

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 (T_r) 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 $T \sim 1000$ 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

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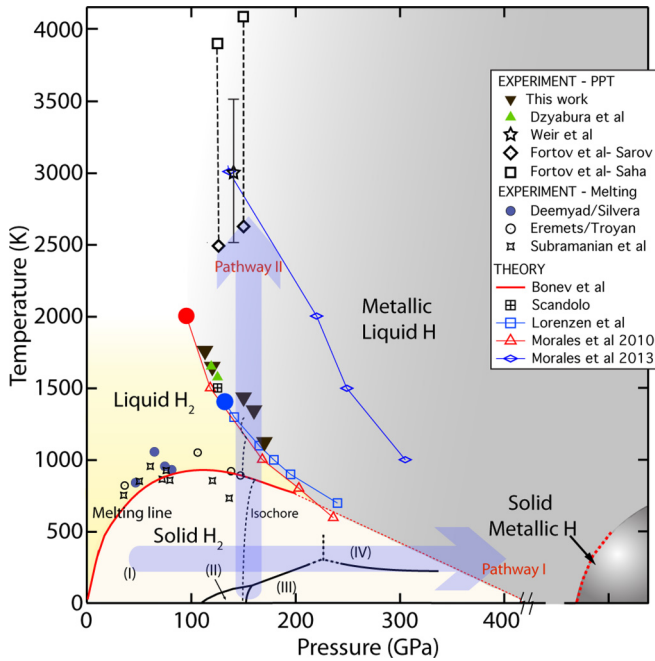


FIG. 1. Phase diagram showing several theoretical predictions of the plasma phase transition as well as established phases in the solid at lower temperatures and the theoretical melting line with confirming experimental data. Our pressure/temperature plateau data points (solid black triangles) delineate a phase boundary, and optical measurements confirm the metallic nature of this transition. Circles at the low-pressure end of the theoretical phase lines are critical points. The calculated temperatures for the pressures for deuterium by Fortov *et al.* are connected by dashed lines. A possible isochoric thermodynamic path is shown. The random uncertainty for plateau temperatures is ± 25 K and falls within the size of the symbols; however there may be systematic uncertainties (see the text).

article we describe our recently reported [14] achievement of producing MH at high T and high static pressures in a diamond-anvil cell.

Early theory, focused on planetary modeling, predicted a point for the PPT at $\sim 15\,000$ K and ~ 60 GPa [40]. Density functional theory (DFT) [41–43] predicted somewhat higher pressures (P) and temperatures (T) almost an order of magnitude lower, shown in Fig. 1. Morales *et al.* [44] then included nuclear effects and found an increase in the PPT pressure of ~ 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 P/T 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 ($\sim 10\text{--}50 \times 10^3$ 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. S11 [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 higher 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 ~ 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 ~ 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 μm 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_c/T_c values (P_c and T_c are the values at the plateaus) represent the PPT phase line, and that for $T \geq T_c$ 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_c/T_c 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-

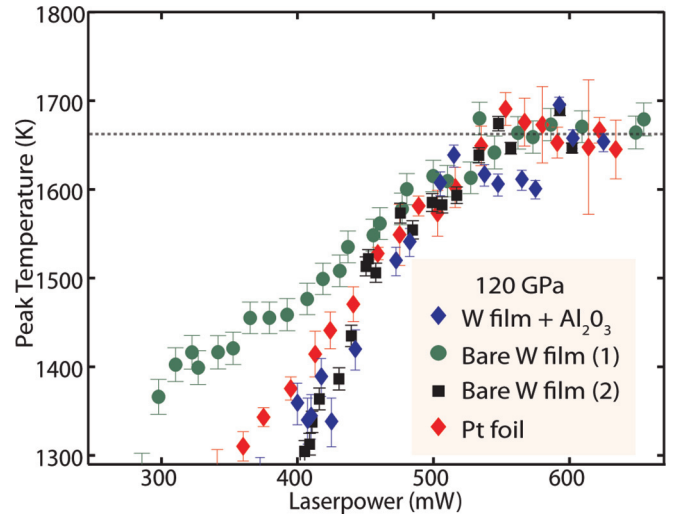


FIG. 2. Overlapping of plateaus on heating curves for several different laser absorber surfaces at a fixed pressure of 120 GPa. Each point represents the peak temperature achieved for a given laser power.

drogen. Einaga *et al.* [64], who also see anomalies for hydrogen samples pressed against gold absorbers, have demonstrated plateau-free heating curves with an inert medium on gold.

Here we report on a method to measure the optical properties of transparent dense matter. We use a thin (~ 8.5 -nm) semitransparent film of W deposited on the diamond culet as our laser absorber shown in the inset of Fig. 3 or Supplemental Material Fig. S3 [57]. This layer enables transmittance and reflectance of the hydrogen to be measured while pulsed laser heating the absorber. The diamond is insulated from

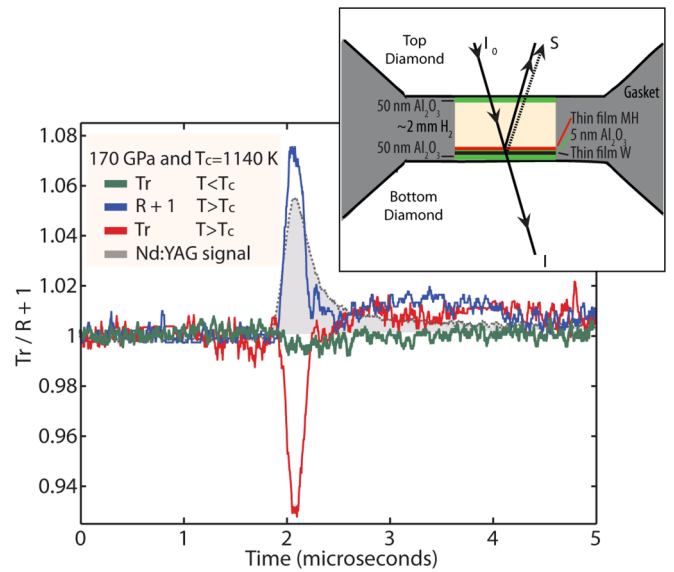


FIG. 3. The transmittance and reflectance (980-nm light) of hydrogen vs time at 170 GPa and 1280 K when hydrogen is heated into the region beyond the plateau. The trace of the 280-ns-wide Nd:yttrium aluminum garnet pulse indicates the period of time when the hydrogen is hottest. The trace in the insulating phase is just below T_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.

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 multilayer 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

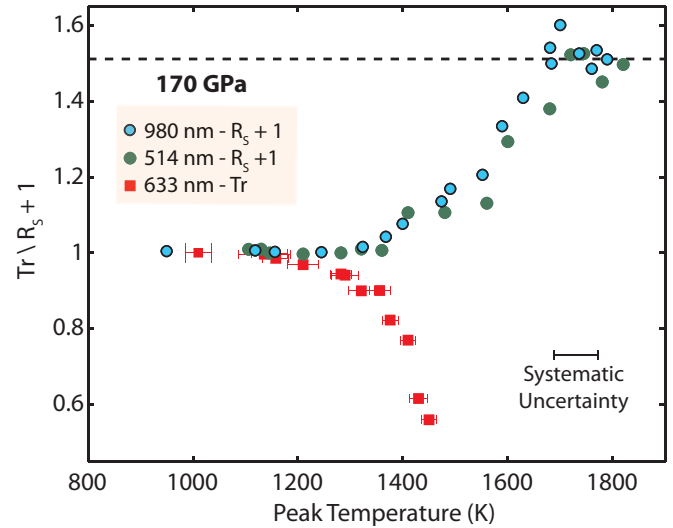


FIG. 4. Transmission and normalized reflectance signal as a function of peak temperature for three wavelengths, traversing from the thin MH film to the thick-film limit and saturating the reflectance for the 170-GPa measurement cycle. The plateau temperature is 1140 K (see the Supplemental Material [57]). Systematic uncertainty is discussed in the Supplemental Material [57].

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 ~ 50 nm. The drop in Tr and increase in R grows with temperature (or 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 $\sim 1.25 \times 10^{-5}$ 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 ~ 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 Tr/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 Tr/R might fall/rise for T above 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 $5\text{-}\mu\text{m}$ thick, is heated from both sides, and develops a temperature gradient. The absorber is surrounded by $2.5\text{-}\mu\text{m}$ -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 Tr/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] (± 500 K) or Fortov *et al.* [55] (± 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 Tr and R at this transition, for all wavelengths, consistent with a Drude model of a metal. The sharp increase in Tr/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 [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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