Observation of Metal-Insulator and Metal-Metal Transitions in Hydrogen Iodide under Pressure

J. van Straaten and Isaac F. Silvera

Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

Hydrogen iodide has been studied up to pressures of 70 GPa at low temperatures in a diamond-anvil cell. Electrical-conductivity and optical measurements have been used to observe pressure-induced phase transitions which are interpreted as follows: First a metal-insulator transition takes place in the molecular solid; with increased pressure a metal-metal molecular-to-atomic transition occurs. An additional transition due to intrinsic impurities has been observed. Implications for metallic hydrogen are discussed.

Metal-insulator (MI) transitions in solids are currently of great experimental and theoretical interest. H_2 is the prototype for molecular solids and is predicted to have transitions due to band-gap closure from molecular insulator to molecular metal to atomic metal[1] at very high pressure; such transitions have been observed in I_2.[2] A second type of MI transition occurs in heterogeneous systems such as doped semiconductors when the density is such that the electrons in effective Bohr orbits of the impurity atoms overlap.[3] Our observations on HI under pressures up to 70 GPa indicate two transitions at pressures of 42.5 and 51 GPa. The first we interpret as a molecular-insulator to molecular-metal transition; the second as a molecular-metal to atomic-metal transition. In addition, light, pressure, and elevated temperatures stimulate the formation of intrinsic impurities that we believe are I_3^- anions in acceptor states. We have also observed MI transitions in doped HI at sufficiently high pressure or impurity density. Our experimental techniques have included optical and uv transmission, Raman scattering, four-terminal electrical conductivity, and photoconductivity in a diamond-anvil cell at temperatures down to 5 K.

HI is an aggressive toxic gas at room temperature, freezing as a clear solid at 222 K in an fcc structure[4] with a zero-pressure molar volume of 34.9 cm^3/mole at $T = 5$ K.[5] Two structural phase transitions take place at lower pressures and temperatures; although the structures are not known, they are probably similar to the other hydrogen halides.[6] The molar volume at which a MI transition takes place can be estimated by a simple model. In the Herzfeld approach[7] the dielectric constant becomes infinite at the MI transition, or, by use of the Lorentz-Lorenz relationships,

$$(n^2 - 1)/(n^2 + 2) = (\epsilon - 1)/(\epsilon + 2) = R/V, \qquad (1)$$

which is equal to 1 at the MI transition. If the molar refraction, R, is independent of pressure then $R = V_m$, the metallization volume. The index of refraction of

liquid HI is 1.466[8] at an estimated volume of 49.76 cm^3/mole,[9] which yields $V_m = 13.76$ cm^3/mole. Although the equation of state of HI has not been measured, Stewart[10] has studied HCl and HBr to 20 kbar. Assuming the equation of state of HI to be similar, with a zero-pressure volume V_0 of 34.9 cm^3/mole,[5] we find[11] for the metallization pressure corresponding to V_m, $P_m = 51.4$ GPa. We can check the result for V_m by considering HI as one of a family of metal hydrides.[12] In this case it can be shown[11] that $V(HI) = V(H) + V(I)$, where $V(X)$ is the molar volume of metallic species X. We take $V(H) = 1.7$ cm^3/mole and $V(I) = 12.2$ cm^3/mole (the molar volume of solid I at this metallization pressure of HI), with the result $V = 13.9$ cm^3/mole or 14.09 cm^3/mole when corrected for charge transfer.[12]

We have studied HI down to $T = 5$ K using a diamond-anvil cell and cryostat described elsewhere.[13] Raman and optical-uv studies were performed with a conventional system. The cell was difficult to load with HI, but best results were achieved with a cell temperature of 190 K while the loading capillary was heated to prevent blockage. 98% HI gas (Matheson) contains a few percent I_2 impurity. It was important to purify this to obtain sensible results. This was done by freezing to 77 K in a trap made of Monel and distilling off the HI.

Upon pressurizing of the HI to $p \geq 20$ GPa the sample became visibly opaque which is interpreted as being due to a reduction of the valence-conduction band gap of energy E_g. Results of transmission (T) measurements for one of several runs are shown in Fig. 1(a), where we plot $-\ln T = \alpha d$ (d is the unknown sample thickness) versus frequency. The band-gap energy E_g is taken as the kink in the curve of αd, indicated by the arrows. Residual absorption at low frequency is assumed to arise from impurities.

It is interesting to predict a pressure for which $E_g = 0$. We extrapolate using an empirical relationship[14] which seems to hold for alkali halides, alkali
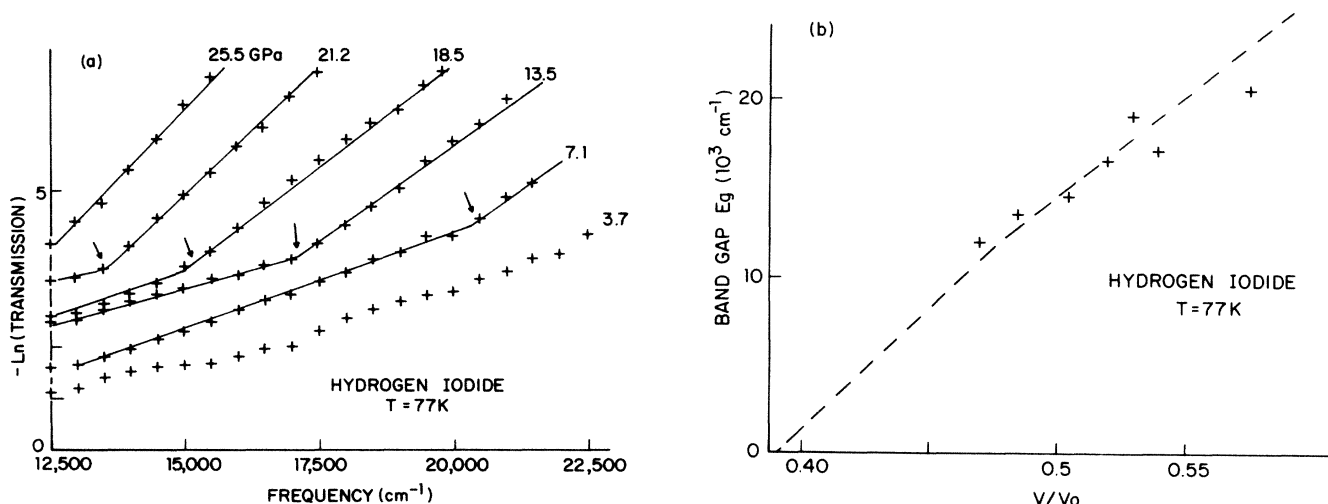

FIG. 1. (a) Logarithm of the transmission as a function of frequency for several pressures. (b) Energy band gap as a function of molar volume; V_0 is the zero-pressure volume. The dashed curve is a fit by Eq. (2).

chalcogenides, and rare-gas solids, $n^2 E_g = D$, where n is the index of refraction, $D = 21.1$ eV, and E_g is in electronvolts. Combining with Eq. (1) yields

$$E_g = D(V - V_m)/(V + 2V_m). \qquad (2)$$

In Fig. 1(b) we show the fitted extrapolation with Eq. (2), which yields $V_m = 13.59$ cm³/mole or $P_m = 54$ GPa. Such predictions are encouraging, but too weak of a basis to claim metallization of HI.

A technique was developed for electrical and photoconductive measurements on cryocrystals, which combines a modification of a four-lead electrical method[15] with techniques for loading cells with cryocrystals.[13] The essential features which will be described in detail elsewhere[11] are shown in Fig. 2. Four pie-shaped zirconium leads were sputtered onto one of the diamonds. The diamonds were sealed in insulating Bakelite holders with four sputtered gold leads connected to the diamond leads with silver epoxy. The leads proved to be most vulnerable to damage at the diamond bevel edge. Nevertheless, they were rugged and survived several pressure cycles up to as high as 70 GPa with the loss of only one lead.

The gasket consists of a T301 stainless-steel girdle and an inner heart of an insulating mixture of Al_2O_3 (75%) and NaCl (25%). This mixture is prestressed, drilled, and again prestressed to yield a sample hole about 100 μm in diameter and about 40–50 μm thick. A Teflon cylinder seals the two Bakelite holders and the HI enters through a Monel capillary.

Results of resistance measurements on a relatively high-purity HI sample at 77 K are shown in Fig. 3(a). In run a, a large discontinuous drop in resistance occurred at 42 GPa. The sample cycled back to higher resistance values at lower pressures. Since the highest reported pressure yet achieved for resistive measure-

ments in a diamond-anvil cell was 48.5 GPa,[15] and as a result of a number of failures of earlier versions of our system at high pressure, great caution was used. In run b the pressure was extended. The first resistive drop occurred at 45 GPa; a second smaller one occurred at 51 GPa. The sample again cycled back to high resistance at low pressure. To establish that the phenomenon is due to band-gap closure, we measured the photoconductivity using 10 mW power at a wavelength of 5145 Å. The photoconductivity as a function of pressure is shown in Fig. 3(b). The arrow indicates the pressure corresponding to $E_g = h\nu$ with E_g defined by the kink in Fig. 1; i.e., the onset of conductivity begins when $h\nu = E_g$.

We interpret the data in analogy with x-ray observations on I_2 and predictions for H_2. The first drop in resistivity corresponds to a molecular-insulator to molecular-conductor transition; the second corresponds to a transition to a metallic atomic state. X-ray
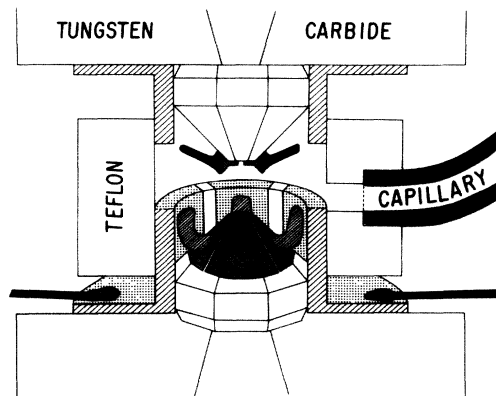

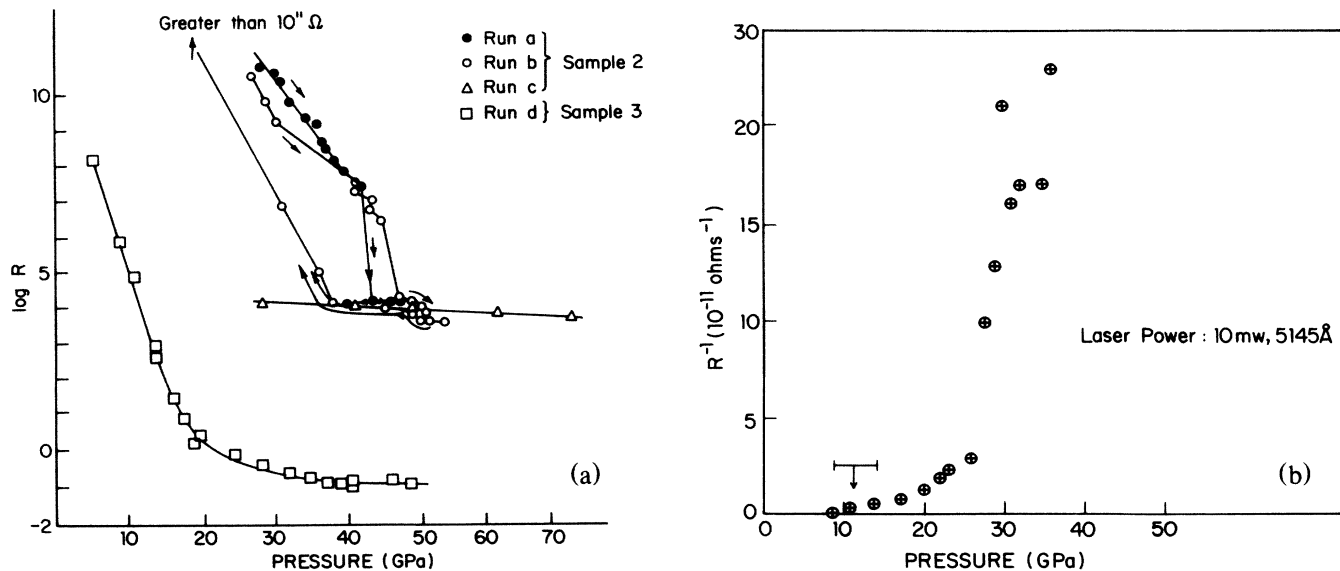FIG. 2. Schematic diagram of the diamond anvils used for making electrical-conductivity measurements.

FIG. 3. (a) Resistance in HI at $T = 77$ K as a function of pressure. Sample 2 was a two-lead measurement; sample 3, four-lead. (b) Photoconductivity at 77 K as a function of pressure on sample 2.

confirmation of these observations would be useful.

One of the great initial difficulties in studying this system has been the buildup of intrinsic impurities. We now believe that this adds a rich new aspect to the problem. In optical or resistive observations at low pressure and as a function of time the sample was visually observed to transform from a pale yellow to a deep red to an opaque solid. This was accelerated by high pressure, high temperature, and in particular, laser light (5145 Å) illumination. In part the impurity was identified as I_2 by use of Raman scattering. We also observed an absorption peak in the uv at 22 000 cm^{-1} which corresponds to absorption due to the I_3^- complex.[16] A possible description of the chemistry is $2HI \rightleftharpoons H_2 + I_2$; $I_2 + HI \rightleftharpoons HI_3$; $2HI_3 \rightleftharpoons 2H^+ + 2I_3^-$ $\rightleftharpoons H_2 + 2p + 2I_3^-$. At any rate I_3^-, H_2, and holes (p) are formed. The I_3^-, which has been identified elsewhere as a stable complex in iodine compounds,[17] is an acceptor level and forms holes in the valence bands. This gives rise to semiconducting behavior. At a high enough concentration (this can be built up by illumination) or density n_i, a MI transition occurs (when $n_i a^* \sim 0.26$, where a^* is the effective Bohr radius). In Fig. 3(a), runs c and d, the resistivity is seen to have taken on a very low value. This behavior was observed in several samples. Measurements down to 5 K show a slow increase in conductivity with falling temperature. For higher-resistivity samples the temperature dependence of the conductivity is very complex as a result of thermally activated reactions, protonic conduction, and hole conduction. We thus have observed three transitions in HI.

The metallization of HI can have implications for metallic hydrogen, other than the fact that the lattice is half atomic H. By embedding of a hydrogen molecule in a metallic lattice with extended overlapping s electrons, the $^3\Sigma$ orbitals may be partially occupied since the $^1\Sigma$ orbitals are saturated, thereby weakening the hydrogen bond. We believe that we might be able to make samples of $(H_2)_{1-x}HI_x$ which will become an alloy of metallic hydrogen $H_{(2-x)}I_x$ at higher pressures. A reduction of the metallization pressure by doping of H_2 has been suggested by Carlson and Ashcroft[18] and one of the authors.[19]

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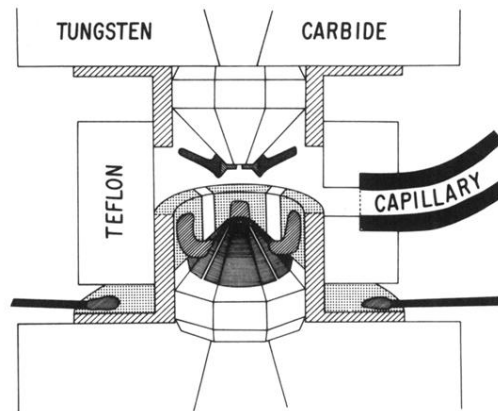
[19]I. F. Silvera, unpublished.

FIG. 2. Schematic diagram of the diamond anvils used for making electrical-conductivity measurements.