Classifying superconductivity in compressed H₃S

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Abstract

The discovery of high-temperature superconductivity in compressed H₃S by Drozdov and co-workers (A. Drozdov, et. al., Nature 525, 73 (2015)) heralded a new era in superconductivity. To date, the record transition temperature of $T_c = 260$ K stands with another hydrogen-rich compound, LaH₁₀ (M. Somayazulu, et. al., arXiv:1808.07695) which becomes superconducting at pressure of $P = 190$ GPa. Despite very intensive first-principle theoretical studies of hydrogen-rich compounds compressed to megabar level pressure, there is a very limited experimental dataset available for such materials. In this paper, we analyze the upper critical field, $B_{c2}(T)$, data of highly compressed H₃S reported by Mozaffari and co-workers (S. Mozaffari, et. al., LA-UR-18-30460, DOI: 10.2172/1481108) by utilizing four different models of $B_{c2}(T)$. In result, we find that the ratio of superconducting energy gap, $\Delta(0)$, to the Fermi energy, $\varepsilon_F$, in all considered scenarios is $0.03 < \Delta(0)/\varepsilon_F < 0.07$, with respective ratio of $T_c$ to the Fermi temperature, $T_F$, $0.012 < T_c/T_F < 0.039$. These characterize H₃S as unconventional superconductor and places it on the same trend line in $T_c$ versus $T_F$ plot, where all unconventional superconductors located.
Classifying superconductivity in compressed H$_3$S

I. Introduction

Experimental discovery a superconductivity above $T = 200$ K in highly compressed H$_3$S by Drozdov et al [1] is one of the most fascinating confirmation of the Bardeen-Cooper-Schrieffer (BCS) theory [2] and the phonon-mediated pairing scenario which can sustain superconductivity at such high temperature [3,4]. Moreover, recent experimental results on another hydrogen-rich compound of LaH$_{10}$ [5,6], further showed that BCS electron-phonon pairing mechanism works at much higher temperatures, and highest observed in experiment superconducting transition temperature, $T_c$, for LaH$_{10}$ compound is $T_c = 260$ K [6]. Historical aspects of the discovery, included the astonishing theoretical prediction of Ashcroft [7], and reviews of theoretical works in the field can be found elsewhere [8-13].

Most theoretical works [10,12,13-18] came to conclusion that H$_3$S is strong coupled superconductor with BCS ratio:

$$\frac{2\Delta(0)}{k_B T_c} = \alpha = 4.5 - 4.7$$

(1)

where $\Delta(0)$ is ground state of the superconducting energy gap, $k_B$ is the Boltzmann constant. In contrast to this, our analysis [19] of experimental self-field critical current density, $J_c(sf,T)$ (reported by Drozdov and co-workers in [1]), showed that the BCS ratio (Eq. 1) for H$_3$S is more likely to be very close to the weak-coupling limit of 3.53, and we deduced value for $\Delta(0) = 28$ meV [19,20], while many theoretical works came to predicted values in the range of $\Delta(0) = 40$-45 meV. Modern spectroscopic techniques have been applied to H$_3$S [21], which confirmed theoretically calculated energy spectrum for energies above 70 meV.

In this paper, we analyse recently released experimental upper critical field, $B_{c2}(T)$, data [22] for highly compressed H$_3$S with the purpose to deduce the Fermi velocity, $v_F$, and Fermi energy, $\varepsilon_F$, for this material.
II. Description of models

In the Ginzburg-Landau theory, the upper critical field is given by following expression:

\[ B_{c2}(T) = \frac{\phi_0}{2\pi \xi^2(T)} \]  \hspace{1cm} (2)

where \( \phi_0 = 2.07 \times 10^{-15} \) Wb is flux quantum, and \( \xi(T) \) is the coherence length. There is a well-known BCS expression [2]:

\[ \xi(0) = \frac{\hbar v_F}{\pi \Delta(0)} \]  \hspace{1cm} (3)

where \( \hbar = h/2\pi \) is reduced Planck constant, and \( v_F \) is the Fermi velocity. Thus, from deduced \( B_{c2}(0) \) and \( T_c \) and assumed \( \alpha \) (Eq. 1), one can calculate the Fermi velocity, \( v_F \):

\[ v_F = \frac{\pi}{2} \cdot \xi(0) \cdot \frac{\alpha \cdot k_B \cdot T_c}{\hbar}, \]  \hspace{1cm} (4)

the Fermi energy, \( \varepsilon_F \):

\[ \varepsilon_F = \frac{m^*_{e_f} v_F^2}{2}, \]  \hspace{1cm} (5)

where \( m^*_{e_f} \) is effective mass (for H\textsubscript{3}S we used \( m^*_{e_f} = 2.76 \) \( m_e \) [10]), and the Fermi temperature, \( T_F \):

\[ T_F = \frac{\varepsilon_F}{k_B}, \]  \hspace{1cm} (6)

where \( k_B \) is Boltzmann constant.

One of conventional models to analyse \( B_{c2}(T) \) was given by Werthamer-Helfand-Hohenberg (WHH) [23,24]:

\[ \ln \left( \frac{T}{T_c(B=0)} \right) = \psi \left( \frac{1}{2} \right) - \psi \left( \frac{1}{2} + \frac{\hbar \cdot D \cdot B_{c2}(T)}{2 \cdot \phi_0 \cdot k_B \cdot T} \right), \]  \hspace{1cm} (6)

where \( D \) is the diffusion constant of the normal conducting electrons/holes, with two free fitting parameters of \( T_c(B=0) \) and \( D \). Baumgartner et al [25] proposed simple and accurate analytical expression for \( B_{c2}(T) \) within WHH model:

\[ B_{c2}(T) = \frac{1}{0.693} \cdot \frac{\phi_0}{2 \pi \xi^2(0)} \cdot \left( 1 - \frac{T}{T_c} \right) - 0.153 \cdot \left( 1 - \frac{T}{T_c} \right)^2 - 0.152 \cdot \left( 1 - \frac{T}{T_c} \right)^4 \]  \hspace{1cm} (7)
where $\xi(0)$ and $T_c \equiv T_c(B=0)$ are two free fitting parameters. We will designate this model as B-WHH.

In addition, there are several analytical expressions which are in a wide use too [26-28]. For instance, there are classical two-fluid Gorter-Casimir model [29]:

$$B_{c2}(T) = \frac{\phi_0}{2\pi \xi^2(0)} \left( 1 - \left( \frac{T}{T_c} \right)^2 \right)$$  \hspace{1cm} (8)

and Jones-Hulm-Chandrasekhar (JHC) model [30]:

$$B_{c2}(T) = \frac{\phi_0}{2\pi \xi^2(0)} \left( \frac{1 - \left( \frac{T}{T_c} \right)^2}{1 + \left( \frac{T}{T_c} \right)^2} \right)$$  \hspace{1cm} (9)

There is also a little-known equation from Gor’kov for $B_{c2}(T)$ [31] which was referred by Gor’kov as a good analytical interpolative approximation over the whole temperature range:

$$B_{c2}(T) = \frac{1}{1.77} \cdot \frac{\lambda(0)}{\xi(0)} \left( 1.77 - 0.43 \cdot \left( \frac{T}{T_c} \right)^2 + 0.07 \cdot \left( \frac{T}{T_c} \right)^4 \right)$$  \hspace{1cm} (10)

where $B_c(T)$ is the thermodynamic critical field, and $\lambda(0)$ is the ground state London penetration depth. Eq. 8 was re-written by Jones et al [30] in following form:

$$B_{c2}(T) = \frac{1}{1.77} \cdot \frac{\phi_0}{2\pi \xi^2(0)} \left( 1.77 - 0.43 \cdot \left( \frac{T}{T_c} \right)^2 + 0.07 \cdot \left( \frac{T}{T_c} \right)^4 \right) \left( 1 - \left( \frac{T}{T_c} \right)^2 \right)$$  \hspace{1cm} (11)

We will designate Eq. 9 as G model.

In this paper, we utilise Eq. 8 in a different way. If we take in account, the Ginzburg-Landau (GL) theory expressions:

$$B_{c2}(T) = \sqrt{2} \cdot \frac{\lambda(T)}{\xi(T)} \cdot B_c(T)$$  \hspace{1cm} (12)

we can conclude that the Gor’kov’s equation (Eq. 8) means that:

$$\kappa(T) = \frac{\lambda(T)}{\xi(T)} = \frac{1}{1.77} \cdot \frac{\lambda(0)}{\xi(0)} \left( 1.77 - 0.43 \cdot \left( \frac{T}{T_c} \right)^2 + 0.07 \cdot \left( \frac{T}{T_c} \right)^4 \right)$$  \hspace{1cm} (13)

By utilising another GL theory expression:

$$B_{c2}(T) = 2 \cdot \left( \frac{\lambda(T)}{\xi(T)} \right)^2 \cdot \frac{B_{c2}(T)}{\ln(\kappa(T)) + 0.5} = \left( \frac{\lambda(T)}{\xi(T)} \right)^2 \cdot \frac{\phi_0}{2\pi \lambda^2(T)} = \left( \frac{\phi_0}{2\pi \lambda^2(T)} \right) \cdot \frac{\phi_0}{2\pi \lambda^2(T)}$$  \hspace{1cm} (14)

and BCS expression for $\lambda(T)$ for $s$-wave superconductor:
\[
\lambda(T) = \frac{\lambda(0)}{\left(1 - \frac{1}{2k_B T} \int_0^\infty \frac{de}{\cosh^2 \left( \frac{\sqrt{e^2 + \Delta(T)^2}}{2k_B T} \right)} \right)}^{1/2}
\]

where the temperature-dependent superconducting gap \( \Delta(T) \) equation can be taken from Gross et al [32]:

\[
\Delta(T) = \Delta(0) \cdot \tanh \left( \frac{\pi k_BT_c}{\Delta(0)} \cdot \sqrt{\eta \cdot \frac{\Delta C}{C} \cdot \left( \frac{T_c}{T} - 1 \right)} \right)
\]

where \( \Delta C/C \) is the relative jump in electronic specific heat at \( T_c \), and \( \eta = 2/3 \) for s-wave superconductors [32], one can obtain expression for the temperature dependent upper critical field:

\[
B_{c2}(T) = \frac{\phi_0}{2\pi \xi^2(0)} \left[ \left( \frac{1}{T_c} \right)^2 + 0.7 \left( \frac{T}{T_c} \right)^4 \right]^{1/2} \cdot \frac{1}{1 - \frac{1}{2k_B T} \int_0^\infty \frac{de}{\cosh^2 \left( \frac{\sqrt{e^2 + \Delta(T)^2}}{2k_B T} \right)} \right]^{1/2}
\]

Thus, four fundamental parameters of superconductor, i.e. \( \xi(0), \Delta(0), \Delta C/C \) and \( T_c \), can be deduced by fitting experimental \( B_{c2}(T) \) data to Eq. 17. We need to clarify that \( \xi(0) \) determines absolute value of \( B_{c2}(0) \) amplitude, while \( \Delta(0) \) and \( \Delta C/C \) are deduced from the shape of \( B_{c2}(T) \) curve (which is the part of Eq. 17 in square brackets).

In this paper we fit experimental \( B_{c2}(T) \) data for compressed sulfur hydride to Eqs. 7, 9, and 11, 17 with the purpose to deduce/calculate fundamental superconducting parameters of this material.

III. Results and Discussions

Mozaffari et al [22] in their Fig. 1(a) defined two values for the upper critical field:

1. At the onset of superconductivity, which we will designate as \( B_{c2}(T) \) (in accordance with Mozaffari et al [22] definition).
2. At zero-resistance point, which we will designate as \( B_{c2,R=0}(T) \) for the clarity.
In Figs. 1-4 we show raw upper critical field data and data fits to four models:

Panel a: B-WHH model [24] (Eq. 7);
Panel b: JHC model [30] (Eq. 9);
Panel c: G model [31] (Eq. 11);
Panel d: this work model (Eq. 17).

In Figs. 1,2 we show results for Sample #1 compressed at $P = 150$ GPa. In Figs. 3,4 we show results for Sample #2 compressed at $P = 170$ GPa. In Figs. 1,3 we analysed $B_{c2,R=0}(T)$ data, and in Figs. 2,4 we analysed $B_{c2}(T)$ data. Results of all fits are presented in Table 1.

In general (Figs. 1-4, Table 1), we can conclude that all four models provide good fit quality, $R$, and deduced values of $T_c$ and $\xi(0)$ for all four models are in reasonable agreement with each other. The most interesting thing we found is that fits to Eq. 17 reveal for all four $B_{c2}(T)$ datasets the value for superconducting energy gap of $\Delta(0) = 25$-$28$ meV which all are in excellent agreement with the value we deduced by the analysis of critical current densities in H$_3$S in our previous work [19], $\Delta(0) = 28$ meV. The latter was deduced for different H$_3$S sample [1] with $T_c = 203$ K, while in present work we analysed data for samples with lower $T_c$.

All deduced $B_{c2}(0)$ values (Fig. 1-4) are well below Pauli limit of:

$$B_p(0) = \frac{2\Delta(0)}{g\mu_B} = 430 - 500 \; T \gg B_{c2}(0)$$

where $g = 2$ and $\mu_B = \frac{e\hbar}{2m_e}$ is the Bohr magneton. Following Gor’kov’s note [33], Eq. 18 means that the mean-free path, $l$, of the electrons is large compared with the coherence length:

$$l \gg \xi(T) > \xi(0) \sim 2.5 \; nm$$

(19)
Figure 1. Superconducting upper critical field, $B_{c2,R=0}(T)$, data (blue) for compressed $H_3S$ Sample #1 at pressure $P = 150$ GPa (raw data are from Ref. 22). (a) Fit to B-WHH model [24] (Eq. 7), fit quality is $R = 0.9832$. (b) Fit to JHC model [30] (Eq. 9), fit quality is $R = 0.9785$. (c) Fit to G model [31] (Eq. 11), fit quality is $R = 0.9827$. (d) Fit to this work model (Eq. 17), fit quality is $R = 0.9832$. 

- **(a) B-WHH fit**
  - $\xi(0) = 2.46 \pm 0.02$ nm
  - $T_c = 150 \pm 1$ K

- **(b) JHC fit**
  - $\xi(0) = 2.40 \pm 0.03$ nm
  - $T_c = 157 \pm 2$ K

- **(c) G fit**
  - $\xi(0) = 2.55 \pm 0.02$ nm
  - $T_c = 149 \pm 1$ K

- **(d) Eq. 17 fit**
  - $\xi(0) = 2.67 \pm 0.05$ nm
  - $T_c = 150 \pm 3$ K
  - $\Delta(0) = 26.1 \pm 3.6$ meV
  - $\Delta C / C = 1.7 \pm 0.4$
  - $2\Delta(0)/k_B T_c = 4.0 \pm 0.6$
Figure 2. Superconducting upper critical field, $B_{c2}(T)$, data (blue) for compressed $\mathrm{H}_3\mathrm{S}$ Sample #1 at pressure $P = 150$ GPa (raw data are from Ref. 22). (a) Fit to B-WHH model [24] (Eq. 7), fit quality is $R = 0.9850$. (b) Fit to JHC model [30] (Eq. 9), fit quality is $R = 0.9908$. (c) Fit to G model [31] (Eq. 11), fit quality is $R = 0.9806$. (d) Fit to this work model (Eq. 17); fit quality is $R = 0.9914$. 

- **B-WHH fit**
  - $\xi(0) = 2.10 \pm 0.02$ nm
  - $T_c = 164.9 \pm 1.6$ K

- **JHC fit**
  - $\xi(0) = 2.06 \pm 0.01$ nm
  - $T_c = 172 \pm 2$ K

- **G fit**
  - $\xi(0) = 2.18 \pm 0.02$ nm
  - $T_c = 163 \pm 2$ K

- **Eq. 17 fit**
  - $\xi(0) = 2.21 \pm 0.03$ nm
  - $T_c = 171 \pm 4$ K
  - $\Delta(0) = 24.8 \pm 2.0$ meV
  - $\Delta G/C = 1.2 \pm 0.3$
  - $2\Delta(0)/k_B T_c = 3.4 \pm 0.3$
Figure 3. Superconducting upper critical field, $B_{c2,R=0}(T)$, data (blue) for compressed H$_3$S Sample #2 at pressure $P = 170$ GPa (raw data are from Ref. 22). (a) Fit to B-WHH model [24] (Eq. 7), fit quality is $R = 0.9901$. (b) Fit to JHC model [30] (Eq. 9), fit quality is $R = 0.9978$. (c) Fit to G model [31] (Eq. 11), fit quality is $R = 0.9879$. (d) Fit to this work model (Eq. 17); fit quality is $R = 0.9979$. 

$\xi(0) = 1.88 \pm 0.01$ nm, 
$T_c = 182.5 \pm 0.9$ K

$\xi(0) = 1.79 \pm 0.01$ nm, 
$T_c = 187.0 \pm 0.5$ K

$\xi(0) = 1.97 \pm 0.02$ nm, 
$T_c = 182 \pm 1$ K

$\Delta(0) = 26.1 \pm 2.3$ meV, 
$\Delta C / C = 1.2 \pm 0.1$, 
$2\Delta(0)/k_B T_c = 3.3 \pm 0.3$
Figure 4. Superconducting upper critical field, $B_{c2}(T)$, data (blue) for compressed H$_3$S Sample #2 at pressure $P = 170$ GPa (raw data are from Ref. 22). (a) Fit to B-WHH model [24] (Eq. 7), fit quality is $R = 0.990$. (b) Fit to JHC model [30] (Eq. 9), fit quality is $R = 0.9978$. (c) Fit to G model [31] (Eq. 11), fit quality is $R = 0.9886$. (d) Fit to this work model (Eq. 17); fit quality is $R = 0.9981$. 

**Equations:**

- **B-WHH fit**
  - $\xi(0) = 1.79 \pm 0.01$ nm
  - $T_c = 185.2 \pm 0.9$ K

- **JHC fit**
  - $\xi(0) = 1.68 \pm 0.01$ nm
  - $T_c = 189.0 \pm 0.5$ K

- **G fit**
  - $\xi(0) = 1.88 \pm 0.02$ nm
  - $T_c = 181.9 \pm 0.9$ K

- **Eq. 17 fit**
  - $\xi(0) = 1.86 \pm 0.10$ nm
  - $T_c = 190 \pm 4$ K
  - $\Delta(0) = 28.8 \pm 5.9$ meV
  - $\Delta C/C = 1.2 \pm 0.2$
  - $2\Delta(0)/k_BT_c = 3.5 \pm 0.7$
This is interesting result, if we take into account that H₃S is formed by chemical reaction which occurs within the diamond anvil volume:

\[ 3H_2S \rightarrow 2H_3S + S \]  \hspace{1cm} (20)

and pure sulfur is always presented as post-reacted product in the studied sample.

However, Eq. 18 tells us that two phases, i.e. H₃S and S, are reasonably well separated from each other and there is a very low level of atomic disordering within superconducting H₃S phase, which has lattice parameter of \( a = 0.3092 \) nm [34].

The next step of the analysis is the comparison of \( v_F \), \( \varepsilon_F \), \( T_F \) values calculated directly by Eq. 3 (because fits to Eq. 17 provide both required quantities, i.e. \( \xi(0) \) and \( \Delta(0) \)) with \( v_F \) values calculated by Eq. 4 in assumption of two extreme coupling strength scenario of \( \alpha = 3.53 \) and \( \alpha = 4.70 \). Overall, deduced/calculated \( v_F \) for H₃S are in the range of \( v_F = (2.0 - 3.8) \times 10^5 \) m/s which equals to \( v_F \) of nickel and cobalt at normal conditions [35] and is approximately equal to the universal nodal Fermi velocity of the superconducting cuprates [36].

**Table 1.** Deduced parameters for H₃S superconductor. We assumed that electron effective mass in H₃S is \( m_{eff} = 2.76 \) \( m_e \) [10].

| Pressure (GPa) | Raw data | Model | Deduced \( T_c \) (K) | Deduced \( \xi(0) \) (nm) | Assumed/deduced | \( \Delta C/ C \) | \( v_F \) (10⁵ m/s) | \( \Delta(0) / eV \) | \( \varepsilon_F / eV \) | \( \Delta(0)/\varepsilon_F \) | \( T_F / (10^3 K) \) | \( T_c / T_F \) |
|---------------|----------|-------|------------------------|---------------------------|----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| 150           | B-WHH    | 150 ± 1 | 2.46 ± 0.02            | 3.53                      | 2.68 ± 0.03   | 22.8 ± 0.2     | 0.56 ± 0.01    | 0.040 ± 0.001  | 6.5 ± 0.2       | 0.023 ± 0.001  | 0.013 ± 0.001  |
|               |          |        |                        |                           |               | 4.70            | 3.57 ± 0.04    | 30.4 ± 0.04    | 1.00 ± 0.02     | 0.030 ± 0.001  | 11.6 ± 0.4     | 0.023 ± 0.001  |
| 150           | JHC      | 157 ± 2 | 2.40 ± 0.03            | 3.53                      | 2.74 ± 0.03   | 23.9 ± 0.4     | 0.59 ± 0.03    | 0.041 ± 0.002  | 6.8 ± 0.2       | 0.023 ± 0.001  | 0.013 ± 0.001  |
|               |          |        |                        |                           |               | 4.70            | 3.65 ± 0.05    | 31.8 ± 0.4     | 1.04 ± 0.02     | 0.030 ± 0.002  | 12.1 ± 0.5     | 0.023 ± 0.001  |
| 150           | G        | 149 ± 1 | 2.55 ± 0.02            | 3.53                      | 2.76 ± 0.03   | 22.7 ± 0.2     | 0.60 ± 0.01    | 0.038 ± 0.002  | 6.9 ± 0.2       | 0.021 ± 0.001  | 0.012 ± 0.001  |
|               |          |        |                        |                           |               | 4.70            | 3.68 ± 0.04    | 30.2 ± 0.3     | 1.06 ± 0.02     | 0.028 ± 0.001  | 12.3 ± 0.5     | 0.021 ± 0.001  |
| 150           | Eq. 16   | 150 ± 3 | 2.67 ± 0.05            | 4.0 ± 0.6                 | 3.33 ± 0.45   | 26.1 ± 3.6     | 0.87 ± 0.12    | 0.030 ± 0.004  | 10.1 ± 1.4      | 0.015 ± 0.002  | 0.012 ± 0.001  |
|               |          |        |                        |                           | 3.53          | 2.51 ± 0.03    | 25.1 ± 0.3     | 0.50 ± 0.01    | 0.051 ± 0.002  | 5.8 ± 0.2      | 0.029 ± 0.001  |
| $B_{c2}(T)$ | $B_{c1}$ | $T_c$ | $2.10 \pm 0.02$ | $4.70$ | $3.35 \pm 0.03$ | $33.4 \pm 0.3$ | $0.88 \pm 0.02$ | $0.038 \pm 0.002$ | $10.2 \pm 0.2$ | $0.016 \pm 0.001$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| B-WHH | 165 ± 2 | 3.53 | $2.57 \pm 0.03$ | $26.2 \pm 0.3$ | $0.52 \pm 0.01$ | $0.050 \pm 0.002$ | $6.0 \pm 0.2$ | $0.029 \pm 0.001$ |
| JHC | 172 ± 2 | 4.70 | $3.42 \pm 0.03$ | $34.8 \pm 0.3$ | $0.92 \pm 0.02$ | $0.038 \pm 0.001$ | $10.7 \pm 0.2$ | $0.016 \pm 0.001$ |
| G | 163 ± 2 | 4.70 | $3.53$ | $24.8 \pm 0.3$ | $0.52 \pm 0.02$ | $0.048 \pm 0.002$ | $6.0 \pm 0.2$ | $0.027 \pm 0.001$ |

| $B_{c2,001}(T)$ | $B_{c1}$ | $T_c$ | $1.87 \pm 0.01$ | $1.86 \pm 0.01$ | $3.30 \pm 0.02$ | $36.8 \pm 0.1$ | $0.85 \pm 0.02$ | $0.043 \pm 0.002$ | $9.9 \pm 0.3$ | $0.018 \pm 0.001$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| B-WHH | 182.5 ± 0.9 | 1.88 ± 0.01 | 3.53 | $2.50 \pm 0.03$ | $27.8 \pm 0.1$ | $0.49 \pm 0.01$ | $0.057 \pm 0.002$ | $5.7 \pm 0.2$ | $0.032 \pm 0.002$ |
| JHC | 187.0 ± 0.5 | 4.70 | $3.32 \pm 0.02$ | $37.0 \pm 0.2$ | $0.87 \pm 0.01$ | $0.043 \pm 0.001$ | $10.0 \pm 0.2$ | $0.018 \pm 0.001$ |
| G | 182 ± 1 | 4.70 | $3.53$ | $28.4 \pm 0.1$ | $0.46 \pm 0.01$ | $0.062 \pm 0.001$ | $5.4 \pm 0.1$ | $0.035 \pm 0.001$ |

| $B_{c2}(T)$ | $B_{c1}$ | $T_c$ | $1.97 \pm 0.02$ | $1.92 \pm 0.05$ | $3.3 \pm 0.3$ | $1.2 \pm 0.1$ | $2.4 \pm 0.2$ | $26.1 \pm 2.3$ | $0.44 \pm 0.05$ | $0.059 \pm 0.006$ | $5.0 \pm 0.5$ | $0.037 \pm 0.004$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| B-WHH | 185.2 ± 0.9 | 1.79 ± 0.01 | 3.53 | $2.40 \pm 0.01$ | $28.2 \pm 0.1$ | $0.45 \pm 0.01$ | $0.062 \pm 0.001$ | $5.3 \pm 0.1$ | $0.035 \pm 0.001$ |
| JHC | 189.0 ± 0.5 | 4.70 | $3.20 \pm 0.01$ | $37.5 \pm 0.1$ | $0.80 \pm 0.02$ | $0.047 \pm 0.002$ | $9.3 \pm 0.2$ | $0.020 \pm 0.001$ |
| G | 181.9 ± 0.9 | 4.70 | $3.30 \pm 0.02$ | $36.8 \pm 0.1$ | $0.85 \pm 0.02$ | $0.043 \pm 0.002$ | $9.9 \pm 0.3$ | $0.018 \pm 0.001$ |

Examination of the values in Table I led us to three important findings:

1. The ratio of the superconducting energy gap, $\Delta(0)$, to the Fermi energy, $\varepsilon_F$, in all considered scenarios (including direct deduction by Eq. 17) is within interval of $0.03 < \Delta(0)/\varepsilon_F < 0.07$. These values characterize H$_3$S material as an unconventional superconductor, by illustration, conventional niobium, Nb, has the ratio which is at least two orders of magnitude lower, i.e. $\Delta(0)/\varepsilon_F = 3 \times 10^{-4}$ [37].

2. The most straightforward way to see our conclusion that H$_3$S is unconventional superconductor is to add $T_c$ and $T_F$ data for H$_3$S on the plot of $T_c$ versus $T_F$ where other
superconductors are shown. In this plot (Fig. 5) (data in Fig. 5 were adopted from Uemura [38], Ye et al [39], Qian et al [40], and Hashimoto et al [41]) all unconventional superconductors are located within a narrow band of $0.01 < T_c/T_F < 0.05$. We note that Uemura [38] stated that there is the upper limit for $T_c/T_F = 0.05$ for all known superconductors. In all considered scenarios, H$_3$S has ratios within interval of $0.012 < T_c/T_F < 0.039$ (Fig. 5 and Table 1). It is clearly visible in Fig. 5 that H$_3$S is in the same band where all unconventional superconductors, particularly heavy fermions and cuprates, are. In this regard, H$_3$S is located just above Bi-2223 phase. In this regard, H$_3$S is the material which is located at the position where majority of others unconventional superconductors placed.

![Figure 5](image_url)

**Figure 5.** A plot of $T_c$ versus $T_F$ obtained for most representative superconducting families. Data was taken from Uemura [38], Ye et al [39], Qian et al [40], and Hashimoto et al [41].

3. We also can see that despite of very different assumptions and varieties of the upper critical field data definition, the Fermi velocity is within reasonably narrow interval of $v_F = (2.1-3.7) \times 10^8$ m/s. This value is about two times lower than $v_F$ of alkali metals at normal
conditions [35,37] and it approximately equals to the universal nodal Fermi velocity of the superconducting cuprates [36]. This is another manifestation that H$_3$S should be classified as unconventional superconductor.

Even though the original paper from Drozdov et. al. [1] stated that H$_3$S is conventional superconductor, and this point of view was very quickly widely accepted by the scientific community [3], we must note that at that time there were no available experimental data which supported this point of view. One of prerequisites of phonon mediated mechanism in H$_3$S is the strong-coupling electron-phonon interaction (references on original papers can be found in Ref. 13), which we cannot confirm neither by the analysis of experimental critical current densities [20], nor by the analysis of experimental upper critical field data presented herein. Instead our analysis gives clear evidence that H$_3$S is weak-coupled superconductor, with the ratio:

$$3.3 \pm 0.3 < \frac{2\Delta(0)}{k_BT_c} < 4.0 \pm 0.6 \quad (21)$$

and average value of

$$\frac{2\Delta(0)}{k_BT_c} = 3.55 \pm 0.31 \quad (22)$$

which is remarkably closed to weak-coupling limit of BCS theory of 3.53. Average absolute value of the ground state superconducting energy gap is:

$$\Delta(0) = 26.5 \pm 1.7 \, meV \quad (23)$$

This value is in a very good agreement with $\Delta(0) = 27.8$ meV which we deduced in our previous paper by the analysis of critical current density in H$_3$S [19] for sample with $T_c = 203$ K.

**IV. Conclusion**

In this paper, we analysed the upper critical field data for compressed H$_3$S which were recently released by Los-Alamos Laboratory [22]. Result of our analysis showed that
compressed H$_2$S should be classified as another member of unconventional superconductor family.

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