can be determined by using the following relation:

\[
m Z_m^1 \approx m_e^\ast = \frac{\rho(0)}{Z_m^1}.
\]

where \( Z_m^1 \) is the maximum value of the wave function renormalization factor and \( m_e \) denotes the band electron mass.

The wave function renormalization factor as well as its maximum value are presented in figures 2(a)–(d) as functions of the temperature for the selected values of \( \mu^\ast \). By using equation (1) we estimate the \( m_e^\ast \) value for the PtH alloy to be 1.84 \( m_e \), which is relatively high as for the phonon-mediated superconductors.

The determined dependence of the \( Z_m^1 \) function on the temperature allows us next to calculate the normalized free energy difference between the superconducting and normal state as:

\[
\frac{\Delta F}{\rho(0)} = \sqrt{8\pi \Delta F/\rho(0)}.
\]

Like in the case of the \( \Delta F/\rho(0) \) function, the normalized thermodynamic critical field strongly depends on the assumed \( \mu^\ast \) value, and decreases together with increasing \( \mu^\ast \). The \( H_C/\sqrt{\rho(0)} \) function and the specific heat for the normal state \( (C_N) \) given by:

\[
C_N(T) = \frac{k_B \gamma}{\beta}.
\]

where \( \gamma \equiv \frac{2}{3} \pi^2 (1 + \lambda) \) is the Sommerfeld constant, can next be used to estimate the first characteristic thermodynamic ratio, familiar in the BCS theory. In particular, the ratio of interest for the critical magnetic field is defined as:

\[
R_H = \frac{T_C C_N(T_C)}{H_C^2(0)}.
\]

and takes the constant value of \( R_H^{\text{BCS}} = 0.168 \) within the BCS theory [5, 6]. However, for the PtH alloy at 100 GPa our calculations predict that \( R_H \approx (0.155, 0.167) \) for \( \mu^\ast \approx (0.05, 0.15) \), showing deviation from the BCS predictions.

The relations given in equations (2) and (9), can next be used to address the normalized difference between the specific heat of the superconducting \( (C_S) \) and normal \( (C_N) \) state,

Figure 2. (a)–(c) The wave function renormalization factor on the imaginary axis \( (Z_m) \) as a function of \( m \) for the selected values of temperature \( (T) \) and coulomb pseudopotential \( (\mu^\ast) \). (d) The maximum value of the wave function renormalization factor on the imaginary axis \( (Z_m^1) \) as a function of the temperature for the selected values of the coulomb pseudopotential.

Figure 3. (a)–(c) The normalized free energy difference \( (\Delta F/\rho(0)) \) (lower panel) and the thermodynamic critical field \( (H_C/\sqrt{\rho(0)}) \) (upper panel) as a function of the temperature \( (T) \) for the selected values of the coulomb pseudopotential \( (\mu^\ast) \).
as given by:

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

(6)

where \( \Delta C = C^S - C^N \). In what follows, the specific heat of the superconducting state can be determined. In figures 4(a)–(c) we present the obtained functional behavior of the \( C^S \) on the temperature for the three considered \( \mu^* \) values. For comparison and systematic purposes, the \( C^N \) function is also presented. It can be observed that the \( C^S \) function rises faster then \( C^N \) as the temperature grows, presenting a characteristic jump at \( T_C \). Moreover, the normalized specific heat of the superconducting state strongly depends on the \( \mu^* \) value, decreasing when the \( \mu^* \) grows.

For the results given in figure 4, the second dimensionless characteristic thermodynamic ratio can be calculated, by using:

\[
R_C \equiv \frac{\Delta C(T_C)}{C^N(T_C)},
\]

(7)

Similarly, like in the case of the \( R_M \) ratio, the obtained \( R_C \) values exceed the BCS limit. In particular, \( R_C \in (1.88, 1.82) \) for \( \mu^* \in (0.05, 0.15) \), whereas \( R_C^{\text{BCS}} = 1.43 \).

The last remaining characteristic ratio, which corresponds to the energy gap value at the Fermi level \( 2\Delta(T) \), where \( \Delta(T) \) is the order parameter on the real axis, can be calculated by solving the Eliashberg equations in the mixed representation (see [20] and [21] for more details). Such analysis is required in order to provide the quantitative values of the \( \Delta(T) \) function, given by the following expression:

\[
\Delta(T) = \text{Re} \left[ \Delta(\omega = \Delta(T), T) \right].
\]

(8)

In figure 5, we summarize our calculations on the real axis by presenting the results of the total normalized density of states (NDOS(\( \omega \))) for \( T = T_0 = 3 \text{ K} \) and the selected values of the coulomb pseudopotential. We note, that the

**Figure 4.** The normalized specific heat of the superconducting \( (C^S/k_B\rho(0)) \) and normal \( (C^N/k_B\rho(0)) \) state as a function of the temperature \( (T) \) for the selected values of the coulomb pseudopotential \( (\mu^*) \).

**Figure 5.** The normalized total electronic density of states (NDOS) at \( T_0 = T = 3 \text{K} \) for the selected values of coulomb pseudopotential \( (\mu^*) \).

NDOS(\( \omega \)) function is related to the \( \Delta(T) \) solutions as:

\[
\text{NDOS}(\omega) = \frac{\text{DOS}_S(\omega)}{\text{DOS}_N(\omega)} = \text{Re} \left[ \frac{\left| \omega - i \Gamma \right|}{\sqrt{(\omega - i \Gamma)^2 - \Delta^2(\omega)}} \right],
\]

(9)

where \( \text{DOS}_S(\omega) \) and \( \text{DOS}_N(\omega) \) are, respectively, the density of states of the superconducting and normal state, whereas \( \Gamma \) stands for the pair breaking parameter and equals to 0.15 meV.

As already mentioned, results presented in figure 5 are depicted for \( T = T_0 \) due to the fact that only the maximum value of the order parameter is relevant for our discussion. By comparing plots for different considered values of \( \mu^* \), we can clearly observe the decrease of the superconducting gap towards the metallic character of the discussed alloy. This outcome is in qualitative agreement with the results presented previously in figures 1(a)–(d).

On the basis of the obtained results we first estimate the value of the the zero-temperature energy gap at the Fermi level \( 2\Delta(0) \equiv 2\Delta(T_0) \). In the case of the PtH alloy at the pressure of 100 GPa the calculated values are: \( 2\Delta(0) \in (6.87, 5.31, 4.28) \text{ meV} \) for \( \mu^* \in (0.05, 0.1, 0.15) \).

In the context of the BCS theory, the \( 2\Delta(0) \) parameter can next be used to determine the thermodynamic ratio for the zero-temperature energy gap at the Fermi level \( (R_A) \). In particular:

\[
R_A \equiv \frac{2\Delta(0)}{k_B T_C}.
\]

(10)

Again, the BCS theory predicts a constant value of the \( R_A \) ratio equal to 3.53, whereas our results for the PtH material under the discussed conditions give \( R_A \in <3.98, 3.84> \) for \( \mu^* \in <0.05, 0.15> \). In what follows, similarly to the case of
the $R_H$ and $R_C$ ratios, the $R_A$ differs from the BCS suggestions.

4. Summary

In the present paper we address the vague experimental data for the high-pressure silane superconductor given by Eremets et al in [13] and the consequences of these results in terms of the platinum hydride alloy. In particular, we perform calculations of the thermodynamic properties of the PtH hydride and reveal several crucial facts concerning the possibility of the existence and properties of the superconducting phase in this material. In order to assure the creditability of our results, calculations are performed at the pressure of 100 GPa and within the hcp structure (with the $P_6_3$ space group), which match exactly the conditions of the experiment conducted in [13].

In the first place, the calculated values of the critical temperature for three different $\mu^*$ present good agreement with the experimental data. In particular, it is shown that the experimental value of $T_C$ can be obtained for the $\mu^*$ equal to $\sim 0.1$. This is a physically relevant value that additionally agrees with the predictions of Ashcroft given for hydrogen-dense materials in [8]. In what follows, our results suggest that the experimental data obtained in [13] may be ascribed to the PtH alloy rather than the SiH$_4$ material. This outcome is in agreement with the previous qualitative results for $T_C$ presented in [15–18]. At this point we would like to also note that the former results [22, 23] predicted from the first principles and the analytical McMillan formula, show that the value of the critical temperature for the SiH$_4$ at 100 GPa ($\mu^* = 0.1$) is around three times higher than in the experiment by Eremets et al. In the context of the above results, subsequent experimental clarification of the discussed issue is timely and of crucial importance for the field.

Our further calculations allow us to determine other thermodynamic properties of the PtH at 100 GPa such as the thermodynamic critical field, the specific heat for the superconducting and normal state, the value of the energy gap at the Fermi level, and others.

It is convenient to summarize these results by estimating the values of the characteristic thermodynamic ratios. We show that all calculated ratios exceed predictions given by the BCS theory, in particular $R_H \in <$0.155, 0.167>, $R_C \in <$1.88, 1.82>, and $R_A \in <$3.98, 3.84>, which correspond to the range of $\mu^* \in <$0.05, 0.15>. The differences between our estimations and the BCS theory indicate a significant role of the retardation and strong-coupling effects in PtH at the pressure of 100 GPa. In what follows, the analysis of the discussed material cannot be conducted within the BCS theory, reinforcing the relevancy of our results and chosen theoretical approach. We note also, that the increase of the value of the Coulomb pseudopotential reduces the mentioned discrepancies, which is the physically plausible effect.

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