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Insulator-metal transition of fluid molecular hydrogen

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Dynamically compressed fluid hydrogen shows evidence for metallization at the relatively low pressure of 140 GPa (1.4 Mbar) while experiments on solid hydrogen made in a diamond-anvil cell have failed to detect any evidence for gap closure up to a pressure of 230 GPa (2.3 Mbar). Two possible mechanisms for metalliclike resistivity are put forward. The first is that as a consequence of the large thermal disorder in the fluid ($kT \sim 0.2$–0.3 eV) short-range molecular interactions lead to band tailing that extends the band edge into the gap, resulting in closure at a lower pressure than in the solid. The second mechanism argues that molecular dissociation creates H atoms that behave similar to n-type donors in a heavily doped semiconductor and undergo a nonmetal-metal Mott-type transition. [S0163-1829(96)51838-2]

Weir *et al.*[1] recently reported electrical resistivity measurements for liquid H_2 and D_2 compressed by multiple shocks to calculated pressures of 93–180 GPa (0.93–1.8 Mbar) and temperatures of the order 3000 K. Over this range the resistivity decreases by almost four orders of magnitude to a value of 5×10^{-4} Ω cm at a pressure of 140 GPa and a calculated volume of 3.2 $\text{cm}^3/\text{mol}\,H_2$. This resistivity is typical of a liquid alkali metal. Weir *et al.* interpreted the metallic conductivity at 140 GPa as resulting from thermal electron activation across the molecular semiconducting band gap. They assume that at the semiconducting band gap (E_g) at this pressure equals the thermal energy (kT), or $E_g = kT = 0.3$ eV. At these conditions the conduction electrons are partially degenerate. Using tabular values for the Fermi-Dirac integrals[2] leads to the prediction of a carrier density of $n_c \sim 10^{21}$ electrons/cm^3. This value is comparable to that estimated from the Mott criteria for expanded Cs near its nonmetal-metal transition[3] and the carrier density of an alkali metal at room temperature.

At ambient pressure molecular hydrogen is an insulator with a band gap of about 17 eV.[4] Theoretical calculations predict that with increasing density the band gap decreases continuously and goes to zero at predicted pressures ranging from 150 to 300 GPa,[5,6] depending on the orientation of the molecules in the crystal.[6] For an orientationally disordered phase calculations place metallization close to 300 GPa and at a volume of 1.9 cm^3/mol.[5] Optical experiments on solid hydrogen made in a diamond-anvil cell have failed to detect any evidence for gap closure up to a pressure of 230 GPa.[7]

The purpose of this study is to understand why dynamically compressed hydrogen shows evidence for metallization at the relatively low pressure as 140 GPa. The key feature that distinguishes dynamic experiments from static is that dynamic compression generates partially dissociated high-temperature states with molecular collisions occurring at much shorter separations than in the solid. On the basis of these facts we put forward two possible mechanisms for metalliclike resistivity. The first is that the short range molecular interactions lead to band tailing which extends the band edge into the gap resulting in closure at a smaller volume than in the solid phase. The second is that H atoms created by molecular dissociation form an n-type impurity conduction band that is analogous to the metallic state of a highly doped semiconductor. This is essentially the extension to very high donor concentrations of an idea first put forth by Mott.[8]

In order to attain 140 GPa dynamically, Weir *et al.* first shocked a thin layer of liquid hydrogen sandwiched between two sapphire anvils to 4.7 ± 0.2 GPa and allowed the shock to reverberate between the anvils. This process was simulated by a hydrodynamics computer program using a hydrogen equation of state[9] to provide the final temperature and density. It is well known that a series of multiple shocks approach an isentrope and provides a method to attain a very high pressure dynamically without the very high temperature accompanying a single strong shock.

In the present paper we approximated this process, without using a hydro program, by first calculating the Hugoniot to a pressure of 4.7 GPa and temperature of 1451 K followed by an isotrope from these starting conditions. The present calculations were made using the more recent hydrogen model described in Holmes *et al.*,[10] which was normalized to fit the reflected shock at a temperature $T\sim5000$ K and a pressure of about $P=84$ GPa while retaining the agreement with all the previous lower pressure shock data. The results from the shock-isentrope calculation for hydrogen are shown in Fig. 1. The final temperature ($\sim$2600 K) obtained at 140 GPa is somewhat lower than that of Weir *et al.* mainly because of the improved molecular dissociation physics. The model predicts that at the reported metallization pressure the volume is 2.9 cm^3/mol, also smaller than previously calculated. But the essential points made in this report are not sensitive to these differences. At higher pressures, isentropic temperatures decrease with increasing pressure. This results because in a constant energy or entropy dynamic process molecular dissociation absorbs kinetic energy thereby lowering the temperature. In this case the entropy is maintained at a constant value by the increase in the number of particles.

The theoretical model[10] uses a modified hard-sphere reference system to calculate the radial distribution function and a reference free energy. The hard-sphere packing fraction, $\eta=\pi\rho d^3/6$ is used as a variational parameter to minimize the total free energy. ρ is the density, N/V, and d is the

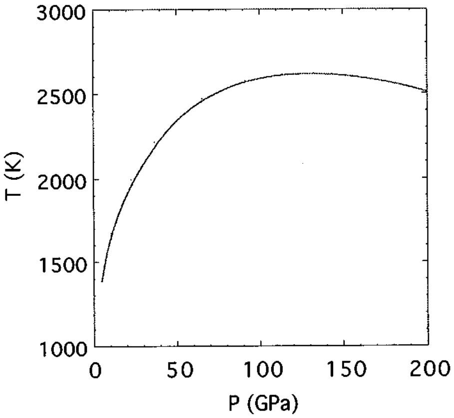

FIG. 1. Calculated liquid hydrogen isentrope: pressure versus temperature.

hard sphere diameter. Figure 2 shows a plot of the hard sphere radial distribution function, $g(r,\eta)$ of fluid hydrogen at these conditions. At a pressure of 140 GPa, $\eta = 0.377$ and $d = 1.5$ Å. d represents the distance of closest approach between colliding molecules. For the purpose of comparison, we also denote the nearest-neighbor separation, $r_{nn} = 1.64$ Å, for hydrogen molecules on an hcp lattice at 0 K and a pressure of 300 GPa and a volume of 1.9 cm^3/mol. At this volume Chacham and Louie[5] predicted that a solid of freely rotating hydrogen molecules will metallize by band gap closure. The striking feature emerging from the plot of $g(r)$ is that each hydrogen molecule in fluid is surrounded by about five neighbor molecules at distances between $r = 1.5$ and 1.8 Å. These separations are comparable to the nearest neighbor distance in the solid at Chacham and Louie's predicted metallization density. Such states will lower the gap enhancing the degree of thermal electron excitation or even close it leading to metallic properties. This feature is similar to the origin of band tails in disordered lattices and impurity bands in semiconductors which show a high density of states extending from the band edge of the ideal crystal and decrease exponentially into the band gap.[11]

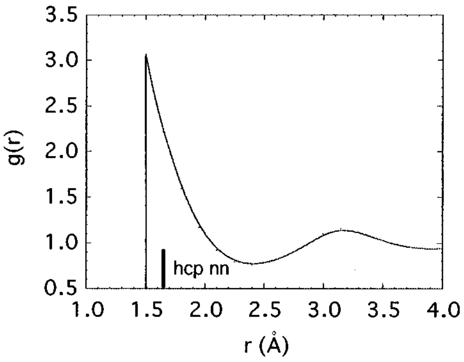

FIG. 2. Calculated $g(r)$ at $\eta = 0.377$, $T = 2600$ K, and 140 GPa. Indicated on the r axis as "hcp nn" is the separation between nearest neighbor molecules on an hcp lattice at 0 K.

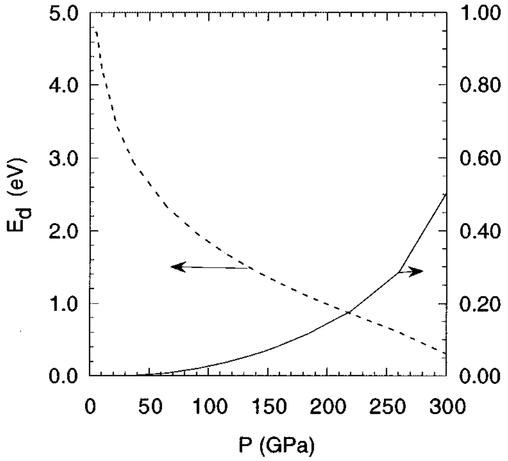

FIG. 3. Pressure versus energy of dissociation (E_d) and fraction of molecules dissociated (x_d).

Molecular dissociation is a second mechanism which could lead to metallic resistivity at lower pressures than band gap closure. Figure 3 shows a plot of the fraction of hydrogen molecules dissociated (x_d) and energy of dissociation (E_d) as a function of pressure along the isentrope. The model[10] predicts that the dissociation energy decreases with increasing density, and goes to zero near 320 GPa. The density dependence of the dissociation energy can be understood by recognizing that while a low density dissociation leads to atoms in the gas phase, high density atoms recombine in a condensed system and some of the energy used to break the bond is returned. This leads to a lowering of the dissociation energy with increasing density and an enhanced degree of dissociation at all pressures. Lowering of the dissociation energy is the molecular analog of the lowering of the electron band gap, and happens for the same reason. That is, the electron kinetic energy increases with increasing density destabilizing the covalent diatomic bond and broadening the valence band thereby narrowing the band gap and decreasing the dissociation energy. At 140 GPa, E_d decreases to 1.5 eV and $x_d = 6.4\%$. Since each dissociated molecule provides two atoms this means that the atom or donor electron concentration, $n_c = N/V$, is 2.7×10^{22} electrons/cm^3 and has a free-electron Fermi energy of 3.26 eV. For comparison with the alkali metals the electron density in solid potassium and sodium are, respectively, 1.34 and 2.5×10^{22} electrons/cm^3 (Ref. 12) and the Fermi energies are 2.1 and 3.1 eV. Even a 2% dissociation of hydrogen will lead to a Fermi energy of 1.5 eV, that is equal to that of solid cesium. The alkali metal Fermi energies are very nearly the same as for the hydrogen donor system. The reason for the near equality is that although the number of free electrons in the hydrogen fluid may be only 0.1 the number of electrons in an alkali metal conduction band, the molar volume of hydrogen (2.9 cm^3) is also only about 0.1 the volume of K and Na (45 and 24 cm^3, respectively). Simple free-electron theory predicts that given similar electron densities the electrical resistivities should be similar, or in this case metalliclike.

The electronic behavior of alkali metal-alkali halide melts is another example of a fluid system exhibiting a nonmetal-metal transition.[13] The alkalis are simple nearly free-electron metals and the halides are completely dissociated closed shell ions. One of the best studied systems is that of fluid K-KCl at 800 °C. At low metal concentrations ($x_m < 0.2$) the electrical conductivity is characteristic of the ionic conductivity of the pure molten salt and above $x_m \sim 0.2$ (n~2

$\times 10^{21}$ cm^{-3}) it rapidly increases reaching metallic character. Except for the Coulombic interaction between ions this system is very similar to a fluid of partially dissociated hydrogen.

A connection can also be made between fluids with ''impurity'' atoms and standard semiconductor physics. It is well known that n-type donor impurity states are near the conduction band edge. If a large number of donors are introduced the electron concentration may induce a metalliclike behavior. The donors will form bandlike states near the conduction edge, and the Fermi level will reside within this band. Transitions from insulating to metallic behavior have been observed to occur in a number of systems. One of the best understood examples is that of n-type silicon and germanium in which the insulator to metal transition is produced by increasing the concentration of group V donors, P, As, or Sb.[14] For donor concentrations below some concentration, n_c, electrons are bound to single donor atoms or small cluster of atoms. Above a second concentration, n_{cb}, the Fermi level of the donor electrons passes into the host crystal conduction band and the system acquires properties characteristic of a metal. The insulator-metal transition in doped semiconductors is generally believed to be a continuous phase transition. By compressing molecular hydrogen at a high temperature a self-doping process occurs in which n-type hydrogen atom donors are created by molecular dissociation and the electrons pass into the conduction band just as in the case of a highly doped group IV semiconductor. Because of the very high density of molecular hydrogen even a dissociation of about 6% in the pressure range near 140 GPa will produce metalliclike electron densities and electrical resistivity.

Iodine is another diatomic molecule, which has been found to metallize in the liquid at a lower pressure than in the solid.[15] In the solid a sharp rise in the electrical conductivity and closure of the optical gap has been observed near 18 GPa.[16] Iodine remains diatomic at that pressure and undergoes a continuous structural change becoming a monoatomic metal near 21 GPa.[17] In molten iodine, near freezing ($T \sim 1000$ K), the electrical conductivity was found to increase by four orders of magnitude between 3 and 4 GPa.[15] Over this narrow pressure range the shape of the melting curve undergoes a drastic change with dT/dP decreasing by a factor of 2. This could be explained by molecular dissociation. Since, $dT/dP = T\Delta V/\Delta H$, where ΔV is the volume change on melting and ΔH is the enthalpy change. Dissociation above 3 GPa would increase ΔH and decrease dT/dP. Given the rapid advances in high temperature diamond-anvil research, I_2 with its small band gap (1.3 eV) and low dissociation energy (1.54 eV), should provide a favorable case for studying the insulator-metal fluid transition. The appearance of similar behavior in hydrogen and iodine suggests this is a general phenomena. In summary, high temperature provides a continuous path from molecular to metal, which differs fundamentally from that of the solid.

In summary, two mechanisms have been proposed to explain why metalliclike electrical conductivity is observed in fluid hydrogen at 140 GPa, a considerably lower pressure than in the solid. These are: (1) disorder induced band tailing and (2) dissociation-induced H impurity band conduction. While it is likely that both mechanisms are operative over some range of conditions, our calculation of the fraction of molecular dissociation predicts that the electron density of the H impurity band at 140 GPa is comparable to that of an alkali metal at ambient conditions which is sufficient to cause metallic conductivity, with or without a further contribution from induced band gap tailing.

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