Reply to “Comment on Nature 586, 373 (2020) by E. Snider et al.”

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In this paper, we respond to a recent criticism of our work on CSH, (1,2) raised by Hirsch and van der Marel on the arXiv (3). We point out that their non-peer reviewed critique stems from either a lack of scientific understanding or a failure to appropriately analyze raw data. We explain that the use of their “Unwrapped” method was inappropriately performed. (3) We present scientific evidence that this basic and fundamental failure used in their method results in the false representations set forth in Ref (3). We also note that the raw data of Refs (1,2) were made available to Hirsch before he and van der Marel posted their comments on the arXiv. (3) We stand by the findings and conclusions of Refs (1,2) and remain committed to the integrity in scientific research.

We aim to provide an understanding of the incorrect analysis of our work on CSH, (1) the first reported room temperature superconductor, by Hirsch and van de Marel as recently posted in the arXiv. (3) We will demonstrate that their use of “unwrapped” method is merely a misinterpretation of our measurements. Figure 1 is a graphical representation of their approach of obtaining a “null” signal for Fig 2g in Ref (3). We will clearly show that such an approach has no scientific merit or validity, and that their analysis in fact provides a null signal for any arbitrary signal.

![Fig. 1 Summary of the calculation carried out by the authors in Ref (3)](image)

Fig. 1 Summary of the calculation carried out by the authors in Ref (3) showing the steps of their "unwrapped" signal method. (left) Is the raw data – our user defined background (UDB_1). This is Col(B) of the excel file in Ref (3). (middle) Col(I) of the excel file in Ref (3), which is mathematically equivalent to the numerical integration from high temperature to low temperature of the differentiated signal of Col(B). This results in ~ mirror of the original signal. (right) Sum of the two data sets of the other two figures: (Col (J)) = signal (Col (B)) + ~ mirror of the signal (Col(I)); resulting in a null result for any arbitrary signal.
We once again emphasize the method of selecting the background as we described in the Ref. (2). In the side-by-side coil magnetic susceptibility experiments, the large background signal is unique to each experiment, is temperature dependent, can have varying profiles, and is a consequence of the makeup of the DAC (diamond anvil cell). However, the background can be approximated as linear in the region of the transition, and the susceptibility of the sample extracted after the background signal is subtracted from the raw data (as shown in Fig 2a). We described this in more detail by looking at the AC susceptibility data for CSH at 138 GPa in Ref. 2. In the raw data a temperature region immediately above and below the transition is selected (as highlighted in blue and shown in Fig 2b). The background profile is kept true but scaled to match the same signal strength of the raw data. This background profile is then subtracted from the raw data, providing a baseline value of zero for the susceptibility above $T_c$ (as shown in Fig 2b).

We further describe the user defined background. The background arises from fluctuating currents in the normal sample and the surrounding metals such as the gasket and cell; these give rise to a voltage in the pickup coil. We selected the background after carefully investigating the temperature dependence of the non-superconducting CSH sample at 108 GPa, the closest pressure prior to the superconducting transition. We note here that we did not use the measured voltage values of 108 GPa as the background. We use the temperature dependence of the measured voltage above and below the $T_c$ of each pressure measurement and scale to determine a user defined background (Fig. 2a). The scaling is such that one achieves an approximately zero signal above the transition temperature; the subtracted background isolates the signal due to the sample. We call this method “user defined background method 1 (UDB_1)” in this report. With UDB_1, one finds a signal as a function of temperature comparable to what one observes on a large sample where the background is insignificant. This procedure is either not understood or intentionally ignored by Hirsch and van der Marel in their recent comments on the arXiv. (3) In other words, the background is not an independently measured signal as Hirsch and van der Marel incorrectly claim. See Fig. 2. We chose the UDB_1 background as opposed to a simple linear function, which we

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**Fig. 2 AC susceptibility data.** (a) Raw data measured at 160 GPa. The profile of the regions highlighted in blue are used as part of the UDB_1. (b) Measured voltage from the susceptibility measurement explained in experimental details section in Ref. 1 and 2 for 160 GPa. Raw data (red), UDB_1 (blue) and raw data – UDB_1 (black).
examine later, to make sure we captured the response of the unknown background contributions. Furthermore, the temperature vs time profiles are extremely difficult to accurately replicate between runs and hence why we use the profiles from the same dataset, before and after the superconducting transition to generate a user defined background profile. We will show that the function of the background, although subtly affects the signal to noise, does not detract from the clear presence of the raw, measured susceptibility response of the superconducting transition that clearly matches the independent electrical transport measurements. The user defined background for subtraction is qualitative in nature and does not represent a physical quantity, and we will demonstrate other methods later in this paper.

Next, we calculate a susceptibility increments plot, a notation invented and defined by Hirsch and van der Marel in their comments on the arXiv as follows:

\[
\Delta \chi_i = \chi_{i-1} - \chi_i \tag{Eq. 1}
\]

Here, we note that this quantity \( \Delta \chi_i \) is approximately proportional to the numerical derivative with respect to temperature of a data set (assuming \( T_{i-1} - T_i \) is approximately the same for all points). Here we defined the equation 1, to match the sign of the figure 2b of reference (3). In typical susceptibility data, the numerical derivative (or \( \Delta \chi_i \)) is supposed to show a discontinuity near the superconducting transition temperature.

![Fig. 3. Calculated susceptibility increments \( \Delta \chi_i \) (Eq. 1.) where \( \chi_i \) is the Raw data - UDB_1.](image)

We first show \( \Delta \chi_i \) using the Raw data – UDB_1. The discontinuity near the superconducting transition temperature is visible even here around 170 K. We will later show how this compares to the differentiated raw signal. We thus suspect that Hirsch and van der Marel failed to perform analysis on the raw data that was readily available to them.

As a consequence of the approach, we used to define the user defined background, “UDB_1”, (1) the results show a stepwise effect, which is highlighted in Hirsch and van der Marel’s comments.
(3) This effect is a consequence of the user defined background, which, as noted, Hirsch and van der Marel incorrectly identified as an independently measured data set.

Subsequently, we further show this by plotting the quantity $\Delta \chi_i$ in three different ways as follows:

1. using raw data (measured voltage)
2. using raw data – user defined background method 2 (UDB_2)
3. using raw data – user defined background method 3 (UDB_3)

With this methodology, user defined background method 2 (UDB_2), user defined background method 3 (UDB_3) are defined as described below. By using different backgrounds, we demonstrate that irrespective of the background used, the superconducting signal is clearly visible both in raw data and any of background subtracted data.

User defined background method 2 (UDB_2)

We fit the data just before the superconducting transition, $170.311 \text{ K} < T < 173.0403 \text{ K}$, using a linear fit, $Y = -1.3629 x + 8267.6168$. We use this linear equation to generate background points for each corresponding temperature point of the raw data.

User defined background method 3 (UDB_3)

We apply a shift to the raw data after the superconducting transition, $166.9137 \text{ K} < T < 169.5824 \text{ K}$, with a shift to match the trend of the raw data before the transition $170.3110 \text{ K} < T < 173.0403 \text{ K}$. We use these two ranges as a combined data set and using a linear fit, $Y = -0.67088 x + 8148.6442$. We use this linear equation to generate background points for each corresponding temperature point of the raw data.

These two methods are illustrated in Figure 4.

![Figure 4](image.png)

Fig. 4. Illustration of the background used as (a) “UDB_2” (b) “UDB_3” as described in the text for the measurement at 160 GPa.
Figure 5 shows the signal (raw data – background) after using “UDB_1”, “UDB_2” and “UDB_3” as the background. It is clearly visible that depending on the user defined background, the absolute values show slight differences in each method. However, the overall behavior of the transition is readily visible irrespective of the choice of the background. That is, the signal (raw data – background) above the transition T > 170.5 K fluctuates around zero due to noise in the extreme experimental conditions at 160 GPa and shows a clear drop at the superconducting transition temperature (Tc). For T < 169 K, the signal again shows fluctuations due to the experimental noise. This is the well-established behavior of high-pressure AC-susceptibility data, and this is common knowledge in the field of high-pressure superconductivity. However, considering the misplaced concern raised by Hirsch and van der Marel, we feel compelled to elaborate and further explain these fundamental concepts.

We also note here that the artifacts of Figure 2 (c) and (d) of the Ref (3) by Hirsch and van der Marel are due to the user defined background subtraction method 1 (explained above). As shown in below Figure 6, there is no artifact when the Background Method 2, Background Method 3 are used to obtain the signal. Therefore, it is obvious that the original user defined background for 160 GPa created the artifacts.
Fig. 6. (a), (b) Signal (raw data – background) after using “UDB_1”, “UDB_2”, and “UDB_3” as the background. (c), (d) Figure 2 (c) and (d) of the Ref. 3 (arXiv:2201.07686v1).

Fig. 7. (a) Calculated susceptibility increments $\Delta \chi_l$ (Eq. 1.) with $\chi_l$ used as (i) the Raw data (ii) the Raw data – UDB_1 (iii) the Raw data – UDB_2 (iv) the Raw data – UDB_3. (b) Derivative of the raw data.
Next in Figure 7, we show the calculated susceptibility increments (Eq. 1.) using user defined backgrounds.

For Raw data, Raw data – UDB_2 and the Raw data – UDB_3, the quantity $\Delta\chi_l$ is randomly scattered around a slightly positive average value, with a peak at the superconducting transition temperature $T_c$. This is exactly the behavior one should expect for an AC susceptibility signal. No artifacts or stepwise effect is visible for (1) the Raw data, the Raw data – UDB_2 and the Raw data – UDB_3. This again shows that the artifact of $\Delta\chi_l$ questioned by Hirsch and van der Marel is due to the user defined background (UDB_1) we describe above. And we again emphasize that, irrespective of which analysis method is used, an unbiased and scientifically informed reader can easily see the susceptibility signal.

Next, we show susceptibility data of a new sample (unpublished) with $T_c \sim 235$ K and a similar analysis. This data shows a clearer signal due to less extreme conditions and a larger sample size.

![Graphs showing susceptibility data and analysis](image)

Fig. 8. Susceptibility data of a new sample (unpublished) and its analysis of (a) Raw data (b) Linear fit to determine the background (c) Raw data – Background (d) and (e) Calculated susceptibility increments $\Delta\chi_l$ (Eq. 1.) with $\chi_l$ used as (d) the Raw data (e) the Raw data – Background.
Now that we have demonstrated that the artifact shown in Ref. (3) by Hirsch and van der Marel is due to a user-defined background, we will discuss how they arrived at their conclusions. In particular, we will show that the analysis by Hirsch and van der Marel is non-scientifically based.

Hirsch and van der Marel included the Excel sheet from which they did their calculations. We paste a snapshot of the Excel sheet and their explanation for each column in the readme sheet. The link to their original spreadsheet, as of today, is as follows:

http://dirkdavendamarel.ch/wp-content/uploads/chi.xlsx.

If we examine each column, we see that:

A(j) = Temperature
B(j) = Signal = Raw data – user defined background 1
E(j) = B(j-1) – B(j)
F(j) = E(j)/arbitary factor
*arbitary factor used by Hirsch and van der Marel in Ref. 3 = 0.1655
G(j) = Hirsch and van der Marel changed this value by hand by looking at the artifacts of F(j) in a non-scientific way. We note here that this is equivalent to rounding to the nearest integer of F(j). Below we plot (Fig. 9) and show that even with mathematical rounding, their method follows the same procedure.
H(j) = H(j-1) + G(j) This is the cumulative summation of column G.
I(j) = H(j) x arbitary factor (0.1655)
J(j) = B(j) + I(j) This is their “Unwrapped Signal,” which in simple terms is the background subtracted signal + cumulative summation of \( \Delta \chi \) (~ summation of approximate derivative of signal)
K(j) and L(j) is irrelevant for our analysis.

We show in Figure 9 the calculations done by Hirsch and van der Marel in their Figure 2 e-g of Ref. 3 for their hypothesized “Unwrapping” method. Black points represent our user defined background 1 subtracted signal (raw data – UDB 1). Red points represent the quantity they calculated in column I(j) of their Excel file, which is just the cumulative summation of \( \Delta \chi \). Here we point out that in their intermediate step column, G(j), they hand pick values without any scientific basis. For comparison, we carried out the same steps with rounding off to the nearest integer, since 97.77% of the values are the same as rounding off column I(j). They handpick values for temperatures between 172.2331 and 172.1116 K. This is evident from the magenta and red curves of Figure 9. Red and magenta curves deviate only after 172.2331 K. Therefore, rounding off I(j) is identically the same for their method. We emphasize this point applying their incorrect analysis to both our raw data of CSH 160 GPa and the 0 GPa data of the well-known superconductor MgB\(_2\) (Figure 10).
Before moving into further analysis of our raw data and MgB$_2$, we discuss the behavior of the steps Hirsch and van der Marel employed and the resulting “unwrapped” curve. We note here that their calculated quantity $I(j)$ is nothing but **right to left integration** of the derivative of any data set. As a result, $I(j)$ shows the mirror image of the data around the y-axis. Therefore, when $I(j)$ is added to the data set, the resulting curve will cancel out. Hirsch and van der Marel could have easily visualized this if they had followed our approach for our Figure 9.

![Figure 9](image)

**Fig. 9.** Analysis done by Hirsch and van der Marel in their figure 2 e-g for Ref. 3. We show here the steps of their hypothetical “Unwrapping” method. See legend and text for the information of each curve.

![Figure 10](image)

**Fig. 10.** Similar analysis done by Hirsch and van der Marel (3) figure 2 e-g for our raw data of CSH 160 GPa and for 0 GPa data of the well-known superconductor MgB$_2$.

Figure 10 shows that even for the well-known MgB$_2$ system, the superconducting signal becomes null when using the “Unwrapped” method of ref 3.
Finally, we would like to point out that the main accusation made by Hirsch and van der Marel is based on their inappropriate reverse engineering process of the data they describe in Ref. 3:

“By shifting continuous segments of the curves by an amount 0.16555n, with n integers that can be read off from Fig. 2b, it is a simple and straightforward task to ‘unwrap’ the vertical offsets [6]. The result for the two separate ranges above and below 170 K is displayed in Fig. 2e and f, and for the full range in panel g. Comparing panel e to c, and f to d we can verify that the resulting curves are extremely smooth and completely free of discontinuities. Comparing panel g to a we see that the steep rise at 170 K is absent from panel g.”

To the best of our knowledge, it appears that Hirsch and van der Marel created an “unwrap” methodology of using the background subtracted data to be presented to the scientific community as raw data as shown in Figure 2g of Ref (3). They then allege that we manipulated the data to make it look like Figure 2a. (3) In simple mathematical terms, Hirsch and van der Marel performed a numerical integration of the derivative of the background subtracted signal. However, they evaluate the integral from the right end point to the given value which resulted in a mirror signal for column I(j) in their excel file. After adding the signal to the integrated signal (mirror signal), the final answer is a null result. Their calculation is true for any arbitrary function and has no scientific value in terms of our research and conclusions related to CSH superconductivity. In addition, conclusions they made on the observed artifacts in $\Delta \chi$ are misleading since they ignored the raw data (measured voltage) and instead performed their calculations on the already subtracted background data. Had they paid sufficient attention to the raw data, they would have observed that the raw data clearly shows what is expected in terms of the measured superconducting signal. We have clearly demonstrated here that irrespective of the method of selecting the background the superconducting signal is clearly visible.

We expect the scientists’ intent on critiquing our project would, at the very least, consider their own fundamentally simple linear background (example shown in Fig. 4) for the raw data that we made publicly available in Ref (2). By seemingly ignoring our raw data in their assessment and performing an inaccurate method to show a null signal, authors of Ref (3) misled the scientific community. For these reasons, the scientific community should perform their own analyses, leading to a rejection of Hirsch and van der Marel’s hastily posted and scientifically unsubstantiated arXiv comments. (3)

(1) E. Snider, N. Dasenbrock-Gammon, R. McBride, M. Debessai, H. Vindana, K. Vencatasamy, K. Lawler, A. Salamat, and R. Dias, Nature 586, 373 (2020).

(2) R. Dias and A. Salamat, “Standard Superconductivity in Carbonaceous Sulfur Hydride”, arXiv:2111.15017, Dec. 28, 2021.

(3) D. van der Marel and J. Hirsch “Comment on Nature 586, 373 (2020) by E. Snider et al”. https://arxiv.org/pdf/2201.07686.pdf (2022).