Neutron structural investigations of solid parahydrogen at pressures up to 24 kbar

S. N. Ishmaev, I. P. Sadikov, A. A. Chernyshov, B. A. Vindryaevskiĭ, V. A. Sukhoparov, A. S. Telepnev, and G. V. Kobelev

I. V. Kurchatov Institute of Atomic Energy, Moscow; Institute of High-Pressure Physics, Academy of Sciences of the USSR, Moscow

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The crystal structure of solid parahydrogen at pressures between 0 and 24 kbar and temperatures between 4.2 and 100 K has been investigated by the neutron time-of-flight diffraction method with a pulsed source. Only a hexagonal close-packed structure ($c/a = 1.631 \pm 0.002$) was observed throughout the ranges studied, in contrast to a number of proposals about the possibility of a phase transition. The zero volume is determined as $V_0 = 23.00 \pm 0.02$ cm^3 mole^{-1}. The dependence of the lattice parameters on pressure was found and the low-temperature equation of state set up: $P(V) = \alpha\beta[2.786 + 6.331\beta]$, where $\alpha = (V_0/V)^{5/3}$; $\beta = (V_0/V)^{2/3} - 1$, and the pressure is measured in kbar. This equation can be extrapolated reliably to the region up to 100 kbar.

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1. INTRODUCTION

There has recently been heightened interest in studying the condensed state of hydrogen. It has been stimulated largely by the prospect of using hydrogen and its isotopes in energy programs of the future, and also by the problem of the transition of molecular hydrogen into a metallic phase under megabar pressures. From the fundamental point of view, hydrogen is attractive as an example of a simple molecular crystal which has quantum properties, anomalous compressibility, large isotopic mass difference and presents a unique possibility for studying the properties of a crystal consisting of molecules in different modifications: in the ortho- and para-states. At low temperatures the thermodynamically stable state is the one with minimum rotational energy, i.e., para-H_2 (spin $I = 0$, rotational quantum number $J = 0$). Para-H_2 molecules have spherical symmetry and their interactions are mainly isotropic. Ortho-H_2 molecules ($I = 1$, $J = 1$) are metastable at low temperatures, but can exist for an appreciable time because of the low rate of ortho-para conversion in a crystal (1.9% per hour). They have an electric quadrupole moment which gives rise to an anisotropic part of the intermolecular interaction potential. This difference in the nature of the interaction leads to the structural properties of solid molecular hydrogen that depend on the ortho-para composition.

Although the first x-ray diffraction studies on parahydrogen were made half a century ago,[1] the pressure and temperature range in which the phase diagram was studied was very limited and the results obtained by different methods sometimes contradict one another. The situation arrived at before the present work was undertaken is described below, while a more detailed account of the history of the problem can be found in recent reviews,[2,3] where a comprehensive bibliography can be found.

It was quite reliably established that at pressure $P = 0$ and temperature $T \leqslant 14$ K molecular hydrogen crystallizes with the hexagonal close-packed (hcp) structure, which remains stable down to the lowest temperatures studied ($T = 0.17$ K) for ortho-H_2 concentrations $x < x_c \approx 50\%$. For large ortho-H_2 concentrations $50 < x < 100\%$, a phase transition takes place from a hexagonal to a face-centered cubic (fcc) lattice at temperatures $0 < T_c < 3$ K, respectively. Such a structural transition results from the anisotropic electric quadrupole-quadrupole interaction of the ortho-molecules and is accompanied by their orientational ordering in the crystal. These conclusions were confirmed[1)] by direct x-ray structural investigations.[4–6]

At the same time, the possibility of a structural phase transition in pure parahydrogen under pressure was also proposed on the basis of a number of indirect data: both at helium temperature in the region of 0.8 kbar (from optical results on Raman scattering[8]) and near the melting curve around 30–100 bar (from measurements of compressibility and the observation of anomalous thermal expansion in para-H_2[9–11]). By analogy with the known phase diagram of solid helium,[12] it was assumed that this indicated an hcp to fcc transition. Doubt was cast on conclusions about the possibility of such a transition at helium temperature[8] by neutron scattering measurements up to 1.8 kbar[13] and infrared absorption up to 10 kbar,[14] in which no change in the hcp structure was found.

As regards the melting region, observation of the coexistence of hcp-fcc phases from x-ray studies at $P = 80$ to 100 bar was reported,[15] but the specimens in this experiment did not consist of pure parahydrogen but were obtained by condensation from a gaseous He-H_2 mixture. Finally, no anomalies near the melting region were found in isochore measurements (for hydrogen of composition 50% ortho and 50% para) in the range $10\ \mathrm{K} < T < T_m$ and $P < 1.8$ kbar[16]), and it was suggested that they could have been produced in the earlier experiments by errors in the method. An attempt to relate these very contradictory data to the well known results at $P = 0$ has been undertaken[2] and a possible rough structural phase diagram of solid hydrogen was proposed.

The present work was started with the intention of solving this problem by direct structural studies of solid parahydrogen under pressure, using the slow neutron diffraction

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method with time of flight for a pulsed source.[17] Thanks to the relatively large neutron scattering cross section for hydrogen, a relatively low (compared with other forms of radiation) attenuation of the beam by the material of the pressure chamber can be achieved, and when the whole source spectrum is used this method is especially suitable for experiments at high pressures. The first results on neutron diffraction in the pressure range up to 5 kbar[18] showed the existence of only the hcp structure for a para-H_2 crystal. Further improvement in the method enabled the range of the investigation to be broadened both in the direction of higher pressures, up to24 kbar, and to low temperatures, down to 4.2 K, and to test new theoretical predictions[19] of the form of the parahydrogen structural diagram, published during the course of the experiment. The results obtained in the present work on the change in the lattice parameters with pressure also enabled the low-temperature equation of state of solid parahydrogen at $T \ll T_m$ to be determined by independent means.

2. EXPERIMENTAL TECHNIQUE

The measurements were carried out on two experimental facilities based on a pulsed neutron beam from the "Fakel" accelerator in the I. V. Kurchatov Institute of Atomic Energy. Both used the same gas system for preparing the parahydrogen specimen to be studied, which consisted of the successive stages of a purification system at $T = 77$ K, an ortho-para converter with $Fe(OH)_3$ catalyst at $T \approx 20$ K and a thermal compressor for preliminary pressurization of the hydrogen or for producing gaseous helium pressure on the specimen.

The first apparatus, which included a hydraulic press and helium cryostat[20] with a high-pressure piston and cylinder chamber, has been described in detail.[17] Studies on parahydrogen were carried out with it in the pressure range from 0.4 to 25 kbar at temperatures from 14 K upwards. Three high-pressure chambers were used: one made of V96-T aluminum alloy ($P_{\max} = 5$ kbar, specimen volume $V = 15$ cm^3), one of heat treated BrB2 beryllium bronze ($P_{\max} = 17$ kbar, $V = 4$ cm^3), and one of Ti-Zr alloy in a steel support with windows for the incoming and scattered neutron beam ($P_{\max} = 25$ kbar, $V = 0.7$ cm^3). The Ti-Zr alloy has zero amplitude for coherent neutron scattering so that the signal-to-noise ratio can be considerably improved. The solid hydrogen specimen itself, condensed into the chamber from the gas phase at $P \approx 0.4$ kbar, acted as the pressure transmitting medium. The pressure in the chamber was determined by measuring the dependence of piston displacement on load during forward and backward movement, as in experiments on the compressibility of hydrogen.[21–25] The friction at maximum load did not exceed 12% and corrections were calculated for elastic deformation of the walls of the chamber channel. Taking account of all errors, the accuracy in determining pressure was not worse that 2.5%. The degree to which the pressure distribution in the specimen was hydrostatic was monitored by the breadth of the diffracted reflections. No noticeable broadening of them was observed on raising the pressure, indicating the good uniformity of the pressure in the chamber. During an experiment the temperature was maintained stable to within 0.3°.

The second apparatus was specially constructed for more accurate measurement at low temperatures (down to 4.2 K) and pressures (0 to 0.6 kbar). The gas pressure chamber was a V99-T alloy tube (with inner space 1.5 cm diameter, height 8.5 cm and wall thickness 0.3 cm) suspended in a helium cryostat on a narrow stainless steel capillary. Hydrogen was first fed along the capillary and condensed to liquid at $T \approx 20$ K to fill the chamber to about 80% of its height. The chamber temperature was then lowered to 4.2 K and the gaseous helium pressure, provided by a thermal compressor, was applied to the parahydrogen specimen. The capillary could be heated to prevent blocking; experiments at $P > 0.14$ kbar were carried out at $T = 8$ to 10 K, i.e., above the helium solidification temperature. The cryostat design allowed the specimen chamber either to be cooled by liquid helium or to be maintained at a higher temperature by using a heat-exchange gas. The uniformity of temperature distribution in the chamber was checked by two germanium resistance thermometers and the pressure was measured with a standard gas manometer with an accuracy of ± 0.6 bar. The cryostat could be moved vertically by remote control and the degree of filling could be determined by illumination with a narrow neutron beam, with an accuracy of ± 2 mm. It is known that the solubility of helium in liquid hydrogen is small[26] and in our experiments gaseous helium acted on solid parahydrogen. Nevertheless, only the part of the specimen 1 to 2 cm below the "helium-hydrogen" boundary was irradiated with the neutron beam to remove this uncertainty. In addition, experiments at $P = 0$ were carried out twice: before helium was let into the chamber and after a cycle, spread over several days, of raising and lowering the pressure. Both measurements gave results which agreed within the experimental errors.

Each apparatus has a neutron spectroscopy facility so that the transmission, diffraction and inelastic scattering could be measured simulataneously on one specimen, using the whole show neutron spectrum of the pulsed source with the time-of-flight technique.[17,27] The measurement of the neutron transmission by the direct beam detector was used for an operational determination of the macroscopic density and ortho-para constitution of a specimen[27] to an accuracy of 1 to 2%. In a number of experiments at low temperatures, an iron hydroxide catalyst was also included directly in the pressure chamber to ensure the maximum para-concentration in the specimen.

On crystallization, hydrogen usually forms a coarse-grained textured specimen. This can complicate a reliable structure analysis and can even lead to incorrect interpretation of the results.[28] Our neutron structure studies were made with a multi-detector diffractometer using time-of-flight (neutron wavelength λ variable, scattering angle 2θ fixed). In each experiment up to 16 diffraction pictures (as a function of λ) were measured for various scattering angles in the range $2\theta = 99$ to 165°. Such a series of pictures measured at the same angles allowed not only a reliable monitoring of the texture of the polycrystalline specimen, but also led to high accuracy (0.03 to 0.05%) in determining the crystal lattice parameters. The diffractometer scale was calibrated, i.e. the relation between the time of flight and the corresponding value of the interplanar distance in the crystal, by special measurements on standard polycrystalline specimens of silicon and germanium to an accuracy of 0.2%. Mesurement of neutron diffraction by molecular hydrogen is much complicated by a large background of incoherent scattering. Pure coherent scattering can, however, be observed with parahydrogen if the long wavelength part of the spectrum ($\lambda > 3$ Å) is used, where the neutron energy is insufficient to excite the $J = 0 \rightarrow J = 1$ rotational transition with spin inversion.[13,17] This region of the spectrum is also favorable from the point of view of the smaller diffraction background from the chamber material. From 5 to 8 reflections with the largest interplanar spacing of the hydrogen lattice could be reliably observed in aluminum alloy pressure chambers. Measurements at high pressures were very difficult because of the relatively small dimensions of the specimen and the appreciable neutron absorption by the chamber material (in an experiment the intensity was reduced by about 25). However, even under these conditions three diffraction reflections from parahydrogen could be recorded sufficiently accurately.

3. EXPERIMENTAL RESULTS

The region of the parahydrogen *P-T* diagram studied is shown in Fig. 1. The full line corresponds to the melting curve and the points show the pressures and temperatures at which neutron-diffraction measurements were carried out. The boundaries which have been suggested[2,19] for the hcp-fcc transition are shown by the dashed lines. Theoretical calculations,[19] based on a quantum mechanical cell model, predict that this transition can occur at a pressure about an order of magnitude higher than proposed by Mills.[2]

The region from 50 to120 bar close to the melting curve was studied in special detail. From experiments at $P = 0$ and low temperatures, in which the hcp-fcc transition in orthohydrogen was studied,[4–6] it was known that this transition is of martensitic nature, has noticeable temperature hysteresis, and often forms mixed phases. Special care was therefore taken in the preparation of the specimen. The direction of the heating-melting-cooling and pressure raising-lowering cycles was varied, as was the rate of crystallization from the liquid or fluid state. The main measurements at high pressures were made at $T \approx 16$ K; in a number of experiments the specimen was maintained under pressure for 3 to 4 days, and its temperature was raised to 100 K. We were well placed to observe recrystallization processes and the oriented growth of blocks in the polycrystal, but all experiments showed the existence of only the hcp structure for parahydrogen. Impurity of another crystal phase at a 3% level could have been observed. It can thus be concluded that in the temperature range 4.2 to 100 K and pressures 0 to 24 kbar, solid parahydrogen has only the hcp structure.

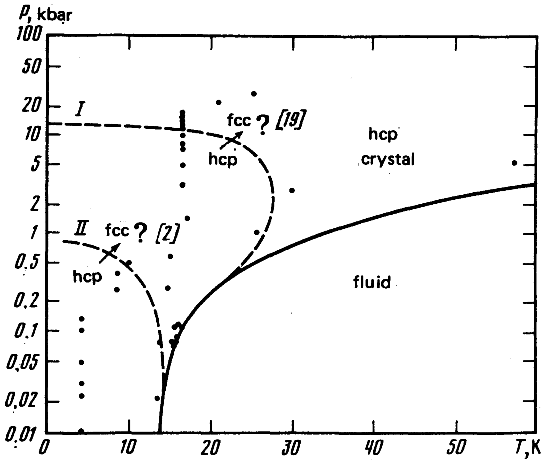

FIG. 1. *P-T* diagram for parahydrogen (full line—melting curve, dashed line—suggested boundaries of the structural phase transition[2,19]). The sole existence of the hcp crystal structure was determined by neutron diffraction measurements for values of the thermodynamic parameters shown by the points.

TABLE I. Hcp lattice parameters of parahydrogen crystals as a function of pressure.

P, kbar	*T*, K	*a*, Å	c, Å	c/*a*	*V*, cm^3 mol^{-1}
0	4,2	3.782(2)	6.167(3)	1.631(1)	23.00(2)
0.0276(6)	4.2	3.767(2)	6,136(3)	1.629(2)	22.71(3)
0.0235(6)	4.2	3.761(2)	6.154(2)	1.636(2)	22.70(3)
0.0488(6)	4.2	3,755(2)	6,119(3)	1.630(2)	22.50(3)
0.1024(6)	4.2	3.720(1)	6.078(2)	1,634(1)	21.93(2)
0.1294(6)	4.2	3.713(1)	6.056(1)	1.631(1)	21.77(1)
0,253(1)	8.3	3.661(1)	5.972(2)	1.631(1)	20.87(2)
0.252(1)	8,5	3.659(1)	5.975(2)	1.633(1)	20,86(2)
0.381(2)	8.6	3.619(1)	5.905(2)	1.632(1)	20.17(2)
0.488(2)	10.0	3.591(1)	5.863(1)	1.633(1)	19.72(1)
1.40(4)	17.3	3.435(1)	5.594(6)	1.629(2)	17.21(3)
3.00(4)	16.6	3.300(1)	5,366(6)	1.626(3)	15.24(3)
4.80(4)	16:6	3.207(3)	5.206(6)	1,623(3)	13.96(3)
7.0(1)	16.0	3.119(2)	5,086(3)	1.631(2)	12,90(3)
9.4(2)	16.5	3.059(2)	4.993(3)	1.632(2)	12.18(6)
11.9(2)	16,8	2.998(3)	4.893(4)	1.632(3)	11.47(7)
13.8(3)	16.2	2,979(2)	4.853(3)	1.629(3)	11.23(7)
15.1(4)	16.5	2.953(3)	4.809(4)	1.629(3)	10.93(7)
16.9(4)	16.4	2.929(2)	4.780(3)	1 632(3)	10.59(6)
24.0(4)	25.5	2.850(2)	4.640(3)	1.628(3)	9.83(6)

The experimentally determined values of the hcp crystal lattice parameters of parahydrogen as a function of pressure are shown in Table I. The uncertainty in the last significant figure is indicated in the parentheses. It can be seen

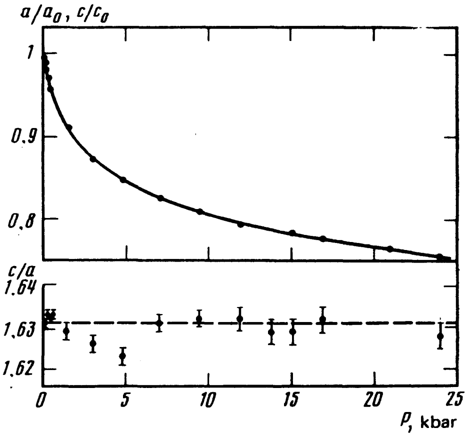

FIG. 2. Relative change in the hcp lattice parameters of para-hydrogen with pressure.

from Fig. 2 that the lattice parameters decrease monotonically with pressure and that the ratio c/a stays practically constant within the limits of experimental error and is little different from the ideal value for the hcp structure: 1.631 ± 0.002. A somewhat smaller value of c/a was sometimes found in a number of earlier experiments.[18] This may have been produced by the presence of 2 to 3% orthohydrogen impurity in the specimen (for hydrogen of composition 75% ortho and 25% para at $P = 0$, c/a was found from x-ray studies[4] to be 1.623). The influence of orthohydrogen on the anisotropic hcp lattice of solid hydrogen is a rather interesting question and requires further study. Unfortunately the possibilities of the neutron diffraction method are limited because of the strong increase in the incoherent scattering background in orthohydrogen.

The results shown in Table I were obtained for temperatures appreciably less than the corresponding melting temperature, when the contribution of the thermal pressure (due to thermal vibrations of the lattice) is relatively small. The magnitude of this contribution can be estimated from the results of measuring the $P_v(T/T_m)$ isochores of solid hydrogen.[16] For $P < 0.15$ kbar the difference between $P_v(T/T_m = 0.3)$ and $P(0)$ is not more than 0.3 bar; for $P \lesssim 0.5$ kbar this difference is between 1.7 and 2.5 bar and for higher pressures it is between 7 and 4 bar. It can be seen that this correction is less than or comparable with the accuracy of our pressure measurements in the corresponding ranges. The results given can therefore be considered as a completely justified extrapolation to the "zero" isotherm with $T = 0$.

4. DETERMINATION OF THE LOW-TEMPERATURE EQUATION OF STATE

Until now, experimentally determined equations of state for solid molecular hydrogen have been based mainly on results obtained by the piston displacement method. Such measurements have been made at low temperature, $T = 4.2$ K, in the range 2 to 20 kbar,[21] 0.5 to 25 kbar,[22] 1 to 5 kbar,[23] at $T = 77$ K from 5 to 30 kbar[24] and in the fluid phase from 2 to 20 kbar.[25]

The appreciable friction in the piston-cylinder system is a difficulty of this method; only the relative change in volume can be measured reliably, while the low-pressure region (where the compressibility of hydrogen is especially high) is inaccessible. It is therefore necessary to use an extrapolation and to include results obtained by other methods when constructing an equation of state. Measurements of the $P_v(T)$ isochores[16] and the heat capacity[29] $C_v(T)$ have recently been carried out up to 2 kbar. Both groups of authors[16,29] have proposed somewhat different variants of an equation of state for solid parahydrogen in the pressure region up to 25 kbar by using their own results combined with measurements of the relative compressibility. We should mention two factors which introduce some uncertainty into the earlier results. The first is connected with the effect of the ortho-para composition. Only two of the experiments mentioned above[23,29] were carried out on predominantly parahydrogen while the concentration of ortho-molecules in the others was not controlled and was between 75 and 50%. The correction for the contribution to the pressure from the interaction of the ortho-molecules has to be made by calculation.[16] The second factor is the appreciable scatter in the value of V_0, the molar volume at zero pressure, determined by different authors. As far as we know, sufficiently accurate and direct diffraction measurements have not been made of this quantity for pure parahydrogen. The value of V_0 was found by extrapolation and was sometimes one of the adjustable parameters in constructing the equation of state. On comparing various results, divergences were thus observed which often exceeded the uncertainties indicated by the authors.

We have tried to determine the equation of state for parahydrogen at $T = 0$ by an independent method, based only on results of absolute measurements of volumes by neutron diffraction. The $P = P(V)$ dependence for $T = 0$ has traditionally been expressed in the form of the Birch series[30] in work on the equation of state of molecular hydrogen:

$$P(V) = (V_0/V)^{5/3} \sum_{n=1}^{N} A_n[(V_0/V)^{2/3} - 1]^n \ldots \tag{1}$$

with two parameters ($N = 2$). We have also analyzed our results on the basis of this equation. The best approximation of the experimental results of Table I (taking account of the uncertainties) to Eq. (1) with $N = 2$ and $N = 3$ was found by the method of least squares. It turned out that for $N = 3$, the coefficient A_3 was effectively zero and there is no point in taking it into account over the range investigated. The values of the parameters for the parahydrogen zero isotherm—the initial bulk modulus $B_0 = -V(\partial P/\partial V)_{P=0} \equiv 2/3A_1$ and the coefficient A_2, obtained in this work, are shown in the bottom column of Table II.

The parameters A_1 and A_2 are stable relative to a variation in the value of V_0 within the limits of its experimental uncertainty, and their correlation coefficient

$$r = \langle \delta A_1 \delta A_2 \rangle / (\langle \delta A_1^2 \rangle \langle \delta A_2^2 \rangle)^{1/2} = -0.9,$$

was calculated by estimating the resulting error in the equation of state. We give numerical relations for calculating the pressure P and the bulk modulus $B = -V\partial P/\partial V$ on the basis of these parameters:

$$P(V) = \alpha\beta(2.786 + 6.331\beta) \ [\text{kbar}],$$

$$B(V) = 1.857\alpha(1-\beta) + \alpha\beta(16.799 + 18.993\beta) \ [\text{kbar}], \ldots \tag{2}$$

$$\alpha = (V_0/V)^{5/3}; \ \beta = (V_0/V)^{2/3} - 1; \ V_0 = (23.00 \pm 0.02) \ \text{cm}^3/\text{mol}^{-1}.$$

Comparison the results with the earlier ones (see Table

TABLE II. Parameters of the "zero" isotherm of the parahydrogen equation of state determined in various experiments.

Method	V_0, cm^3 mol^{-1}	B_0, kbar	A_2, kbar
Piston displacement[21] (1956)	–	2.00	5,70
Piston displacement[22] (1974)	–	1.70	6.185
Piston displacement[23] (1975)	–	2.01	5.44
Measurement of $P_v(T)$[16] + piston displacement[22] (1979)	23.14±0.08	1.858	6.334
Measurement of $C_v(T)$[29] + piston displacement[22] (1980)	23.23±0.05	1.759	5.869
Neutron diffraction, results of the present work	23.00±0.02	1.857±0.03	6.331±0,2

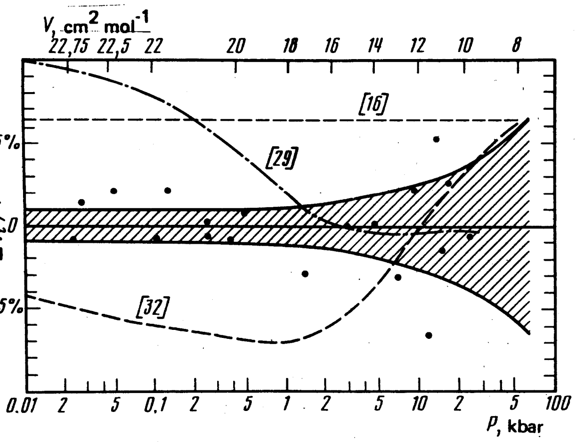

FIG. 3. Comparison of the experimental[16,29] and theoretical[32] results for the low-temperature equation of state of solid parahydrogen with the results of the present work.

II) shows the good agreement with the parameters B_0 and A_2 determined by Driessen *et al.*[16] The agreement with the value $B_0 = (1.860 \pm 0.067)$ kbar, found from measurements of the isothermal compressibility of parahydrogen in the range up to 0.2 kbar,[31] is an additional argument in favor of their reliability. There is, however, some difference (outside the experimental uncertainty) between the value of the zero volume measured by us and the experimental calculations of Driessen *et al.*[16] and of Krause and Swenson.[29]

The scale of the agreement and disagreement between the recently published results for the zero isotherm and our results is shown in Fig. 3 for a fairly wide pressure range. The comparison is conveniently carried out in the form of relative deviations:

$$\Delta V_i(P)/V(P)=[P_i(V)-P(V)]/B(V),$$

where $P(V)$ and $B(V)$ are calculated from Eq. (2) and $P_i(V)$ are the results of Refs. 16, 29, and 32. The shaded area shows the estimated accuracy of our determination of the zero isotherm and the points indicate the scatter of the experimental results in Table I from the best approximation to them [Eq. (2)]. It should first of all be noticed that overall the disagreements are small. In our view, the systematic ($\sim 0.6\%$) disagreement of the results of Driessen *et al.*[16] is completely explained by inaccuracy in determining V_0 in that work. There is appreciable error in Krause and Swenson's results[29] at relatively low pressures (up to 1 kbar). There is, however, remarkably good agreement with the results obtained over the remaining pressure range, although a clearly higher value of V_0 is used combined with slightly lower parameters B_0 and A_2.

There is a considerably larger amount of theoretical than experimental work devoted to calculating the equation of state of solid molecular hydrogen. This shows that this problem has not found a satisfactory solution after a long time. In any case the disagreement between various theories and experiment often exceeded the scale of Fig. 3. At present the completely semi-empirical isotropic pair potential with a correction for many body interactions[32] must evidently be considered the most successful. Its parameters were chosen on the basis of experimental values for the sublimation energy at $P = 0$ and the pressure for $V = 10$ cm³ mol⁻¹. The calculation then gave $V_0 = 22.90$ cm³ mol⁻¹. Comparison with the equation of state calculated[32] on the basis of this potential shows (see Fig. 3) that a noticeable disagreement with experiment remains in the low-pressure region. In so far as the accuracy of our measurements is higher here, they can serve as a good basis for refining the theory.

The situation as regards the higher pressure region is so far less certain. While this work was being completed, the results of optical studies on solid hydrogen in diamond cells at $T = 295$ K up to 200 kbar[33] and at $T = 5$ K up to 370 kbar[34] were published. We should note the reasonable agreement on extrapolating our results to 100 kbar with the low-temperature results.[34] For example, for $V = 8$ and 7 cm³ mol⁻¹, calculation according to Eq. (2) gives values of the pressure 55.0 and 91.8 kbar, compared with the values 54.1 and 87.8 kbar.[34] At the same time, appreciable disagreement is observed on comparing the results[33,34] for smaller specific volumes:

112 kbar[33] and 149 kbar[34] for $V = 6$ cm³ mol⁻¹
187 kbar[33] and 271 kbar[34] for $V = 5$ cm³ mol⁻¹
354 kbar[33] and 537 kbar[34] for $V = 4$ cm³ mol⁻¹

Further efforts must obviously be made to improve the equation of state in this region so that the pressure for the transition of molecular hydrogen into the metallic phase can be predicted more reliably.

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[1] It is possible that for $x < x_c$ at low temperatures a frozen-in phase of the "quadrupole glass" type,[7] with no long-range orientational order, may exist but the crystalline hcp structure is then preserved.[6]

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