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Index of refraction, polarizability, and equation of state of solid molecular hydrogen

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The index of refraction and the equation of state (EOS) of hydrogen have been measured to high pressures, leading to a determination of the pressure dependence of the polarizability to greater than 1 mbar. A simple method for measuring the index allows for straightforward extension of both the index and EOS measurements to the highest pressures achievable in a diamond-anvil cell. [S0163-1829(98)05322-3]

Solid hydrogen and its isotopes have been intensively studied for decades; one of the primary goals is to reach the ultra-high-pressure metallic state of hydrogen. This elusive material has been the subject of numerous experimental and theoretical studies.[1] Although there have been several claims of experimental observation, none has survived rigorous analysis; theories attempt to predict the transition pressure, but the range of predicted metallization pressures remains large, both for the metallic molecular and metallic atomic forms. Two important properties of hydrogen are the index of refraction and the equation of state (EOS); the interpretation of experimental data and development of reliable theoretical predictions have been hampered by the limited range over which these quantities are known experimentally. The refractive index of high-pressure solid hydrogen provides important constraints on electronic structure calculations of high-pressure properties of hydrogen.[2] Moreover, the index is a key piece of data, important to the interpretation of optical spectra of high-pressure hydrogen and its behavior has been extrapolated into the megabar region,[3,4] although measurements only extended up to 37 GPa.[5] At present the semiempirical method of predicting the transition pressure to the atomic metallic phase compares the Gibbs free energy derived from the experimental pressure-volume EOS to the theoretical predictions for the atomic metallic phase.[5,6] This method has had two problems; first, there are a number of theories with different predictions for the phases and EOS and second, until recently, reliable experimentally determined EOS's extended only to about 40 GPa,[5,7] requiring an extrapolation to the region of interest (200–500 GPa), leading to large uncertainties in the predicted metallization pressure. In recent advances, the EOS of hydrogen and deuterium have been studied by x-ray diffraction to greater than 100 GPa.[6] In this report we present measurements of the index of refraction of solid hydrogen in a diamond-anvil cell (DAC) at pressures approaching 100 GPa; using the Lorenz-Lorentz model we determine the polarizability of hydrogen to a pressure of 130 GPa. We also present results of an improved version of an earlier method of determining the EOS. Together our data supports the idea that the index of refraction of diamond hardly changes over this pressure range. Our measurements can be easily extended to the highest achievable pressures in a DAC.

The most accurate method of determining an EOS is by x-ray diffraction, yielding volume precisions of better than a few tenths of a percent. The principal difficulty of this technique at high pressure is the production and maintenance of single crystals, required to achieve sufficient x-ray intensity. The previous pressure limitation of approximately 25 GPa was imposed by fracturing of the hydrogen crystal as the pressure was increased. The pressure at which this fracturing occurs has been increased by growing crystals embedded in a compressible medium (helium); deuterium crystals have been maintained in pristine form to 119 GPa, while hydrogen has been studied to 109 GPa.[6] At present, the 100 GPa region seems to be the limit for this technique. By contrast our method seems to be limited by failure of the diamonds and promises to extend to the 200–300 GPa region.

Van Straaten and Silvera[5,8] determined the EOS by optically measuring the volume of the sample in a DAC as a function of pressure. The pressure was determined using the ruby fluorescence scale.[9] A sample in a DAC can be modeled as a volume of height d and cross sectional area A. The area of the sample was determined photographically and the thickness by measuring the interference fringes produced by the Fabry-Perot (FP) cavity formed between the two diamond-sample interfaces within the DAC. The fringe spacing yielded the product of the index of refraction n and the sample thickness d. By measuring this fringe pattern as a function of the angle of incidence of the illumination, n and d could be determined independently. This technique was successfully applied to hydrogen and deuterium at low temperatures and pressures up to 37 GPa to determine both the index of refraction and the EOS. An important limitation arose because the index of refraction of hydrogen matches that of diamond at 130 GPa (Refs. 10 and 11) so that the fringe contrast goes to zero; however, it was found that already at 40–50 GPa the contrast had dropped enough that accurate measurements could not be made. This limitation was imposed by two sources: (1) the technique of varying the angle of incidence loses sensitivity as the difference in indices of refraction decreases and (2) interference patterns arising from the windows of the cryostat disrupt the interference pattern of the hydrogen sample when its contrast is reduced. The principal sources of error were from the thickness measurement and any systematic error from the manual determination of the area. An additional source of systematic error was in determining if the hole was a right parallelepiped, as it can be significantly deformed by the large compression and modest amounts of material can be concealed in terracelike structures at the sample edge. In these measurements the volume accuracy was estimated to be about 5%. Although this method is not as accurate as the x-ray method it is simple to implement and it is not hindered by the polycrystalline nature of the samples.

In this work we have made several improvements and modifications to the technique of van Straaten and Silvera, enabling us to make measurements over an increased pressure range and achieving improved precision for the EOS. We have adapted modern charge-coupled device (CCD) camera capabilities to improve the accuracy of the areal measurement. All six windows in the cryostat were wedged MgF_2 windows (4° wedge) to suppress their FP interference patterns which otherwise obscure the fringes from the sample. We also use a simple method to measure the index of the hydrogen sample, maintaining accuracy when the FP fringe pattern contrast is poor.

Three separate runs were made. Samples of ultra-high-purity hydrogen (99.999%) were cryogenically loaded into a DAC along with a few ruby chips. The DAC employed pairs of 0.2 carat double beveled (6°/9°) diamond anvils selected for low birefringence and low fluorescence. The pairs of anvils had culet flat diameters of 50–75 μm. Rhenium gaskets with initial hole diameters of $\sim 50\ \mu$m and thicknesses of $\sim 25\ \mu$m were used. The DAC was maintained in a cryostat at 80–90 K throughout the course of the experiments. The loading technique, DAC, and details of the cryostat are described elsewhere.[12] The pressure was determined using the quasihydrostatic ruby fluorescence pressure scale[9] corrected for low temperatures.[12] The volume percentage of ruby in the samples was estimated to be $\sim 2.5\%$ at the maximum pressures achieved. All of the runs were concluded by failure of the diamonds; data were collected at pressures up to 60, 72, and 34 GPa, respectively.

At each pressure, optical data was taken using the system depicted in Fig. 1. Light from the sample was collected using a Wild Model 420 long working distance microscope objective. Collimated light from a quartz-tungsten halogen lamp was used for measurement of the FP fringes from the sample and for photography. An argon ion laser focused to a spot size of 5 μm was used for ruby fluorescence and index of refraction measurements (described below). A videograph of the sample was taken using a CCD monochrome camera (Pulnix TM-7CN) and digitized and stored using a frame grabber (Scion LG-3). Two spectrometers, a Spex 0.6 m triplemate and an ISA 320 mm single-grating spectrograph, coupled to an EGG Model 455 intensified diode array dispersed and detected the optical spectra.

The index of refraction was measured by a simple method which compares the reflectivity of the diamond-vacuum interface with that of the diamond-hydrogen interface. A laser beam (5145 Å) was aligned to pass through the microscope and coincide in focus with the visual focus; the microscope was first focused at the diamond table, as shown in the Fig. 1 inset. The focus was then translated to the diamond-hydrogen interface. The image of the focused laser was spatially filtered with a pinhole to select an area of 5 μm in the object plane, and the intensity of the collected light signal was measured with a silicon photodiode, using a chopper and a lock-in amplifier for increased sensitivity and background rejection. The combination of the focused laser beam, i.e., divergent away from its focus, and the spatial filter reject light reflecting from all but the interface at the focus. As a test, the focus was shifted to points within the diamond where one would not expect any light to be reflected. The collected signal levels from inside the diamond were more than an order of magnitude below the signal at the interface when the optical system was focused only 1 mm away.

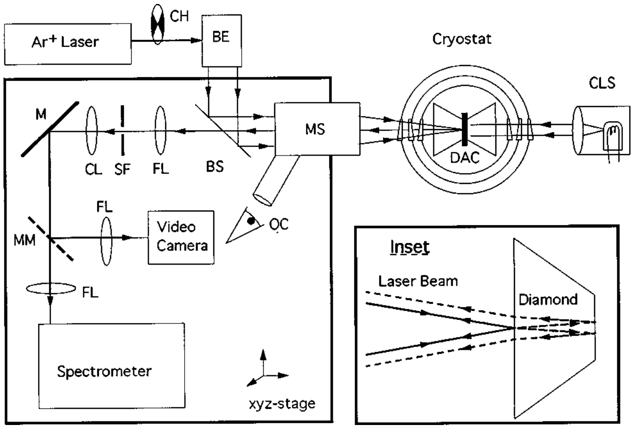

FIG. 1. Schematic diagram of the optical system used to collect the optical images and spectral data. Abbreviations: MS = microscope, OC = ocular, BS = beamsplitter, FL = focusing lens, CL = collimating lens, M = mirror, MM = moveable mirror, SF = spatial filter, BE = beam expander, CH = chopper, CLS = collimated light source. Inset, expanded view of reflection of focused laser beam from diamond table.

The index of refraction of hydrogen was determined as follows. The signal, $V_{\text{diam-vac}}$, detected when the optical system is focused on the diamond-vacuum interface is given by Eq. (1), and the Fresnel reflection formula, Eq. (2), approximated to normal incidence:

$$V_{\text{diam-vac}} = K I_0 R_{\text{diam-vac}} \tag{1}$$

$$R_{\text{diam-vac}} = (n_{\text{diam}} - n_{\text{vac}})^2 / (n_{\text{diam}} + n_{\text{vac}})^2. \tag{2}$$

Here I_0 is the incident laser intensity, and K represents the losses in the optical system. The signal when focused at the diamond-hydrogen interface is reduced by the above reflection loss, and additional corrections for reflections within the sample. Equation (3) expresses this signal, accounting for a single reflection:

$$V_{\text{diam-H}_2} = K I_0 (1 - R_{\text{diam-vac}})^2 R_{\text{H}_2\text{-diam}}, \tag{3}$$

$$R_{\text{H}_2\text{-diam}} = (n_{\text{H}_2} - n_{\text{diam}})^2 / (n_{\text{H}_2} + n_{\text{diam}})^2. \tag{4}$$

In the analysis, three additional terms for successive reflections within the sample chamber were included. Higher order corrections effect the intensity by less than 1%. The ratio of Eqs. (1) and (3) may be solved for the one unknown $R_{\text{H}_2\text{-diam}}$ which allows one to solve Eq. (4) for the index of hydrogen

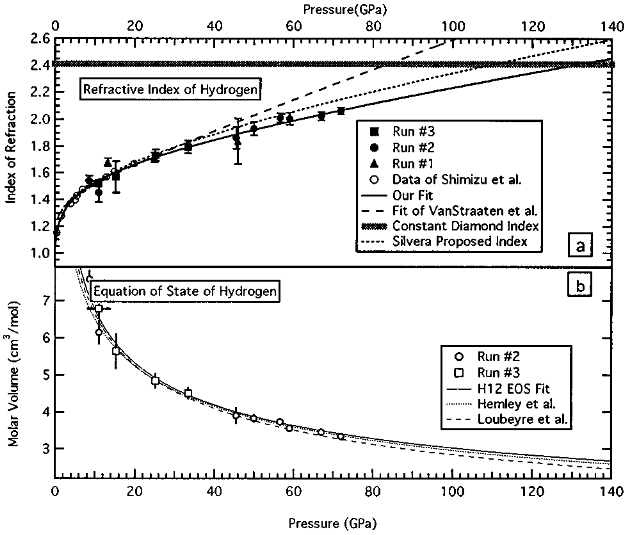

FIG. 2. (a) The pressure dependence of the index of refraction. Solid symbols represent data collected in this work. The long dashes are the fit of van Straaten and Silvera (Ref. 5), the short dashes are the dependence proposed by Silvera (Ref. 3), and the solid line is the fit to our data and the data of Shimizu *et al.* (Ref. 14). The solid band represents the proposed pressure independent index of diamond. (b) The EOS of solid hydrogen at 80–90 K. The squares and circles represent the data. The solid line is a fit using the H12 functional form with parameters as given in the text. The long dashed line is the fit of Hemley *et al.* (Ref. 7), and the short dashed line is the fit of Loubeyre *et al.* (Ref. 6).

if the index of diamond is known. At the diamond-sample interface the index of diamond may decrease slightly at high pressure (estimated to decrease by 2.5% at 200 GPa),[13] however, a pressure independent value of 2.41 has been used.

The volume of the hydrogen sample was determined by measuring the thickness and the area of the sample in the DAC. The thickness was determined by measuring the FP fringe spacing produced by the hydrogen sample illuminated at normal incidence with transmitted white light. This yields the product of the index of refraction and thickness, which, when divided by the experimentally measured index, yielded the thickness of the sample d. The area of the sample was determined by computer analysis of the digitized image. The systematic error arising from determination of the edge of the sample area was greatly reduced by using a fixed gray level as the edge determination criterion. This criterion was determined by making measurements of objects of known area, similar in size to the hydrogen samples, and determining the appropriate gray level to reproduce the known area.

The results of the our measurements of the index of refraction of solid hydrogen are shown in Fig. 2(a) along with previous literature measurements. Run No. 1 used the method of rotating the sample described by van Straaten and Silvera,[5] while run Nos. 2 and 3 used the simple reflection method described above. The behavior proposed by Silvera[3] based on the 130 GPa index matching of hydrogen and diamond comes quite close to the observed experimental behavior. The deviation is probably due to the fact that the point at 130 GPa was not weighted strongly enough to constrain the fit to pass through that point.

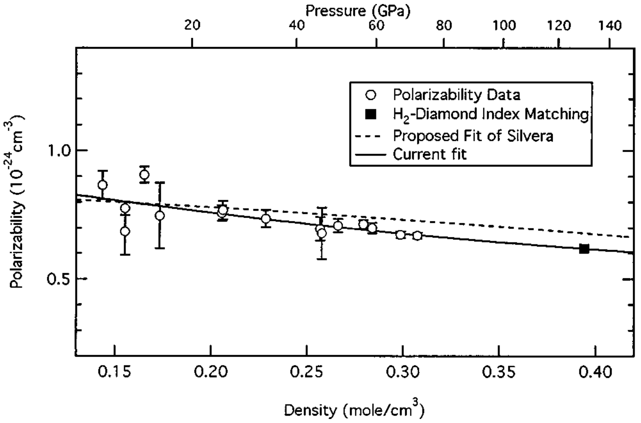

FIG. 3. The pressure dependence of the polarizability. Symbols represent data from this work. The line is a fit to this data using the quadratic form derived from the Lorenz-Lorentz equation.

We have fit our index of refraction data and the low pressure data of Shimizu *et al.*[14] to a functional form based on consistency with the Lorentz-Lorentz relation as proposed by van Straaten and Silvera.[5] The results of this fit are

$$n = -0.687343 + 0.00407826P + 1.86605(0.29605+P)^{0.0646222}. \tag{5}$$

The uncertainty of our measurements was less than 2.5% using the simple reflection method, and as high as 10% using the rotation technique. The decreased accuracy of the rotation technique was principally due to the decreased fringe contrast and concomitant decreased accuracy in determining the fringe extrema. It is noteworthy that the fit extrapolates to an index of 2.40 at 130 GPa which is consistent with the observed index matching between the hydrogen sample and the diamond.[11]

An important property of the hydrogen molecule under pressure is the polarizability α related to the index of by the Lorenz-Lorentz equation. Solving for the polarizability

$$\alpha = \frac{3}{4\pi\rho}\left(1 - \frac{3}{n^2+2}\right), \tag{6}$$

where ρ is the molar density and n is the index. Using our index data and the EOS of Loubeyre *et al.* we can extract the pressure dependence of the polarizability of solid hydrogen. Based on the observed index matching of hydrogen and diamond at 130 GPa, we have also included the index of refraction of hydrogen at this pressure. We assign it a value equal to the assumed pressure-independent index of diamond. This analysis yields the density dependence for the polarizability shown in Fig. 3. The low-pressure points exhibiting a strong deviation from the fit were determined by the lower accuracy rotation technique. The curve fits the data well.

The P-V measurements from a given run establish relative values of the volume at measured values of pressure. To fix the absolute volumes, an experimentally known reference volume V_{ref} at pressure P_{ref} is used. If a V_{ref} corresponding to very low pressure is used, large systematic errors can accrue as the sample has undergone of order tenfold compression at a megabar, and as mentioned earlier the gasket hole sample might not be in the form of a right cylinder and contain concealed terraces. In the present technique this source of systematic error is greatly suppressed. It is important to understand the performance of a gasket. For a gasket that sticks to the opposing diamonds, if a material more compressible than the gasket is pressurized, so that the sample volume gets smaller, then the gasket wall intrudes into the sample so that it is somewhat parabolic in cross sectional shape. As the pressure increases the sample becomes much less compressible and as the gasket thins the wall pushes back out. This effect is reduced when the starting thickness of the sample is smaller. In our case we start with thin samples (at some cost of absolute accuracy because the initial volume is smaller). Most important, however, is choosing a high-pressure reference volume for extending the EOS to higher pressures. In this case the cavity is thinner and better behaved as only modest compression accrues with increasing pressure; moreover, the hidden parts of the sample are very small and the systematic error due to hidden sample is thrown to the low-pressure region, which is already known. By choosing a reference volume corresponding to high pressure, greater accuracy is achieved in the higher-pressure region where the EOS is not known. Because we now have accurate x-ray data at high pressure, a high-pressure reference volume can be chosen, greatly increasing the absolute accuracy of our method.

In order to compare to the recent megabar pressure x-ray measurements, we use a reference volume close to 26.2 GPa, the maximum pressure of an earlier x-ray measurement.[7] For extending the EOS to even higher pressures than discussed in our current work, one would choose the smallest possible V_{ref} from x-ray data. Another source of error is the deformation of the diamond culet flat at high pressure;[5] this source of error was suppressed by using a small sample (mean diameter approximately 35 μm at 89 GPa). The resulting EOS for hydrogen with comparison to other data is shown in Fig. 2(b).

We have fit our EOS data using the H12 fitting form proposed by Holzapfel.[15] This has the advantage that at very high pressure it properly approaches the Fermi-gas limit so that an extrapolation is constrained to exhibit the proper limiting behavior. The form and fit parameters of this EOS are

$$P = 3K_0 x^{-5}(1-x)e^{(cx+c_0)(1-x)}, \tag{7}$$

where $x=(V/V_0)^{1/3}$, $V_0=34.536$, $K_0=0.19625$ GPa, $c_0=5.1106$, and $c=-4.7831$. The quality of the fit is quite good and matches the data points to their measured accuracies.

Sources of error have been evaluated for their level of impact on our measurements. Corrections have not been made to the pressure-volume measurements for the thermal pressure, cupping of the diamonds or volume occupied by ruby. The thermal pressure at 80 K, for pressures above a few GPa, amounts to a pressure correction much less than the accuracy of our pressure measurements, ~ 0.8 GPa. As noted above, our samples were sufficiently small that noncylindrical samples due to deformation of the diamond tips or hidden areas were strongly suppressed. The dominant systematic error was due to the presence of ruby in the sample volume, but this is significantly less than the statistical error of the measurements. The quality of the sample imaging for areal measurements was not high, but the reproducibility was verified using known standards, and uncertainty was confirmed to be below 0.5%.

The EOS determined in this study exhibits a slight systematic deviation toward a harder character than the x-ray determined EOS's of Loubeyre *et al.*[6] and Hemley *et al.*[7] The difference from that of Hemley *et al.* is well within the accuracy of our data, while there is a noticeable deviation relative to the EOS of Loubeyre *et al.* In analyzing this difference one finds that agreement between the EOS determined in this study and the x-ray EOS is entirely dependent on which of the x-ray EOS's is used for the reference volume determination, e.g., had we used the EOS of Loubeyre *et al.* to establish our reference volume at 26 GPa we would have observed excellent agreement with the Loubeyre *et al.* EOS. This circumstance arises because the technique we have used is not as precise as the x-ray determination and cannot distinguish subtle differences in the EOS. The power of this technique lies in its simplicity and ability to be easily extended to significantly higher pressures.

The assumptions made in the determination of the index from the reflectivity data, i.e., diamond index does not vary significantly with pressure, is strongly supported by the good agreement of the EOS determined in this study with the x-ray determined EOS. Differences in the EOS's could be reconciled by dropping our assumption of a constant index for diamond, and modeling it such that the index of hydrogen would change and cause our thickness measurement to yield a volume consistent with the x-ray EOS. One would arrive at this correction by assuming that the discrepancy between our data and the high precision x-ray EOS is due to an incorrectly determined index of hydrogen. From this difference one can then back calculate the index of hydrogen, and correct the assumed index of diamond to be consistent with the observed reflectivity. While there is a small systematic difference in the EOS's, the accuracy of the data collected in this study does not warrant presentation of a detailed analysis to extract a corrected index of refraction for hydrogen.

In conclusion, we have measured the index of refraction and EOS of solid hydrogen to compressions greater than sevenfold. We have demonstrated a technique for making ultra-high-pressure index and EOS measurements of optically transparent materials that shows no pressure limitations. The results of these measurements have been used to extract the pressure dependence of the polarizability of hydrogen up to 130 GPa. Our measurements show good agreement with high-pressure x-ray EOS measurements, and the index measurements are consistent with the index matching of hydrogen with diamond at 130 GPa and the proposed very weak variation of the index of diamond with pressure.

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