Infrared Reflectance Measurements of the Insulator-Metal Transition in Solid Hydrogen

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Reflectance measurements on solid hydrogen to 177 GPa (1.77 Mbar) have been performed from near-infrared to ultraviolet wavelengths (0.5 to 3 eV). Above 150 GPa characteristic free-electron behavior in the infrared region is observed to increase sharply with increasing pressure. Analysis of volume dependence of the plasma frequency obtained from Drude-model fits to the spectra indicates that the pressure of the insulator-metal transition is 149($\pm$10) GPa at 295 K. The measurements are consistent with metallization by closure of an indirect gap in the molecular solid.

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The formation of a metallic modification of solid hydrogen by application of pressure has been a problem of certain prominence in condensed-matter physics since its theoretical prediction by Wigner and Huntington in 1935.[1] In the original theoretical treatment, the transition from the insulating molecular phase to a metallic form takes place by a molecular dissociation to a higher-density monatomic form. More recently, an alternative mechanism for metallization has been proposed, one in which the solid retains its distinct molecular components with metallic character achieved by overlap of the valence and conduction bands.[2] During the past two years, we have conducted a series of studies with the diamond-anvil cell that have permitted the containment of hydrogen samples at pressures above 200 GPa and the measurement of spectroscopic properties *in situ* under these conditions.[3-6] Vibrational Raman measurements have indicated that the molecular form persists into this pressure range, estimated from equation-of-state data to be in excess of tenfold compression ($V/V_0 < 0.1$). Measurements carried out at lower pressures and temperatures (e.g., 77 K) have also revealed that a phase transition occurs at 150 GPa.[3,4,7] Further, dramatic changes in the optical properties of the hydrogen occur at higher pressures: There is a gradual increase in absorption at visible wavelengths, and at the highest pressures the samples have absorption coefficients in excess of 10^3 cm^{-1}. We interpreted the absorption as arising from closing of the direct band gap at pressures above 200 GPa.[5] It was further pointed out that the absorption could also arise from free-carrier excitation if an indirect gap has closed at lower pressures, perhaps in the vicinity of 150 GPa. In fact, this interpretation was consistent with preliminary visible reflectance and absorption measurements reported at that time[5] and with theoretical predictions of band-gap closure below 200 GPa.[8]

A critical test of the onset of metallization by a band-crossing mechanism is the measurement of the free-electron behavior in the infrared wavelengths. In fact, should hydrogen become metallic below 200 GPa, the small change in optical properties in the visible would indicate that the plasma frequency ω_p would be in the infrared range at these pressures. In this Letter, we report the extension of our optical measurements on dense solid hydrogen to infrared wavelengths. Measurements of infrared reflectivity were carried out to 177 GPa. We demonstrate that hydrogen exhibits free-electron behavior with increasing pressure above about 150 GPa at room temperature. Assuming the spectra can be described by a Drude model, we determine the metallization pressure of hydrogen to be 149($\pm$10) GPa at 295 K.

The hydrogen was pressurized in a modified megabar-type diamond-anvil cell with anvil geometries and gasketing materials described previously.[9] The sample chambers were 30-50 μm in diameter. The optical measurements were carried out using a scanning uv-visible-infrared system employing Si-diode and PbS detectors with a wavelength range of 0.4-2.5 μm similar to that described by Syassen and Sonnenschein.[10] Pressure was determined by ruby R_1 fluorescence from small grains of ruby estimated to be less than 5% of the total sample volume, and by Raman measurements of the vibron frequency, which has been calibrated against the ruby-pressure scale.[11,12] Measurements were performed on three separate samples of hydrogen that reached pressures above 150 GPa. In addition, we performed identical (control) measurements on solid neon to 165 GPa. The experimental parameters for each run are listed in Table I.

Reflective spectra of hydrogen at the maximum pressures achieved in the three hydrogen runs are shown in Fig. 1. A pair of perfectly parallel diamond anvils with a transparent sample in between reflects as a Fabry-Pérot interferometer and produces an interference pattern. The interference pattern is obtained in hydrogen run No. 2 to 161 GPa, and is used for calculating the index of refraction and its dispersion. The results indicate that the direct band gap of hydrogen remains wide within the pressure range of the present study. The disappearance of the interference pattern at 120 GPa and its reappear-

TABLE I. Experimental parameters. Reflectance spectra were measured through the top diamond; A, bevel diameter; B, culet diameter; θ, bevel angle.

Run No.	Sample	Top diamond			Lower diamond			Sample diameter (μm)	Maximum pressure (GPa)
		A (μm)	B (μm)	θ	A (μm)	B (μm)	θ		
1	H_2	513	50	9°	515	54	9°	40	177
2	H_2	296	74	9°	307	71	9°	40	161
3	H_2	485	103	10°	490	47	7°	30	172
4	Ne	500	48	7°	510	105	10°	40	165

ance at 140 GPa further shows that the refractive index of hydrogen crosses the refractive index of diamond at about 130 GPa. In order to obtain pure reflectivity spectra, the interference pattern could be eliminated by experimentally spoiling the interferometer with a small amount (5%) of fine ruby powder uniformly distributed in the hydrogen sample, such as in run No. 1.

In each run a significant rise in reflectivity in the infrared is observed at the maximum pressure. Figure 2 shows that this rise starts at pressures above 150 GPa. No structure besides the interference pattern in run No. 2 is observed towards the visible spectral range, consistent with previous measurements.[5] At higher energies the signal drops as a result of diamond absorption at these energies. The behavior in the near infrared is clearly indicative of Drude-like reflectivity with a plasma frequency in the infrared. A very important observation in this regard is the systematic increase in the near-infrared signal with pressure (Fig. 2). The solid clearly remains molecular at these pressures, as indicated by the presence of a strong intramolecular stretching mode (vibron) observed in the Raman spectrum measured at

each point.

Since these are the first measurements of this type reported for hydrogen, it is prudent to consider a number of possible artifacts that could contribute to this signal. This is especially important because the optical properties of diamond anvils at very high stresses have not been fully characterized. For this reason, we conducted a series of experiments with different samples to check for reproducibility. Also, different pairs of diamonds were used for each run; this is significant because there is a natural variability in optical properties of the type-Ia di-

FIG. 2. Reflectance spectra of hydrogen as a function of pressure in the near infrared (run No. 1). The experimental data are given by the open circles; the solid lines correspond to calculated spectra with the following best-fit parameters: for $P = 158$ GPa, $\omega_p = 1.11(\pm 0.40)$ eV, $\hbar/\tau = 0.65(\pm 0.50)$ eV, $\epsilon_{IB} = 12.7(\pm 1.0)$, $n_D = 3.29$; $P = 167$ GPa, $\omega_p = 1.70(\pm 0.30)$ eV, $\hbar/\tau = 0.75(\pm 0.20)$ eV, $\epsilon_{IB} = 14.8(\pm 0.5)$, $n_D = 3.33$; $P = 177$ GPa, $\omega_p = 2.42(\pm 0.20)$ eV, $\hbar/\tau = 0.77(\pm 0.20)$ eV, $\epsilon_{IB} = 17.3(\pm 0.5)$, $n_D = 3.42$. The values for $\hbar/\tau$ obtained in these fits are large (see also Refs. 17–20); hence we consider τ to be only a phenomenological fitting parameter. In the visible range (above 1.5 eV) the calculated spectra tend to deviate from the measurements because of the neglect of dispersion effects and absorption in diamond.
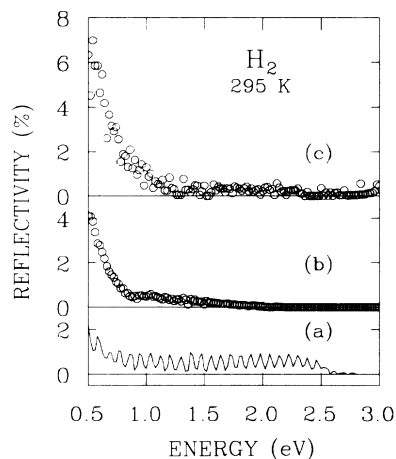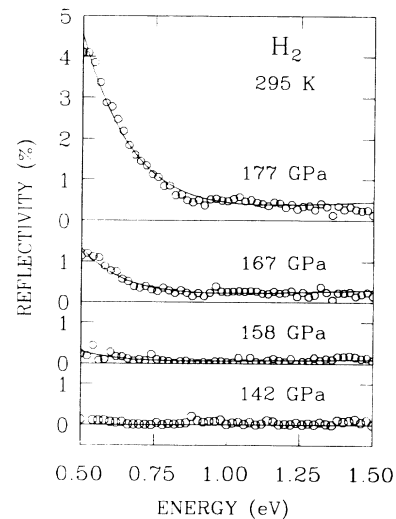

FIG. 1. Reflectance spectra of hydrogen, measured at the maximum pressures achieved in the three hydrogen runs: (a) Run No. 2, 161 GPa. (b) Run No. 1, 177 GPa. (c) Run No. 3, 172 GPa.

amonds that are used. Finally, at the very high stresses of these experiments there can be a significant deformation of anvils at the diamond-sample interface. This deformation is dependent on the geometry of the tip, the strength of the gasket and sample, and the conditions of sample preparation (e.g., preindenting). These factors were therefore varied in each of the runs.

All three runs on hydrogen show the dramatic increase in infrared reflectivity above 150 GPa. The three runs show similar behavior; the differences are within the experimental errors of the measurements and arise principally from uncertainties in the pressure and stress conditions. Sampling aperture sizes were varied from 13 to 6 μm to verify that the high reflectivity did not arise from the metal gasket. In addition, reflectance spectra of the sample and the gasket differ: The gasket is reflective through the infrared and visible region, whereas the high-pressure hydrogen has low reflectivity in the visible. At 177 GPa in run No. 1, moreover, the reflectivity of the hydrogen sample at 0.5 eV exceeded that measured from the rhenium gasket.[13] Finally, solid neon was studied as a control experiment because it is a weak solid at high pressure,[12] and is therefore likely to cause similar diamond-anvil deformation at high stresses. On the other hand, its metallization pressure is predicted to be approximately 3 orders of magnitude higher than that of hydrogen,[14] so changes in the optical properties are expected to be minimal at these pressures. Because of the large difference in the refractive index of neon and diamond even at high pressures, the neon sample showed a strong interference pattern. However, the increase in reflectivity in the infrared documented for hydrogen was not observed in neon to the maximum pressures studied (165 GPa).

We fitted a simple Drude free-electron model[15] to the experimental spectra for pressures above 150 GPa. In this model, the real and imaginary parts of the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ are given by

$$\epsilon_1(\omega) = \epsilon_{1B} - \omega_p^2\tau^2/(1+\omega^2\tau^2),$$

$$\epsilon_2(\omega) = \omega_p^2\tau/\omega(1+\omega^2\tau^2),$$

where ω_p is the plasma frequency, τ is an effective free-carrier scattering time, and ϵ_{1B} is the contribution to the dielectric function arising from direct interband transitions at higher frequency, which is taken to be real and constant. The reflectivity is given by the Fresnel equation

$$R = |[\epsilon(\omega)^{1/2} - n_D]/[\epsilon(\omega)^{1/2} + n_D]|^2,$$

where n_D is the refractive index of diamond. Its pressure dependence was determined by an effective oscillator model. We also took into account the observation that the refractive index of hydrogen exceeds that of diamond for pressures above 130 GPa. Further details of the calculation will be presented in a subsequent paper.[16] Simi-

lar models have been used successfully to describe the infrared optical properties of CsI,[17] Xe,[18] and O_2 (Ref. 19) during band-gap closure at pressures above 100 GPa.

The results of the fits for run No. 1 are shown by solid lines in Fig. 2. The model accurately reproduces the rise in infrared reflectivity and transmission in the visible at pressures above 150 GPa. The result is consistent with excitation of free carriers originating from an indirect valence-conduction band overlap. From 158 to 177 GPa, ω_p increases from 1.1($\pm$0.4) to 2.4($\pm$0.2) eV. To estimate the transition pressure, we assume that the energy bands are parabolic[20] and shift linearly with volume over the range of these measurements.[21] A plot of $\omega_p^{4/3}$ vs V in the vicinity of metallization reveals the point of band overlap (the volume at which $\omega_p = 0$). The results are shown in Fig. 3, where we have used the recently determined x-ray equation of state for hydrogen.[22] A linear trend is apparent, with $\omega_p^{4/3}$ rising steeply with decreasing volume. Linear extrapolation yields $\omega_p = 0$ at $V = 2.52(\pm 0.03)$ cm^3/mol; this corresponds to a pressure of 149($\pm$4) GPa. Considering the additional uncertainty associated with the pressure calibration, the error in the transition pressure is estimated to be $\pm$10 GPa. The frequency of molecular vibron measured in each of the hydrogen samples shows a continuous shift with pressure, with no sign of the discontinuity found at lower temperatures[3,4,7] (to 177 GPa). Hence, the data suggest that the insulator-metal transition is continuous at 295 K.

In conclusion, we have presented direct experimental evidence consistent with metallization of hydrogen by a band-overlap mechanism. The results are also in accord with previous optical observations and measurements in the visible.[5] The observation that the sample is transparent in the visible at the point of band overlap indicates that the band gap is indirect at closure, with the direct transitions still at high energies in the ultraviolet. The optical spectra in the low-energy range can be fitted suc-
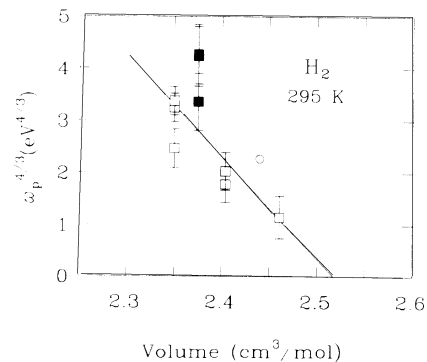

FIG. 3. Plot of $\omega_p^{4/3}$ vs molar volume: open squares, run No. 1; open circle, run No. 2 (estimated from the rise in the infrared reflectivity); and solid squares, run No. 3.

cessfully with a simple free-electron model. An analysis based on both absorption and reflectance measurements will be presented in a later publication. It may be of interest to point out that though the band-overlap mechanism of metallization was not explicitly examined in the original study of Wigner and Huntington,[1] they suggested that intermediate forms may be stable prior to full molecular dissociation. We may consider the molecular metallic phase, for which we now have evidence, to be of this type.

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