Unconventional superconductivity in highly-compressed unannealed H₃S

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Abstract

While great scientific efforts focus on the synthesis and studies of near-room-temperature (NRT) superconductors exhibited record superconducting transition temperatures (for instance, laser annealed H₃S, LaH₁₀ and YH₆ (n = 4,6,7,9) with Tc > 200 K), unannealed low-Tc counterparts of NRT superconductors stay in the background. However, unannealed highly-compressed hydrides are part of hydrogen-rich superconductors family and the success in understanding of NRT superconductivity depends on the study of these materials too. In this paper we analyse experimental temperature dependent upper critical field data, B_{c2}(T), reported by Drozdov et al (Nature 525, 73 (2015)) for unannealed highly-compressed (P = 155 GPa) H₃S with Tc = 46 K and show that this material is unconventional superconductor which exhibits the ratio of Tc to the Fermi temperature, T_F, in the range of 0.02 ≤ Tc/T_F ≤ 0.05.
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I. Introduction

The discovery of near-room-temperature (NRT) superconductivity in highly compressed sulphur hydride, H$_3$S, by Drozdov et al. [1] and in lanthanum decahydride, LaH$_{10}$, by Somayazulu et al. [2], raises a wide public interest and great scientific efforts to study pressure-induced superconductivity in hydrogen-rich materials [3-7]. It should be noted, that the discovery of the effect of pressure-induced superconductivity in non-superconducting materials is attributed to Jörg Wittig [8] who converted elemental cerium into superconductor at pressure of $P = 5$ GPa. During this, more than fifty years, long research journey, pressure-induced superconductivity was found in dozens of non-superconducting elements and compounds (details can be found in recent reviews [3,9-11]).

It is important to note, that all known NRT superconductors (which exhibits record superconducting transition temperatures, $T_c$) are synthesized by the laser annealing technique of highly-compressed hydrogen-rich precursors in the diamond-anvil cell (DAC) [1,2,10-15]. At the same time, some unannealed phases, and particularly H$_3$S [1], are also superconductors with, however, much lower $T_c$. The latter is this reason why these superconducting phases are in the background of its NRT counterparts. Independent of its lower $T_c$’s, these low-$T_c$ unannealed phases are highly-compressed hydrogen-rich superconductors and there is an interest to understand the superconductivity in these compounds too.

In this paper we analyse temperature dependent upper critical field data, $B_{c2}(T)$, for unannealed H$_3$S phase ($P = 155$ GPa) reported by Drozdov et al. in their first milestone paper [1]. In the result, it is found that unannealed H$_3$S phase has the ratio of $T_c$ to the Fermi temperature, $T_F$, in the range of $0.02 \leq T_c/T_F \leq 0.05$, and, thus, this superconductor falls in the unconventional superconductor band of the Uemura plot [16-18] together with heavy fermions, fullerens, cuprates, pnictides and NRT superconductors.
II. Extrapolative models for ground state upper critical field

Ground state upper critical field, $B_{c2}(0)$, is given in the Ginzburg-Landau theory [19] by following expression:

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

where $\phi_0 = 2.068 \cdot 10^{-15}$ Wb is magnetic flux quantum, and $\xi(0)$ is the ground state coherence length. To deduce $\xi(0)$ value from real world measurements (which very often perform at high reduced temperatures) several models were proposed. In this paper, to deduce $\xi(0)$ value for unannealed H$_3$S phase we will use classical two-fluid Gorter-Casimir model (GC model) [20]:

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

as well as model proposed by Gor’kov [21] (Gor’kov model):

$$B_{c2}(T) = B_{c2}(0) \cdot \left( \frac{1.77 - 0.43 \left( \frac{T}{T_c} \right)^2 + 0.07 \left( \frac{T}{T_c} \right)^4}{1.77} \right) \cdot \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right] =$$

$$\frac{\phi_0}{2 \pi \xi^2(0)} \cdot \left( \frac{1.77 - 0.43 \left( \frac{T}{T_c} \right)^2 + 0.07 \left( \frac{T}{T_c} \right)^4}{1.77} \right) \cdot \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]$$  \hspace{1cm} (3)

and modified Werthamer, Helfand, and Hohenberg (WHH) [22,23] model proposed by Baumgartner et al [24] (B-WHH model):

$$B_{c2}(T) = B_{c2}(0) \cdot \left( \frac{1 - \frac{T}{T_c} - 0.153 \left( \frac{T}{T_c} \right)^2 - 0.152 \left( \frac{T}{T_c} \right)^4}{0.693} \right) =$$

$$\frac{\phi_0}{2 \pi \xi^2(0)} \cdot \left( \frac{1 - \frac{T}{T_c} - 0.153 \left( \frac{T}{T_c} \right)^2 - 0.152 \left( \frac{T}{T_c} \right)^4}{0.693} \right)$$  \hspace{1cm} (4)

III. $B_{c2}(T)$ analysis for unannealed H$_3$S $(P = 155$ GPa)

Drozdov et al [1] in their Figure 3(a) reported the temperature dependent magnetoresistance, $R(T,B)$, for unannealed H$_3$S sample pressurised at $P = 155$ GPa. To
deduce raw \( B_{c2}(T) \) data we processed \( R(T,B) \) data (Figure 3(a), upper insert) by utilising a criterion of \( R(T) = 345 \) m\( \Omega \). Raw \( B_{c2}(T) \) data and results of fits to three models (Eqs. 2-4) are shown in Fig. 1 and Table 1.

\[ \begin{align*}
\xi(0) &= 3.6 \pm 0.1 \text{ nm} \\
T_c &= 45.9 \pm 0.1 \text{ K}
\end{align*} \]

\[ \begin{align*}
\xi(0) &= 3.3 \pm 0.1 \text{ nm} \\
T_c &= 45.9 \pm 0.1 \text{ K}
\end{align*} \]

\[ \begin{align*}
\xi(0) &= 3.1 \pm 0.1 \text{ nm} \\
T_c &= 45.9 \pm 0.1 \text{ K}
\end{align*} \]

**Figure 1.** Superconducting upper critical field, \( B_{c2}(T) \), data and fits to three models (Eqs. 2-4) for unannealed \( \text{H}_3\text{S} \) phase compressed at pressure of \( P = 155 \text{ GPa} \) (raw data is from Ref. 1). (a) fit to GC model, the fit quality is \( R = 0.989 \). (b) fit to Gor’kov model, \( R = 0.991 \). (c) fit to B-WHH model, \( R = 0.991 \). 95% confidence bars are shown.
Table I. Deduced and calculated parameters for unannealed H₃S compressed at \( P = 155 \) GPa. Deduced critical temperature for all models (Eqs. 2-4) is \( T_c = 45.9 \pm 0.1 \) K. Assumed charge effective mass is \( m^*_{e\text{ff}} = 2.76 \cdot m_e [32] \). Smallest and largest values for \( \frac{T_c}{T_F}, \frac{T_c}{T_{\text{fluc,phase}}} \) and \( \frac{T_c}{T_{\text{fluc,amp}}} \) are marked in bold.

| Model       | Deduced \( \xi(0) \) (nm) | Assumed \( z(0) \) \( k_B T_c \) | \( T_c/T_F \) | Assumed \( k \) | \( T_{\text{fluc,phase}} \) (10⁴ K) | \( T_{\text{fluc,amp}} \) (10⁴ K) | \( T_c/T_{\text{fluc,phase}} \) | \( T_c/T_{\text{fluc,amp}} \) |
|-------------|----------------------------|---------------------------------|---------------|----------------|----------------|----------------|----------------|----------------|
| GC          | 3.6 ± 0.1                  | 3.53                            | 1.3 ± 0.1     | 0.035 ± 0.002 | 60             | 1.88 ± 0.05    | 0.50 ± 0.02   | 0.024 ± 0.001 | 0.091 ± 0.003 |
| Gor’kov     | 3.3 ± 0.1                  | 3.53                            | 1.1 ± 0.1     | 0.042 ± 0.002 | 60             | 2.05 ± 0.06    | 0.35 ± 0.01   | 0.022 ± 0.001 | 0.083 ± 0.003 |
| B-WHH       | 3.1 ± 0.1                  | 3.53                            | 0.97 ± 0.06   | 0.047 ± 0.004 | 60             | 2.18 ± 0.07    | 0.59 ± 0.02   | 0.021 ± 0.001 | 0.078 ± 0.002 |

IV. Unannealed H₃S (\( P = 155 \) GPa) in Uemura plot

From deduced \( \xi(0) \) values (Fig. 1 and Table 1), we calculated the Fermi temperature, \( T_F \), for unannealed H₃S phase by utilising the Bardeen-Cooper-Schrieffer theory expression [33]:

\[
T_F = \frac{\varepsilon_F}{k_B} = \frac{\pi^2}{8} \cdot m^*_{e\text{ff}} \cdot \xi^2(0) \cdot \left( \frac{\alpha k_B T_c}{\hbar} \right)^2,
\]

(5)

where \( \alpha = \frac{2\Delta(0)}{k_B T_c} \), \( \Delta(0) \) is the amplitude of the ground state energy gap, \( \varepsilon_F \) is the Fermi energy, \( \hbar = \hbar/2\pi \) is reduced Planck constant, \( k_B \) is the Boltzmann constant, \( m^*_{e\text{ff}} \) is the charge carrier effective mass (\( m^*_{e\text{ff}} = 2.76 \cdot m_e \) for H₃S at \( P = 155 \) GPa [32]).

For H₃S phase \( \alpha = 3.53-4.7 \), where the lower bound was reported by Kaplan and Imry [34] and in our previous works [35-37], and the upper bond was reported by other authors [3,32]. Due to for all three models deduced \( T_c = 45.9 \pm 0.1 \) K in Table I we show only the \( T_c/T_F \) ratios.

As the result, unannealed H₃S (\( P = 155 \) GPa) phase in all considered scenarios (Table 1) has \( 0.02 \leq T_c/T_F \leq 0.05 \) and falls in unconventional superconductors band of the Uemura plot [16-18] in close proximity to other NRT counterparts [1,2,12-15] (Fig. 2), including annealed
H₃S with transition temperature $T_c \sim 190$ K [1,38]. Two characteristic lines for Bose-Einstein condensates (BEC) (for which $T_c/T_F = 0.22$) and the Bardeen-Cooper-Schrieffer (BCS) superconductors (for which $T_c/T_F \leq 0.001$) are shown in Fig. 2 for clarity.

![Figure 2](image)

**Figure 2.** A plot of $T_c$ versus $T_F$ where the most representative superconducting families are shown. Raw data is taken from [18,37,39-41]. Characteristic lines for the Bose-Einstein condensate (BEC) and the Bardeen-Cooper-Schrieffer (BCS) superconductors are shown for clarity.

Most of NRT superconductors have severe influence of thermodynamic fluctuations on the superconducting order parameter and, thus, on the observed superconducting transition temperature, $T_c$ [39-41]. There are two types of the thermodynamic fluctuations in superconductors, the phase fluctuations of the order parameter, which have characteristic temperature [42]:

$$T_{fluc,phase} = \frac{0.55 \phi_0^2}{\pi^{3/2} \mu_0 k_B} \left( \frac{1}{\kappa^2 \xi(0)} \right)$$  \hspace{1cm} (6)
where \( \kappa = \lambda(0)/\xi(0) \) is Ginzburg-Landau parameter, and \( \lambda(0) \) is the ground state London penetration depth; and the amplitude fluctuations of the order parameter [43], with characteristic temperature of:

\[
T_{\text{fluc,amp}} = \frac{\phi_0^2}{12\pi\mu_0\kappa_B \cdot \frac{1}{\kappa^2\xi(0)}}
\] (7)

To calculate \( T_{\text{fluc,phase}} \) and \( T_{\text{fluc,amp}} \) we make an assumption that unannealed H\(_3\)S phase has the Ginzburg-Landau parameter in the range of \( \kappa = 60-120 \) which covers all superconductors with transition temperature above \( T_c = 20 \) K [42,44-46].

Examination of obtained values for \( T_{\text{fluc,phase}} \) and \( T_{\text{fluc,amp}} \) (Table I) leaded us to an important conclusion that thermodynamic fluctuations are not make influence on the observed \( T_c \) in this compound, which is different from the case of annealed H\(_3\)S phase where the ratio of \( T_c/T_{\text{fluc,amp}} \) in some scenarios can be as high as \( T_c/T_{\text{fluc,amp}} = 0.7 \) [39].

V. Conclusions

In summary, in this paper we analyse experimental \( B_c^2(T) \) data of unannealed highly-compressed H\(_3\)S compound and find that this superconductor exhibits unconventional superconductivity. In addition, we show that thermodynamic fluctuations do not affect the observed critical temperature \( T_c = 46 \) K in this superconductor.

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