

The Behavior of Solid Hydrogen at 342 GPa

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Theoretical calculations indicate that the hydrogen molecule should depair at high pressures and eventually form a new alkali metal. The resultant alkali metal sample in the diamond anvil cell would not be transparent in the visible. Experimentally, we find that hydrogen is still transparent at 342 GPa. This represents over a 50% increase in the static pressure at which scientific studies have been made by other groups.

[estimated metallic transition pressure, optical transmission at pressure, refractive index at pressure, molar refraction at pressure]

1. Introduction

Ashcroft [1], using a semiquantitative approach which utilizes experimental Raman frequency vs. pressure, has estimated that depairing of the hydrogen molecule should occur in the 300-340 GPa range. Natoli et al. [2], utilizing first principle calculations, find a transformation to a diamond cubic structure, which may be a gapless semiconductor or a semimetal, around 340 GPa. They calculate that this phase transforms to a simple cubic structure around 650 GPa and to a body centered cubic structure around 900 GPa. The later phases are expected to be metallic.

2. Refractive index to 155 GPa

In Reference 3 the refractive index, n , of hydrogen versus density, ρ , was obtained using the existing equation of state of hydrogen. Now that a new and more accurate equation of state has been obtained [4] the present authors have obtained a new relation $n = 1 + 3.0445\rho + 1.077\rho^2$ on the range of pressures up to 155 GPa where ρ has the units of moles/cm³. The linear coefficient is three-halves of the low pressure limit of the molar polarization or molar refraction. Figure 1 shows the calculated reflectivity at a stressed diamond anvil-sample interface. The

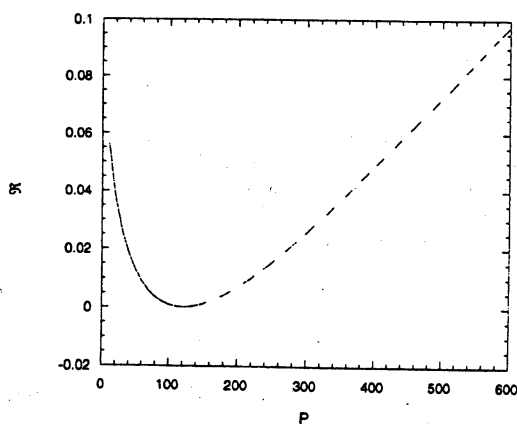


Fig. 1. Computed reflectivity at a diamond-hydrogen interface versus pressure. The dashed portion involves extrapolation.

refractive index of diamond as a function of pressure is from Reference 5. The reflectivity remains low over this range. It should be noted that the refractive index of the diamond at the center of the surface of the tip is a function of the stress state at the center of the surface of the tip; this depends only on the maximum pressure and not the pressure distribution. The dashed line is an extrapolation to a density which corresponds to a pressure of 600 GPa [4]. Figure 2 shows the molar refraction versus pressure calculated from the Clausius-Mossotti, Lorentz-Lorenz equation. It is clear that the molar refraction decreases as density increases and that, if the extrapolation is justified, the molar refraction never equals the molar volume, i.e., no dielectric catastrophe is expected for the molecular phase [6]. There is a need for experimental refractive index studies at higher pressures. Loubeyre et al. [4] extrapolate their equation of state for the molecular phase from 109 GPa to 600 GPa to calculate the change in the Gibbs free energy $\int VdP$ and on this basis show that the Gibbs free energy of the molecular phase equals that of the metallic phase at 600 GPa.

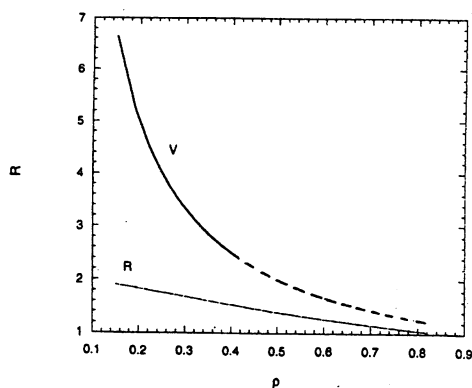


Fig. 2. Molar refraction versus density and volume versus density. The dashed line involves extrapolation. Note the absence of an intersection, i.e., of a dielectric catastrophe.

3. Experiments

The present group of authors made studies on hydrogen which led to failure of fifteen pairs of diamonds. Of these, three exceeded 250 GPa; failures occurred at 255 GPa, 275 GPa and 342 GPa. There was no evidence of alkali metal formation, i.e., the specimens were transparent at the highest pressures. The first two involved tips of 35 μm . We next used a pair of 20 μm tips. It should be noted that tip size is very important to reaching high pressures. Earlier experiments on Mo, W and Pt which significantly exceeded the pressure of 361 GPa at the earth's core [7,8] also utilized 20 μm tips.

This experiment differs from that carried out by others on hydrogen in the following ways:

- (1) 20 μm tips were used.
- (2) Tungsten was used as a gasket because our studies showed it does not react with H_2 .
- (3) The sample hole was 11 μm and was centered to $\pm 1/4 \mu\text{m}$ on the flat, when observed from both sides.
 - (a) This means that the diamonds stay aligned during the preindenting process and suggests they stay aligned during subsequent loading.
 - (b) The fact that the sample area is small compared to the tip area means that tungsten is located between most of the area of the diamond flats. (At the highest pressure 90% of the area is covered by tungsten.)
- (4) The sample hole was smooth with no burrs.
- (5) The time from which the sample was clamped in the cell and the pressure reached 275 GPa was only 30 minutes.

At the initial clamping the cell was loaded to about 50 GPa. The sample hole was circular and, of course, smaller, since, with a compliant sample, the gasket intrudes inward initially. The rate of hole shrinkage with change of pressure decreases as the pressure increases and essentially stops around 200 GPa. If the diamonds were rigid, the sample diameter would grow after the shrinkage stopped. Cupping of the diamond prevents this. On further rapid loading to a pressure estimated to be about 250 GPa from the birefringence pattern and previous experience, the sample hole became elliptical and moved off center. The pressure was then measured by the x-ray marker method on the tungsten adjacent to the sample hole using the equation of state of tungsten obtained from shock data [9,10] and fitted by the Birch equation of state [11] with $B_0 = 311.8 \text{ GPa}$ and $B_0' = 3.826$. Detailed and thorough first principle calculations of the equation of state of Mo [12] and W [13] were made to 600 GPa. In each case the computed equation of state was in excellent agreement with the experimental data.

From the diffraction data the pressure was found to be 275 GPa. The pressure was subsequently increased and measured several times. A nonhydrostatic correction [14] of 29.0 GPa gave a mean normal stress of 351.2 GPa in the tungsten at the highest pressure based on a yield stress at atmospheric pressure of $\sigma_{00} = 8 \text{ GPa}$ and on the pressure strengthening factor for tungsten, calculated as a function of pressure as shown in Reference 12 using the results of [13]. Recently measurements have shown the yield strength of tungsten in a DAC at 200 GPa to be about 20 GPa [15], while the aforementioned pressure strengthening factor yields 20.4 GPa. The pressure in the hydrogen, 342 GPa, is the mean normal stress in the tungsten minus one-third the yield stress of the tungsten at a mean normal

stress of 351 GPa; the yield stress was calculated to be 27.9 GPa from the pressure strengthening factor.

The heavily stressed tungsten pushes inward against the outward acting pressure of the hydrogen. **WITH THE GEOMETRY USED BY THE PRESENT AUTHORS, WERE THE HYDROGEN SUPPORT TO LEAK AWAY, THE TUNGSTEN WOULD IMMEDIATELY FILL THE HOLE.** This would be the case even if the tungsten, for whatever reason, attained the strength of a perfect crystal.

4. Results: Still the reluctant alkali at 342 GPa

A photograph taken using illumination for both reflection and transmission is shown in Figure 3. Figure 4 shows transmission through the sample. This transmission appears yellow. Previous control experiments on diamond to 421 GPa [16] show that absorption by the diamonds at 342 GPa makes incident white light appear yellow in transmission.

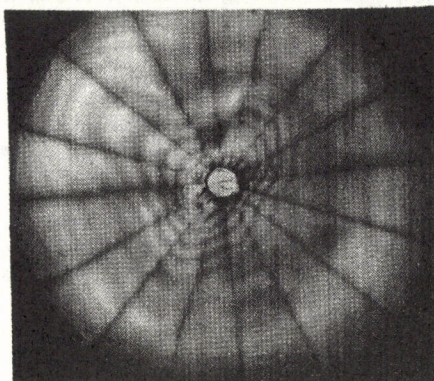


Fig. 3. Reflection-transmission photo of the diamond anvil sample system at 327 GPa. The nearly circular central areas represents the initially flat tip (20 μm diameter). (Computer scan of original colored reflection transmission photo.)

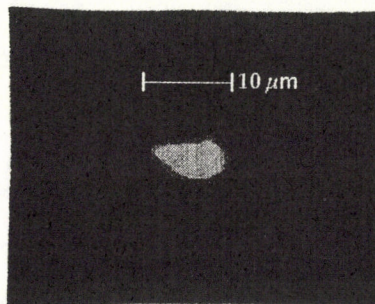


Fig. 4. Light transmission through the sample at 327 GPa. The transmission at 342 GPa was essentially the same as was the transmission after the torque was increased to raise the pressure above 342 GPa. Fracture occurred while the torque was being entered in the notebook. It produced a near-deafening noise. (Reproduced by computer scan from original colored photo.)

Were hydrogen to transform to an alkali metal, the hydrogen sample, which is approximately 2 μm thick, would not transmit any radiation in the visible. Since hydrogen still readily transmits such light it is not yet an alkali metal at 342 GPa. This pressure is over 50% higher than the 216 GPa [17] and the 191 GPa [18] in the March 15, 1996 issue of *Phys. Rev. Lett.* which disclaim earlier claims of metallization.

This pressure is in the neighborhood of the pressure at which depairing should occur [1,2] although the structure that is formed may be a semimetal or a gapless semiconductor [2], which may be transparent in the visible.

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