

Electronic Energy Gap of Molecular Hydrogen from Electrical Conductivity Measurements at High Shock Pressures

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Electrical conductivities were measured for liquid D₂ and H₂ shock compressed to pressures of 10–20 GPa (100–200 kbar), molar volumes near 8 cm³/mol, and calculated temperatures of 2900–4600 K. The semiconducting energy gap derived from the conductivities is 12 eV, in good agreement with recent quasiparticle calculations and with oscillator frequencies measured in diamond-anvil cells.

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The density dependence of the electronic energy band gap of hydrogen is of great current interest with respect to the insulator-metal (IM) transition. Since the valence-conduction band gap of solid hydrogen is about 15 eV at zero pressure, very high pressures are required to close the gap and achieve metallization. Low-temperature phase transitions [1,2] and increases in infrared reflectivity and absorption [3,4] have been reported near and below 150 GPa in diamond-cell experiments. It has been suggested that the 150-GPa transition is caused by closure of the indirect band gap in the molecular solid [3]. Measurements of the frequency dispersion of the refractive index $n(\omega)$ of solid hydrogen in a diamond cell yield effective oscillator frequencies ω_1 which correlate closely with the energies of direct valence-conduction band transitions [5–7]. Values of ω_1 in the range 4–12 eV were obtained by fitting $n(\omega)$ for photon energies below 3–4 eV, the absorption edge of diamond. Electronic structure calculations for some structures indicate that orientationally ordered states of H₂ favor smaller band gaps and metallization pressures [8]. However, consideration of other structures indicates that the commonly assumed structure [8] is energetically unfavorable and that lower-energy structures have wider band gaps to higher densities [9]. Quasiparticle calculations of the H₂ band gap place the IM transition at 150 and 300 GPa, respectively, for *c* axis aligned and orientationally disordered H₂ in the hcp phase at 0 K [10]. The quasiparticle method is the most effective in calculating experimental band gaps of semiconductors. Intermolecular potentials derived from Raman vibron data [11] indicate that the fully dissociated metallic transition occurs at about 300 GPa [12].

The purpose of this Letter is to report measurements of electrical conductivities of hydrogen at high pressures. Because shock compression is used, the associated high temperatures activate electron carriers and enable determination of the semiconducting energy gap E_g . Also, the high shock temperatures cause nearly constant-volume states in D₂ over the pressure range of these measurements. Thus, shock pressure is changed primarily to vary temperature and carrier concentration. Electrical con-

ductivities of dense fluid H₂ are needed for calculations of the external magnetic fields of Jupiter and Saturn, which are caused by convective dynamo motion of conducting H₂ at pressures up to a few hundred GPa and temperatures up to several thousand K [13]. Thus, these conductivity data are important for comparison with theoretical calculations of H₂ energy gaps and for scaling the electrical conductivity of H₂ to extreme conditions in the interiors of the giant planets.

Liquid-hydrogen specimens were used and the high shock temperatures achieved correspond to the dense fluid phase. Previous work with liquid Ar and Xe showed that shock-compression curves calculated theoretically by including electronic excitations across the 0-K density-dependent electronic band gap of the solid are in good agreement with experiments [14–16]. Thus, comparison of energy gaps derived from shock experiments in the fluid phase with calculations for the 0-K solid has been validated. A major issue to be resolved is the substantial difference between H₂ energy gaps calculated theoretically by the local density approximation (LDA) [8,9,17,18] versus quasiparticle methods [10] using various crystal structures and molecular orientations [12]. At the volumes of our experiments the LDA and quasiparticle [19] energy gaps are about 7 and 12 eV, respectively.

Theoretical analysis [20] of equation-of-state data of single-shocked liquid H₂ and D₂ [21–23] showed that the molecule is stable in the fluid phase to above 20-GPa shock pressure and that shock temperatures range up to 4600 K (0.4 eV) at 20 GPa for D₂. Since the molar volume of D₂ decreases threefold at 20-GPa shock pressure, E_g should decrease from its initial value of about 15 eV [24] to the 12-eV range [19]. Thus, shocked liquid D₂ and H₂ are semiconducting fluids with $E_g/k_B T > 30$. E_g can be derived from measured electrical conductivities σ using the equation for a liquid semiconductor [25],

$$\sigma = \sigma_0 \exp(-E_g/2k_B T). \quad (1)$$

Since the shock temperatures T are small compared to the gap energy, the highest possible shock temperatures are required to induce measurable conductivities. Most experiments were performed, therefore, with liquid-D₂

specimens, because the maximum available shock pressures and temperatures are appreciably higher for D_2 than for H_2 [20,23]. The electronic structure of hydrogen depends on the molar volume of molecules, independent of isotopic composition.

Shock compression was achieved by accelerating planar Ta impactors with a two-stage light-gas gun [26] to measured velocities in the range 5.2–6.7 km/s and impacting them onto Al specimen holders [27]. The cryogenic holders were cooled with liquid H_2 at 20 K [23]. High-purity D_2 or H_2 liquid specimens were condensed from gas [27] to insure that intrinsic conductivities are measured. Electrical conductivities were measured using a two-probe method, similar to that used for liquid O_2 and N_2 [28,29]. Both thin insulated Au-plated Mo electrodes in the conductivity cell are connected by coaxial cables to the differential amplifier of a fast oscilloscope through a battery-charged isolated capacitor and an optional resistive signal attenuator. When a shock wave transits the liquid hydrogen between the electrodes, the liquid becomes conducting and the capacitors discharge through the hydrogen. Each signal cable is also connected in parallel to one side of one of two 50 Ω termination resistors at the inputs to the differential amplifier. The other sides of both 50 Ω resistors are connected to the common ground of the differential amplifier. To increase dynamic range, several oscilloscopes and fast digitizers are used. Measured cell resistances range from 50 to 40000 Ω . Signal levels are a few 0.1 V and signal durations are about 100 ns. Conductivity cell calibration is a two-step process prior to each shot. Cell resistance is obtained from measured voltage by replacing the conductivity cell with various standard resistors in series with a fast switch. Cell resistance is related to fluid conductivity by measuring cell resistances for standard salt solutions with known electrical conductivities. Also, cell resistance was calculated from equipotential curves calculated using a three-dimensional representation of the electrodes. The calibration and the calculation are in good agreement.

Five conductivity points for shocked D_2 are plotted in Fig. 1 as $\log(\sigma)$ vs T^{-1} . These data fit Eq. (1). Shock pressures and molar volumes obtained by shock-impedance matching [27,29] are 20.4, 18.7, 15.5, 15.2, and 13.3 GPa and 7.17, 7.29, 7.57, 7.60, and 7.83 cm^3/mol , respectively. Calculated shock temperatures are 4560, 4160, 3430, 3360, and 2920 K, respectively [20]. The variation in molar volume is small, especially compared to the initial liquid volume of 23.6 cm^3/mol . Thus, these compressions are quasi-isochoric and the variation in E_g with volume can be neglected. The variation of shock temperature, however, causes a variation in conductivity of almost 4 orders of magnitude. The least-squares line in Fig. 1 corresponds to $E_g = 11.7$ eV and $\sigma_0 = 1.1 \times 10^6$ (Ωcm) $^{-1}$. Experimental uncertainties in σ correspond to ± 0.5 eV in E_g . Uncertainties in calculated shock temperatures of simple molecular hydrogen are a nominal 5%, which cause a systematic uncertainty of ± 0.6 eV.

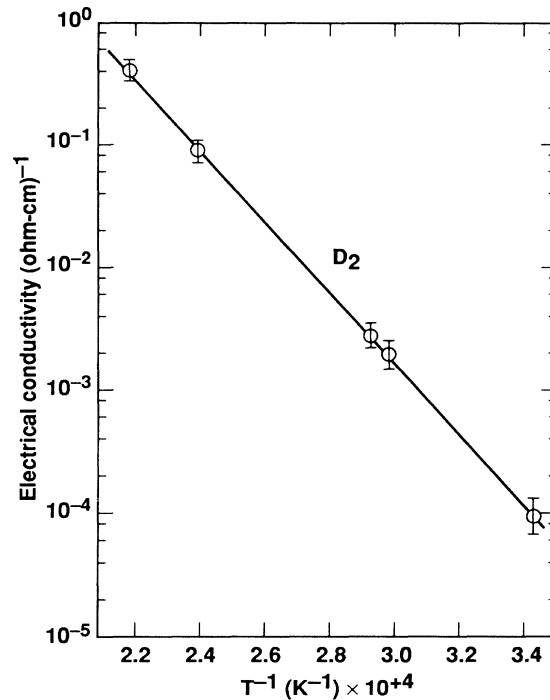


FIG. 1. Logarithm of electrical conductivity of shock-compressed liquid D_2 vs reciprocal shock temperature.

Thus, $E_g = 11.7 \pm 1.1$ eV at 7.5 ± 0.3 cm^3/mol . The D_2 conductivities are plotted versus shock pressure in Fig. 2.

One experiment was performed with liquid H_2 at maximum impact velocity of 6.7 km/s, corresponding to 9.96 GPa, 9.04 cm^3/mol , and 3020 K. Because of the low H_2 shock temperature and somewhat larger energy gap (12.4 eV) [19], the conductivity is very small; the same impactor velocity produces a D_2 conductivity which is 10^4 greater. Nevertheless, as shown in Fig. 2 the measured H_2 conductivity agrees with the exponential pressure dependence of the conductivity of shocked liquid H_2 predicted from the quasiparticle band gaps at the H_2 shock volume [19], the calculated shock temperatures of H_2 [20], and σ_0 obtained from the D_2 data.

Our energy gap of D_2 is plotted in Fig. 3 along with density dependences of the quasiparticle [19] and LDA [17] band gaps. Our gap is in good agreement with the quasiparticle curves for the hcp phase. The experimental uncertainty does not resolve the difference between the orientationally disordered and the c -axis cases. The molar volumes of our experiments are in the range in which solid D_2 is in the hcp phase [30] with low-frequency molecular rotational bands [31] indicative of orientational disorder. A broadened hcp-like pair distribution is expected to persist in the dense molecularly disordered fluid. Thus, results for the fluid are most relevant to the orientationally disordered hcp case. Also, our values of E_g agree well with optical oscillator frequencies of about 12 eV at 7 cm^3 of solid H_2 [5–7]. At the densities of our

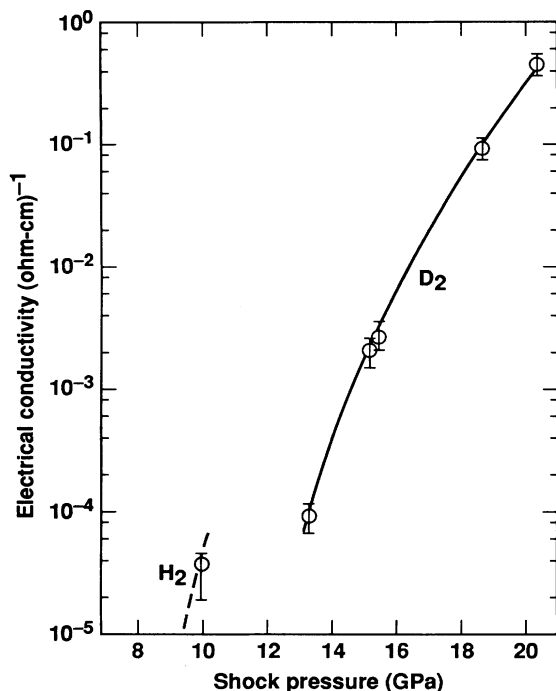


FIG. 2. Logarithm of electrical conductivity of shock-compressed liquid D₂ and H₂ vs shock pressure. Solid curve through D₂ data is a linear fit in Fig. 1, with shock pressure related to shock temperature by theoretical calculations of Ref. [20]. Dashed curve through the H₂ data point is calculated from D₂ data as described in text. Agreement between the H₂ point and the predicted exponential dependence of dashed curve is evidence that both the calculated quasiparticle energy gap and shock temperatures are quite accurate.

experiments the energy gap is weakly sensitive to structure, solid or liquid, because bonding between molecules is weak, as indicated by relatively flat electronic energy bands.

A carrier concentration of $10^{15}/\text{cm}^3$ is estimated in fluid D₂ at 4000 K with $E_g = 11.7$ eV, using semiconductor statistics with effective masses of five free-electron masses for electrons and holes ($m_e = m_h$); H₂ bands are relatively flat, which implies relatively large effective masses. Electronic scattering times estimated from $\tau_e = m_e \sigma / ne^2$ are 10^{-12} s. Electronic mobilities estimated from $\mu_e = e\tau_e/m_e$ are $400 \text{ cm}^2/\text{Vs}$, which is a factor of 4 smaller than electron mobilities of crystalline Si and diamond.

Since the dissociation energy of hydrogen is 4.5 eV, molecules dissociate in the shock state. The calculated dissociation fraction of D₂ is $< 1\%$ at 20 GPa [20]. The ionization energy of an H atom is 13.5 eV, larger than the molecular energy gap of 11.7 eV. Since the densities of these experiments are insufficient to have a substantial effect on the atomic ionization energy, carrier activation from the 100 times more numerous molecules is expected to dominate over that from atoms.

To achieve higher densities, H₂ and D₂ must be multi-

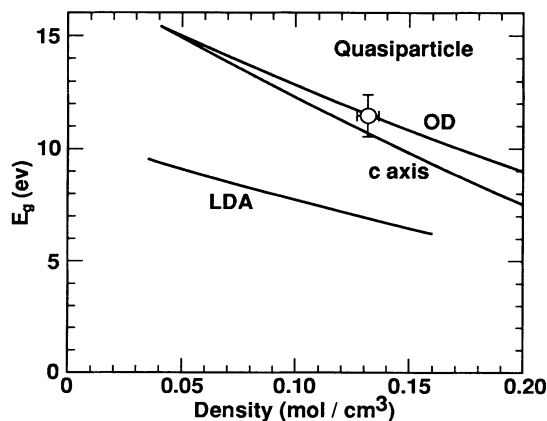


FIG. 3. Measured energy gap of D₂ (open circle) plotted vs density with theoretical density dependences calculated by the quasiparticle [Ref. [19]: hcp structure; OD (orientationally disordered) and *c* axis aligned molecules] and LDA methods (Ref. [17]: *Pa*3 structure). LDA results of Refs. [17] and [18] are quite similar on this scale. At the densities of these experiments the gap is expected to be weakly sensitive to solid or liquid structure.

ply shocked by a reverberating shock wave. This process maintains shock temperatures at a few 0.1 eV, which is appropriate for measuring few-eV gaps by electrical conductivities. The prefactor σ_0 in Eq. (1) is expected to vary slowly with density, provided band curvature is small, because the density dependence of σ_0 should be dominated by $(m_e m_h)^{3/4}$ from the expression for intrinsic carrier concentration.

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