CaLi$_2$ superconductor under the pressure of 100 GPa: the thermodynamic critical field and the specific heat

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Abstract

In this paper the thermodynamic properties of the CaLi$_2$ superconductor have been studied at a pressure of 100 GPa. The thermodynamic critical field ($H_C$) and the specific heats for the superconducting and normal states ($C_S$ and $C_N$) have been obtained. The calculations have been made within the framework of the Eliashberg approach for a wide range of the Coulomb pseudopotential: $\mu^* \in (0.1, 0.3)$. It has been shown that the low-temperature critical field and the specific heat jump at $T_C$ strongly decrease if $\mu^*$ increases. The value of the dimensionless ratio $R_C \equiv (C_S - C_N)/C_N$ at the critical temperature differs significantly from the value predicted by the Bardeen–Cooper–Schrieffer (BCS) model. In particular, the parameter $R_C$ decreases from 1.83 to 1.73 with the increase of the Coulomb pseudopotential value. In the paper, the interpolation formulas for the functions $T_C(\mu^*)$ and $R_C(\mu^*)$ have also been given.

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

1. Introduction

Calcium (Ca) under compression exhibits the anomalous behaviour associated with structural transitions. In particular, Ca gets transformed from the fcc to the bcc structure at 19.5 GPa [1]. A simple cubic structure exists in the pressure ($p$) range from 52 to 113 GPa. Above these values the Ca-IV phase exists [2]. Several other higher pressure phases like Ca-V (at $p = 139$ GPa [2]), Ca-VI (at $p = 158$ GPa [3]) and Ca-VII (at $p = 210$ GPa [4]) have also been confirmed in the experimental way.

At $p = 44$ GPa (the sc phase), the superconductivity with the critical temperature ($T_C$) close to 2 K has been observed [5]. The critical temperature in Ca increases with the pressure [6], and reaches the maximum value equal to 25 K at 161 GPa [7]—the highest value of the critical temperature for simple elemental superconductors.

Ca can create compounds with many other elements. The theoretical studies have predicted that a hydrogen-rich compound, like CaH$_6$ ($p = 150$ GPa), can be a high temperature superconductor with an extremely high value of critical temperature: $T_C \in (220 - 235)$ K [8]. However, this result has still not been confirmed by the experimental data.

On the other hand, the superconducting state in CaLi$_2$ has been experimentally observed at a pressure above 11 GPa. Between 11 and 45 GPa, the critical temperature increases to the maximum value equal to 12.9 K, then $T_C$ slowly decreases to 9 K at 81 GPa [9]. The full dependence of the critical temperature on the pressure has been presented in figure 1.

The superconducting state in CaLi$_2$ has also been studied theoretically [10].

In the first step, it has been shown that the crystal structure of the CaLi$_2$ compound possesses the decomposition–recombination oscillating behaviour.

In particular, the hexagonal Laves phase, which is stable for $p \in (10, 20)$ GPa, decomposes in the pressure range of 20 – 35 GPa. At the pressure between 35 – 54 GPa and 54 – 105 GPa, the two structures, with space groups $C2/c$ and $P21/c$ are stable. Next, the CaLi$_2$ superconductor decomposes into elemental Ca and Li above 105 GPa. The stable phases of CaLi$_2$ have been marked in figure 1.

A previous paper [10] has proved that the superconducting state in CaLi$_2$ is characterized by a high value of the electron–phonon coupling constant ($\lambda$).

A detailed form of the function $\lambda(p)$ has been plotted in figure 1. It is easy to see that for $p \in (36, 80)$ GPa,
the coupling constant is of the order of 1. Above 80 GPa, λ strongly increases with the pressure and assumes the value of 2.73 for \( p = 100 \) GPa. In the considered cases, the electron–phonon coupling constant is so large that the mean-field Bardeen–Cooper–Schrieffer (BCS) theory cannot be used \[11\]. For this reason, the calculation of the thermodynamic properties of the superconducting state in CaLi_2 should be conducted in the framework of the Eliashberg formalism \[12\].

In the literature the full analysis of the thermodynamic properties of the superconducting state in CaLi_2 has been performed for the pressure values between 45 GPa (\( T_C = 12.9 \) K) and 60 GPa (\( T_C = 10.6 \) K) \[13, 14\].

In the first case (the \( C2/c \) space group and \( \lambda = 1.14 \)), it has been shown that the Coulomb pseudopotential (\( \mu^* \)) has an exceptionally high value, equal to 0.23. We underline that the function \( \mu^*(p) \) has high values (\( \approx 0.15 \)), also in the pressure range from 28 to 60 GPa. From a physical point of view, the above result means that the depairing electronic correlations in CaLi_2 are strong for the considered values of \( p \). Additionally for \( p = 45 \) GPa, the remaining thermodynamic parameters differ significantly from the BCS predictions. In particular, the zero-temperature energy gap to the critical temperature is equal to 3.95, and the ratio of the specific heat jump to the normal state specific heat assumes the value of 2.01.

For \( p = 60 \) GPa, the superconducting state gets induced in the structure with the space group \( P2_1/c \). In this case, the values of \( \lambda \) and \( \mu^* \) are slightly smaller (\( \lambda = 0.96 \) and \( \mu^* = 0.2 \)) than for \( p = 45 \) GPa. It has also been shown that the thermodynamic parameters of the superconducting phase are beyond the BCS predictions. Although not as far beyond as for \( p = 45 \) GPa.

The situation changes very significantly just before the final decomposition of CaLi_2 (\( p = 100 \) GPa), where the electron–phonon coupling constant reaches the maximum, and CaLi_2 is in the extreme strong-coupling regime. In this case, the determination of the superconducting thermodynamic parameter is especially interesting.

For this reason, in the presented paper we have calculated the values of the thermodynamic parameters of the CaLi_2 superconductor for \( p = 100 \) GPa. The numerical analysis has been made in the framework of the Eliashberg formalism.

### 2. Formalism

The Eliashberg equations on the imaginary axis can be written in the following form:

\[
\Delta_n Z_n = \frac{\pi}{\beta} \sum_m K(n, m) \frac{-\mu^* 0}{\sqrt{\omega_m^2 + \Delta_n^2}} \Delta_m
\]

and

\[
Z_n = 1 + \frac{\pi}{\beta \omega_n} \sum_m \frac{K(n, m)}{\sqrt{\omega_m^2 + \Delta_n^2}} \omega_m,
\]

where the symbols \( \Delta_n \equiv \Delta(i\omega_n) \) and \( Z_n \equiv Z(i\omega_n) \) denote the order parameter and the wave function renormalization factor, respectively. The \( n \)th Matsubara frequency is given by the expression \( \omega_n = \frac{\pi}{\beta} (2n - 1) \), where \( \beta = 1/k_B T \) and \( k_B \) is the Boltzmann constant.

The electron–phonon pairing kernel \( K(n, m) \) is given by

\[
K(n, m) \equiv 2 \int_0^{\Omega_{\text{max}}} \frac{d\Omega}{(\omega_n - \omega_m)^2 + \Omega^2} \alpha^2 F(\Omega),
\]

where the Eliashberg function \( (\alpha^2 F(\Omega)) \) and the maximum phonon frequency \( (\Omega_{\text{max}} = 113.1 \text{ meV}) \) has been determined in another paper \[10\]. In particular, the crystal structure for the CaLi_2 compound has been obtained by using the \textit{ab initio} evolutionary algorithm USPEX \[15–17\]. This method has also been discussed in detail in the papers \[18–20\]. The structural relaxations and the electronic properties calculations have been carried out using the density functional theory \[21–23\] (the VASP code \[24\]). The lattice dynamics and the electron–phonon coupling have been analyzed with the help of the QUANTUM-ESPRESSO package \[25\].

In the presented paper, the depairing electronic interaction has been described by the Coulomb pseudopotential; the symbol \( \theta \) denotes the Heaviside unit function and \( \omega_c \) is the cut-off frequency (\( \omega_c = 3\Omega_{\text{max}} \)).

Due to the absence of the experimental value of the critical temperature, we have assumed a wide range of the Coulomb pseudopotential: \( \mu^* \in (0.1, 0.3) \). This choice is connected with the fact that the value of the Coulomb pseudopotential in Ca and Li is high \[26, 27\]. For example: \( [\mu^*]^{(\text{Ca})}_{p=161\text{ GPa}} = 0.24 \) and \( [\mu^*]^{(\text{Li})}_{p=22.3\text{ GPa}} = 0.22 \) or \( [\mu^*]^{(\text{Li})}_{p=29.7\text{ GPa}} = 0.36 \) \[28, 29\].

The Eliashberg equations have been solved for 2201 Matsubara frequencies by using the iteration method, described in the papers \[30, 31\]. In the considered case, the functions \( \Delta_n \) and \( Z_n \) are stable for \( T \geq T_0 \), where the temperature \( T_0 \) is equal to 2.32 K.

### 3. Results

In figure 2, the solutions of the Eliashberg equations on the imaginary axis have been presented. We have chosen the temperature range from \( T_0 \) to \( T_C \) for the selected values of the Coulomb pseudopotential.

In figures 2(A)–(C), the dependence of the order parameter values on the successive Matsubara frequencies
...and the normal states, respectively. The normal states at the Fermi surface. The symbols $Z_m$ denote the wave function renormalization factors for the superconducting and the normal states, respectively. The normal states at the Fermi surface. The symbols $Z_m$ denote the wave function renormalization factors for the superconducting and the normal states, respectively. The normal states at the Fermi surface. The symbols $Z_m$ denote the wave function renormalization factors for the superconducting and the normal states, respectively. The normal states at the Fermi surface. The symbols $Z_m$ denote the wave function renormalization factors for the superconducting and the normal states, respectively. The normal states at the Fermi surface. The symbols $Z_m$ denote the wave function renormalization factors for the superconducting and the normal states, respectively.

The thermodynamic properties of the superconducting phase depend on the free energy difference between the superconducting and the normal states ($\Delta F \equiv F^S - F^N$) [32]:

$$
\frac{\Delta F}{\rho(0)} = -\frac{2\pi}{\beta} \sum_{n} \left( \sqrt{\omega_n^2 + \Delta_n^2} - |\omega_n| \right) \times \left( Z_n^S - Z_n^N \right),
$$

where $\rho(0)$ represents the value of the electron density of states at the Fermi surface. The symbols $Z_n^S$ and $Z_n^N$ denote the wave function renormalization factors for the superconducting and the normal states, respectively.

In figure 3, the dependence of $\Delta F/\rho(0)$ on the temperature for the selected values of the Coulomb pseudopotential have been plotted. The negative values of the considered ratio prove that the superconducting state is thermodynamically stable to the critical temperature. Additionally, it can be noticed that $\Delta F(T_0)$ strongly decreases with $\mu^*$:

$$
[\Delta F (T_0)]_{\mu^*=0.3} / [\Delta F (T_0)]_{\mu^*=0.1} \simeq 0.41.
$$

The thermodynamic critical field can be calculated in the following way [33]:

$$
\frac{H_C}{\sqrt{\rho(0)}} = -8\pi \left[ \frac{\Delta F}{\rho(0)} \right].
$$

In figure 4, the temperature dependence on the ratio $H_C/\sqrt{\rho(0)}$ has been shown. It is easy to see that the low temperature value of the critical field strongly decreases if the Coulomb pseudopotential increases:

$$
[\Delta F (T_0)]_{\mu^*=0.3} / [\Delta F (T_0)]_{\mu^*=0.1} \simeq 0.65.
$$

The specific heat difference between the superconducting and the normal states ($\Delta C \equiv C^S - C^N$) should be calculated...
by using the expression
\[
\frac{\Delta C(T)}{k_B \rho(0)} = \frac{1}{\beta} \frac{d^2 \{\Delta F/\rho(0)\}}{d(k_B T)^2}.
\]  

Figure 4. The thermodynamic critical field as a function of the temperature for selected values of the Coulomb pseudopotential.

Whereas, the specific heat in the normal state can be obtained from the formula: \(C^N(T) = \frac{\rho(T)}{\beta} \), where the Sommerfeld constant is given by: \(\gamma = \frac{\pi^2}{3} (1 + \lambda)\). From the physical point of view, the use of the expressions for \(\Delta C\) and \(C^N\) means that the clean phononic component of the specific heat has been omitted in the presented study.

In Figure 5, the form of the specific heat has been shown. Let us notice that at low temperatures, the specific heat in the superconducting state is exponentially suppressed. At a higher temperature, \(C^S\) rapidly increases and significantly exceeds the value of \(C^N\). At the critical temperature the characteristic jump has been observed.

Furthermore, we can see that at the critical temperature the specific heat jump decreases with the growth of the Coulomb pseudopotential:
\[
\frac{[\Delta C(T_C)]_{\mu^* = 0.3}}{[\Delta C(T_C)]_{\mu^* = 0.1}} \simeq 0.60.
\]  

The knowledge of the functions \(C^S\) and \(C^N\) enables the determination of the parameter:
\[
R_C = \frac{\Delta C(T_C)}{C^N(T_C)}.
\]  

Figure 5. The dependence of the specific heats in the superconducting and the normal state on the temperature for selected values of the Coulomb pseudopotential. The vertical line indicates the position of the specific heat jump at \(T_C\). The clean phononic component of the specific heat has been omitted.

For the CaLi\(_2\) compound under the pressure of 100 GPa, we have obtained \(R_C \in (1.83, 1.73)\) if \(\mu^* \in (0.1, 0.3)\). The above result strongly differs from the value predicted by the BCS model: \([R_C]_{\text{BCS}} = 1.43\) [34]. The observed difference between the predictions of the BCS and the Eliashberg theory is connected with the existence of the strong-coupling and retardation effects in the CaLi\(_2\) compound. These effects are measured by the parameter: \(k_B T_C/\omega_{\text{phon}}\) where the symbol \(\omega_{\text{phon}}\) denotes the logarithmic phonon frequency [35]. In the BCS limit, we have \(k_B T_C/\omega_{\text{phon}} \rightarrow 0\). On the other hand, in the framework of the Eliashberg theory, we can obtain \(k_B T_C/\omega_{\text{phon}} \in (0.656, 0.404)\) for \(\mu^* \in (0.1, 0.3)\). We would like to note that the critical temperature has been calculated from the formula determined in the appendix, and \(\omega_{\text{phon}} = 3.87\) meV.

It is also worth calculating the dependence of \(R_C\) on the electron–phonon coupling constant. The numerical results have shown that the ratio \(R_C\) strongly increases if \(\lambda\) increases.

In order to determine the value of \(R_C\), it was necessary to make complicated calculations. For this reason, we have presented the convenient interpolation formula also for \(R_C\) in order to reconstruct the precise numerical result:
\[
\frac{R_C}{R_{\text{BCS}}} = 1 + 53 \left(\frac{0.158 k_B T_C}{\omega_{\text{phon}}}ight)^2 \ln \left(\frac{1.073 \omega_{\text{phon}}}{k_B T_C}\right).
\]  

In Figures 6(A) and (B), we have presented the ratio \(R_C\) as a function of the Coulomb pseudopotential and the electron–phonon coupling constant. It is easy to see that the formula (11) correctly reproduces the numerical data.

Figure 6. The value of the ratio \(R_C\) as a function of the Coulomb pseudopotential (A) and the electron–phonon coupling constant (B). The circles represent the exact Eliashberg result. The solid line has been obtained on the basis of the expression (11). Additionally, the BCS result has been shown.
4. Summary

In summary, we have used the Eliashberg equations to calculate the thermodynamic critical field and the specific heat of the CaLi$_2$ superconductor under the pressure of 100 GPa. We have shown that the low-temperature value of the critical field and the value of the specific heat jump at $T_C$ strongly decreases if the Coulomb pseudopotential increases. The ratio $R_C$ for the characteristic values of the functions $C^S$ and $C^N$ cannot be described correctly by the conventional BCS theory. In particular, $R_C \in (1.83, 1.73)$, where $\mu^* \in (0.1, 0.3)$. The numerical results for the functions $T_C(\mu^*)$ and $R_C(\mu^*)$ have been supplemented by the interpolation formulas.

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Appendix. The formula for the critical temperature

The interpolation formula for the critical temperature takes the form

$$k_B T_C = f_1 f_2 \frac{\omega_{\text{fn}}}{1.45} \exp \left[ \frac{-1.172 (1 + \lambda)}{\lambda - \mu^*} \right] .$$

(A.1)

where $f_1$ and $f_2$ denote the strong-coupling correction function and the shape correction function, respectively [35]:

$$f_1 = \left[ 1 + \left( \frac{\lambda}{\Lambda_1} \right)^{1.5} \right]^{1/2} \quad \text{and} \quad f_2 = 1 + \left( \frac{\sqrt{\omega_2} - 1}{\lambda^2 + \Lambda_2^2} \right).$$

(A.2)

The quantities $\Lambda_1$ and $\Lambda_2$ have the form

$$\Lambda_1 = 2 - 2.6 \mu^* \quad \text{and} \quad \Lambda_2 = (0.31 + 1.41 \mu^*) \left( \frac{\sqrt{\omega_2}}{\omega_{\text{fn}}} \right).$$

(A.3)

The parameter $\sqrt{\omega_2}$ is equal to 34.95 meV.

The formula (A.1) has been prepared based on 300 exact values of the function $T_C(\mu^*)$. We have used the last square method and we have considered the range of $\mu^*$ from 0.1 to 0.3.

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