

Absorption and Reflectance in Hydrogen up to 230 GPa: Implications for Metallization

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(Received 24 September 1990)

We have measured optical absorption and reflectance in the visible and near infrared in hydrogen up to 230 GPa between 77 and 295 K. Our data show no evidence that hydrogen metallizes near 150 GPa, as has been recently reported from reflectance data. We analyze both experiments and conclude that the metallization of hydrogen remains an open question.

PACS numbers: 71.30.+h, 62.50.+p, 78.20.Dj

Observation of the pressure-induced insulator-to-metal (IM) transition in solid hydrogen has been an experimental challenge since it was first predicted in 1935.¹ Subsequent theoretical studies^{2,3} predicted that hydrogen first transforms to a semimetallic molecular state by closing of an indirect band gap, with the atomic metallic state occurring at higher pressures. In 1988, Hemley and Mao⁴ observed a transition in solid molecular hydrogen at 145 GPa (100 GPa = 1 Mbar), which they believed to be an extension of the low-pressure, electric-quadrupole-quadrupole-induced transition to an orientationally ordered state. Lorenzana, Silvera, and Goettel⁵ subsequently identified this as a transition to a new phase called the hydrogen-*A* (H-*A*) phase, which exists only above 149 GPa. Eggert, Goettel, and Silvera⁶ presented indirect evidence from dielectric measurements that hydrogen may become metallic in this pressure region. Mao and Hemley⁷ observed visual darkening of hydrogen above 200 GPa, although this is not proof of metallization.⁸ Recently, Mao, Hemley, and Hanfland⁹ (MHH) measured the reflectance of hydrogen to 177 GPa at room temperature. Using a Drude model, they concluded that the IM transition occurs at 149 GPa. In this Letter we present results of optical measurements up to 230 GPa from 77 to 295 K. We find no evidence of Drude behavior, which leaves the question of the nature of the H-*A* phase open.

Several authors have presented additional arguments consistent with the H-*A* phase being the molecular metallic phase. Theoretical³ and experimental^{10,11} studies indicate that the structure of the H-*A* phase may be hcp with the molecular axes oriented along the *c* axis. A calculation based on the hcp structure¹² has shown that the band gap for orientationally ordered hydrogen is significantly smaller than the gap for disordered hydrogen, with the gap closing at 180 ± 20 GPa for ordered hydrogen. Lorenzana, Silvera, and Goettel¹⁰ provided evidence that the H-*A* phase is orientationally ordered, lending support to the idea that H-*A* might be metallic. In addition, when entering the H-*A* phase there is a

discontinuous shift to lower frequencies for the vibron.^{4,5} This is consistent with the existence of an IM transition, since a transfer of bound electrons into free-electron states would weaken the molecular binding and hence soften the vibron.

In the metallic phase we expect a rise in the infrared absorption and reflectance, characteristic of a Drude free-electron metal, as observed in Xe.^{13,14} The isotropic Drude model with equal electron and hole masses¹⁵ yields expressions for the real and imaginary parts of the dielectric constant, $\epsilon \equiv \epsilon_1 + i\epsilon_2$:

$$\begin{aligned}\epsilon_1 &= n^2 - k^2 = \epsilon_{1B} - \omega_p^2 \tau^2 / (1 + \omega^2 \tau^2), \\ \epsilon_2 &= 2nk = \omega_p^2 t / \omega (1 + \omega^2 \tau^2).\end{aligned}\quad (1)$$

$N \equiv n + ik$ is the complex refractive index, ϵ_{1B} is the dielectric contribution from interband transitions, ω_p is the plasma frequency, and τ is the electron relaxation time.¹⁶ The absorption coefficient is given by $\alpha = (2\omega/c)k$. The absorption [in terms of optical density (OD)] is given by Beer's law, $A = \ln(I_0/I) = 0.434\alpha d$, and the reflectance for normal incidence is given by the Fresnel equation, $R = |n + ik - n_d|^2 / |n + ik + n_d|^2$, where d is the sample thickness and n_d is the refractive index of diamond.

In a diamond-anvil cell (DAC), optical studies are restricted to a small frequency range so that caution must be used in interpreting a low-frequency rise as a "Drude edge." Since causality relates absorption and reflectance, confidence in the applicability of the Drude model is provided by demonstration of internal consistency of the absorption and reflectance data. In metallic xenon,¹³ it was significant that both absorption and reflectance were well fitted by the Drude model.

We measured absorption and reflectance in hydrogen up to 230 GPa between 77 and 295 K. The DAC techniques and sample loading were similar to those reported elsewhere.^{5,13} We used double-beveled diamonds with 50- μm central flats and a rhenium gasket.¹⁷ We measured pressure using the quasihydrostatic ruby scale¹⁸

corrected for use at 77 K. Ruby grains, $\sim 1 \mu\text{m}$ in size, were concentrated at the edge of the gasket hole; a ruby-free hydrogen sample about $17 \mu\text{m}$ in diameter was always present. The ruby appeared dark at all pressures, except between 30 and 60 GPa where index matching of the ruby and the hydrogen occurred. Above 118 GPa we used the time-resolved chopping technique¹⁹ to isolate ruby fluorescence from pressure-induced diamond fluorescence.

Our optical studies employed experimental techniques similar to those used by Goettel *et al.*¹³ in xenon. We measured absorption and reflectance spectra from 0.7 to 3.0 eV using a Ge detector and a diode array. Using a spatial filter, we limited our sampling-area diameter to $5 \mu\text{m}$ in the visible. We referenced the absorption data to a spectrum taken at 75 GPa, where there was negligible absorption. We referenced the reflectance of the hydrogen-diamond interface to the vacuum-diamond interface at the table of the near diamond.

At all pressures, except between 120 and 160 GPa where index matching of hydrogen and diamond occurred,⁹ we observed Fabry-Pérot (FP) fringes in the visible reflectance [Fig. 1(a)]. We determined the dispersion of the refractive index of hydrogen to our highest pressures, reproducing the earlier measurements^{6,20} at lower pressures. These results will be presented elsewhere. From the fringe measurements, we determined the product of the index of refraction and the sample thickness. Using the extrapolated index of refraction for hydrogen,²¹ we estimated our sample thickness to be about $2.3 \mu\text{m}$ at 230 GPa.²²

Our absorption and reflectance (Fig. 1) measurements at 77 K exhibit no Drude evidence for the H-A phase being metallic up to 220 GPa. The reflectance [Fig. 1(a)] as a function of energy, down to 0.85 eV, is less than 5% and, shows no significant rise in the infrared. Accuracy in our measurement of reflectance was somewhat impaired due to wavelength-dependent scatter from our cryogenic-optical system. The absorption [Figs. 1(b) and 1(c)] is less than 0.5 OD at 0.7 eV for all pressures, and shows no evidence for a pressure-dependent rise in the infrared. The reproducibility of the absorption data was better than 0.2 OD. The apparent fall in reflectance and the rise in absorption with increasing energies are due to stress-induced absorption in the diamond anvils, and become more pronounced at higher pressures. The consistent signatures in both the absorption and reflectance data imply that the absorption is in the diamond, not in the hydrogen.

MHH (Ref. 9) have recently reported reflectance measurements from 0.5 to 3.0 eV for hydrogen up to 177 GPa at 295 K; however, no absorption data were presented. Most of their measurements were performed on samples with ruby distributed throughout the hydrogen to suppress interference fringes. They observed a pressure-dependent rise in infrared reflectance with a

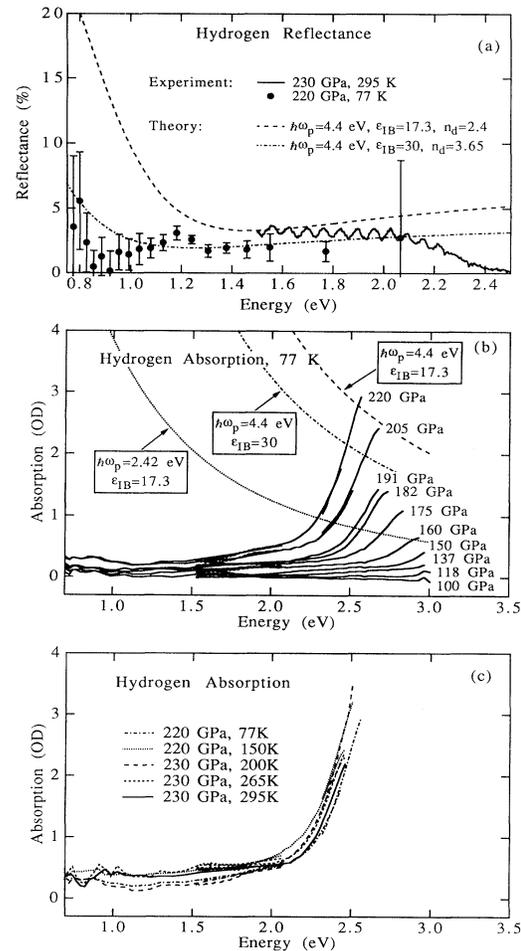


FIG. 1. (a) The reflectance and (b),(c) the absorption vs photon energy at various pressures. The fall in reflectivity and the rise in absorption at higher energy is due to absorption in the diamond anvils. The dashed curves are calculated from the Drude model using $\hbar/\tau=0.77 \text{ eV}$, and the values shown for ω_p and ϵ_{IB} . (a) Reflectance data at our highest pressures. The data for 230 GPa and 295 K (solid line) were taken with a visible Si diode array detector. The data for 220 GPa and 77 K (solid circles) were taken with an ir Ge diode detector. The bars represent statistical error. In addition, there is an estimated systematic error of up to a factor of 2 in the absolute value due to base-line normalization corrections. (b) The absorption data for all pressures at 77 K. (c) Absorption spectra at several temperatures.

maximum reflectance of about 6%. Fitting their reflectance data by the Drude model, they found plasma frequencies as high as 2.42 eV at 177 GPa. Extrapolating the plasma frequency to zero, MHH inferred metallization at 149 GPa. If hydrogen is exhibiting Drude behavior, then the reflectance measurement of MHH necessarily determines our complementary absorption measurements. We shall show that the two data sets are inconsistent, within the scope of the Drude model.

Extrapolating MHH's values of $(\omega_p)^{4/3}$ with density, we obtain $\hbar\omega_p=4.4$ eV at 220 GPa. In Fig. 1(a), we plot Drude-model reflectance curves using this value for $\hbar\omega_p$, and $\hbar/\tau=0.77$ eV (the 177-GPa value is from MHH). Varying the refractive index of diamond between the 1-bar value of 2.4 and an estimated value of 3.65 using a simple model,⁶ we find drastically different curves, given reasonable values of ϵ_{1B} [Fig. 1(a)]. Since the absorption is independent of the refractive index of diamond, the uncertainty in the behavior of diamond is much less important, as illustrated by the absorption curves in Fig. 1(b) using identical parameters to those used in the reflectance curves in Fig. 1(a). For this reason we shall stress our absorption measurements.

Our experimental absorption limit of less than 0.5 OD at 0.75 eV, allows us to set bounds on the plasma frequency at 220 GPa. Using values for $1/\tau$ and ϵ_{1B} similar to the values found by MHH yields an upper limit for $\hbar\omega_p$ of about 0.8 eV at 220 GPa. MHH's fit of their data by the Drude model suggests that at 177 GPa for a sample 2.3 μm thick, absorption should rise to 5.5 OD (3×10^5 attenuation in transmission) at 0.75 eV as shown in Fig. 1(b). Using the extrapolated value at 220 GPa of $\hbar\omega_p=4.4$ eV and MHH's 177-GPa values for \hbar/τ and ϵ_{1B} implies an absorption of 22 OD at 0.75 eV [also shown in Fig. 1(b)]. We would have easily observed such absorption. At the highest pressures in our experiment, the optical path length in the hydrogen sample was 2 to 3 μm , while the optical path length in the stressed diamond anvils was about 4 mm. We note that our measurements show an absence of absorption, and uncertainties regarding absorption of diamond at high pressure cannot explain our lack of absorption. Additionally, reasonable variations of $1/\tau$ and ϵ_{1B} do not alter our conclusions.

Considering the possibility that unexpectedly large thermal effects were causing the apparent discrepancies, we raised the sample temperature to 150 K at 190 GPa and to 295 K at 230 GPa.²³ We did not observe any Drude behavior in the absorption at higher temperatures as shown in Fig. 1(c). Thus, based on optical data, we do not confirm the conclusion of MHH that hydrogen is in the metallic state above 149 GPa.

We have demonstrated that our data are inconsistent with the Drude-model interpretation of MHH. We now present an analysis which shows that MHH's data itself is incompatible with the Drude model they used; this analysis implies that their sample had little absorption in the infrared, as we have observed. Given the Drude-model parameters ω_p , τ , and ϵ_{1B} , the refractive index $N=n+ik$ is determined. By accounting for a complex refractive index in the derivation of the FP fringe equation,²⁴ absorption may be included in the expression for the reflected intensity,

$$\frac{I_r}{I_0} = R \frac{(1-T)^2 + 4T \sin^2(\delta/2)}{(1-TR)^2 + 4TR \sin^2(\delta/2)}. \quad (2)$$

Here, $T \equiv \exp(-ad)$, $\delta \equiv 4\pi nd/\lambda$ for normal incidence. We plot one of MHH's reflectance traces (from run No. 2, 161 GPa) in Fig. 2. In this run, unlike their other two, the sample was not covered with ruby, and the reflectance shows FP fringes in the infrared, as well as a rise in infrared reflectance (similar to their other runs). We also plot a least-squares fit to the reflectance data of MHH, using Eq. (2). In the infrared region of rising reflectance, the corresponding increase in absorption, demanded by the Drude model, rapidly damps the FP fringes. The existence of infrared fringes in this region of the MHH data implies a sample absorption below 1.0 OD (as opposed to 3.3 OD at 0.5 eV, predicted by the Drude model). In this analysis we fixed the value for ϵ_{1B} , taken from Ref. 11, and varied the other parameters shown in Fig. 2. Our value of ω_p corresponds closely to that given by MHH, and our general conclusions are not sensitive to variations in the fitting parameters. This analysis shows that the rise in the infrared reflectance in MHH's data, run No. 2, is not consistent with the Drude model, and thus cannot be interpreted as either a Drude edge or evidence for metallization.

In conclusion, we propose two explanations for our optical results in hydrogen: (1) The H-A phase is metallic, but the characteristics of the bands which overlap are such that ω_p remains small, either through a small free carrier density or a large effective mass. In this case the indirect arguments for H-A being metallic would be correct, although Drude behavior would not be observable in the energy range we have studied. (2) The H-A phase may not be metallic. In this case our observations are not surprising; however, the question of the identification of the H-A phase remains unresolved.

Our results do not provide any evidence for the metallization of hydrogen in the spectral range studied to a pressure of 230 GPa. This does not prove that the H-A phase is not metallic. However, with our data, and a reanalysis of MHH's data, we have shown that hydrogen

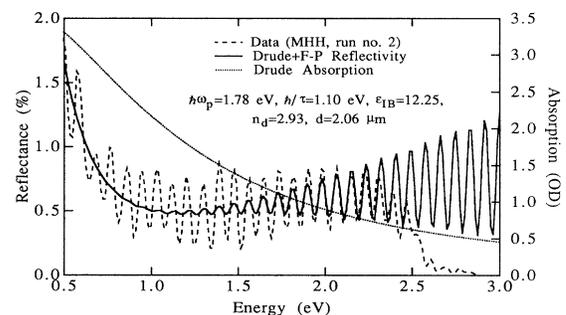


FIG. 2. The MHH reflectance data. We show a least-squares fit to this data using Eq. (2). The resulting Drude absorption is plotted against the right-hand scale. The high-energy attenuation in the data is due to absorption in the diamond and was not included in the fit.

does not exhibit the characteristic Drude behavior expected of a metal, in the spectral range studied.

We thank M. Cohen, A. Garcia, A. Lagendijk, S. Louie, J. Mester, E. Meyer, and A. Ruoff for useful discussions. We gratefully acknowledge financial support from the U.S. Air Force Astronautics Laboratory, Contract No. F04611-89-K-0003, and the Harvard Materials Research Laboratory, NSF Grant No. DMR-14003. One of us (W.J.E.) was also supported by the Fannie and John Hertz Foundation.

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²³Our diamonds failed spontaneously after spending five days at 295 K and 230 GPa. From an analysis of the failure mode of many hydrogen experiments, we feel that the most likely explanation is temperature-dependent diffusion and embrittlement by hydrogen of the diamond anvils.

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