

Comment on “Evidence of a first-order phase transition to metallic hydrogen”

Ross T. Howie,¹ Philip Dalladay-Simpson,¹ and Eugene Gregoryanz^{1,2,3}

¹Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China

²Key Laboratory of Materials Physics, Institute of Solid State Physics, CAS, Hefei 230031, China

³Centre for Science at Extreme Conditions and School of Physics and Astronomy,
University of Edinburgh, Edinburgh EH9 3FD, United Kingdom

(Received 28 December 2016; published 4 October 2017)

A recent article by Zaghoo *et al.* [*Phys. Rev. B* **93**, 155128 (2016)] presented high-pressure high-temperature optical experiments claiming the observation of a first-order transition to atomic liquid metallic hydrogen. Here, we demonstrate that the experimental evidence presented is unsubstantial for such a claim. Furthermore, the claimed results and conclusions contradict previously published works, including those by the same research group.

DOI: [10.1103/PhysRevB.96.157102](https://doi.org/10.1103/PhysRevB.96.157102)

Zaghoo *et al.* [1] adopts an indirect method in an attempt to observe the latent heat of the hydrogen molecules' dissociation to determine a phase transition in liquid H₂. The phase-transition criterion used is a claimed plateau in the tungsten coupler's temperature dependence with laser power. Reference [1] provides the transmission of the sample with 633-nm laser light and reflectance with 514- and 980-nm laser light at 170 GPa, stating that the observed decrease in transmission and increased reflectivity constitute a first-order transition in the hydrogen sample to a metallic state. The authors employ a meaningless procedure to normalize their transmission/reflectivity spectra at 170 GPa measuring a different empty cell ‘for the index of air in the gap between diamonds’ to correct for that of ‘high-pressure hydrogen’, which is unknown. The study does not provide any convincing measurements of the samples' physical properties and is therefore highly arguable. The validity of the employed technique is also questionable as discussed by previous appraisals [2]. Failure to provide any measurements directly related to hydrogen itself is a serious issue considering the difficulties associated with pressurizing and heating hydrogen in a diamond-anvil cell. The authors do not provide clear or complete Raman spectra *before* and *after* any heating run but only vibrational modes as a function of pressure [see Fig. SI2 in Supplemental Materials in Ref. [1]], thereby failing to demonstrate that the sample did not react with its surroundings. Instead, the authors present isolated isobaric data sets collected from the coupler and provide arbitrary *guides to the eye* to justify their claimed plateaus. However, when these *guides to the eye* are removed and the data sets are considered as a whole (see Fig. 1; we also have added the data from the group's previous study [3]), the plateaus become completely indistinguishable, inconsistent with one another and easily attributed to the technique's inherent experimental error.

Indeed, the authors themselves admit that the plateau could be either “*interpreted as being due to heat of transformation (energy goes into latent heat) or due to increases in reflectance*”, both of which are highly speculative, by no means conclusive, and contradict their own previous study on the melting line [4]. Comparing these studies immediately raises the concern that, if the plateau in Fig. 2 of Ref. [1] is due to latent heat, then why are there not two plateaus demonstrating both the solid-liquid melt and the previously claimed liquid-liquid transition? We also note that the finite

element analysis (FEA) studies [5,6] suggested that in the given experimental configuration (e.g., not enough hydrogen in the sample chamber) the phase transition would, at best, manifest itself not by a plateau but by a gradient change in the temperature curve vs laser power. This is interesting when reviewing the literature as the authors' have previously changed their argument to suit the FEA findings [5,6], inconsistently citing it as an explanation for the absence of the plateau [3], whereas completely disregarding their previous work observing a plateau-like nature [4]. We also remark that when the authors present the phase diagram they show a smooth melting curve [1,3] which does not have a sharp maximum at ~65 GPa [7,8] as they previously claimed using the questionable latent heat measurement method [4].

If one assumes that the plateau is due to an increase in reflectance, then the authors cannot rule out chemical

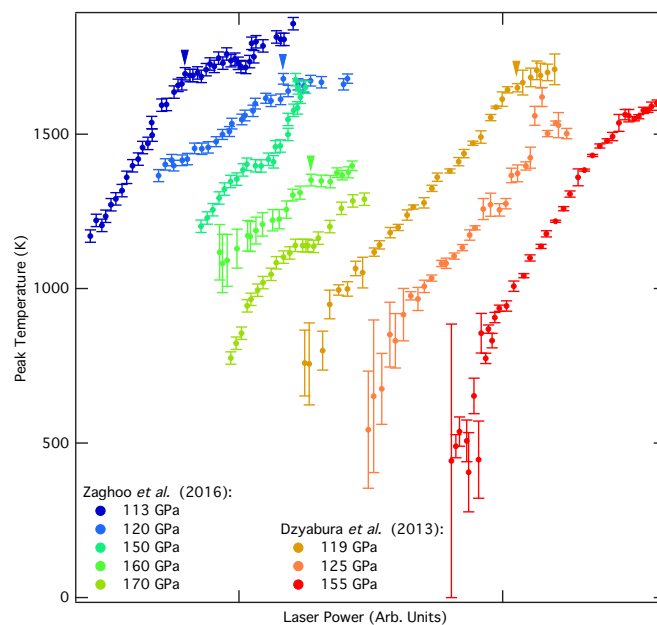


FIG. 1. Combined coupler temperature vs laser power from both Refs. [1,3] illustrating no obvious or consistent plateaus (where the corresponding arrows represent the authors' designation) when the datasets are presented together and the authors' *guide to the eye* is not used.

reactivity among the hydrogen, the diamond coatings, and the absorber (see also above). This change is far more likely the cause of the change in absorbance, and hence the perceived temperature plateau. Indeed, the authors critically admit in the Supplemental Material (see Fig. SI7 in Ref. [1]) that in some runs the absorber would deteriorate, causing a plateau at a much different temperature and laser power. The authors simply cannot claim a phase transition, based

solely on experimental data that can be so wildly altered ($\Delta 200$ K, $\Delta 200$ mW) by changes in the absorber under heating and upon consideration, does not come from the sample.

In conclusion, the experimental evidence presented for a “*first-order phase transition to metallic hydrogen*” state by Zaghoo *et al.* [1] is unsubstantial, which renders the claim as purely speculative.

-
- [1] M. Zaghoo, A. Salamat, and I. F. Silvera, *Phys. Rev. B* **93**, 155128 (2016).
[2] A. Goncharov, R. J. Hemley, and E. Gregoryanz, *Phys. Rev. Lett.* **102**, 149601 (2009).
[3] V. Dyzabura, M. Zaghoo, and I. F. Silvera, *Proc. Natl. Acad. Sci. USA* **110**, 8040 (2013).
[4] S. Deemyad and I. F. Silvera, *Phys. Rev. Lett.* **100**, 155701 (2008).
[5] J. Montoya and A. F. Goncharov, *J. Appl. Phys.* **111**, 112617 (2012).
[6] Z. Geballe and R. Jeanloz, *J. Appl. Phys.* **111**, 123518 (2012).
[7] R. T. Howie, P. Dalladay-Simpson, and E. Gregoryanz, *Nature Mater.* **14**, 495 (2015).
[8] P. Dalladay-Simpson, R. T. Howie, and E. Gregoryanz, *Nature (London)* **529**, 63 (2016).