TECHNICAL COMMENT

HIGH-PRESSURE PHYSICS

Comment on "Observation of the Wigner-Huntington transition to metallic hydrogen"

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Dias and Silvera (Research Article, 17 February 2017, p. 715) claim the observation of the Wigner-Huntington transition to metallic hydrogen at 495 gigapascals. We show that neither the claims of the record pressure nor the phase transition to a metallic state are supported by data and that the data contradict the authors' own unconfirmed previous results.

ias and Silvera (1) present only one experimental run claiming a record pressure of 495 GPa. The paper presents two figures of the phase diagram, iPhone photos of the sample, and the deduced reflectivity of four wavelengths only at the highest pressure point. The supplementary materials provide processed and fitted infrared (IR) absorption spectra from 135 to 335 GPa, the pressure versus force curve assuming a linear dependence, and the Raman spectra of the stressed diamond from 1200 to 2200 cm⁻¹. The absence of data combined with the uncritical claims have led to the unprecedented three comments (2–4) written within a month of publication of (1).

In the past 5 years, we have conducted ~120 experiments on hydrogen reaching above 200 GPa (5-10). In ~30 runs out of 120, the pressure exceeded 300 GPa, and in only 5 out of 120, the pressure exceeded 350 GPa. The extensive statistics show that the diamond culet sizes of 30 μ m diameter [used in (1)] could be used to reach maximum pressures of $\sim 315 \pm 10$ GPa with the probability of 20%. To reach pressures close to 400 GPa, with lower probability of 10%, the culet sizes of 15 µm must be used with the sample contracting to 2 to 3 µm at the highest pressure. Our statistics are in excellent agreement with other groups working on hydrogen at high pressure (11-13). The authors of (1) had two experimental runs in the past year using culets of 30 µm diameter (1, 14) claiming the unsubstantiated pressures of 420 and 495 GPa.

Dias and Silvera (I) claim that a combination of annealing, fine polishing, and coating the culet with Al_2O_3 has led to an increase in the maximum pressure with larger culets (and

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samples), compared with previous studies (5–13). Those techniques would likely decrease the probability of the premature failure due to hydrogen diffusion, but there is no supportive evidence that these techniques would improve the mechanical stability of diamond. The record pressure of 600 GPa was recently achieved on metals using a novel double-stage approach, with the pressure-generating area having a diameter of $3 \ \mu m$ (*15*) [smaller by a factor of 100 than the area in (*1*)].

Figure 1 shows the pressure-versus-load curve from (1), (4), and our own data. Dias and Silvera (1) use three different, nonoverlapping calibration methods at ~100 and ~300 GPa. Measuring pressure by estimating the load is not a direct method, as it does not probe the sample and/or calibrant in situ. The loading curve is unique for each experimental run and depends on the size of the culets, angles of the bevels, and compressibility of the gasket and sample. The dependency cannot be linear, as shown in (1), but always consists of three distinct regimes, each of which is sublinear with differing gradients: (i) plastic deformation of the gasket, (ii) sharp rise of pressure beyond the plastic deformation, followed by (iii) the much slower pressure increase due to the bending of the diamonds.

To make the dependence linear, Dias and Silvera (*I*) take a point from a different experiment (*I4*), rescaling it from 420 to 400 GPa, and plot four additional meaningless points of "visual observation." Pressures of 495 and 420 GPa were deduced from a single Raman spectrum, which does not cover a wide energy range showing the signal from hydrogen and/or pressure-induced fluorescence. This rules out any critical assessment



Fig. 1. Pressure versus load. (**A**) Our data and data from (4). (**B**) Data from Dias and Silvera (1). (**C**) Some raw IR absorption spectra provided but not plotted in (1) (in color). The black curves are normalized spectra taken from figure S1 in (1). We note that the intensity and frequency of the raw spectra at 338 GPa do not match those displayed in figure S1 in (1).

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Fig. 2. Photos of the sample from (1) and (14). (A) Photo of the semitransparent sample at 420 GPa from (14). (B) Photo of the dark sample at 415 GPa from (1). (C and D) Photos of the samples at 205 and 495 GPa from (1). We have used the 30 μ m stated by (1) as being the size of the culet as the scale to estimate the size of the sample. In the vertical direction, the sample reaches 15 μ m, which is almost twice as large as the 8 to 10 μ m stated in (1). For comparison, the size of the hydrogen sample at 390 GPa was ~2 μ m; see figure 3 in (10).

that the sample did not diffuse out and that the peak assigned to the stressed diamond is not due to any other factors.

The IR absorption data are consistent with the loss of the sample and contradict the authors' own previous claims (14). In Fig. 1, we plot the raw data provided by but not plotted in (1), together with the normalized spectra. The sample was clearly diffusing out between the claimed pressures of 314 and 338 GPa and ultimately was completely lost above this. The lack of IR transmission above 338 GPa and the fact that the "sample" appears dark at 415 GPa correlate with the gasket flow scenario we describe below. In (14), the authors present the same IR data up to 420 GPa but do not provide any explanation for why their results are so different in two consecutive experiments. Also, no explanation is given as to why there was no IR transmission/ absorption between 335 and 495 GPa, the pressure range in which hydrogen is semiconducting.

The analysis of the photos provided is also very consistent with the loss of the sample at an earlier stage in the experiment (Fig. 2). The sample at 415 GPa is expanded under pressure and is slightly bigger than at 205 GPa, whereas it is the same size at 495 GPa. In (8), we demonstrate, with photos of the sample up to 280 GPa, the flow of the metal gasket in the sample chamber as H₂ diffuses out of the chamber. As the chamber closes, the thin layer of hydrogen between the collapsed gasket and the diamond gives the dark appearance [compare figure 2B in (1) and figure 3 in (8)]. With the increasing pressure, all hydrogen diffuses out of the chamber, and the dark area, which could partially be rhenium hydride. becomes shiny as it bridges the anvils but would have different reflectivity from the rest of the gasket, as in figure 2C in (*I*) [see also the photo of "metallic hydrogen" in figure 3D in (*II*)]. Because the raw reflectivity spectra or their pressure dependence are not given, it is not possible to confirm the self-consistency of the measurements, as well as the claim of the increased reflectivity of the "sample" versus the rest of the gasket.

The presented phase diagrams [figures 1 and 4 in (1)] show an unconfirmed H₂-PRE phase for which no data are presented in the paper. The existence of this phase was surmised in (14), and even though no supporting data are given, Dias and Silvera (1) state, "after the 335-GPa pressure point resulted in our sample starting to turn black (Fig. 2B) as it transitioned into the H₂-PRE phase," which the authors claimed to be transparent [see figure 3S in (14)]. Furthermore, (1) cites one of the authors' own publications on the melting curve but, without any explanation, plots the smooth melting curve (see Fig. 1), contradictory to the authors' earlier claim about the existence of the sharp peak at 60 GPa.

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