Faulty evidence for superconductivity in ac magnetic susceptibility of sulfur hydride under pressure

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It is generally believed that sulfur hydride under high pressure is a high temperature superconductor [1–7]. In National Science Review 6, 713 (2019) Huang and coworkers Ref. [8] reported detection of superconductivity in sulfur hydride through a highly sensitive ac magnetic susceptibility technique and an unambiguous determination of the superconducting phase diagram. In this paper we present evidence showing that the experimental results reported in that paper [8] do not support the conclusion that sulfur hydride is a superconductor.

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I. INTRODUCTION

In 2015, Drozdov and coworkers reported the discovery of high temperature superconductivity in sulfur hydride [1]. The result is generally assumed to be true [2–7]. Independently, Huang and coworkers measured ac magnetic susceptibility of sulfur hydride [8] and in appearance confirmed the existence of superconductivity. According to ref. [9], that work “sets a new standard for experimental studies of superconductivity at high pressure”.

However, we have recently argued that the experimental evidence supporting superconductivity in sulfur hydride presented in ref. [1] is not convincing [10], and that neither is the one presented in refs. [11, 12] concerning the Meissner effect [13, 14]. In this paper we argue that the ac susceptibility measurements of ref. [8] provide no support for the existence of superconductivity in sulfur hydride either. No other studies of ac magnetic susceptibility nor of other magnetic properties of sulfur hydride besides those mentioned above have been reported so far.

Ac magnetic susceptibility is a superior test for superconductivity in materials under high pressure [15–20]. A superconductor excludes magnetic flux, so upon cooling into the superconducting state a sharp drop in the ac magnetic susceptibility is observed. For experiments under high pressures, because of the smallness of the sample required by the geometry of the diamond anvil cell, the detected signal is a tiny drop in a large signal arising from the superposition of the sample and the background magnetic responses, with the background signal being several orders of magnitude larger than the sample signal [15, 16, 18, 20]. For that reason, it is customary to subtract from the total signal (the so-called ”raw data”) the background signal, according to the relation

\[ \text{data} = \text{raw data} - \text{background signal}. \]  

(1)

The background signal is usually obtained by measuring the susceptibility at a pressure value such that no superconducting transition occurs in the temperature range of interest [18].

Reference [8] reports measurements of ac magnetic susceptibility measurements for sulfur hydride at seven different pressure values. It only shows results for ac susceptibility for four values of pressure. These results (figure 2 of ref. [8]) are reproduced in Fig. 1. The drops in the signals seen in the figure were interpreted as due to the onset of superconductivity at the critical temperatures \( T_c \) shown in the figure [8].

![FIG. 1: Magnetic susceptibility signals of sulfur hydride at various pressures, Fig. 2 of ref. [8].](image)

II. THE MEASURED RAW DATA

The results shown in Fig. 1 are for the left side of Eq. (1), i.e. are obtained by subtracting a background signal from raw data. In order to assess the validity and significance of these results, we requested from the authors the raw data and background signal measured, from which the results shown in Fig. 1 were obtained. Following generally accepted proper scientific practice, the authors kindly sent us these data recently as well as gave us ad-
FIG. 2: Top panels: raw data and background signal for Fig. 2a of ref. [8] plotted from data supplied by the authors [21]. The lower left panel shows the difference between the upper left and right panels, in agreement with the published results shown on the lower right panel.

FIG. 3: Top panels: raw data and background signal for Fig. 2b of ref. [8] plotted from data supplied by the authors [21]. The lower left panel shows the difference between the upper left and right panels, in agreement with the published results shown on the lower right panel.

FIG. 4: Top panels: raw data and background signal for Fig. 2c of ref. [8] plotted from data supplied by the authors [21]. The lower left panel shows the difference between the upper left and right panels, in agreement with the published results shown on the lower right panel.

FIG. 5: Top panels: raw data and background signal for Fig. 2d of ref. [8] plotted from data supplied by the authors [21]. The lower left panel shows the difference between the upper left and right panels, in agreement with the published results shown on the lower right panel.

ditional details of the measurements upon our request [21].

From the data supplied by the authors, we made plots of the raw data and the background signal and of their difference according to Eq. (1). These are shown in Figs. 2 to 5. It can be seen that the difference calculated from the raw data and background signal supplied by the authors properly reproduces the data plotted in Fig. 2 of ref. [8].

We also learn from these figures that the background signal, which was collected separately for each temperature range at a lower pressure [21], is smooth in all cases, with nearly constant slope around the region where the transition occurs. This is what one expects for these measurements, as also seen for example in ref. [20]. As a consequence, the raw data shown in the top left panels of Figs. 2 to 5 show similar slope versus temperature above and below $T_c$.

This is in stark contrast with the raw data for ac magnetic susceptibility of a carbonaceous sulfur hydride (CSH) under pressure, claimed to be superconducting at room temperature, shown in ref. [22]. For that mate-
rial, the published raw data for ac magnetic susceptibility (Extended Data Fig. 7 d of ref. [22]) show a very significant change in slope across the transition, similar to what such data look like for the element europium at low temperature [23]. I have suggested that this implies that the published data for ac susceptibility of CSH are invalid [24–26]. Instead, the authors of ref. [22] state that the background signal is responsible for this unusual behavior [27]. This would imply a very anomalous background signal, qualitatively different from that seen in Figs. 2-5 here, arguably impossible [26]. The authors of ref. [22] have declined to supply their raw data and background signal measurements to verify or disprove their claim.

III. FURTHER ANALYSIS

To further examine the validity and significance of the susceptibility data for sulfur hydride reported in [8] under discussion here, we have made graphs of the measured temperature versus line number in the data files supplied by the authors [21]. The authors did not give us a time track record for each measurement, but informed us that data were taken at a constant rate of temperature change, mostly about 0.1 K/min, sometimes no bigger than 0.5 K/min [21]. With the reasonable assumption that data were taken at regular time intervals, we would expect a smooth curve for the temperature as a function of line number on the data file. Indeed, that is what we see for the background signal measurements, shown in Fig. 6.

Instead, when we do the same plots for the different temperature ranges shown in Fig. 1 at the pressure values given in Fig. 1 where the supposed superconducting transitions occur, we find the very surprising results shown in Fig. 7. Particularly for cases (a) and (b), a sharp break in the temperature versus line number in the file occurs right at the point where the assumed superconducting transition takes place.

The behavior shown in Fig. 7 is very unexpected. It suggests that the rate of temperature change is not constant in time, contrary to what we were told was the experimental protocol [21]. Indeed, in Fig. 8 we plot $\Delta T$, the change in temperature between two subsequent lines in the data file, versus temperature for two cases. There is a sharp break at the critical temperature, with the temperature changing faster above than below $T_c$.

If the system is being heated at a constant rate, as we were informed [21], the sudden increase in the temperature change could indicate that the heat capacity of the system suddenly decreased. For a superconducting transition this is in fact expected: the specific heat jump at the critical temperature is given by $(c_s - c_n)/c_n = 1.43$, with $c_n$ and $c_s$ the heat capacities in the normal and superconducting states.

However, the temperature sensor cannot be placed in the diamond anvil cell next to the sample, that is physically impossible [28]. Assuming the temperature sensor
is located at a distance $R \sim 1\text{cm}$ from the sample, the temperature measured would correspond to that of a volume of order $\sim 10^7$ times larger than the volume of the sample, so it cannot possibly be influenced to the degree shown in Fig. 8 by a change in the heat capacity of the sample.

Therefore, we have to conclude that the sudden change in the temperature increment coinciding with the assumed critical temperature is an experimental artifact. This indicates that the observed change in slope in the ac susceptibility observed at those temperatures is a consequence of the same experimental artifact and cannot be taken as evidence of a superconducting transition.

Fig. 9 shows the corresponding plots for the other two values of pressure, 149 GPa and 155 GPa. There is also evidence here that there are changes in the rate of temperature change right at the assumed superconducting transitions, which again is not expected and casts doubt on the conclusion that the observed drops in Figs. 1c and 1d indicate superconductivity.

**IV. SPECULATION ON A POSSIBLE SCENARIO**

In this section we ask: assuming the sample did not go superconducting at the $T_c$'s indicated in Fig. 1, what could be a possible scenario that led to the obtention of Fig. 1, which indicates that there were superconducting transitions when in fact there were none?

Given the anomalous temperature steps found in Fig. 8, we hypothesize that there may also have been a problem with the temperature determination, i.e. that the readings in the thermometer did not accurately reflect the temperature of the sample. As a simple scenario, let us assume that for 117 GPa the temperature step at the sample location was in fact constant below $T_c$, given by the average value of what was measured below $T_c$, $\Delta T = 0.0068K$, and jumped up by a factor of three at $T_c$, similarly to what the left panel of Fig. 8 shows, remaining constant above $T_c$. This is indicated by the dashed red lines on the left panel of Fig. 10, which is not too different from what was measured (black lines). The resulting raw data versus this new temperature scale are shown on the right panel of Fig. 10, and no longer show the structure near $T_c$ that the original raw data showed (top left panel of Fig. 2). If we now subtract the background, we obtain what is shown on the left panel of Fig. 11. The steep susceptibility drop at a temperature interpreted as the superconducting transition temperature has disappeared.

For 130 GPa, we assume again that the step was constant below $T_c$ and above $T_c$, but here we will assume that the value was the same below and above $T_c$, given by the average of the step value over the entire temperature range.

**FIG. 10:** Left panel: we assume that the temperature steps were in reality given by the red dashed lines, constant below and above $T_c$, changing by a factor of 3 at $T_c$. The right panel shows the resulting raw data plotted versus this new temperature scale.

**FIG. 11:** The left panel shows the susceptibility after background subtraction assuming the raw data given in the right panel of Fig. 10, i.e. with the new temperature scale. Note that the jump reported to occur around 38 K, shown in the right panel, is no longer there.

**FIG. 12:** Left panel: we assume that the temperature steps were in reality given by the red dashed line, i.e. the same for all temperatures. The right panel shows the resulting raw data plotted versus this new temperature scale.
Fig. 13: The left panel shows the susceptibility after background subtraction assuming the raw data given in the right panel of Fig. 12, i.e., with the new temperature scale. Note that the jump reported to occur around 55 K, shown in the right panel, is no longer there.

A magnetic susceptibility measurement of sulfur hydride has not been independently reproduced. In view of the results presented here, we urge that these experiments be repeated to establish whether or not they provide support for the claimed superconductivity of sulfur hydride. We predict they will not. Nor has other claimed magnetic evidence for superconductivity of sulfur hydride been independently reproduced, and its validity has been questioned.

V. CONCLUSIONS

In this paper, we have analyzed the raw data [21] associated with the ac magnetic susceptibility measurements of sulfur hydride [8] that were interpreted as providing evidence that sulfur hydride under pressure became superconducting [8, 9], supporting the claim of ref. [1]. We concluded that the published data were correctly inferred from raw susceptibility data and background signal by subtraction, as given by Eq. (1).

However, when considering the rate of change of temperature of the system shown in the raw data for the cases where a superconducting transition was supposedly detected, we found an anomalous jump that exactly lines up with the inferred transition temperature. This, and the fact that the anomaly is not found in the background signal measurements, strongly suggests that the observed change in slope of the susceptibility curve is not an indication of a superconducting transition but instead is an experimental artifact.

Furthermore, we hypothesized that as a consequence of this experimental problem the measurements of the temperature were not necessarily accurate, and with small modifications of the temperature scale we showed for two cases that the jumps interpreted as indicating a superconducting transition completely disappear.

It should also be noted that the rise in the amplitude of the signal right before the assumed superconducting transition as the temperature is lowered seen in Fig. 1b, for 130 GPa, is anomalous. The drop in susceptibility due to the onset of superconductivity should not be preceded by a susceptibility rise. In the raw data, this is signaled by the flattening of the curve seen in the upper left panel of Fig. 3. This fact alone should cast doubt on the validity of the results reported in Fig. 1b, even in the absence of the other anomalies pointed out in this paper.

Ac magnetic susceptibility measurements of sulfur hydride have not been independently reproduced. In view of the results presented here, we urge that these experiments be repeated to establish whether or not they provide support for the claimed superconductivity of sulfur hydride. We predict they will not. Nor has other claimed magnetic evidence for superconductivity of sulfur hydride been independently reproduced, and its validity has been questioned.

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Appendix A: Additional information

A shortened version of this paper [29] (due to length constraints in the journal) was published in Nat. Sci. Rev. as a Comment to Ref. [8]. In a Reply [30], the authors of Ref. [8] argued that “our measured data demonstrate that there are no relationships between the superconducting transitions and those temperature breaks.”

To address this point, we show in Fig. 14 the measured raw susceptibility data and the temperature increments, with high resolution, for two values of the pressure. It can be seen in Fig. 14 that the temperature values where the susceptibility sharply changes its slope and where the temperature increments sharply change, coincide to better than 1 part in 1000 for both pressure values. We argue that this indicates that with very high probability there is a relationship between the superconducting transition signals and the temperature breaks, contrary to what the authors say in their Reply [30].
FIG. 14: Comparison of the position of the breaks in the temperature increments $\Delta T$ and the kinks in the raw susceptibility data for pressure values 117 GPa and 130 GPa.

[1] A.P. Drozdov, M.I. Eremets, I.A. Troyan, V. Ksenofontov and S.I. Shylin, ‘Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system’, Nature 525, 73-76 (2015).
[2] W.E. Pickett and M.I. Eremets, “The quest for room-temperature superconductivity in hydrides”, Physics Today 72, 5, 52 (2019).
[3] J. A. Flores-Livas et al., “A perspective on conventional high-temperature superconductors at high pressure: Methods and materials”, Physics Reports 856, 1-78 (2020).
[4] K. Shimizu, “Investigation of Superconductivity in Hydrogen-rich Systems”, J. Phys. Soc. Jpn. 89, 051005 (2020).
[5] V. S. Minkov, V. B. Prakapenka, E. Greenberg and M. I. Eremets, “A Boosted Critical Temperature of 166°K in Superconducting $D_3S$ Synthesized from Elemental Sulfur and Hydrogen”, Angew. Chem. Int. Ed. 59, 18970 (2020).
[6] S. B. Zhang, M. Zhang and H. Y. Liu, “Superconductive hydrogen-rich compounds under high pressure”, Applied Physics A 127, 684 (2021).
[7] Y. Sun, H.Y. Liu and Y. M. Ma, “Progress on hydrogen-rich superconductors under high pressure”, Acta Physica Sinica 70, 017407 (2021).
[8] X. Huang et al., “High-temperature superconductivity in sulfur hydride evidenced by alternating-current magnetic susceptibility”, Nat. Sci. Rev. 6, 713 (2019).
[9] D. Semenok and A. R. Oganov, “Measuring the Meissner effect at megabar pressures”, Nat. Sci. Rev., Volume 6, 856 (2019).
[10] J. E. Hirsch and F. Marsiglio, “Absence of magnetic evidence for superconductivity in hydrides under high pressure”, Physica C 584, 1353866 (2021).
[11] I. Troyan et al., “Observation of superconductivity in hydrogen sulfide from nuclear resonant scattering”, Science 351, 1303 (2016).
[12] V. Struzhkin, “Squeezing into superconductivity”, Science 351, 1260 (2016).
[13] J. E. Hirsch and F. Marsiglio, “Meissner effect in non-standard superconductors”, Physica C 587, 1353896 (2021).
[14] J. E. Hirsch and F. Marsiglio, “Flux trapping in superconducting hydrides under high pressure”, Physica C 589, 1353916 (2021).
[15] S. Klotz, J.S. Schilling and P. Müller, Frontiers of High-Pressure Research 286, 473 (1991).
[16] Y. A. Timofeev et al., Rev. Sci. Inst. 73, 371 (2002).
[17] D. D. Jackson et al., Rev. Sci. Inst. 73, 2467 (2003).
[18] J. J. Hamlin, “Superconductivity studies at extreme pressure”, Dissertation, Washington University, 2007.
[19] M. Debessai, J.J. Hamlin and J.S. Schilling, “Comparison of the pressure dependences of $T_c$ in the trivalent $d$-electron superconductors Sc, Y, La, and Lu up to megabar pressures”, Phys. Rev. B 78, 064519 (2008).
[20] J. Song et al., “Pressure-Induced Superconductivity in Elemental Ytterbium Metal”, Phys. Rev. Lett. 121, 037004 (2018).
[21] X. Huang and T. Cui, private communications to author, 8/15/2021, 8/18/2021.
[22] E. Snider et al., ‘Room-temperature superconductivity in a carbonaceous sulfur hydride’, Nature 586, 373 (2020).
[23] M. Debessai, T. Matsuoka, J. J. Hamlin, J. S. Schilling and K. Shimizu, “Pressure-Induced Superconducting State of Europium Metal at Low Temperatures”, PRL 102, 197002 (2009).
[24] J. E. Hirsch, “About the Pressure-Induced Superconducting State of Europium Metal at Low Temperatures”, Physica C 583, 1353805 (2021).
[25] J. E. Hirsch, arXiv:2012.07537 v3(2020).
[26] J. E. Hirsch, arXiv:submit/3896758 [cond-mat.supr-con] 24 Aug 2021, arXiv:2110.12854v1 (2021).
[27] Ranga Dias, in “Feeling the Pressure”, by R. F. Service, Science Vol. 373, Issue 6558, p. 954 (2021).
[28] D. Semenok, private communication to author (2020).
[29] J. E. Hirsch, “Faulty evidence for superconductivity in ac magnetic susceptibility of sulfur hydride under pressure”, *National Science Review*, 9, nwac086 (2022).

[30] X. Wang, X. Huang, Y. Gao and T. Cui, “Reply: Faulty evidence for superconductivity in ac magnetic susceptibility of sulfur hydride under pressure”. *National Science Review*, 9, nwac087 (2022).