PHYSICAL REVIEW B VOLUME 42, NUMBER 10 1 OCTOBER 1990

Equation of state of solid hydrogen and deuterium from single-crystal x-ray diffraction to 26.5 GPa

R. J. Hemley, H. K. Mao, L. W. Finger, A. P. Jephcoat,* R. M. Hazen, and C. S. Zha†
Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, N.W., Washington, D.C. 20015

(Received 29 December 1989)

Pressure-volume equations of state of solid normal hydrogen and deuterium are determined from single-crystal x-ray diffraction measurements to maximum pressures of 26.5 GPa (265 kbar) at 300 K. Experimental data for deuterium are presented and used with the previously reported results for hydrogen. The measurements for deuterium indicate that the structure remains hexagonal closed packed to at least 14.2 GPa at 300 K. The P-V data are analyzed with both phenomenological equation-of-state formalisms and pair-potential models. The thermal contributions are calculated from a Mie-Gruneisen model and from lattice-dynamics calculations using effective potentials. A P-V equation of state is determined that accurately describes both the high-pressure diffraction data (to $V/V_0 = 0.2$) and previous low-pressure compression results ($V/V_0 = 1.0$ to 0.4). There is a significant softening of the equation of state relative to the predictions of lattice-dynamics calculations using previously reported pair potentials, and several effective potentials are examined. Possible corrections to the equation of state at higher pressures, above the range of the present experiments, include effects associated with order-disorder transitions, vibron softening, and band overlap.

I. INTRODUCTION

One of the intriguing characteristics of solid hydrogen is its extremely high compressibility, a property that arises from its anharmonic, quantum-solid behavior at low pressures.[1,2] At 1 GPa (10 kbar), for example, the molar volume is reduced by a factor of 2 relative to that at zero pressure ($V/V_0 = 0.5$), and a compression close to $V/V_0 \approx 0.4$ is reached at pressures of 2.5 GPa.[3,4] This pressure effect is several orders of magnitude higher than that of most common materials. As a result of its high compressibility, studies of hydrogen as a function of pressure provide useful information on the evolution of microscopic and bulk properties of solids in general with increasing density. Measurements of the pressure-volume equation of state (EOS) of hydrogen have therefore assumed a critical role in understanding the properties of this solid.

Diffraction measurements provide accurate determination of molar volume as well as unit-cell structure. X-ray and neutron diffraction measurements in the low-pressure range (< 1 GPa) have shown that structural stability in solid hydrogen is controlled in part by the rotational state of the molecules, which at low temperatures are forced into even (J=0) and odd (J=1) states as a result of the coupling of the nuclear spin and molecular rotation. It is now established that para-H_2 (J=0) and normal-H_2 (ortho-para mixtures) crystallize in the hexagonal close-packed (hcp) structure at low temperatures (4 K);[5] in contrast, H_2 samples with high concentration of J=1 species (o-H_2 or p-D_2) undergo an ordering transition to a cubic structure (space group $Pa3$) at lower temperatures, which in turn is a function of density. More recent work has shown that p-H_2 and o-D_2 are stable in the hcp structure to 2.5 GPa, with no sign of order-disorder (or other) transitions.[6,7] For both the pure J=0 solids and ortho-para mixtures, the intermolecular potential is dominated by isotropic rather than anisotropic terms. With increasing density the anisotropic terms dominate, and the vibrational dynamics of the solid evolve from an anharmonic, quantum solid to a harmonic, classical system.[2]

Efforts to understand the properties of solid hydrogen at higher pressures require an accurate determination of its structure and equation of state in this regime. In this pressure range, the determination of accurate intermolecular potentials for solid hydrogen has received considerable attention, primarily because of their use in high-temperature simulations; comparisons between experimental and theoretical equations of state have been used as stringent tests of the form of new potentials. Experimental determinations of the EOS at pressures above 10 GPa include Brillouin scattering,[8] optical measurements of relative volume,[9] magnetic compression,[10] and shock-wave techniques.[11] It is important to emphasize that these measurements provide no direct structural information; in addition, these measurements either provide only an indirect determination of molar volume or have unacceptably large uncertainties.

Recent work has demonstrated for the first time that x-ray diffraction can be used to determine directly structural and equation-of-state information on solid hydrogen in a diamond-anvil cell in the gigapascal pressure range using a conventional x-ray source.[12] For higher-pressure measurements, a smaller sample volume must be used. In addition, higher pressures generally cause the hydrogen crystal to fragment under compression, thereby reducing the intensity of the diffraction peaks. A solution to this problem is afforded by the higher x-ray intensities and narrow beam collimation of synchrotron radiation. A new experimental method was designed based on a combination of single-crystal methods and the energy-dispersive scattering technique. With this technique[13] the lattice parameters and P-V relations for hydrogen were measured to a pressure of 26.5 GPa at 300 K.[14]

Accurate structural and EOS measurements in this higher-pressure range are also relevant to understanding the behavior of hydrogen at ultrahigh pressures (above 100 GPa) where significant changes in electronic properties (metallization) are predicted to occur.[15,16] These changes are expected to occur at $V/V_0 \approx 0.1$. Phase transitions at ultrahigh pressure have been observed in hydrogen[17] and deuterium[18] at these densities (beginning at 150 GPa), and recent optical measurements indicate that metallization by band overlap occurs at these pressures.[19] The EOS in this pressure range has not yet been examined by experimental techniques. At these pressures one must rely on the extrapolations of lower-pressure EOS and on the predictions of theoretical calculations. In fact, EOS calculations have been performed[20] based on effective intermolecular potentials parametrized using poorly constrained experimental P-V data; the refinement of such potentials in view of the new experimental data is therefore of interest. During the past few years, the EOS has also been calculated by the use of electronic structure techniques based on a variety of different approximations.[21–25] Considerable differences in the predicted equations of state are evident. Detailed comparisons with the accurate experimental data provide a test of the accuracy of these theoretical methods.

In this paper we present single-crystal x-ray diffraction results for n-D_2 to 14.2 GPa together with an analysis of the data for both n-H_2 and n-D_2 using phenomenological EOS formalisms and effective pair-potential models. The accurate P-V data now available over a large range of compression (V/V_0 to 0.21) allow us to examine critically the validity of phenomenological equations of state parametrized by low-pressure elastic properties. The volume dependence of the thermal pressure is calculated from the Mie-Gruneisen model. Equations of state are calculated from a variety of effective pair potentials developed for dense hydrogen. From the pair potentials, lattice-dynamics calculations can be performed to provide an additional check on the calculation of the thermal pressure. We examine the accuracy of extrapolating the calculated EOS to high compression. These comparisons are useful for estimating the stability of the molecular phase relative to the predicted metallic phases at very high pressures.

The remainder of the paper is organized as follows. The experimental technique is reviewed in Sec. II, and the experimental results for D_2 are presented in Sec. III. The thermal pressure as a function of pressure is considered in Sec. IV. In Sec. V the phenomenological EOS treatment is given. The results of the pair-potential calculations of the equation of state, including a discussion of the lattice dynamics, are presented in Sec. VI. Comparisons with the results of previous experimental equation-of-state studies are described in Sec. VII. Section VIII contains a discussion, including comparisons with theoretical results and implications for the equation of state at higher pressures.

II. EXPERIMENTAL METHODS

The x-ray diffraction measurements reported here for deuterium were performed on beam line X13A (now X7A) at the National Synchrotron Light Source, Brookhaven National Laboratory. The experimental technique has been outlined previously,[14,26,27] so it is reviewed only briefly here. The collimation of the x-ray beam is accomplished with a pair of adjustable slits, which result in a beam size down to 10–30 μm^2.[28] The x rays are incident on the sample in the diamond cell which is mounted on a translation stage which is in turn mounted on a goniometer head. The diffracted x rays are detected by a Ge solid-state detector at a fixed 2θ angle from the incident beam. Along with the higher intensity, however, the background radiation (primarily from the diamond) also increases. Improved collimation of the receiving slits enhanced the sensitivity for measurement of diffraction from the sample.

The solid hydrogen was pressurized using a diamond-anvil pressure cell designed for x-ray diffraction.[29] The cell was loaded in a pressure vessel containing fluid deuterium at 0.2 GPa and 300 K.[30] The sample was confined by a stainless steel gasket having a hole diameter of 50–150 μm and a thickness of 50 μm. The smaller sample size was used for the higher-pressure measurements. The pressure in the diamond cell was increased to 6.3 GPa, which is above the 300 K freezing point[31] to form a single crystal of deuterium. Orientation of the sample and searching for reflections were accomplished by mounting the single-crystal cell in a rotation stage (for the χ circle rotation), which was then mounted on the goniometer head of the diffractometer on the beamline (for the ω circle rotation). A given reflection was found as a peak in the energy-dispersive spectrum when the diffraction condition was satisfied for a specific combination of χ and ω.[14,26]

The pressure was determined by ruby fluorescence[32,33] with an optical system consisting of a microscope, 0.18 m spectrometer, and optical multichannel analyzer; the measured ruby fluorescence was induced directly by the incident x-ray beam.[34] The quasihydrostatic ruby pressure scale is used to calculate the pressure from the wavelength shift of the ruby R_1 band.[33,34]

III. X-RAY DIFFRACTION OF DEUTERIUM

Diffraction patterns measured for deuterium at high pressure are shown in Fig. 1. Diffraction patterns at six pressures up to 14.2 GPa were measured. The angular relationships between the diffraction peaks indicated that the structure is hexagonal close packed,[13] consistent with lower-pressure measurements for deuterium[5] and low- and high-pressure results for hydrogen.[13,15] The orientation of the crystal was found to shift slightly with increasing pressure in the lower-pressure range. Significantly larger shifts were observed at higher pressures. There was no evidence of any major phase transitions having occurred (for example, to an orientationally ordered cubic structure).[1,2] At the highest pressures the reflections weakened as a result of breakup of the single crystal. Nevertheless, the number of reflections measured was sufficient to calculate a volume on the basis of a hexagonal cell. With pressures measured by x-ray induced ruby fluorescence, the pressure dependence of the lattice parameters and molar volume from 6.5 to 14.2 GPa at 300 K were directly determined. The results are tabulated in Table I.

The pressure dependence of the c/a ratio for D_2 is plotted in Fig. 2. No systematic change in the c/a ratio with pressure is evident, within the experimental uncertainty, to 14.2 GPa. Previous measurements for n-H_2 carried out to 26.5 GPa indicated a systematic decrease in the axial ratio c/a with pressure; this change becomes particularly pronounced above 15 GPa.[14] A c/a ratio close to the ideal value of 1.633 is observed for both isotopes near ambient pressure and low temperature.[5]

Recently Glazkov *et al.*[35] have reported neutron diffraction measurements for n-D_2 to 30.9 GPa at 300 K. They report that c/a remains constant at 1.62 over this pressure range, which is consistent with our results. There is thus evidence that hydrogen and deuterium show different behavior in the 15–30 GPa pressure range. Although these differences could arise from intrinsic structural differences between the two isotopes at high pressure, it is necessary to confirm these results with further measurements. The measured deviation in c/a from ideal in hydrogen could be associated with nonhydrostatic strains; these may differ from one sample to the next due to different states of annealing at high pres-

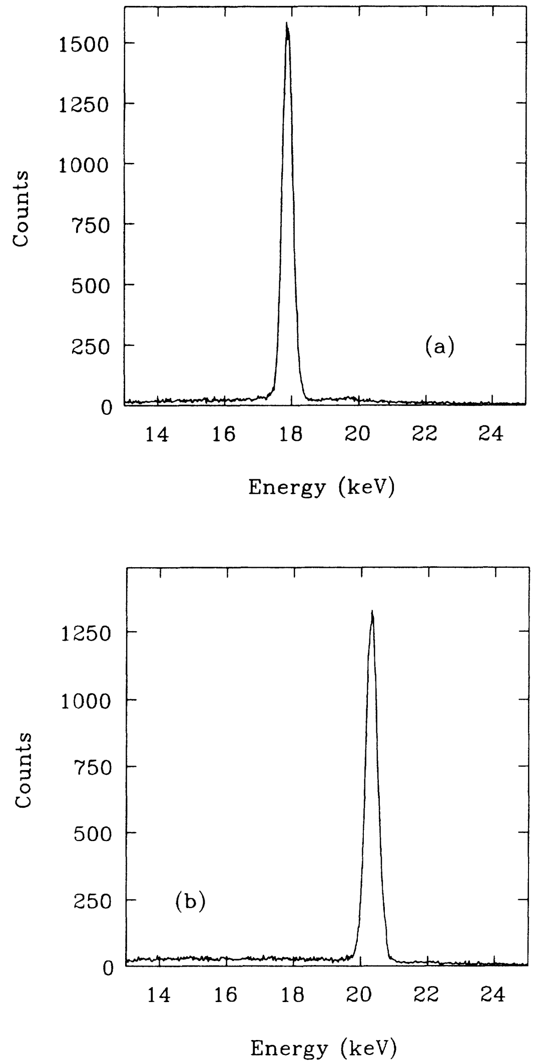

FIG. 1. Examples of diffraction patterns for n-D_2 at 9.2(±0.1) GPa. (a) 100 class reflection. (b) 101 class reflection. The intensity scale is total counts; the spectra were collected over 2–3 min of exposure time.

TABLE I. Lattice parameters and molar volume of n-D_2 (300 K). Uncertainties are given in parentheses. The principal source of error in the absolute values in the lattice parameters (and molar volumes) is that due to uncertainty in the angle calibration for the energy-dispersive measurements. This uncertainty was largest for the measurements at the first three pressures (~0.8%). The error in pressures is that due to the wavelength calibration of the monochromator used in the ruby fluorescence measurements.

a (Å)	c (Å)	c/a	V (cm^3/mol)	P (GPa)
2.623(22)	4.252(35)	1.621(3)	7.63(11)	6.5(1)
2.574(20)	4.201(33)	1.632(3)	7.26(10)	7.3(1)
2.512(21)	4.108(35)	1.635(5)	6.76(10)	9.2(1)
2.493(2)	4.050(5)	1.625(5)	6.56(1)	10.2(1)
2.442(5)	3.963(7)	1.623(2)	6.16(2)	12.3(1)
2.406(5)	3.894(8)	1.618(3)	5.88(2)	14.2(2)

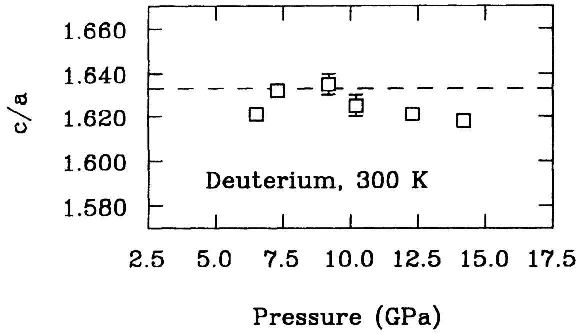

FIG. 2. Pressure dependence of the c/a ratio in n-D_2 (300 K). The ideal value (1.633) is shown by the dashed line.

sure, different sample sizes, and differences in the materials used in the diamond-anvil cell. It is also possible that this behavior reflects differences in ortho-para content in normal hydrogen and deuterium at 300 K. Under equilibrium conditions, there is a higher concentration of molecules in odd (e.g., $J=1$) relative to even (e.g., $J=0$) states in n-H_2 than in n-D_2 at 300 K (75%–25% and 33%–67%, respectively, at zero pressure).[2] This difference could result in a more anisotropic structure for H_2 at a similar compression; such a possibility can be tested by x-ray diffraction measurements of the temperature dependence of the lattice parameters at high pressure.

The observed pressure dependence of the c/a ratio in n-H_2 may be indicative of continuous partial alignment of the H_2 molecules in the hcp structure at high pressure, with the rotation axis parallel to c. Recent density functional calculations by Barbee *et al.*[25] predict a continuous ordering of H_2 molecules in the hcp structure, instead of a first-order orientational ordering transition.[2,16] They predict that the c/a ratio reaches a limiting value of 1.56 under pressure for the fully ordered solid. On the other hand, the Hartree-Fock calculations of Raynor[24] predict an increase in c/a with pressure (>1.78). These calculations were performed for the static lattice with a frozen molecular bond (i.e., zero-point motion was neglected), and no distinction is made for ortho or para species. It is also important to emphasize that the calculations of Barbee *et al.* predict metallization by band overlap to occur at a very low pressure (40 GPa), in poor agreement with experiment.[19]

We wish to point out that on the basis of current x-ray diffraction data for hydrogen and deuterium, we cannot rule out the possibility of mixed layer polytype structures based on hexagonal close-packed layers. The x-ray intensities for the supercell diffractions would be too small to be observed. There is evidence for the persistence of such metastable structures in hydrogen at low pressures.[36] Moreover, we have documented the existence of such intermediate structures of close-packed materials at high pressure by diamond-anvil cell x-ray diffraction techniques.[37] On the other hand, the volumes of such structures are expected to be close to that of the hcp solid, so the existence of such intermediates should not have a large effect on the calculated equations of state (e.g., Ref. 37), which is the central focus of the present study.

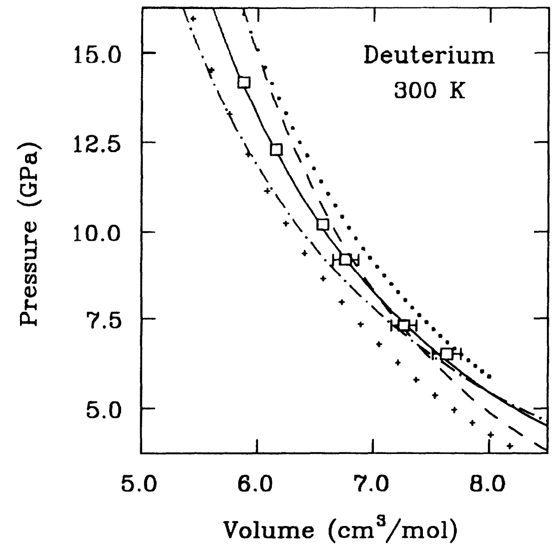

FIG. 3. Pressure-volume data and equation of state of deuterium at 300 K. ——, Vinet *et al.*, fit to the present data; . . . ., van Straaten and Silvera (Ref. 9); – . –, Shimizu *et al.* (Ref. 8); + + + +, extrapolation of Anderson and Swenson Birch-Murnaghan EOS (Ref. 4); – – –, extrapolation of Anderson and Swenson data using the Vinet *et al.* EOS.

In Fig. 3 we compare the present data for D_2 with previously determined equations of state plotted in the same P-V range at room temperature. The lower curve is the room-temperature EOS given by Shimizu *et al.*,[8] which was calculated from the pressure dependence of the sound velocity measured by Brillouin scattering. The van Straaten *et al.*[9] EOS was based on low-temperature optical measurements with a Mie-Gruneisen model used for the thermal correction for room temperature. We also show the results of extrapolations of the earlier EOS data of Anderson and Swenson[4] using EOS formalisms described below.[38–40] The new data at higher pressures lie between the earlier determinations. A comparison between the previously reported results for hydrogen and earlier equations of state showed similar discrepancies. The calculation of the EOS shown in Fig. 2 is described in Sec. V.

IV. THERMAL PRESSURE

In order to compare our results with equation of state determined at low temperatures and with theoretical models, a thermal pressure term P_{th} for 300 K must be subtracted from our measured pressures. In this calculation, we use the Mie-Gruneisen approximation,[41] a model that has been applied to dense solid hydrogen in a number of previous studies (see Ref. 2). The results are also compared with lattice-dynamics calculations using intermolecular potentials.

The pressure $P(V,T)$ is given as the volume derivative of the Helmholtz free energy F. In the Mie-Gruneisen model, the total pressure is written

$$-\left(\frac{dF}{dV}\right)_T = P(V,T) = P_S(V)+P_{ZP}(V)+P_{th}(V,T) \qquad (1)$$

where $P_S(V)$ is the static-lattice pressure, and the second and third terms are the zero-point and thermal pressures given as

$$P_{ZP}(V) = 9R\Theta_D\gamma/8V, \qquad (2)$$

$$P_{th}(V,T) = (3RT\gamma/V)\ D(\Theta_D/T). \qquad (3)$$

Here γ is the thermal Gruneisen parameter, Θ_D is a characteristic (Debye) temperature, $D(\Theta_D/T)$ is the Debye function, and R is the gas constant. In this analysis we determine the pressure at $T = 0$ K, $P_0 = P_S + P_{ZP}$, which is a function of volume only, for each of the experimental points.

The volume dependence of the Gruneisen parameter has been studied by numerous investigators. Krause and Swenson[42] have determined the volume dependence of γ to 10 cm^3/mol from heat capacity measurements. Wijngaarden *et al.*[43] have approximated γ at higher compression by measurements of the mode-Gruneisen parameter for the E_{2g} optical phonon obtained from high-pressure Raman and infrared spectroscopy and scaling the results of lattice-dynamics calculations. Driessen and Silvera[44] and Hemmes *et al.*[45] have used these results in their calculations of the EOS. Recently, we have obtained measurements of the pressure dependence of the optical phonon to pressures above 100 GPa.[46] In the present analysis, we estimate the pressure dependence of γ by fitting the frequency shift of the phonon over this large pressure range. In the pressure range of the present x-ray data the result is similar to that reported previously,[41] although the volume dependence differs because an extrapolated low-pressure EOS (Ref. 47) was used to analyze the data in that study. It is useful to point out that for $T \gg \Theta_D$ the thermal pressure becomes

$$P_{th} = (3RT\gamma/V)[1 - \tfrac{3}{8}(\Theta_D/T) + \tfrac{1}{20}(\Theta_D/T)^2 + \cdots], \qquad T \gg \Theta_D. \qquad (4)$$

The effective Θ_D for hydrogen at zero pressure ($T \to 0$ K) is 99 K, increasing to ~400 K at 1.5 GPa, and ~1250 K at 20 GPa.

The volume dependence of the thermal pressure calculated from the Mie-Gruneisen model in shown in Fig. 4. All models indicate a significant increase in P_{ZP} with applied pressure. There are significant discrepancies in P_{ZP} between the Mie-Gruneisen model and the lattice-dynamics calculation with the exp-6 potential (α=10.9; see below). On the whole, a softer potential produces a lower P_{ZP} at higher pressure. However, the thermal pressure is less sensitive to these differences, and there is good agreement in the calculation of volume dependence of P_{th} using the effective potentials considered here and the Mie-Gruneisen model. Since these differences are close to, or in some cases less than, the uncertainty in measured pressures (~0.1 GPa), there does not appear to be any additional uncertainty added to the equation-of-state calculation in the temperature reduction of the pressures to $T = 0$ K. Similar thermal corrections for hydrogen in this pressure range were obtained by Ross *et al.*[20] from lattice-dynamics calculations. The temperature-reduced pressures obtained in this study for H_2 and D_2 are listed in Table II.

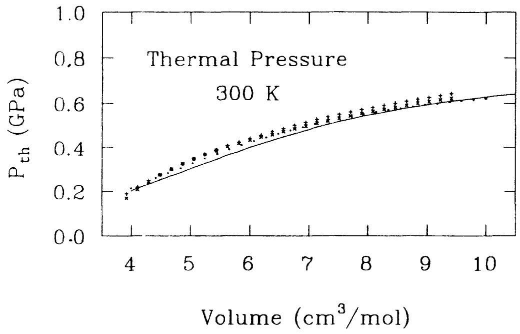

FIG. 4. Thermal pressure as a function of volume for H_2. ——, Mie-Gruneisen model. We parametrize the Debye temperature as $\Theta_D(V) = \Pi \exp(A_k x^k)$, with $x = \ln(V/V_a)$ and $V_a = 23.0$ cm^3/mol. The Gruneisen parameter is thus $\gamma(V) = -\sum_{k=0}^{3} kA_k x^k$. The parameters obtained from the fit are $A_0 = 4.599$, $A_1 = -2.161$, $A_2 = -0.3736$, and $A_3 = -0.029\,84$. . . . ., Mie-Gruneisen result of Hemmes *et al.* (Ref. 45). + + + +, lattice-dynamic calculation with the Silvera-Goldman potential (see text); × × × ×, lattice-dynamics calculation with the exp-6 potential with α=10.9 (see text).

The ortho-para concentration introduces some ambiguity into the equation-of-state fit in the low-pressure range. The concentration of odd-J species c_1 is 75% for n-H_2 at room temperature, whereas for $T \approx 0$ K $c_1 = 0$ at equilibrium (the ground state for the solid at $P = 0$). The

TABLE II. Pressures at 300 and 0 K as functions of volume for n-H_2 and n-D_2.

V (cm^3/mol)	P (GPa) (300 K)	P (GPa) (0 K)[a]
	H_2	
7.992(1)	5.40(3)	4.84
6.671(4)	10.1(1)	9.6
5.799(10)	15.0(1)	14.6
5.145(23)	21.4(1)	21.1
4.791(22)	26.5(1)	26.2
	D_2	
7.63(11)	6.5(1)	5.7
7.26(10)	7.3(1)	6.5
6.76(10)	9.2(1)	8.5
6.56(1)	10.2(1)	9.5
6.16(2)	12.3(1)	11.6
5.88(2)	14.2(2)	13.5

[a] Calculated pressure from the Mie-Grüneisen model.

presence of $J=1$ impurities introduces a small negative quadrupolar pressure P_Q which reduces the zero pressure V_0. The magnitude of the change, however, is much less than the spread in values reported for V_0 for pure p-H_2.[2] Perhaps the most accurate determination of V_0 is that of Ishmaev and co-workers[6,7] who reported values of 23.00 (± 0.02) cm^3/mol and 19.933 (± 0.015) cm^3/mol for p-H_2 and o-D_2, respectively. For hydrogen, Silvera[2] prefers $V_0 = 23.14$ (± 0.12) cm^3/mol for p-H_2, with $V_0 = 22.91$ cm^3/mol for n-H_2 (but see Krause and Swenson[42]). In view of the uncertainties in this quantity, we have adopted $V_0 = 23.00$ cm^3/mol for our fit, but also show results of using the lower value. The value reported by Ishmaev *et al.*[7] for deuterium is close to previous determinations; $V_0 = 19.93$ cm^3/mol is used in the fit.

V. EQUATION OF STATE

With the temperature-reduced P-V data, we can analyze the results by the use of phenomenological equations of state. The Birch-Murnaghan[38] equation of state has been used in a number of EOS studies of hydrogen (see Silvera[2]). To fourth order in the strain energy, the equation of state is written,

$$P = 3K_0(V_0/V)^{5/3} f(1 + af + bf^2), \tag{5}$$

where f is the Eulerian strain, $f = \frac{1}{2}[(V_0/V)^{2/3} - 1]$, and

$$a = \tfrac{3}{2}(K_0' - 4),$$

$$b = \tfrac{3}{2}[K_0 K_0'' + K_0'(K_0' - 7) + \tfrac{143}{9}].$$

A fit of $F = P(V/V_0)^{5/3} f$ versus f can be used to obtain the bulk modulus K_0 and its pressure derivatives K_0' and K_0''. If the EOS is truncated at third order (linear F-f relation), K_0'' is constrained by $K_0 K_0'' = -(K_0')^2 + 7K_0' - \frac{143}{9}$. Grover *et al.*[39] have proposed the following EOS for P-V data at high compressions:

$$P = \frac{K_0}{K_0' + 1}\{(V/V_0)\exp[K_0'(1 - (V/V_0)] - 1\}. \tag{6}$$

This function has been shown to accurately represent compressional data to $V/V_0 \approx 0.4$.[39] More recently, Vinet *et al.*[40] have proposed an EOS of the form

$$\begin{aligned} P = {} & 3K_0(V/V_0)^{-2/3}[1 - (V/V_0)^{1/3}] \\ & \times \exp\{\eta[1 - (V/V_0)^{1/3}]\}, \end{aligned} \tag{7}$$

where $\eta = \frac{2}{3}(K_0' - 1)$. They have shown that this function is capable of fitting the EOS of a wide variety of materials to high compression. With this formulation, it is useful to note that $K_0 K_0'' = -(K_0'/2)^2 - (K_0'/2) + \frac{19}{36}$; in the Grover *et al.*[39] EOS $K_0 K_0''$. The Birch-Murnaghan EOS can be represented in terms of an expansion of a $1/r^n$ interatomic potential such as the Lennard-Jones form $(r^{-6}$–$r^{-12})$.[48] In contrast, the latter two EOS functions are based on a repulsive interatomic potential.

TABLE III. Equation-of-state parameters.

EOS	V_0 (cm^3/mol)	K_0 (GPa)	K_0'	$K_0 K_0''$ [a]	Pressure range (GPa)	Data source and notes
			H_2			
Vinet *et al.*	23.00	0.172(4)	7.19(4)	[−16.0]	5.4–26.5	This work n-H_2
Vinet *et al.*	22.91	0.169(4)	7.26(4)	[−16.3]	5.4–26.5	This work n-H_2
Vinet *et al.*	22.91	0.166	7.29(2)	[−16.4]	0.05–26.5	Ref. 4 + Ref. 14 n-H_2
Vinet *et al.*	23.00	0.186(5)	7.07(2)	[−15.5]	0.05–2.5	Ref. 4 n-H_2[b]
Birch (3rd)	23.00	0.170(6)	7.0(3)	[−15.9]	0.05–2.5	Ref. 4 n-H_2[c]
Birch (3rd)	23.00(2)	0.1857(30)	7.03(28)	[−16.1]	0–2.4	Ref. 6 p-H_2[d]
Birch (3rd)	23.00	0.362(3)	4.71(3)	[−5.1]	5.4–26.5	This work n-H_2
Grover *et al.*	23.00	0.066(2)	8.43(1)	[−8.4]	5.4–26.5	This work n-H_2
			D_2			
Vinet *et al.*	19.93	0.35(3)	6.6(2)	[−13.7]	6.5–14.2	This work n_2-D_2
Vinet *et al.*	19.93	0.336(1)	6.78(1)	[−14.4]	0–14.2	Ref. 7 o-D_2 + this work n-H_2
Vinet *et al.*	19.93	0.330(1)	7.01(1)	[−15.3]	0–2.5	Ref. 7 o-D_2
Birch (3rd)	19.933(15)	0.3347(53)	6.86(17)	[−14.9]	0–2.5	Ref. 7 o-D_2[d]
Birch (3rd)	19.93	0.315(6)	6.7(3)	[−13.9]	0.05–2.5	Ref. 4 n-D_2[c]
Birch (3rd)	19.93	0.46(5)	5.2(2)	[−6.5]	6.5–14.2	This work n-D_2
Grover *et al.*	19.93	0.22(2)	7.1(1)	[−7.1]	6.5–14.2	This work n-D_2

[a] Parameter is constrained by K_0' according to the specific form of the EOS (see text).

[b] A similar result was obtained by Vinet *et al.* (Ref. 40), who performed an unweighted fit.

[c] Values for K_0 and K_0' reported by Anderson and Swenson (Ref. 4).

[d] Best-fit parameters reported by Ishmaev and co-workers (Refs. 6 and 7).

We performed weighted nonlinear least-squares fits of the temperature-reduced P-V data listed in Table II to each of these equation-of-state formalisms. In each case, V_0 was assumed, and K_0 and K_0' were adjusted. The resulting equation-of-state parameters are listed in Table III. Previous studies have shown that the third-order Birch EOS is sufficient to represent the P-V data for hydrogen to pressures of 2.5 GPa.[4–7] When combined with the previous low-pressure results, we find that the P-V data for both isotopes is not well represented by a third-order Birch-Murnaghan expansion; specifically, a distinct curvature in the F-f plot develops above $f = 0.6$. Hence, at least a fourth-order expansion is required to adequately represent the data. With the fourth-order parametrization, however, the F-f curve passes through a maximum at $f \sim 1.0$, which is unphysical; hence the fourth-order EOS is not likely to be useful for extrapolation to higher pressures.

We find that the Vinet *et al.*[40] form is superior to both the Birch-Murnaghan and Grover *et al.* fits to the same data. When the low-pressure data of Anderson and Swenson[4] or Ishmaev and co-workers[6,7] are used to constrain K_0 and K_0', the agreement between the extrapolated Vinet *et al.* EOS and the new higher-pressure data is quite close, as shown in Figs. 5 and 6. If used in combination with the low-pressure data of Ishmaev *et al.* (for p-H_2), the result is similar to the Vinet *et al.* fit; but K_0K_0'' becomes more negative. On the other hand, there is no need for higher-order terms (beyond K_0'') in the latter EOS. This result for H_2 was suggested by preliminary work reported by Vinet *et al.*,[40] who analyzed the Anderson and Swenson P-V results and the original optical EOS data of van Straaten *et al.*[9] The present analysis indeed shows that the two-parameter Vinet *et al.* EOS provides a better fit to H_2 data over a large compressional range than was suggested by the previous work of these authors.[40]

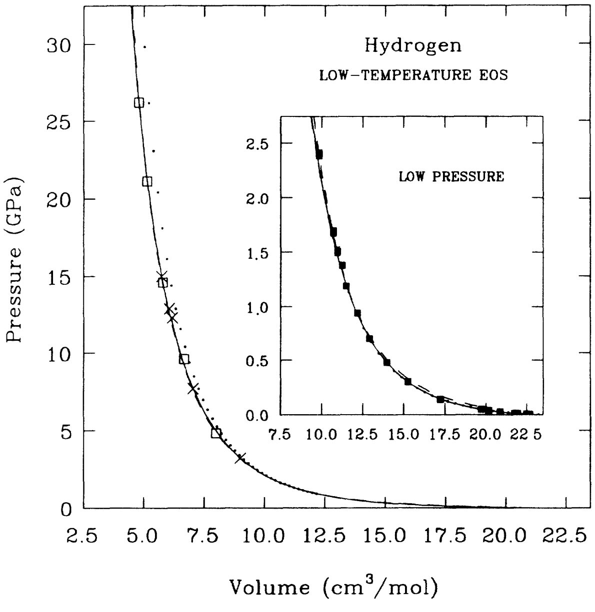

FIG. 5. Temperature-reduced ($T = 0$ K) EOS for H_2. □, x-ray data (high-pressure); ■, neutron data of Ishmaev *et al.* (Ref. 6) (low pressure); ×, Mateev *et al.* (Ref. 10); ——, Vinet *et al.* fit to the present data; – – –, van Straaten and Silvera (Ref. 9); . . . ., extrapolation of Anderson and Swenson EOS (Ref. 4).

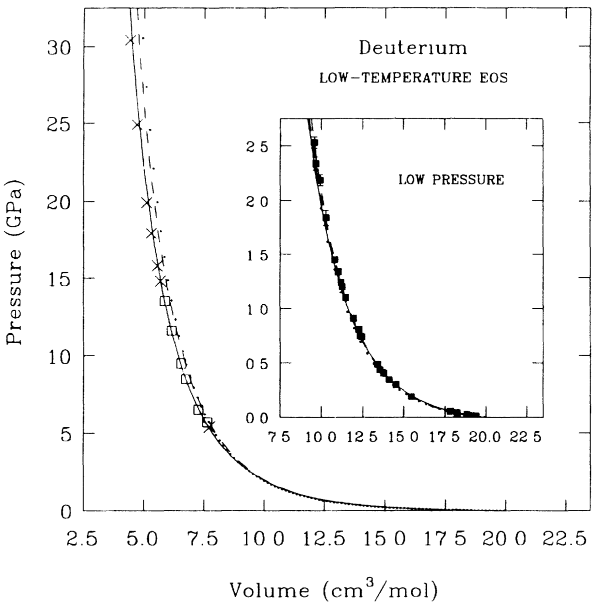

FIG. 6. Temperature-reduced ($T = 0$ K) EOS for D_2. □, x-ray data (high-pressure); ■, neutron data of Ishmaev *et al.* (Ref. 7) (low pressure); ×, Glazkov *et al.* (Ref. 35); ——, Vinet *et al.* fit to the present data; – – –, van Straaten and Silvera (Ref. 9); . . . ., extrapolation of Anderson and Swenson EOS (Ref. 4).

The present analysis shows that given the same values for K_0 and K_0', the two-parameter forms of the three EOS begin at $V/V_0 = 0.8$; this is consistent with Jeanloz's[49] general analysis of these EOS functions. It is useful to note that the values for K_0' obtained from both the Vinet *et al.* and third-order Birch-Murnaghan forms are similar. $K_0' \approx 7$ was obtained for H_2 and D_2; when $K_0' = 6.76$, the $K_0'K_0''$ terms for the two EOS are equal. There are currently no ultrasonic data for K_0'' which could be used to assess the extent to which the values so obtained are physically meaningful.

VI. COMPARISONS WITH PREVIOUS EXPERIMENTAL RESULTS

One of the tests of an equation-of-state fit such as those described above is the accuracy in the zero-pressure parameters. Since these are merely fitting parameters in the EOS, they may not necessarily correspond to actual values obtained independently by low-pressure elasticity measurements (e.g., ultrasonic or Brillouin scattering). It is therefore useful to note that the values obtained for K_0 from the fit of the x-ray diffraction data agree with those determined from ultrasonic measurements by Udovidchenko and Manzhelli[50] and by Wanner and Meyer[51] [$K_0 = 0.174\ (\pm 0.010)$ GPa]. For D_2, we find that the K_0 obtained from the fit of the neutron- and x-ray diffraction data from 0 to 15.5 GPa is also close to the ultrasonic result[51] [$K_0 = 0.337\ (\pm 0.020)$ GPa]. Ultrasonic results for H_2 are also close to those measured by Brillouin scattering at zero pressure and 4 K by Thomas *et al.* [$K_{0S} = 0.173(1)$ GPa (adiabatic); corrected to $K_{0T} = 0.162$ GPa (isothermal)].[52]

The quality of the equation-of-state fits to the x-ray diffraction data can be assessed further by the comparison of the results in the low-pressure region (Figs. 5 and 6). Here we compare the temperature-reduced equations of state with the P-V data of Anderson and Swenson, which were obtained for n-H_2 and n-D_2 by a piston displacement technique to 2.5 GPa at 4.2 K. These data were not included in the present fit. The Vinet *et al.* form accurately reproduces the low-pressure data. As discussed previously,[14] very good agreement with the present equation of state for H_2 is obtained if K_0 is set equal to the original zero-pressure values reported by Anderson and Swenson in their Birch-Murnaghan fit.[4] For hydrogen (Fig. 5), we also show the results of the fit that included the Anderson and Swenson data in addition to the high-pressure diffraction points reported in Ref. 14 (see Table III). The result is nearly indistinguishable from the present fit.

The most accurate EOS data in the low-pressure range appear to be the neutron-diffraction measurements of Ishmaev *et al.*[6,7] These authors examined the $J=0$ (para-H_2 and ortho-D_2) solids at 4-40 K. Anderson and Swenson[4] found no dependence on c_1 in their measured isotherms. The effect of ortho-para concentration on the equation of state has been studied by Driessen *et al.*[44] For the low-density solid, increasing ortho concentration affects the EOS by the introduction of a quadrupolar pressure. This correction is small on the scale of the present measurements, and decreases with applied pressure above ~0.05 GPa.

We recall that there is less uncertainty in the V_0 for D_2. The EOS reported by Ishmaev *et al.*[7] for D_2 is significantly less compressible than the results of Anderson and Swenson[4] and Driessen *et al.*[44] (who used the data of Anderson and Swenson). It is interesting to note that when the x-ray diffraction data alone are used in the fit, the resulting equation of state is close to that of Ishmaev *et al.*[7] This suggests that there may be a systematic error in the relative volume measurements reported in Ref. 4. In support of this conjecture is the overestimate of the compressibility predicted for D_2 using the extrapolated Vinet *et al.* EOS fit to the Anderson and Swenson data (Figs. 5 and 6); in contrast, a similar analysis of the H_2 result accurately predicts the EOS in the region of the direct x-ray diffraction measurements.

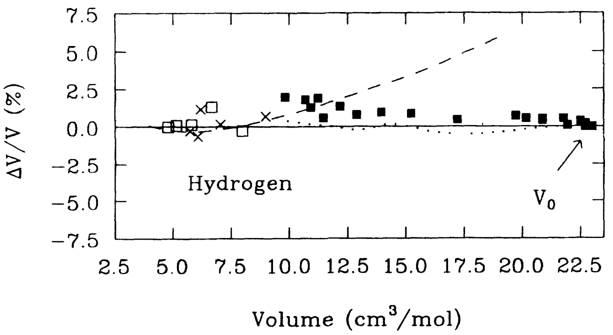

FIG. 7. Deviation of relative volume of EOS for H_2 at a given pressure. □, x-ray data (high pressure); ■, neutron data of Ishmaev *et al.* (Ref. 6) (low pressure); ×, Mateev *et al.* (Ref. 10); ——, Vinet *et al.*, fit to the present data; – – –, van Straaten and Silvera (Ref. 9); . . . ., Anderson and Swenson EOS (Ref. 4); ×, Mateev *et al.* (Ref. 10).

The deviations between the EOS calculated from the present data for H_2 and D_2 and those determined in previous investigations are illustrated in Figs. 7 and 8. In these figures the percent difference in volume at a given pressure is plotted as a function of volume. For H_2 we note the revised EOS of van Straaten and Silvera[9] is in much better agreement with the x-ray diffraction results than was the earlier version (see Ref. 14). The closeness of the two results actually extends well outside the range of both measurements (less than 1% difference at 300 GPa). This agreement is partly fortuitous since the error in the optical technique is estimated to be on the order of ~5% as a result of the large uncertainty in the determination of the index of refraction by this technique. It is not surprising then that their equation of state for deuterium differs considerably from the x-ray diffraction result (e.g., the volume is overestimated by 5% at 5 cm^3/mol). The neutron diffraction result of Glazkov *et al.*[35] is in good agreement with the present results over the range where the two sets of measurements overlap (6–8 cm^3/mol); however, at higher pressures the volumes determined by neutron diffraction are somewhat smaller than that predicted by the EOS extrapolated from the x-ray data.

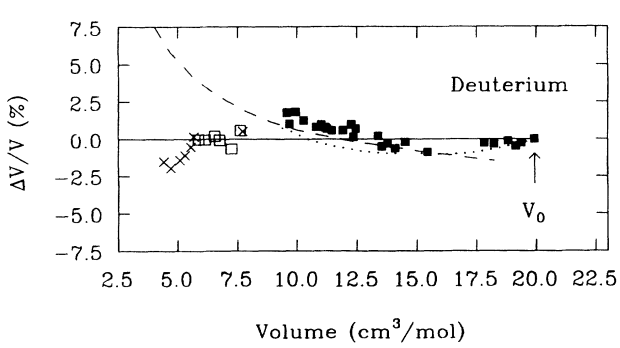

FIG. 8. Deviations of relative volume of the EOS for D_2 at a given pressure. □, x-ray data (high pressure); ■, neutron data of Ishmaev *et al.* (Ref. 7) (low pressure); ×, Glazkov *et al.* (Ref. 35); ——, Vinet *et al.*, fit to the present data; – – –, van Straaten and Silvera (Ref. 9); . . . ., Anderson and Swenson EOS (Ref. 4).

VII. LATTICE DYNAMICS AND EFFECTIVE POTENTIALS

The determination of an accurate pair potential for solid molecular hydrogen for the calculation of the equation of state and other thermodynamic properties has been the subject of a large number of studies. The isotropic potential is a pair potential obtained from low-pressure data for the gas phase; all angular terms averaged out. It is well known that a quasiharmonic treatment is insufficient to describe the highly anharmonic quantum character of low-Z solids such as helium and hydrogen at low densities.[1,2,53] Although the quasiharmonic treatment is insufficient to describe the dynamics of low-Z solids at low pressure (where they are quantum solids), it is well known that the harmonic expansion becomes accurate at higher pressures (e.g., Ref. 54). If the intramolecular dynamics are neglected, at the moderate range of compressions of interest here, hydrogen may be considered a nonquantum solid.[2] Hence we use a quasiharmonic approximation to estimate the thermal correction to the static equation of state. The Helmholtz free energy is given[41] as

$$F(V,T) = \Phi(V) + \tfrac{1}{2}\sum_i \hbar\omega_i(V) + k_B T \sum_i \ln\{1 - \exp[-\hbar\omega_i(V)/k_B T]\}, \quad (8)$$

where the static-lattice energy $\Phi(V)$ and harmonic normal mode frequencies ω_i are determined from the pair potentials and are summed over the Brillouin zone. To obtain the total vibrational pressure $P_{\text{vib}} = P_{\text{ZP}} + P_{\text{th}}$, we calculate the volume derivative of the vibrational free-energy calculated from the lattice dynamics, $P_{\text{vib}} = -(dF_{\text{vib}}/dV)$. The individual terms are written

$$P_{\text{ZP}} = -\tfrac{1}{2}\sum_i \gamma_i(V)\hbar\omega_i(V), \quad (9)$$

$$P_{\text{th}} = -k_B T \sum_i \gamma_i(V)\hbar\omega_i(V), \quad (10)$$

where γ_i is the mode-Gruneisen parameter of the ith vibrational mode, $-d\ln\omega_i/d\ln V$. The components of the pressure were calculated by differentiation of polynomial fits to the free-energy terms as a function of volume. We use several potentials constructed for H_2 (Fig. 9). Calculations were performed for the hcp solid. Since spherical potentials are used, the minimum energy configuration at a given volume will occur at the ideal c/a ratio (1.633); all calculations were therefore performed with this constraint. The results of lattice-dynamics calculations of the EOS using a variety of pair potentials for hydrogen and deuterium are shown in Figs. 10 and 11.

Isotopic pair potentials for H_2 have been obtained from fitting gas-phase data and from *ab initio* calculations. These potentials may be considered pure two-body interaction potentials; that is, they do not include possible many-body effects associated with molecules in condensed phase. A large number of such pair potentials have been proposed for hydrogen over the years (see Ref. 2 for a review); the potential of Ahlrichs *et al.*[55] is representative of this class. Both this potential and the *ab initio* result of Ree and Bender[56] overestimate the volumes at high pressure. Similar conclusions were reached by Ross *et al.*[20] in comparing the results of lattice-dynamics calculations with the previous, less accurate equation-of-state data for the solid.

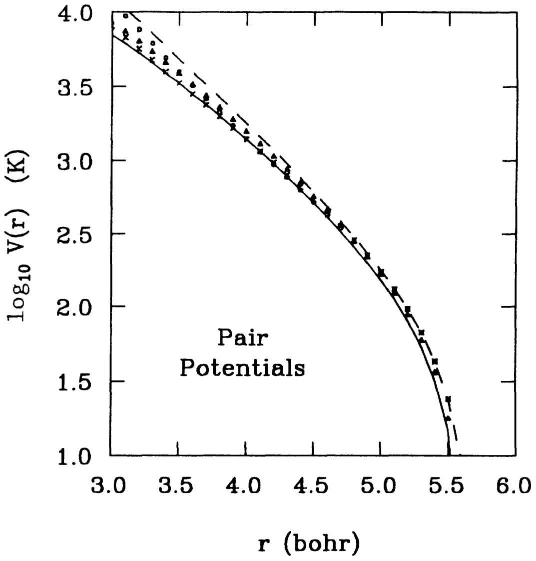

FIG. 9. Comparison of effective pair potentials for hydrogen. ——, modified potential (this work); – – –, exp-6 with α=11.1 (this work); . . . ., Silvera-Goldman (Ref. 47); × × × ×, exp-6 of Ross *et al.* (Ref. 20) (α=11.1); + + + +, Young-Ross (Ref. 20).

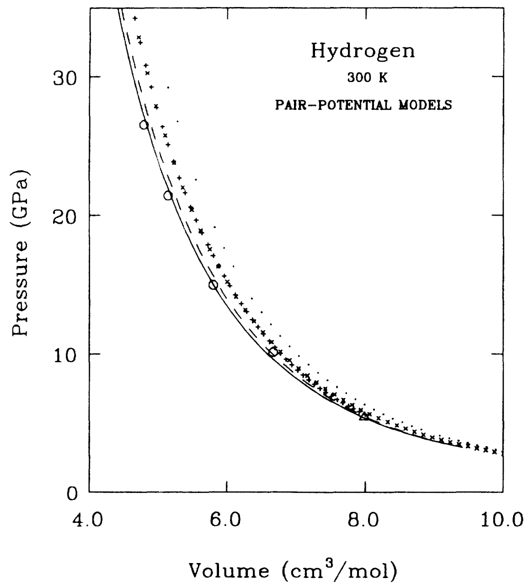

FIG. 10. Comparison of 300 K equations of state for hydrogen calculated from effective pair potentials. ——, modified potential (this work); – – –, exp-6 with α=11.1 (this work); . . . ., Silvera-Goldman (Ref. 47); × × × ×, exp-6 of Ross *et al.* (Ref. 20) (α=11.1); + + + +, Young-Ross (Ref. 20).

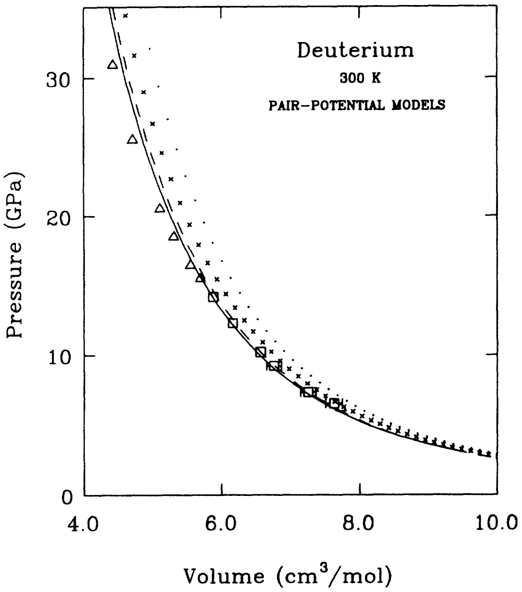

FIG. 11. Comparison of 300 K equations of state for deuterium calculated from effective pair potentials. ——, modified potential (this work); – – –, exp-6 with α=11.1 (this work); . . . ., Silvera-Goldman (Ref. 47); × × × ×, exp-6 of Ross *et al.* (Ref. 20) (α=11.1).

Early potentials for hydrogen were of the Lennard-Jones type.[2] Such potentials, however, were found to be far too inflexible in fitting both low- and high-pressure data.[2] A particularly useful form has been the modified Buckingham, or exp-6, potential,

$$V_{\text{exp-6}}(r) = \frac{\varepsilon}{\alpha - 6}\{6\exp[\alpha(1 - r/r^*)] - \alpha(r^*/r)^6\}, \tag{11}$$

This potential has been shown to be more flexible in fitting condensed phase data. The calculation with the isotropic pair potential for hydrogen shows large deviations with the experimental data for the solid. Such a discrepancy was first shown in earlier calculations of the EOS measured to 2 GPa.[2] The potential developed by Silvera and Goldman[47] was shown to fit the experimental data to 2 GPa. This potential is written

$$\begin{aligned} V_{\text{SG}}(r) &= \exp(\alpha - \beta r - \gamma r^2) \\ &\quad - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}}\right) f(r) + \frac{C_9}{r^9} f(r), \end{aligned} \tag{12}$$

where $f(r)$ is a damping function,

$$f(r) = \begin{cases} \exp[-(1.28r_m/r - 1)^2], & r \le r_m, \\ 1, & r > r_m. \end{cases} \tag{13}$$

The parameters have the following values (atomic units): α = 1.713, β = 1.5671, γ = 0.00993, C_6 = 12.14, C_8 = 215.2, C_9 = 143.1, C_{10} = 4813.9, and r_m = 6.444 bohr. They used self-consisent phonon methods for the low-density solid where anharmonic effects are particularly large.[2]

Ross *et al.*[20] calculated the equation of state of hydrogen and deuterium with lattice-dynamics models with a variety of pair potentials. They compared the results with the equation-of-state data available at that time, including both indirect static results[8,9] and shock-wave data.[11] They showed that the equation of state of hydrogen predicted by previously proposed pair potentials for solid hydrogen causes a significant overestimation of the pressure at high compression. This discrepancy indicates that attractive many-body forces become significant in hydrogen at high densities. To account for this effect, they modified effective potentials that fit low-density data by softening the potential at short range. This included a modified exp-6-type potential[20] parametrized to fit shock-wave data for hydrogen to 10 GPa and deuterium to 76 GPa;[11] for this potential ε/k_B = 36.4 K, r^* = 3.42 Å, and α = 11.1. Ross *et al.* also modified the Silvera-Goldman[47] potential for static pressure calculations (Young-Ross potential V_{YR}). The potential at short range (below 2.55 Å) has a softer repulsive exponential term; i.e.,

$$\begin{aligned} V_{\text{YR}}(r) &= V_{\text{SG}}(r), \quad r \ge r_c \\ &= A\exp[-B(r - r_c) - C(r - r_c)^2 - D(r - r_c)^3 \\ &\quad - E(r - r_c)^3(r - r_1)], \quad r < r_c, \end{aligned} \tag{14}$$

where $A = 3.98823 \times 10^{-14}$ erg, B = 4.769 40 Å^{-1}, C = 2.254 57 Å^{-2}, D = 0.955 189 Å^{-3}, E = 0.248 158 Å^{-4}, r_1 = 1.2 Å, and r_c = 2.55 Å. The results obtained with these potentials were in good agreement with the earlier EOS of van Straaten *et al.*, which is significantly stiffer than their revised equation[9] and the synchrotron x-ray diffraction results (see also Ref. 14). The comparison with the present data for the two isotopes is shown in Figs. 10 and 11.

Because of the inadequacy of these effective potentials to fit the high-pressure data for both hydrogen and deuterium, we have obtained a new effective potential for hydrogen. In the spirit of previous work we propose a new modification of the potential of Silvera and Goldman at short range. We simply add to the SG potential an *ad hoc* short-range term V_{SR} of the form

$$V_{\text{SR}}(r) = \begin{cases} a_1(r - r_c)^3 + a_2(r - r_c)^6, & r \le r_c \\ 0, & r > r_c. \end{cases} \tag{15}$$

This correction term is similar to that proposed by Kim *et al.*[57] in their study of the high-pressure EOS of xenon and krypton. We find that such a correction with $a_1 = -4.287 \times 10^{-2}$ hartree/bohr^3 and $a_2 = 6.718 \times 10^{-4}$ hartree/bohr^6, with r_c = 5.291 bohr, accurately represents the room-temperature x-ray diffraction data for both isotopes. The results are shown in Figs. 10 and 11.

VIII. DISCUSSION

We have obtained an EOS for H_2 and D_2 that fits the accurate compression data for the two solids over a wide compression range ($V/V_0 \approx 0.2$). We find that two-parameter EOS functional forms based on exponential repulsive interactions may be superior to those based on $1/r^n$ interactions (e.g., Lennard-Jones form). In fact, the two-parameter Vinet *et al.* EOS is capable of representing both the low- and high-compression data as successfully as the low-compression data alone with the same parametrization. The values for the bulk modulus that are obtained from such an analysis are in excellent agreement with the best experimental estimates based on cryogenic sound velocity measurements performed near zero pressure. The extent to which the higher-order parameters obtained from such a fit (K_0' and K_0'') are close to physically meaningful elasticity parameters measured at zero pressure remains to be tested by further zero-pressure measurements. In spite of uncertainties associated with effects of variable ortho-para ratios and the zero-pressure reference volume, our analysis has permitted us to assess the accuracy of previous P-V measurements carried out to $V/V_0 \approx 0.4$ (2.5 GPa).

The overestimation of the pressure (or volume) in the pair-potential calculations in comparison with the new high-pressure data is a general feature of the results presented above. These discrepancies reflect inadequacies of the form of the repulsive part of the potential. Similar results have been noted for helium,[26] neon,[34] and xenon.[57] It has been proposed that at high densities many-body exchange terms soften the repulsive forces in the solid, causing a decrease in the pressure. An alternative approach is based on the concept that the charge density of the component atoms contract in the crystal, thereby softening nearest-neighbor repulsive interactions (see Ref. 34). We emphasize that the effective potentials may not be useful for describing properties other than the equation of state; use of the modified SG or exp-6 potentials to calculate the pressure dependence E_{2g} hcp phonon, for example, significantly underestimates the frequency at high compression (e.g., by as much as 45% at 6 cm^3/mol); similar results have been obtained by Wijngaarden *et al.*[43] with the SG potential. An additional complication for the use of effective potentials arises from the observed softening of the Raman-active vibron,[17,18,58] which indicates that the intermolecular interactions become more complex at high densities. The inadequacy of a pairwise description of the forces in polarizable systems in general at high compression, of which dense solid hydrogen is an excellent example, has been analyzed by Maggs and Ashcroft.[59]

The potentials obtained by Ross *et al.*[20] fit shock-wave data[11] for hydrogen up to 10 GPa and for deuterium to 76 GPa. At the highest pressures reached on deuterium, however, the errors in the pressure are considerable; hence, the effective potential is actually rather poorly constrained by these data. It is useful to note that even the Young-Ross potential appears to overestimate the pressure slightly for the highest compression points on the Hugoniot. It is likely that the effective potentials proposed will fit the shock-wave points within the uncertainty of the measurements, although this must be tested by a direct calculation. At highest pressures along the Hugoniot, where the high temperatures reach a maximum of 7100 K, the effect of the weakened intramolecular bond may be appreciable; this bond-weakening effect should be included in the EOS calculation.

The large differences in the EOS of hydrogen and deuterium at low pressures (<1 GPa) arise from quantum effects.[2] It is useful to investigate whether or not there are differences in the EOS at higher pressures. The observed differences in the pressure of the phase transition at 150–170 GPa (Refs. 17 and 18) and the pressure dependence of the vibron frequency[59] for hydrogen and deuterium indicate that there are significant isotope effects on the energetics at very high compressions. Within the accuracy of the present x-ray data we cannot currently resolve any differences in the P-V curve of the two isotopes over the pressure range of our measurements. On the other hand, comparison of the x-ray diffraction results for hydrogen with the neutron-diffraction data for deuterium of Glazkov *et al.*[35] suggests a higher compressibility for the heavier isotope. This difference is systematic and outside the error limits of the two studies. Differences in ortho-para concentration could also contribute, as discussed above in regard to the pressure dependence of axial ratios. Moreover, since the results were obtained using two different techniques, further measurements are required to examine this question.

Although a large number of electronic structure calculations for the high-density monatomic phase have been performed over the years,[15,16] it is only fairly recently that comparable calculations have been done for the

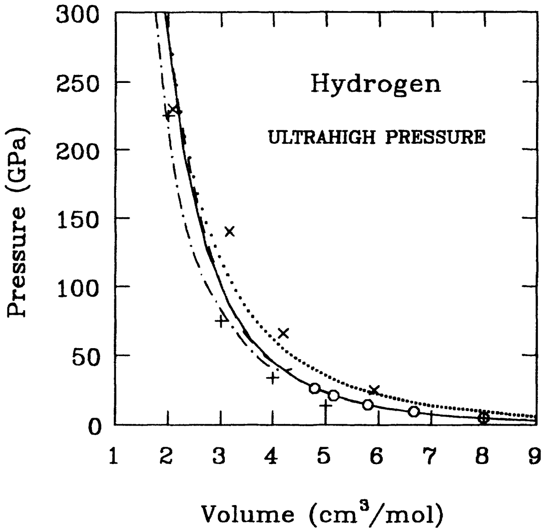

FIG. 12. Comparison between the theoretical and experimentally determined equations of state for hydrogen at ultrahigh pressures. ——, extrapolation of present EOS; – – –, extrapolation of van Straaten and Silvera (Ref. 9) EOS; – . –, Min *et al.* (Ref. 22) (cubic $Pa3$ structure); ×, Ceperley and Alder (Ref. 23) (cubic $Pa3$ structure >100 GPa; rotationally disordered fcc <100 GPa); . . . ., Raynor (Ref. 24) (ordered hcp structure); +, Barbee *et al.* (Ref. 25) (ordered hcp structure).

molecular phase. Min *et al.*[22] and Barbee *et al.*[25] have performed density functional calculations for the molecular solid in the orientationally ordered structures, and Ceperley and Alder[23] have examined ordered and disordered molecular phases by Monte Carlo techniques (at $T = 0$ K). Raynor[24] investigated the phase stability, vibrational properties, and equation of state with Hartree-Fock self-consistent field methods. The equations of state calculated from these models are compared with the experimentally constrained $T = 0$ K equations of state in Fig. 12. In the extrapolation to higher pressure, we neglect the effect of possible band overlap, as well as vibron softening, both of which could cause a softening of the compression (negative pressure term) at high pressure. There are considerable differences among the calculations and between theory and experiment at low pressures, but the discrepancies tend to decrease in the higher-pressure range (> 100 GPa). The Min *et al.*[22] and Barbee *et al.*[25] calculations tend to give smaller volumes than does the extrapolated Vinet *et al.* EOS at high pressure. Other theoretical calculations are found to give larger volumes at high pressure, as are the EOS calculated from the previously proposed pair-potential models.[20]

Recently, we showed that there is a gradual increase in optical absorption in the molecular solid above 200 GPa.[19] We proposed that this represents decreasing energy of the direct band gap, with the indirect gap closing at lower pressures. In view of the possibility of structural and order-disorder transitions outside the P-T range of the present measurements, and the possible softening of the equation of state associated with vibron shifts and band overlap, we emphasize that the present EOS measurements are strictly valid only in the moderate-pressure range (to $\sim$30 GPa). In addition, although we have calculated the effect of temperature reduction to $T = 0$ K, we cannot rule out the possibility of such transitions at lower temperatures within the pressure range of our measurements. Low-temperature Raman studies suggest that a transition of this type occurs in D_2 at $\sim$28 GPa (10 K).[60] Direct structural investigation by x-ray diffraction is required for definitive study of these transitions. Such variable P-T measurements are now possible with diamond-anvil cell and synchrotron x-ray diffraction techniques.

ACKNOWLEDGMENTS

We thank D. E. Cox for assistance in the experiments reported here, and Y. Wu for computational help. We are also grateful to M. Hanfland and N. W. Ashcroft for useful discussions. This work was supported in part by the National Science Foundation under Grant Nos. EAR-8608941 and DMR-8912226, by the National Aeronautics and Space Administration under Grant No. NAGW1722, by the U.S. Department of Energy, Division of Materials Research (Contract No. DE-AC-2-76CH00016), and by the Carnegie Institution of Washington.

---

[*] Present address: Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, United Kingdom.

[†] Present Address: Institute for Fundamental Physics, University of Science and Technology of China, Hefei, Anhui, The People's Republic of China.

[1] J. van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).

[2] I. F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[3] J. W. Stewart, J. Phys. Chem. Solids **1**, 146 (1956).

[4] M. S. Anderson and C. A. Swenson, Phys. Rev. B **10**, 5184 (1973).

[5] R. L. Mills and A. F. Schuch, Phys. Rev. Lett. **15**, 722 (1965); R. L. Mills, A. F. Schuch, and D. A. Depatie, *ibid.* **17**, 1131 (1966).

[6] S. N. Ishmaev, I. P. Sadikov, A. A. Chernyshov, B. A. Vindryaevskii, V. A. Sukhoparov, A. S. Telepnev, and G. V. Kobelev, Zh. Eksp. Teor. Fiz. **84**, 394 (1983) [Sov. Phys. JETP **57**, 228 (1983)].

[7] S. N. Ishmaev, I. P. Sadikov, A. A. Chernyshov, B. A. Vindryaevskii, V. A. Sukhoparov, A. S. Telepnev, G. V. Kobelev, and R. A. Sadykov, Zh. Eksp. Teor. Fiz. **89**, 1249 (1985) [Sov. Phys. JETP **62**, 721 (1985).]

[8] H. Shimizu, E. M. Brody, H. K. Mao, and P. M. Bell, Phys. Rev. Lett. **47**, 128 (1981); H. Shimizu, in *High Pressure in Science and Technology,* edited by C. Homan, R. K. MacCrone, and E. Whalley (North-Holland, New York, 1984), Vol. II, p. 57.

[9] J. van Straaten, R. J. Wijngaarden, and I. F. Silvera, Phys. Rev. Lett. **48**, 97 (1982); J. Van Straaten and I. F. Silvera, Phys. Rev. B **37**, 1989 (1988).

[10] V. V. Matveev, I.V. Medvedeva, V.V. Prut, P.A. Suslov, and S. A. Shibaev, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 219 (1984) [JETP Lett. **39**, 261 (1984)].

[11] W. J. Nellis, A. C. Mitchell, M. van Thiel, R. J. Trainor, and N. Brown, J. Chem. Phys. **79**, 1480 (1983); W. J. Nellis, M. Ross, A. C. Mitchell, M. van Thiel, D. A. Young, F. R. Ree, and R. J. Trainor, Phys. Rev. A **27**, 608 (1983), and references therein.

[12] R. M. Hazen, H. K. Mao, L. W. Finger, and R. J. Hemley, Phys. Rev. B **36**, 3944 (1987).

[13] H. K. Mao, L. W. Finger, R. M. Hazen, A. P. Jephcoat, R. J. Hemley, C. S. Zha, and D. E. Cox (unpublished).

[14] H. K. Mao, A. P. Jephcoat, R. J. Hemley, L. W. Finger, C. S. Zha, R. M. Hazen, and D. E. Cox, Science **239**, 1131 (1988).

[15] Early work on dense solid hydrogen has been reviewed by M. Ross and C. Shishkevish, *Molecular and Metallic Hydrogen* (Rand Corporation, Santa Monica, 1977).

[16] I. F. Silvera, in *Simple Molecular Systems at Very High Densities*, edited by P. Loubeyre, A. Polian, and N. Boccara (Plenum, New York, 1989), pp. 33–46.

[17] R. J. Hemley and H. K. Mao, Phys. Rev. Lett. **61**, 857 (1988).

[18] R. J. Hemley and H. K. Mao, Phys. Rev. Lett. **63**, 1393 (1989); R. J. Hemley, H. K. Mao, and M. Hanfland (unpublished).

[19] H. K. Mao and R. J. Hemley, Science **244**, 1462 (1989).

[20] M. Ross, F. H. Ree, and D. A. Young, J. Chem. Phys. **79**,

1487 (1983).

[21] S. Chakravarty, J. H. Rose, D. Wood, and N. W. Ashcroft, Phys. Rev. B **24**, 1624 (1981).

[22] B. I. Min, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **33**, 6383 (1986).

[23] D. M. Ceperley and B. J. Alder, Phys. Rev. B **36**, 2092 (1987).

[24] S. Raynor, J. Chem. Phys. **87**, 2795 (1987).

[25] T. W. Barbee, A. Garcia, M. L. Cohen, and J. L. Martins, Phys. Rev. Lett. **62**, 1150 (1989).

[26] H. K. Mao, R. J. Hemley, Y. Wu, A. P. Jephcoat, L. W. Finger, C. S. Zha, and W. A. Bassett, Phys. Rev. Lett. **60**, 2649 (1988).

[27] H. K. Mao, in *Simple Molecular Systems at Very High Densities*, edited by P. Loubeyre, A. Polian, and N. Boccara (Plenum, New York, 1989), pp. 221–236.

[28] A. P. Jephcoat, H. K. Mao, C. S. Zha, P. M. Bell, L. W. Finger, and D. E. Cox, National Synchrotron Light Source Annual Report, 1986 (unpublished).

[29] H. K. Mao and P. M. Bell, Carnegie Inst. Washington Yearb. **79**, 409 (1980).

[30] A. P. Jephcoat, H. K. Mao, and P. M. Bell, in *Hydrothermal Experimental Techniques*, edited by G. C. Ulmer and H. L. Barnes (Wiley-Interscience, New York, 1987), Chap. 19.

[31] H. K. Mao and P. M. Bell, Science **203**, 1004 (1979); V. Diatschenko, C. W. Chu, D. H. Liebenberg, D. A. Young, M. Ross, and R. L. Mills, Phys. Rev. B **32**, 381 (1985).

[32] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[33] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

[34] R. J. Hemley, C. S. Zha, A. P. Jephcoat, H. K. Mao, L. W. Finger, and D. E. Cox, Phys. Rev. B **39**, 11 820 (1989).

[35] V. P. Glazkov, S. P. Besedin, I. N. Goncharenko, A. V. Irodova, I. N. Makarenko, V. A. Somenkov, S. M. Stishov, and S. Sh. Shil'steyn, Pis'ma. Zh. Eksp. Teor. Fiz. **47**, 661 (1988).

[36] A. F. Schuch, R. L. Mills, and D. A. Depatie, Phys. Rev. **165**, 1032 (1968).

[37] A. P. Jephcoat, H. K. Mao, L. W. Finger, D. E. Cox, R. J. Hemley, and C. S. Zha, Phys. Rev. Lett. **59**, 2670 (1987).

[38] F. Birch, Phys. Rev. **71**, 809 (1947); J. Geophys. Res. **57**, 227 (1952); **83**, 1257 (1978).

[39] R. Grover, I. C. Getting, and G. C. Kennedy, Phys. Rev. B **7**, 567 (1973).

[40] P. Vinet, J. Ferrante, J. R. Smith, and J. H. Rose, J. Phys. C **19**, L467 (1986); P. Vinet, J. Ferrante, J. H. Rose, and J. R. Smith, J. Geophys. Res. **92**, 9319 (1987).

[41] M. Born and Y. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1956); V. N. Zharkov and V. A. Kalinin, *Equations of State of Solids at High Pressures and Temperatures* (Consultants Bureau, New York, 1971).

[42] J. K. Krause and M. S. Swenson, Phys. Rev. B **21**, 2533 (1980).

[43] R. J. Wijngaarden, V. V. Goldman, and I. F. Silvera, Phys. Rev. B **27**, 5084 (1983).

[44] A. Driessen, J. de Waal, and I. F. Silvera, J. Low Temp. Phys. **34**, 225 (1979); A. Driessen and I. F. Silvera, *ibid.* **54**, 361 (1984).

[45] H. Hemmes, A. Driessen, and R. Griessen, J. Phys. C **19**, 3571 (1986).

[46] R. J. Hemley, H. K. Mao, and J. F. Shu (unpublished).

[47] I. F. Silvera and V. V. Goldman, J. Chem. Phys. **69**, 4209 (1978).

[48] F. Birch, J. Phys. Chem. Solids **38**, 175 (1977).

[49] R. Jeanloz, Phys. Rev. B **38**, 805 (1988).

[50] B. G. Udovidchenko and V. G. Manzhelli, J. Low Temp. Phys. **3**, 429 (1970).

[51] R. Wanner and H. Meyer, J. Low. Temp. Phys. **11**, 715 (1973).

[52] P. J. Thomas, S. C. Rand, and B. P. Stoicheff, Can. J. Phys. **56**, 1494 (1978).

[53] H. R. Glyde, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, New York, 1974), pp. 382–504.

[54] E. L. Pollock, T. A. Bruce, G. V. Chester, and J. A. Krumhansl, Phys. Rev. B **5**, 4180 (1972).

[55] R. Ahlrichs, R. Penco, and G. Scoles, Chem. Phys. **19**, 119 (1977).

[56] F. H. Ree and C. F. Bender, J. Chem. Phys. **71**, 5362 (1979).

[57] J. H. Kim, T. Ree, and F. H. Ree, J. Chem. Phys. **91**, 3133 (1989).

[58] H. K. Mao, P. M. Bell, and R. J. Hemley, Phys. Rev. Lett. **55**, 99 (1985).

[59] A. C. Maggs and N. W. Ashcroft, Phys. Rev. B **36**, 7586 (1987).

[60] I. F. Silvera and R. J. Wijngaarden, Phys. Rev. Lett. **47**, 39 (1980).