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Metastable Solid Metallic Hydrogen

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Abstract

Hydrogen reaches the mimimum electrical conductivity of a metal at 140 GPa (1.4 Mbar), 0.6 g/cm^3 (ninefold compression of initial liquid-H_2 density), and 3000 K in the fluid phase. The quest for metallic hydrogen over the past 100 years is reviewed briefly. Possible scientific and technological uses of metastable solid metallic hydrogen (MSMH) are speculated upon in the unlikely event that the metallic fluid can be quenched to MSMH at ambient pressure and temperature: a quantum, metallic solid with novel physical properties, including room-temperature superconductivity; a very light-weight structural material; a fuel, propellant, and explosive, depending on the rate of release of stored energy; a dense fuel for higher energy yields in inertial confinement fusion; and an aid in the synthesis of novel hard materials. Some of the formidable difficulties to synthesize MSMH are discussed.

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. One hundred years later, solid metallic hydrogen at 300 K has not been observed at experimental pressures up to 340 GPa (3.4×10^6 bar) (Narayana et al, 1998) and the required pressure might be as large as 600 GPa (Loubeyre et al, 1996). In contrast, metallic fluid hydrogen has been observed at 3000 K and 140 GPa achieved with a reverberating shock wave (Weir et al, 1996).

Because of the difficulty in achieving the metallic state, hydrogen has become a prototypical system for the insulator-to-metal (IM) transition. Solid molecular hydrogen is a wide bandgap insulator at ambient (E_g = 15 ev). Thus, extremely high pressures are required to close this gap. Condensed hydrogen is extremely difficult to treat theoretically because it is a quantum system with substantial zero-point energy and motion. In the crystalline diatomic solid, the amplitude of the zero-point motion of the molecule about its equilibrium lattice point is ~15 % of the lattice parameter (Silvera, 1980). The hydrogen molecule can be treated as a quantum mechanical harmonic oscillator because the first few lowest lying vibrational levels are separated by ~6000 K (Kolos and Wolniewicz, 1968), which means the vibrational energy of the ground state of the diatomic molecule is ~3000 K. The associated vibrational amplitude of H_2 is ~0.1 A, calculated from the square root of the expectation value of the square of the displacement of an harmonic oscillator with a mass equal to the reduced mass of two protons and an energy of 3000 K. Solid hydrogen is difficult theoretically because of these zero-point energies and because of phase transitions in molecular orientation and crystal structure (Edwards and Ashcroft, 1997).

Shortly after quantum mechanics was developed, Wigner and Huntington (1935) predicted that the insulating molecular solid would transform isostructurally to a conducting monatomic solid at sufficiently high pressure P and density ρ at temperature T = 0 K. They assumed a simple cubic lattice, which means a filled band with 2 electrons for the molecular insulator and a half-filled band with 1 electron for the monatomic metal. The predicted pressure of this transition at 0 K has varied from 25 GPa (Wigner and Huntington, 1935) to 2,000 GPa (Alder and Christian, 1960). The question still remains as to whether metallization occurs by a first-order phase transition from a diatomic to monatomic solid or whether metallization occurs by band overlap within the diatomic solid.

By heating hydrogen to ~3000 K the mimimum electrical conductivity of a metal was observed at 140 GPa, 0.6 g/cm^3 (ninefold initial liquid-H_2 density), and 3000 K. These conditions lasted for 100 ns and were achieved with a reverberating shock wave (Weir et al, 1996; Hemley and Ashcroft, 1998). 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 ps. Since the time resolution of the diagnostic system and the time to achieve thermal and electrical equilibrium are all ~1 ns or less, the conductivity of equilibrated hydrogen was measured. Hydrogen is a quantum fluid at these conditions because T/T_F ~ 0.02, where T_F is the Fermi temperature of the electron system, and T = ~3000 K is comparable to the ground state vibrational energy of the diatomic molecule and 0.5 the spacing between the first few lowest-lying vibrational levels of the molecule. Thus, the fluid is primarily molecular H_2 with some in an excited state and ~10 at.% H (Nellis et al, 1998a).

In contrast, heating hydrogen statically to such high temperatures has not been possible because hydrogen is optically transparent, electrically insulating, and hydrogen at high temperatures has an enormous mass 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.

The pressure required to achieve metallization is lower in the fluid than in the ordered solid because orientational and crystalline phase transitions, which inhibit metallization in the ordered solid, do not occur in the disordered fluid. In the fluid, charge clouds on neighboring dimers and/or monomers are compressed until they overlap and electrons are delocalized; that is, a Mott transition occurs (Hensel and Edwards, 1996). The electronic excitation energy, E_g, to the conducting state is reduced by pressure until E_g ~ kT, at which point the depression in the density of states around the Fermi level is filled in by thermal disorder to produce a metallic density of states with a Fermi surface and the minimum conductivity of a metal. The measured value of metallic conductivty, 2000 $(\Omega\text{-cm})^{-1}$, is consistent with the minimum conductivty of a metal (Mott and Davis, 1971), the Ziman model of a liquid diatomic metal (Nellis et al, 1998a), and tight-binding molecular dynamics (Kress et al). Implications of metallic fluid hydrogen for Jupiter have been discussed (Nellis et al, 1996, 1998b; Nellis, in press)

POSSIBLE SCIENCE AND TECHNOLOGY

It is not known how, nor even whether, metallic hydrogen could be quenched to ambient pressure and temperature. However, the potential scientific and technological benefits are enormous if it could be. Speculations about such possibilities are discussed in this section and difficulties in synthesizing metastable solid metallic hydrogen (MSMH) are discussed in the next section.

MSMH has been predicted to be a room-temperature superconductor in both the monatomic (Ashcroft, 1968) and diatomic (Richardson and Ashcroft, 1997) crystalline phases. In general the electrical, magnetic, optical, thermal, and mechanical properties are expected to be very unusual for this novel quantum, metallic solid.

We assume that the degree of metastability of MSMH will be tuneable. That is, high metastability means that reversion to the equilibrium phase is very unlikely, such as the high metastability of diamond relative to its reversion to graphite, the equilibrium phase at ambient; low metastablity means that reversion to the equilibrium phase is easily induced. Highly metastable MSMH might be useful as a light-weight structural material, provided it has strength. At high pressures metallic fluid hydrogen exists at ~10 times molecular-solid density, or ~0.7 g/cm^3. So, we assume that MSMH will have a comparable density. Thus, its density is comparable to the density of water, is ~3 times lighter than Al and ~10 times lighter than iron. So, automobiles and other vehicles made of light-weight MSMH would need substantially less hydrocarbon fuels than currently.

Because of its high number density, MSMH would have a high density of stored energy which would be released on reversion to H_2. Since the primary reaction product is H_2, MSMH would be environmentally clean, provided additives required to synthesize it are. Depending on the rate of energy release, this energy could be used as a fuel, propellant, or explosive. If this energy were released relatively slowly, MSMH might be used to replace hydrocarbon fuels currently used for autos, trains, and airplanes. If the energy were released somewhat faster, then MSMH could be used as a propellant. For example, the predicted specific impulse (Mead, 1972) of MSMH is ~2000 seconds, about 5 times that of liquid H_2/O_2 fuel now used to launch rockets into space (Frisbee, 1997). This large increase in specific impulse would greatly facilitate space travel (Cole, 1997).

If the stored energy were released extremely rapidly, MSMH could be used as an explosive.

Hydrogen in the form of deuterium and tritium (DT) is used as the fuel in laser-driven inertial confinement fusion (ICF). MSMH targets would produce substantially higher fusion yields than other forms of DT, not because it is metallic but because of its high density. The higher the starting density of the DT fuel pellet, the higher is the energy yield produced by the nuclear fusion of deuterium and tritium. The extremely high density of metallic DT means that substantially more fuel could be packed into a given space than targets with gases or cryogenic molecular solids. Since metallic DT targets would increase substantially the energy produced in laser-driven ICF (Pollaine, 1997), new giant lasers would have an even larger margin for success than expected previously and cryogenics would not be necessary to fabricate fuel pellets.

By way of comparison, ICF targets at LLNL's NOVA laser are gaseous at 8-50 atmospheres of pressure, which corresponds to a DT gas density of 0.002-0.011 g/cm^3. The cryogenic solid molecular DT layer to be used at the LLNL NIF laser (National Ignition Facility), now under construction, will have a density of 0.25 g/cm^3. MSMH for DT would have a density of ~1.5 g/cm^3, plus the density of any additives necessary to synthesize it. Possible additives are a potential problem for ICF. That is, if the required density of additives is too high, they will cool the laser plasma and reduce the nuclear yield; if additives make MSMH too brittle, it might not be possible to machine the targets sufficiently smoothly to inhibit hydrodynamic instabilities at very high compressions, which reduce yield. In any event, the high density of MSMH makes it attractive as a possible fuel for ICF.

Since some of the hydrogen in metallic fluid hydrogen is in the form of monomers, atomic hydrogen produced by this method might aid the synthesis of new superhard materials. For example, diamond grows at conditions where it is metastable using various chemical vapor deposition methods. Atomic hydrogen plays a major role in this process (Angus et al, 1993). Since atomic hydrogen is produced by a reverberating shock wave, it is possible that atomic hydrogen produced by this technique might lead to the synthesis of other novel metastable forms of carbon, other light elements, and their mixtures.

SYNTHESIS ISSUES

Quenching metallic fluid hydrogen from high pressures and temperatures is a formidable problem. While it is not possible to quench solid monatomic metal from high pressures (Salpeter, 1972), perhaps the metallic fluid could be quenched. If so, then producing the metallic fluid by shock compression has the advantage that large quantities of MSMH might be made using large systems of explosives, as DuPont shock-synthesizes industrial diamond powders in a cylindrical system 4 m high and 1 m in diameter (Bergmann, 1984). In order to do this, the initial size and shape of the hydrogen sample and quenching medium must be known so that metallic hydrogen temperature is quenched by thermal conduction before shock pressure is released, thus decreasing thermal energy to drive the back transformation.

The hydrogen phase diagram must be known at high pressures and temperatures in order to determine an optimal quenching system. That is, the probability of recovering material successfully increases inversely with shock pressure. Thus, it is important to know the lowest shock pressure and temperature required to reach the metallic state in order to maximize the probability of quenching MSMH in a successful shock recovery experiment.

The phase diagram of hydrogen (Nellis et al, 1998a) is illustrated schematically in Fig. 1. The metallization point measured in the fluid is the point at 140 GPa and 2600 K (Weir et al, 1996). The triple point of insulating solid phases I, II, and III was measured by Cui et al (1994) and by Mao and Hemley (1994). The melt line was calculted by Ross et al (1983) and by Hubbard et al (1997). The slope of the metallization curve is assumed to be negative because metallization pressure at 0 K is predicted to be about 300 GPa (Ashcroft, 1990) and observed to be greater than 340 GPa at 300 K (Narayana, 1998). At sufficiently high temperatures hydrogen will be completely dissociated and ionized to produce an electron/proton plasma.

Since only crystalline solid insulators have been observed to date, it is quite likely that if the metallic fluid is simply cooled below the melt line, it will crystallize into an ordered solid insulator. One possible way to retain the metallic nature of the disordered fluid is to quench into a disordered solid, namely, metastable metallic hydrogen glass. In this way it might be possible to take advantage of the fact that the disordered fluid is metallic at unexpectedly lower pressures (~100 GPa) than thought previously for the solid (~400 GPa). To do this would probably require additives, such as B and P metalloids are added to Pd to make a metallic glass.

Several formidable difficulties are involved in quenching MSMH from the metallic fluid:

1) The basic metallization process in the fluid must be determined in order to know what needs to be quenched. The densities and temperatures of the metallic fluid occur at the confluence of thermal and quantum effects which link metallization, ionization, molecular dissociation, and possible cluster formation. The relative importance of dissociation, for example, must be determined to know if monomers are required for metallization or if a purely diatomic phase conducts at ~150 GPa if it is disordered.

2) Quenching the roughly spherical electronic distribution of a metal is difficult in a system which tends toward an insulating diatomic molecular state in the solid.

3) The quench must be stable against zero-point intramolecular and intermolecular quantum motions, the amplitudes of which are a few 0.1 A. Such disturbances might cause MSMH to revert to an insulating diatomic solid phase.

4) Additives will probably need to be found which quench in the desired density and metallic conductivity. It is advantageous to find different additives to produce different degrees of metastability.

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CAPTION

Fig. 1. Schematic hydrogen phase diagram at high pressures and temperatures. Metallization point 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.

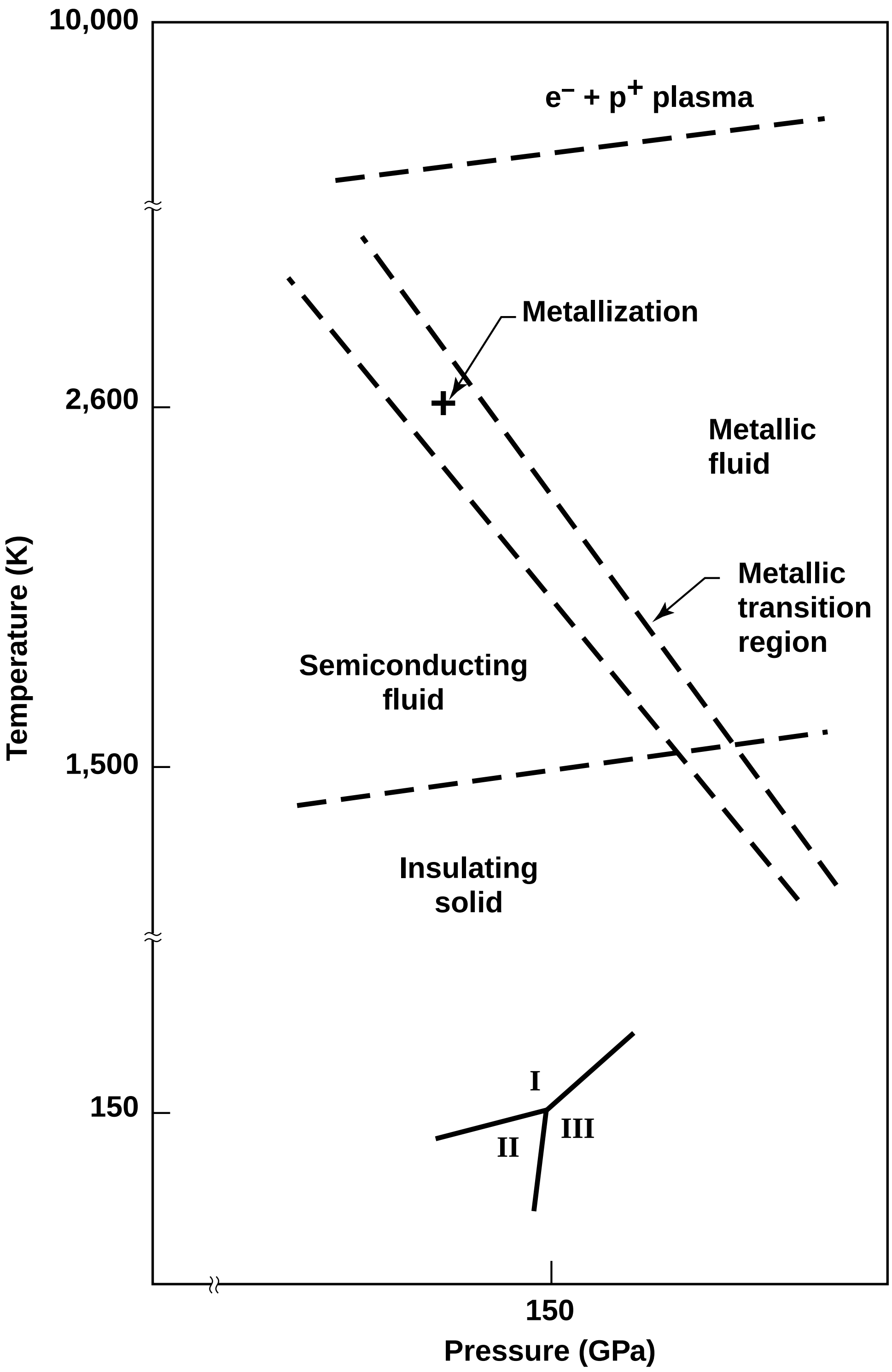
10,000
e⁻ + p⁺ plasma
Metallization
2,600
Metallic fluid
Metallic transition region
Semiconducting fluid
1,500
Insulating solid
I
II
III
150
Temperature (K)
150
Pressure (GPa)

Fig. 1
Nellis