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Study of the High-Pressure Superconducting State in H_3Se at 300 GPa

E.A. Drzazga*

Institute of Physics, Częstochowa University of Technology, al. Armii Krajowej 19, 42-200 Częstochowa, Poland

In the present paper, the selected thermodynamic properties of the superconducting state in H_3Se compound are theoretically characterized. In the considered system, the superconducting state is induced under the pressure of 300 GPa. The numerical calculations are conducted in the framework of the Eliashberg formalism, due to the relatively high value of the electron–phonon coupling constant, $\lambda = 1.05$. In a result, the numerical values of the superconducting order parameter and the wave function renormalization factor, as a function of temperature, are obtained. It is found that the critical temperature value is $\sim$ 120 K; for the Coulomb pseudopotential equal to 0.1. Moreover, the difference between free energy for the normal and superconducting state, the critical magnetic field, as well as the specific heat for the superconducting and normal state on the temperature are determined. In a conclusion, it is suggested that the strong-coupling and retardation effects play pivotal role in the analyzed superconducting phase, similarly to what can be found in the breakthrough hydrogen sulfide material.

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PACS/topics: superconductivity, thermodynamic properties, high-pressure effects, hydrogen-based compounds

1. Introduction

In 2014, Drozdov et al. reported that the ultra-dense phase of sulfur hydride (H_3S) may exhibit superconducting properties at $\sim$ 150 GPa, with transition temperature (T_c) equal to 203 K [1]. This observation started the wave of new discoveries. In a few next years, researchers have found a large number of potential hydrogen rich compounds, which could be superconducting with a high value of T_c, e.g. PH_3 with $T_c = 103$ K at 207 GPa [2], SnH_4 with $T_c = 91$ K at 220 GPa [3] and ScH_6 with $T_c = 147$ K at 285 GPa [4]. These discoveries confirm Ashcroft's prediction that hydrogen-based compounds may exhibit high-temperature superconducting state [5] at relatively low pressure values, when comparing to the pristine hydrogen case [6].

Currently, one of the most promising hypothetical hydrogen-based superconductors are compounds of hydrogen and selenium, which under high pressure conditions show rather good thermodynamical properties. In this regard, special attention should be given to H_3Se, which is the most thermodynamically stable structure among all known superconducting hydrogen selenides [7]. Moreover, the empirical McMillan formula [8] suggest that in H_3Se at 300 GPa, the value of T_c can exceed the level of 100 K [7], which is almost three times higher than in the prominent MgB_2 compound [9]. Next, the electron–phonon coupling value, found within the density functional theory (DFT) calculations [7], is of the order of unity ($\lambda = 1.05$) and positions H_3Se in the strong-coupling regime, similarly to the groundbreaking hydrogen sulfide. Interestingly, the latter one is not the sole similarity shared by hydrogen-based superconductors with selenium and sulphur, respectively. In particular, both selenium [10, 11] and sulfur [12, 13] are predicted to be superconducting as a standalone chemical elements. Furthermore, selenium is a similar and isoelectronic to sulfur; both are chalcogenides in the same group of periodic table. In what follows, the experimental realization of H_3Se and its derivatives may be realistically possible in the close future, toward extending the existing groups of already verified hydrogen-based superconductors i.e. H_3S [1, 14, 15], PH_3 [2, 14], and PtH [16–19].

In this context, the in-depth analysis of the thermodynamic properties of H_3Se is crucial for the further developments in this field. First, to verify the existing qualitative theoretical studies of this compound, and second to provide guidelines for future corresponding experimental studies. Herein, such theoretical investigations are provided within the state-of-art Eliashberg formalism for the strong-coupling superconductors [20, 21]. Specifically, all the most important thermodynamical properties of the discussed state are comprehensively analyzed, to give their quantitative temperature-dependent estimates. The analysis is supplemented by pertinent conclusions.

2. Theory

As mentioned above, the thermodynamic properties of H_3Se are determined here in the framework of the Eliashberg equations. In the isotropic case, they constitute a set of two equations, namely: the equation for the order parameter function ($\Delta_n = \Delta(i\omega_n)$) and equation for the wave function renormalization factor ($Z_n = Z(i\omega_n)$), where $\omega_n = (\pi/\beta)(2n-1)$ denotes the Matsubara frequency and $\beta = 1/k_BT$ with k_B being the Boltzmann constant. Explicitely, described set of equations take the following form:

*corresponding author; e-mail: edrzazga@wip.pcz.pl

$$\Delta_n Z_n = \frac{\pi}{\beta} \sum_{m=-M}^{M} \frac{K(\omega_n - \omega_m) - \mu^\star(\omega_m)}{\sqrt{\omega_m^2 + \Delta_m^2}}, \quad (1)$$

$$Z_n = 1 + \frac{\pi}{\beta} \sum_{m=-M}^{M} \frac{K(\omega_n - \omega_m)}{\sqrt{\omega_m^2 + \Delta_m^2}} \frac{\omega_m}{\omega_n} Z_m. \quad (2)$$

The $K(\omega_n - \omega_m)$ function in Eqs. (1) and (2) denotes the electron–phonon pairing kernel and is defined by:

$$K(\omega_n - \omega_m) \equiv 2 \int_0^{+\infty} \mathrm{d}\Omega \frac{\alpha^2 F(\Omega)\Omega}{(\omega_n - \omega_m)^2 + \Omega^2}, \quad (3)$$

where the electron–phonon spectral function ($\alpha^2 F(\Omega)$) was adopted from [7]; wherein it has been calculated in the framework of the DFT, as implemented in the Quantum Espresso package [22].

For the considered superconductor the electron–electron depairing interactions are modeled by the Coulomb pseudopotential ($\mu^\star \equiv \mu^\star \theta(\omega_c - |\omega_m|)$) parameter; the θ denotes Heaviside's function, the value of cut-off for the phonon frequency is $\omega_c = 10\Omega_{\max}$ and $\omega_{\max}$ stands for its maximum value which is equal to 322.12 meV. In the case of H_3Se the $\mu^\star$ parameter is assumed to be 0.1, in accordance with the Ashcroft predictions for hydride superconductors [5].

3. Results

In the present paper, the Eliashberg equations are solved using the in-house developed numerical methods described in [20, 23–25]. It is instructive to note that the numerical analysis is conducted here for the 2201 Matsubara frequencies, in order to reach the numerical stability of computations. Accordingly, the physically-relevant results are obtained for $T \geq T_0$, where $T_0 = 7$ K.

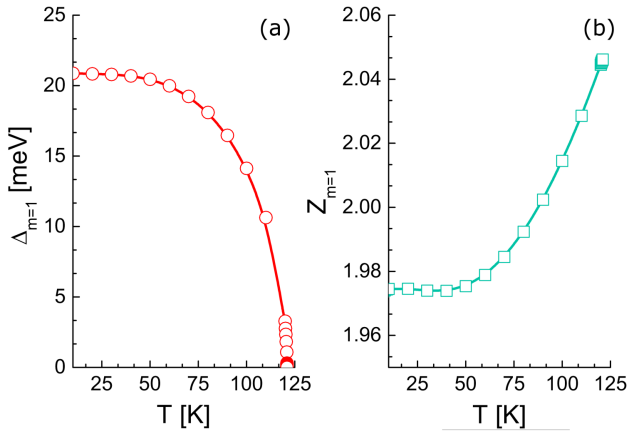

Fig. 1. (a) The maximum value of the order parameter as a function of the temperature and (b) the corresponding maximum value of the temperature-dependent wave function renormalization factor.

In what follows, the first step of analysis concerns the solutions of Eqs. (1) and (2) on the imaginary axis. In a result of the numerical computations, the temperature-dependent maximum values of the order parameter function ($\Delta_{m=1}$) and the wave function renormalization factor ($Z_{m=1}$) are obtained, as depicted in Fig. 1a and b, respectively. It can be easily observed that the calculated points resemble typical behavior of the $\Delta_{m=1}$ and $Z_{m=1}$ functions for the phonon-mediated superconductors [23]. Moreover, results depicted in Fig. 1a allow to determine the critical temperature value (T_c) for the considered compound; specifically at the critical temperature, the order parameter takes on the zero value, which marks the superconductor-metal phase transition. In the discussed case, the T_c value is estimated to 121 K. Note that the determined temperature is about 10 K higher than corresponding prediction of the empirical McMillan formula [8], presented in [7]. Furthermore, $\Delta_{m=1}$ function can be approximately interpreted as the half-value of the energy gap at the Fermi level ($\Delta(0)$), whose maximum for the H_3Se material is 20.9 meV at T_0. On the other hand, the wave function renormalization factor, depicted in Fig. 1b, is related to the effective mass of electrons by the following formula: $m_e^\star \simeq Z_{m=1}(T) m_e$, where symbol m_e represents the electron band mass. In this context, for $T = T_c$ it is obtained that $m_e^\star / m_e \simeq 1 + \lambda \simeq 2.05$. Notably, this value is in agreement with other estimate, namely: $Z_{m=1}(T_c) \sim 2.05$; which to some extent confirms the high precision of numerical calculations presented here.

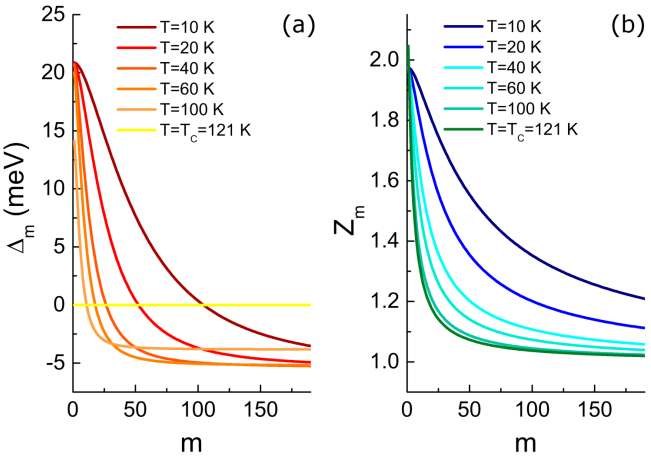

Fig. 2. (a) The order parameter and (b) the wave function renormalization factor for the selected values of the temperature, as a functions of m.

Figure 2 presents the characteristics of (A) the order parameter and (B) the wave function renormalization factor as a function of m for the selected values of temperature. It is observed that both functions become saturated above 150 Matsubara frequencies. Moreover, with the increase of the temperature, the saturation occurs for the lower values of m. This fact ensures that assumed number of the Matsubara frequencies is sufficient to obtain convergence for the analyzed thermodynamic properties. Note additionally that the determined results can be transparently compared with the predictions of the BCS theory, by calculating the characteristic ratios for the thermodynamic properties. First of such ratios is conventionally defined as:

$$R_\Delta \equiv \frac{2\Delta(0)}{k_B T_c}, \tag{4}$$

and equals to 4.01 for the analyzed superconductor. It should be noted that the BCS theory predicts much lower value i.e. $R_\Delta = 3.53$. The two remaining parameters for the thermodynamic critical field and the specific heat are calculated below.

On the basis of the above solutions, the normalized free energy difference between the superconducting and normal state can be calculated from the following formula [26, 27]:

$$\frac{\Delta F}{\rho(0)} = -\frac{2\pi}{\beta}\sum_{n=1}^{M}\left(\sqrt{\omega_n^2+\Delta_n^2}-|\omega_n|\right) \times (Z_n^S - Z_n^N \frac{|\omega_n|}{\sqrt{\omega_n^2+\Delta_n^2}}). \tag{5}$$

In the above equation symbol $\rho(0)$ is the value of the electron density of states at the Fermi level, whereas Z_n^S and Z_n^N stand for the wave function renormalization factor of the superconducting state and the normal state, respectively. The numerical results for the $\Delta F/\rho(0)$ function are presented in the lower part of Fig. 3a. It can be easily observed that the $\Delta F/\rho(0)$ takes negative values for the entire range of temperature, which indicates the thermodynamical stability of the superconducting phase in H_3Se at 300 GPa. Moreover, the function described by Eq. (5), allows next to determine the temperature-dependent normalized thermodynamic critical field as

$$\frac{H_c}{\sqrt{\rho(0)}} = \sqrt{-8\pi\left[\Delta F/\rho(0)\right]}. \tag{6}$$

In correspondence, the upper part of Fig. 3a shows the $H_c/\sqrt{\rho(0)}$ ratio as a function of temperature. Contrary to the $\Delta F/\rho(0)$, the normalized thermodynamic critical field takes the positive values for the entire temperature range. However, as a main outcome, discussed parameter

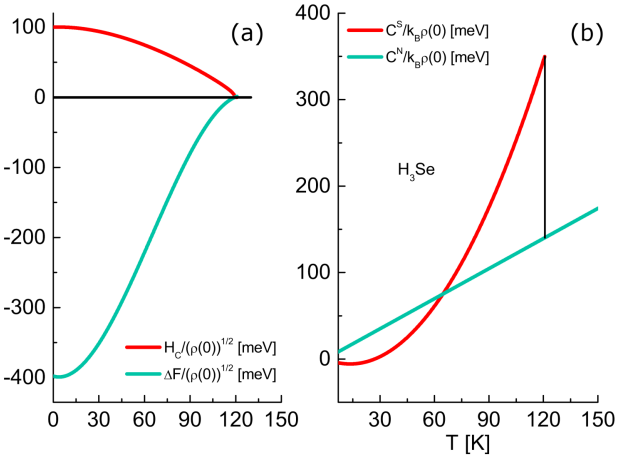

Fig. 3. (a) The thermodynamic critical field as a function of the temperature (upper part) and the dependence of the free energy value on the temperature (lower part), (b) the temperature-dependent specific heat of the superconducting state and the normal state.

allows to determine the second dimensionless ratio, toward its comparison with the canonical BCS predictions. In particular, the corresponding ratio reads

$$R_H \equiv \frac{T_c C^N(T_c)}{H_c^2(0)}. \tag{7}$$

In the case of H_3Se, it is received that $R_H = 0.148$, which is notably lower than the estimate of the BCS theory which suggests that $R_H = 0.168$.

Similarly, the calculation of the normalized specific heat difference (ΔC) between the superconducting (C^S) and normal state (C^N) leads to the last remaining characteristic ratio within the BCS theory. Specifically, the normalized $\Delta C(T)/k_B\rho(0)$ is given as

$$\frac{\Delta C(T)}{k_B\rho(0)} = -\frac{1}{\beta}\frac{\mathrm{d}^2\left[\Delta F/\rho(0)\right]}{\mathrm{d}\left(k_B T\right)^2}, \tag{8}$$

where the specific heat in the normal state reads: $C^N(T)/k_B\rho(0) = \gamma/\beta$ assuming that the Sommerfeld constant is written as $\gamma = \frac{2}{3}\pi^2(1+\lambda)$. The temperature dependence of the $\Delta C(T)/k_B\rho(0)$ function is depicted in Fig. 3b, and exhibits the characteristic *jump* at critical temperature, which is marked by vertical black line. To this end, the aforementioned characteristic ratio for the specific heat is defined as:

$$R_C \equiv \frac{\Delta C(T_c)}{C^N(T_c)}. \tag{9}$$

Herein, the numerical calculations give $R_C = 1.68$, whereas BCS theory predicts that $R_C = 1.43$. Therefore, another dimensionless ratio visibly differ from the BCS theory estimates.

4. Summary

In the present paper the thermodynamic properties of the H_3Se compound under high pressure (300 GPa) were analyzed within the Eliashberg formalism. In this context, one of the most crucial observations correspond to the critical temperature value, which appeared to be around 10 K higher than the estimation given in the

TABLE I

The adopted and obtained values of the most important parameters which characterize superconducting state in H_3Se at 300 GPa.

	Quantity	Value	Unit
adopted	p	300	GPa
	m	2201	–
	$\mu^\star$	0.1	–
	λ	1.05	–
obtained	$\Omega_{\max}$	322.12	meV
	T_0	7	K
	T_c	121	K
	$\Delta_{m=1}(T_0)$	21	meV
	$Z_{m=1}(T_c)$	2.05	K
	R_Δ	4.01	–
	R_C	1.68	–
	R_H	0.148	–

framework of the empirical McMillan formula. Similarly the characteristic ratios for the order parameter, the thermodynamic critical field and the specific heat showed discrepancies with the estimates of the BCS theory.

Above observations suggest that the strong-coupling and retardation effects play pivotal role in the H_3Se at 300 GPa. In other words, analyzed material is a strong-coupling superconductor, which cannot be described within the mean-field BCS theory toward quantitative determination of the most important superconducting properties.

To this end, values of all component thermodynamic parameters, which enters formulae for the above ratios, were determined and their estimates are given explicitly in Table I.

References

[1] A.P. Drozdov, M.I. Eremets, I.A. Troyan, V. Ksenofontov, S.I. Shylin, *Nature* **525**, 73 (2015).

[2] A.P. Drozdov, M.I. Eremets, I.A. Troyan, arXiv:1508.06224 (2015).

[3] M.M.D. Esfahani, Z. Wan, A. Oganov, H. Dong, Q. Zhu, S. Wang, M. Rakitin, X. Zhou, *Sci. Rep.* **6**, 22873 (2016).

[4] K. Abe, *Phys. Rev. B* **96**, 144108 (2017).

[5] N.W. Ashcroft, *Phys. Rev. Lett.* **92**, 187002 (2004).

[6] N.W. Ashcroft, *Phys. Rev. Lett.* **21**, 1748 (1968).

[7] S. Zhang, Y. Wang, J. Zhang, H. Liu, X. Zhong, H.-F. Song, G. Yang, L. Zhang, Y. Ma, *Sci. Rep.* **5**, 15433 (2015).

[8] W.L. McMillan, *Phys. Rev.* **167**, 331 (1968).

[9] A.A. Golubov, J. Kortus, O.V. Doglov, O. Jepsen, Y. Kong, O.K. Andersen, B.J. Gibson, K. Ahn, R.K. Kremer, *J. Phys. Condens. Matter* **14**, 1353 (2002).

[10] D. Zhou, C. Pu, D. Szczęśniak, G. Zhang, C. Lu, G. Li, J. Song, *Chin. Phys. Lett.* **30**, 027401 (2013).

[11] D. Szczęśniak, I.A. Wrona, E.A. Drzazga, A.Z. Kaczmarek, K.A. Szewczyk, *J. Phys. Condens. Matter* **29**, 445602 (2017).

[12] S. Rudin, A. Liu, J. Freericks, A. Quandt, *Phys. Rev. B* **63**, 224107 (2001).

[13] A.P. Durajski, R. Szczęśniak, M.W. Jarosik, *Phase Transit.* **85**, 727 (2012).

[14] A.P. Durajski, *Sci. Rep.* **6**, 38570 (2016).

[15] R. Szczęśniak, A.P. Durajski, *Sci. Rep.* **8**, 6037 (2018).

[16] M.I. Eremets, I.A. Trojan, S.A. Medvedev, J.S. Tse, Y. Yao, *Science* **319**, 1506 (2008).

[17] O. Degtyareva, J. Proctor, C. Guillaume, E. Gregoryanz, M. Hanfland, *Solid State Commun.* **149**, 1583 (2009).

[18] D. Szczęśniak, T.P. Zem la, *Supercond. Sci. Technol.* **28**, 085018 (2015).

[19] R. Szczęśniak, D. Szczęśniak, K. Huras, *Phys. Status Solidi B* **251**, 178 (2014).

[20] G.M. Eliashberg, *Sov. Phys. JETP* **11**, 696 (1960).

[21] R. Szczęśniak, E.A. Drzazga, A.M. Duda, *Solid State Commun.* **166**, 50 (2013).

[22] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. De Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, Ch. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, *J. Phys. Condens. Matter* **21**, 395502 (2009).

[23] J.P. Carbotte, F. Marsiglio, in: *The Physics of Superconductors*, Eds. K.H. Bennemann, J.B. Ketterson, Springer, Berlin 2003.

[24] R. Szczęśniak, *Acta Phys. Pol. A* **109**, 179 (2006).

[25] R. Szczęśniak, D. Szczęśniak, T. Zem la, *Physica B Condens. Matter* **495**, 106 (2016).

[26] J. Bardeen, M. Stephen, *Phys. Rev.* **136**, A1485 (1964).

[27] R. Szczęśniak, D. Szczęśniak, *Chin. Phys. Lett.* **31**, 117401 (2014).