

# Metallization of fluid hydrogen at 140 GPa (1.4 Mbar) by shock compression

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**Abstract.** Shock compression was used to produce the first observation of a metallic state of condensed hydrogen. The conditions of metallization are a pressure of 140 GPa (1.4 Mbar),  $0.6 \text{ g/cm}^3$  (ninefold compression of initial liquid- $\text{H}_2$  density), and 3000 K. The relatively modest temperature generated by a reverberating shock wave produced the metallic state in a warm fluid at a lower pressure than expected previously for the crystallographically ordered solid at low temperatures. The relatively large sample diameter of 25 mm permitted measurement of electrical conductivity. The experimental technique and data analysis are described.

**Key words:** Metallic state of hydrogen, Shock compression

## 1 Introduction

The quest for metallic hydrogen has been going on for over one hundred years. Hydrogen was first liquified in 1898 and solidified in 1899 by James Dewar. Both these condensed phases are transparent insulators. Prior to their syntheses many scientists had predicted that the condensed phases would be metals at atmospheric pressure (Mendelssohn 1966). This prediction was based on the assumption that hydrogen would be a monatomic alkali metal, as the elements below hydrogen in the first column of the Periodic Table. Instead, hydrogen turned out to be a diatomic insulator, as the halogens in the seventh column of the Periodic Table. Later, Wigner and Huntington (1935) predicted theoretically that the insulating molecular solid would transform to a metallic monatomic solid at sufficiently high pressure  $P$  and density  $D$  at temperature  $T = 0 \text{ K}$ . Over the years the predicted pressure of this transition has varied from 25 GPa (Wigner and Huntington 1935) to 2,000 GPa (Alder and Christian 1960). Experimentally, solid metallic hydrogen has not been observed at pressures up to 340 GPa ( $3.4 \times 10^6 \text{ bar}$ ) (Narayana et al. 1998) and the required pressure might be as large as 600 GPa (Loubeyre et al. 1996). Optical spectroscopy measurements at  $\sim 250 \text{ GPa}$  at 300 K also do not indicate hydrogen metallization (Chen et al. 1996; Hemley et al. 1996; Ruoff 1996).

Because of the difficulty in achieving the metallic state, hydrogen has become a prototypical system for the insulator-to-metal transition. Since solid molecular hydrogen is a wide bandgap insulator at ambient ( $E_g = 15 \text{ eV}$ ),

extremely high pressures are required to close this gap and reach a metallic state. Solid hydrogen is difficult to understand theoretically because of phase transitions in molecular orientation and in crystal structure, which inhibit metallization (Edwards and Ashcroft 1997). In fact, in the solid the question still remains as to whether metallization occurs by a first-order phase transition from a diatomic to monatomic state, as suggested by Wigner and Huntington, or whether metallization occurs by electron band overlap within the diatomic solid.

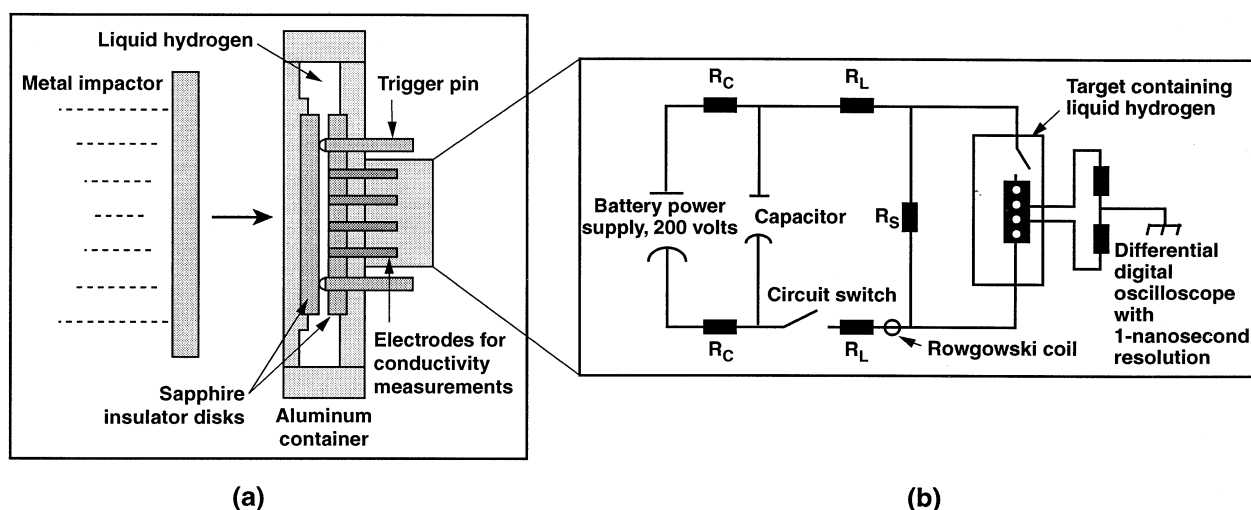
A metallic state has been achieved with a reverberating shock wave, which heats as well as pressurizes hydrogen. The minimum electrical conductivity of a metal was observed at 140 GPa,  $0.6 \text{ g/cm}^3$  (ninefold initial liquid- $\text{H}_2$  density), and 3000 K (Weir et al. 1996; Nellis et al. 1999). At this pressure, the temperature is about twice the melting temperature and hydrogen is in the fluid phase. Heating occurs adiabatically on shock compression and the temporal width of a shock front is  $< 1 \text{ ps}$ . Since the time resolution of the diagnostic system and the time to achieve thermal and electrical equilibrium are all  $\sim 1 \text{ ns}$  or less, the conductivity of equilibrated hydrogen was measured.

In contrast to this dynamic method, heating hydrogen statically to such high temperatures is not possible because hydrogen has a very large diffusion coefficient and high chemical reactivity with solids. That is, at static high temperatures and pressures hydrogen either diffuses out of and/or reacts chemically with its container before an accurate measurement can be made (Datchi and Loubeyre 1996).

Hydrogen is of great importance for planetary science because its cosmological abundance is about 90 at.%. Ju-

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**Fig. 1a,b.** Schematic of electrical conductivity experiments on fluid metallic hydrogen. Metal impactor is launched by 20 m long two-stage gun. Four electrodes in **a** are connected to circuit in **b**. Sapphire disks are 25 mm in diameter; liquid hydrogen layer between sapphire disks is initially 0.5 mm thick. For conductivities lower than metallic, two probes were used. Trigger pins turn on recording system. All cables are coaxial

Jupiter and Saturn together contain over 400 Earth masses, most of which is hydrogen in the metallic fluid. Implications for Jupiter of our recent hydrogen measurements have been discussed (Nellis et al. 1996; Nellis 1999a).

The equation of state of fluid hydrogen is important for inertial confinement fusion (ICF). In laser-driven ICF a fuel pellet composed of the hydrogen isotopes deuterium and tritium is placed in a hohlraum and radiated by a multisteped, high-intensity laser pulse (Lindl et al. 1992; Lindl 1995). The first step of the laser pulse produces a  $\sim 100$  GPa shock and the successive pulses comprise a quasi-isentrope, similar to the compressive process used in these conductivity experiments. In order to achieve efficient nuclear-fusion reaction of deuterium and tritium, it is necessary to achieve the highest possible areal mass density of the deuterium/tritium fuel. In order to achieve a relatively high areal mass density with a relatively low investment of laser energy, it is necessary to compress most of the deuterium/tritium fuel on an isentrope with the smallest possible entropy. This is best accomplished by achieving maximum first-shock density with the lowest possible entropy. These electrical conductivity measurements yield electronic excitation energies which are needed to calculate the equation of state of hydrogen in this regime of importance to ICF.

Scientific and technological possibilities for metastable solid metallic hydrogen, if it could be quenched to ambient, are discussed elsewhere, including room-temperature superconductivity (Ashcroft 1968; Richardson and Ashcroft 1997); a very light-weight structural material; a fuel, propellant, or explosive, depending on the rate of release of stored energy; a dense fuel for higher energy yields in ICF; and an aid in the synthesis of novel hard materials (Nellis 1999b).

In summary, the metallic state of hydrogen is of great scientific and potential technological importance. The first

observation of a metallic state of hydrogen has been made using shock compression.

## 2 Finite temperatures

Because the metallic state of hydrogen has not been observed in the solid at room temperature, it is advantageous to look for metallization in the fluid at higher temperatures. Since the melting temperature is  $\sim 1500$  K at  $\sim 100$  GPa (Ross et al. 1983), temperatures need to exceed  $\sim 2000$  K. Hydrogen is so mobile that when it is heated statically above 500 K, it rapidly diffuses out of the sample chamber and into the solid walls of the diamond anvil cell (Datchi and Loubeyre 1996). Thus, it is essential that hydrogen be heated for only a very brief time, say  $\sim 100$  ns, which is both sufficiently long that hydrogen is in thermal and electrical equilibrium and sufficiently fast that hydrogen cannot be lost by diffusion nor by chemical reactions, nor do Richtmyer-Meshkov instabilities have time to grow at the planar boundaries between hydrogen and the adjacent optically-flat crystal anvils.

On the other hand a temperature of 3000 K is a relatively low temperature for metallic fluid hydrogen. Because the density required to reach the metallic state is so high, 9 times initial liquid- $H_2$  density, the Fermi energy  $E_F$  of the metal is 12 eV, which corresponds to a Fermi temperature of  $T_F = 140,000$  K. Because  $T/T_F \ll 1$ , the electrons are degenerate, as in a simple metal. Also, 3000 K is a sufficiently low temperature that the molecular nature of hydrogen is essentially maintained. That is, because the lowest lying vibrational levels of the molecule are separated by  $\sim 6000$  K, the hydrogen molecule can be treated as a quantum mechanical harmonic oscillator. Thus, the vibrational energy of the ground state of the diatomic molecule is half this energy spacing or  $\sim 3000$  K.

Calculations indicate that at  $0.6 \text{ g/cm}^3$  and 3000 K this fluid is  $\sim 90\%$  molecular  $\text{H}_2$  and  $\sim 10 \text{ at.}\%$  H, with some of the molecules in an excited vibrational state (Nellis et al. 1998).

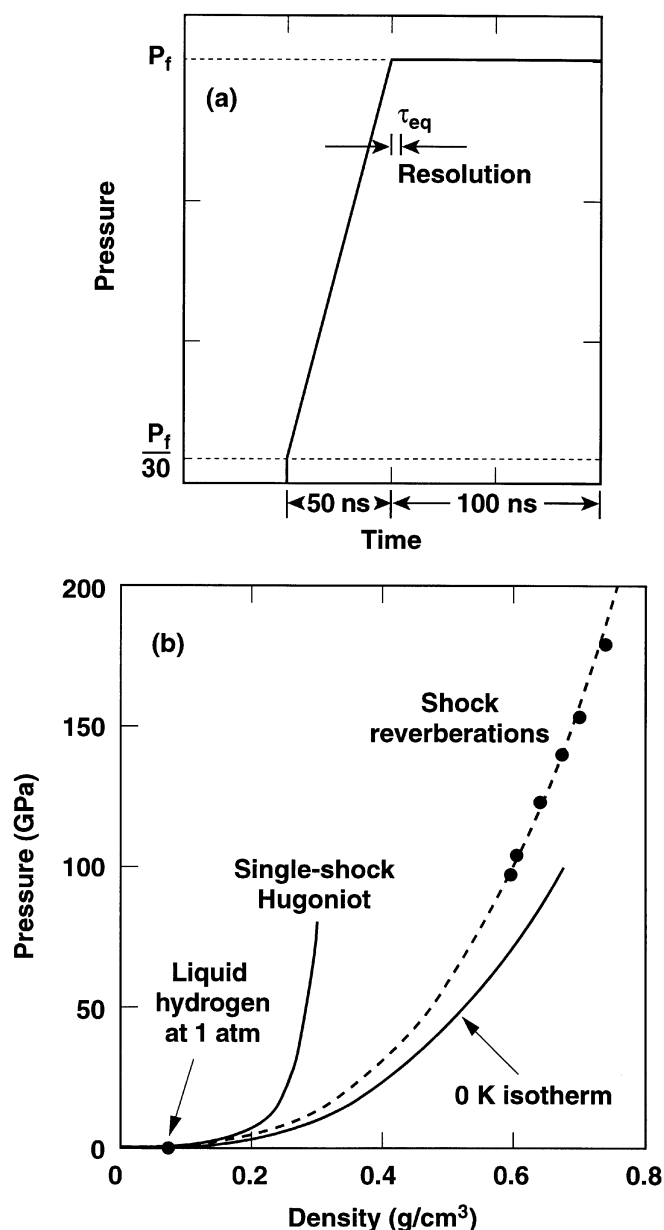
### 3 Metallization experiments

The experimental configuration is illustrated in Fig. 1. A 0.5 mm thin layer of liquid  $\text{H}_2$  or  $\text{D}_2$  is compressed dynamically by a high-pressure shock wave reverberating between two stiff, electrically-insulating sapphire (single-crystal  $\text{Al}_2\text{O}_3$ ) disks, or anvils, 25 mm in diameter. The two sapphire anvils are contained between two Al plates, which are part of a cryostat at 20 K. The compression is initiated by a shock wave generated when a metal plate, launched by a two-stage light-gas gun at velocities up to  $\sim 7 \text{ km/s}$ , impacts the Al plate on the left in Fig. 1. This gas gun is 20 m long, with a projectile diameter of 28 mm. The impact shock is amplified when it is transmitted into the first sapphire disk. The first shock pressure in the liquid is  $\sim 30$  times lower than the shock incident from the sapphire. The shock then reverberates quasi-isentropically between the two anvils until the final hydrogen pressure equals the shock pressure initially incident in the sapphire.

The P-D states achieved by shock reverberation are illustrated in Fig. 2. The loading path consists of an initial weak shock followed by a quasi-isentrope. The quasi-isentrope, which is actually achieved by a series of discrete reverberating shocks, is represented by the ramp in time in Fig. 2a. The final temperature produced by a reverberating shock is about 1/10 what it would be for a single shock to the same pressure (Ogilvie and Duvall 1983). Figure 2 shows that states achieved by shock reverberation are relatively close to the 0 K isotherm and at much higher densities than the single-shock Hugoniot. The calculated temperatures achieved in these states are about twice the calculated melting temperatures.

Electrical resistance of the hydrogen sample was measured versus time by inserting electrodes through the anvil on the right in Fig. 1. Either  $\text{H}_2$  or  $\text{D}_2$  samples were used, depending on the final density and temperature desired,  $\text{H}_2$  giving lower final temperatures than  $\text{D}_2$ . That is, because the initial mass densities of liquid  $\text{H}_2$  and  $\text{D}_2$  differ by a factor of 2.4, the final shock-compressed densities and temperatures also differ. Thus,  $\text{H}_2$  and  $\text{D}_2$  were used to obtain different final densities and temperatures and not to look for an isotope effect.

At present there is no way to measure hydrogen density and temperature because the high-rate deformations caused by the reverberating shock render the sapphire anvil opaque. As a result conventional optical diagnostics are not possible yet. Thus, density and temperature were calculated using two reasonable equations of state of Ross (Holmes et al. 1995) and of Kerley (1983). The calculated density of metallization agrees within 2% for both of these equations of state. The conservative uncertainties derived from these calculations are 5% in density and 30% in temperature. The experimental data (Weir et al. 1996)



**Fig. 2a,b.** Effect of rise time on pressure-density states. **a** First pressure in hydrogen is  $\sim P_f/30$ , where  $P_f$  is incident shock pressure in  $\text{Al}_2\text{O}_3$  as well as the final pressure in hydrogen. Successive reverberations comprise quasi-isentrope up to pressure  $P_f$ . This quasi-isentrope is represented by ramp over  $\sim 50 \text{ ns}$  from  $P_f/30$  up to  $P_f$ . After reverberation is complete,  $P_f$  is held for  $\sim 100 \text{ ns}$ . If  $P_f$  were achieved in one jump, a state at much higher temperature would be achieved on single-shock Hugoniot. **b** Equation-of-state curves plotted as pressures versus densities: 0 K isotherm, points reached in these experiments by shock reverberations, and single-shock Hugoniot. Initial point is liquid  $\text{H}_2$  at 1 atm

are plotted in Fig. 3 as electrical resistivity versus pressure,  $P_f$  in Fig. 2a. Electrical resistivities measured under single-shock compression up to 20 GPa were reported previously (Nellis et al. 1992).

## 4 Results

The slope change at 140 GPa in Fig. 3 is indicative of the transition to the metallic state. In the semiconducting fluid range of 93-120 GPa, the data were fit to the dependence of a thermally activated semiconductor:

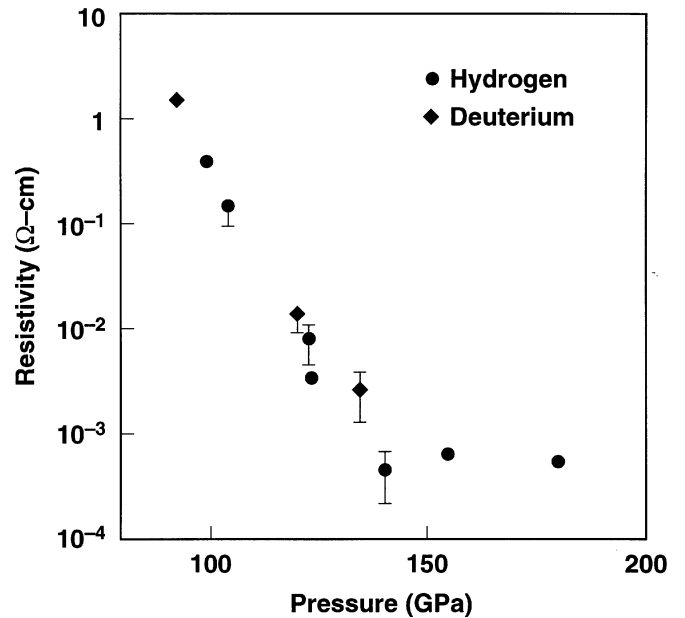
$$\sigma = \sigma_0 \exp(-E_g(D)/2k_B T),$$

where  $\sigma$  is electrical conductivity,  $\sigma_0$  depends on density  $D$ ,  $E_g(D)$  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. This fit gives the result  $E_g(D) = 1.22 - (62.6)(D - 0.30)$ , where  $E_g(D)$  is the activation energy in eV and  $D$  is in mol/cm<sup>3</sup>.  $E_g(D)$  derived from this fitting procedure and  $k_B T$  are equal at a density of 0.32 mol/cm<sup>3</sup> (9-fold initial liquid-H<sub>2</sub> density) and a temperature of  $\sim 2600$  K (0.22 eV). At 0.32 mol/cm<sup>3</sup> and 2600 K the calculated pressure is 120 GPa, close to 140 GPa at which the slope changes in the electrical resistivity (Fig. 3). At pressures of 140 to 180 GPa the measured hydrogen resistivity is essentially constant. Thus, fluid hydrogen undergoes a continuous transition from a semiconducting to metallic fluid at 140 GPa, 0.32 mol/cm<sup>3</sup> and  $\sim 2600$  K (0.22 eV). Metallization occurs by thermal smearing of the mobility gap,  $E_g(D) \sim k_B T$ , which produces a Fermi surface and the minimum metallic conductivity of a disordered metal, 500  $\mu\Omega$ -cm.

## 5 Discussion

This metallic value of 500  $\mu\Omega$ -cm is essentially the same resistivity as that of the fluid alkali metals Cs and Rb at 2000 K undergoing the same nonmetal-metal transition (Hensel and Edwards 1996). This minimum metallic conductivity of fluid Cs, Rb, and hydrogen is achieved at essentially the same Mott-scaled density of  $D_m^{1/3} a^* = 0.30$ , where  $D_m$  is the density at metallization and  $a^*$  is the Bohr radius. Mott's preferred value is 0.25 (Mott and Davis 1971). Since the Bohr radius is the same for H<sub>2</sub> and H (Barbee 1996), the difference in the Mott-scaled density between the diatomic and monatomic states is simply a factor of  $2^{1/3}$ . Thus, this relationship cannot distinguish whether hydrogen is in the form of molecules or atoms. Since the size and shape of H<sub>2</sub> and H are very similar (Barbee 1996), the two are probably miscible at 3000 K in the fluid. Thus, the measured energy gap is probably that of the mixture of H<sub>2</sub> and H.

Iodine is a molecular element, as hydrogen, which also metallizes at much lower pressure in the liquid, 3 GPa (Brazhkin et al. 1992), than in the solid, 16 GPa (Riggleman and Drickhamer 1963). The measured pressure dependences of the resistivities at metallization are very similar for iodine and hydrogen (Hemley and Ashcroft 1998).



**Fig. 3.** Logarithm of electrical resistivity of H<sub>2</sub> and D<sub>2</sub> samples plotted versus pressure. Slope change at 140 GPa is transition from semiconducting to metallic fluid. H<sub>2</sub> and D<sub>2</sub> samples are used to obtain different final densities and temperatures

Based on Ross' bulk thermodynamic calculations, an estimated 5% of the molecules are dissociated (Weir et al. 1996). Tight-binding molecular dynamics simulations (Lenosky et al. 1997; Kress et al. 1998) also show that fluid metallic hydrogen at these temperatures is essentially molecular. Neglecting dissociation and assuming one conduction electron per H<sub>2</sub> molecule at metallization density (analogous to one electron per alkali atom), the free-electron Fermi energy of metallic fluid hydrogen is  $\varepsilon_F \sim 12$  eV, as for solid Al. Since at metallization  $T/T_F \sim 0.02$ , metallic fluid hydrogen is degenerate, highly-condensed matter.

The measured value of 500  $\mu\Omega$ -cm is bracketed by simple theoretical models. The minimum electrical conductivity of a metal is given by  $\sigma = 2\pi e^2/3hd$ , where  $e$  is the charge of an electron,  $h$  is Planck's constant, and  $d$  is the average distance between particles supplying the electrons (Mott and Davis 1971). In this case  $d = D_m^{-1/3}$ . The calculated minimum conductivity corresponds to a resistivity of 250  $\mu\Omega$ -cm, which is within a factor of only 2 of the measured value.

The electrical conductivity of fluid metallic hydrogen has been calculated using tight-binding molecular dynamics (Kress et al. 1998). At 140 GPa and temperatures in the range 1500 to 3000 K, the calculated resistivities are 500 to 250  $\mu\Omega$ -cm, respectively, in good agreement with experiment.

Since all these calculations produce electrical resistivities close to the measured value, our measurement of 500  $\mu\Omega$ -cm is quite reasonable.

The pressure required to achieve metallization is lower in the fluid than in the ordered solid probably because orientational and crystalline phase transitions, which inhibit

metallization in the ordered solid (Ashcroft 1995) do not occur in the disordered fluid. In the fluid, charge clouds on neighboring molecules and/or atoms are compressed until they overlap and electrons are delocalized; that is, a Mott transition occurs from a nonmetal to a state with the minimum conductivity of a metal (Hensel and Edwards 1996).

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