Absence of evidence of superconductivity in sulfur hydride in optical reflectance experiments

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In ref. 1, Capitani and co-workers reported infrared optical reflectance measurements that provided evidence for a superconducting transition in sulfur hydride (H3S) under 150 GPa pressure, and that this transition is driven by the electron–phonon interaction. Here we argue that the measured data did not provide evidence that the system undergoes a transition to a superconducting state, nor do the data support any role of phonons in driving a transition. The data are instead consistent with the system remaining in the normal state down to a temperature of 50 K, the lowest temperature measured in the experiment.

We requested all the raw data used in ref. 1 from the corresponding authors. We obtained data for temperatures of 50 K, 100 K, 150 K, 240 K and 320 K. The paper also presented data for temperatures 200 K, 130 K and 170 K, but we did not receive them.

Figure 1 shows raw data for H3S. These data represent an intensity detected at the spectrometer, and comprise a combination of black-body source radiation and reflectance off the sample and diamond anvil apparatus (T. Timusk and P. Roy, personal communication). In Fig. 1d we show for comparison the (presumably raw) reflectance data from a cuprate sample1. To remove non-intrinsic signals from the H3S data, the authors of ref. 1 plotted ratios of the intensity at different temperatures. This is shown in Fig. 1b, while the corresponding procedure for the cuprates is given in Fig. 1c.

At low temperatures, the cuprate reflectance flattens and approaches unity on the scale given by the superconducting energy gap \( \Delta \), estimated as \( \Delta \approx 43.4 \text{ meV} \) for that case. All cuprate reflectance curves, below and above the critical temperature \( T_c \), monotonically increase with decreasing frequency/energy (except for some sharp dips due to phonons) and approach unity at low frequency/energy. For a given frequency, the reflectance monotonically decreases as the temperature increases. In Fig. 1c, which shows the ratio of the reflectance for the two lowest temperatures for the cuprate, a peak is present, consistent with the expectation given in fig. 1b of ref. 1. One of these curves is at a temperature above \( T_c \), and also shows a gap, consistent with the original authors’ interpretation of their normal state data in terms of a pseudogap. By contrast, the reflectance ratios for H3S shown in Fig. 1b display a more complicated pattern.

The usual technique of evaporating gold on a free-standing sample to obtain an absolute reflectance is not feasible here (T. Timusk and P. Roy, personal communication). It is clear that the main intensity in Fig. 1a has large contributions from sources other than the H3S sample. Capitani and colleagues corrected the spectrum for an admixture with light reflected from the NaCl-coated gasket. Using equation (3) in the supplementary information of ref. 1 we could relate the ratio of the sample reflectance in the superconducting and normal state to the ratio of intensities at the same two temperatures:

\[
\frac{R_s}{R_n} = \frac{I_s}{I_n} - \frac{\alpha}{R_n} \left( 1 - \frac{I_s}{I_n} \right),
\]

where the parameter \( \alpha = 0.13 \) if we use the values for \( R_s \) and \( \alpha \) provided in ref. 1. \( R_s/R_n \) is the reflectance ratio and \( I_s/I_n \) is the intensity ratio. Note that in ref. 1, \( \alpha \) is the fraction of the nominal sample beam that misses the sample surface and falls on the NaCl gasket, and \( R_c \) is the reflectance of the NaCl gasket. As the second term on the right-hand-side of equation (1) is at most on the order of 2% and tends to correct the ratio towards unity, we approximated the ratio of reflectances by the ratio of intensities. Thus, a comparison between Fig. 1b and Fig. 1c suggests that the reflectance ratios in the case of H3S do not indicate superconductivity.
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To zoom in on this issue, in Fig. 2 we show the intensity raw data and ratios in the energy range 65–100 meV that was used in ref. 1 to infer that H$_3$S undergoes a superconducting transition. The solid curves on the right panel are taken from fig. 2b of ref. 1; however, to match the measured data we had to shift the blue curve given in ref. 1 downwards by 0.042 and the red curve upwards by 0.016, which are significant shifts on the scale shown. The fact that the low-temperature reflectance ratio is smaller than the high-temperature reflectance ratio, opposite to what ref. 1 showed, directly contradicts the interpretation that these features are “in good agreement with the theoretical gap structure”1,4. Figure 2a shows that both the temperature and energy dependence of the measured curves are dominated by effects not coming from the H$_3$S sample. Thus, Fig. 2 indicates that the curves shown in the paper were not “the measured $R_n(T)/R_n^{\infty}$ as claimed in ref. 1, but instead the measured $R(T)/R^{\infty}$ shifted as described above. This shift is crucial as the published data in ref. 1 report a temperature dependence that is opposite to what the measured raw data show. The authors concluded from their fig. 2b that “the intensity of this feature and its temperature dependence are in good agreement with the theoretical behaviour of the superconducting gap”. Instead, we conclude that the data plotted in fig. 2b of ref. 1 resulted from an alteration of the measured data, which otherwise provide no support for the existence of a superconducting gap.

Ref. 1 also presents reflectance ratios in fig. 3b in the energy range 450–600 meV, reproduced here in Fig. 3b. The authors claim that their positive slope and temperature dependence is in agreement with theoretical calculations and that it “demonstrates that H$_3$S is an Eliashberg superconductor, driven by the electron–phonon interaction with strong coupling to high phonons of order of 200 meV”. However, in Fig. 3a we plot the indicated reflectance ratios obtained from the raw data sent by the authors. The red points in Fig. 3a should correspond to the light blue curve in Fig. 3b, whereas the blue points in Fig. 3a, for a lower temperature, should have a steeper positive slope than the dark blue curve in Fig. 3b. Instead, both sets of points in Fig. 3a show a relatively noisy and flat behaviour that is qualitatively different from the behaviour in Fig. 3b in the same energy range (450–600 meV). For energies below 450 meV, not shown in Fig. 3b, the low-temperature (blue) curve in Fig. 3a shows a sudden sharp drop that is not predicted by the theory used in ref. 1 (see the dashed blue line in fig. 3a of ref. 1). It has been suggested that this is due to ice depositing on the diamond surface at low temperature (T. Timusk and P. Roy, personal communication). We argue that the measured data shown in Fig. 3a provide no support for the assertion of ref. 1 that the slope of the measured data in the region 450–600 meV is a signature of the expected behaviour for a superconductor. We found the same qualitative behaviour in other datasets shared by the authors of ref. 1 for different temperatures (two sets for $T=50$ K and $T=240$ K, three for $T=150$ K).

In summary, we argue that ref. 1 presents a misleading picture. Data for carefully selected small energy windows were chosen, ratios of measured quantities, rather than absolute values, were plotted, and measured data were altered in unexplained ways to arrive at the published data. The reader of ref. 1 is left with the impression that the reported optical measurements provided confirmation that (1) H$_3$S is a high-temperature conventional superconductor and (2) the electron–phonon interaction drives its superconductivity. Instead, we have shown here that the measured data provided support for neither conclusion. The measured data have major contributions from unknown sources that render them incapable of supplying any information about the existence or nonexistence of superconductivity in H$_3$S.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of
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Competing interests
The authors declare no competing interests.

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