Conductivity and dissociation in liquid metallic hydrogen and implications for planetary interiors

Mohamed Zaghoua* and Isaac F. Silvera*1

*Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138

Published under the PNAS license

Published in PNAS

PNAS November 7, 2017 | vol. 114 | no. 45 | 11873–11877

www.pnas.org/cgi/doi/10.1073/pnas.1707918114

Abstract

Liquid metallic hydrogen (LMH) is the benchmark Coulomb system that is the simplest and the lightest of all liquid metals. However, despite its apparent simplicity and fundamental significance, its thermodynamic and transport properties continue to pose outstanding challenges. Unlike other alkali metals, atomic metallic hydrogen is exceptional in possessing no bound electrons. Moreover, the low mass of its protonic system gives rise to a substantial zero-point motion. LMH is ubiquitous in the universe, making up about 60%–70% of our solar planetary structure and the vast interiors of extrasolar giant planets (1).

In recent decades remarkable progress has been made in determining dense hydrogen’s thermodynamic equation of state in the region relevant to planetary conditions (1, 2). However, the transport properties of LMH remain less well understood (2, 3). A key long-standing issue that pertains to these properties is the mechanism of electronic conduction: thermal excitation of carriers across a reduced mobility gap (4–6) versus conduction by free electrons in an atomic system (7, 8). The central question is whether metallization at these conditions occurs in the molecular phase or if it proceeds by dissociation into a conducting atomic phase (2). Accurate determination of the plasma frequency, and thus the carrier density, from the reflectance, as well as the density dependence of optical conductivity, are experimental probes that can distinguish between these two models of metallization (5). The confine of quantum and thermal effects, as well as the strong coupling between the electrons and the protons, make it difficult to accurately calculate electrical and thermal conductivity. Theoretical models have to rely on different assumptions about the ionic system structure (7, 9, 10), the degree of ionization (3, 10, 11), and proton–proton correlations (8), all of which remain challenging to adequately describe. Ab initio density-functional theory (DFT) simulations differ substantially in their calculated conductivities, depending on the functionals used (12) (see also discussions in the supporting information of ref. 13). Experimentally, pioneering shock-wave experiments have reported plateauing of electrical conductivity at values around 2,000 S/cm in the region 1.4–1.8 Mbar (6). It was argued that the plateau of conductivity was due to thermal smearing of the band gap and that metallization occurs in the molecular phase with 5–10% dissociation fraction (5, 6). We note that the reported values of conductivity are a factor of 5 less than the Mott–Ioffe–Regal (MIR) minimum metallic conductivity criterion, 6,000 S/cm (4, 14), and a factor of 5–10 lower than values predicted with different theoretical models for fully ionized metallic liquids (3, 5, 7–9, 15).

Here we report measurements of the optical conductivity of bulk LMH at planetary interior conditions in the pressure region of 1.4–1.7 Mbar and measured temperatures of 1,800–2,700 K, which are comparable to the conditions studied by Nellis et al. (4, 5) and Weir et al. (6), but at higher temperatures than those inferred for deuterium studies by Knudson et al. (13). Pressurized hydrogen was pulse-laser heated and time-resolved spectroscopy was used to measure the optical reflectance in eight optical runs using an experimental setup shown in Supporting Information. Unlike previous static and shock-wave work, the energy dependence of optical reflectance was measured simultaneously with temperature, thus removing systematic uncertainties that arise from separate measurements of reflectance and temperature. The duration of the laser pulse, 290 ns, is sufficiently long to achieve local thermal equilibrium yet short enough to inhibit sample diffusion into metallic gasket and diamonds.

Optical reflectance of hot dense hydrogen samples was measured simultaneously or separately (in different experiments) at three wavelengths: 514, 633, and 980 nm. We observed an abrupt increase in reflectance above a certain transition temperature consistent with previous results (16) (Fig. 1). At threshold, the LMH film is thin and semitransparent (Supporting Information).

Significance

Liquid metallic hydrogen (LMH) is a fundamental system in condensed matter sciences and the main constituent of gas giant planets. Because of exceptional challenges in experimentation and theory, its transport properties remained poorly understood. We have conducted experimental determination of the optical conductivity of bulk LMH using spectrally resolved reflectance measurements on statically compressed and heated hydrogen. Metallic hydrogen’s mechanism of metallization is largely dissociative to an atomic state, rather than the previously held experimental model, ionization of molecules. We find that LMH’s electrical conductivity is substantially higher, a factor of 6–8, than the only experimentally reported value in the literature, measured in the dc limit. The implications of the current results to Jovian giants planetary models are discussed.

Author contributions: M.Z. and I.F.S. designed research, performed research, analyzed data, and wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

Published under the PNAS license.

1To whom correspondence should be addressed. Email: silvera@physics.harvard.edu.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1707918114/-/DCSupplemental.

PNAS: 07/01/17; 114:45; 11873-11877
As the laser power is increased, the film heats and thickens until the transmission is essentially zero and reflection corresponds to that of a bulk metal. This value of reflectance is consistent with values obtained in previous shock-wave and static experiments (13, 16–18). Once the reflectance saturates, it is weakly dependent on temperature, as expected in a degenerate metallic system. We further compare our observed reflectance in Fig. 1 to that expected for hydrogen if it was semiconducting with a finite gap and the carriers are thermally activated, as previously suggested (6). The strong disagreement with our measurements enables us to reject a semiconductor model.

Optical reflectance measurements are amenable to a Fresnel analysis. The measured reflectance at a given frequency is

\[ R(\omega) = \left| \frac{N_D - N_D^0}{N_D + N_D^0} \right|^2, \]

where \( N_D \) is the index of refraction of molecular hydrogen/diamond layer and \( N_D^0 \) is the complex index of refraction of LMH. The observed saturation of optical reflectance, conditions of electron degeneracy (\( T << T_F \), the Fermi temperature; Supporting Information), and the characteristic wavelength dependence of the conduction are important conditions for application of the free-electron model. We have thus analyzed the optical response of LMH, only in the limit of saturated reflectance, using the Drude free-electron model, which has previously been extensively used for LMH (7, 15, 19). Use of this model is further justified below. In this model, \( N_D^0 = 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} \), where \( \omega_p \) is the plasma frequency, which is directly related to the carrier density \( n \) by \( \omega_p^2 = 4\pi n e^2/m_e \), and \( \tau \) is the electron relaxation time. We define a dissociation/ionization fraction \( Z \) as the ratio of the carrier to ion density. Thus, if all molecules are dissociated, \( Z = 1 \), while if all molecules are ionized or half atomic-molecular, \( Z = 1/2 \). Accurate measurements of \( R(\omega) \) can thus be used to determine \( \omega_p \) and \( \tau \) from which the carrier density or the degree of dissociation can be deduced. We performed a least-squares nonlinear fit of our measured \( R(\omega) \) to extract these parameters (Fig. 2).

We have determined the Drude parameters at 140 and 170 GPa. At 140 GPa, our reflectance data are best fit to \( \omega_p = 20.4 \pm 1.6 \text{ eV} \) and \( \tau = 1.3 \pm 0.2 \times 10^{-16} \text{ s} \), yielding a dissociation fraction \( Z \) of \( 0.65 \pm 0.15 \). We determine \( \sigma_{dc} = 11,000 \pm 1,100 \text{ S/cm} \), a factor of 2 higher than Mott’s minimum metallic conductivity at this pressure (Supporting Information). At 170 GPa, our data, as well as those reported in ref. 16, are best fit to \( \sigma_{dc} = 21.8 \pm 2.8 \text{ S/cm} \) and \( \tau = 1.6 \pm 0.3 \times 10^{-16} \text{ s} \), yielding a \( Z = 0.57 \pm 0.14 \). This corresponds to \( \sigma_{dc} = 15,500 \pm 1,500 \text{ S/cm} \). We contrast our optical reflectance and the Drude fits to that expected for LMH using the minimum relaxation times \( \tau_{min} \) prescribed by the MIR limit. Such a limit, which is often employed by shock-wave experiments (4), cannot account for the observed reflectance of LMH shown in Fig. 2.

Several ab initio calculations have suggested that at the onset of the insulator–metal transition, the fluid may exhibit a non-free-electron-like density of states (7, 12, 19). Our optical data present experimental evidence for such behavior, where we show that in the transition onset region in which the reflectance is rapidly rising, the data cannot be fit to the Drude model (Fig. 2, Top Left). As the dissociation fraction increases, LMH becomes more Drude-like and the free-electron character is established. This result provides a further justification for the validity of the Drude model in the degeneracy region. The real part of the optical conductivity is plotted in Fig. 2, where the determined relaxation time is assumed to be frequency independent. We have investigated a possible deviation from this assumption through the empirical Smith–Drude (SD) model (20). In this model, a backscattering term is introduced that

**Fig. 1.** Dense hydrogen reflectance as a function of temperature plotted for three wavelengths: 514, 633, and 980 nm. Above a certain transition temperature, liquid hydrogen metallizes and reflects incident probe light. Lines are guides to the eye. The relatively larger scatter in the 170 GPa LMH bulk reflectance data, shown in detail (Inset), is because each wavelength measurement was collected separately, while for 140 GPa reflectances at 514 and 980 nm were measured simultaneously. (Bottom) For comparison, calculations are shown of expected reflectance due to thermally activated carriers plotted against temperature if hydrogen were semiconducting with a 0.3-eV band gap. The sharp step is absent for this case.
shifting the Drude Lorentzian peak to a nonzero frequency. An effort to fit to the SD model is shown in Fig. 2, Top. A best fit is quite poor and only crosses one data point on the curve, shifting the peak to the infrared (below our measured 1.2 eV) and will only have a minor effect on the determined dc conductivity.

It is instructive to compare our LMH Drude parameters to those recently reported for the Wigner–Huntington transition at ~500 GPa and cryogenic temperatures (21). The higher plasma frequency, ~30 eV, found from these experiments is consistent with the higher carrier densities at the higher pressures ($\omega_p \propto \sqrt{n}$). Moreover, the difference in the relaxation times, a factor of 6 shorter for LMH, is likely related to the temperature difference between LMH at ~2,000 K and the cryogenic temperature metallic phase. We further compare our results to those obtained experimentally for warm dense xenon. In those shock-wave experiments, the energy dependence of the optical reflectance in compressed xenon was measured as a function of pressure and Brewster angles (22, 23). Fitting the free-electron model to this pressure dependence yielded relaxation times on the order of $2.655 \times 10^{-15} - 3.6 \times 10^{-15}$ s (22). These values are almost an order of magnitude longer than those obtained from our experiments. Moreover, it is unclear whether those longer relaxation times are attributed to an experimental effect, related to broadening of shock-wave fronts, or to the physics of xenon at the reported conditions (24).

In highly degenerate systems, such as LMH, thermal transport is very likely dominated by conduction electrons. Thermal conductivity could thus be related to electrical conduction through the Lorentz proportionality constant. We have calculated the electronic contribution to thermal conductivity of LMH using the Wiedemann–Franz law, whose application is all the more supported by theoretical models (3).

In Fig. 3, we compare our electrical and thermal conductivity values to several theoretical predictions using various models of different degrees of sophistication. Our LMH dc conductivities and
relaxation times are in very good agreement with DFT-molecular dynamics (7, 15) and correlated electron-ion Monte Carlo (CEIMC) calculations that predict $\sigma_{dc} = 13,000$ S/cm and $\tau = 3.0 \times 10^{-16}$ s and $\sigma_{dc} = 8,600$ S/cm and $\tau = 3.1 \pm 0.3 \times 10^{-16}$ s, respectively, as well as those calculated for fully ionized hydrogen plasmas, albeit at higher $T$ (11).

Our electrical conductivities are a factor of 6–8 higher than those previously reported by Weir et al. (6). The uncertainties in those measurements ranged from 25 to 50% (6). The exact origin of discrepancy is unknown, with temperature being an unlikely factor, since our optical data show a clear saturation as a function of increasing $T$. Moreover, assuming that conductivity may suffer a reduction until a layer of LMH is encountered. The conductivity of dense central core (1). As the atmosphere is entered, composed of a fluid hydrogen space probes. The gas giants, which are largely atomic and degenerate. The transition is also abrupt and reflectance rises to metallic-like values, ~0.3, within ~100 K (Supporting Information). Additionally, we have not observed any concomitant interband transitions in the frequency range investigated, consistent with a first-order transition. Our results thus do not support a conduction mechanism by thermal smearing of a reduced Mott–Hubbard gap. A mechanism of band overlap in the molecular phase has also been suggested where one electron per molecule contributes to conduction or the equivalent of 50% dissociation fraction (5). Within the uncertainties of our fit, the current measurements cannot conclusively distinguish between a mixed atomic-molecular metal and a fully molecular metal. Additional low-frequency reflectance measurements could resolve this uncertainty. Apart from their fundamental significance, the determined properties of LMH have important consequences to dynamo and thermal models of hydrogen-rich planets. These models await new magnetic and gravitational observations by the Juno and Cassini space probes. The gas giants, which are ~90% hydrogen, are composed of a fluid hydrogen–helium envelope and possibly a dense central core (1). As the atmosphere is entered, $P$ and $T$ increase until a layer of LMH is encountered. The conductivity of LMH reported here is representative of $P$-$T$ conditions at ~0.84 of Jupiter’s radius, $R_J$, and 0.63 of Saturn’s radius, $R_S$ (25). It corresponds to a magnetic diffusivity of $\sim 0.56 \times 10^7 \text{cm}^2/\text{s}$, a factor of 8 lower than previously inferred from Weir et al. (6), and now roughly similar to new estimates of Earth’s iron core. The addition of 9% helium is most likely unimportant for these conductivity
estimates (Supporting Information). Our experimental values are also considerably higher than the ab initio transport values calculated along the Jovian adiabat at similar pressures (26), where the used DFT functionals employed evidently underestimate conductance. Since the interaction of the magnetic field with the fluid flow (Ohmic dissipation) scales linearly with electrical conductivity, higher conductivities should result in substantially more dissipation at this transition than currently assumed. This should render recent estimates on the penetration depth of the zonal winds to even shallower bounds than their quoted 0.84 \( R_j \) or 0.63 \( R_j \) (25, 27).

Precise gravitational measurements of low-order harmonics expected by Cassini should further confine this boundary. The Jovian dynamo is also most likely to operate out to a pressure that is much lower than that at 0.84 \( R_j \) into a regime where hydrogen is not fully ionized. If metallization along the Jupiter adiabat is continuous, as both theory and previous experiments suggest, then the depth at which hydrogen conductivity reaches values corresponding to a magnetic diffusivity sufficient to sustain the dynamo \((10^7 \text{ cm}^2/\text{s})\) may extend to more than 0.91. This dynamo depth is much lower than most previous estimates (28–30) and even likely lower than the value inferred by recent dynamo simulations (31, 32) based on the ab initio transport results (26). Since the effect of the dynamo origin depth on the observed magnetic spectrum is mostly manifested at the higher harmonic contributions, the Juno magnetic measurements should provide much tighter observational constraints to future dynamo models, where electrical conductivity profiles remain the key input. In this respect, the dissociation-based picture revealed in this article is particularly important as it means that LMH transport coefficients should scale with increasing density or Jovian radius, consistent with our observation for optical conductivity. This is remarkable for most anelastic dynamo simulations that otherwise prescribe a characteristic constant conductivity for depths below the metallic transition region (29).

Our inferred thermal conductivity values are also considerably lower by a factor of 4–6 than the theoretical estimates in current use for heat-transfer models of Jovian-like planets (9, 33). Revised estimates should thus provide a crucial experimental benchmark for future models, particularly those proposing layered convection as a likely origin for Saturn’s strikingly higher luminosity (34) or the anomalously large radius of several extrasolar transiting hot Jupiters (35).

Materials and methods are available as Supporting Information.

ACKNOWLEDGMENTS. We thank Ashkan Salamat, Ranga Dias, Ori Noked, and Rachel Husband as well as Bill Nellis for discussions. NSF Grant DMR-1308641, the DOE Stockpile Stewardship Academic Alliance Program, Grant DRDoD W911NF-19-1-C0090, and NASA Earth and Space Science Fellowship Program, Award NNX14AP17H, supported this research. Preparation of diamond surfaces was performed in part at the Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Infrastructure Network, which is supported under NSF Award ECS-0335765. CNS is part of Harvard University.