Evidence of a first-order phase transition to metallic hydrogen

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The insulator-metal transition in hydrogen is one of the most outstanding problems in condensed-matter physics. The high-pressure metallic phase is now predicted to be liquid atomic from the low-temperature limit with the system in the ground state to very high temperatures. We have conducted measurements of optical properties of hot dense hydrogen in the region of 1.1–1.7 Mbars and up to 2200 K. We present evidence supportive of a first-order phase transition accompanied by changes in transmittance and reflectance, characteristic of a metal. The phase line of this transition has a negative slope in agreement with theories of the so-called plasma phase transition.

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I. INTRODUCTION

Theory and experiment have worked closely together for decades on the problem of metallic hydrogen. In 1935, 80 years ago, Wigner and Huntington predicted that solid molecular hydrogen would transform to atomic metallic hydrogen (MH) if pressurized to 0.25 Mbars (1 Mbar = 100 GPa) [1]. MH is predicted to have spectacular properties, such as room-temperature superconductivity [2], possible metastability, and a prediction that the megabar pressure atomic metallic phase may be a liquid in the limit that temperature approaches zero [3]. If metastable so that it exists at ambient conditions, MH would revolutionize rocketry as a remarkably light and powerful propellant [4]. In addition, the high-pressure molecular phase is also predicted to be metallic and superconducting [5,6]. Currently, static experiments at over 300 GPa have failed to reveal MH [7–11]. Modern calculations yield a transition pressure of 400–500 GPa for MH (see Refs. [12,13]). After briefly reviewing recent and historical developments we present an innovative method that allows measurement of transmittance (Tr) and reflectance (R) of hydrogen statically pressurized and heated to a metallic phase, reported recently [14].

In recent decades a remarkable change has developed for the phase diagram of hydrogen, shown in Fig. 1. The hydrogen melting line was predicted to have a nonclassical dome shape with a maximum at \( T \sim 1000 \text{ K} [15] \), confirmed by experiment [16–19]. The melting line was extrapolated to the low-temperature limit, to be consistent with earlier predictions (dashed line in Fig. 1) [3]. At high pressures, above the melting line in the liquid molecular hydrogen field there is a predicted line of a first-order liquid-liquid phase transition to atomic metallic hydrogen, involving dissociation of the molecules [20] and latent heat as the transition line is crossed. This has been named the plasma phase transition (PPT). Early considerations by Landau and Zeldovich [21] discussed a first-order insulator-metal transition (IMT) in mercury with a critical point. This was studied for dense matter by Norman and Starostin [22] (theories for hydrogen will be discussed later). In Fig. 1 the PPT line has also been extrapolated to meet the melting line; for higher pressures, solid molecular hydrogen melts to liquid MH. At lower pressures and higher temperatures it is predicted to have a critical point so that for pressures below the critical pressure, the dissociative transition is continuous. The PPT is a Mott transition to a metallic liquid, whereas, for example, a low to modest density of hydrogen can electrically conduct as a plasma at very high temperatures [23] but is not a metal! A common IMT in an ordered system involves overlapping energy bands; in disordered systems there are mobility bands. Mott has shown that metallization of disordered samples satisfies a minimum metallic conductivity condition [24].

As one traverses to ever-higher temperatures at high densities there is no phase line that separates a low-temperature metal from a high-temperature plasma [25]; a well-defined Fermi surface is a reasonable demarcation. Such regions are critical for understanding the state of most of the hydrogen in planetary systems where it is estimated that 60%–70% of the planetary mass in our solar system is dense fluid metallic hydrogen [26]. An important question is as follows: does dense liquid hydrogen metallize as a continuous transition, or does it undergo a sharp first-order transition with a discontinuous increase in density? The importance of this question for our understanding of the structure of the astrophysical gas giants Saturn and Jupiter cannot be overstated [27] and is answered in this paper.

The modern predictions for the PPT line in Fig. 1 show a broad field of liquid MH in the phase diagram (gray region), ranging from the high-temperature to the low-temperature limit with the system in its ground state. In this figure two pathways for achieving metallic hydrogen are indicated: I and II. Pathway I is at lower temperatures in the solid state; metallization requires static pressures not yet achieved on hydrogen in a diamond-anvil cell (DAC). However, four phases have been identified along this pathway, named I, II, III [28–30], and IV [9,10]. These are structural phase transitions of orientational-order of the molecules in which the solid remains insulating. There have been several earlier reports of the observation of metallic hydrogen under static pressure conditions [9,31–34], but none have found acceptance in the scientific community [35–39].

The broad field of MH shown in Fig. 1 can also be entered at lower more accessible pressures along pathway II, but very high temperatures are required. Achieving such temperatures is a challenge for high-pressure hydrogen in a DAC. In this
More recently, DFT computational approaches have been benchmarked [47] with the result that the theoretical curves should fall in the original lower pressures of nuclear effects and found an increase in the PPT pressure of functional theory (DFT) [41–43] predicted somewhat higher pressures (≈100 GPa). A diffusion Monte Carlo calculation indicated that pressures of −650 GPa would be required [45], and subsequent analysis predicted metallization a few hundred GPa lower [46] (not shown in Fig. 1). More recently, DFT computational approaches have been benchmarked [47] with the result that the theoretical curves should fall in the original lower PPT regions, shown in Fig. 1. An experimental determination of the PPT is still lacking and would resolve these large differences in theoretical predictions.

Hydrogen and deuterium have also been studied by dynamic shock-wave techniques that achieve high pressures at much higher temperatures (∼10–50 × 10³ K) for periods of 10–100 ns [48–52]. Optical measurements show a continuous rising reflectivity, consistent with metallic behavior. A phase transition, such as the PPT has not been observed. Such measurements were unable to distinguish between atomic or molecular conductivity. Experiments using reverberating shock waves by Weir et al. [53] found the conductivity of hydrogen to saturate at a pressure of 140 GPa and a calculated temperature estimated to be 2500–3500 K with minimum metallic conductivity [54]. Shock experiments with optical measurements find a much lower density for the transition to metallic behavior, possibly due to higher temperatures. Fortov et al. [55] observed a density change in shocked deuterium, believed to be due to the PPT. Neither this, nor the experiment of Weir et al. measured temperature, and the density data in the work of Fortov et al. are too sparse to conclude a discontinuous behavior with large uncertainties in calculated temperatures (Fig. 1). The PPT line for deuterium is expected to differ from that of hydrogen due to differences in zero-point energy.

II. EXPERIMENTAL TECHNIQUES

Our optical determination of metallization of hydrogen is based on a Drude model. In this model a metal has a plasma frequency. For frequencies higher than the plasma frequency the metal is transparent, whereas for lower frequencies the transmittance decreases and the reflectance approaches 100%. We cannot directly measure the plasma frequency because the diamond anvils of the DAC are opaque in the region where the plasma frequency is expected (around 20 eV) [56]. We have studied optical properties using several laser lines (cw laser light at 514, 633, 808, and 980 nm), covering almost a factor of 2 in wavelength, using the optical system shown in the Supplemental Material, Fig. SI1 [57]. The optical method is often used in dynamic [48,51] and static high pressure studies of IMTs [58–60]. Measurement of electrical conductivity as an experimental method for a first observation of MH was rejected as the metallic leads might contaminate the hydrogen [39].

A DAC is an adjustable isochoric (fixed volume) cell; an isochore is the thermodynamic path of P and T for a fixed volume. For example, in the low-temperature limit, for any given pressure, the volume (or density) can be fixed, say at V(P, T = 0), whereas the pressure will vary with temperature, called the thermal pressure. For this volume, as temperature is raised, the sample follows an almost vertical thermodynamic path shown in Fig. 1. In a given phase, pressure increases weakly with temperature. Heating along this trajectory, hydrogen first melts to a molecular liquid, then at high temperatures the PPT line is crossed and molecules are predicted to dissociate to liquid atomic MH. Since the slopes of the phase lines traversed are negative, the pressure falls back when crossing such lines (Clausius-Clapeyron relation), somewhat compensating the thermal pressure. We measure the pressure at room temperature as representative of the pressure at high temperatures. Pressure is determined either by ruby fluorescence or the shift of the Raman-active vibron of the hydrogen (see Supplemental Material Fig. S2 [57]), always measured before and after a heating cycle to confirm the presence of hydrogen.

The challenge of studying high-P, T hydrogen arises from hydrogen diffusion. At high P/T, hydrogen is very reactive and can diffuse into the metallic gasket or diamond; diamond anvils can embrittle and fail. This makes it very challenging to study high-P, T hydrogen at a steady high temperature since...
diffusion is an activated process and the rate increases at high $T$. We have developed methods to inhibit diffusion of hydrogen at high temperatures using pulsed laser heating and coating the diamonds with alumina that acts as a diffusion barrier. Laser pulses are $\sim 280$-ns long; this is sufficient time to achieve local thermal equilibrium in the hydrogen (electron/phonon relaxation times are on the order of 10 ps or less [61]) but too short for serious diffusion to ensue. We use a small tabletop laser with pulse energies less than 2 mJ to heat the already dense hydrogen. This results in powers as high as $\sim 7$ kW/pulse, much larger than what is needed to heat our samples. We measure $P$, $T$, and optical properties, transmission and reflection, that confirm the long-predicted transition to a liquid metallic phase.

Hydrogen is pressurized in a DAC at room temperature. A rhenium gasket confines the sample, which in our many runs ranged from 10–30 $\mu$m in diameter. Since hydrogen is transparent one can laser heat an embedded absorber that in turn heats the hydrogen pressed against its surface as was performed in Refs. [16,19]. The surface of the hydrogen sample was heated to peak temperatures as high as 2200 K. At high pressures the molecular hydrogen is a few microns thick, whereas we estimate that the heated part of the sample that metallizes is a few to tens of nanometers for low-energy pulses and thickens for higher-energy pulses. The energy/pulse is small, so the sample and diamonds remain at room temperature, on average. The temperature of the absorber and adjacent hydrogen is determined by collecting the blackbody irradiance and fitting to an appropriate curve based on the Planck radiation law to yield the peak temperature due to the heating pulse [62].

In earlier experiments by Dzyabura et al. [19] a laser heated absorber embedded in the hydrogen heated the hydrogen pressed against its surface. In this configuration a phase-transition line was observed in agreement with some of the theoretical lines for the PPT. They measured heating curves, i.e., plots of peak temperature vs heating power. For such curves, if there is no phase change the temperature increases monotonically with laser power. They observed plateaus at $P$, $T$ values (constant $T$ as laser power is increased) interpreted as being due to heat of transformation (energy goes into latent heat) or due to increases in reflectance as both of these mechanisms require increased laser power to maintain the temperature. However, they presented no evidence of metallic behavior. In this article our objective is to show that $P$, $T$ values ($P_\text{c}$ and $T_\text{c}$ are the values at the plateaus) represent the PPT phase line, and that for $T \geq T_\text{c}$, the optical properties are that of a metal, i.e., MH. An example of a plateau for a fixed pressure is shown in Fig. 2; for other pressures see Supplemental Material Fig. S15 [57]. These $P$, $T$ points are plotted in Fig. 1.

It is important to demonstrate that the plateaus arise from hydrogen and not the absorber. In Fig. 2 we show plateaus for absorbers made of platinum, tungsten (W), and W with a 5-nm alumina layer between the W and the hydrogen to inhibit hydrogen diffusion and chemical activity (such as dissociation of molecular hydrogen on a metallic surface). At high $P$, $T$, tungsten forms tungsten hydride [63], whereas the protected W should be tungsten. There is excellent overlap in the data for the various surfaces, establishing that the plateaus arise from hy-

![FIG. 2. Overlapping of plateaus on heating curves for several different laser absorber surfaces at a fixed pressure of 120 GPa. Each point represents the peak temperature achieved for a given laser power.](image)

![FIG. 3. The transmittance and reflectance (980-nm light) of hydrogen vs time at 170 GPa and 1280 K when hydrogen is heated into the region beyond the plateau. The trace of the 280-ns-wide Nd:YAG pulse indicates the period of time when the hydrogen is hottest. The trace in the insulating phase is just below $T_\text{c}$. The laser signal is on an arbitrary scale. The inset (upper right) shows the interior of the cell (not to scale), described in the text.](image)
the heated W by a 50-nm layer of (amorphous) alumina. Thus, one can continuously shine optical light on the sample while repetitively (20-kHz) heating the hydrogen with the pulsed laser. During the pulse, the heated sample traverses the isochoric line shown in Fig. 1, rising and falling in temperature. With sufficient laser power the PPT region can be reached. The transmitted (or reflected) light is detected with a Si photodetector with a 3-ns rise time. The optical light Tr through the W film and hydrogen as well as the R are measured during the pulse. The waveform is recorded and averaged on an oscilloscope for several microseconds, synced to the laser pulse (the optical setup is shown in Supplemental Material Fig. S1 [57]). The pulsed laser light used for heating is filtered out. The Tr/R signals due to the hydrogen can be separated from that of the W film. The transmittance of the cell in the light path is temperature dependent (thermotransmittance), and this is taken into account in the analysis (see the Supplemental Material [57]).

Figure 3 shows the Tr/R, below and above the plateau region for a given pressure load. Data analysis requires a detailed description. First, we scale the Tr/R signals to 1 for each laser wavelength (for times before or after the laser pulse when the sample is at room temperature). This represents the transmittance and reflectance (we plot $R + 1$ of the W, molecular hydrogen, and diamonds so that losses or reflectance due to the cell are normalized out (see the Supplemental Material [57]). To get absolute Tr of the metallic hydrogen, we measure the transmitted signal for laser power pulses at a temperature $T$ on or above the plateaus (see Fig. 2), and these time traces are divided by the signals for temperatures lower than $T_c$, just below the plateaus (for raw data see Supplemental Material Fig. S4 [57]). This is important as it removes the temperature dependence of the transmittance of the cell. With this normalization the transmission of the molecular hydrogen before it metallizes is 1, even during the heating pulse (see the Supplemental Material [57] for detailed analysis). The reflectance is more complicated. We define $R_S$ as the ratio of the detected signal $S(t)$ at or above $T_c$ to that below $T_c$, reflected off of the W film. For a thick film of MH this yields $R$ as the laser power is fully attenuated before it reaches the W. However, for a thin film the signal $S$ contains light reflected off of the MH plus light transmitted through the MH and reflected off of the tungsten back through the film and to the detector, twice attenuated by the MH (see Fig. 3, inset). We analyze the multifilm reflectance using Fresnel equations to extract $R$ (see the Supplemental Material [57]). The W layer may be converted to tungsten hydride (due to diffusion) [63], and its complex index of refraction is unknown. As a consequence we measured the reflectance of the tungsten layer at high pressure, which is needed for the analysis (see the Supplemental Material [57]).

In total for this article 11 runs were carried out (see the Supplemental Material [57]), all consistent with each other. When the absorber film was overly heated it could deteriorate so that we conservatively studied the transition to MH mainly in the vicinity of the plateau where the MH film is thin, on the order of a few to several nanometers and the changes in Tr/R values are only several percent (see the scale in Fig. 3). However, at higher pressures, the plateau is at a lower temperature, and we safely heated substantially above the plateau temperature to measure Tr/R, shown in Fig. 4. Since transmittance decreases exponentially with the absorption coefficient times the thickness (see the Supplemental Material [57]), the explanation of decreasing transmission is that the film of MH becomes thicker with increasing power. We see that as the film thickens (higher peak temperature) the reflectance is saturated to bulk values of about 0.55; this is consistent with shock measurements [49] on thick deuterium samples. From calculations of Tr/R for thin films using a dielectric function for hydrogen, the estimated thickness at saturation is $\sim$50 nm. The drop in Tr and increase in R grows with temperature (pulsed laser power). Note that both reflectance and transmittance changes are very small in the plateau region as the film of MH is very thin. We estimate that $\sim 2 \times 10^{-7}$ mj of energy is required to dissociate a monolayer of hydrogen with the area of our sample at 150 GPa or about $\sim 1.25 \times 10^{-2}$ mj for a 10-nm film (see the Supplemental Material [57] for details). The energy in a laser pulse falling on the sample can easily be varied in small increments so that it is well matched to heat the sample and scan a heating curve involving a phase transition (see the Supplemental Material [57]). Our pulses are carefully tailored to have just sufficient energy to metallize a thin film of hydrogen; very large energy pulses would result in large temperature rises and could “wash out” the plateau. We compare this to shock-type measurements that use energies $\sim$megajoules and may be insensitive to small changes arising from latent heat.

III. DISCUSSION

The PPT is predicted to be a first-order phase transition to MH with latent heat due to dissociation of molecules and the formation of MH. Transmittance/reflectance data for all of our studied wavelengths, spanning a factor of $\sim 2$ in frequency (see Supplemental Material Fig. S6 [57]), are
supportive of the Drude model of a metal. For measurements with plateaus at lower pressures there was some dispersion in these results, possibly due to systematic uncertainties in temperature measurement (see the Supplemental Material [57]). To determine the nature of the transition (first or second order) one generally plots the temperature dependence of an order parameter or establishes latent heat at the transition. We find that $T_{r}/R$ change abruptly as hydrogen is heated into the plateau region and above (Fig. 3), but these quantities are not order parameters. We believe that the plateaus we observe in our heating curves arise from latent heat of dissociation, associated with a first-order phase transition. Due to systematic uncertainty in the position of the plateaus relative to the onset of changes in the optical properties, at this time we cannot unequivocally determine that these occur simultaneously so that $T_{r}/R$ might fall/rise for $T > T_{c}$; this will be resolved in future measurements with reduced systematic uncertainties.

When we first observed metallization of hydrogen using our technique, we were concerned that the large thermal gradient in the cell could also lead to a nonuniform electron density in the MH, and this would require a special analysis to extract the dielectric function. Such an analysis was carried out in the accompanying paper [65]. The result was that for thin films of several nanometers thicknesses, the optical properties were unchanged from the properties of a uniform block of MH. On the other hand, thick films with a smoothly increasing electron density could have strongly attenuated reflectance and essentially 100% absorption. Our observation of reflectance for thick films (Fig. 4) shows the reflectance expected for a block of MH with very little smoothing. We believe that the high thermal conductivity of MH levels the gradient in this part of the sample, whereas a large gradient exists in the low thermal conductivity molecular hydrogen.

Plateaus in heating curves can arise from latent heat due to a phase transition, increased reflectivity so that additional laser power is required to maintain the temperature, or reduced emissivity or absorption. In our experiments, at the region of the plateaus, reflectance is very small, and the absorption grows when the plateau is entered. Therefore the latent heat remains as the probable source of the plateaus. There have been a couple of finite element analyses (FEAs) to understand the source of plateaus in heating curves. Geballe and Jeanloz [66] did an FEA with the main result that latent heat was not responsible for plateaus. However, their FEA is not relevant to our experimental system. They consider a laser absorber that is 5-μm thick, is heated from both sides, and develops a temperature gradient. The absorber is surrounded by 2.5-μm-thick transparent insulating layers (for pressurization) that are not transformed by the heating and they consider the transition of the absorber, not the pressurization medium. They analyze both cw and pulsed heating and indeed do find the possibility of latent heat induced plateaus for pulsed heating (see their Fig. 1). Similar remarks can be made for an FEA by Montoya and Goncharov [67]. In our case the absorber is much thinner than the laser attenuation length, and its temperature is uniform; it follows the power of the laser pulse. For our experiment, it is the hydrogen pressurization medium that undergoes a phase transition, not the absorber.

We have observed no evidence of interband transitions. Using a dielectric model of a metal, assuming full dissociation at 170 GPa and 1250 K, the dc Drude conductivity is found to be $(2.1 \pm 1.3) \times 10^{3} (\Omega \text{cm})^{-1}$, satisfying Mott’s criterion for the minimum metallic conductivity for hydrogen. We are developing techniques to simultaneously measure $T_{r}/R$ at multiple wavelengths, and this should eliminate the large systematic uncertainties and enable a reduction in the uncertainty in the dielectric function and the dc conductivity.

After this paper was submitted, two papers relevant to our studies have been published, and we comment here in the proofs of our paper. Ohta et al. [68] studied hydrogen in a DAC using cw laser heating with gold as an absorber and found anomalies in heating curves consistent with the $P/T$ points for plateaus in the study of Dzyabura et al. [69] and our studies here. Recently, Knudson et al. published a paper on metallization of deuterium using reverberating shock and ramp compression [70]. They observed metallization of deuterium at about 300 GPa, detected by reflectance measured to be about 0.45 in the visible. The substantially higher pressure for the observation of metallic reflectance in deuterium, relative to our observations in hydrogen, can possibly be explained as quantum effects since molecular deuterium has less zero-point energy than molecular hydrogen. However, there is no explanation for the large differences relative to the transition conditions observed in earlier shock experiments. It is important to compare and explain the differences with the results of Fortov et al. [55] (see Fig. 1), Weir et al. [53], and other shock observations on deuterium. A pressure/temperature phase line for the PPT is presented in their Fig. 1, however the temperature was not measured in the experiment, so it is difficult to assess their evidence for the PPT phase line. They use calculated temperatures and do not give uncertainties in their calculated values. In other shock experiments large uncertainties were given in calculated temperatures: Weir et al. [53] $(\pm 500$ K) or Fortov et al. [55] $(\pm 750$ K) (see Fig. 1). Finally, in their Fig. 2, they observe a large region in time (or on their ramp) where the optical signal used to measure reflectance is attenuated to zero and they ascribe this to interband transitions for a closing energy gap. They also state that there is a transient region of spatial heterogeneity in the density. We have no evidence of interband absorption in our measurements, nor do we find this in their data as such a claim should require a spectroscopic determination. In Ref. [65] we present another plausible explanation. A thick inhomogeneous plasma can have almost 100% absorption (and no transmission), and this may be the case as their sample transforms from molecular to metallic deuterium.

To summarize, the results we report provide strong evidence for the IMT in dense liquid hydrogen. A phase line with a negative slope has been observed that separates the insulating phase from the higher-temperature metallic phase, in agreement with some theoretical models. We observe abrupt changes in $T_{r}$ and $R$ at this transition, for all wavelengths, consistent with a Drude model of a metal. The sharp increase in $T_{r}/R$ is indicative of a first-order phase transition. However, it is the plateaus that can be explained as arising from latent heat that are supportive of a first-order phase transition with coexisting phases. A characteristic of the PPT is a critical point and a
discontinuity in density; our pressure range may have been too high to observe the critical point. Discontinuous changes in density, characteristic of a first-order phase transition, are not observable in an isochoric (fixed volume, thus fixed density) cell, such as a DAC chamber. Our results show that the transition to a conducting phase is not continuous as has been reported in shock experiments. At this point in our studies we cannot experimentally distinguish between a molecular metal and an atomic metal, but the correlation between our data and theory indicates atomic MH \cite{41–43}. Temperatures in this set of experiments were too high to expect to observe metastable MH. We also do not expect to detect high \( T_c \) superconductivity at these temperatures. Future measurements at higher pressures, implying lower transition temperatures, may enable observation of these predicted properties.

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A First-order Phase Transition to Metallic Hydrogen

Supplementary Information

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DAC and Optical System

The data on the plateaus and optical properties were obtained in 13 runs, including earlier studies (details are given in Table I). The DACs are of the design described in Ref. (1) but made of Vascomax. In all runs, diamonds were type Ia, selected for low fluorescence with 75 or 100 µm culet flats. Samples were cryogenically loaded and then warmed to room temperature and removed from the cryostat to be mounted on an optical table for measurements. The layout of the optical system is shown in Fig. S11. This system allows for pulsed laser heating with temperatures determined from the thermal irradiance of the pulse heated laser absorbers. This light is collected with a Schwarzschild objective, magnified and imaged on a 200 µm diameter spatial filter and then reimaged on the slits of a prism spectrometer, detected with an InGaAs diode array responsive in the 0.8 to 1.7 µm spectral region.

Thermal irradiances were fitted to a grey-body curve in the spectral region of 1.33-1.7 µm using techniques described elsewhere (2). The transfer function used to correct the spectral irradiance from our samples to the response of the optical system was measured using an ohmically heated thin tungsten film deposited on a diamond anvil in an inert environment, to best match the desired condition of the experiment. The high emissivity of the W films, ~4 times that of bulk foils resulted in higher signals and allowed for temperature measurements as low as 800 K, with a duty cycle of ~1.5×10⁻³. The system included an optical spectrometer used for pressure determination from ruby fluorescence or Raman spectra of the hydrogen vibron, shown in Fig. S12. Above 1 Mbar, all the pressure points reported within this article are based on the hydrogen Raman shift as a pressure marker using a calibration from Ref. (3). Four different CW probe laser beams could be sequentially imaged on the sample by flipping of mirrors. Each probe laser was aligned to be collinear with the pulsed laser beam. In general the DAC was oriented so that the beams go through the hydrogen sample before hitting the semi-transparent W film (see Fig S13). The transmittance and reflectance signals of these laser beams was detected by fast Si detectors; the output was recorded and averaged on a 100 MHz bandwidth multichannel oscilloscope, synced to the heating laser pulse. For reflectance measurements, the DAC was rotated 10 degrees from the normal so that the central mirror of the Schwarzschild did not block the reflected beam. Various important filters and dichroic mirrors are shown in Fig. S11. A computer controlled beam stop and polarization rotator aided automated data acquisition. Fig S13 shows the heart of the DAC with the multilayer films, also shown as an inset in Fig. 3. For clarity this figure is not to scale.
<table>
<thead>
<tr>
<th>Runs</th>
<th>Pressures studied</th>
<th>Absorber material</th>
<th>Data collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run1</td>
<td>140-155 GPa</td>
<td>Pt foil + Alumina</td>
<td>Plateaus, Ref. (2)</td>
</tr>
<tr>
<td>Run2</td>
<td>119-129 GPa</td>
<td>Pt foil</td>
<td>Plateaus, Ref. (2)</td>
</tr>
<tr>
<td>Run3</td>
<td>110-125 GPa</td>
<td>W thin film</td>
<td>Plateaus</td>
</tr>
<tr>
<td>Run4</td>
<td>120-130 GPa</td>
<td>W thin film</td>
<td>Testing/calibration</td>
</tr>
<tr>
<td>Run5</td>
<td>120-176 GPa</td>
<td>W thin film</td>
<td>Plateaus + testing optical data acquisition/analysis</td>
</tr>
<tr>
<td>Run6</td>
<td>120-125 GPa</td>
<td>W thin film</td>
<td>Plateaus</td>
</tr>
<tr>
<td>Run7</td>
<td>120-135 GPa</td>
<td>W thin film</td>
<td>Plateaus + optical data</td>
</tr>
<tr>
<td>Run8</td>
<td>130-135 GPa</td>
<td>W thin film + Alumina</td>
<td>Plateaus + optical data</td>
</tr>
<tr>
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<td>130-170 GPa</td>
<td>W thin film + Alumina</td>
<td>Plateaus and optical data</td>
</tr>
</tbody>
</table>

Table I. A compilation of experimental runs that were carried out for measurements on high-pressure pulse heated hydrogen.
Fig. SI1. The optical layout for studies of pulse heated hydrogen.
Fig. SI3. Interior of the cell showing the various layers and light vectors, including secondary reflections. The tungsten film is ~8 nm thick (layers are not to scale). For some samples a 5 nm layer of alumina was deposited on the W film. For clarity we do not show the bending of rays at interfaces.

Fig. SI2. Raman spectra of the hydrogen vibron mode used for pressure measurements. Pressure was measured before and after each optical measurement.
Transmittance and Reflectance Analysis

In the DAC sample in Fig. SI3, only tungsten and MH have the dominant emissivity in the spectral region of interest, 0.8-1.7 μm, whereas that of diamond, amorphous alumina, and molecular hydrogen are negligible. Thus, the response of transmittance and reflectance signals are dependent mainly on the tungsten thermo-optical properties at lower temperatures. This is valid unless hydrogen undergoes a phase transition that changes its electronic/optical properties. The W film is much thinner than the optical attenuation length so it is uniformly heated and thermalizes in the order of ten picoseconds; its temperature essentially follows the power of 280 ns wide laser pulse. Moreover, the W film and alumina layers are much thinner than the wavelengths of the laser light (>500 nm), so that there is little phase shift of the light and no interference fringes in the layers. The layer of hydrogen adjacent to the W film is in local thermal equilibrium with the W during this relatively long pulse, with a small temperature offset when the absorber has a thin alumina coating. When the hydrogen is sufficiently hot to become metallic, we observe a dip in the transmittance, with an increase in the reflectance for higher temperatures (see Figs. 3,4). The raw data for such a situation is shown Fig. SI4a. The pulse energy flows into the molecular hydrogen (a few microns thick) and into the diamond with the W/alumina coating. The molecular hydrogen has a large heat capacity and longer thermal time constant. Thus, the temperature of the molecular hydrogen rises and falls; after the laser pulse ends the temperature of the W follows that of the molecular hydrogen (consider injecting a finite amount of energy into a mass in a delta function in time; the temperature of the mass rises and falls with its thermal time constant). In Fig. SI4 we observe a thermal response of a few microseconds, much longer than the time of the heating pulse.

In order to isolate the optical properties of the hydrogen film adjacent to the tungsten, for a multilayer system such as depicted in Fig. SI3, one needs to calculate the transmitted and reflected electric fields using the Fresnel equations and squaring to get the transmittance and reflectance. We have done this for our optical pathway, simulating a metallic hydrogen film. We find that for nanometer thick films we can use an “intensity approximation”, that is, propagate the intensity through the multifilm system. T

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function in time; the temperature of the mass rises and falls with its thermal time constant). In Fig. SI4 we observe a thermal response of a few microseconds, much longer than the time of the heating pulse.

I(t,T) = I_0 exp[-(\alpha_{diamond} + \alpha_H + \alpha_{alumina} + \alpha_W(T) + \delta_{H}(t)\alpha_{H}(t,T))] (1.1)

where we incorporate the reflective losses (due to the diamond tables and W film) in Rf; \alpha_i = \alpha, d_i with d_i the thickness of layer i, \delta_{H} = \alpha \text{ if } x = H \text{ and } 0 \text{ if } x = H2, and t, T are time and temperature. We incorporate the thickness in \alpha_{H(t,T)}, not only for ease of notation, but because we do not measure the thickness of the H film. Now consider a transmittance signal in time for a temperature T below the PPT transition temperature T_c, and call this I(t,T < T_c) with x = H, and another for a temperature above the transition temperature I(t,T > T_c) with x = H. Then, the transmittance at T_c is

Tr = I(t,T > T_c) / I(t,T < T_c) = exp[-\alpha_{H(t,T > T_c)}]] (1.2)
For $T<T_c$, hydrogen is in the insulating molecular phase with $x=H_2$ and the transmittance is 1 (we have normalized out the transmission of the W film). A similar approach is used for the reflectance signals to measure the absolute reflectance of a layer of metallic hydrogen on top of a reflective W surface. In this case let $R_w$ be the reflectance off of the tungsten film (geometry of Fig. SI3) and $R$ the reflectance off of the metallic hydrogen. Then the reflectance signals are

$$S(t, T > T_c) = I_o R f (R + T_r^2 R_w)$$

(1.3a)

$$S(t, T < T_c) = I_o R f R_w.$$  \hspace{1cm} (1.3b)

Normalizing gives

$$R_S = \frac{R + (T_r)^2 R_w}{R_w} \text{ or } R = R_w [R_S - (T_r)^2]. \hspace{1cm} (1.4)$$

As explained in the text we normalize $R_w$ to 1, so in this case eq. 1.4 becomes

$$R = [R_S - (T_R)^2]. \hspace{1cm} (1.5)$$

The second term in Eq. 1.3a or 1.4 for $T>T_c$ is due to the light that passes through the H film and is reflected back by the W film. When hydrogen is in the insulating phase $R$ is zero and $T_r = 1$; with this normalization $R_S = 1$ (Eq. 1.4). In the thick film limit the transmission goes to zero and $R=R_S$. We plot reflectance of our MH films as $R+1$ for convenience.

Fig. SI4. (a) Raw transmittance signals during the heating pulse at two different temperatures lower than and in the $T_c$ region. Normalized transmission of the hydrogen (blue trace) is the ratio of the high temperature to the low temperature signals. (b) Plots of $S(t, T > T_c)$ (red) and $S(t, < T_c)$ (green), both normalized to $I_o R f$. The inset shows $R+1$, where $R_S$ has been corrected for the secondary reflection off of the W film.
In order to determine the absolute value of R using Eq. 1.4, we need to determine $R_w$. We measured the transmittance through the tungsten film in the DAC at 170 GPa, and prepared another DAC without the W film but with diamonds coated with alumina and a gasket with the same size hole. Normalization gives the transmittance of W (we correct for the index of air in the gap between diamonds in the second DAC to have that of high pressure hydrogen). Normalizing we have $T_{w} = I(t, T < T_c) / I_0 R_f$ which enables the determination of $I_0 R_f$, using the measured signal. Then $R_w = S(t, T < T_c) / I_0 R_f$, and we find $R_w = 0.29$. This enabled us to extract the reflectance of MH from the measured reflectance of the multilayer sample.

The method of normalization (for example, Eq. 1.2) corrects for the temperature dependence of transmittance and reflectance of the heated W region. An example of raw data is shown in Fig. SI4.

Plateaus in the heating curves, attributed to the latent heat of dissociation of the PPT, are shown in Fig. SI5. The P,T points for the plateaus are plotted in Fig. 1.

Figure SI6 shows some examples of transmittance at different pressures. Due to experimental constraints the transmittance and reflectance measurements as a function of wavelength were not all conducted simultaneously, but sequentially. In some cases we measured the temperature as a function of pulsed laser power, and subsequently used the power to imply the temperature. For some of the transmittance measurements we could not measure the temperature simultaneously with the transmittance signal. This was because the longer wavelength laser light could not be completely filtered out of the blackbody light used to determine the temperature and the two contributions could not be separated. We have conducted systematic studies on the uncertainty of the temperature measured for a given laser power over a period of time. For time intervals of ~1 hour, for the same measured laser power, the temperature uncertainties are on the order of ±50 K. This systematic uncertainty is attributed to mechanical instabilities, where slight spatial shifts could change the position of the focus of the heating laser relative to the sample by few microns.
Fig. S15. Several heating curves showing the rise in temperature of the hydrogen as power is increased for the different pressure points reported in Fig. 1. For every pressure reported, three different heating curves were measured, often in different runs (details in Table 1). The temperature uncertainty bars represent the standard deviation of the fitted temperatures; the straight lines at plateaus are guides to the eye.
Fig. S16. Collection of transmittance and reflectance data versus peak temperature at pressures. At a given plateau temperature corresponding to the plateaus in the heating curves, the data shows a drop in transmittance for the different wavelengths of the probe lasers. Notice that at the lower pressure points, the data shows less drop in transmission at increasing wavelength. The error bar on each point represents uncertainty in the blackbody fit, while the large error bar represents systematic error for the temperature values at the longer wavelengths.
Origin of the Plateaus

Here we estimate the latent heat of transformation due to dissociation of molecules. The dissociation energy of a free molecule of a hydrogen, \( E_{\text{diss}} \), is 4.67 eV. Upon compression, many-body interactions lower \( E_{\text{diss}} \) and the dissociated atoms interact repulsively so the latent heat of dissociation, \( L_{\text{diss}} \), is estimated to be 0.1 eV/molecule (4, 5) for dense hydrogen at a pressure of \(~150\) GPa. The energy required to dissociate a monolayer of hydrogen molecules compressed in our sample cavity (\(~20\) micron diameter) is the number of molecules in a monolayer times the dissociation energy, \( N \times E_{\text{diss}} \approx 2 \times 10^{-7} \) mJ, where \( N \) is calculated from the equation of state of hydrogen \(~2.4 \times 10^{23}\) molecules/cc (6). The spacing between monolayers is \(~1.6\) Å, so there are \(~6.25\) monolayers of molecular hydrogen in 1 nm. Thus, a 10 nm layer requires about \(1.25 \times 10^{-5}\) mJ for dissociation. We now compare the pulse energy in our experiment to the latent heat. In Fig. SI5 about 50 mW of additional average power is required to traverse the plateau. \( P_{\text{avg}} \) is the rate of energy flow over the period of our repetition rate and is measured with a power meter. The power from the laser is divided by a beam-splitter so that 80% goes to the DAC and 20% to the power meter, thus the power change in the beam is 5\times50\ mW= 250 mW. The actual power that does the heating is peak power (\( P_{\text{peak}} \)) in a pulse, the rate of energy flow over the pulse width of 280 ns. \( P_{\text{avg}} \) is related to \( P_{\text{Peak}} \) by the duty cycle \((6 \times 10^{-3})\), where \( P_{\text{avg}} = P_{\text{peak}} \times \text{duty cycle} \). This yields about 44 Watts of peak power, so that the increased energy/pulse to cross the plateau is about \(2.3 \times 10^{-3}\) mJ. However, this is not all delivered to the sample. Our beam is defocused so \(~1/2\) falls on the absorber; and of this, \(~1/2\) is absorbed in the semi-transparent tungsten film. The energy absorbed by the tungsten film is divided into a flux into the hydrogen and into the W coated diamond. Estimating the thermal conductivity of the molecular hydrogen and the diamond, we calculate that about 1/50th goes into the hydrogen. All told, \(~1.2 \times 10^{-5}\) mJ is delivered to the hydrogen. Since we are able to adjust the pulsed laser power to generate a heating curve we can easily vary the peak temperature to resolve points below, at, and above the plateau. Thus, our pulses are well matched to achieve the temperatures of the plateaus and make incremental steps to probe this part of the heating curves. If the energy per pulse was substantially greater, the temperature of the heating curve would rapidly rise during a pulse and minimize the plateau.

Sample Integrity

One of the problems encountered with our measurements was the deterioration of the tungsten film with time, when the pressure was above a megabar. As a consequence we studied 13 samples to ensure reproducibility, of which 12 gave consistent results. One could visually observe that the initially smooth W film slowly became textured within a few weeks, shown in Fig. SI7. Tungsten is known to form tungsten hydride at high pressure and temperature (7), which might be responsible. Other possibilities are stress in the underlying alumina layer that cause the texturing or due to the cupping of the diamond at high pressure. For some of our runs we covered the tungsten absorber with a layer of alumina and this effectively slowed the hydrogen diffusion. A general consequence of the deterioration was that pulsed laser power had to be increased to achieve the same measured temperature; if we considered the measurements to be unreliable the runs were terminated. The measurements at 130 GPa were conducted twice on two different samples, using tungsten+alumina coated absorbers. Each run yielded a different value for the plateau (Fig. SI7-c). Visual observation of the W absorber under a microscope showed serious deterioration of the film. The runs were terminated and data discarded.
References and Notes