Reports

Optical Studies of Hydrogen Above 200 Gigapascals: Evidence for Metallization by Band Overlap

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Direct optical observations of solid hydrogen to pressures in the 250-gigapascal (2.5-megabar) range at 77 K are reported. Hydrogen samples appear nearly opaque at the maximum pressures. Measurements of absorption and Raman spectra provide evidence that electronic excitations in the visible region begin at \sim 200 gigapascals. The optical data are consistent with a band-overlap mechanism of metallization.

HE INSULATOR-METAL TRANSFORmation in solid hydrogen at high pressure has long been of considerable interest to researchers in condensedmatter physics. As a result, experimental and theoretical studies of hydrogen at high densities continue to represent a primary goal of high-pressure research. Theoretical predictions that molecular hydrogen will dissociate to form a monatomic metal at high pressure date back to the 1935 calculation of Wigner and Huntington (1). Recent theoretical calculations (2) indicate that the transition may occur in the 250- to 400-GPa range (2.5 to 4.0 megabars), an estimate that is consistent with current experimental constraints (3, 4). In addition, there has been a great deal of interest in the possibility that below the pressure of molecular dissociation, the gap between the valence and conduction bands will decrease and eventually vanish under compression so that a conducting molecular solid is formed. Recent calculations predict this transformation to occur at 170 to 250 GPa (2). The absorption edge in the solid at zero pressure arises from excitonic peaks at 11 eV, with the conduction band edge at 15 eV (5). Should pressure-induced band overlap occur in the molecular solid, the optical properties of hydrogen at high pressure may be characterized by increasing absorption in the visible region of the spectrum (1.5 to 3.0 eV) prior to closure of the gap.

Experimental studies of hydrogen at very high pressures have proven both challenging and controversial over the years. Dynamic compression studies have provided evidence for a transition to a conducting state in fluid hydrogen at very high pressures and temperatures (6), but there is considerable uncertainty in the estimation of the pressuretemperature conditions attained in these experiments, and the implications of these results for the behavior of the low-tempera-

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ture solid have not been established. Claims for the formation of a high-pressure conducting state under low temperatures and static pressures (7) remain controversial; these experiments involved the use of electrical resistance measurements that can produce spurious results because of the possibility of electrical short-circuiting in the highpressure apparatus. A fundamental limitation of all of these investigations—both dynamic and static—has been the lack of direct visual observation of the sample under pressure.

Sustained static pressures well into the megabar range can be generated with the diamond-anvil high-pressure cell (8). In this device diamonds serve both as anvils to generate ultrahigh pressures and as windows through which to view the sample under pressure. Recently, we reported the results of static compression studies of hydrogen above 200 GPa using diamond-anvil cell techniques (4). The experiments were performed at liquid nitrogen temperature to improve sample stability at ultrahigh pressures. By the use of Raman scattering spectroscopy, we demonstrated that the molecular solid is stable to at least 200 GPa at 77 K, as evidenced by the presence of the H-H molecular stretching mode (vibron) in the Raman spectra measured at these pressures. Here we report the results of additional optical measurements performed on these samples. Optical transmission, reflection, and Raman spectra, in addition to visual observation, indicate that electronic excitation in the visible region of the spectrum begins in the 200-GPa range (77 K). The optical data can be interpreted in terms of a decreasing band gap to form a high-pressure metallic molecular solid.

The experiments were performed at 77 K using megabar-type diamond-anvil cells with single-bevel diamonds having central flats ranging from 25 to 100 μ m (Fig. 1)

(8). Pressures were determined principally by the use of the ruby technique (quasihydrostatic scale) (9). When a nearly pure hydrogen sample (that is, with minimal ruby) is compressed between small diamond tips in a gasket, the sample tends to thin out appreciably, with most of the hydrogen flowing away from the region of peak pressure. As in previous studies (4, 10), ruby (Cr³⁺:Al₂O₃) was used as a secondary support to stabilize the hydrogen within the gasket (T301 stainless steel) and to increase sample thickness at high compressions. The pressures reported correspond to measurements on small ($\leq 1 \mu m$) grains of ruby suspended in the hydrogen; spectra from these grains are characterized by wellresolved ruby R_1 bands, which are not broadened by large nonhydrostatic stresses of the ruby in contact with the diamonds.

Extra precaution is needed for optical studies in diamond-anvil cells above 150 to 200 GPa. At these pressures, a stress-induced red shift of the absorption edge, new fluorescence, and new Raman peaks become apparent in the diamond windows (12). In order to distinguish between optical phenomena associated with the hydrogen sample and those of the diamond, we used an optical system with high spatial resolution. We compared absorption, reflection, and Raman spectra of hydrogen with reference spectra of the alumina and the metal gasket 5 to 10 μ m from the hydrogen in the sample. Optical properties of hydrogen were monitored as a function of pressure determined by the ruby fluorescence. Seven sets of experiments were performed in which hydrogen was pressurized to at least 200 GPa. In addition, an equal number of runs were made on hydrogen-free samples to these pressures to obtain further information on changes in the optical properties of the diamonds and to provide additional pressure calibration.

Changes in the optical properties of the hydrogen were first observed as an enhancement of the intensity of Raman scattering of the molecular vibron. This intensity enhancement occurred at about 180 GPa, or at pressures above the previously reported phase transformation (4). Initially the enhancement (estimated to be up to tenfold) was observed upon changing the excitation wavelength from 488.0 nm to 514.5 nm. The intensity increase suggests a resonance effect (11) attributable to the presence of electronic transitions near the laser excitation energy at that pressure (for example, 2.54 eV at 180 GPa). At still higher pressures (~ 200 GPa) the intensity of the bands

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Fig. 1. Configuration of the sample of solid hydrogen and Al_2O_3 (ruby) in the diamond-anvil cell. (**a**) Photomicrograph of sample. (**b**) Side and top view. The diameters of the diamond flats (A and A') used in this experiment are 25 and 50 μ m, with a culet diameter B of 500 μ m. (**c**) Map of the sample at a peak pressure of 250 to 300 GPa, which is attained in the region within the small diamond flat (A). The hydrogen is localized in veins throughout the sample. In the region of peak pressure the hydrogen, which has an estimated sample thickness of 1 μ m, is nearly opaque. The sample was uniformly transparent at low pressures.

excited with 514.5-nm excitation decreased. With increasing pressure, the intensity of the vibron peak decreased and the resonance frequency appeared to shift to longer wavelengths; this behavior is indicative of a red shift of electronic transitions in the hydrogen with increasing absorption at shorter wavelengths. The phenomenon is clearly associated with changes in the electronic structure of the hydrogen since the hydrogen vibron intensity was affected (11).

No discontinuous changes in the absorption properties of the hydrogen were evident with increasing pressure (4). Above the phase transition at ~ 150 GPa, however, light transmission through the hydrogen-containing regions at the highest pressures

gradually decreased. This increase in absorption is clearly illustrated in the photomicrograph of one of the hydrogen/Al₂O₃ composite samples above 250 GPa in Fig. 1, a and c. It should be cautioned that the increasing index of refraction of the hydrogen relative to the Al₂O₃ with pressure results in increasing contrast at the interfaces between the two materials; this could also cause an apparent darkening of small regions containing hydrogen and can be mistakenly interpreted as bulk absorption. In the present samples that contained sufficiently large volumes of hydrogen (for example, 5 µm in linear dimensions), however, increasing optical absorption could be distinguished from this effect, which begins at 30 GPa where the refractive indices of the hydrogen and ruby are identical.

Representative micro-optical spectra of the hydrogen samples measured through the diamond-anvils with a spatial resolution of 2 μ m are shown in Fig. 2. The molecular vibron was clearly evident in the hydrogencontaining regions (Fig. 2a). With increasing pressure, visible transmission spectra showed a decreasing signal at short wavelengths (below 550 nm) because of the red shift of the effective absorption edge of nitrogen impurities in the type Ia diamond anvils. In addition to this effect, a nearly uniform decrease in transmission at longer wavelengths was measured in the hydrogen areas (Fig. 2b). At the highest pressure regions shown in Fig. 1a, we estimate that the absorption coefficient α exceeds $\sim 10^3$ cm⁻¹ for hydrogen in this wavelength range. This calculation is based on the intensity of light transmitted through hydrogen relative to that through the nearby Al₂O₃. A hydrogen sample thickness of 1 µm was assumed on the basis of white-light interference fringes observed at lower pressures. No measurable absorption was detected in the Al_2O_3 in this spectral range. The estimate for α is likely to be a lower bound because of sample inhomogeneity; in addition, it is probable that stray light transmitted through the alumina surrounding the hydrogen was also picked up by the detector as a result of defocusing of the light by the highly strained diamonds. The spectrum of the hydrogen appears broad and largely structureless below the diamond-absorption edge. In some cases, however, a weak increase in absorptivity was observed above 800 nm.

Additional experiments were performed on samples without hydrogen to confirm that the observed effects are associated with the hydrogen and to obtain further information on the spectral contributions of the diamond anvils under these conditions (12, 13). Experiments were performed on rare gases, oxides, alkali halides, and metals using the same anvil geometries and diamond types. Spectra were compared at similiar pressures to those obtained in the hydrogen experiments, with the pressures determined by ruby fluorescence and, in some cases, by x-ray diffraction of Pt contained within the samples (13). No increase in absorption at 600 to 850 nm was found in samples of Ne, Al₂O₃, SiO₂-stishovite, and NaCl compressed to 200 GPa, for example, and no absorption features other than the red-shifted ultraviolet impurity edge of the diamond were observed. On the other hand, the decreasing light transmission of the sample under pressure for hydrogen is similar to that measured for molecular nitrogen com-



Fig. 2. (a) Raman spectrum of the molecular vibron of hydrogen; the pressure given by the ruby fluorescence in the same region of the sample was 197 GPa. The spectrum was measured with approximately 50 mW of 514.5-nm radiation with a 30-s exposure. (b) Representative optical spectra of hydrogen at high pressure from 690 to 870 nm. The solid line (curve A) is a transmission spectrum of hydrogen at ~210 GPa obtained by normalizing the signal transmitted through the hydrogen to that measured for the Al₂O₃ in the sample at the same pressure (see text). The dotted curves are relative reflectivity spectra of hydrogen at 140 GPa (curve B) and 210 GPa (curve C). These spectra were obtained by taking the ratio of the signal reflected from the diamond-hydrogen interface (R_{D-H}) to that measured at the diamond-gasket interface (R_{D-G}). The optical spectra were measured with a tungstenhalogen lamp, 0.32-meter spectrograph, and optical multichannel analyzer. A Leitz reflecting-optics attachment was used in the reflection measurements.



Fig. 3. Volume dependence of the band gap in solid hydrogen. The location of the absorption threshold for the lowest energy exciton and the band gap are from Inoue *et al.* (5). The dashed line shows the result of a low-pressure optical study by van Straaten and Silvera, who used a dielectric model to obtain an effective absorption threshold energy to 28 GPa (17). The crosses correspond to the band gap calculated theoretically by Friedli and Ashcroft (18), and the circles represent the theoretical result of Min *et al.* (19). The Pa3 structure was assumed in both theoretical calculations.

pressed to 180 GPa (14). The molecular vibron, indicative of molecular bonding, is also found to persist into the absorbing state in both materials; in addition, a decrease in Raman signal occurs at higher pressures in both, consistent with increasing absorption by the sample and diamond. From these measurements, we conclude that the uniform increase in visible absorption shown in Figs. 1 and 2 is due to the hydrogen.

The gradual increase in absorptivity suggests that the electronic excitation threshold in hydrogen [10.9 eV at zero pressure (5)] has decreased under pressure into the visible region (15). The lack of a sharp absorption

edge may be indicative of closure of an indirect band gap, as predicted theoretically (2). The prediction of an indirect gap, however, is dependent on the choice of crystal structure, which is currently unknown for the high-pressure phase. Figure 3 summarizes the experimental and theoretical information on the volume dependence of the band gap and absorption threshold (16-19). For the experimental data, we use the P-V(pressure and volume) equation of state determined recently by single-crystal x-ray diffraction (3) [the phase transformation at 145 GPa, which is expected to have a small effect on the volume (4), is neglected]. The Herzfeld criterion gives a predicted metallization volume of 2.02 cm³/mol, corresponding to a pressure of 270 GPa (16). If we interpret the resonance Raman effects observed at 180 GPa (2.40 cm³/mol) as tracking the band edge, or excitons near the edge (5) at this pressure, the estimated gap ($E_g =$ 2.5 eV) at that volume is consistent with the Herzfeld prediction. Alternatively, because the precise point of band overlap may be difficult to detect optically, a transition at lower pressures cannot be ruled out, as suggested by the theoretical results (18, 19)plotted in Fig. 3. In fact, band overlap may be associated with the structural transition at 145 GPa (at which point no absorption has yet been detected). If so, hydrogen above 145 GPa would initially be a diatomic semimetal. The optical properties and mechanism of band overlap of hydrogen may be analogous to the behavior of xenon, which is nearly transparent at the reported metallization transition at 130 to 150 GPa (20). Above 200 GPa hydrogen appears to exhibit significantly more absorption in the visible than has been observed in xenon samples (20, 21).

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In principle, the onset of metallization can also be determined by measurements of reflectivity in the visible or infrared at the sample-diamond interface. Our reflectivity measurements at the diamond-hydrogen interface do show an increase in signal above 800 nm at \sim 150 GPa (Fig. 2b), similar to the change in reflectivity observed in metallization of Xe (20) and CsI (22). We have found, however, that an increase in diamond-sample reflectivity with increasing pressure can also be observed in other samples (for example, Ne, SiO_2 and Al_2O_3) that remain essentially transparent and are believed to remain insulators at these pressures. These effects may be associated with strains at the diamond-anvil tips (12). Hence, possible increases in reflectivity attributable to metallic (or semimetallic) molecular hydrogen alone at these pressures cannot yet be determined quantitatively.

The maximum pressures achieved on hydrogen in these experiments are estimated to be above 250 GPa. The ruby pressure scale has been calibrated only to 180 GPa (9). We have found that the R_1 ruby peaks above 230 GPa are generally very weak and difficult to measure, even when light-chopping techniques are used to remove background diamond fluorescence (23). In some runs, the hydrogen sample remained in the highest pressure region (on the central flat) without ruby. A lower bound on the pressures in these cases was estimated at ~ 250 GPa by measurement of the ruby pressure profiles in the gasket (24). In addition, x-ray diffraction measurements performed on hydrogen-free samples containing Pt as a pressure calibrant gave peak pressures of 280 to 310 GPa (13). These pressures are in the range expected for dissociation of the molecular bond (12) as well as the simple Herzfeld model predictions for metallization. We are not able to observe the molecular vibron in the Raman spectrum of the very dark hydrogen samples at the highest pressures. Although it is possible that dissociation has occurred, these results are not conclusive because intense new fluorescence bands in the diamonds (12) and the high absorptivity of the hydrogen complicate the Raman measurements. Characterization of hydrogen in the 300 GPa range thus remains a challenging prospect for high-pressure physics.

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Rates of Tectonometamorphic Processes from Rubidium and Strontium Isotopes in Garnet

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Measurement of the radial variation of the ⁸⁷Sr/⁸⁶Sr ratio in a single crystal from a metamorphic rock can be used to determine the crystal's growth rate. That variation records the accumulation of ⁸⁷Sr from radioactive decay of ⁸⁷Rb in the rock matrix from which the crystal grew. This method can be used to study the rates of petrological processes associated with mountain building. It is applied to garnet crystals in rocks from southeast Vermont that were metamorphosed about 380 million years ago. The average growth rate measured for three garnets is $1.4^{+0.92}_{-0.45}$ millimeters per million years and the average time interval of growth is 10.5 ± 4.2 million years. Garnet and its mineral inclusions provide a sequential record of temperature change, strain, and chemical reactions during metamorphism; therefore, the technique offers the potential for determination of the rates of those processes as well. The growth interval and observed amount of rotation recorded by inclusion trails in one garnet indicate that the mean shear strain rate during garnet growth was $2.4^{+1.6}_{-0.7} \times 10^{-14}$ per second.

UNDAMENTAL TO AN UNDERSTAND-✓ ing of metamorphism is knowledge of the rates of concurrent processes affecting the rocks such as heating, increase in pressure, devolatilization, deformation, and recrystallization. Quantitative measurement of these rates has proved elusive because continued metamorphism acts to overprint or to erase earlier metamorphic phenomena. We have overcome this difficulty by measuring the growth rate of a widespread metamorphic mineral, garnet, that commonly resists overprinting. We determine the growth rate by precisely measuring the radial variation of the 87 Sr/ 86 Sr ratio (1) in single crystals of garnet. This variation reflects the rate of accumulation of ⁸⁷Sr in the rock matrix caused by radioactive decay of ⁸⁷Rb during the time of growth of the garnet crystal.

We chose garnet because it grows by dehydration reaction during metamorphism in common rocks, because it preferentially incorporates Sr relative to Rb, and because its low cationic diffusivity (2) helps to preserve the isotopic record. Garnet also preserves other information important in characterizing metamorphism. For example, there is the possibility of estimating the pressure and temperature history of the rock during garnet growth from mineral inclusions in garnet (3, 4), oxygen-isotope thermometry (5), and chemical zoning profiles (6). Garnet can also record progressive deformation of its surrounding matrix (7, 8)because it is rigid, equant, and commonly inclusion-bearing. Thus measurement of growth rates of metamorphic garnet may provide a direct measure of rates of temperature-pressure change, chemical reaction, dehydration, and deformation during metamorphism.

Determination of the growth interval of a mineral by our method requires that (i) the mineral had a much lower ⁸⁷Rb/⁸⁶Sr ratio than the matrix from which it grew; (ii) changes in the ⁸⁷Sr/⁸⁶Sr ratio of the matrix were due solely to in situ decay of ⁸⁷Rb in the matrix and were not significantly influenced by infiltrating fluid or exchange with neighboring rock units with contrasting ⁸⁷Sr/⁸⁶Sr and ⁸⁷Rb/⁸⁶Sr ratios; (iii) the local source matrix sampled by the growing mineral was homogeneous with respect to ⁸⁷Sr/ ⁸⁶Sr and ⁸⁷Rb/⁸⁶Sr ratios during growth; (iv) Sr diffusion in the mineral was suffi-

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