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1998 J. Phys.: Condens. Matter 10 11147

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Metallization of fluid hydrogen by multiple shock compression

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Received 1 June 1998

Abstract. The electrical conductivity of fluid, molecular hydrogen is studied to a density of 0.38 mol cm^{-3} , which is about a tenfold compression from the initial, ambient-pressure, liquid hydrogen state. The hydrogen was compressed by means of a reverberating shock wave. By compressing the hydrogen with a rapid series of relatively weak shock waves instead of a single strong shock wave, we minimize the heating of the sample and achieve very high densities. Calculated densities were in the range $0.29\text{--}0.38 \text{ mol cm}^{-3}$, and calculated temperatures were in the range $1600\text{--}3100 \text{ K}$. The data indicate that hydrogen undergoes a continuous transition from a fluid, molecular semiconductor to a fluid, molecular metal at a pressure of 1.4 Mbars and a calculated temperature of 2600 K .

1. Introduction

The study of hydrogen under ultra-high pressures has been the focus of much experimental and theoretical effort. Although static high-pressure technology has now reached the stage where experiments can be routinely performed on H_2 and D_2 at pressures far exceeding 1 Mbar , the pressure-induced insulator-to-metal (I–M) transition has not yet been observed in static high-pressure experiments to at least 3.4 Mbars [1]. The search for metallic hydrogen has, however, led to the discovery of a number of other interesting phase transitions and has deepened our appreciation of the true complexity of this apparently simple system, in which electron correlation effects and large zero-point energies play important roles.

While most recent ultra-high-pressure experiments on hydrogen have been static pressure diamond anvil cell experiments, high-pressure hydrogen has also been studied using dynamic compression [2]. Dynamic high-pressure experiments using shock waves to compress a sample offer advantages and disadvantages with respect to static high-pressure experiments, and so dynamic experiments nicely complement static high-pressure research efforts. One advantage of a dynamic compression approach is that electrical conductivity experiments can be readily performed by careful design of the sample chamber and the measurement electronics. Although the time duration of the compression may be very short (typically less than $1 \mu\text{s}$), it is sufficiently long to (1) allow the sample to come to thermodynamic equilibrium, and (2) to make an electrical conductivity measurement before the sample depressurizes. One of the biggest concerns associated with studying hydrogen by dynamic experiments is the fact that hydrogen is extremely compressive, which results in a large amount of irreversible heat being generated as the sample is shock compressed. A key feature of our experiments on hydrogen was the use of reverberating shock waves. By subjecting the sample to a rapid series of relatively weak shock waves instead of a single

large shock wave, irreversible heating of the sample is greatly reduced and so we refer to the locus of thermodynamic states that are accessible by this technique as a 'quasi-isentrope'. Thus, molecular dissociation is minimized. Also, since thermal pressures are minimized, very high compressions are achievable. In this way, it is possible to perform electrical conductivity experiments on hydrogen dynamically compressed by a factor of ten while keeping the temperatures relatively low (1600–3100 K).

2. Experiment

Minimizing the amount of sample heating through the use of multiple-shock compression is very important for achieving high hydrogen densities. In previous single-shock electrical conductivity experiments on hydrogen by Nellis *et al* [3], thin electrical probes extended into the hydrogen sample in order to immediately measure the conductivity of the hydrogen as the shock wave swept through it. The single-shock nature of these experiments limited the compression of hydrogen to molar densities of about 0.13 mol cm^{-3} (about threefold compression from the starting liquid hydrogen state) due to the sharp rise in irreversible heating as the shock pressure increases beyond about 10–20 GPa [3].

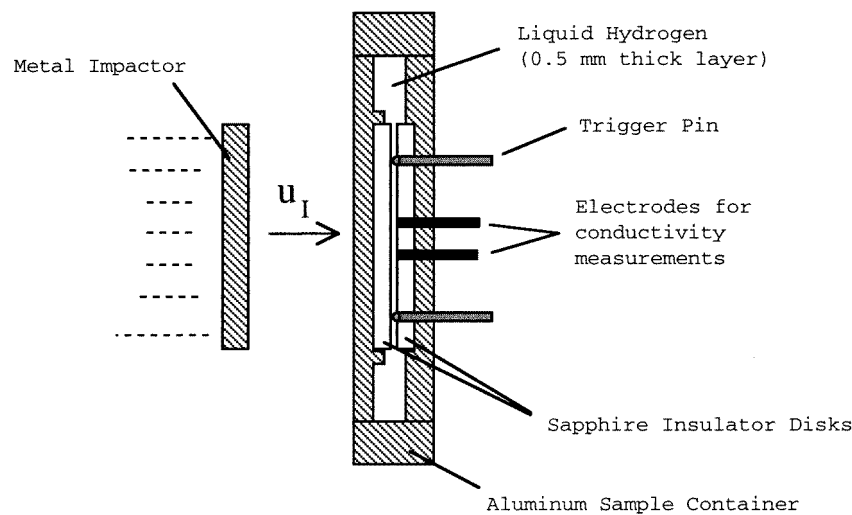


Figure 1. Schematic diagram of the target chamber used for multi-shock experiments. A layer of liquid hydrogen 0.5 mm thick is sandwiched between two 2.54 mm diameter, 2 mm thick sapphire disks. Trigger pins measure the time of shock arrival, and electrodes inserted through the rear sapphire disk make electrical contact to the hydrogen sample. A planar shock wave is generated by the high-speed impact of a metal impactor plate.

A schematic diagram of the sample region of the reverberating shock chamber used in our experiments is shown in figure 1. A planar shock wave is generated in the Al base plate by the impact of a high-speed projectile launched by a two-stage light-gas gun. This planar shock wave propagates through the base plate and the first sapphire disk, and then enters the hydrogen sample. Due to the large mass density and shock impedance mismatch between the sapphire and hydrogen, the shock pressure drops dramatically upon entering the hydrogen. For instance, if the shock pressure generated in the sapphire is 100 GPa, it drops to only ≈ 5 GPa when the shock front passes into the hydrogen. However, this target

chamber was not designed to measure the conductivity of this first shocked state but, rather, the final shock compressed state *after* the shock wave was allowed to reverberate between the two hydrogen–sapphire interfaces multiple times and compress the hydrogen sample to ultra-high densities. This experimental approach is reflected in the design of the sample chamber. Thus, instead of using thin metal foils projecting into the sample region, we opted for a more robust design in which thick steel electrical probes (=0.75 mm diameter) are used, with the electrodes mounted flush with the surface of the rear sapphire disk. Figure 2 shows the calculated pressure against time history for the hydrogen. Again, the first shock pressure is relatively small, but is quickly followed by a rapid series of reshocks within 100 ns which bring the sample pressure up to the initial shock pressure generated in the sapphire, which, for this example is 1 Mbar. The sample then remains at 1 Mbar for a few hundred ns, which is long enough for the sample to come to thermodynamic equilibrium and to perform a conductivity measurement before the pressure releases.

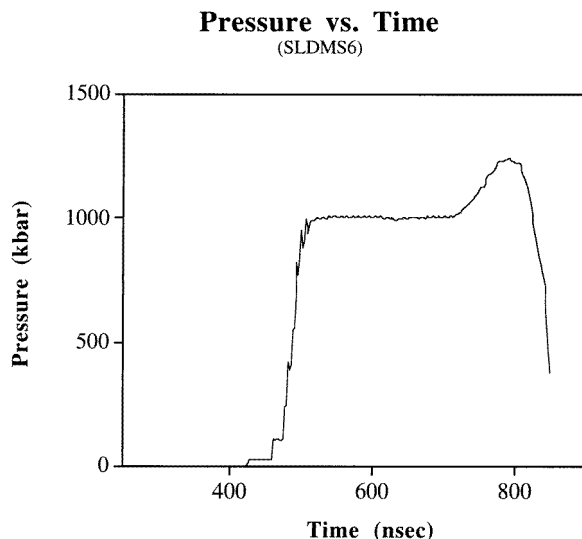


Figure 2. A hydrocode simulation of the pressure against time history of the H₂ sample. The shock wave enters the hydrogen at approximately 420 ns after impact of the metal impactor onto the target chamber. The shock pressure in the sapphire disk is 1 Mbar (=1000 kbar), but due to the large shock impedance mismatch between sapphire (density = 3.98 g cm⁻³) and H₂ (density = 0.071 g cm⁻³), the first shock pressure in H₂ is only about 50 kbars (5 GPa). However, the shock wave then reverberates between the sapphire disks and successive shock waves compress the H₂ sample up to 1 Mbar. The sample remains at this pressure for several hundred ns before axial release waves depressurize the sample.

In the design of the reverberating shock chamber shown in figure 1, we had to address a number of design concerns including: (1) the possible premature depressurization of the sample by axial pressure release waves; (2) the possible premature depressurization of the sample by lateral release waves; (3) ensuring that the magnetic flux diffusion time associated with driving an electrical current through the sample was sufficiently short compared to the duration of the experiment; (4) ensuring that the electrical conductivity of shocked sapphire did not electrically short the electrodes or otherwise affect the accuracy of the measurements; and (5) ensuring that the conductivity measurements were not affected by possible sample-to-electrode contact resistances.

To address concerns (1) and (2), we performed an extensive number of one-dimensional (1D) hydrocode simulations[†] and adjusted the dimensions of the sample chamber to ensure that the electrical measurement would be completed by the time the axial and lateral release waves approached the sample region near the electrodes. This necessitated making the sample chamber fairly thin (only 0.5 mm thick) so that the time duration of the reverberation process would be very short. Also, the electrodes were placed sufficiently close to the central axis of the sample so that the measurement would not be affected by lateral release waves. Another concern was (3), the finite magnetic flux diffusion time. When an electrical current is driven through the sample, the current initially flows predominantly along the outer surfaces of the sample due to the high-frequency skin effect. A more uniform, steady-state electrical current distribution is established only after times t greater than τ , the magnetic flux diffusion time, which was calculated to be not more than 0.5 ns for the conductivities and length scales encountered in our experiments. Since the electrical measurements extend over several hundred ns, magnetic flux diffusion is not a concern and we can assume that a steady-state current distribution has been established by the time the measurement is made. This assumption is important for relating the measured sample resistances to sample conductivities. The electrical conductivity of shocked sapphire and how this might affect the apparent conductivity of the hydrogen sample was another important concern (4). Since the electrical probes extend through the rear sapphire disk, they will be partially shorted by any electrical conductivity which may be present in shocked sapphire. Thus, in our hydrogen conductivity experiments we recognized that the measured resistances reflected the effects of conductivity through both shocked hydrogen and shocked sapphire. However, in our supplemental experiments examining the electrical conductivity of shocked sapphire [4], we found that its electrical conductivity was two to four orders of magnitude lower than the conductivity of the sample in the pressure range 90–180 GPa. This results in about 10% correction in hydrogen conductivity at 90 GPa, and a negligibly small correction at higher pressures. The possibility of significant sample-to-electrode contact resistance was also a concern (5), and so many of the experiments were performed using four-probe geometry, which effectively eliminates the effects of contact resistances. However, we found that the sample conductivities calculated by four-probe measurements were in very good agreement with those calculated with just two of the probes in the same experiment, and so we were able to conclude that any hydrogen-probe contact resistances were so small that they did not significantly affect the measurements.

A very brief summary of how the experiments were performed is as follows. A more complete description of how the experiments were performed will be published [5]. First, the sample chamber was lowered to a temperature of 20 K and a sample of liquid H₂ or D₂ was condensed in the sample chamber from high-purity H₂ or D₂ gas. The electrodes and the transmission lines attached to them were then electrically charged, and a planar shock wave was generated by the impact of a high-speed projectile launched from a two-stage, light-gas gun. When the hydrogen sample became electrically conducting, the electrodes and their attached transmission lines discharged through the sample. The discharge current was measured with a Rowgowski coil, and the voltage drops across the electrical probes were measured with high-speed digital oscilloscopes (Tektronix DSA 602A) connected to the sample chamber by transmission lines. Typical currents were 1–3 A, and typical current densities in the sample were in the neighbourhood of ≈ 500 A cm⁻². Voltage drops across the probes were typically in the ≈ 10 mV range. In this way, H₂ and D₂ sample resistances were measured at a number of pressures along their multi-shock quasi-isentropes.

[†] Hydrocode simulations used in the target design were performed using a 1D finite-element hydrocode and the hydrogen equation-of-state of Kerley [10].

To relate the measured resistances to sample conductivities, the geometry of the sample and the positions of the electrodes must be considered. We performed 3D simulations of the current flow through the sample in its as-compressed geometry [6], and from these simulations we were able to determine the sample conductivities from measured resistances.

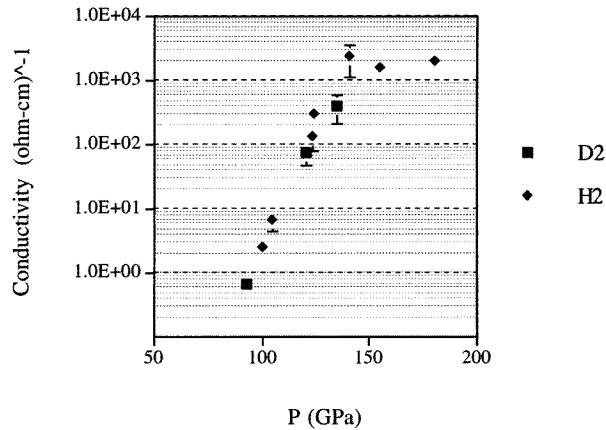


Figure 3. Electrical conductivity of multi-shocked hydrogen against pressure.

3. Data

Data collected on the conductivity of multi-shocked hydrogen are summarized in figure 3. Pressures were determined by shock impedance matching and were confirmed with hydrocode computational simulations [5]. The conductivity increases rapidly with increasing pressure and temperature before saturating at a conductivity of $2000 \Omega^{-1} \text{ cm}^{-1}$ at 140 GPa. Conductivity measurement uncertainties were typically in the range $\pm 20\%$, but ranged up to $\pm 50\%$ for some data points. These uncertainties were primarily due to the dispersion and distortion of the electrical conductivity signals by low thermal conductance steel coaxial cables used to connect the oscilloscopes to the liquid hydrogen cooled target chamber.

Since, at present, experimental techniques have not been developed for measuring the densities and temperatures of the multi-shocked states, hydrocode simulations using a new hydrogen equation-of-state model developed by Holmes, Ross, and Nellis (HRN) [9] were used to calculate the final state densities and temperatures. Although this introduces the concern of systematic uncertainties in density and especially temperature, it will be shown the band-gap analysis is rather insensitive to uniform, systematic shifts in temperature.

A conductivity against temperature plot of the hydrogen data below 1.4 Mbar is shown in figure 4. It was shown in previous single-shock experiments that the observed conductivity was consistent with conduction by thermal excitation of charge carriers across the reduced band gap of hydrogen [3]. The trend of increasing conductivity with increasing temperature is also evident in the multi-shock data of figure 4 for both H₂ and D₂ data points. The offset between H₂ data and D₂ data needs to be explained, however. Due to the smaller mass density of the starting liquid H₂ sample as compared to liquid D₂ (0.071 g cm^{-3} against 0.171 g cm^{-3}), the shock impedance mismatch between the sapphire plates and the sample

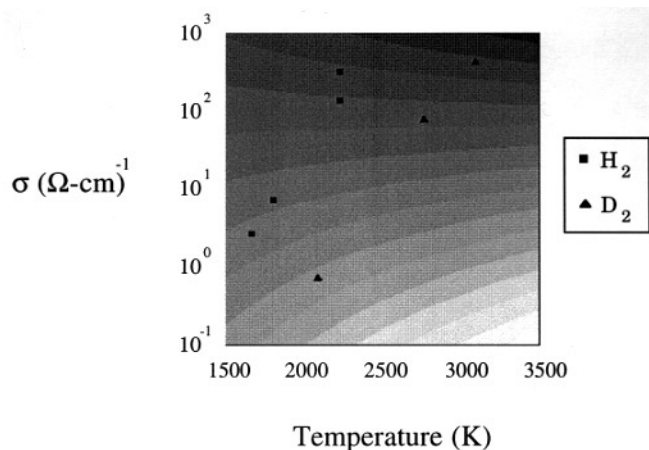


Figure 4. Electrical conductivity of hydrogen against temperature. Only points in the semiconducting region ($P < 1.4$ Mbar) are plotted. The varying molar density is indicated by the shaded bands, with darker regions corresponding to higher densities. Data here were taken over a range of densities from $0.291 \text{ mol cm}^{-3}$ to $0.326 \text{ mol cm}^{-3}$.

is greater for H_2 than for D_2 . As a result, H_2 and D_2 are compressed along different quasi-isentropes by the multi-shock process. If, for example, an H_2 sample and a D_2 sample are both multi-shocked to the same final-state pressure, the H_2 will have a lower temperature than the D_2 sample. For a given final-state temperature, H_2 will be compressed to a *higher* density than D_2 and, therefore, the fact that the H_2 data points lie above the D_2 data points in figure 4 indicates that the electrical conductivity of hydrogen *increases* with increasing density[†].

4. Analysis

As shown in previous shock wave experiments on hydrogen in the range 10–20 GPa, the electrical conductivity of shock compressed hydrogen is consistent with the thermal excitation of charge carriers across the mobility band gap of fluid hydrogen [3]. At 1 atm the band gap of hydrogen is 15 eV. Single-shock conductivity experiments to approximately three fold compression showed a conductivity against temperature behaviour which was consistent with a fluid semiconducting model in which the band gap had been reduced to 11.7 eV. As stated, the offset between H_2 and D_2 data points in figure 4 clearly shows that the conductivity in the range of our multi-shock experiments has a strong density dependence. The conductivity of a fluid semiconductor is described by [7]

$$\sigma = \sigma_0 \exp\left(\frac{-E_g}{2k_B T}\right) \quad (1)$$

where σ_0 is typically $\approx 200\text{--}300 \text{ } \Omega^{-1} \text{ cm}^{-1}$ for liquid semiconductors, E_g is the mobility gap, and T is the temperature. To take into account the density dependence of the conductivity, we assumed a density dependent band gap which could be approximated by a linear function

[†] We assume here that we can neglect differences in the zero-point energies of H_2 and D_2 , and so the band structures and electrical properties of these two molecular fluids should be identical for identical molar density–temperature conditions.

of the molar density ρ over the density range of the semiconducting behaviour region of our experiments. Thus, we assume

$$E_g = A + B \cdot \rho \quad (2)$$

for ρ in the semiconducting density region of the experiments ($0.29 \text{ mol cm}^{-3} < \rho < 0.33 \text{ mol cm}^{-3}$). We then determined the values of the parameters A , B , and σ_0 for our experiment by performing a least-squares fit to minimize

$$\chi^2 = \sum_i [w_i \cdot (\ln(\sigma_i^{(expt)}) - \ln(\sigma_i^{(fit)}))^2] \quad (3)$$

where

$$\sigma_i^{(fit)}(\rho_i, T_i; \sigma_0, A, B) = \sigma_0 \cdot \exp(-(A + B \cdot \rho_i)/(2k_B T_i)) \quad (4)$$

is the calculated conductivity for the i th data point, and $\sigma_i^{(expt)}$ is the measured conductivity for the i th data point. Also, w_i is the least-squares weighting for the i th data point, which is obtained from the conductivity measurement error associated with each point. From this fit we obtained $A = 19.445 \pm 0.802 \text{ eV}$, $B = -61.03 \pm 2.92 \text{ eV cm}^3 \text{ mol}^{-1}$, and $\sigma_0 = 71.0(-34.8/ + 68.3) \Omega^{-1} \text{ cm}^{-1}$. Figure 5 shows a comparison of the calculated conductivities (the $\sigma_i^{(fit)}$) using these parameters with the measured conductivities ($\sigma_i^{(expt)}$).

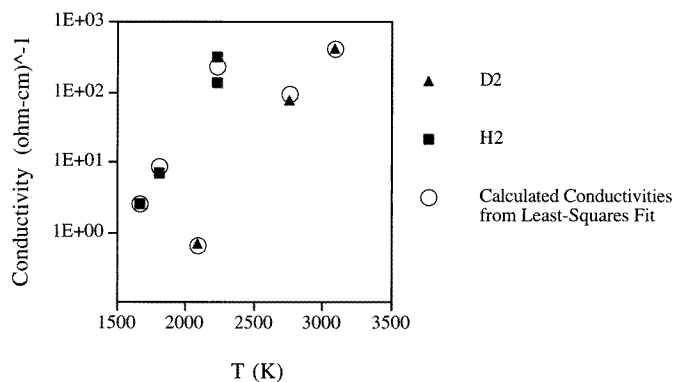


Figure 5. Electrical conductivity against temperature. The measured conductivities for H₂ and D₂ are plotted together with the $\sigma_i^{(fit)}$ calculated conductivities from the least-squares fit of equation (3).

A number of facts now present a consistent argument for metallization of fluid hydrogen in our experiments at a pressure of 1.4 Mbars. (1) According to the fit to a fluid semiconducting model, the mobility band gap E_g closes to $k_B T$ ($\approx 0.2 \text{ eV}$) at a density of $\rho = 0.32 \text{ mol cm}^{-3}$, indicating a band overlap metallization transition at this density. (2) The conductivity saturates to a plateau at a density of $\approx 0.34 \text{ mol cm}^{-3}$, which is very close to the metallization density indicated by the closing mobility band gap. (3) The saturation conductivity of $2000 \Omega^{-1} \text{ cm}^{-1}$ is typical of conductivities observed in other molten alkali metals. (4) The rate of band closure with density obtained from our fit is $dE_g/d\rho = -61.03 \pm 2.92 \text{ eV cm}^3 \text{ mol}^{-1}$, which is a reasonable value and compares well with the value of $40 \text{ eV cm}^3 \text{ mol}^{-1}$ calculated for the rate of band closure near the metallization density for molecularly disordered hexagonal close packed (hcp) hydrogen at

0 K [8]. (5) The σ_o obtained from our fit lies in the range 36–139 $\Omega^{-1} \text{ cm}^{-1}$, which compares very well with values in the range 200–300 $\Omega^{-1} \text{ cm}^{-1}$ for typical liquid semiconductors.

When taken together, these facts all present a very strong case for metallization of hydrogen in the vicinity 0.32 mol cm^{-3} at a pressure of 1.4 Mbars and a temperature of ≈ 2600 K along the quasi-isentrope. According to the model used to calculate the equation of state (EOS) [9], the fluid is predominantly molecular at the transition, with the amount of dissociation being about 5–10%.

4.1. Systematic errors

As stated, since there are no techniques currently available for measuring the temperature or the density of the multi-shocked states, we must rely on calculated equations-of-state for hydrogen for determining these temperatures and densities. This, of course, introduces the problem of systematic errors, especially in calculated temperatures, and of how these systematic errors may affect our analysis. However, if one examines the expression for $\sigma_i^{(fit)}$ in equation (4), it is apparent that a systematic shift in all calculated temperatures T_i by a fixed percentage will result in a proportional shift in *both* fitting parameters A and B . Thus, systematically changing all of the temperatures T_i by a fixed factor does not affect the calculated density of band gap closure ($= -A/B$), although it will change the calculated rate of band gap closure ($=B$). Therefore, the new fitting based on the EOS of Holmes, Ross, and Nellis (HRN) [9] gives very similar results for the density of band closure to that obtained from the Kerley EOS [10] used in our initial analysis [11], even though the calculated temperatures according to the HRN EOS are about 20% lower than those obtained from the Kerley EOS. For the density for band closure, using the HRN EOS gives 0.315 mol cm^{-3} whereas the Kerley EOS gave 0.309 mol cm^{-3} , a 2% difference.

4.2. Plasma phase transition

No clear sign of a discontinuity in the conductivity which might indicate the presence of a hydrogen plasma phase transition [12] is observed in our experiments. However, since the current resolution of the conductivity experiments is ± 20 –50% and some of the points are widely spaced, the possibility cannot be completely ruled out. Future hydrogen conductivity experiments with higher measurement accuracy would be very useful for examining this point further.

4.3. Dissociation induced conductivity

It has been suggested [13, 14] that the observed conductivity arises from the dissociation of hydrogen molecules at high temperature and density, with the monomers contributing to the density of states near the Fermi level, i.e. the hydrogen atoms form an impurity band within the fluid molecular hydrogen. Lenosky *et al* [14] showed that according to this model, the conductivity should be proportional to the square of the dissociation fraction. A plot of our measured conductivities against dissociation fraction is shown in figure 6. There is no clear direct correlation between the dissociation fraction and the conductivity, as would be expected if the conductivity were predominantly determined by monomer concentration. For example, although there are both H_2 and D_2 data points with calculated dissociation fractions of around 0.05, the measured conductivities of these points differ by over an order of magnitude. However, as was shown, the observed dependence of the electrical conductivity with density and temperature can be readily explained in terms of

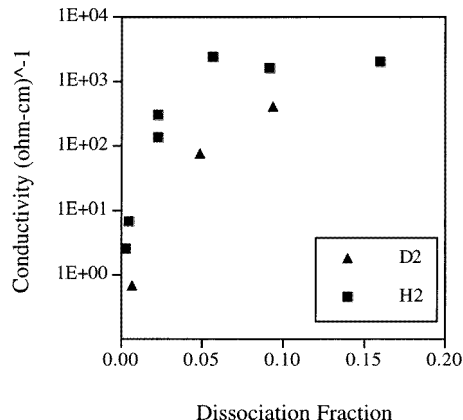


Figure 6. Electrical conductivity against calculated dissociation fraction.

a very simple liquid semiconductor model, and the model parameters thus obtained are in excellent agreement with those expected for liquid semiconducting systems.

5. Summary and future experiments

In summary, we have performed electrical conductivity experiments on quasi-isentropically compressed hydrogen to a pressure of 1.8 Mbars and a calculated temperature of 3100 K. These measurements indicate that hydrogen undergoes a continuous phase transition from a fluid, molecular semiconductor to a fluid, molecular metal at a pressure of 1.4 Mbars, a calculated temperature of 2600 K, and a calculated density of 0.34 mol cm^{-3} , which corresponds to almost a tenfold compression from the initial, ambient-pressure, liquid hydrogen state. The fluid is predominantly molecular at this transition, with a calculated molecular dissociation of $\approx 5\text{--}10\%$.

There are clearly many ways in which to extend electrical conductivity experiments on quasi-isentropically compressed hydrogen. So far, the conductivity along just two quasi-isentropes have been explored corresponding to sapphire/H₂/sapphire geometry and sapphire/D₂/sapphire geometry. The quasi-isentropes were determined by the shock impedance mismatches at these hydrogen-insulator boundaries. By choosing insulators of different densities for the reverberation chamber, different quasi-isentropes can be selected. For example, a smaller hydrogen/chamber density mismatch can be obtained by using LiF (density = 2.60 g cm^{-3}) insulating disks for the reverberation chamber. These experiments would access hotter quasi-isentropes. Additional quasi-isentropes could be accessed by performing experiments on HD or H₂-D₂ mixtures.

The experiments can also be extended to higher pressures to examine the metallic conductivity at higher pressures and temperatures. These experiments will first require that the accuracy of the measurements be improved, however, from the current $\approx 20\text{--}50\%$.

Finally, it would be highly desirable to be able to measure the density and, especially, the temperature along these multi-shock quasi-isentropes. Although single- and double-shocked hydrogen temperatures have been measured [9], there appear to be serious difficulties to extending these experiments to multi-shocked states because of the loss of transparency in the shocked optical window used for the optical pyrometry studies. However, direct measurements of the temperatures and densities of states along the hydrogen quasi-isentropes

would provide very valuable data on hydrogen molecule dissociation and on the possible existence of any first-order plasma phase transition in hydrogen involving volume collapse.

Acknowledgments

The multi-shock hydrogen conductivity data resulted from a collaboration between A C Mitchell, W J Nellis, and myself. Important experimental contributions were also provided by P McCandless, E See, J Crawford, S Weaver, K Stickle and W Brocius. We thank R Kays of Lockheed-Martin for providing a storage dewar for liquid-H₂ coolant and R Silva for technical assistance. The multi-shock hydrogen project was performed with support from the LLNL Directed Research and Development Program under the auspices of the US Department of Energy, contract No W-7405-ENG-48.

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