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

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Zaghoo *et al.* [Phys. Rev. B **93**, 155128 (2016)] report on the observation of a first-order phase transition to metallic hydrogen at pressures of 100–170 GPa and high temperatures of 1100–1800 K. Here, based on the analysis of their optical spectroscopy data and finite element calculations, we show that the presented data do not support the existence of such a transition at their claimed T_c and are likely related to a continuous band-gap reduction.

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A recent paper by Zaghoo *et al.* [1] presents optical data at high pressures and high temperatures and interprets the data as evidence for a first-order phase transition to metallic hydrogen during heating.

Here we argue that the presented data are contradictory with these claims. Elucidating this issue is important for building a coherent picture that is emerging as the result of theoretical calculations of various levels [2–4] and experimental investigations employing static and dynamic compression techniques [5,6]. In this context, the use of adequate probes of the electronic and chemical states is crucial. Optical probes [1] that do not address the energy-dependent conductivity while making multiple references to the Drude model are highly speculative. Indeed, the available dynamic and static compression data and theoretical modeling show that the study of energy-dependent conductivity is important for understanding the nature of hot dense hydrogen (see Ref. [6] and references therein). We stress that the available information about *P-T* conditions of the plasma transition and position of the critical points is contradictory [3–5] thus making it very important to obtain the reliable experimental results. Below we concentrate on inconsistencies in the interpretation of data in Ref. [1], which call for careful examination of their claims and further detailed investigations. We analyze their optical data and use finite-element (FE) calculations and argue that the high-temperature state studied in Zaghoo *et al.* [1] well above their claimed transition temperature T_c (at least 10%) is not metallic and that the data cannot discriminate between a first-order phase transition and a continuous phase transition or even a band-gap drop within one phase.

Observations of plateaus in temperature versus heating power are the purported evidence for a first-order phase transition. In particular, Zaghoo *et al.* [1] suggest that a 0.1-eV/molecule latent heat of dissociation of H_2 molecules is plausible and could explain the plateau. The latter argument is based on an energy balance estimate with limited analysis of heat transport from the tungsten laser absorber into the hydrogen medium. Our FE calculations of heat transport, on the other hand, show that latent heat must be orders of magnitude larger than 0.1 eV/molecule to cause plateaus similar in magnitude to those shown in the measurements of Zaghoo *et al.* [1]. In particular, we assume the physical properties and sample chamber geometry of Table I, a laser pulse with a shape of Ref. [1] shown in Fig. 1, and the finite-element solver of Ref. [7]. We find that the latent heat of a transition at 1140 K and 170 GPa must be ∼3.8 eV/molecule to reproduce the measurements of Zaghoo *et al.* [1] (Fig. 2). A latent heat of ∼3.8 eV/molecule is implausibly high because the molecular binding energy (4.75 eV at ambient pressure) has been shown (both experimentally and theoretically) to decrease with pressure to much lower values [8,9]. We conclude that the observed plateaus are due to something besides latent heat. Figure 2 shows that an onset of absorption at $T_c = 1140$ K with a peak absorption coefficient of 0.1 μm^{-1} [6] is an alternative and more plausible cause of the plateaus. The plateau emerges as a result of change in the absorption mechanism in the cavity causing a gradual time-dependent growth of an absorbing hydrogen layer, reaching 270 nm in thickness in our calculations (Fig. 1). The presence of the absorbing hydrogen creates a different temperature profile in the sample cavity with less laser power reaching the tungsten absorber and laser energy being distributed into the sample causing the temperature to increase less than it would otherwise. This rearrangement results in a change in slope of the measured temperature versus the laser power remarkably similar to that of Zaghoo *et al.* [1] (Fig. 2). In this Comment these measurements have been modeled quantitatively based on physical principles, ruling out previous qualitative interpretations.

Decreases in optical transmission by 3%−20% and increases in reflection of up to 13% in the plateau region are interpreted as being due to the transformation of thin layers of hydrogen to a metallic state. In particular, Zaghoo *et al.* [1] estimate electrical conductivity of 2100 S/cm at 1250 K and 170 GPa. A 10-nm thickness of the transformed hydrogen is assumed. However, our heat-flow models show that the

TABLE I. Material properties and thickness of layers assumed in our finite-element calculations at 170 GPa.

	Hydrogen	Alumina	Diamond	Tungsten
Thermal conductivity (W/m/K)	100 and 10	100	2000	226
Specific heat capacity (J/kg/K)	15000	880	509	134
Density (kg/m^3)	772	5500	3500	30000
Layer thickness (μm)	0.270 and 0.090	0.05	30	0.01

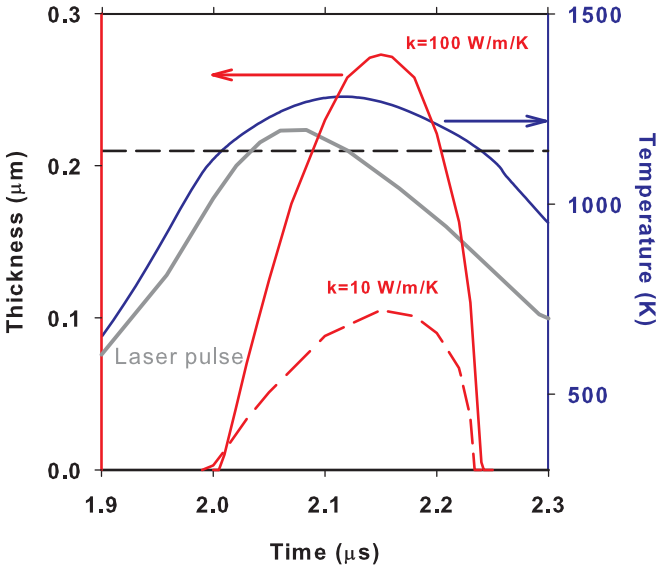

FIG. 1. The calculated thickness of transformed sample when heated to a maximum temperature of 1280 K, as in the experiments of Ref. [1]. The results for the hydrogen thermal conductivity of 100 and 10 W/m/K are shown by solid and dashed lines, respectively. The transformation temperature $T_c = 1140$ K, above which hydrogen begins absorbing is shown by a horizonatal dashed line.

thickness of transformed hydrogen reaches ∼200 nm (∼80 nm if the thermal conductivity of hydrogen is 10 W/m/K, which should be considered as a lowest reasonable value for this parameter) when the peak temperature exceeds the reported transition temperature by ∼100 K (as in the data used to esti-

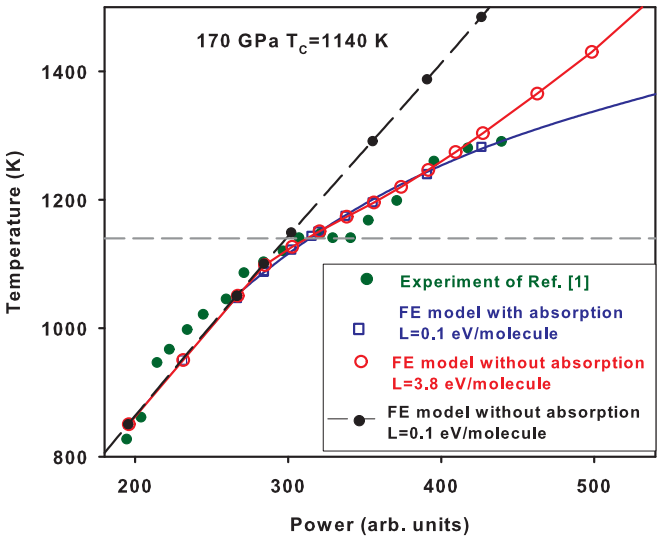

FIG. 2. The sample temperature versus the laser power measured radiometrically in Ref. [1] compared to FE calculations that assume that hydrogen absorbs above $T_c = 1140$ K and with no absorption. The calculations take into account the variable latent heat (L) associated with the transition at T_c (broadened by 100 K using the Gauss error function).

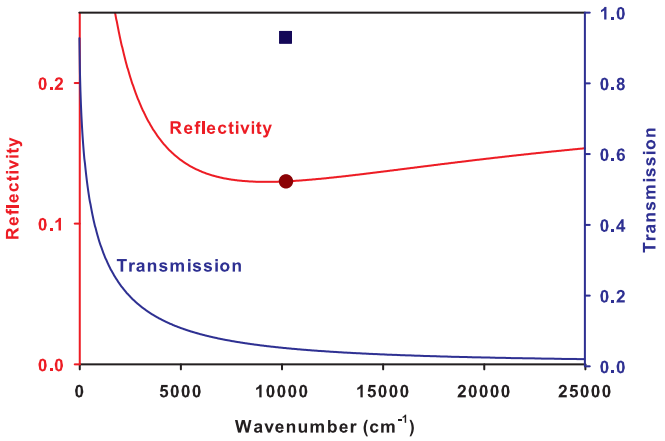

FIG. 3. The optical properties of hot hydrogen calculated using the Drude model with the following parameters: $W_p = 14.4$ eV, scattering time $\tau = 1.4 \times 10^{-17}$ s. The sample thickness is 200 nm. The solid points (the circle reflectivity and the square transmission) are from Ref. [1] for 980 nm, 170 GPa, $T = 1280$ K.

mate electrical conductivity in Ref. [1]). A 10-nm-thick sample can only be obtained in the regime of very small overheating of approximately 2 K above the T_c, which is experimentally not achievable. We present in Fig. 3 the Drude model that matches the observed reflectivity (13%) and assumes a "full dissociation" of hydrogen molecules but strongly disagrees in transmission value (5% versus 93% measured) requiring the sample to be only 4.9-nm thick to match the reported transmission. We find that the Drude model parameters of Fig. 3 yield the dc conductivity of 590 S/cm suggesting semiconductor or bad metal behavior. The electrical conductivity is even lower if non-Drude semimetal optical properties are accounted for [6].

To summarize, we refute the claim of Zaghoo *et al.* [1] that "Our pulses are carefully tailored to have just sufficient energy to metallize a thin film of hydrogen." Rather, relatively large increases in heating power and in peak temperature are needed to build up a layer of absorbing hydrogen that is measurable, meaning that a relatively thick layer (∼200 nm) is created. The reported plateau is unlikely due to latent heat as even such a thick layer does not produce an anomaly in temperature versus the laser power that would be consistent with plausible latent heat values. The optical properties of the layer of transformed hydrogen in the ∼140 K above the purported T_c are inconsistent with those of metal as reflectivity is too small and transmission is too large, making the claims of a sharp metallization premature. Hence, we find no reliable evidence for the adjectives in the paper's title; the hydrogen at high-temperature even 140 K above T_c is not necessarily metallic, and the detected transformation need not be a phase transition, much less a first-order phase transition. On the other hand, Zaghoo *et al.* [1] do show interesting changes in the optical properties of hydrogen that warrant further study.

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