METALLIZATION OF FLUID HYDROGEN AT 140 GPa (1.4 Mbar) BY SHOCK COMPRESSION

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The minimum electrical conductivity of a metal was produced in dense hydrogen using shock compression. Metallization occurs at 140 GPa (1.4 Mbar), 0.6 g/cm³ (ninefold compression of initial liquid-H₂ density), and 3000 K. The relatively modest temperature generated by a reverberating shock wave produced the metallic state in a warm quantum fluid at a lower pressure than expected previously for the crystallographically ordered solid at low temperatures. Future research directions are discussed. Possible scientific and technological uses of metastable solid metallic hydrogen are speculated upon in the unlikely event that the metallic fluid can be quenched to this state at ambient pressure and temperature.

Keywords: Hydrogen; metallization; shock experiments

INTRODUCTION

The quest for metallic hydrogen has been going on for over one hundred years. Hydrogen was first liquefied in 1898 and solidified in 1899 by James Dewar. Both these condensed phases are transparent insulators. Prior to their discovery many scientists had predicted that the condensed phases would be metals at atmospheric pressure. This prediction was based on the assumption that hydrogen would be a monatomic alkali metal, like the elements below hydrogen in the first column of the Periodic Table. Instead, hydrogen turned out to be a

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diatomic insulator, like the halogens in the seventh column of the Periodic Table. In 1935 it was predicted theoretically that the insulating molecular solid would transform to a metallic monatomic solid at sufficiently high pressure $P$ and density $\rho$ at temperature $T = 0\,\text{K}$ [1]. Over the years the predicted pressure of this transition has varied from 25 to 2,000 GPa [1, 2]. Solid metallic hydrogen has not been observed optically at static high pressures up to 340 GPa in a diamond-anvil cell [3] and, based on X-ray diffraction experiments, the required pressure might be as large as 620 GPa [4]. Metallic electrical conductivities have not been found at dynamic pressures up to $\sim 200\,\text{GPa}$ at temperatures of $\sim 300\,\text{K}$ using isentropic magnetic-flux compression [5, 6].

Because of the difficulty in achieving its metallic state, hydrogen has become the prototypical system for the insulator-to-metal transition. Since solid molecular hydrogen is a wide bandgap insulator ($E_g = 15\,\text{eV}$) at ambient conditions, extremely high pressures are required to close this gap and reach a metallic state. In fact, in the solid the question still remains whether metallization occurs by a first-order phase transition from a diatomic to monatomic state 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 g/cm$^3$ (ninefold initial liquid-H$_2$ density), and 3000 K [7, 8]. At this pressure, the temperature is about twice the melting temperature and hydrogen is in the fluid phase. Heating occurs adiabatically upon 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 or reacts chemically with its container before an accurate measurement can be made.

Hydrogen is of great importance for planetary science because its cosmological atomic abundance is about 90%. Jupiter and Saturn
together contain over 400 Earth masses, most of which is hydrogen in the metallic fluid.

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 multistepped, high-intensity laser pulse. The first step of the laser pulse produces a ∼100 GPa shock and the successive pulses comprise a quasi-isentrope [9], similar to the compressive process used in these conductivity experiments. 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.

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, which means ∼2000 K at ∼100 GPa. 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. Thus, it is essential that hydrogen be heated for only a very brief time, say ∼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 or by chemical reactions.

On the other hand, a temperature of 3000 K is relatively low for metallic fluid hydrogen, and this metallic fluid is quantum in nature. That is, 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 essentially the ground state vibrational energy of the H$_2$ molecule. Thus, 3000 K is a sufficiently low temperature that the molecular nature of hydrogen is essentially maintained. Calculations indicate that at 0.6 g/cm$^3$ and 3000 K this fluid is ∼90% molecular H$_2$ and ∼10% H, with some of the molecules in an excited vibrational state [10, 11].
METALLIZATION EXPERIMENTS

The experimental configuration is illustrated in Figure 1. A 0.5 mm-thin layer of liquid H₂ or D₂ is compressed dynamically by a high-pressure shock wave reverberating between two stiff, electrically-insulating sapphire (single-crystal Al₂O₃) anvils, 25 mm in diameter. The initial state is liquid in order to obtain a relatively high final density. 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 as shown in Figure 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 \( P-\rho \) states achieved by shock reverberation are illustrated in Figure 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 Figure 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 [12]. Figure 2 show 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 \textit{versus} time by inserting electrodes through the anvil on the right in Figure 1. Either H₂ or D₂ samples were used, depending on the final density and temperature desired, H₂ giving lower final temperatures than D₂. That is, because the initial mass densities of liquid H₂ and D₂ differ by a factor of 2.4, the final shock-compressed densities and temperatures also differ. Thus, H₂ and D₂ 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
FIGURE 1 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. For the lowest conductivities, the shunt resistor $R_s$ was omitted. Trigger pins turn on recording system. All cables are coaxial.
FIGURE 2  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 $\sim 50$ ns from $P_f/30$ up to $P_f$. After reverberation is complete, $P_f$ is held for $\sim 100$ 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.
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 [13] and of Kerley [14]. 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 are plotted in Figure 3 as electrical resistivity versus pressure, \( P_f \) in Figure 2a. Electrical resistivities measured under single-shock compression up to 20 GPa were reported previously [15].

RESULTS

The slope change at 140 GPa in Figure 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:

\[ \sigma = \sigma_0 \exp\left(-\frac{E_g(\rho)}{2k_B T}\right), \]  

(1)

where \( \sigma \) is electrical conductivity, \( \sigma_0 \) depends on density \( \rho \), \( E_g(\rho) \) 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. This fit gives the result \( E_g(\rho) = 1.22 - 62.6 \times (\rho - 0.30) \), where \( E_g(\rho) \) is the activation energy in eV and \( \rho \) is in mol/cm\(^3\). \( E_g(\rho) \) derived from this fitting procedure and \( k_B T \) are equal at a density of 0.32 mol/cm\(^3\) (9-fold initial liquid-H\(_2\) density) and a temperature of \( \sim 2600 \) K (0.22 eV). At 0.32 mol/cm\(^3\) 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\(^3\) and \( \sim 2600 \) K (0.22 eV). Metallization occurs by thermal smearing of the mobility gap, \( E_g(\rho) \sim k_B T \), which produces a Fermi surface and the minimum metallic conductivity of a disordered metal, 500 \( \mu \Omega \)-cm.

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 [16]. This minimum metallic conductivity of fluid Cs, Rb, and hydrogen is achieved at essentially the same Mott-scaled density of \( \rho_m^{1/3} a^* = 0.30 \), where \( \rho_m \) is the density at metallization and \( a^* \) is the radius of maximum electron probability. Mott's preferred value is 0.25 [17]. Since the radius is the same for H\(_2\) and H [18], 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\(_2\) and H are very similar [18], the two are probably miscible at 3000 K in the fluid. Thus, the measured energy gap is probably that of the mixture of H\(_2\) and H.

Iodine is a molecular element, like hydrogen, which also metallizes at much lower pressure in the liquid, 3 GPa [19], than in the solid, 16 GPa [20]. The measured pressure dependences of the resistivities at metallization are very similar for iodine and hydrogen [21].
Based on Ross' bulk thermodynamic calculations, an estimated 5% of the molecules are dissociated [7]. Tight-binding molecular dynamics simulations [22, 23] also show that fluid metallic hydrogen at these temperatures is essentially molecular. Neglecting dissociation and assuming one conduction electron per H₂ 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, similar to 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 bracketed by simple theoretical models. The minimum electrical conductivity of 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 [17]. In this case $d = \rho_m^{-1/3}$. The calculated minimum conductivity corresponds to a resistivity of 250 $\mu\Omega$-cm, which is within a factor of 2 of the measured value.

The electrical conductivity of fluid metallic hydrogen has been calculated using tight-binding molecular dynamics [23]. 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 [24], do not occur in the disordered fluid. In the fluid, charge clouds on neighboring molecules 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 [16].

**FUTURE RESEARCH AND APPLICATIONS**

Thermodynamic states achieved in these and previous gas-gun experiments, with the Nova laser [25] and with diamond anvil cells [4] are shown in Figure 4. These data are all at comparable pressures and densities; the temperatures range up to $\sim 1$ eV. Since many of
FIGURE 4 Pressure-volume curves for (i) fluid states achieved in this work in H$_2$ (open circles) and D$_2$ (solid circles); (ii) solid states achieved in diamond anvil experiments at 300 K on H$_2$ (open squares) and D$_2$ (solid squares); theoretical 0 K isotherm (solid curve) calculated for H$_2$ hcp phase; D$_2$ Hugoniot points obtained with gas gun under single shock (solid diamonds) and double shock (open diamonds); D$_2$ Hugoniot points obtained with Nova laser (solid triangles).

these data are in a fully quantum regime and since it is not now possible to treat this entire regime with a fully quantum theory, a quantum theory for dense hydrogen at temperatures up to $\sim 1$ eV needs to be developed. In order to develop the required theory and the resulting improved equation of state, it is essential to understand the basic interactions and phase transitions. Thus, a wider range of data
and more accurate equation-of-state data are required, including the phase diagram, illustrated schematically in Figure 5, to put accurate constraints on the theory to be developed.

![Figure 5](image)

**FIGURE 5** Schematic hydrogen phase diagram at high pressures and temperatures. Metallization point (this work) observed by conductivity experiments in shock-compressed fluid, solid phases I–III observed in optical experiments in diamond-anvil cells, and calculated melting curve are indicated. Other phase lines are schematic estimates.
Scientific and technological speculations for metastable solid metallic hydrogen, if it could be quenched to ambient conditions, include room-temperature superconductivity; 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 [26].

Implications of these data for the interior of Jupiter have been discussed elsewhere [27, 28].

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References

[1] Wigner, E. and Huntington, H. B. (1935). J. Chem. Phys., 3, 764.
[2] Alder, B. J. and Christian, R. H. (1960). Phys. Rev. Lett., 4, 450.
[3] Narayana, C., Luo, H., Orioff, J. and Ruoff, A. L. (1998). Nature, 393, 46.
[4] LouBayre, P., LeToullec, R., Hausermann, D., Hanfland, M., Hemley, R. J., Mao, H. K. and Finger, L. W. (1996). Nature, 383, 702.
[5] Hawke, R. S., Burgess, T. J., Duerre, D. E., Huebel, J. G., Keeler, R. N., Klapper, H. and Wallace, W. C. (1978). Phys. Rev. Lett., 41, 994.
[6] Pavlovskii, A. I., Boriskov, G. V., Bykov, A. I., Dolotenko, M. I., Egorov, N. I., Karpikov, A. A., Kolokolchikov, N. P. and Mamyshev, V. I. (1987). In: Megagauss Technology and Pulsed Power Applications, Eds., Fowler, C. M., Caird, R. S. and Erickson, D. J. (New York: Plenum), p. 255.
[7] Weir, S. T., Mitchell, A. C. and Nellis, W. J. (1996). Phys. Rev. Lett., 76, 1860.
[8] Nellis, W. J., Weir, S. T. and Mitchell, A. C. (1999). Phys. Rev. B, 59, 3434.
[9] Lindl, J., McCrory, R. L. and Campbell, E. M., Physics Today, September 1992, p. 32.
[10] Ross, M. (1996). Phys. Rev. B, 54, R9589.
[11] Nellis, W. J., Louis, A. A. and Ashcroft, N. W. (1998). Proc. Roy. Soc. London A, 356, 119.
[12] Ogilvie, K. M. and Duvall, G. E. (1983). J. Chem. Phys., 78, 1077.
[13] Holmes, N. C., Ross, M. and Nellis, W. J. (1995). Phys. Rev. B, 52, 15835.
[14] Kerley, G. I. (1983). In: Molecular-Based Study of Fluids, Eds., Haile, J. M. and Mansoori, G. A. (American Chemical Society, Washington), pp. 107–138.
[15] Nellis, W. J., Mitchell, A. C., McCandless, P. C., Erskine, D. J. and Weir, S. T. (1992). Phys. Rev. Lett., 68, 2937.
[16] Hensel, F. and Edwards, P., Phys. World, April 1996, p. 43.
[17] Mott, N. F. and Davis, E. A. (1971). Electronic Processes in Non-Crystalline Materials (Oxford, London), p. 81.
[18] Barbee III, T. W. (1996). Private communication.
[19] Brazhkin, V. V., Popova, S. V., Voloshin, R. N. and Umnov, A. G. (1992). High Pressure Res., 6, 363.
[20] Riggleman, B. M. and Drickamer, H. G. (1963). J. Chem. Phys., 38, 2721.
[21] Hemley, R. J. and Ashcroft, N. W., *Physics Today*, August 1998, p. 26.
[22] Lenosky, T. J., Kress, J. D., Collins, L. A. and Kwon, I. (1997). *Phys. Rev. B*, 55, R11907.
[23] Kress, J., Collins, L., Lenosky, T., Kwon, I. and Troullier, N. (1998). In: *Proceedings of the Conference on Strongly Coupled Coulomb Systems*, Eds., Kalman, G. J., Rommel, J. M. and Blagoev, K. (Plenum, New York), pp. 331–334.
[24] Ashcroft, N. W., *Phys. World*, July 1995, p. 43.
[25] Da Silva, L. B., Celliers, P., Collins, G. W., Budil, K. S., Holmes, N. C., Barbee III, T. W., Hammel, B. A., Kilkenny, J. D., Wallace, R. J., Ross, M. and Cauble, R. (1997). *Phys. Rev. Lett.*, 78, 483.
[26] Nellis, W. J. (1999). *Phil. Mag. B*, 79, 655.
[27] Nellis, W. J., Weir, S. T. and Mitchell, A. C. (1996). *Science*, 273, 936.
[28] Nellis, W. J. (1999). *Planetary and Space Science* (in press).