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## Low-Temperature Equation of State of Molecular Hydrogen and Deuterium to 0.37 Mbar: Implications for Metallic Hydrogen

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The  $T = 5$  K isotherms of molecular  $H_2$  and  $D_2$  as well as the index of refraction to 370 kbar have been measured with a diamond-anvil cell. The hydrogens are somewhat softer than predicted from extrapolation of low-pressure measurements and the transition to the metallic atomic state is predicted to fall between 1.9 and 5.6 Mbar.

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The advent of the diamond-anvil cell (DAC) has made it possible to study molecular hydrogen and its isotopes up to pressures,  $P$ , approaching 1 Mbar.<sup>1,2</sup> However the physically meaningful parameter density, or molar volume  $V$ , was known experimentally only to about 25 kbar. We have measured the  $P, V$  relation, or the equation of state (EOS), as well as the index of refraction  $n$ , of molecular hydrogen and deuterium, to pressures of 370 kbar at  $T = 5$  K in a DAC. We have compressed  $H_2$  by more than a factor of 5 from its zero-pressure volume of 23.16 to 4.6 cm<sup>3</sup>/mole. The hydrogens are found to be softer at high pressures than extrapolations would suggest. Our results have important implications for metallic hydrogen. In the past 46 years there have been of order two dozen calculations of the transition pressure of insulating molecular hydrogen to the conducting atomic state with predicted pressures ranging between 0.25 and 20 Mbar. Much of the uncertainty was due to the unknown EOS of  $H_2$  at high pressure. We can now make the first prediction of the transition pressure based upon a high-pressure experimental EOS; we find the transition to fall between 1.9 and 5.6 Mbar. We also show that up to 400 kbar the EOS can be based on an effective pair potential.

The  $P, V$  relation can be measured in a DAC by a number of methods. Pressure determination is straightforward and makes use of the calibrated pressure dependence of the frequency of the ruby  $R$  line, observed in fluorescence.<sup>3</sup> A number of techniques for determining the volume are conceivable. X-ray diffraction can be used to measure the lattice parameter; however, this technique is difficult because of the small x-ray cross section for  $H_2$  and the small sample size in a DAC ( $\sim 10^{-4}$  mm<sup>3</sup>). Brillouin scattering can be used to measure the velocity of sound, which under a number of assumptions can be integrated to yield the  $P, V$  relation.<sup>4</sup> We have chosen a simple

and direct technique of measuring the sample volume by a combination of photographic and interferometric methods.

Our DAC is mounted in a cryostat with an optical tail, having a temperature range of 1.1–300 K. Most measurements were performed at  $T = 5$  K. The maximum pressure achieved in these measurements was 590 kbar; however, useful data were taken only up to 370 kbar. Samples of  $p$ - $H_2$  and  $o$ - $D_2$  were confined in a cylindrical channel (effective diameters ranged from 40 to 150  $\mu$ m and thickness,  $d$ , from 6 to 120  $\mu$ m) in a stainless-steel gasket between optically flat and parallel culets of two diamonds, along with ruby grains for pressure measurements. The channel volume varies with pressure and we assume that it remains a right cylinder with area,  $A$ , of arbitrary shape so that  $V = Ad$ . The area is measured *in situ* by microphotographic techniques. Photographs include the area of the culet which is used as a reference. Errors in areal measurement were estimated to be as large as 5%, due mainly to the limited spatial resolution of our microscope which required a long focal length as it is external to the cryostat. Possible systematic errors which underestimate the volume could arise from nonuniform channel walls and deviations from a right-cylindrical channel geometry. The profiles of used gaskets were studied with a scanning electron microscope. No serious problem was detected and no corrections were made. For the determination of  $d$ , we measure optical interference fringes in transmission.<sup>5</sup> The sample hole is illuminated with a collimated source of visible white light. Transmitted light is focused into a spectrometer (Spex 1401) with a resulting fringe pattern in which the peaks are separated (in wave number) by

$$\Delta\bar{\nu} = \Delta m / (2nd \cos \gamma), \quad (1a)$$

where  $m$  is the fringe order,  $n$  the index of re-

fraction of the sample, and  $\gamma$  the angle of the wave vector of the light in the sample with respect to the normal of the culet. For the conditions of our experiment the fringe pattern is essentially a sine wave in wave number  $\bar{\nu}$  whose phase depends upon the angle  $\gamma$ . Both  $n$  and  $d$  are unknown; however, they can in principle be determined by measurement at two values of the angle  $\gamma$  from Eq. (1a). Since the range of  $\gamma$  is quite small in our system, accuracy is improved by measuring the fringe shift  $\delta\bar{\nu}$  for a series of angles. Using Snell's law  $\sin\alpha = n \sin\gamma$ , where  $\alpha$  is the angle of the light incident on the diamond, it is easily shown that for small angles

$$\delta\bar{\nu} = (\bar{\nu}/2n^2)\alpha^2. \quad (1b)$$

A plot of  $\delta\bar{\nu}$  vs  $\alpha$  can be fitted by a parabola to determine  $n$  and then  $d$  from Eq. (1a). In our apparatus  $\alpha$  was limited to  $3.5^\circ$  and could be measured to an accuracy  $\delta\alpha/\alpha \approx 0.002$ . The principal inaccuracy in the determination of  $d$  arose from error in  $n$  determined by Eq. (1b) which is then used in Eq. (1a). The error in  $n$  was due to the limited range of  $\alpha$  and reduced fringe contrast at high pressure which led to inaccuracies in measuring the shift,  $\delta\bar{\nu}$ .

Two runs were made on both  $H_2$  and  $D_2$ , one for low ( $P < 50$  kbar) and the other for high pressure. The low-pressure runs had substantially larger gasket holes and thus higher precision. These runs were used to compare to the known EOS and for a control of the accuracy of our technique. The measured values of  $n$  for  $p$ - $H_2$  and  $o$ - $D_2$  are shown in Fig. 1 as a function of pressure. Because of the large scatter, it is desirable to smooth the data. One expects the modified isotropic Lorenz-Lorentz relation,

$$[(n^2 - 1)/(n^2 + 2)]3V/4\pi\alpha_\infty = S(V), \quad (2)$$

to be a reasonable representation of  $n$ . Here  $\alpha_\infty$  is the single-molecule polarizability.  $S(V)$  is a normalized [ $S(\infty) = 1$ ] decreasing function of  $\rho = V^{-1}$  in our pressure regime and arises from many-body forces and spatial confinement of the molecules.<sup>6</sup> Considering the size of the error in  $n$ , the most useful way of smoothing the data was to treat all of the  $H_2$  and  $D_2$  data together (at high pressure the densities of  $H_2$  and  $D_2$  are about equal at the same pressure). These were fitted with a curve which was constrained such that the left-hand side of Eq. (2) was less than or equal to one, yielding

$$n = -0.7 + 0.0009P + 1.83(1.37 + P)^{0.03}$$

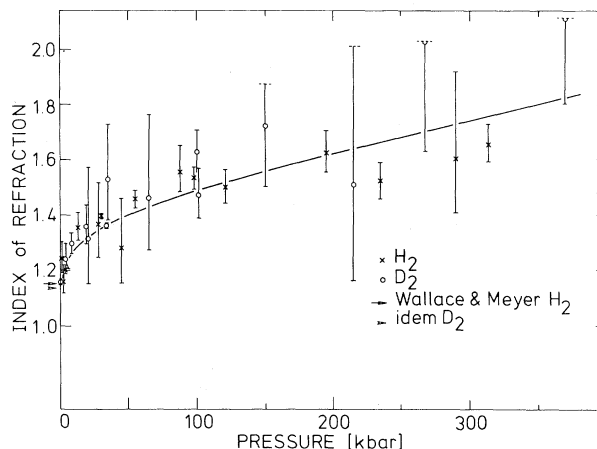


FIG. 1. Measured index of refraction as a function of pressure. The line is a fit to the data. Upper limits on some of the data points were determined from the fringe contrast.

for both  $H_2$  and  $D_2$ . This curve gives surprisingly good agreement with precision low-pressure data from other sources.<sup>7</sup> These values of  $n$  vs  $P$  are then used to determine  $d$  of Eq. (1a). In order to determine the EOS we require the true value of the molar volume,  $V$ , whereas in the experiment we only measure a scaled value  $V' = \eta V$ . The scale factor  $\eta$  is determined by fitting low-pressure data of a given run to the known low-pressure Birch relation for the EOS of  $H_2$  and  $D_2$  from Driessen *et al.*<sup>8</sup> The experimental values of the EOS so determined are shown in Fig. 2. The bars represent estimates of statistical error. The dashed lines represent the EOS according to the Birch relation<sup>8</sup> which closely fits precision experimental data to 25 kbar (Ref. 9) and can be safely extrapolated to  $P \approx 100$  kbar. The rather good agreement between our data and this curve provides confidence in our technique.

We would now like to fit our  $P, V$  data with a curve to allow extrapolation to higher pressures. Although the Birch relation does a splendid job of fitting up to 25 kbar, we expect that this form, which is based on a power-series intermolecular potential, will not have the proper repulsive behavior to extrapolate to ultrahigh pressure where the known exponential form of the repulsive part of the pair potential,  $\phi$ , will dominate. We propose a new form for the EOS. For hydrogen  $T = 5$  K corresponds to the  $T = 0$  K limit. At  $T = 0$  K the pressure is given by  $P = -\partial F/\partial V$ , where  $F = F_s + F_z$  is the free energy. The static part is equal to the lattice energy,  $F_s = U$ , and the zero-

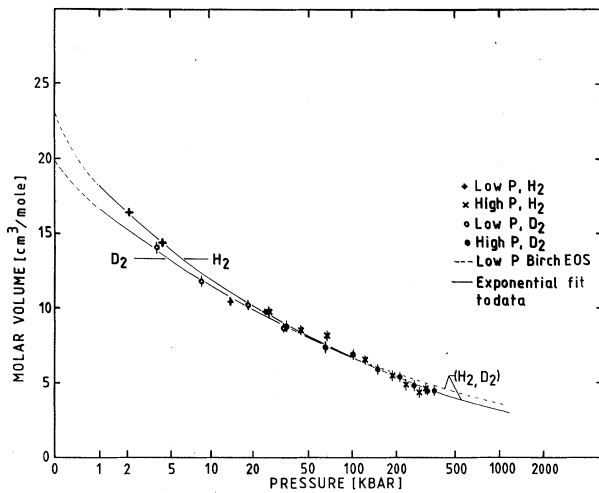


FIG. 2. The  $T = 5$  K isotherms of  $H_2$  and  $D_2$ . High-pressure lines beyond the data points are extrapolations. We use a quasilogarithmic scale by adding a constant 1 kbar to plot all the data and emphasize the high pressures.

point part

$$F_{\mathbf{z}} \propto \hbar \langle \omega \rangle / 2 = D [R^{-1}(\partial/\partial R)(R\partial/\partial R)U]^{1/2},$$

where  $D$  is a constant proportional to  $M^{-1/2}$  ( $M$  is the molecular mass) and  $\langle \omega \rangle$  is an average phonon frequency. For  $U$  we use a form inspired by a simplified form of the potential of Silvera and Goldman,<sup>10</sup>  $U = A \exp(-\beta R) - CR^{-6}f$ , where  $R$  is the intermolecular distance in angstroms and  $f = \exp[-(8.24/R - 1)^2]$  is a function which attenuates the attractive van der Waals term at short distances. The first term of  $U$  represents the repulsive core. Straightforward differentiation ( $f$  is taken as a constant for this operation) yields an expression

$$P = P_s(A, \beta, C, V/V_0) + DP_{\mathbf{z}}(A, \beta, C, V/V_0),$$

where  $V_0$  is a reference volume corresponding to  $P = P_0$ . This form is inadequate at  $P = 0$  because of the extreme quantum nature of  $H_2$  and thus we restrict it to  $P \gtrsim 1$  kbar. The expression for  $P$  (which is a bit lengthy and is available from the authors on request) is then the least-squares fit to our data of  $H_2$  and  $D_2$ ; in the region 1–25 kbar we use the more accurate data of Anderson and Swenson.<sup>9</sup> These curves are shown in Fig. 2 (solid lines) and a tabulation is given in Table I. We see that  $H_2$  is softer than predicted by extrapolating the Birch relation to high pressure (Fig. 2—compare  $\Delta P$  at a constant  $V$ ). From the fit parameters, we find  $\beta_{D_2} = 2.854 \text{ \AA}^{-1}$  and  $\beta_{H_2} = 2.907 \text{ \AA}^{-1}$ , which we compare to the slightly “harder” value  $\beta = 2.958 \text{ \AA}^{-1}$  of Ref. 10; also

TABLE I.  $T = 5$  K isotherms of  $H_2$  and  $D_2$  of this work compared with extrapolations based on low-pressure isotherms. For  $V < 5 \text{ cm}^3/\text{mole}$  the present work is extrapolated using the EOS discussed in the text.

$V$ ( $\text{cm}^3/\text{mole}$ )	Pressure (kbar)			
	Present Work $D_2$	Present Work $H_2$	Ref. 10 $H_2$	Birch (Ref. 8) $H_2$
10	20.0	22.7	22.6	22.9
9	31.2	34.6	35.1	35.3
8	49.9	54.1	56.3	56.6
7	82.5	87.8	93.8	94.3
6	142	149	165	167
5	262	271	312	320
4	528	537	656	702
3	1216	1220	1614	1854
2	3513	3482	5151	6940
1.6	5972	5892		

$D_{H_2}/D_{D_2} = 1.48 \approx (M_{D_2}/M_{H_2})^{1/2}$  supporting our model in which the zero-point pressure is explicitly included in the EOS. These results show that, at least to 400 kbar, the effective pair potential remains a valid approximation for thermodynamic properties of solid  $H_2$ .

Our results have important implications for the prediction of the pressure  $P_c$  of the insulator-metal transition. This has had two sources of uncertainty: the EOS of the insulating phase and that of the conducting phase. Previously the former had been extrapolated from 25 kbar or has been calculated, also based on questionable approximations; our EOS removes much of these uncertainties. The EOS of the metallic phase has been calculated in various approximations giving a spread of values. Ross and McMahan<sup>11</sup> have recently pointed out an additional large uncertainty due to electron correlation energy. We have determined  $P_c$  by calculating the Gibbs free energy,  $G$ , from our EOS and using a spread of values of  $G$  for the metallic phase (after McMahan<sup>12</sup>). From Fig. 3 we see that  $P_c$  ranges between 1.9 and 3.6 Mbar and can be as high as 5.6 Mbar if the correlation energy is reduced by 2 (dashed line). Recently the possibility of a transition to a conducting molecular state has been considered.<sup>13</sup> This would occur at a pressure lower than  $P_c$ .

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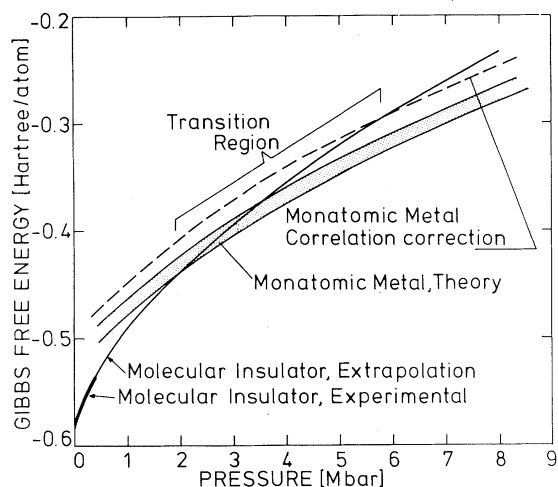


FIG. 3. The Gibbs free energy for atomic metallic and molecular insulating hydrogen. Metallization occurs where the curves for the molecular and atomic phases cross.

*Note added.*—Subsequent to the submission of this Letter, an article on the room-temperature high-pressure isotherm of  $H_2$  and  $D_2$  by Shimizu *et al.* has been published.<sup>14</sup>

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## Structural Determination of the Symmetry-Breaking Parameter in *trans*-(CH)<sub>x</sub>

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The magnitude of the symmetry-breaking dimerization distortion has been determined by analysis of x-ray scattering data from *trans*-(CH)<sub>x</sub>,  $u_0 \approx 0.03$  Å. This distortion can account for the magnitude of the energy gap, implying that electron-electron interactions do not dominate the physics of long-chain polyenes.

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The infinite polyene chain has been a subject of both theoretical and experimental investigation since the early work of Lennard-Jones<sup>1</sup> and that of Coulson.<sup>2</sup> Whether the work was focused on the question of dimerization of the linear chain,<sup>3</sup> the

role of Coulomb correlation,<sup>4</sup> or the recent proposals of topological excitations<sup>5-7</sup> (solitons), the existence and magnitude of the bond alternation has been the crucial and fundamental issue remaining to be resolved. That such a basic ques-