

Micro- and macrodensity of solid parahydrogen under pressure

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Neutron diffraction and transmission methods are used for precision measurements of micro- and macrodensities of solid parahydrogen under pressure of up to 2 kbar with an aim at refining the data on their systematic difference. No density differences that can be attributed to the influence of zero-point defects in quantum crystals have been found at the 0.3% level.

1. INTRODUCTION

Small mass and weak intermolecular coupling, which lead to unusual physical properties, are responsible for the significant role played by zero-point atom vibrations in such substances as condensed helium and hydrogen. In Ref. 1 some features of quantum crystals were predicted, such as superplasticity and a possible existence of zero-point defectons down to the lowest temperatures. The difference between isotope masses makes it possible to study objects with different degrees of quantization which also depend on pressure.

In preceding works we have studied the role of zero-point vibrations in physical properties of solid and liquid hydrogen and their isotopic mixture. Thus, in Refs. 2 and 3, using experimental low-temperature equations of state for parahydrogen ($p\text{-H}_2$) and orthodeuterium ($o\text{-D}_2$), we have estimated the contribution of zero-point vibrations to the total crystal lattice energy. Neutron studies of liquid isotopic $(p\text{-H}_2)_x(o\text{-D}_2)_{1-x}$ solutions have revealed that they differ from ideal and have a weak tendency to isotopic stratification, which is due to the difference between the zero-point vibrations of hydrogen and deuterium molecules and leads to short-range order concentration fluctuations.³

For a long time physicists have been intrigued by a noticeable ($\sim 0.5\text{--}1\%$) difference, beyond the experimental error limits, difference between the values found by different methods for the molar volume of solid molecular $p\text{-H}_2$ at atmospheric pressure. For solid $p\text{-H}_2$ diffraction

experiments^{4,5} give smaller values than thermodynamic ones,^{6–8} whereas for $o\text{-D}_2$ no significant difference in micro- and macrodensities has been found.^{7,9–14} (Table I).

The molar volume of solid $p\text{-H}_2$ under pressure was found in specific heat experiments⁸ and by neutron diffraction.⁴ Differing by 1% at $P=0$, the equations of state $V(P)|_{T=0\text{ K}}$ drew closer with pressure and practically coincided for $V \approx 16\text{ cm}^3 \cdot \text{mol}^{-1}$ ($P \approx 2\text{ kbar}$). This could have been attributed to macroscopic defects in the specimen at low pressure and, partially, to so-called zero-point vacancies,¹ which must disappear as the quantization decreases with pressure.

In this connection, the macro- and microdensity measurements on one specimen and their comparison for different pressures seemed to be of interest. The experimental setup^{4,14,15} built for neutron studies of cryocrystals made possible such measurements, with the microdensity found from neutron diffraction data and the macrodensity from neutron transmission spectra. The aim was to check experimentally whether the above-mentioned difference in densities really existed.

2. EXPERIMENTAL DETAILS

The measurements were carried out in a high-pressure gas chamber made of Ti–Zr alloy ("zero"-matrix for coherent neutron scattering¹⁶) placed in a helium cryostat. Gaseous hydrogen was rid of impurities in a purification block at $T \approx 77\text{ K}$, converted into the para-modification at

TABLE I.

$V_0^{p\text{-H}_2}$, $\text{cm}^3 \cdot \text{mol}^{-1}$	$V_0^{o\text{-D}_2}$, $\text{cm}^3 \cdot \text{mol}^{-1}$	Method	References
23,10	$20,03 \pm 0,07$	Dielectric constant measurements, conversion to density	[8, 14]
$23,14 \pm 0,08$	$19,87 \pm 0,09$	Isochore measurement	[9]
$23,23 \pm 0,05$	—	Heat-capacity measurement	[10]
$23,063 \pm 0,016$	$19,930 \pm 0,016$	X-ray diffraction	[7, 13]
$23,00 \pm 0,02$	$19,933 \pm 0,015$	Neutron diffraction	[16, 6]
—	19,94	Neutron scattering	[11]
—	20,02	Neutron diffraction	[12]
—	$19,998 \pm 0,013$	Neutron diffraction	[15]

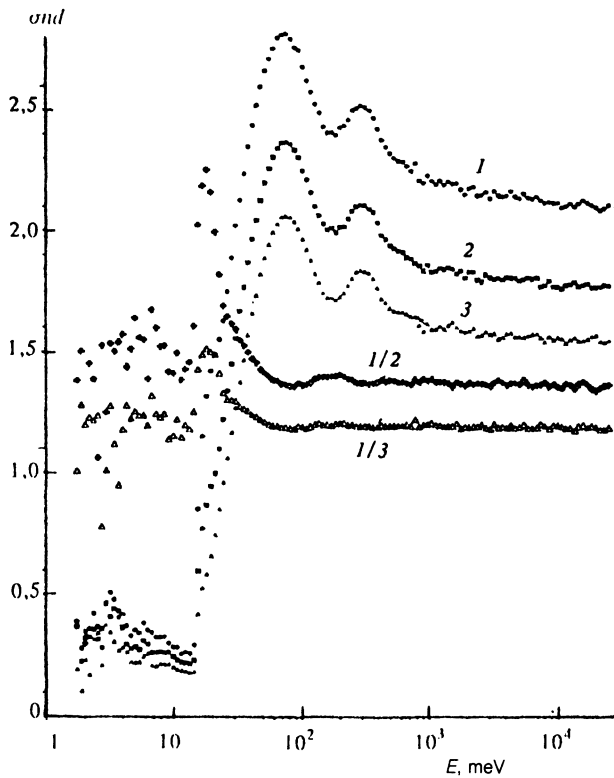


FIG. 1. Experimental values of σnd versus energy for solid $p\text{-H}_2$ under pressure equal to 1.765 kbar (1), 0.453 kbar (2), and 0.013 kbar (3) and cross-section ratios (1/2, 1/3) at corresponding pressure.

$T \approx 20$ K [with $\text{Fe}(\text{OH})_3$ catalyst], pressurized to a maximum pressure ~ 2 kbar by a ball membrane compressor, and condensed along a capillary into the high-pressure chamber cooled to a temperature 2–3 K higher than the solidification temperature corresponding to the given pressure. The pressure chamber was then cooled abruptly to the helium temperature to obtain a fine-grained polycrystal for precise diffraction measurements. To preserve the specimen quality, the measurements were carried out at decreasing pressure, i.e., without adding hydrogen to the chamber. In some experiments, to monitor a possible influence of macrodefects on the measured macrodensity of the specimen, the latter was annealed at temperature 1–2 K lower than the melting point. A noticeable change in the specimen block structure manifested itself in a change in diffraction maximum intensities, but neutron transmission was not seriously affected. The specimen was 18 mm in diameter and its height was 50 mm.

TABLE II.

P , kbar	Diffraction volume, $\text{cm}^3 \cdot \text{mol}^{-1}$	σnd	$(V_M - V_\mu)/V_\mu$
Run of measurements No. 1			
1,77	$16,665 \pm 0,010$	$2,1545 \pm 0,0023$	$0,0043 \pm 0,0012$
0,453	$19,855 \pm 0,014$	$1,8153 \pm 0,0025$	$-0,0011 \pm 0,0015$
0,013	$22,843 \pm 0,017$	$1,5804 \pm 0,0020$	$-0,0032 \pm 0,0015$
Run of measurements No. 2			
1,98	$16,359 \pm 0,010$	$2,4439 \pm 0,0022$	$-0,0021 \pm 0,0011$
0	$23,002 \pm 0,021$	$1,7288 \pm 0,0028$	$0,0021 \pm 0,0019$

The measured effect being small, stringent requirements were imposed on the volume-measurement accuracy ($\sim 0.1\%$). Whereas we had already measured diffraction on $p\text{-H}_2$ to this accuracy,⁴ to measure transmission we had to significantly refine the procedure to permit prolonged stable operation of the channels detecting the incident and transmitted neutron beams.

It must be noted that in our transmission experiment we did not aim at measuring the absolute value of macrodensity, since it was very difficult to find the effective thickness of the specimen placed into the high-pressure chamber and cryostat to the necessary accuracy. It was enough to analyze relative variations of macrodensity with pressure. We measured the quantity σnd , where $\sigma = \sigma_s + \sigma_a$ is the total cross section of neutron interaction with an H_2 molecule and consists of the scattering (σ_s) and absorption (σ_a) cross sections, n is the macrodensity, and d is the specimen effective thickness. A correction for expansion of the high-pressure chamber body was introduced, according to elasticity theory, for the case of an infinite hollow cylinder.¹⁷ This correction was practically independent of the Poisson ratio for the chamber material and amounted to $\delta d/d \approx 0.0012 \delta P$ (if the pressure difference σP is expressed in kilobars and the Young's modulus is taken equal to 2.2 Mbar), thus not exceeding 20% of the greatest possible effect.

Two kinds of instabilities of the measuring channels presented the main difficulty in neutron transmission measurements: a slow drift and rare random overshoots. The problem of precise determination of the source integral intensity is a fundamental one, since the quantity σnd was found from the relation

$$\sigma nd = \ln \left(\frac{N_c(E) M_H}{N_H(E) M_c} \right),$$

where $N_c(E)$ and $N_H(E)$ are the spectra of neutron transmission by the empty high pressure chamber in the cryostat and the chamber filled with parahydrogen respectively, while M_c and M_H are the corresponding monitored values of these spectra. The relative measurement errors for M_c and M_H ($\delta M_c/M_c$ and $\delta M_H/M_H$) for sufficient statistics of the $N_c(E)$ and $N_H(E)$ spectra give the absolute error

$$\delta(\sigma nd) = \left(\frac{1}{N_c} + \frac{1}{N_H} + \left(\frac{\delta M_c}{M_c} \right)^2 + \left(\frac{\delta M_H}{M_H} \right)^2 \right)^{1/2}.$$

To provide lasting stability of the spectrometric equipment (better than 0.15% for more than 100 hours of con-

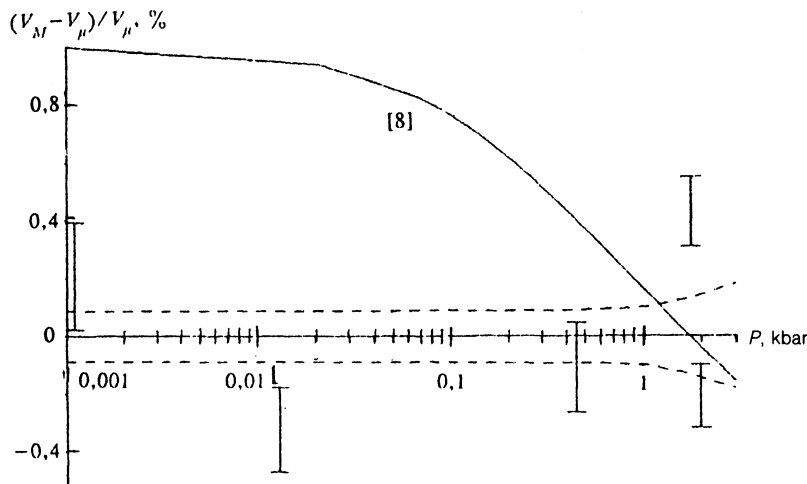


FIG. 2. The deviation of experimental dependence of the p - H_2 molar volume found by macroscopic method (see Ref. 8) from the "microscopic" dependence,⁴ whose region of reliability is shown by dashed lines. The results of the present study are shown by points. To place them, it has been arbitrarily assumed that mean values of relative deviations of macrovolumes from diffraction ones in each run are equal to zero (see Table II).

tinuous operation) we introduced a large amount of dc feedback in the preamplifiers of the monitor and of the main detectors and also took steps to stabilize in temperature the thresholds of the discriminator-shapers of the above mentioned channels. The computer program included control of random equipment overshoots: the sums of pulses registered by the monitor and main detectors over definite time intervals were compared and a decision was made either to add this information to the balance file or to reject it.

Note also that to increase the accuracy we enhanced the quality of the neutron beam: the inlet and outlet collimators were moved right up to the cryostat. Extra reliability of the data was achieved by duplication of both the monitor and the direct beam detector channels.

In the final analysis, the refinements introduced into the method at the equipment and program levels made it possible to achieve a controlled accuracy 0.2–0.3% of macro-density determination.

3. RESULTS

Figure 1 shows experimental values of σnd versus energy for different pressures and also the ratios of these values. In the energy range ~ 500 meV the ratios are practically independent of energy, which made it possible to use them to find the relative change in macro-density, though the cross sections themselves have not yet reached their asymptotic values corresponding to scattering by free protons. In the low-energy region the changes of the cross sections are related not only to density variations but also to consecutive inclusion of new scattering channels connected with rotational excitation of hydrogen molecules, and changes in the molecule oscillation spectrum in the crystal. Therefore the detailed information on total cross sections obtained in this experiment can be also used for analysis of pressure induced changes in some integral characteristics of the phonon p - H_2 spectrum (such as the rms molecular displacement and the Debye temperature) found from higher intensity measurements than the measurements of inelastic incoherent neutron scattering.¹⁸

Table II and Fig. 2 show the results found for the macro- and microdensities of solid p - H_2 . We carried out

two runs in which the specimen quality and its location on the neutron beam differed slightly. The macrodensities from different runs were not related to one reference value and only their relative changes with pressure (within each run) were analyzed, a comparison being made with similar changes in the diffraction volume.

Analyzing the experimental point distribution, we may conclude that there is no systematic difference between the pressure dependences of macro- and microvolumes at the level of 0.3%. Thus, it seems unlikely that the macro- and microdensities differ by 1%. As far as the possibility of a noticeable quantity of equilibrium defects existing at "zero" temperature is concerned, further precision measurements are needed.

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