Experimental compressions for normal hydrogen and normal deuterium to 25 kbar at 4.2 K

M. S. Anderson and C. A. Swenson

Ames Laboratory, United States Atomic Energy Commission
and Department of Physics, Iowa State University, Ames, Iowa 50010

(Received 5 August 1974)

The piston-displacement technique has been used to determine the pressure-volume relations for normal hydrogen (n-H_2) and normal deuterium (n-D_2) at pressures to 25 kbar at 4.2 K. The accuracy of the relative compressions V/V_0 ranges from $\pm 10^{-3}$ at low pressures to $\pm 3 \times 10^{-3}$ at 25 kbar. The data, especially for n-H_2, agree well with earlier 20-kbar results, and the extrapolated $P = 0$ bulk moduli, 1.70 ± 0.06 kbar for n-H_2 and 3.15 ± 0.06 kbar for n-D_2, are consistent with recent ultrasonic data. The shapes of the pressure-volume relations resemble more closely those for the helium isotopes than those for the heavier-rare-gas solids, and suggest that the two-body repulsive interaction for hydrogen molecules (and helium atoms) varies more slowly with intermolecular spacing than that for the heavier-rare-gas atoms. These experiments also give maximum values for the pressure-dependent shear yield stress of solid hydrogen.

I. INTRODUCTION

Stewart[1] in 1956 published 4.2-K pressure-volume relations to 20 000 atm for solid hydrogen and deuterium. These results have been used extensively for testing model potentials and cohesive-energy calculations for hydrogen and deuterium, and, until recently, the same pair potential could not be used to explain both the nonideal-gas properties and the compressions of the solid phases. England *et al.*[2] now have shown by explicit calculation that these difficulties are related to the anisotropic nature of the interaction between orthohydrogen molecules. While a spherically averaged potential may be used in the solid phase, the anisotropies must be included when considering gasphase collisions involving ortho molecules, since the rotational frequency is comparable with the collision times. Much of the current interest in the equations of state (EOS) of the molecular phases of hydrogen and deuterium is related to calculations of the metallic-phase-transition pressure in these solids. Marvin Ross[3] has analyzed molecular-hydrogen shock-compression experiments in terms of various forms of intermolecular potentials, and concludes that 2.2 Mbar is a reasonable lower limit for this transition. These papers by England *et al.*[2] and Ross,[3] which are quite different in emphasis, can serve as an excellent introduction to previous work on the equations of state of the hydrogen isotopes. Roder *et al.*[4] have given a survey of the literature (in some instances up to mid-1973) describing experimental work on the hydrogen isotopes at temperatures below the critical point.

The present experiments were initiated to provide independent confirmation of Stewart's[1] measurements and to extend both their range and accuracy. Our piston-displacement technique, which was used for high pressure EOS studies of the rare-gas solids (RGS),[5,6] is very similar to Stewart's[1] in that the sample serves as its own pressure transmitter. Solid hydrogen and deuterium both have very low shear yield strengths,[7,8] so the approximations which are involved in the use of this technique appear to be minimal. Stewart[1] used a Bridgman unsupported area seal with a potassium metal gasket to prevent extrusion of these highly plastic solids through the gap between the piston and the cylinder walls. The present experiments were somewhat easier to carry out than were his, since we were able to make effective seals using only small, highly flexible, triangular extrusion rings.[6] Our results, as well as those of Stewart, are given only for 4.2 K since the present sample holders cannot be used for temperatures above the triple-point temperature for any solid.

Figure 1 compares on a relatively insensitive plot the present results (the solid lines) and those of Stewart[1] (the solid points). The agreement is excellent for hydrogen with only a slight difference in shape. The differences for deuterium are roughly proportional to the compression, and could arise through the uncertainty in Stewart's absolute-sample-length determination. The disagreement is not serious, and lies within Stewart's estimated experimental accuracy.

The present data, and presumably those of Stewart,[1] were obtained for samples with room-temperature equilibrium (normal) ortho-para concentrations for both hydrogen (n-H_2: $\frac{3}{4}$ ortho, $\frac{1}{4}$ para) and deuterium (n-D_2: $\frac{2}{3}$ ortho, $\frac{1}{3}$ para), since the conversion rates to the low-temperature equilibrium concentrations (pure parahydrogen, p-H_2, and pure orthodeuterium, o-D_2) are relatively slow,
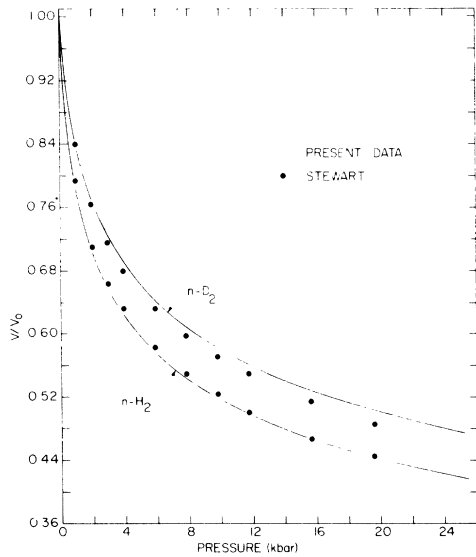
FIG. 1. Comparison of the relative-volume changes
for solid hydrogen and solid deuterium which were found
in the present experiments and the smoothed values
(solid dots) which are given by Stewart (Ref. 1).

with a conversion from n-H_2 to 0.50 p-H_2 in rough-
ly 50 h.[9] The 4.2-K equilibrium molar volume of
p-H_2 is greater than that of n-H_2 by approximately
1%,[9] so the compressions of these two solids (and
their $P=0$ bulk moduli) could be observably differ-
ent. Wanner and Meyer,[10] however, have shown
from their single-crystal ultrasonic measurements
that the bulk modulus for hydrogen increases at
constant volume as the p-H_2 concentration in-
creases. Since the $P=0$ volume also increases
with increasing p-H_2 concentration, with a corre-
sponding purely mechanical decrease in the bulk
modulus (see the discussion of the Murnaghan rela-
tion in Sec. II), these two effects tend to compen-
sate, and indeed our single isotherm for a p-H_2
sample is identical with that for the n-H_2 samples.
The difference between the molar volumes of o-D_2
and n-D_2 is only 0.3%,[11] with a correspondingly
smaller effect on the compressions and bulk modu-
li. The sensitivity of the present experiments is
not sufficient to make the actual ortho-para con-
centrations of our samples an important factor.

II. EXPERIMENTAL DETAILS AND DATA ANALYSIS

High-pressure data were obtained at 4.2 K for
n-H_2 and n-D_2 for sample holders with diameters
of 0.500, 0.354, and 0.250 in., and corresponding
maximum available pressures of 7, 14, and be-
cause of sample-holder-strength considerations,
25 kbar. Only one run was made with p-H_2 using
the 0.354-in.-diam sample holder. The experi-
mental apparatus (including the sample holders),
the procedures for taking data, and the data analy-

sis all are identical with those used for the RGS,[5,6]
so they will not be described here.

The final experimental results for a given sam-
ple are expressed in terms of relative-sample-
length changes as a function of pressure, $L(P)/
L(P_0)$, where $L(P_0)$ is an absolute sample length
which is determined at a reference pressure P_0;
P_0 is the same for all samples of a given isotope,
and was 1.10 kbar for H_2 and 4.00 kbar for D_2.
Since the area of the cylinder is assumed to be
independent of the pressure (a reasonable assump-
tion for sintered tungsten-carbide sample holders),[6]
these relative-length changes are equal to the rela-
tive-volume changes $V(P)/V(P_0)$. Friction forces
in the sample holder and in the press limit the
minimum pressure at which data can be taken, so
in practice it is not possible to choose $P_0=0$.
Hence, least-squares fits of empirical relations
to the data are used to extrapolate the results to
$P=0$, and to obtain the ratio $V(P_0)/V(P=0)$, which
is required to be able to express the results as
$V(P)/V_0$, with $V_0 = V(P=0)$.

The present results could not be represented
satisfactorily by the form of the power series
which was used successfully with the RGS data[6]
and which was suggested by the volume dependence
of the Lennard-Jones 6-12 potential. A fit was ob-
tained within the precision of the data, however,
with only the first two terms ($N=2$) of a modified
power-series form of the Birch relation,[12]

$$P(V) = P_0 + y^5 \sum_{n=1}^{N} A_n(y^2 - 1)^n ,$$ (1)

with $y = [V(P_0)/V(P)]^{1/3}$. This expression was fit to
the combined data for all three sample holders for
each solid using a procedure which minimized in a
least-squares sense the relative-sample-length
or relative-volume deviations.[5,6] The coefficients
then were used for an extrapolation to $P=0$ to ob-
tain $V(P_0)/V_0$. The data now were expressed as
$V(P)/V_0$, and Eq. (1) was refit to them with $P_0=0$
and $y = [V_0/V(P)]^{1/3}$ to obtain a smoothed 4.2-K
isotherm, $P(V/V_0)$, and the volume or pressure
dependence of the bulk modulus, $B_T(V/V_0)$
$= - V(\partial P/\partial V)_T$.

Table I contains the coefficients for Eq. (1) (with
$P_0=0$) which represent the complete data for each
solid, together with the root-mean-square (rms)
deviation of the fit (in terms of V/V_0) and the ex-
trapolated $P=0$ value of the bulk modulus, B_0.
The deviations of the input data for each sample
for each solid from these representations are pre-
sented in Fig. 2. Table II gives the resulting
$P(V/V_0)$ relations for each of the solids, with the
parentheses indicating the region where the results
are calculated from the extrapolation of the experi-
mental data. The calculated bulk moduli also are
given. The deviations of the single p-H_2 run from

TABLE I. The coefficients for Eq. (1) which with P_0 = 0 can be used to represent the experimental results for n-H$_2$ and n-D$_2$. The rms deviation is in terms of V/V_0 and is dimensionless. For these representations, $(V/V_0)_{P=0} = 1.0000$ and $B_0(V_0)$ is as given. The uncertainties in the parentheses represent the limits of these two quantities which are obtained by other extrapolations.

	n-H$_2$	n-D$_2$
A_1 (kbar)	2.54974	4.72497
A_2 (kbar)	6.18536	10.21948
rms dev. (in V/V_0)	6×10^{-4}	3×10^{-4}
$(V/V_0)_{P=0}$	1.000($\pm$0.002)	1.000($\pm$0.002)
B_0 (kbar)	1.70($\mp$0.06)	3.15($\mp$0.06)

TABLE II. Smoothed values of the pressure-volume relation and bulk modulus for n-H$_2$ and n-D$_2$ as calculated from Eq. (1) and the coefficients given in Table I. The values in parentheses are extrapolated.

|	n-H$_2$		n-D$_2$	
V/V_0	$P(V/V_0)$ (kbar)	$B_T(V/V_0)$ (kbar)	$P(V/V_0)$ (kbar)	$B_T(V/V_0)$ (kbar)
1.0000	(0.0000)	(1.700)	(0.0000)	(3.150)
0.9500	(0.1048)	(2.414)	(0.1925)	(4.406)
0.9000	(0.2602)	(3.375)	0.4743	6.086
0.8500	0.4887	4.677	0.8844	8.355
0.8000	0.8240	6.461	1.4807	11.448
0.7500	1.3172	8.933	2.3513	15.719
0.7000	2.0479	12.408	3.6327	21.70
0.6800	2.4328	14.181	4.3050	24.75
0.6600	2.8861	16.233	5.0953	28.27
0.6400	3.4216	18.614	6.0266	32.34
0.6200	4.0557	21.39	7.1273	37.09
0.6000	4.8091	24.63	8.4326	42.64
0.5800	5.7074	28.44	9.9858	49.14
0.5700	6.2206	30.60	10.8720	52.81
0.5600	6.7826	32.94	11.8416	56.80
0.5500	7.3988	35.48	12.9037	61.14
0.5400	8.0750	38.26	14.0684	65.86
0.5300	8.8182	41.29	15.3471	71.02
0.5200	9.6359	44.60	16.7529	76.65
0.5100	10.5367	48.23	18.3004	82.81
0.5000	11.5306	52.20	20.0063	89.56
0.4900	12.6287	56.56	21.8894	96.96
0.4800	13.8436	61.35	23.9714	105.09
0.4745	...	...	25.2100	109.91
0.4700	15.1902	66.63		
0.4650	15.9179	69.47		
0.4600	16.6849	72.45		
0.4550	17.4938	75.59		
0.4500	18.3472	78.89		
0.4450	19.2479	82.36		
0.4400	20.1991	86.02		
0.4350	21.2040	89.87		
0.4300	22.2662	93.92		
0.4250	23.3896	98.20		
0.4200	24.5783	102.72		
0.4165	25.4517	106.03		
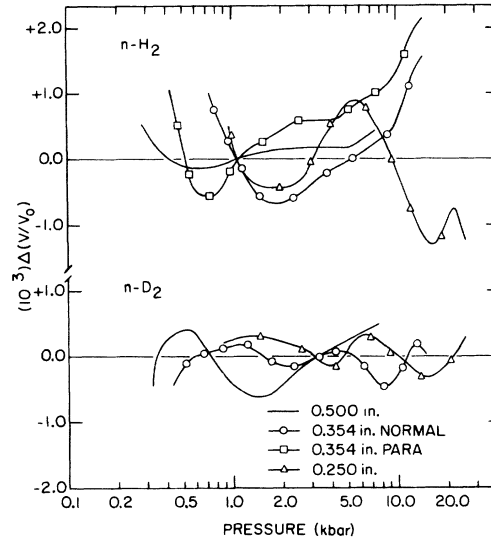
FIG. 2. Deviations of the experimental data for the various samples from the empirical relations for hydrogen and deuterium [Eq. (1) with coefficients from Table I]. The actual lengths in inches for each sample at P_0 (1.10 kbar for H$_2$, 4.00 kbar for D$_2$) are as follows, in order of decreasing sample diameter: n-H$_2$: 0.333, 0.298, 0.209; p-H$_2$: 0.304; n-D$_2$: 0.257, 0.325, 0.177.

the n-H$_2$ fit relation are shown in Fig. 2 to indicate that the data for the two solids are identical.

The results of the extrapolations to $P = 0$ depend slightly on the form which is assumed for the pressure-volume relation. The uncertainties in V/V_0 at $P = 0$ and in B_0 which are indicated in Table I arise from the use of different extrapolation procedures, including fits to the data of the relation $P(V/V_0) = \sum_{n=1}^{3} B_n (V_0/V)^n$. In each case, the rms deviation was close to that in Table I, and B_0 and V/V_0 at $P = 0$ were within the indicated limits, especially when the upper limit of the fit was truncated, for instance, to correspond to only $\frac{1}{2}$ the total compression, or at roughly 2.5 kbar (Fig. 1).[5]

An empirical observation that the bulk modulus is a linear function of the pressure for many solids (the so-called Murnaghan relation)[13] also can be used to extrapolate these data to $P = 0$, since if

$$B_T(P) = B_0 + \eta P , \qquad (2)$$

with

$$\eta = \left(\frac{\partial B_T}{\partial P}\right)_T = -\left(\frac{\partial \ln B_T}{\partial \ln V}\right)_T , \qquad (3)$$

then

$$P(V/V_0) = (B_0/\eta)[(V_0/V)^\eta - 1] . \qquad (4)$$
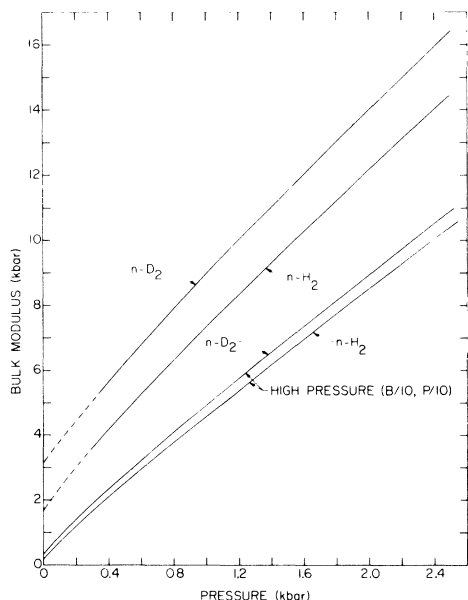
The bulk modulus is plotted as a function of pres-

FIG. 3. Pressure dependences of the bulk moduli for solid hydrogen and deuterium as determined in these experiments. The dashed lines below 0.4 kbar are extrapolations using Eq. (1) and the coefficients in Table I.

sure for each solid in Fig. 3, using scales which differ by a factor of 10 for the low-pressure (below 2.5-kbar) and high-pressure (to 25-kbar) data. The solid lines are for the experimentally accessible region (Fig. 2) and represent a differentiation of the data which is independent (to 1%) of the form of the fit relation which is used. The dashed lines below 0.4 kbar are calculated from Eq. (1) and the coefficients of Table I. The slope varies smoothly from $\eta \approx 7$ at $P = 0$ to $\eta \approx 4$ for pressures above 10 kbar, so the use of Eq. (4) does not appear to be justified for these solids. If this equation is assumed to apply at low pressures, however, with a linear interpolation between the end of the solid lines in Fig. 3 and the $P = 0$ values of the bulk moduli in Table I, the resulting values of V/V_0 at $P = 0$ are slightly larger (1.002) than those corresponding to the representations which we have used. This procedure serves to illustrate an extreme limit for the extrapolation procedure.

The internal consistency of the various sets of data for a given solid are shown in Fig. 2 to be of the order of 10^{-3} in V/V_0. This corresponds approximately to the sensitivity (5×10^{-4} in.) with which length changes could be determined for the roughly 0.40-in.-long (at $P = 0$) samples which were used with the two lower-pressure sample holders. The absolute sample lengths for these lower-pressure experiments were taken as an average of those determined from two methods,[6] with a possible error of $\pm 10^{-3}$ in. which is given by the

internal consistency. Greater differences were found between sample lengths as determined by the two methods for experiments with the smallest-diameter (highest pressure) sample holder. An effective sample length was defined for these experiments by arbitrarily choosing $L(P_0)$ so that the relative compressions agreed with the results for the other two sample holders. This effective length in each case differed from the average by less than 1%. If the absolute sample lengths are assumed to be accurate to ± 0.5%, and the sample-length changes are accurate to $\pm 10^{-3}$ in V/V_0, the uncertainties in the compressions given in Table II range from $\pm 10^{-3}$ in V/V_0 at low pressures to $\pm 3 \times 10^{-3}$ in V/V_0 at the highest pressures. The relative importance of the absolute-sample-length determination increases appreciably as the compressions become greater. Since, except for pure p-H_2, three sets of data are averaged in the determination of the final results, the relative values for $V(P)/V_0$ undoubtedly are more accurate than this below 14 kbar.

The H_2 gas was obtained from a cylinder of H_2 "zero gas" which was obtained from the Matheson Co. For our purposes, the purity of this gas (better than 99.99% in an absolute sense from a typical analysis) is more than adequate. The n-H_2 samples were condensed directly from this cylinder, and in no instance were they kept below 20 K for longer than 4 h. The nominal 3:1 ortho-para ratio of these samples should have changed very little in this time.[4] Pure p-H_2 was obtained by using liquid helium as a refrigerant to condense several liquid cm³ of this gas into a glass container which contained about an equal volume of activated chromium-impregnated alumina pellets.[4] The conversion of the n-H_2 to pure p-H_2 was assumed to be complete after $\frac{1}{2}$ h or so, after which the liquid p-H_2 was evaporated, warmed to room temperature, and then condensed immediately into the sample holder. The D_2 gas was supplied by the Bio-Rad Laboratories, and was specified as better than 99.65-at.% D. We found it necessary to pass this gas over charcoal at liquid-nitrogen temperatures to prevent blockage of the capillary to the sample holder.[6] The density difference between n-D_2 and the low-temperature equilibrium phase o-D_2 is sufficiently small (0.3%)[11] that conversion in the charcoal or in the solid samples should not affect the pressure-volume results.

III. DISCUSSION

The present results have been compared with those of Stewart[1] in Fig. 1, with satisfactory agreement. Hence, any theoretical calculations which were fit to his H_2 results will agree with the present also. The extrapolated $P = 0$ bulk moduli B_0 in Table I also can be compared with direct low-

TABLE III. Summary of recent determinations of the isothermal bulk modulus B_T and its pressure derivative η for the hydrogen isotopes at $P = 0$ and 4.2 K.

	B_T (kbar)	$\eta = \left(\dfrac{\partial B_T}{\partial P}\right)_T$	Method Refs.
n-H_2	1.70(± 0.06)	7.0(± 0.3)	Present results
n-H_2	1.74(± 0.1)[a]	5.4(± 1.3)	Ultrasonic, Ref. 10
p-H_2	1.82(± 0.06)	6.9(± 0.3)	Diel. const., Ref. 13
p-H_2	2.1	···	Neutron scatt., Ref. 15
n-H_2	2.6[b]	···	Ultrasonic, Ref. 16
p-H_2	2.4[b]	···	Ultrasonic, Ref. 18
n-D_2	3.15(± 0.06)	6.7(± 0.3)	Present results
n-D_2	3.37(± 0.2)	5.4(± 2)	Ultrasonic, Ref. 10
o-D_2	4.0	5.8(± 1)	Neutron scatt., Ref. 15
n-D_2	4.8[b]	···	Ultrasonic, Ref. 17

[a]Single-crystal data.

[b]Polycrystalline data, with the assumption that $B_S = B_T$ at 4.2 K (Ref. 10).

pressure bulk-modulus determinations for these solids. Wanner and Meyer[10] describe the results of constant-density ultrasonic measurements on single-crystal samples of both n-H_2 and n-D_2 for two densities, and they also give a detailed discussion of previous results and theoretical work. Other published results have involved dielectric-constant determinations as a function of pressure by Udovidchenko and Manzhelii[14] for p-H_2, inelastic neutron scattering by Nielsen[15] for both p-H_2 and o-D_2, and polycrystalline ultrasonic measurements by Bezuglyi and Minyafaev for n-H_2 (Ref. 16) and n-D_2,[17] and by Bezuglyi, Plakhotin, and Tarasenko[18] for p-H_2. These various results are summarized in Table III. Some of these experiments also determined the pressure dependence of the elastic constants, so the pressure dependence of the bulk modulus [η, Eq. (3)] also is given where appropriate.

The agreement between the present results and those of Wanner and Meyer[10] is within the combined experimental uncertainties in B_0 and η for both n-H_2 and n-D_2. The other bulk-modulus determinations appear to give higher values for B_0 which are independent of ortho-para concentrations, while no serious discrepancy exists for the η's. Wanner and Meyer[10] have measured the p-H_2 concentration dependence of the sound velocities for H_2 at fixed density near $P = 0$ at 4.2 K, and suggest an increase in B_0 of roughly 0.035 kbar from n-H_2 to pure p-H_2. The equivalent constant-pressure experiment at $P = 0$ would have resulted in a simultaneous volume increase of 0.8%[9] (as recalculated on the basis of $B_0 = 1.7$ kbar instead of 2.0 kbar), and, consequently, a decrease in B_0 of 0.09 kbar, using the definition of η in Eq. (3). Hence, the bulk modulus for pure p-H_2 at 4.2 K and $P = 0$

should be smaller than that for n-H_2 by from 0.05 to 0.06 kbar, or roughly 3%. None of the experiments listed in Table III is sufficiently precise so that this difference could be observed, and it is reasonable that our measurements on the compression of pure p-H_2 should give the same results as those for n-H_2 (see Fig. 2).

Durana and McTague[19] have performed high-pressure Raman scattering measurements on solid p-H_2 at 4.2 K and have observed a phase transition (presumably from hcp to fcc) which occurs between 0.4 and 0.89 kbar. Other indications of phase transitions near the melting line have been reported by Manzhelii et al.[20] and by Roder.[21] We did not find any indications of a phase transition in the present experiments, presumably because the volume difference between these two close-packed structures is expected to be very small.

The present experiments also give a measure of the pressure dependence of the shear yield stress for solid hydrogen, since this quantity should be a limiting factor in the magnitude of the pressure hysteresis which occurs between the pressure-increasing and pressure-decreasing portions of the raw data for an isotherm. Bignell[7] gives shear yield stresses for solid hydrogen which increase to 0.3 kbar at a pressure of 1.5 kbar, and which are almost an order of magnitude greater than those of Towle.[8] The half-widths of the present hysteresis curves must be greater than the shear yield stress since friction both in the sample holder and in other parts of the apparatus also will cause hysteresis. Our actual half-widths at 1.5 kbar varied from 0.1 kbar for the largest-diameter sample holder to 0.37 kbar for the smallest; and hence suggest that Bignel's[7] results are too large, and that Towle's[8] experiments are more likely to be correct. Bignel's experiments involved observations of hysteresis in resistivity data when solid hydrogen was used as a pressure transmitter, with the complication that considerable sample deformation occurred. Solid hydrogen also was used as a pressure transmitter to 10 kbar by Jennings and Swenson[22] in measurements of the effect of pressure on superconducting transition temperatures. These experiments gave reversible results (in contrast with those of Bignel[7]), and suggested pressure differences along the superconducting samples which increased to 0.4 kbar at the maximum pressure. These observations are consistent with those from the present experiments and with the results of Towle,[8] but not with those of Bignel.[7]

The two-body interactions for H_2 and D_2 molecules (neglecting ortho-para effects) are expected to be identical, with the cohesive energies of the solids, differing primarily due to the much larger zero-point energy of the lighter isotope, H_2. This
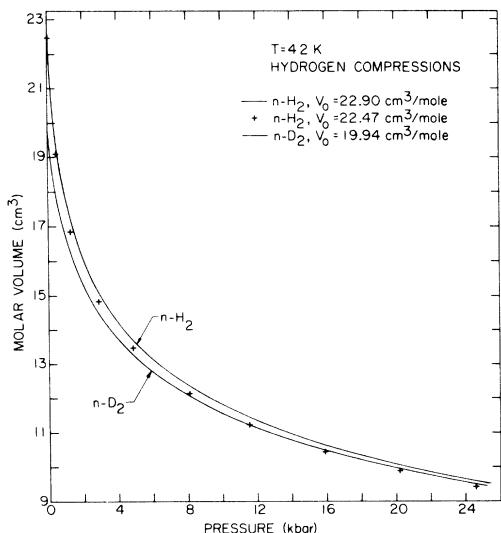
FIG. 4. Pressure-volume relations for the hydrogen isotopes as derived from Table I using various values of the $P = 0$ molar volume V_0. See the text for details.

effect can be used to account qualitatively for the roughly 14% difference in the $P = 0$ molar volumes for these isotopes. The implication is that for any pressure the zero-point energy difference should result in a greater molar volume for H_2 than for D_2, with the absolute difference tending to disappear at very high pressures where the repulsive forces are large. The present results can be used to construct a molar-volume-vs–pressure plot for each of the hydrogen isotopes using the appropriate 4.2-K $P = 0$ molar volumes V_0. This procedure is not straightforward, however, since, as Wanner and Meyer[10] point out, inconsistencies exist in the published data for V_0 which are more serious for H_2 than for D_2. Roder et al.[4] suggest the use of $V_0 = 22.65$ cm^3/mole for p-H_2 (22.47 cm^3/mole for n-H_2), based on an average of a number of recent and quite old determinations, while Mills[23] prefers $V_0 = 23.08$ cm^3/mole for p-H_2 (22.90 cm^3/mole for n-H_2), based primarily on x-ray experiments. Two recent neutron scattering experiments[11,15] are consistent with $V_0 = 19.94$ (+0.05) cm^3/mole for n-D_2, roughly 1% greater than Roder et al.[4] suggest. Figure 4 gives the pressure-volume relations for n-H_2 and n-D_2 as derived from these molar volumes. The larger value of V_0 for n-H_2 clearly gives the more consistent picture, since, as described above, the molar volume for H_2 always should be greater than that for D_2 for the same pressure.

A law of corresponding states for the pressure-volume relations for a class of solids results when the cohesive-energy-vs–volume relations of these solids all have the same shape. Thus, if

$$E_{coh}(V) = E_0 f(V/V_0) ,\qquad (5)$$

then

$$P(V) = B_0(V_0)f'(V/V_0) ,\qquad (6)$$

with $f'(1) = 0$ and $B_0(V_0) = (E_0/V_0)f''(1)$. Conversely, if a law of corresponding states is valid for the pressure-volume relations for a class of solids, their cohesive energies will have the form of Eq. (5) and will differ only by characteristic values of E_0 and V_0. Laws of corresponding states (different in each case) apply, for instance, to the compression data for the heavy-rare-gas solids argon, krypton, and xenon,[6] for the alkali metals lithium, sodium, and potassium,[24] and for the four alkali halides LiF, NaF, NaCl, and NaI.[25] Figure 5 contains a plot of Eq. (6) for the present data for n-H_2 and n-D_2 as calculated from Table II. The slight systematic differences which appear at high pressure (5% in P/B_0) are slightly outside the combined experimental uncertainties in the B_0 values. The extrapolation procedure which were used result in the coupling of the uncertainties in B_0 and V/V_0 at $P = 0$ (Table I), so any adjustment of the B_0's to produce a better agreement must be carried out self-consistently. The difference in Fig. 5 may be real, since the spherical averaging of the two-body potentials in the solid[2] could result in slightly different forms for the cohesive energy even for the $T = 0$ equilibrium configurations.

Equation (4) represents a reduced equation of state which appears to have fairly universal validity.[13,24,25] The parameter η [Eq. (3)] determines the shape of the reduced relation and therefore is characteristic of a class of solids. This parameter is pressure dependent for the hydrogen isotopes (Fig. 3) and for the rare-gas solids[6] (including helium[26]), but in each case it approaches a con-
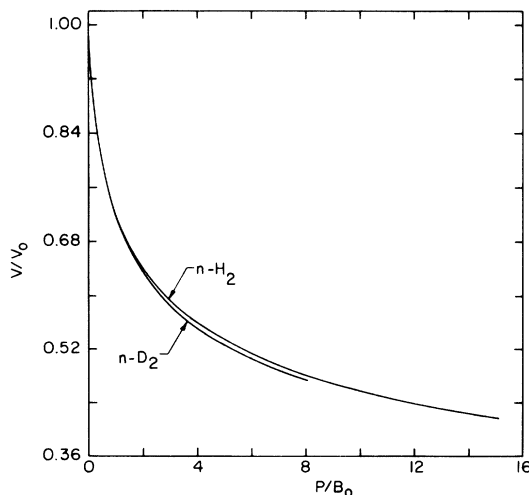

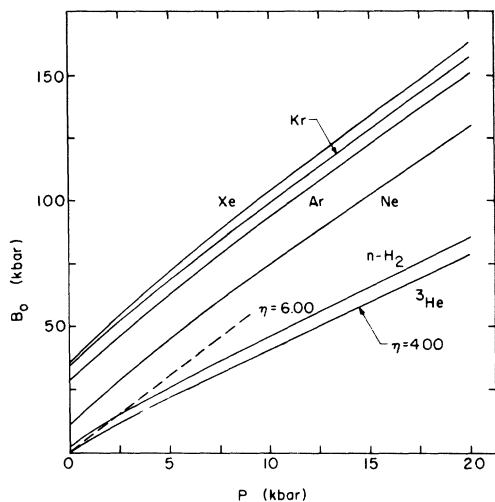FIG. 5. Reduced plot of the data in Table II, using the values of B_0 given in Table I.

FIG. 6. Comparison of the low-temperature-bulk-modulus-vs-pressure relations for the rare-gas solids and hydrogsn. See the text for details.

stant value at high pressures (above 10 kbar). This behavior is shown in Fig. 6, where only ^{3}He and n-H_2 are plotted for comparison with the heavier-rare-gas solids, since on this scale the differences between isotopes are small. The high-pressure limiting value of η is identical for the three heaviest-rare-gas solids ($\eta = 5.6$), is slightly smaller for neon, and is appreciably smaller ($\eta = 4$) for helium and hydrogen. These results suggest that the repulsive interactions for the two lightest solids are very similar, and are softer than those for the heavier solids; "hard core" effects are more important for the heavy-rare-gas solids than for helium and hydrogen. The two-body potentials which are most suitable for calculations with solid hydrogen[2] and helium[27,28] reflect this softness when compared with the commonly used (though incorrect[2,28]) Lennard-Jones potential.

The identification of the high-pressure value of η for these six solids with the repulsive part of their interaction energy can be justified by noting that in each case the nearest-neighbor distance at 20 kbar is sufficiently small that the two-body energy is positive. For helium, this occurs at 2 kbar. If the repulsive energy is assumed to vary as V^{-n}, then in this limit $\eta = n + 1$. The pressure-volume data thus suggest that between 10 and 20 kbar the volume dependence of the cohesive energy of the heavy-rare-gas solids can be approximated by $V^{-4.6}$, while that for hydrogen and helium is remarkably similar and varies as V^{-3}.

Additional support for the above picture can be found in values of η which are obtained from pressure-dependent ultrasonic measurements for the

alkali halides, since the closed-shell repulsions for these solids should be similar to those for the rare-gas solids. McLean and Smith[29] report a common value $\eta = 5.4(\pm 0.15)$ for 16 alkali halides which is very close to the limiting value for the rare-gas solids. Gerlich and Smith[30] recently have carried out similar measurements on LiH, and find $\eta = 3.8(\pm 0.15)$. This difference between LiH and the other alkali halides is identical with that which could have been predicted from Fig. 6, since the repulsive interactions for LiH should correspond to those in helium.

The differences in the limiting, or probably more appropriately the average, value of η also can be used to understand why the same type of power series cannot be used to represent the pressure-volume isotherms for the heavier-rare-gas solids and for hydrogen and helium. The dominant terms in the $T = 0$ power-series representations for the heavy-rare-gas solids[6] are those which correspond to the Lennard-Jones 6-12 potential, V^{-3} and V^{-5}, with η descreasing to 5 at the highest pressures. Equation (1) has the property that only A_1 is required if $\eta = 4$,[12,13] so it is more appropriate for a description of a solid such as hydrogen, or for solids such as the alkali metals, which have (limiting) values of η in this range. A "reduced" plot such as Fig. 6 for both experimental results and possible analytical pressure-volume relations can serve as a useful guide to the optimum choice of the functional representation for a set of data. A more complex version of Eq. (2) has been used[31] which involves an expansion to terms in P^2. This expansion implies a linear dependence of η on pressure, and cannot apply to the present results for which η appears to approach a constant value at high pressure.

Grover et al.[32] have shown that

$$\ln B/B_0 = \alpha(V_0 - V)/V_0 = \alpha[1 - (V/V_0)] \qquad (7)$$

applies to data for many solids, with α a constant. This relationship holds to approximately 2% for the n-H_2 results for $V/V_0 \geq 0.55$ (or to approximately 8 kbar), after which deviations occur which are in the same direction as those for less-compressible solids.[32] This relation also applies to better than 1% to 20 kbar for the heavy-rare-gas-solid data,[6] although deviations occur at high pressure for solid neon[5] which are of the same sign as for hydrogen. The representation of experimental results in a form which is suggested by either Eq. (2) or Eq. (5) is extemely useful for a reduced comparison of data for different solids (see Fig. 3), but, unfortunately, both of these relations are empirical in nature, and neither of them follows explicitly from any actual calculation of the equation of state for a solid.

IV. CONCLUSIONS

The present results for hydrogen are almost identical with those of Stewart,[1] and are within his stated experimental accuracy for deuterium. Hence, no changes need be made in calculations for molecular hydrogen which are based on his results. The increased accuracy of the present results as compared with his (by a factor of between 5 and 10) can provide a much more sensitive test of the accuracy of theoretical models for molecular hydrogen which are used to determine the metallic-transition pressure. The effects of relative ortho-para concentrations on the compression of hydrogen appear to be smaller than our experimental precision. A comparison of the hydrogen and deuterium results using a reduced representation suggests that the two-body intermolecular potentials might be slightly different in these two solids. Both hydrogen and deuterium resemble helium in that the repulsive contribution to their two-body interaction is somewhat softer than that which is found for the heavier-rare-gas solids.

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

[2]W. England, R. D. Etters, J. Raich, R. Danilowicz, Phys. Rev. Lett. 32, 758 (1974).

[3]Marvin Ross, J. Chem. Phys. 60, 3634 (1974).

[4]H. M. Roder, G. E. Childs, R. D. McCarty, and P. E. Angerhofer, NBS Technical Note 641, available as SD Catalog No. C13.46:641 from the Superintendent of Documents, U. S. GPO, Washington, D. C.

[5]M. S. Anderson, R. Q. Fugate, and C. A. Swenson, J. Low Temp. Phys. 10, 345 (1973).

[6]M. S. Anderson and C. A. Swenson, J. Phys. Chem. Solids (to be published).

[7]N. Bignell, Cryogenics 13, 30 (1973).

[8]L. C. Towle, J. Phys. Chem. Solids 26, 659 (1965).

[9]J. Jarvis, D. Ramm, and H. Meyer, Phys. Rev. Lett. 18, 119 (1967).

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

[11]J. L. Yarnell (private communication).

[12]L. Thomsen, J. Phys. Chem. Solids 31, 2003 (1970).

[13]O. L. Anderson, J. Phys. Chem. Solids 27, 547 (1966).

[14]B. G. Udovidchenko and V. G. Manzhelii, J. Low Temp. Phys. 3, 429 (1970).

[15]M. Nielsen, Phys. Rev. B 7, 1626 (1973).

[16]P. A. Bezuglyi and R. Kh. Minyafaev, Fiz. Tverd. Tela 9, 624 (1967) [Sov. Phys.-Solid State 9, 480 (1967)].

[17]P. A. Bezuglyi and R. Kh. Minyafaev, Fiz. Tverd. Tela 9, 3622 (1967) [Sov. Phys.-Solid State 9, 2854 (1968)].

[18]P. A. Bezuglyi, R. O. Plakhotin, and L. M. Tarasenko, Fiz. Tverd. Tela 13, 309 (1971) [Sov. Phys.-Solid State 13, 250 (1971)].

[19]S. C. Durana and J. P. M. McTague, Phys. Rev. Lett. 31, 990 (1973).

[20]V. G. Manzhelii, B. G. Udovidchenko, and V. B. Esel'son, Zh. Eksp. Teor. Fiz. Pis'ma Red. 18, 30 (1973) [JETP Lett. 18, 16 (1973)].

[21]H. M. Roder, Cryogenics 13, 439 (1973).

[22]L. D. Jennings and C. A. Swenson, Phys. Rev. 112, 31 (1958).

[23]R. L. Mills (private communication).

[24]C. A. Swenson, J. Phys. Chem. Solids 27, 33 (1966).

[25]C. S. Smith and K. O. McLean, J. Phys. Chem. Solids 34, 1143 (1973).

[26]C. A. Swenson, in Rare Gas Solids, edited by M. L. Klein and J. A. Venables (Academic, New York, 1974), Chap. 11.

[27]J. P. Hansen and E. L. Pollock, Phys. Rev. A 5, 2651 (1972).

[28]J. A. Barker, in Ref. 26, Chap. 4.

[29]K. O. McLean and C. S. Smith, J. Phys. Chem. Solids 33, 279 (1972).

[30]D. Gerlich and C. S. Smith, J. Phys. Chem. Solids (to be published).

[31]J. Ross Macdonald, Rev. Mod. Phys. 41, 316 (1969).

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