The thermodynamic critical field and specific heat of superconducting state in phosphorene under strain

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In this work we present the thermodynamic properties of the superconducting state in phosphorene. In particular, we have examined the electron doped (n_D = 1.3 \times 10^{14}\text{cm}^{-2}) and biaxially strained (4\%) monolayer of black phosphorous, which exhibits best thermodynamic stability and highest superconducting critical temperature (T_c) among all monolayer phosphorene structures. Due to the confirmed electron-phonon pairing mechanism and relatively high electron-phonon coupling constant in the studied material, we carried out the calculations in the framework of the Eliashberg formalism for a wide range of the Coulomb pseudopotential \mu^* \in (0.1, 0.3). We have determined the thermodynamic critical field (H_c), and the specific heat difference (\Delta C) between superconducting (C^S) and normal state (C^N) as the functions of the temperature. In addition, we have calculated the dimensionless parameters R_C = \Delta C(T_c)/C^N(T_c) and R_H = T_cC^N(T_c)/H^2_c(0), and also found their significant deviation from the expectations of the BCS theory. In particular, R_C \approx (2.724, 1.899) and R_H \simeq (0.133, 0.155) for \mu^* \in (0.1, 0.3).

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I. INTRODUCTION

Phosphorene - the monoatomic layer of the black phosphorous - has been paid a special attention by the world of science due to its interesting physical properties that can be used in the nano- and opto-electronics including applications in the nanoscale superconducting devices [1–3]. In 2014, it was possible to experimentally separate the one-atom layer of black phosphorus within the mechanical exfoliation [4, 5] and the plasma-assisted fabrication [6]. Theoretical predictions have shown that phosphorene is a semiconductor whose size of the energy gap depends on the number of material layers: 0.59 eV for 5 layers [5] and 1.59 eV for the monolayer [7]. These results confirm the applicability of phosphorene in the field-effect transistors [8, 9].

The superconducting state in phosphorene, as in graphene, cannot be induced due to the zero density of states at the Fermi level. In 2014, Shao et al. theoretically predicted that by doping with electrons n_D = 1.3 \times 10^{14}\text{cm}^{-2} the superconducting state in phosphorene can be induced, and is characterized by the critical temperature T_c = 4 K. Accordingly, it is considered that phosphorene can find application in the nanoscale superconducting devices, including superconducting quantum interference devices and superconducting transistors [11, 12].

Subsequent studies have shown that the puckered structure of phosphorene can withstand a wide range of strain [13, 14], what can be used to strengthen the electron-phonon coupling and the superconducting state in phosphorene. Recent experimental data only confirmed such predictions. In an experiment investigating the superconducting state in the bilayer phosphorene [12] it was found that the critical temperature equals T_c \sim 3.8 K and it is the same regardless of the intercalant alkali metal. This experiment confirms the supposition that superconductivity in phosphorene results only from its structure. In 2015, Ge et al. have analyzed the superconducting state in phosphorene depending on the uniaxial and biaxial straining with different intensity. The increase in the critical temperature to about 16 K was shown for typical doping n_D and the biaxial straining at a rate of 4\% [15].

Motivated by the results of the experiment and strain effects of the two-dimensional phosphorene, we have decided to examine selected thermodynamic properties of the superconducting state in the case of the biaxial straining (4\%) and in the typical doping n_D = 1.3 \times 10^{14}\text{cm}^{-2}. To our knowledge, the literature data show that such phosphorene is the most stable one, and reaches the highest critical temperature among all known cases.

II. THE ELIASHBERG EQUATIONS

All results contained in this work have been determined basing on the Eliashberg equations in the isotropic limit for the half-filled electron band (\langle n \rangle = 1). This is due to the relatively high electron-phonon coupling constant (\lambda = 1.6 \text{[9]}) in phosphorene. These equations take the
known as the order parameter, and functions, and
\( \mu \) where
\( \beta \) is the Coulomb potential, and
\( n \) solutions of the Eliashberg equations are stable for
in works \[26–28\]. In the case under consideration, the
1100 Matsubara frequencies, using the methods described
values
perconducting state in the monolayer phosphorene, we
tronic density of states on the Fermi surface.
The function
\( \theta \) constant. The symbol
\( \omega \) the wave function renormalization factor. The Mat-
help of the Coulomb pseudopotential function:
the studied material \[24, 25\].

The depairing electron correlations are described with
help of the Quantum Espresso package, which uses the
electron-phonon interaction. It was designed with the
non-interacting phonons. The Eliashberg function
energy difference
\( \Delta \) and the specific heat difference
\( \Delta C \) between the superconducting state and the normal
state, and the thermodynamic critical field
\( H_c \).
The kernel of the electron-phonon interaction takes the
form:
\[ K(z) = 2 \int_0^{+\infty} d\omega \frac{\omega}{\omega^2 - z^2} \alpha^2 F(\omega). \]  

In the considered case we assume that the function
\( K(z) \) has been derived in the approximation of the gas
of the non-interacting phonons. The Eliashberg function
\( \alpha^2 F(\omega) \), taken from the work \[9\], quantitatively models
the electron-phonon interaction. It was designed with the
help of the Quantum Espresso package, which uses the
density functional theory to determine structural, elec-
tronic, vibrational and superconducting properties of the
studied material \[24, 25\].

The depairing electron correlations are described with
the help of the Coulomb pseudopotential function:
\[ \mu^* = \frac{\mu}{1 + \mu \ln \left( \frac{\omega_C}{\omega_{\mu}} \right)}. \]

where \( \mu = U \rho(0) \) denotes the direct Coulomb repulsion,
\( U \) is the Coulomb potential, and \( \rho(0) \) determines the
electronic density of states on the Fermi surface.

Due to the lack of the experimental data on the super-
conducting state in the monolayer phosphorene, we
adopted a wide range of the Coulomb pseudopotential
values \( \mu^* = (0.1, 0.3) \), in order to get an overview of all
possible physically-relevant cases.
The Eliashberg equations have been solved for
1100 Matsubara frequencies, using the methods described
in works \[26, 28\]. In the case under consideration, the
solutions of the Eliashberg equations are stable for
\( T \geq T_0 \), where \( T_0 = 2 \) K.

\[ \varphi_n = \frac{1}{\beta} \sum_{m=-M}^M \frac{K(i\omega_n - i\omega_m - \mu^* \theta(\omega_n - |\omega_m|))}{\omega^2_m Z_m^2 + \varphi_m^2} \varphi_m \]

and
\[ Z_n = 1 + \frac{1}{\omega_n \beta} \sum_{m=-M}^M \frac{K(i\omega_n - i\omega_m)}{\omega^2_m Z_m^2 + \varphi_m^2} \omega_m Z_m. \]

The function \( \varphi_n = \varphi(i\omega_n) \) in the equations above is
known as the order parameter, and \( Z_n = Z(i\omega_n) \) is the
wave function renormalization factor. The Matsubara
frequencies are given by the following formula:
\( \omega_n \equiv \frac{\pi}{\beta} (2n - 1) \), where \( \beta = \frac{1}{\pi T} \), \( k_B \) is the Boltzmann
constant. The symbol \( \theta \) in (1) denotes the Heaviside
functions, and \( \omega_C \) is the characteristic cut-off frequency
\( \omega_C = 3\Omega_{\text{max}}, \text{where} \ \Omega_{\text{max}} = 47.332 \text{ meV} \).

The Eliashberg equations on the imaginary axis allow
to determine the thermodynamic properties of the super-
conducting state in phosphorene, such as: the free
energy difference \( \Delta F \) and the specific heat difference
\( \Delta C \) between the superconducting state and the normal
state, and the thermodynamic critical field \( H_c \).

The kernel of the electron-phonon interaction takes the
form:
\[ K(z) = 2 \int_0^{+\infty} d\omega \frac{\omega}{\omega^2 - z^2} \alpha^2 F(\omega). \]  

In the considered case we assume that the function
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\( T \geq T_0 \), where \( T_0 = 2 \) K.

\[ \Delta F = -2\pi k_B T \sum_{n=1}^M \left[ \sqrt{\omega_n^2 + \left( \varphi_n / Z_n \right)^2} - |\omega_n| \right] \]  

\[ \times \left[ Z_n^{(S)} - Z_n^{(N)} \right] \frac{|\omega_n|}{\sqrt{\omega_n^2 + \left( \varphi_n / Z_n \right)^2}}, \]

where \( Z_n^{(S)} \) and \( Z_n^{(N)} \) denote the wave function renor-
amalization factor for the superconducting state \( (S) \) and
the normal state \( (N) \). The given expression \[16–23\] is nor-

![FIG. 1: The free energy difference between the superconduct-
ing state and normal state as a function of the temperature
for three selected values of the Coulomb pseudopotential.](image1)

![FIG. 2: The dependence of the thermodynamic critical field
on the temperature for three selected values of the Coulomb
pseudopotential.](image2)

**III. THE NUMERICAL RESULTS**

The free energy difference between the superconduct-
ing state and the normal state \( \Delta F \), presented in figure
was determined by applying the formula: \[29\]:

\[ \frac{\Delta F}{\rho(0)} = -2\pi k_B T \sum_{n=1}^M \left[ \sqrt{\omega_n^2 + \left( \varphi_n / Z_n \right)^2} - |\omega_n| \right] \]  

\[ \times \left[ Z_n^{(S)} - Z_n^{(N)} \right] \frac{|\omega_n|}{\sqrt{\omega_n^2 + \left( \varphi_n / Z_n \right)^2}}, \]

where \( Z_n^{(S)} \) and \( Z_n^{(N)} \) denote the wave function renor-
amalization factor for the superconducting state \( (S) \) and
the normal state \( (N) \). The given expression \[16–23\] is nor-
Expression (6) determines the thermodynamic critical field. Its values are always positive and decrease with increasing temperature. A significant decrease in value of \( H_c \) in relation to \( \mu^* \): \( [H_c(T_0)]_{\mu^*=0.1}/[H_c(T_0)]_{\mu^*=0.3} \simeq 1.67 \) can be seen in figure 2. The specific heat difference \( \Delta C = C^S - C^N \) between the superconducting state \( (C^S) \) and the normal state \( (C^N) \) is presented with the help of formula (7). The specific heat for the normal state can be determined using the formula: \( C^N/k_B \rho(0) = \gamma/\beta \), where \( \gamma = \frac{2}{3}\pi^2(1+\lambda) \) is the Sommerfeld constant. Figure 3 presents the dependence of the specific heat on the temperature for three selected values of the Coulomb pseudopotential. It can be seen that \( C^S \) for the low temperatures increases exponentially, while at higher temperatures - almost linearly. At the critical temperature it reaches the value of \( C^N \). At the \( T_c \) it is possible to observe a specific heat jump and the decrease in the temperature’s value, at which this jump occurs relative to \( \mu^* \): \( [\Delta C(T_c)]_{\mu^*=0.1}/[(\Delta C(T_c))_{\mu^*=0.3} \simeq 1.64 \).

The knowledge of the thermodynamic functions \( C^S \), \( C^N \) and \( H_c \) gives the opportunity to determine the basic dimensionless parameters of the BCS theory:

\[
R_C = \frac{\Delta C(T_c)}{C^S(T_c)} \quad \text{and} \quad R_H = \frac{T_c C^N(T_c)}{H^2_c(0)}, \tag{8}
\]

where \( H_c(0) \simeq H_c(T_0) \). Their dependence on the Coulomb pseudopotentail is presented in figure 4. Dashed lines mark the values of those parameters for the BCS theory, and these values are: \( R_C \simeq 1.43 \) and \( R_H \simeq 0.168 \) [31, 31]. For phosphorene subjected to a biaxial strain we have received \( R_C \simeq (2.724, 1.899) \) and \( R_H \simeq (0.133, 0.155) \) for \( \mu^* \in (0.1, 0.3) \). Such a large deviation from the predictions of the BCS theory is related to the strong electron-phonon coupling and the strong retardation effects in two-dimensional phosphorene.

IV. SUMMARY

In the presented work we have solved the Eliashberg equations on the imaginary axis to be able to determine the selected thermodynamic properties of the superconducting state in phosphorene. In the paper, we have presented the dependencies of the free energy, the thermodynamic critical field and the specific heat on the temperature. In addition, we have presented the parameter values \( R_C \) and \( R_H \) as the functions of the Coulomb pseudopotential. In particular, we have obtained \( R_C \simeq (2.724, 1.899) \) and \( R_H \simeq (0.133, 0.155) \) for \( \mu^* \in (0.1, 0.3) \). This result confirms the strong-coupling character of the superconducting state in phosphorene.

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