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# Superconducting state in bromium halide at high pressure

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ABSTRACT

The thermodynamic properties of the superconducting state in bromium halide (HBr) compound have been analyzed in the framework of the Eliashberg formalism. In particular, for the range of the pressure ($p$) from 140 GPa to 200 GPa, it has been shown that the critical temperature increases significantly: $T_C(p) \in \langle 28.8, 55.1\rangle$K, whereas the Coulomb pseudopotential ($\mu^\star$) is equal to 0.1. Together with the increase of $p$, the values of the thermodynamic parameters such as: the ratio of the energy gap at the temperature of zero Kelvin to the critical temperature ($R_\Delta \equiv 2\Delta(0)/k_B T_C$), the ratio of the specific heat jump at the critical temperature to the electronic specific heat of the normal state ($R_C \equiv \Delta C(T_C)/C^N(T_C)$), and the ratio related to the thermodynamic critical field ($R_H \equiv T_C C^N(T_C)/H_C^2(0)$) increasingly deviate from the predictions of the BCS model: $R_\Delta(p) \in \langle 3.79, 4.05\rangle$, $R_C(p) \in \langle 1.94, 2.27\rangle$, and $R_H(p) \in \langle 0.157, 0.147\rangle$. It should be noted that the increase of $\mu^\star$ visibly lowers $T_C$ and significantly reduces the difference between the results of the Eliashberg and BCS theory.



## 1. Introduction

The thermodynamic properties of the superconducting state induced by the electron–phonon interaction can be modeled by the Fröhlich Hamiltonian [1,2]:

$$H = H_e + H_{ph} + H_{e-ph}, \tag{1}$$

where $H_e$ denotes the operator of the band electrons of the energy $\epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m_e^\star}$. The symbol $\mathbf{p}$ represents the momentum of the electron and $m_e^\star$ is the electron band mass. The term $H_{ph}$ describes the free phonons and $H_{e-ph}$ models the linear electron–phonon interaction. In the simplest case, after the application of the canonical transformation, in order to eliminate the phonon degrees of freedom, the Fröhlich operator transforms into the BCS Hamiltonian with the explicitly specified pairing potential [3–5]. However, the most interesting results can be obtained by analyzing the Fröhlich operator in the framework of the formalism of the matrix Matsubara–Green functions (Eliashberg approach) [6]. The result is the set of the nonlinear equations used to determine the values of the order parameter function, the wave function renormalization factor, the energy shift function, and the chemical potential. It should be emphasized that with the help of the Eliashberg equations, the quantitative agreement between the theoretical predictions and the experimental data has been usually obtained. In essence, this fact is related to the accurate description of the structure of the electron–phonon interaction by the spectral function ($\alpha^2(\Omega)F(\Omega)$), which is the input parameter to the Eliashberg equations.

It is currently believed that the highest value of the critical temperature ($T_C$) is taken by the superconducting state in the metallic hydrogen under the influence of the extremely high pressure ($p$) [7–11]. In particular, the *ab initio* calculations suggest that the metallization of the molecular hydrogen occurs for the pressure at ~400 GPa ($p_m$) [12]. In the pressures range from ~400 GPa to ~500 GPa, the maximum of the critical temperature ($T_C$ = 242 K) is placed in the vicinity of 450 GPa [13–15]. It should be noted that for the lower pressures ($p$=414 GPa), the critical temperature is also high ($T_C$ = 84 K), whereby the superconducting phase is induced by the highly anisotropic electron–phonon interaction. As a result one can expect the significant deviation of the thermodynamic properties of the superconducting condensate from the expectations of the classical BCS model [16].

The fact that the high-temperature superconducting state in hydrogen can be obtained only for the extremely high values of the pressure surely draws the attention. These values are difficult to achieve, even in the highly specialized physical laboratories. For this reason, in 2004 it was suggested that the crystal lattice of the foreign elements could be used for the reduction of the metallization pressure of hydrogen (so-called chemical pre-compression) [17]. To this day the two related experimental reports has been published; first suggesting the existence of the superconducting state with the critical temperature equal to 17.5 K ($p$=96 GPa) in

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$SiH_4$ compound [18], and the second one which predicts value of $T_C$ as high as 203 K in $H_2S$ at $p=155$ GPa [19,20]. However, in the case of the former experimental studies, some researchers argue that actually observed superconducting phase has been formed in platinum electrodes highly saturated with hydrogen (PtH) [21]. On the other hand, results presented for the $H_2S$ compound may constitute huge breakthrough in research on the high-temperature phonon-mediated superconductivity. We note, that the theoretical models clearly predict even higher critical temperature values for the superconducting state in hydrogen-containing compounds, at the pressure values similar to the one reported for $H_2S$. Of particular interest are the results for $CaH_6$ compound ($p=150$ GPa), where the proposed value of the critical temperature may reach 235 K [22,23].

In the case of the hydrogen-containing compounds (not only the hydrogenated compounds but also hydrides), the complex series of the structural transformations induced by the high pressure should be expected to exist [24,25]. Phase transitions of this type are of fundamental importance for the superconducting state, as its thermodynamic properties substantially depend on the crystal structure in which it occurs. The present paper discusses the properties of the superconducting state in bromium halide (HBr) compound under the influence of the high pressure. In the case of HBr, the information on the sequence of the low-temperature phase transitions is available only via theoretical calculations, and the most recent data can be found in [26,27]. In particular, for $p \in \langle 0, 25\rangle$ GPa, the calculations presented in [26] predicts the formation of the $Cmc2_1$ structure. For the higher pressure values, the *Cmcm* structure appears to be stable for $p \in \langle 25, 134\rangle$ GPa and $p \in \langle 20, 125\rangle$ GPa as proposed in [26] and [27], respectively. However, in the case of the results given in [27], the *Cmcm* structure for $p \in \langle 100, 125\rangle$ GPa is competitive against two others types of symmetries, namely the *I*-42*d* and *P*-1 structures. Above the pressure values which mark the existence of the *Cmcm* symmetry, both discussed reports found the monoclinic-prismatic class of systems, specifically the $P2_1$ and $C2/m$ symmetries for [26] and [27], respectively. Both systems are considered to be superconducting, however results presented in [26] show the $Br_2+H_2$ decomposition scheme above 200 GPa, whereas symmetries given in [27] are predicted to be stable at least up to 300 GPa. Nevertheless, the critical temperature values proposed in [27] has been calculated for only two values in the region of $p$ from 140 to 200 GPa, which marks possibly the highest $T_C$values for HBr due to the works in both [26] and [27]. Note that above 200 GPa for $C2/m$ the critical temperature values are suggested to be relatively low [27]. In what follows, we have concentrated on the pressure region from 140 to 200 GPa, which is fairly well sampled within the $P2_1$ symmetry structure, as described in [26]. In particular, it has been found that critical temperature, in this region, increases together with the increase of $p$ from about 27.7 K to 51.4 K, which has been associated with the decreasing distance between the adjacent hydrogen atoms [26,28,29]. In the presented paper, the calculations of the thermodynamic parameters in HBr have been conducted in the framework of the Eliashberg formalism.

## 2. Formalism and computational details

The half-width of the electron band in HBr is so large (~10 eV) that for the calculations one can use the Eliashberg equations determining only the order parameter function ($\phi_n \equiv \phi(i\omega_n)$) and the wave function renormalization factor ($Z_n \equiv Z(i\omega_n)$) [26]. Note that in this case, due to the half-filled electron band, the energy shift function and the chemical potential take the value of zero. The symbol $i$ denotes the imaginary unit and $\omega_n$ represents the $n$-th Matsubara frequency: $\omega_n \equiv (\pi/\beta)(2n-1)$, whereas $\beta \equiv (k_B T)^{-1}$, $k_B$ is the Boltzmann constant. The corresponding set of the Eliashberg equations has the following form [6]:

$$\phi_n = \frac{\pi}{\beta}\sum_{m=-M}^{M}\frac{\lambda(i\omega_n - i\omega_m) - \mu^{\star}\theta(\omega_c - |\omega_m|)}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}}\phi_m, \tag{2}$$

$$Z_n = 1 + \frac{1}{\omega_n}\frac{\pi}{\beta}\sum_{m=-M}^{M}\frac{\lambda(i\omega_n - i\omega_m)}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}}\omega_m Z_m, \tag{3}$$

where the values of the pairing kernel can be determined with the help of the formula below:

$$\lambda(z) \equiv 2\int_0^{+\infty} d\Omega\,\frac{\Omega}{\Omega^2 - z^2}\alpha^2(\Omega)F(\Omega). \tag{4}$$

The spectral functions for the considered values of the pressure (140 GPa, 160 GPa, 180 GPa, and 200 GPa) have been calculated in the paper [26], where the Quantum ESPRESSO package has been used [30]. The magnitude of the depairing electronic correlations has been determined parametrically by the Coulomb pseudopotential ($\mu^{\star}$). In the case of the systems, which are under the influence of the high pressure, the Coulomb pseudopotential should be defined by [31]:

$$\mu^{\star} \equiv \frac{\mu + a\mu^2}{1 + \mu\ \ln\left[\frac{\omega_e}{\omega_{ph}}\right] + a\mu^2\ \ln\left[\frac{\alpha\omega_e}{\omega_{ph}}\right]}, \tag{5}$$

where $a=1.38$ and $\alpha \simeq 0.10$. The quantity $\mu$ is the direct Coulomb repulsion parameter. The symbols $\omega_e$ and $\omega_{ph}$ denote the characteristic electron and phonon frequency, respectively. Let us note that the formula (5) is the generalization of the classical Morel–Anderson expression [32], due to the fact that it takes into account the amendments of the order $\mu^2$.

In the case of the high-pressure systems, the predictions based on the formula (5) prove that the retardation effects lead to the lesser reduction of the value of the direct Coulomb repulsion ($\mu \to \mu^{\star}$) than indicated by the Morel–Anderson model. Thus, $\mu^{\star}$ for the compounds located under the influence of the high pressure is usually significantly higher than in the classical low-pressure cases. It should be also noted that the exact calculation of the parameter $\mu^{\star}$ for the real systems is a very complicated issue. Because of this, in the presented paper it has been assumed: $\mu^{\star} \in \langle 0.1, 0.3\rangle$. The Heaviside function in Eq. (2) has been denoted by $\theta$, while the cut-off frequency is equal to: $\omega_c = 3\Omega_{\max}$. The symbol $\Omega_{\max}$ represents the maximum phonon frequency, which is of the order of 200 meV [26].

The Eliashberg equations have been solved for 2201 Matsubara frequencies ($M=1100$). The stability of the solutions has been obtained in the temperature range from $T_0 = 2.5$ K to $T_C$. The numerical methods, tested in the papers [33–38], have been applied. The Eliashberg equations on the imaginary axis have been used for the exact determination of the value of the critical temperature, the free energy, the thermodynamic critical field, and the specific heat jump at the critical temperature. On the other hand, the order parameter and the effective mass of the electron have been calculated using the Eliashberg equations in the mixed representation. These equations have been used for the analytical continuation of the function $\phi_n$ and $Z_n$ on the real axis ($\omega$) [39]: