Metallization of Fluid Molecular Hydrogen at 140 GPa (1.4 Mbar)

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Electrical resistivities were measured for liquid H_2 and D_2 shock compressed to pressures of 93–180 GPa (0.93–1.8 Mbar). Calculated densities and temperatures were in the range 0.28–0.36 mol/cm^3 and 2200–4400 K. Resistivity decreases almost 4 orders of magnitude from 93 to 140 GPa and is essentially constant at a value typical of a liquid metal from 140 to 180 GPa. The data are interpreted in terms of a continuous transition from a semiconducting to metallic diatomic fluid at 140 GPa and 3000 K.

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Hydrogen has been the subject of intense research because it is the prototypical system of the insulator-to-metal (IM) transition [1]. Although condensed molecular hydrogen is a wide band-gap insulator at ambient pressure ($E_g = 15$ eV), at sufficiently high pressure the electronic energy gap is expected to close to zero, resulting in an IM transition. The electrical conductivity of the fluid was measured previously at single-shock pressures up to 20 GPa (200 kbar) and 4600 K [2]. These measurements yielded an energy gap of 11.7 eV at 7.5 cm^3/mol. Electrical conductivity experiments using explosively driven magnetic flux compression to isentropically compress liquid hydrogen showed that the conductivity becomes less than 1 $(\Omega\,\mathrm{cm})^{-1}$ at 200 GPa and 400 K [3]. Measurements at static high pressures on solid hydrogen in a diamond anvil cell are restricted to optical properties to 250 GPa [4,5] and x-ray diffraction to 120 GPa [6].

Calculations of the IM transition with an intermolecular potential derived from shock data [7] and theory of the monatomic metal predict a 0 K IM transition at 300–400 GPa [8,9]. A plasma phase transition to a conducting phase has been predicted to occur at ∼100 GPa and 10 000 K [10]. Intermolecular potentials derived from Raman vibron data of solid hydrogen at static high pressures [11] indicate that full dissociation and metallization occur at about 300 GPa [12]. Electronic band gaps calculated for diatomic hydrogen at 0 K predict metallization pressures in the range 150–300 GPa, depending on molecular orientation in the hcp phase [13,14]. However, the hcp structure is energetically unfavorable and lower energy structures have wider band gaps at high density [15]. Thus important issues are (i) does hydrogen metallize in the monatomic, diatomic, or mixed phase and (ii) what pressure is required to close the energy gap of a given structure.

In this work we used a shock wave reverberating between electrically insulating Al_2O_3 anvils to compress a 0.5 mm thick layer of liquid hydrogen to pressures of 93–180 GPa. In this way we have increased the maximum pressure of our conductivity measurements an order of magnitude over our previous experiments [2]. Hydrogen is in the fluid phase because the calculated temperatures are well above the calculated melting temperatures of ∼1000 K at 100 GPa pressures [8,16]. The shock-compression technique is well suited for measuring electrical conductivity because (i) the high pressure reduces the energy gap; (ii) the reverberating shock maintains temperatures at a few 0.1 eV, ∼10 times lower than the temperature achieved by a single shock to the same pressure; (iii) the relatively low shock temperatures activate sufficient conduction electrons to produce measurable conductivities in the semiconducting state; (iv) electrode dimensions and separations are mm's, which are straightforward to assemble; (v) hydrogen is in thermal equilibrium in these 100 ns experiments [17]; and (vi) uniform electrical current density is established in a time small compared to the duration [18].

The purpose of this Letter is to report measurements of electrical conductivities of fluid hydrogen and deuterium at shock pressures of 93–180 GPa and the derived density dependence of the electronic energy gap. The results are needed for comparison with theoretical calculations of band-gap closure at high pressures. Electrical conductivities are also needed for calculations of the magnetic fields of Jupiter and Saturn, which are caused by convective dynamo motion of conducting fluid hydrogen at pressures up to a few hundred GPa and temperatures up to several thousand K [19].

High shock pressures were generated by impact of a hypervelocity impactor onto the front surface of an Al sample holder [20] containing a thin layer of liquid hydrogen between Al_2O_3 anvils. Hydrogen shock pressure is determined by shock impedance matching the measured impactor velocity and known Hugoniot equations of state of the impactor, Al, and Al_2O_3. The pressure in hydrogen reverberates up to the first shock pressure in the Al_2O_3, independent of the equation of state of hydrogen [21,22]. The uncertainty in pressure is 1%. Electrical resistivity was derived from measured resistance by calibration [23]. The uncertainty in electrical resistivity was typically 25% but ranged up to 50%. This uncertainty is caused primarily by signal dispersion in the low thermal conductance coaxial cables used for the cryogenic target.

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Both hydrogen and deuterium samples were used to obtain different densities and temperatures. Liquid deuterium essentially behaves normally at ambient pressures [24] and hydrogen and deuterium fluids are expected to behave normally at high pressures and temperatures. Al and Cu impactor plates were accelerated with a two-stage light-gas gun. Impactor plates were 2 or 3 mm thick, 25 mm in diameter, and embedded in a Lexan plastic sabot. Impact velocities in the range 5.58–7.33 km/s were measured with flash x radiography [25]. The cryogenic Al sample holders were cooled with liquid H_2 at 20 K [7]. Liquid D_2 or H_2 specimens were then condensed from high-purity gas to insure that intrinsic conductivities are measured. The liquid specimen was initially 0.5–0.6 mm thick and 25.4 mm in diameter. This liquid layer was sandwiched between two z-cut single-crystal Al_2O_3 disks 2 mm thick, which in turn were sandwiched between two Al disks 2 mm thick. The outer Al walls are ductile and strong at 20 K; the Al_2O_3 disks are stiff, electrically insulating anvils. Because of the large density mismatch between hydrogen and Al_2O_3 the first shock pressure in hydrogen is a factor of ~25 lower than the first shock in Al_2O_3. The reverberation of the shock in hydrogen between the Al_2O_3 anvils achieves a final hydrogen temperature of a few 0.1 eV, low compared to the initial energy gap of 15 eV and low compared to molecular dissociation energies of about 2 eV at these pressures [9]. The configuration was illustrated previously [26].

Insulated metal electrodes, either two or four depending on whether the conductivity was expected to be relatively small or large, were inserted through the rear walls and were flush with the rear liquid hydrogen-Al_2O_3 interface. The electrodes were 1 mm in diameter, separated by 3.5 mm, and centered on the axis of the sample holder. Electrical conductivities below $\sim 10\ (\Omega\ \mathrm{cm})^{-1}$ were measured using a constant-voltage two-probe method, similar to that used previously for liquid H_2 [2]. Electrical conductivities above $\sim 10\ (\Omega\ \mathrm{cm})^{-1}$ were measured using a constant-current four-probe method. Signal levels were at least 0.01 V and signal durations were about 200 ns after shock reverberation to final pressure. Supplemental experiments examining the electrical conductivity of shock-compressed Al_2O_3 at 100 GPa shock pressures [27] revealed that the conductivity of hydrogen is 2–4 orders of magnitude greater than that of Al_2O_3, resulting in a small to negligible correction to the hydrogen conductivity data.

The data are plotted as the logarithm of electrical resistivity vs shock pressure in Fig. 1. The resistivities decrease from about 1 Ω cm at 93 GPa to 5×10^{-4} Ω cm at 140 GPa and are constant at 5×10^{-4} Ω cm at 155 and 180 GPa. Figure 1 shows that the resistivity decreases almost 4 orders of magnitude from 93 to 140 GPa and then plateaus at 500 μΩ cm to 180 GPa. The data in the range 93–135 GPa were analyzed using our previous dependence for a fluid semiconductor [2]:

$$\sigma = \sigma_0 \exp[-E_g(\rho)/2k_B T], \tag{1}$$

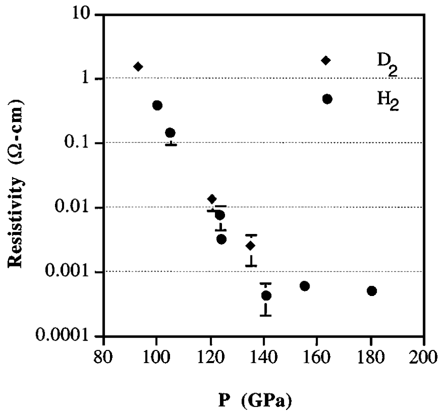

FIG. 1. Electrical resistivity vs pressure for fluid hydrogen and deuterium. The saturation resistivity of 500 μΩ cm above 140 GPa is that of the metallic fluid. Theoretical predictions of this resistivity are a factor of 100 smaller (Refs. [33] and [34]).

where σ is electrical conductivity, σ_0 depends on density ρ, $E_g(\rho)$ is the density-dependent mobility gap in the electronic density of states of the fluid, k_B is Boltzmann's constant, and T is temperature. Because of uncertainties in σ and T and the small number of points, any temperature dependencies in E_g and σ_0 cannot be determined.

The density and temperature were calculated by computationally simulating each experiment using a standard equation of state of hydrogen in the molecular fluid phase [28]. The hydrogen pressures obtained from these computational simulations agree within 1% of those obtained by shock impedance matching. Although a computational model for hydrogen introduces systematic uncertainties in the calculated densities and temperatures [29], the results are useful for understanding the slope change at 140 GPa in Fig. 1. In Fig. 2 the data are plotted as the logarithm of electrical conductivity vs $(2k_B T)^{-1}$. Since $E_g(\rho)$ is an electronic property, it is assumed to be the same for both hydrogen and deuterium. This assumption is expected to be valid in the fluid where possible effects on the band gap caused by different zero-point energies of

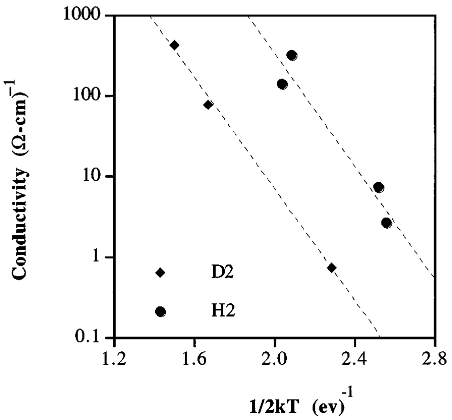

FIG. 2. Electrical conductivity vs $(2k_B T)^{-1}$ for fluid hydrogen and deuterium. For these points, pressure is in the range 93–135 GPa. The dashed lines are guides to the eye.

hydrogen and deuterium are probably smeared out thermally. Figure 2 shows that for a given temperature the conductivities are different for the two isotopes, which means that the density-dependent energy gaps are also different. To derive a density-dependent E_g common to both isotopes, a large decrease in E_g with density is required. Agreement between the conductivities of both isotopes is excellent if the band gap decreases at 70 eV/(mol/cm^3). The calculated rate of band-gap closure near metallization of 0 K of molecularly disordered hcp hydrogen [14] is 40 eV/(mol/cm^3), which shows that our value is comparable to calculated results at 100 GPa pressures. The least-squares fit of Eq. (1) to our experimental data gives $E_g(\rho) = 0.905\ \text{eV} - (67.7\ \text{eV})(\rho - 0.3)$, where the uncertainty is 10% in E_g and ρ is in mol/cm^3. The fit also gives $\sigma_0 = 140\ (\Omega\ \text{cm})^{-1}$; a value of $\sigma_0 \approx 200-300\ (\Omega\ \text{cm})^{-1}$ is typical of liquid semiconductors [30].

$E_g(\rho)$ derived from this fitting procedure and the calculated temperatures are both plotted vs density in Fig. 3. $E_g(\rho)$ is equal to k_BT at a temperature of 0.3 eV and a density of 0.31 mol/cm^3. In this region of density and temperature the energy gap is smeared out thermally, activation of electronic carriers is complete, disorder is already saturated in the fluid, and conductivity is expected to be weakly sensitive to further increases in pressure and temperature. At 0.31 mol/cm^3 the pressure is 120 GPa, which is close to the pressure at which the slope change at 140 GPa occurs in Fig. 1. At higher pressures of 155 and 180 GPa the resistivity is essentially constant at $5 \times 10^{-4}\ \Omega$ cm, a value typical for liquid metals [31]. Also, a saturated resistivity of this order of magnitude has been proposed for a disordered solid at 0 K [32]. Similar ideas are expected for fluid metallic hydrogen. Thus fluid hydrogen becomes metallic at about 140 GPa, 3000 K, and 9 times liquid-H_2 density via a continuous transition from a semiconducting to metallic fluid. These pressures and densities are comparable to those in the solid at which metallization has been predicted theoretically and phase transitions have been observed in diamond anvil cells.

Temperatures of shock-compressed liquid hydrogen have been measured optically [9,17]. At highest pressures and temperatures, 83 GPa and 5200 K, the measured temperatures are substantially lower than predicted for pure molecular hydrogen. We interpret these lower temperatures as caused by energy absorbed in molecular dissociation. The theoretical model derived from those temperature data [9,17] was used to calculate the dissociation fraction in these experiments. At 140 GPa and 3000 K the dissociation fraction is ~5%. Metallization is occurring in the diatomic molecular phase.

The electrical resistivity of metallic hydrogen was predicted theoretically to be about a factor of 100 smaller (5–10 $\mu\Omega$ cm) [33,34] than we measure (500 $\mu\Omega$ cm) at the density and temperature at which we observe metallization. The value predicted theoretically is comparable to that of the solid alkali metals at room temperature.

Our electrical conductivity of 2000 $(\Omega\ \text{cm})^{-1}$ in the metallic fluid phase is essentially the same as that of Cs and Rb in the expanded fluid at 2000 K [35]. This is consistent with the idea that fluids metallize when the mean free path for electrons becomes comparable to the mean distance between the particles providing the electrons. This correspondence is also consistent with electronic conduction in hydrogen caused by electrons delocalized from ${H_2}^+$ ions, a suggestion made previously [36].

The metallization pressure of 140 GPa in the fluid is lower than predicted for the solid at 0 K. At 0 K, hydrogen metallization pressures of 150 to 400 GPa have been predicted recently, depending on whether hydrogen is in the molecular or monatomic phase and on molecular orientation in an ordered structure. A possible explanation for the lower metallization pressure of the fluid relative to that predicted for the solid probably lies in the difficulties involved in closing the band gap in the solid at static pressures achieved thus far in hydrogen, namely, 250 GPa. Several interactions occur in a lattice occupied by diatomic hydrogen molecules which have a high zero-point vibrational energy, orient their molecular axes relative to the crystal structure, and undergo charge transfer [37]. These interactions in the crystal inhibit band-gap closure and are eliminated by melting, thus reducing the metallization pressure. Normally, disorder is expected to delay the onset of metallization from band overlap [38], not to facilitate it.

Available results suggest that the metallization pressure of hydrogen is temperature dependent. At 3000 K the metallization pressure is 140 GPa. At 400 K it is probably about 250 GPa. That is, flux compression experiments indicate that the conductivity of hydrogen is 1 $(\Omega\ \text{cm})^{-1}$ at 200 GPa [3]. Our results indicate that an additional 50 GPa are needed to achieve metallization, at

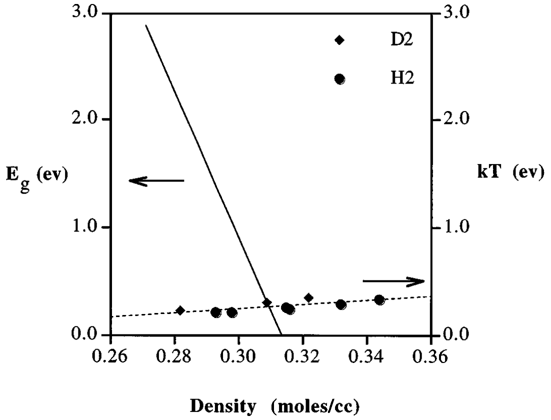

FIG. 3. Electronic energy gap $E_g(\rho)$ obtained from least-squares fitting of the conductivity data and k_BT, where k_B is Boltzmann's constant and T is calculated temperature, plotted vs density for fluid hydrogen and deuterium. The dashed line is a guide to the eye. In the region where the energy gap becomes equal to the temperature, hydrogen undergoes a continuous transition from a semiconducting to a metallic fluid.

least in the fluid. At 0 K the metallization pressure is predicted to be about 300 GPa.

One consequence of our conductivity results is that the first-order plasma phase transition [10] predicted to occur at 100 GPa and 10 000 K between weakly dissociated and substantially dissociated fluid phases probably does not occur. A continuous transition to the metallic fluid occurs within the molecular phase at lower temperatures.

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