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Metallization of Hydrogen and Other Small Molecules at 100 GPa Pressures

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Fluid hydrogen, oxygen, and nitrogen become metallic at 100 GPa (1 Mbar) pressures. Disorder is the primary reason for observing a metal at lower pressures in the fluid than expected for the ordered solid. This metallic transition is similar to those observed in fluid Cs and Rb by Hensel et al. All five undergo a Mott transition from a semiconducting to metallic fluid with the same electrical conductivities. In contrast, water is a proton conductor at pressures up to 200 GPa. Extreme conditions were achieved for ~100 ns with a reverberating shock wave generated with a two-stage light-gas gun.
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I. Introduction

Hydrogen at high pressures has been a major scientific issue ever since it was predicted to undergo molecular dissociation to a monatomic metallic solid at a pressure P of ~25 GPa at temperature T = 0 K [1]. Because Jupiter is composed of ~90 at. % hydrogen, convective dynamo action of metallic fluid hydrogen at high pressures causes the magnetic field of Jupiter [2,3]. Hydrogen becomes metallic via a Mott transition at 140 GPa, ninefold compressed initial liquid density, and 2600 K achieved in the fluid with a reverberating shock wave [4-6]. Both oxygen [7] and nitrogen [8] undergo Mott transitions, as expected. In contrast, dense water is a fluid proton conductor up to 180 GPa, as expected, and predicted to metallize above 300 GPa and 7000 K [9,10].

Temperature is finite because shock compression is fast and adiabatic. Fig. 1 illustrates the effect of pressure rise time. Fig. 1a shows the cases in which pressure increases in one sharp shock and the case in which pressure increases in ~10 shocks to the same final pressure. Single-shock compression produces higher temperatures and modest density, while multiple shocks produce lower temperatures and higher densities close to the 0-K isotherm (Fig. 1b).

Predicted metallization at T=0 K ranges from 25 to 2000 GPa [1,11]. Metal is not observed to 340 GPa [12-14]. Theory puts metallization of the molecular crystal above 430 GPa [15]. The Wigner transition is estimated at ~620 GPa [16]. If a cell is heated statically a few 100 K, hydrogen diffuses out of the cell before a measurement can be made [17]. However, the ~100 ns lifetime of a shock at a few 1000 K is long for thermal equilibrium and too short to lose hydrogen by mass diffusion and chemical reactions.

II. Experiment

Multiple shocks were achieved with a reverberating shock generated with a two-stage gun in a sample sufficiently large to measure dc conductivity [5]. Pressures are known to 1% from measurements. Densities and temperatures were calculated. Resistivities ρ are plotted in Fig. 2 as log (ρ) versus shock pressure P. Similar results were obtained with explosives [18].

III. Mott Transition in Fluid Hydrogen

The change of slope at 140 GPa in Fig. 2 is the nonmetal-metal transition. The regime 93-120 GPa is thermally activated. The data fit gives a mobility gap of $E_g(D) = 1.22 - (62.6)(D - 0.30)$, with $E_g(D)$ in ev and D in mol

H_2/cm^3. Conductivities from this exponential fit differ from measured values within the error bars.

The metallic state is achieved because pressure reduces the 15 ev gap and thermal disorder fills it in until $E_g/k_B = T \sim 2600$ K, where E_g is smeared out thermally and the electronic system has a Fermi surface (E_g = 19 ev). Since $T/T_F \sim 0.01$, metallic hydrogen is highly degenerate. Fluid hydrogen becomes metallic via a continuous transition from semiconductor to metal. Considerations of macroscopic E_g and E_{diss}, the dissociation energy, suggest that these conductivities are sensitive primarily to electronic excitation, with a small amount of dissociation. However, microscopic considerations below suggest that metallic hydrogen is essentially monomeric.

Tight-binding MD [19] shows that metallic hydrogen at 3000 K has a peak in the proton-proton pair distribution function at the separation distance between protons in the molecule and that "molecules" or dimers are short-lived ($\sim 10^{-14}$ s). Kinetic, vibrational, and rotational energies of the transient pairs are comparable. Conduction electrons have a very short mean free path, the distance between adjacent particles (~2A). This is a strong-scattering system characteristic of minimum metallic conductivity.

Fluid Cs, Rb, and H at ~2000 K metallize with a conductivity of 2000 $(\Omega\text{-cm})^{-1}$ at the same scaled density $D_m^{1/3}a^* = 0.38$, where D_m is the density of atoms at metallization and a^* is the effective Bohr radius [20].

IV. Density at Metallization and Minimum Metallic Conductivity

The Herzfeld criterion, which depends only on polarization of the atom [21], gives a metallization density of 0.60 mol H/cm^3, within 7 % of 0.64 mol H/cm^3 determined in III. This agreement and short dimer lifetimes (~10^{-14} s) suggest that fluid metallic hydrogen is essentially monomeric.

Metallic conductivity, 2000 $(\Omega\text{-cm})^{-1}$, is the minimum conductivity of a metal $\sigma_{min} = 2\pi e^2 / (3hd)$, where h is Planck's constant and $d = D_m^{-1/3}$. At metallization density, 0.60 mol H/cm^3, $\sigma_{min} = 6000$ $(\Omega\text{-cm})^{-1}$, in good agreement with experiment. For H_2, $\sigma_{min} = 5000$ $(\Omega\text{-cm})^{-1}$. Conductivity cannot resolve whether hydrogen is monatomic or diatomic. Metallic conductivities in good agreement with experiment were calculated with the Ziman model [22] and with tight-binding molecular dynamics [23]. The latter show that the nonmetal-metal transition in hydrogen is density-driven.

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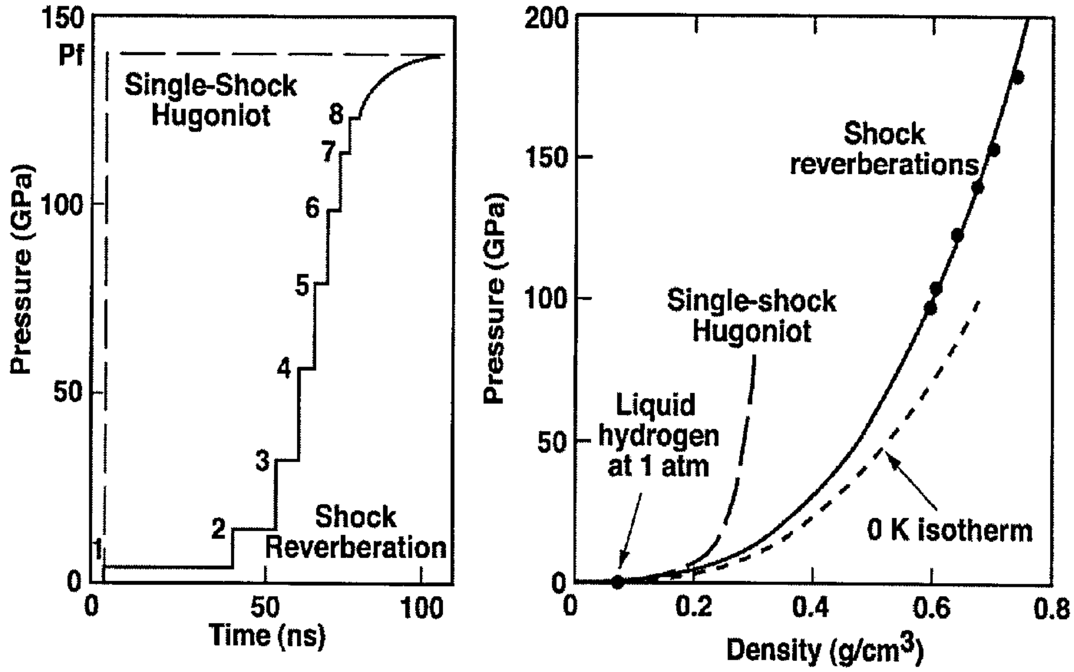

Fig. 1. Effect of time over which pressure is applied on thermodynamic states. One strong shock produces high thermal and total pressures (long-dashed cuve). Many shocks produce substantially lower thermal pressures and higher densities (solid curve) close to 0-K isotherm (short-dashed curve) [5].

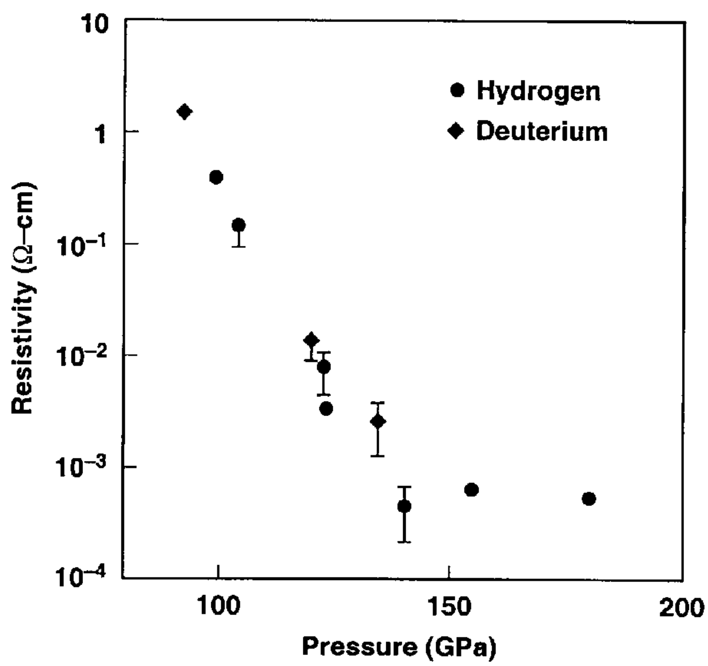

Fig. 2. Logarithm of measured electrical resistivities plotted versus shock reverberation pressure [5]. Similar results are reported in [20].