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Thermodynamics of the hydrogen dominant potassium hydride superconductor at high pressure

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ABSTRACT

In the present paper we report comprehensive analysis of the thermodynamic properties of novel hydrogen dominant potassium hydride superconductor (KH_6). Our computations are conducted within the Eliashberg theory which yields quantitative estimations of the most important thermodynamic properties of superconducting phase. In particular, we observe that together with the increasing pressure all the thermodynamic properties decrease, *e.g.* $T_C \in \langle 72.91, 55.50 \rangle$ K for $p \in \langle 166, 300 \rangle$ GPa. It is predicted that such decreasing behavior corresponds to the decreasing hydrogen lattice molecularization with increasing pressure value. Furthermore, by calculating the dimensionless thermodynamic ratios, familiar in the Bardeen–Cooper–Schrieffer (BCS) theory, it is proved that KH_6 material is a strong-coupling superconductor and cannot be quantitatively described within the BCS theory.

1. Introduction

In the terms of research on the phonon-mediated superconductivity, the hydrogen-based materials [1] experience at present the apogee of the scientific attention [2]. The advent of this high interest is marked by the theoretical work of Ashcroft [3] who predicted that metallic hydrogen, under the influence of high-pressure, can be a superconductor characterized by the high transition temperature (T_C). Such a desirable character of the superconducting phase in hydrogen stems from its light atomic nuclei and the absence of the inner electron shells, resulting in the high value of the electron–phonon coupling constant (λ). However, the pressure value required to induce the superconducting phase in pure hydrogen is beyond any commercial applications.

In this context, the introduction of the heavier atoms into the crystal lattice allows us to lower the metallization pressure, preserving at the same time the extraordinary superconducting properties of hydrogen. In this context, it is possible to supplement the high-temperature superconductors [4], by the ones described within the well-established electron–phonon scenario [5,6]. The true testimonial of the importance of the hydrogen-based superconductors is recent experimental results for the hydrogen sulfide superconductor (H_2S), which report the extremely high transition temperature equal to ~ 190 K, obtained at the relatively moderate pressure value (p) [7,8]. If reproducible, these results may constitute a significant breakthrough in the research on the room-temperature superconductivity.

One of the newest attempts in the research on the superconducting properties of the hydrogen-based compounds considers also application of the alkali metal dopants. The most recent theoretical approach concentrates on using potassium, leading to the thermodynamically stable hydrogen-rich layered material where each six hydrogens hold one potassium atom (the KH_6 compound within the $C2/c$ phase) [9]. In particular, it is theoretically predicted that superconducting phase, in this compound, is stable from ~ 166 GPa up to around 300 GPa. Note that the upper pressure value constitutes the accuracy limit for the projector-augmented plane-wave potentials [10] used within the VASP code [11] for geometry optimization and electronic calculations in [9]. Below the metallization pressure, but above 70 GPa, the KH_6 crystallizes in the metallic $C2/m$ phase. In what follows, the synthesis pressure for KH_6 is expected to be much lower than in the case of the other recently predicted alkali metal hydrides, namely the LiH-family [12]. This fact arises from the faster transfer of electrons to the hydrogen in the KH_6 when compared to the LiH-hydrides, and it is an undisputed advantage of this compound.

In this spirit, present paper reports the analysis of the thermodynamic properties of the KH_6 superconductor, which should be of crucial importance and interest for further design of possible hydride superconductors. The calculations are conducted here for

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three selected pressure values (166 GPa, 230 GPa, and 300 GPa) which sample the entire known superconducting phase of the KH_6 compound. Due to the relatively high values of the electron-phonon coupling constant for all considered pressure values, computations are conducted within the strong-coupling generalization of the Bardeen–Cooper–Schrieffer (BCS) theory, namely in the framework of the Eliashberg equations [13]. This theoretical model allows us to provide the quantitative estimations of all of the most important thermodynamic properties of the superconducting phase such as critical temperature, band gap at the Fermi level, specific heat, thermodynamic critical field, and the electron effective mass. We note that our analysis is based on the isotropic Elishaberg equations, following the character of the Eliashberg function ($\alpha^2F(\omega)$) presented in [9], and adopted for calculations in the present work.

2. Theoretical model and computational details

In order to estimate all desirable thermodynamic properties of the discussed KH_6 superconductor we solve the Eliashberg equations on the imaginary axis and in the mixed representation by using the iterative method presented in [14].

As already mentioned, our calculations based on the Eliashberg spectral functions calculated in [9], by using the QUANTUM ESPRESSO code [15] with the norm-conserving pseudopotentials within the generalized gradient approximation. Such spectral functions yield the electron–phonon coupling constants equal to $\lambda_{p=166\ \mathrm{GPa}} = 0.92$, $\lambda_{p=230\ \mathrm{GPa}} = 0.89$, and $\lambda_{p=300\ \mathrm{GPa}} = 0.79$. Furthermore, we assume that the cutoff frequency is set as $\omega_c = 10\Omega_{\max}$, where $\Omega_{\max}$ stands for the maximum phonon frequency equal to 407.76 meV at 166 GPa and 411.92meV at 230 GPa and 300 GPa.

In our calculations, the electron depairing correlations are described in the terms of the Coulomb pseudopotential (μ^*) equal to 0.1 for all considered cases. The value of $\mu^* = 0.1$ is assumed following the suggestion of Ashcroft given in [1] for the hydrogen dominant metallic alloys. Such scale estimation, given by Ashcroft, is provided using elementary arguments (see [1]) and includes retardation effects necessary in the analysis of the strong-coupling superconductors such as the KH_6 compound. Furthermore, by using the uniform value of μ^* for all considered pressure values, we are able to present transparent comparison between obtained results. These two arguments reinforce our choice of the value of μ^* for the present calculations, and allows us to capture all the most important physical aspects of the superconducting phase in KH_6, even without considering other values of μ^*.

To assure the required precision, our computations are conducted for the 2201 Matsubara frequencies: $\omega_m \equiv \frac{\pi}{\beta}(2m-1)$, with $\beta \equiv 1/k_BT$, and k_B denoting the Boltzmann constant. In what follows, all thermodynamic properties of interest are described quantitatively for $T \geq T_0 \equiv 5$ K.

3. Numerical results

In Fig. 1 we present obtained imaginary-axis results of the (A) maximum value of the order parameter ($\Delta_{m=1}$), (B) the wave function renormalization factor ($Z_{m=1}$), and (C) the normalized electron effective mass (m_e^*/m_e, where $m_e^* \simeq Z_{m=1}m_e$ is the electron effective mass, and m_e denotes the bare electron mass).

In particular, for all considered pressure cases we observe decrease in the values of the $\Delta_{m=1}$, $Z_{m=1}$, and m_e^*/m_e functions with the increasing pressure. In what follows, such a decrease is also observed in the terms of the superconducting transition temperature calculated by using the relation: $\Delta_{m=1}(T_C) = 0$, which gives the T_C values equal to 72.91 K, 70.73 K, and 55.50 K at 166 GPa, 230 GPa, and 300 GPa, respectively. We also note that this decreasing behavior of T_C is slightly more evident in the case of our results than in the predictions presented in [9], which is based on the McMillan formula [16]. Furthermore, results presented in [9] show that for higher electron–phonon coupling constants McMillan formula underestimates the T_C values in KH_6, whereas in the case when λ is close to the weak-coupling limit ($\lambda < 0.3$ [17]) the overestimation can be noticed. This is due to the fact that BCS theory omits the strong-coupling effects, which are present in the Eliashberg theory.

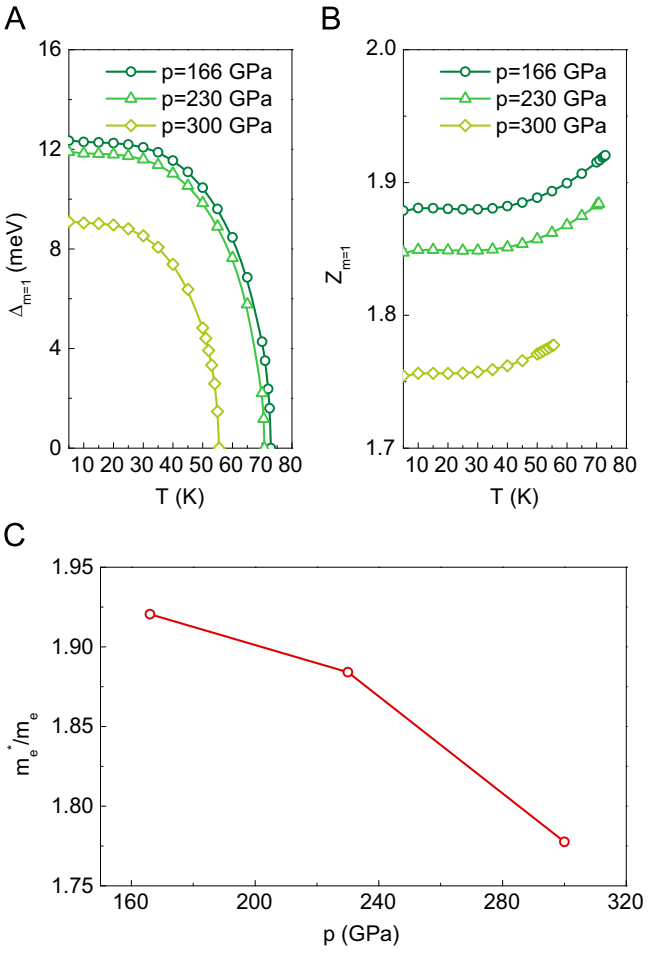

Fig. 1. (color online) The maximum values of the order parameter (A), wave function renormalization factor (B) and the normalized electron effective mass (C). First two parameters are presented as a function of temperature for selected values of pressure. The latter observable is plotted against the pressure value.

The corresponding results for the value of energy gap at the Fermi level are presented in Fig. 2 as a function of pressure. We note that, in the first approximation, such calculations can be done on the basis of the imaginary-axis results presented in Fig. 1, as $2\Delta_{m=1}(0)$, where $\Delta_{m=1}(0) \simeq \Delta_{m=1}(T_0)$. However, in order to obtain the physical value of the energy gap ($2\Delta(0)$, where $\Delta(0) \simeq \Delta(T_0)$) it is required to analytically continue the imaginary-axis results on the real axis (ω). In this context the physical value of the energy gap can be determined by using $\Delta(T) = \mathrm{Re}[\Delta(\omega = \Delta(T), T)]$.

Furthermore, in the inset of Fig. 2 we depict determined values of the characteristic dimensionless ratio of zero-temperature energy gap at the fermi level to the critical temperature ($R_\Delta \equiv 2\Delta(0)/k_BT_C$). We note that for all considered pressure values the R_Δ ratios notably exceed limit set by the BCS theory ($R_\Delta^{\mathrm{BCS}} = 3.53$), [5,6]. In particular, R_Δ equals 3.98, 3.94, and 3.80 for 166 GPa, 230 GPa, and 300 GPa, respectively.

In the next step, our calculations concentrate on the determination of the normalized free energy difference between the