Reply to "Comment on 'Evidence of a first-order phase transition to metallic hydrogen'"

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Howie, Dalladay-Simpson, and Gregoryanz Phys. Rev. B **96**, 157102 (2017) comment on our observation of liquid metallic hydrogen (LMH). All of their objections are answered in our response. The experimental observation of LMH at static pressures stands on firm ground.

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In our experiment to produce liquid metallic hydrogen, we add energy by pulsed-laser power absorbed in a thin semitransparent tungsten film that heats the hydrogen pressed against the film. We measure the corresponding temperature rise of hydrogen and find a plateau that we associate with a predicted phase transition. In principle this would be a direct method, but it is not quantitative, as our cell is not adiabatic and there are heat losses to the diamonds and gasket, discussed in our paper. These temperature vs laser power heating curves slowly change as P,T conditions change, so that the occurrence of a plateau is attributed to the heat of transformation. Earlier, Dzyabura *et al.* [1] found plateaus believed to be associated with the plasma phase transition (PPT) to liquid metallic hydrogen, but had no evidence of metallization at the transition. Howie, Dalladay-Simpson, and Gregoryanz (HDG) [2] quote us as saying "stating that the observed decrease in transmission and increased reflectivity constitute a first-order transition in the hydrogen sample." These words do not occur in our paper. In the abstract we state "We present evidence supportive of a first-order phase transition accompanied by changes in transmittance and reflectance, characteristic of a metal," and in the text "We believe that the plateaus we observe in our heating curves arise from latent heat of dissociation, associated with a first-order phase transition." We identified the phase transition from the plateaus in the heating curves, not the reflectance and transmission.

HDG state "The authors normalised their transmission/reflectivity spectra at 170 GPa to that of high-pressure hydrogen, which is unknown". It is clearly stated in the text (and Supplemental Material) that spectra (at a given pressure) measured above the plateau are normalized to spectra for temperatures below the plateau in which there is no evidence of metallic reflectivity or absorption (see Fig. SI4 of our paper). These spectra are measured and thus known in our experiments. The raw data for such observations are shown in Fig. 1 below, corresponding to data points in Fig. 4 of our paper [3].

They also state "Failure to provide any measurements directly related to hydrogen itself . . . ". In the Supplemental Material, Fig. SI2, we show the characteristic Raman vibron spectra of hydrogen that were measured before each heating curve scan. Similar spectra were measured after each scan to demonstrate the continuity of the sample, but were not shown, only stated in the caption. HDG: " . . . the authors cannot rule out chemical reactivity among the hydrogen, the diamond coatings, and the absorber . . . ". Figure 2 [3] shows heating curves for three absorber surfaces that have the same plateaus, as a demonstration that the plateaus are not due to a reaction of hydrogen with the absorber. Ohta *et al.* [4] used a different surface, gold, and found P,T points that lie on the same line that we found. We measure the transmission/reflectance signals of hydrogen for several wavelengths, shown in Fig. 4 [3]. These are characteristic of a metal for a film of hydrogen that is thickening above the transition temperature, and the thick film reflectance value is in good agreement with theory and earlier shock experiments (references are in our paper). Strong evidence for hydrogen's metallization, which HDG ignore, is hydrogen's high optical reflectance measured in the region of (1–2.33 eV), not only at 980 nm as the comment claims. Analysis of the optical data reveals distinct free-electron behavior [5]; the reflectance of hydrogen increases as a function of increasing wavelength.

HDG replot our heating curve data in their Fig. 1, stating " . . . plateaus become completely indistinguishable, inconsistent with one another . . . ". They also plot earlier data [1] in an experiment using smaller-area, thick, nontransparent Pt absorbers. The latter were the first indication of plateaus and stimulated the development of our technique, enabling the improved measurement of heating curves and of optical properties to demonstrate that metallization occurs at the plateaus. The P,T values of the plateaus are in fact distinguishable and consistent. These are shown in Fig. 1 [3], with the uncertainties falling within the data symbols. The plateau regions are clear in our figures; in their Fig. 1, HDG do not show our original data, but distort our heating curves by stretching the vertical axis to suppress the visual indication of the plateaus.

HDG bring up several points that are clearly discussed in the paper. They state " . . . failing to demonstrate that the sample did not react with its surroundings." As stated above, Fig. 2 of our paper [3] shows that plateaus occur at the same P,T points for three different absorber surfaces, confirming that the plateaus are not due to contamination or chemical activity. HDG state "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". We point out (see Fig. 4 in Ref. [3]) that the reflectance is negligible in the region of the plateaus, leaving heat of transformation as a remaining source of the plateaus. They question why we did not see a plateau for the

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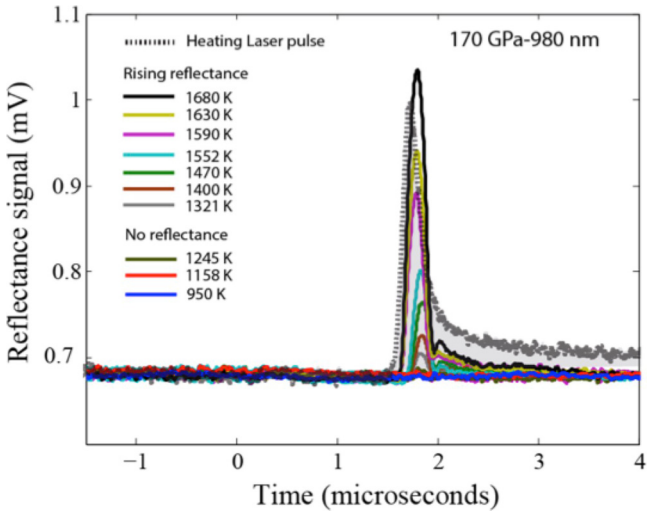

FIG. 1. Raw un-normalized data for the reflectance signal as a function of time, showing rising reflectance when the heating laser pulse is on, for temperatures higher then T_c. The 1680-K curve is in the region of bulk saturation of Fig. 4 in our paper [2]. Normalization yields $R_s + 1$, discussed in Supplemental Material of our paper [2].

melting line, as observed in earlier experiments [6]. In the current experiment, temperatures probed were $\sim 2\times$ higher than those probed for the melting line.

Since the spectral irradiance in a narrow frequency band scales as T^5, the signal-to-noise (SN) for measuring T in the region of melting would be reduced by an enormous factor, ~ 32, requiring a measurement time $(32)^2$ longer to achieve the same SN. Thus, we focused on the region of the PPT. In measurements of the melting line [6], different techniques were used to enhance the signal-to-noise ratio. HDG compare our results to an earlier finite-element analysis (FEA). Those calculations analyzed geometries different from ours. A FEA should include the relevant physics to explain the observed phenomena. They also remark that we use a smoothed curve to represent the melting line in Fig. 1 [3]. This curve was a referenced theoretical curve. The melting line data points from different measurements were shown in Fig. 1 [3], so there should be no confusion. HDG state: "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." Our samples were regularly examined and data from deteriorated absorbers were not used.

To conclude, the comments by HDG do not reveal any flaws in our analysis. We provide evidence of the phase-transition line for the insulator-metal transition in dense fluid hydrogen under static pressure conditions. The observed energy dependence of the optical reflectance is consistent with the free-electron model. Our reported phase line and a recent sophisticated quantum Monte Carlo theory [7] are in good agreement and consistent with other recently reported static [4] measurements. Shock-wave experiments [8–10] on hydrogen or deuterium heat above the PPT phase line to show metallization of hydrogen.

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