Evidence for Band Overlap Metallization of Hydrogen

The report "Optical studies of hydrogen above 200 gigapascals: Evidence for metallization by band overlap" by H. K. Mao and R. J. Hemley (*1*) in my opinion does not present evidence that conclusively demonstrates the metallization mentioned in the title. The most demanding test of such metallization is to show that the dc electrical conductivity remains finite as the temperature goes to zero. One could also show that the sample possesses the optical properties of a metal.

Visual darkening might be expected for a thin metallic film, but by itself the darkening of a sample is not sufficient evidence of metallization, just as a lustery metallic reflectance is not. Good examples are the semiconductors germanium and silicon, which as thin films are dark in the visible, while bulk samples are metallic in appearance. Darkening of a sample can arise from any number of physical mechanisms that cause absorption throughout the visible spectral region. At zero pressure hydrogen has a strong broad-absorption band at 11 eV due to electronic excitons and a valence-conduction band gap absorption at 15.4 eV. When the band gap goes to zero, the solid becomes a metal. As the pressure is increased, both the exciton band and the band gap shift to lower energy. The exciton, if it remains a stable state, is always lower in frequency than the band gap. Thus, when the exciton is in the visible the sample darkens; likewise when the band gap passes through the visible the sample absorbs. Darkening of a sample has been observed in a number of pressurized insulators, which require still higher pressures to become metallic (*2*).

To demonstrate metallization, one could also show that the optical absorption and reflection behave as expected for free electrons with relaxation, including interband transitions, using a Drüde type model for analyses of the data. This evidence was presented in recent metallization experiments on xenon at pressures of 100 to 200 GPa (*3*). In the Drüde model, the plasma frequency ν_p depends on the square root of the free carrier (electron or hole) density. For optical wavelengths longer than $\lambda_p = c/\nu_p$, the sample is highly reflective and absorptive, whereas for shorter wavelengths the reflectivity decreases, as does the absorption coefficient (that is, the transmission of light through the sample increases). On the other hand, the band gap of an insulator is not closed and it is expected that the transmission decreases for shorter wavelengths if the band gap energy is in the spectroscopic region of study.

In the report by Mao and Hemley, the transmission as a function of wavelength shows little structure. There is a weak decrease with increasing frequency. This is the behavior of an insulator, not a metal. A uniform decrease in transmission as a function of wavelength is not expected for a metal, although for the limited spectral region they present, it is difficult to classify the material. Mao and Hemley state that "[i]n some cases . . . a weak increase in absorptivity was observed above 800 nm." Accepted scientific methodology demands reproducibility, especially to show metallization of hydrogen.

The reflectivity spectrum, measured over a limited spectral range, which is shown in figure 2b (curve C of Mao and Hemley) could be that of a metal, but for evidence of metallization, absorption and reflectivity data should be measured as a function of pressure. The region of increasing reflection in a metal should shift to higher frequency with increasing pressure. This is because the band overlap increases with pressure so that the number of free carriers increases, resulting in an increase in the plasma frequency.

In our experience in doing microspectroscopy (*3*), the background normalization of spectra is necessary to obtain correct results. This is especially true for samples with dimensions on the order of the wavelength of light, where frequency-dependent diffraction effects are important. This is exactly the measurement geometry of the samples of Mao and Hemley. We found that normalization of reflectivity spectra to the gasket reflectivity spectrum, as was done by Mao and Hemley was unreliable. Spectra taken from different regions of the gasket differed from each other because of surface inhomogeneities and ruby on the gasket surface. A procedure of normalization of the transmission to that of ruby is also questionable when one does not know the ruby absorption spectrum at the pressures used. For a weakly absorbing indirect band gap insulator, an incorrect normalization can change the slope of transmission/reflection as a function of frequency, so that an insulator appears as a metal and vice versa.

Mao and Hemley discuss the possible red shift of the resonance-enhanced intensity of the vibron Raman scattering signal with increasing pressure as being indicative of a red shift of electronic transitions. They state that it is "clearly associated with changes in the electronic structure of hydrogen"; however, one would actually expect enhancement first at the 488-nm wavelength of laser excitation, before the 514.5-nm wavelength—the opposite of what Mao and Hemley report. Their explanation of the enhanced vibron frequency may be correct; however, it is not evidence of metallization.

Mao and Hemley present the opacity, or darkening of the sample, as evidence of metallization and show a color photograph of a sample in their figure 1. The dark area in the high-pressure central culet region is apparent. But the photograph also shows a large dark region to the right, in the much lower pressure diamond bevel region of the hydrogen-ruby mixture. Although a uniform darkening in this region may be due to the diamond bevel angle, the localized darkening cannot be. One is thus presented with dark regions in both high- and low-pressure regions, without explanation.

The observations of Mao and Hemley are suggestive, but are also compatible with the narrowing down of the band gap in an insulator. I do not believe they fulfill the scientific criteria for establishing metallization.

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REFERENCES AND NOTES

1. H. K. Mao and R. J. Hemley, *Science* **244**, 1462 (1989).
2. See for example, R. Reichlin, M. Ross, S. Martin and K. A. Goettel [*Phys. Rev. Lett.* **56**, 2858 (1986)] for metallization of CsI and J. van Straaten and I. F. Silvera [*ibid.* **57**, 766 (1986)] for metallization of HI.
3. K. A. Goettel, J. H. Eggert, I. F. Silvera, and W. C. Moss [*ibid.* **62**, 665 (1989)] discuss the Drüde model for metallized xenon; R. Reichlin *et al.*, *ibid.*, p. 669.
4. I thank J. Eggert, K. Goettel, and H. Lorenzana for useful discussions. Supported by the Department of the Air Force (AFAL), contract F04611-89-K-003, and by the Harvard Materials Research Laboratory, NSF grant DMR-14003.

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Response: In view of the preceding comments, a review of the principal results and conclusions of our optical study of hydrogen (*1*) is in order. We reported direct optical observations and spectroscopic measurements at ultrahigh pressures which indicated significant absorption at visible wavelengths in hydrogen samples above 200 GPa at 77 K. After evaluating a number of alternative interpretations, we suggested that the increased visible absorption may be due to electronic transitions in hydrogen before closure of the band gap. We also pointed out that the absorption may arise from excitations in a metallic state formed by closure of an indirect gap at lower pressures, perhaps at the 150-GPa structural transition (*2*). We concluded that the optical data are consistent with the theoretically predicted band overlap mechanism of metallization, although indirect evidence for a nonmolecular state (monatomic metal) at the very highest pressures was also presented.

Optical measurements at ultrahigh pressures (above 200 GPa) are not yet routine, so caution must be exercised in the interpretation of new results. We performed 14 separate experiments on a variety of diamond-anvil samples in which pressures greater than 200 GPa were obtained in order to have as much information as possible about artifacts associated with our optical measurements. [In contrast, metallization studies by other groups have been published on the basis of one run, with no "control" experiments reported; for example, reference (*3*) of the preceeding comment.] Numerous test runs indicated that weak diamond absorption occurs throughout the visible, with a significant increase at wavelengths below 600 nm for pressures in the 200-GPa range. Although this complicates the measurements on hydrogen, the changes in optical density in the hydrogen are much larger, as is evident in our figure 1a (*1*). Interpretations included excitation across the band gap (including exciton contributions), with the gap closing at higher pressures, and absorption in the metallic state (excitation by free carriers).

Since free-carrier absorption may show little structure in the visible range (*3*), and since the weak decrease in transmission at shorter wavelengths in our measurements (*1*, figure 2B, curve A) arises from the residual diamond-anvil absorption, Silvera's assertion that our spectra exhibit the behavior of an insulator, not a metal, is inaccurate. Our observations of increased absorption above 800 nm at the highest pressures are particularly interesting in this regard because this may be indicative of metallic behavior with a plasma frequency in the infrared. These measurements were reproducible, but could be made only when the long-wavelength absorption in hydrogen significantly exceeded the contamination of the spectra by stray light, which has the effect of reducing the intensity of the absorption above 800 nm.

Silvera states that one kind of evidence for metallization of hydrogen is the demonstration that the optical absorption and reflection spectra fit a Drüde model. Our evidence for a rise in reflectivity and absorption above 800 nm is indicative of Drüde-type behavior. A quantitative analysis of these effects is premature, however, because of the limited wavelength range of the measurements and, more important, because the optical properties of diamonds under these very high stress conditions are not yet known in sufficient detail. Hence, a model—however physically reasonable—cannot yet be used to extract physically meaningful parameters without further study.

To examine possible changes in material properties, all spectra were measured as a function of pressure to the maximum pressures possible, as we clearly stated (*1*). Silvera's inference that such measurements were not performed is at odds with what we reported. For example, our original figure 2b clearly shows the shift in reflectivity to higher frequency with increasing pressure from 140 GPa (curve B) to 210 GPa (curve C), which is indicative of possible increasing metallic character.

Silvera contends that our procedure for normalizing the absorption and reflectivity measurements is unreliable. As we discussed, background normalization is crucial for obtaining meaningful results. At very high stresses (above 200 GPa), the critical factor is the removal of the effects of the diamond absorption and deformation. For this reason we presented reflectivity spectra from the sample-diamond interface normalized to the adjacent gasket-diamond interface; for our ultrahigh pressure conditions this was found to be more appropriate than the use of reference spectra such as the zero-pressure diamond-air interface (*1*). We performed a large number of measurements in which the transmission through the ruby (plus the diamond anvils) was measured to pressures in the 300-GPa range. No evidence was found for absorption effects in ruby that would complicate our hydrogen measurements in the visible range; any such absorption is significantly smaller than that of the diamond at the anvil tip.

The change in Raman intensity of the hydrogen vibron under pressure was presented as evidence for electronic excitations in hydrogen at visible wavelengths, as clearly stated in our original abstract (*1*). It is likely that the Raman enhancement probably occurs first at 488.0, rather than at 514.5 nm with increasing pressure, as suggested by the decreasing band gap shown in figure 3 (*1*). Enhancement at 488.0 nm could not be confirmed, however, because intensity measurements with the laser lines at wavelengths less than 496.5 nm were complicated by diamond (and possibly sample) absorption. As a result, our discussion concerned intensity changes measured with the longer wavelength laser lines.

Silvera comments on the dark low-pressure region in the photomicrograph of a hydrogen sample in our original figure 1a (*1*). This region is darker because of the high bevel angle of the diamond (*1*, figure 1b), which causes a decrease in transmission because of internal reflection (a feature always observed with bevelled diamond anvils). This effect should not be mistaken for sample absorption, which causes the localized darkening in the high-pressure region. The observations and spectroscopic measurements clearly indicate that significant changes in solid hydrogen occur with increasing pressure, but further work is needed to characterize in detail its optical, electrical, and structural properties under these conditions. This is one of the paramount challenges facing high-pressure physics today.

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