Superconductivity of calcium under the pressure at 120 GPa

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The properties of the superconducting state in calcium under the pressure at 120 GPa were analyzed. By using the imaginary axis Eliashberg equations it has been shown, that the Coulomb pseudopotential reaches the high value equal to 0.215. In the considered case, the critical temperature is not properly described by the Allen-Dynes formula and it should be calculated with an use of the modified expression. In the paper the exact solutions of the Eliashberg equations on the real axis were also obtained. On this basis it was stated, that the effective potential of the electron-electron interaction is attractive for the frequencies lower or equal to the maximum phonon frequency. Then, the dimensionless parameter $2\Delta(0)/k_BT_c = 4.10$ was calculated. In the last step it has been proven, that the ratio of the electron effective mass to the bare electron mass is high and reaches its maximum equal to 2.36 for the critical temperature.

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I. INTRODUCTION

The first mention of the pressure-induced superconducting state in calcium was given by Dunn and Bundy in 1981 [1]. In 1996 Okada et al. have obtained experimentally the dependence of the critical temperature ($T_c$) on the pressure ($p$) [2]. The authors stated, that the critical temperature grows together with an increase of the pressure from the value of about 1 K for $p = 50$ GPa to the value $\sim 20$ K for 150 GPa. The results of Okada were verified in 2006 by Yabuuchi et al. [3]. The significant discrepancy between new and old data was observed (see Fig.1). Most probably the difference between the experimental results comes from the use of the samples of distinct purity or from the different methods of the pressure measuring. The discussion of the considered problem the reader can find in the paper [3].

According to Yabuuchi et al. the superconducting state in calcium can be observed in the following crystal structures: $sc$, Ca-IV and Ca-V. In the structure $sc$ the critical temperature quickly increases together with the growth of the pressure (from the value of about 3 K for $p = 58$ GPa to the value $\sim 23$ K for the pressure equal to 113 GPa). In the case of Ca-IV and Ca-V the increment of $T_c$ is much slower. Although, with the further compression to 161 GPa the critical temperature increases to the value equal to 25 K (the highest observed value of the critical temperature for the simple metals).

The issue of the $T_c$ value for the given pressure seems to be solved by Yabuuchi et al. Unfortunately, the determination of the proper sequence of the structural transitions is still the tangled problem. On the one hand it is connected with the objective experimental difficulties, on the other hand the $ab$ initio calculations are also burdened with the large uncertainty due to the small difference between the values of the enthalpy of the considered crystal structures [8].

Let us point the reader’s attention toward the fact, that some recently published papers partially question above scheme of the structural transitions (see Fig.2(B)-(D)) [7, 8, 9]. On the basis of the presented data it can be easily noticed, that the qualitative agreement between the obtained results exists only for the area of the low pressure’s values (phases $fcc$ and $bcc$). Above $\sim 36$ GPa the differences become significant. Thus at the present stage of the research, it is very difficult to specify which of the presented schemes is proper.

From the physical point of view, the superconducting phase in calcium should have the most interesting properties at the area of high pressures, where $T_c > 20$ K. For that reason, the thermodynamic parameters of the superconducting state under the pressure at 120 GPa were determined. In this case Yin et al. suggest, that structures: $P_{4123}$, $\bar{C}mca$ and $Pnma$ are showing almost identical values of the enthalpy (Fig.3(C)) [8]. The paper of Ishikawa et al. predicts the appearance of the crystal structure $Pnma$ (Fig.3(D)) [9].

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The imaginary axis Eliashberg equations can be written in the following form \[^{[11]}\]:

$$\phi_n = \frac{\pi}{\beta} \sum_{m=-M}^{M} \frac{\lambda(i\omega_n - i\omega_m) - \mu^*\theta(\omega_c - |\omega_m|)}{\sqrt{\omega^2 Z^2 + \phi^2_m}} \phi_m, \quad (1)$$

The pairing kernel for the electron-phonon interaction is described with an use of the formula:

$$Z_n = 1 + \frac{\pi}{\omega_n^2} \sum_{m=-M}^{M} \frac{\lambda(i\omega_n - i\omega_m)}{\sqrt{\omega^2 Z^2 + \phi^2_m}} \omega_m Z_m, \quad (2)$$

where the symbol \(\phi_n \equiv \phi(i\omega_n)\) denotes the order parameter function and \(Z_n \equiv Z(i\omega_n)\) is the wave function renormalization factor; \(m\)-th Matsubara frequency is given by the expression: \(\omega_m \equiv (\pi/\beta)(2n - 1)\), where \(\beta \equiv (k_BT)^{-1}\) and \(k_B\) is the Boltzmann constant. The order parameter is defined as the ratio: \(\Delta_n \equiv \phi_n/Z_n\). The pairing kernel for the electron-phonon interaction is determined in the paper \[^{[8]}\]; the maximum phonon frequency \((\Omega_{\text{max}})\) is equal to 61.68 meV.

In the framework of the Eliashberg formalism, the depairing interaction between the electrons is taken into consideration with an aid of the Coulomb pseudopotential \(\mu^*\). The symbol \(\theta\) denotes the Heaviside unit function and \(\omega_c\) is the cut-off frequency: \(\omega_c = 3\Omega_{\text{max}}\).

The Eliashberg equations were solved for 2200 Matsubara frequencies \((M = 1100)\) with an use of the iteration method, described in the papers \[^{[10, 17]}\]. In the considered case the solutions of the Eliashberg equations are stable for \(T \geq 5\) K.

B. The critical value of the Coulomb pseudopotential

The Coulomb pseudopotential is the second input parameter in the Eliashberg equations. In general, its crit-
In the previous paragraph we have shown that the Allen-Dynes or McMillan formula can not be used in the case of calcium. For that reason, the values of the parameters appearing in the classical Allen-Dynes formula were determined once again. In particular, we were basing on the 200 exact values of $T_C(\mu^*)$ determined with an use of the Eliashberg equations. The following result was received:

$$k_B T_C = f_1 f_2 \frac{\omega_m}{1.45} \exp \left[ -1.03 \left( 1 + \lambda \right) \frac{\left( T - T_C \right)}{\mu^* (1 + 0.06 \mu^*)} \right],$$

where the symbol $f_1$ ($f_2$) is the strong-coupling correction (shape correction) function:

$$f_1 = 1 + \left( \frac{\Lambda}{\Lambda_1} \right)^2 \lambda^2$$

and

$$f_2 = 1 + \left( \frac{\omega}{\omega_m} - 1 \right) \frac{\lambda^2}{\Lambda^2 + \Lambda_2^2}.$$

The parameter $\omega_2$ denotes the second moment of the normalized weight function: $\omega_2 = \frac{1}{2} \int_0^{\Omega_{\text{max}}} d\Omega \omega^2 F(\Omega) \Omega$. The quantity $\omega_m$ is called the logarithmic phonon frequency and $\lambda$ is the electron-phonon coupling constant: $\omega_m = \exp \left[ \frac{2}{\pi} \int_0^{\Omega_{\text{max}}} d\Omega \omega^2 F(\Omega) \ln (\Omega) \right]$ and $\lambda = 2 \int_0^{\Omega_{\text{max}}} d\Omega \omega^2 F(\Omega) \ln (\Omega) \Omega$. For calcium it was achieved: $\omega_2 = 29.81$ meV, $\omega_m = 25.34$ meV and $\lambda = 1.3$. In the paper we have changed also the parametrization of the functions $\Lambda_1$ and $\Lambda_2$. We have obtained:

$$\Lambda_1 \equiv 2 \left( 1 + 4.7 \mu^* \right)$$

and

$$\Lambda_2 \equiv -0.085 \left( 1 - 150 \mu^* \right) \left( \frac{\sqrt{\omega_2}}{\omega_m} \right).$$

In Fig. 3 we present a dependence of the critical temperature on the Coulomb pseudopotential. The results were obtained with an use of the Eliashberg equations, the modified and classical Allen-Dynes formula. Additionally, the values of $T_C$ calculated on the basis of the McMillan formula ($f_1 = f_2 = 1$) are also plotted. It can be easily noticed, that the modified Allen-Dynes formula allows to very precisely reproduce the results of the Eliashberg theory in the whole considered range of $\mu^*$.

### D. The dependence of $\Delta_m$ and $Z_m$ on the temperature

In the paragraph there are presented solutions of the Eliashberg equations on the imaginary axis for the temperature range from 5 K to $T_C$. In particular, in Fig. 4 (A) we have plotted the dependence of the order parameter’s values on the successive Matsubara frequencies. It can be easily noticed, that with the growth of the temperature the maximum of the order parameter’s function ($\Delta_{m=1}$) is decreasing. Additionally, the half-width of the function becomes successively smaller. The last property means, that together with the temperature’s growth less successive Matsubara frequencies commit a relevant contribution to the Eliashberg equations. Let us notice, that
E. The Eliashberg equations in the mixed representation

In order to exactly calculate the value of the energy gap at the temperature of zero Kelvin and electron effective mass one should have the solutions of Eliashberg equations on the real axis. From the mathematical point of view the determination of such type function is a very complicated issue. Usually to do that, one uses the solutions on the imaginary axis and then analytically continues them on the real axis [20]. However, the described procedure has a serious drawback e.g. the obtained functions are stable only for the low values of the frequencies (much lower than the maximum phonon frequency). For that reason, we have used a method of calculation which is deprived of the weak point mentioned above [15]. In particular, the approach is based on the transformation of the Eliashberg equations to the mixed representation, in which the order parameter function and the wave function renormalization factor are defined on both real and imaginary axis. In the considered case the Eliashberg set takes the following form:
\[ \phi(\omega + i\delta) = \frac{\pi}{\beta} \sum_{m=-M}^{M} \left[ \lambda(\omega - i\omega_m) - \mu^{*} \theta(\omega_c - |\omega_m|) \right] \frac{\phi_m}{\omega_m^2 Z_m^2 + \phi_m^2} \]

\[ + i\pi \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' - \omega) \right] \frac{\phi(\omega - \omega' + i\delta)}{\sqrt{(\omega - \omega')^2 Z^2(\omega - \omega' + i\delta) - \phi^2(\omega - \omega' + i\delta)}} \]

\[ + i\pi \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' + \omega) \right] \frac{\phi(\omega + \omega' + i\delta)}{\sqrt{(\omega + \omega')^2 Z^2(\omega + \omega' + i\delta) - \phi^2(\omega + \omega' + i\delta)}} \]

and

\[ Z(\omega + i\delta) = 1 + \frac{i\pi}{\omega} \sum_{m=-M}^{M} \lambda(\omega - i\omega_m) \frac{\omega_m Z_m}{\omega_m^2 Z_m^2 + \phi_m^2} \]

\[ + \frac{i\pi}{\omega} \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' - \omega) \right] \frac{(\omega - \omega') Z(\omega - \omega' + i\delta)}{\sqrt{(\omega - \omega')^2 Z^2(\omega - \omega' + i\delta) - \phi^2(\omega - \omega' + i\delta)}} \]

\[ + \frac{i\pi}{\omega} \int_{0}^{+\infty} d\omega' \alpha^2 F(\omega') \left[ N(\omega') + f(\omega' + \omega) \right] \frac{(\omega + \omega') Z(\omega + \omega' + i\delta)}{\sqrt{(\omega + \omega')^2 Z^2(\omega + \omega' + i\delta) - \phi^2(\omega + \omega' + i\delta)}} \],

where symbols \( N(\omega) \) and \( f(\omega) \) denote the statistical functions of bosons and fermions respectively.

**F. The order parameter on the real axis**

The Eliashberg equations in the mixed representation were solved for identical temperatures like the equations on the imaginary axis. In Fig. 6 we have presented \( \text{Re}[\Delta(\omega)] \) and \( \text{Im}[\Delta(\omega)] \) for the range of the frequencies from 0 to \( \Omega_{\text{max}} \) and selected temperatures. Additionally, the form of the Eliashberg function is also plotted. It can be easily noticed, that for the low frequencies the non-zero is only the real part of the order parameter. From the physical point of view it means the lack of the damping effects, which are described by the imaginary part of the order parameter \( \Phi[21] \). For higher frequencies the functions \( \text{Re}[\Delta(\omega)] \) and \( \text{Im}[\Delta(\omega)] \) are characterized by

![FIG. 6: The dependence of the real and imaginary part of the order parameter on the frequency for the selected temperatures. The rescaled Eliashberg function is also plotted.](image)

![FIG. 7: The values of \( \Delta(\omega) \) on the complex plane for the selected temperatures.](image)
the complicated course which is very plainly correlated with the shape of the Eliashberg function.

The full dependence of the order parameter on the temperature for the range of the frequencies from 0 to \( \omega_c \) can be traced in the most convenient way on the complex plane (see Fig. 7). On the basis of the presented results it can be seen, that the values of the order parameter are forming the characteristic spirals with radius that decreases together with the temperature growth. In particular to achieve the determination of the electron effective mass \( (2\Delta (0)) \) allows to determine the dimensionless ratio \( R_1 \equiv \frac{2\Delta (0)}{\frac{\hbar^2}{m^*}} \) which for the calcium is equal to 4.10. Let us notice, that the real part of the order parameter is connected with the effective pairing potential for the electron-electron interaction \[21\]. Thus, the obtained result means, that only in the range of the frequencies for which the Eliashberg function is defined, the effective potential for the electron-electron interaction is attractive.

Below on the basis of the solution for \( T = 5 \) K we have calculated the value of the order parameter at the temperature of zero Kelvin (\( \Delta (0) \)). In particular to achieve that, the following equation was used:

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

As a result it was obtained: \( \Delta (0) = 4.24 \) meV. The familiarity with the energy gap \( (2\Delta (0)) \) allows to determine the dimensionless ratio \( R_1 \equiv \frac{2\Delta (0)}{\frac{\hbar^2}{m^*}} \) which for the calcium is equal to 4.10. Let us notice, that in the framework of the BCS theory the parameter \( R_1 \) takes considerably smaller value that is equal to 3.53 \[22\].

G. The electron effective mass

In Fig. 8 for selected value of the temperature the functions \( \text{Re}[Z (\omega)] \) and \( \text{Im}[Z (\omega)] \) are presented \( (\omega \in (0, \Omega_{\text{max}})) \). On the basis of the plotted courses it can be easily noticed, that for the low values of \( \omega \) non-zero is only the real part of the wave function renormalization factor; this result is directly correlated with the order parameter’s behavior. For higher frequencies the shape of the real and imaginary part of \( Z (\omega) \) is also plainly dependent on the Eliashberg function’s form.

The values of the wave function renormalization factor on the complex plane for the selected values of the temperature is presented in Fig. 9. In particular, in Fig. 9 (A) we have shown an exemplary low-temperature solution which is characterized by a very complicated course; whereas in Fig. 9 (B) we have placed a few selected "high"-temperature solutions, which are presenting quite similar curves.

In the framework of the Eliashberg formalism the real part of the wave function renormalization factor enables the determination of the electron effective mass \( (m^*) \). In particular, the ratio of \( m^* \) to the bare electron mass \( (m_e) \) is given by: \( m^*/m_e = \text{Re}[Z (0)] \). Let us notice that \( \text{Re}[Z (0)] \) takes the highest value for \( T = T_C \) (similarly as \( Z_{m=1} \)). Thus, \( m^*/m_e \) is equal to 2.36\( m_e \).

III. SUMMARY

The basic thermodynamic quantities for the superconducting phase, that induces in calcium under the influence of the pressure 120 GPa, were determined. All calculations were conducted in the framework of the Eliashberg formalism. In the first step it was shown, that the
Coulomb pseudopotential takes very high value equal to 0.215. Next it was stated, that the classical Allen-Dynes formula significantly underestimates the critical temperature. According to the above, the parameters in the Allen-Dynes formula were determined once again adapting the formula to the strict results predicted by the Eliashberg equations. The dimensionless parameter $R_1 = 4.10$ was also determined. The obtained result means, that the value of the energy gap at the temperature of zero Kelvin considerably exceeds the value predicted by the BCS theory. In the last step, it has been stated that the electron effective mass takes the highest value equal to $2.36m_e$ for $T = T_C$.

The method of analysis based on the Eliashberg equations in the mixed representation allows to determine the dependence of the order parameter on the frequency for the range from 0 to $\omega_c$. On the basis of the conducted calculations it was stated, that the values of $\Delta (\omega)$ on the complex plane lie on the characteristic spirals with the radius decreasing together with the temperature growth. The important notification is related to the fact, that for $\omega \in (0, \Omega_{\text{max}})$ the effective potential of the electron-electron interaction is attractive, while for $\omega \in (\Omega_{\text{max}}, \omega_c)$ is repulsive.

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