Study of the superconducting state in the $Cmmm$ phase of GeH$_4$ compound

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The superconducting state, that gets induced in the GeH$_4$ compound under the pressure at 20 GPa, is characterized by the high critical temperature $T_C(\mu^*) \in (54.5, 31.2)$ K, where $\mu^*$ is the Coulomb pseudopotential, and $\mu^* \in (0.1, 0.3)$. Other thermodynamic parameters for the considered range of the Coulomb pseudopotential significantly differ from the predictions of the BCS model. In particular: (i) the ratio of the energy gap to the critical temperature ($R_\Delta \equiv 2\Delta(0)/k_B T_C$) changes from 4.07 to 3.88; (ii) the value of the parameter $R_C \equiv \Delta C(T_C)/C^N(T_C)$ decreases from 1.85 to 1.69, where $\Delta C$ denotes the specific heat jump, and $C^N$ is the specific heat of the normal state; (iii) the ratio $R_H \equiv T_C C^N(T_C)/H^2_{c2}(0)$ increases from 0.147 to 0.155; $H_C$ represents the thermodynamic critical field.

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In the elements and the chemical compounds under the influence of high pressure ($p$), the electron-phonon interaction can be so strong that the superconducting state is characterized by a high value of the critical temperature. Of particular note are the results obtained for lithium and calcium, where the maximum value of the critical temperature is equal to: $[T_C]_{p=30.2\text{GPa}}^{\text{Li}} = 14 \text{ K}$ and $[T_C]_{p=161\text{GPa}}^{\text{Ca}} = 25 \text{ K}$.

The other thermodynamic parameters of the superconducting state in Li and Ca, as the result of the existence of the retardation and strong-coupling effects, cannot be properly described in the framework of the BCS model.

Probably, the highest value of the critical temperature can be observed in metallic hydrogen. Unfortunately, also at an extremely high pressure. In particular, it has been predicted that hydrogen enters the metallic state at 400 GPa. It exists then in the molecular state, in which the superconducting state with the critical temperature of 240 K has been predicted. Note, that the superconducting state in the molecular hydrogen can be strongly anisotropic in some ranges of the pressure. In the simplest case, the three-band formalism should be used for the description of its properties.

Above 500 GPa, molecular hydrogen dissociates into a single atomic phase. In the examined case, the highest value of $T_C$ is predicted for the pressure at 2000 GPa, where the critical temperature reaches 600 K. For the considered pressure, the low temperature energy gap at the Fermi surface ($2\Delta(0)$) is so large that the dimensionless ratio $2\Delta(0)/k_B T_C$ equals approximately 6.

In order to reduce the pressure of metallization in hydrogen, a method of the chemical precompression has been proposed. Physically, this idea can be realized in the group of the hydrogenated compounds of the following type: SiH$_4$, H$_2$B$_2$H$_6$, B$_2$H$_6$ and PtH.

Typically, the properties of the superconducting state for pressures that exceed the value of 100 GPa have been considered in the literature. Hence, it is difficult to verify the theoretical results in the experimental way.

In the paper, we have determined the basic thermodynamic properties of the superconducting state in the $Cmmm$ phase of the GeH$_4$ compound for the relatively low value of the pressure ($p = 20$ GPa). In the examined case, the critical temperature, calculated on the basis of the modified McMillan formula, equals ~ 47 K.

Let us note that the low value of $p$ will allow in the future an easy comparison of the results obtained in this study with the experimental data.

Numerical calculations have been conducted in the framework of the Eliashberg formalism. On the imaginary axis the Eliashberg equations take the form.

$$
\phi_n = \frac{\pi}{\beta} \sum_{m=-M}^{M} \lambda(i\omega_n - i\omega_m) - \mu^* \theta (\omega_c - |\omega_m|) \sqrt{\omega^2_m - \phi^2_m} \phi_m, \quad (1)
$$
The obtained results prove that
\[ Z_n = 1 + \frac{1}{\omega_n} \sum_{m=-M}^{M} \frac{\lambda(i\omega_n - i\omega_m)}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}} \omega_m Z_m, \] (2)

where \( \phi_n \equiv \phi(i\omega_n) \) denotes the order parameter function, and \( Z_n \equiv Z(i\omega_n) \) is the wave function renormalization factor; \( \omega_n \) stands for the Matsubara frequency: \( \omega_m \equiv (\pi/\beta)(2m-1) \), where \( \beta \equiv (k_B T)^{-1} \); \( k_B \) is the Boltzmann constant. The order parameter is defined by the formula: \( \Delta_n \equiv \phi_n/Z_n \).

The pairing kernel for the electron-phonon interaction can be represented by: \( \lambda(z) = 2 \int_{0}^{\Omega_{\text{max}}} d\Omega \frac{\phi^2(\Omega)}{(\Omega - z)^2 + \phi^2(\Omega)} \), where the Eliashberg function \( (\alpha^2 F(\Omega)) \) has been determined in the paper \[23\]. The value of the maximum phonon frequency \( (\Omega_{\text{max}}) \) is equal to 515.69 meV.

The symbol \( \mu^* \) represents the Coulomb pseudopotential, which models the depairing electron-electron interaction. The quantity \( \theta \) denotes the Heaviside function, and \( \omega_c \) is the cut-off frequency: \( \omega_c = 3\Omega_{\text{max}} \).

The Eliashberg equations have been solved with the help of the numerical methods discussed and used in \[28\]. The convergence of the solutions has been obtained in the temperature range from \( T_0 = 3 \) K to \( T_C; M = 1100 \) has been assumed.

The form of the functions \( \phi \) and \( Z \) on the real axis \( (\omega) \) has been determined by using the Eliashberg equations in the mixed representation \[29\].

\[ \phi(\omega + i\delta) = \frac{\pi}{\beta} \sum_{m=-M}^{M} \left[ \lambda(\omega - i\omega_m - \mu^* \theta(\omega_c - |\omega_m|)) \frac{\phi_m}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}} \right] \]
\[ + i\pi \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' - \omega) \right] \frac{\phi(\omega - \omega' + i\delta)}{\sqrt{(\omega - \omega')^2 Z^2 (\omega - \omega' + i\delta) - \phi^2 (\omega - \omega' + i\delta)}} \]
\[ + i\pi \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' + \omega) \right] \frac{\phi(\omega + \omega' + i\delta)}{\sqrt{(\omega + \omega')^2 Z^2 (\omega + \omega' + i\delta) - \phi^2 (\omega + \omega' + i\delta)}} \]

and

\[ Z(\omega + i\delta) = 1 + \frac{i\pi}{\omega} \sum_{m=-M}^{M} \lambda(\omega - i\omega_m) \frac{\omega_m Z_m}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}} \]
\[ + i\pi \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' - \omega) \right] \frac{(\omega - \omega') Z(\omega - \omega' + i\delta)}{\sqrt{(\omega - \omega')^2 Z^2 (\omega - \omega' + i\delta) - \phi^2 (\omega - \omega' + i\delta)}} \]
\[ + i\pi \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' + \omega) \right] \frac{(\omega + \omega') Z(\omega + \omega' + i\delta)}{\sqrt{(\omega + \omega')^2 Z^2 (\omega + \omega' + i\delta) - \phi^2 (\omega + \omega' + i\delta)}} \]

where the symbols \( N(\omega) \) and \( f(\omega) \) represent the Bose-Einstein and Fermi-Dirac functions, respectively.

A way of solving the equations \[30\] and \[31\] has been discussed in \[31\].

Fig. 1 represents the dependence of the critical temperature on the Coulomb pseudopotential \( (\mu^* \in (0.1,0.3)) \). The obtained results prove that \( T_C \) is high in the whole range of \( \mu^* \) which has been considered. In particular: \( T_C \in (54.5,31.2) \) K. Additionally in Fig. 1 we have plotted the courses of the dependence of \( T_C \) on \( \mu^* \) obtained with the help of the McMillan and Allen-Dynes expression \[24\], \[25\]. It can be easily seen that the analytical formulas significantly underestimate the critical temperature, especially for the high values of the Coulomb pseudopotential.

In Fig. 1 (A)-(C), we have plotted the order parameter on the imaginary axis for the selected values of the temperature and the Coulomb pseudopotential. It has been found that with the increase in the number \( m \), the function \( \Delta_m \) strongly decreases, and then becomes saturated. The influence of the temperature and the Coulomb pseudopotential on the order parameter value can be the most conveniently traced on the example of the course of the function \( \Delta_{m=1}(T, \mu^*) \). It can be parameterized with the help of the formula:

\[ \Delta_{m=1}(T, \mu^*) = \Delta_{m=1}(T_0, \mu^*) \sqrt{1 - \left( \frac{T}{T_0} \right)^2}, \]

where \( \Delta_{m=1}(T_0, \mu^*) = 58.4 (\mu^*)^2 - 44.58 \mu^* + 13.286 \) meV
and $\beta = 3.3$.

It should be noted that the quantity $2\Delta_{m=1}(T, \mu^*)$ with a good approximation reproduces the dependence of the energy gap at the Fermi surface on the temperature and the parameter $\mu^*$. The obtained results have been shown in Fig. 2(D).

The second solution of the Eliashberg equations on the imaginary axis has been presented in Fig. 3(A)-(C). Just as it was in the case of the order parameter, the value of $Z_m$ rapidly decreases with the increasing number $m$. On the other hand, the effect of the temperature and the Coulomb pseudopotential on the wave function renormalization factor is meager.

It is worth noting that for $T = T_C$, the value of $Z_{m=1}$ is independent of the parameter $\mu^*$. In the considered case, it can be calculated analytically using the formula: $Z_{m=1} = 1 + \lambda$, where the symbol $\lambda$ is the electron-phonon coupling constant: $\lambda \equiv 2 \int_0^{\Omega_{\text{max}}} \alpha^2(\Omega) F(\Omega)/\Omega$. For the GeH$_4$ compound $\lambda$ is equal to 1.0324, thus: $[Z_{m=1}]_{T=T_C} = 2.0324$. The identical result has been obtained by using the numerical procedures, indicating a high accuracy of the computation carried out.

From the physical point of view, the wave function renormalization factor for $m = 1$ with a very good approximation reproduces the value of the electron effective mass: $m_e^* \simeq Z_{m=1} m_e$, where the symbol $m_e$ denotes the electron band mass. The results presented in Fig. 3(D) prove that the electron effective mass in GeH$_4$ is high in the entire range of existence of the superconducting state.

The solutions of the Eliashberg equations on the imaginary axis have been used in the calculations of the free energy difference between the superconducting and the
normal state \([31]\): 
\[
\frac{\Delta F}{\rho(0)} = -\frac{2\pi}{\beta} \sum_{n=1}^{M} \left( \sqrt{\omega_n^2 + \Delta_n^2} - |\omega_n| \right) 
\times \left( Z_n^S - Z_n^N \frac{|\omega_n|}{\sqrt{\omega_n^2 + \Delta_n^2}} \right). 
\]  

The symbols \(Z_n^S\) and \(Z_n^N\) denote the wave function renormalization factor for the superconducting state \((S)\) and the normal state \((N)\), respectively.

The thermodynamic critical field has been calculated by the means of the formula: 
\[
\frac{H_C}{\sqrt{\rho(0)}} = \sqrt{-8\pi \left[ \frac{\Delta F}{\rho(0)} \right]} .
\]  

Above the 0 value in Fig. 4 obtained course have been plotted. Also in this case, the depairing electron correlations significantly reduce the values of the function under consideration: \([H_C(0)]_{\mu^*=0.1} / [H_C(0)]_{\mu^*=0.3} = 1.77\), where the designation \(H_C(T_0) \equiv H_C(T_0)\) has been introduced.

The specific heat difference \((\Delta C \equiv C^S - C^N)\) has been estimated on the basis of the formula:
\[
\frac{\Delta C(T)}{k_B \rho(0)} = \frac{1}{\beta} \frac{d^2 [\Delta F/\rho(0)]}{d(k_B T)^2} .
\]

On the other hand, the specific heat of the normal state may be calculated by using the formula: \(\frac{C^N(T)}{k_B \rho(0)} = \frac{C}{\rho}\), where the Sommerfeld constant is derived from: \(\gamma \equiv \frac{2}{3} \pi^2 (1 + \lambda)\).

The results obtained for \(C^S\) and \(C^N\) have been presented in Fig. 5. It can be seen that at higher temperatures the specific heat of the superconducting state far exceeds the value of \(C^N\), which results in the jump at the critical temperature. In addition, we can point out that the specific heat jump strongly depends on the assumed value of the Coulomb pseudopotential: \([\Delta C(T_c)]_{\mu^*=0.1} / [\Delta C(T_c)]_{\mu^*=0.3} = 1.92\).

The considered thermodynamic functions allow us to calculate the values of two dimensionless ratios:
\[
R_H = \frac{T_c C^N(T_c)}{T_c^2 (0)}, \quad \text{and} \quad R_C = \frac{\Delta C(T_c)}{C^N(T_c)}. 
\]

In the framework of the BCS theory, their values are universal and respectively equal to: 0.168 and 1.43 \([4, 7]\). For \(\text{GeH}_4\) compound, it has been obtained: \(R_H \in (0.147, 0.155)\) and \(R_C \in (1.85, 1.69)\), when \(\mu^* \in (0.1, 0.3)\). On this basis, it is clear that the thermodynamic parameters of the superconducting state in \(\text{GeH}_4\) significantly deviate from the expectations of the BCS model.

The physical value of the energy gap at the Fermi level should be determined on the basis of the expression:
\[
\Delta(T) = \text{Re} \left[ \Delta(\omega = \Delta(T)) \right] .
\]

The courses of the order parameter function on the real axis have been obtained by solving the Eliashberg equations in the mixed representation. The results have been presented in Fig. 6.
FIG. 6: The real and the imaginary part of the order parameter on the real axis for the selected values of the temperature and the Coulomb pseudopotential. Additionally, the rescaled Eliashberg function has been plotted.

It can be seen that the order parameter takes complex values. For the lower frequencies, in the area of the applicability of the equation (9), it can be conducted that: \( \text{Re}\left[\Delta(\omega)\right] \gg \text{Im}\left[\Delta(\omega)\right] \). From the physical point of view, this result indicates the existence of the weak damping effects. In addition, we can note that the complex behavior of \( \Delta(\omega) \), in the frequency range from 0 to about 300 meV, is explicitly related to the shape of the Eliashberg function. Above 300 meV the order parameter becomes saturated.

On the basis of Fig. 6, we can also trace the influence of the temperature on the course of \( \Delta(\omega) \). It has been found that together with the increase of \( T \), the outline of the order parameter function becomes more regular, regardless of the value assumed for the Coulomb pseudopotential.

The presented results allowed us to calculate the value of the energy gap at the Fermi level for the lowest considered temperature (2\( \Delta(0) \)). Then, the dimensionless ratio has been estimated: \( R_\Delta = 2\Delta(0)/k_BT_C \). In the case of the Ge\( \text{H}_4 \) compound, the following result has been obtained: \( R_\Delta \in (4.07, 3.88) \), for \( \mu^* \in (0.1, 0.3) \). Let us notice that the BCS theory predicts that: \( R_\Delta = 3.53 \). Therefore, the parameter \( R_\Delta \) for Ge\( \text{H}_4 \) clearly exceeds the value estimated in the framework of the BCS model.

To summarize, we have calculated the values of the specific heat jump at the critical temperature and the low-temperature value of the thermodynamic critical field decreases strongly with the increasing of \( \mu^* \), which has been explicitly presented in table I.

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TABLE I: The values of the thermodynamic parameters of the superconducting state in the GeH$_4$ compound for $p = 20$ GPa.

| $\mu^*$ | $T_C$ (K) | $R_A$, $R_C$, $R_H$ | $\Delta C(T_C)/k_B\rho(0)$ (meV) | $H_C(0)/\sqrt{\rho(0)}$ (meV) |
|---------|-----------|----------------------|-------------------------------|------------------------|
| 0.1     | 54.5      | 4.07, 1.85, 0.147    | 116.31                        | 44.80                   |
| 0.2     | 39.9      | 3.95, 1.79, 0.151    | 82.45                         | 32.30                   |
| 0.3     | 31.2      | 3.88, 1.69, 0.155    | 60.72                         | 25.03                   |

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