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Non-BCS superconducting state in yttrium hydride at a record low value of the external pressure

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ABSTRACT

The *ab initio* calculations suggest that YH_3 compound is a superconductor with the maximum value of the critical temperature (T_C) for the record low external pressure equal to 17.7 GPa. Due to the high value of the electron–phonon coupling constant, the thermodynamic properties of the superconducting state in YH_3 have been determined in the framework of the Eliashberg formalism. It has been shown that T_C changes in the range from 45.91K to 27.29 K, for the value of the Coulomb pseudopotential $\mu^\star \in \langle 0.1, 0.3\rangle$. The parameters of the superconducting phase differ significantly from the values predicted by the BCS theory due to the significant strong-coupling and retardation effects: $k_B T_C/\omega_{\ln} \in \langle 0.138, 0.082\rangle$, where $\omega_{\ln}$ denotes the logarithmic phonon frequency. In particular, the dimensionless ratios: $R_\Delta = 2\Delta(0)/k_B T_C$, $R_C = \Delta C(T_C)/C^N(T_C)$ and $R_H = T_C C^N(T_C)/H_C^2(0)$ take the following values: $R_\Delta \in \langle 4.38, 4.20\rangle$, $R_C \in \langle 2.18, 2.02\rangle$ and $R_H \in \langle 0.151, 0.168\rangle$. The symbol Δ represents the order parameter, ΔC is the specific heat jump, C^N is the specific heat of the normal state, and H_C is the thermodynamic critical field.

The information on the discovery of the high-pressure (p) superconducting state in H_3S compound with the record values of the critical temperature $T_C \sim 200$ K, for $p \sim 150$ GPa was published in December 2014 [1,2]. The undoubted success was the culmination of the years of research on the high-temperature superconducting state in the hydrogen-rich compounds [3–11] and metallic hydrogen [12–21].

The superconducting state in the sulfur trihydride is induced by the classical electron–phonon interaction [8–11,22,23], which is a big surprise, because of the generally prevailing belief that the BCS theory gives a limitation on T_C of the order of 40 K [24,25]. Let us note that the lowest value of the critical temperature at 39.4 K characterized so far MgB_2 compound [26], wherein the superconducting condensate in this case is induced by a highly anisotropic electron–phonon interaction [27,28]. Of course, there are other known groups of the materials with a much higher superconducting critical temperature, cuprates in particular [29] (*i.e.* $HgBa_2Ca_2Cu_3O_{8+\delta}$, where $T_C = 153$ K for p=15 GPa [30,31]), however, the pairing mechanism in these compounds is the most likely related to the pure electron correlations [33,32] or greatly modified interaction of the electron–phonon type [34–37].

This presented work determines the thermodynamic properties of the superconducting state in YH_3 compound. The *ab initio* calculations suggest that the system under inspection transits into the superconducting state ($[T_C]_{\max} \sim 40$ K) at the extraordinary low value of the external pressure (17.7 GPa) [38], which can provide a guidance to achieve the high-temperature superconducting state in the hydrogenated compounds at the lowest possible p. Let us also note that due to the considered value of the external pressure, the theoretical predictions contained in publication [38] and in the presented work may also be relatively easily verified experimentally.

The detailed analysis of the superconducting state in YH_3 has been conducted in the framework of the full Eliashberg formalism [39], due to the high value of the electron–phonon coupling constant ($\lambda = 1.42$) [38]. The wide range of the Coulomb pseudopotential values [40] ($\mu^\star \in \langle 0.1, 0.3\rangle$) was taken under consideration, so that obtained results would adopt the eventually strong depairing effects, often observed in the pressure superconductivity [41–43]. Let us notice that in the case of YH_3 neither the simple BCS theory (too high value of λ), nor the approximate expressions on the critical temperature originated from the Eliashberg formalism (McMillan and Allen–Dynes [44,45]), can be used, because generally they incorrectly determine T_C for higher $\mu^\star$ [46,47].

The detailed numerical calculations have been based on the spectral Eliashberg function ($\alpha^2F(\omega)$) determined in the work [38], whereas the value of the maximum phonon frequency ($\Omega_{\max}$) is equal to 113.77 meV. The cut-off energy for the Coulomb pseudopotential has been adopted in the form: $\omega_c = 5\Omega_{\max}$. The Eliashberg equations' solutions (the order parameter $\Delta_m = \Delta(i\omega_m)$ and the wave function renormalization factor $Z_m = Z(i\omega_m)$) proved to be temperature-depen-

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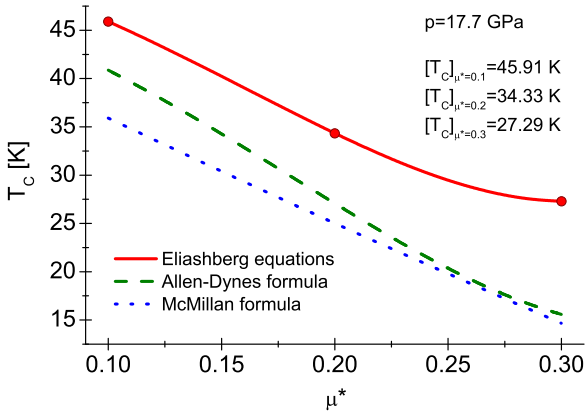

Fig. 1. (Color online) The dependence of the critical temperature for YH_3 on the values of the Coulomb pseudopotential obtained in the framework of the full Eliashberg formalism (the red line). Additionally, the values of T_C obtained with the help of the McMillan and the Allen–Dynes formulas [44,45] (the blue and the green lines) are presented.

dent at $T_0 = 8.12$ K (2201 equations). The symbol i denotes the imaginary unit, and the fermion Matsubara frequency is given by the expression: $\omega_m = (\pi/\beta)(2m-1)$, where $\beta = 1/k_B T$ is the inverted temperature. The detailed description of the Eliashberg formalism and used numerical methods reader can find in the papers [48–51].

Fig. 1 presents the dependence of the critical temperature as a function of the Coulomb pseudopotential. The correctly determined values of T_C are in the range from 45.91K to 27.29 K ($\mu^\star \in \langle 0.1, 0.3\rangle$). Physically it means that, even at relatively strong depairing electron correlations, the critical temperature in YH_3 compound should be comparatively high. Draws attention the fact that the dependence of the critical temperature on the Coulomb pseudopotential cannot be properly reproduced with the help of the McMillan and the Allen–Dynes formulas [44,45], because they significantly underestimate T_C especially in the area of the high values of $\mu^\star$.

The full dependence of the maximum value of the order parameter on the imaginary axis on the temperature present in Fig. 2. The destructive influence of the depairing electron correlations on the superconducting state can be clearly seen. In particular: $\Delta_{m=1}(T_0) \in \langle 8.40, 4.82\rangle$ meV, for $\mu^\star \in \langle 0.1, 0.3\rangle$. The exact values of the order parameter should be calculated in the framework of the Eliashberg formalism on the basis of the equation: $\Delta(T) = \mathrm{Re}[\Delta(\omega = \Delta(T), T)]$, where the function $\Delta(\omega)$ represents the

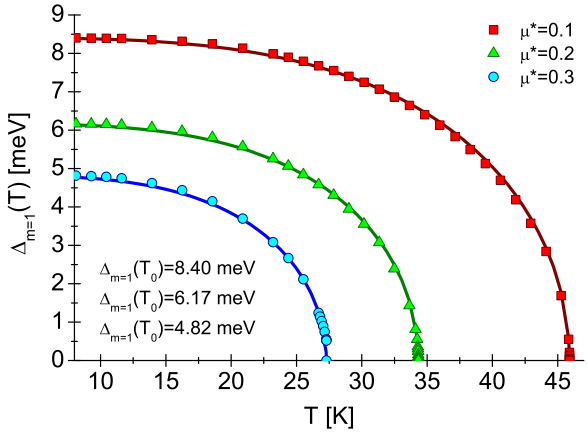

Fig. 2. The maximum value of the order parameter on the imaginary axis (m=1) as a function of the temperature. The symbols were obtained in the framework of the full Eliashberg formalism. The lines can be reproduced with the help of the phenomenological formula: $\Delta_{m=1}(T) = \Delta_{m=1}(T_0)\sqrt{1-\left(\frac{T}{T_C}\right)^{\kappa}}$, where $\kappa = 3.24$. The exponent κ in the BCS theory equals 3 [52].

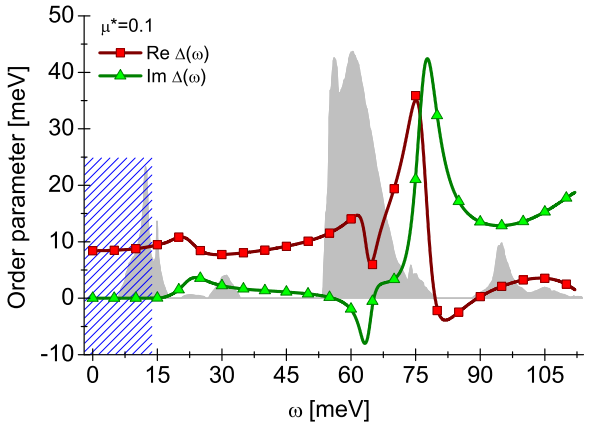

Fig. 3. (Color online) The order parameter on the real axis for $T = T_0$. Blue shaded area corresponds to the value of the frequency, for which the dissipative processes are absent (the static area of the superconducting state: $\Delta(\omega) \simeq \Delta(0)$). The rescaled Eliashberg function is present in the background – the strong correlation between the course of the order parameter and the spectral function is clearly visible.

order parameter determined on the real axis [48]. The detailed form of $\Delta(\omega)$ was obtained with the help of the method of the analytical extension of the Eliashberg equations' solutions from the imaginary axis [54]. For example, Fig. 3 shows the plot of the values of the order parameter on the real axis for $T = T_0$ and $\mu^\star = 0.1$. It can be seen that the dissipative processes ($\mathrm{Im}\,\Delta(\omega) = 0$) are not observed for the low values of the frequency [55]. This means that the superconducting condensate is created by the infinitely long-living Cooper pairs. The damping effects are important at higher power transmissions and they are closely related to the phonon emission and absorption. The form of the Eliashberg function has been plotted in the background of Fig. 3 so reader can easily see the correlations between the course of $\Delta(\omega)$ and $\alpha^2 F(\omega)$.

The performed calculations show that the exact values of the order parameter in the case of YH_3 do not differ significantly from the maximum values of the order parameter on the imaginary axis: $\Delta(T_0) \in \langle 8.67, 4.94\rangle$ meV.

The dimensionless ratio of the energy gap in the single-molecule excitation spectrum to the critical temperature: $R_\Delta = 2\Delta(0)/k_B T_C$, where $\Delta(0) = \Delta(T_0)$ was determined thereafter. The following estimation was obtained: $R_\Delta \in \langle 4.38, 4.20\rangle$ which evidently confirms the fact that the thermodynamic parameters of the superconducting state in YH_3 cannot be correctly calculated in the framework of the classical BCS theory, where $[R_\Delta]_{\mathrm{BCS}} = 3.53$ [24,25]. The reason that causes the BCS theory to work incorrectly for YH_3 compound is the existence of the significant strong-coupling and retardation effects. In the framework of the Eliashberg formalism they can be estimated taking into account the ratio [48]: $r = k_B T_C/\omega_{\ln}$, where the symbol $\omega_{\ln}$ denotes the logarithmic phonon frequency: $\omega_{\ln} = \exp\left[\frac{2}{\lambda}\int_0^{\Omega_{\max}} d\omega \frac{\alpha^2 F(\omega)}{\omega}\ln(\omega)\right]$. The quantity $\omega_{\ln}$ is introduced to the formalism in order to better estimate the characteristic phonon frequency than it takes place with a use of the Debye frequency. In the case of the calculations on the level of the strong coupling theory it was obtained: $r \in \langle 0.138, 0.082\rangle$. Let us notice that in the limit of BCS we obtain: $r \to 0$.

Fig. 4 presents the influence of the temperature on the maximum value the wave function renormalization factor. The relatively weak dependence of the presented function on T draws a special attention. Equally negligible impact on the values of $Z_{m=1}$ posses the depairing electron correlations modeled by the Coulomb pseudopotential. The wave function renormalization factor from the physical side determines the ratio of the electron effective mass ($m_e^\star$) to the electron band mass (m_e). It can be determined in a precise way using the formula [48]: $m_e^\star/m_e = \mathrm{Re}\,Z(\omega = 0)$. However, the approximate values of $m_e^\star/m_e$ are determined by the relation: $m_e^\star/m_e \simeq Z_{m=1}$, which for $T = T_C$ takes the

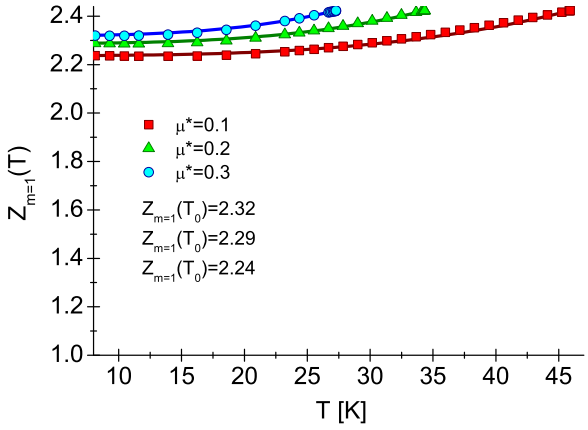

Fig. 4. The maximum value of the wave function renormalization factor on the imaginary axis as a function of the temperature. The symbols were obtained in the framework of the full Eliashberg formalism. The lines can be reproduced with the help of the formula: $Z_{m=1}(T) = Z_{m=1}(0) + [1 + \lambda - Z_{m=1}(0)]\left(\frac{T}{T_C}\right)^{\kappa}$. The electron–phonon coupling constant has a form: $\lambda = 2\int_0^{\Omega_{\max}} d\omega \frac{\alpha^2 F(\omega)}{\omega}$ [48]. Let us note that the value of the wave function renormalization factor for T_C does not depend on $\mu^\star$ and is equal to $1 + \lambda$.

form: $m_e^\star/m_e \simeq 1 + \lambda$. The conducted calculations prove that the electron effective mass is high and takes its maximum value at the critical temperature, whereas $m_e^\star \in \langle 2.83, 2.72\rangle m_e$, for $\mu^\star \in \langle 0.1, 0.3\rangle$.

The thermodynamic critical field (H_C) and the difference between the specific heat of the superconducting state and the specific heat of the normal state ($\Delta C = C^S - C^N$) has been calculated with the help of the formulas below:

$$\frac{H_C}{\sqrt{\rho(0)}} = \sqrt{-8\pi\,[\Delta F/\rho(0)]}\,, \tag{1}$$

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

where $\rho(0)$ denotes the ratio of the value of the electron density of states on the Fermi level ΔF to the free energy difference between the superconducting and normal state:

$$\frac{\Delta F}{\rho(0)} = -\frac{2\pi}{\beta}\sum_{m=1}^{M}\left(\sqrt{\omega_m^2 + \Delta_m^2} - |\omega_m|\right) \times \left(Z_m^S - Z_m^N \frac{|\omega_m|}{\sqrt{\omega_m^2 + \Delta_m^2}}\right). \tag{3}$$

The obtained results are presented in Figs. 5, 6 and 7. It should be noted that increasing depairing electron correlations very strongly underestimate the values of H_C and C^S, which is directly connected

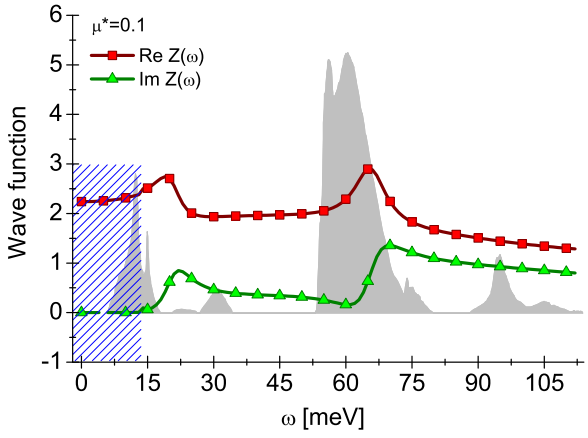

Fig. 5. The wave function renormalization factor on the real axis for $T = T_0$. The Z function in the static area of the superconducting state causes the following renormalization of the electron dispersive relation: $\varepsilon_{\mathbf{k}}/Z(0)$, and also the reduction of the spectral weight of the Green propagator by the factor $1/Z(0)$ [53].

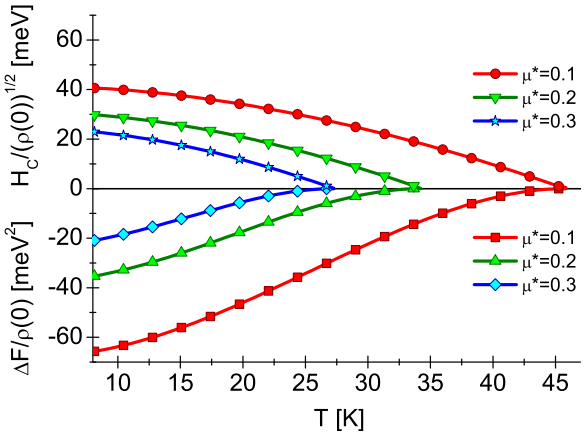

Fig. 6. The free energy difference between the superconducting state and the normal state as a function of the temperature (the lower panel). The negative values of ΔF prove the thermodynamic stability of the superconducting state. The dependence of the thermodynamic critical field on the temperature (the upper panel).

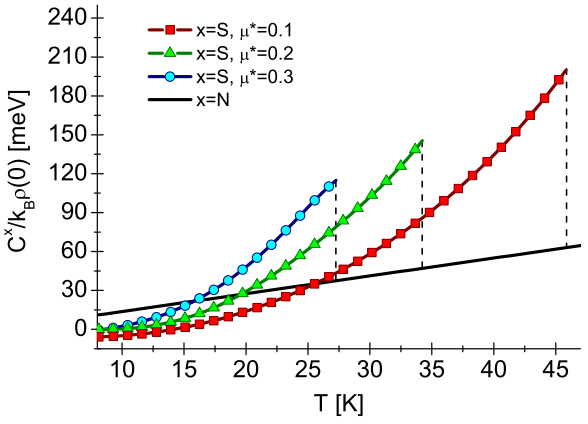

Fig. 7. The specific heat of the superconducting state (S) and the normal state (N) as a function of the temperature. The quantity C^N was estimated on the basis of the formula: $C^N/k_B\rho(0) = \gamma/\beta$, where $\gamma = \frac{2}{3}\pi^2(1 + \lambda)$. It means that the renormalization of the electron specific heat of the normal state by the electron–phonon interaction has been included.

with the destructive influence of $\mu^\star$ on the free energy difference between the superconducting state and the normal state.

Then, the dimensionless ratios: $R_C = \Delta C(T_C)/C^N(T_C)$ and $R_H = T_C C^N(T_C)/H_C^2(0)$, where $H_C(0) = H_C(T_0)$, were estimated on the basis of the determined thermodynamic functions. Due to the significant strong-coupling and retardation effects, R_C and R_H significantly differ from the values predicted by the BCS theory ($R_C = 1.43$ and $R_H = 0.168$) [24,25]. In particular it was obtained: $R_C \in \langle 2.18, 2.02\rangle$ and $R_H \in \langle 0.151, 0.168\rangle$, for $\mu^\star \in \langle 0.1, 0.3\rangle$.

The presented work has determined the thermodynamic properties of the superconducting state that may induce in YH_3 compound for the record low eternal pressure (17.7 GPa). It has been found that the maximum value of the critical temperature is relatively high, even in the case when the depairing electron correlations are large: $T_C \in \langle 45.91, 27.29\rangle$ K for $\mu^\star \in \langle 0.1, 0.3\rangle$. The superconducting state in YH_3 is characterized by the significant strong-coupling and retardation effects that causes its thermodynamic parameters impossible to be correctly calculated in the framework of the classical BCS theory. In particular, the following estimations were obtained for the order parameter, the specific heat and the thermodynamic critical field: $R_\Delta \in \langle 4.38, 4.20\rangle$, $R_C \in \langle 2.18, 2.02\rangle$ and $R_H \in \langle 0.151, 0.168\rangle$, when $\mu^\star \in \langle 0.1, 0.3\rangle$.

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