Neutron-diffraction study of the equation of state of molecular deuterium at high pressures

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'shteĭn
I. V. Kurchatov Institute of Atomic Energy, Moscow; A. V. Shubnikov Institute of Crystallography, Academy of Sciences of the USSR

(Submitted 27 April 1988)
Pis'ma Zh. Eksp. Teor. Fiz. **47**, No. 12, 661–664 (25 June 1988)

The parameters of the unit cell of molecular deuterium have been determined at pressures up to 31 GPa and at room temperature by neutron diffraction and with diamond-anvil apparatus.

Despite the considerable interest in the study of highly compressed hydrogen, which has not waned for many years, dating back to the classic 1935 study by Wigner and Hantington,[1] the experimental progress in this field is still rather modest.

The beginning of real experimental research on highly compressed hydrogen under static pressure should be placed in 1979, when a research team at the Geophysical Laboratory of the Carnegie Institution of Washington successfully recorded Raman, spectra of hydrogen and deuterium at pressures up to ~0.7 Mbar (Ref. 2). This research was subsequently pursued to pressures up to ~1.5 Mbar (Ref. 3). However, a transition of hydrogen to a metallic state was not observed. Theoretical predictions of the pressure at which hydrogen would turn metallic span an extremely broad range.[4–9] The basic difficulties here seem to stem from the difficulties in calculating the properties of the molecular phase. Although noticeable progress has been made in this direction (see Refs. 7, 8, and, especially, 9), an experimental study of the thermodynamic properties and, in particular, the equations of state of the molecular phase of hydrogen and deuterium appeared to be an important step toward a complete understanding of the situation.

The first attempts to study the equations of state of hydrogen and deuterium at ultrahigh pressures were described in Refs. 10 (up to 0.37 Mbar) and 11 (up to 0.2 Mbar). The results of these studies turned out to contradict each other (see also Ref. 12 regarding this situation), but the limits on the possible errors of the methods used in Refs. 10 and 11 were such that it was not possible to make a well-founded choice.

In the present letter we are reporting a study of the equation of state of molecular deuterium at pressures up to 31 GPa, carried out by neutron diffraction and with diamond-anvil apparatus.

It was shown in Refs. 13 and 14 that diamond anvils, combined with the DISK low-background multidetector diffractometer, can be used to observe neutron diffraction despite the extremely small dimensions of the samples. In the present study, in contrast with Refs. 13 and 14, we studied the diffraction by single-crystal samples, so under otherwise equal conditions there was an advantage in terms of the intensities of the reflections. The deuterium single crystals were grown directly in the working

volume of the diamond cell through a recrystallization of individual single-crystal grains which had resulted from spontaneous crystallization of deuterium at room temperature and a pressure ≈ 5.4 GPa.

The diamond chambers were filled with deuterium to a pressure ~ 0.25 GPa by a special apparatus.

All of the diffraction experiments were carried out at room temperature at the IR-8 reactor, with a working power of 6 MW.

In some preliminary experiments on the diffraction of neutrons by samples of large volume (at pressures ≈ 6 GPa) it was found that the deuterium crystals which formed in the diamond chamber have a well-defined orientation, with the c axis of the hcp lattice oriented parallel to the axis of the anvil. This circumstance of course simplified the search for the necessary reflections. The particular neutron wavelength ($\lambda = 1.9$ Å) was chosen in order to maximize the number of reflections in the given experimental geometry. As a result, it was possible to detect seven single-crystal peaks (Fig. 1) from a sample with a volume ~ 0.1 mm^3. The positions of these peaks were determined within $\pm 0.05°$. All the reflections were indexed in an hcp lattice with the parameters $a = 2.6274 \pm 0.0008$ Å, $c = 4.2934 \pm 0.0020$ Å, $a/c = 1.634 \pm 0.001$, and $V = 25.66$ Å^3[11]. The error in the determination of the volume of the unit cell here was $\pm 0.1\%$.

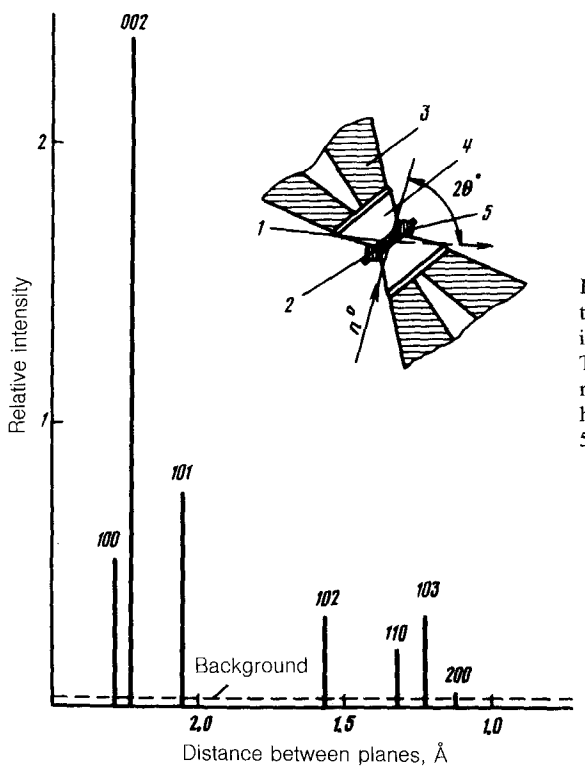

FIG. 1. Relative intensities of the diffraction maxima of a deuterium single cyrstal in an anvil cell at a pressure of 6.17 GPa. The inset shows the experimental arrangement. 1—Sample; 2—copper collar; 3—hard-alloy fulcrum; 4—diamond anvils; 5—stainless-steel spacer.

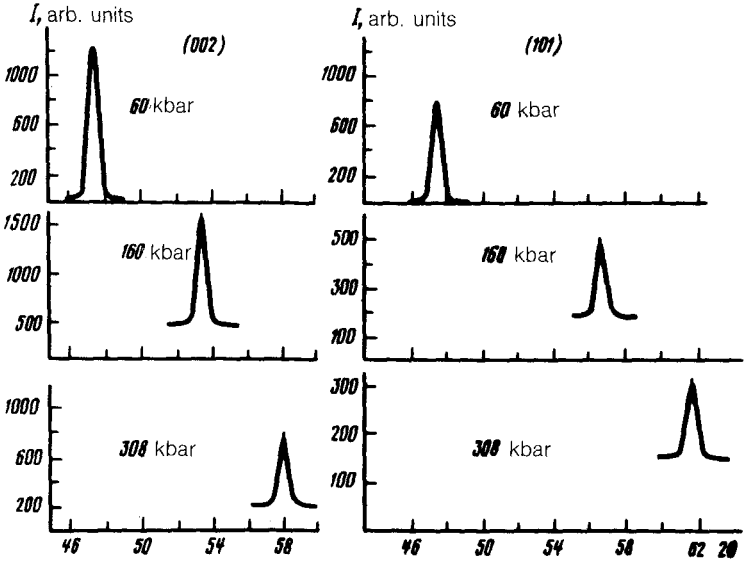

FIG. 2. Diffraction maxima of a deuterium single crystal at various pressures.

In experiments at higher pressures (in which we used samples with a volume $\sim 10^{-2}$ mm^3) we detected only three reflections. Fragments of the corresponding neutron diffraction patterns are shown in Fig. 2. The resultant error in the determination of the parameters of the unit cell from these data are $\delta a/a = \pm 0.1\%$, $\delta c/c = \pm 0.1\%$, and $\delta V/V = \pm 0.3$.

The pressure was determined by a "ruby" pressure gauge with a calibrated scale. To reduce the effect of temporal drift (~ 0.15 GPa/day) on the accuracy of the pressure measurements, we determined the pressure in the diamond chambers before and after the measurements of each reflection. Taking this source of errors into account, we find the overall error in the pressure determination to be ± 0.07–0.1 GPa. Table I and Fig. 3 show data characterizing the dependence of the lattice parameters and the molar volume of deuterium on the pressure, calculated from the present neutron diffraction experiments. The limiting error in the volumes reported here (the error in the pressure determination is taken into account) is 0.5–0.7%. We see that the ratio c/a is close to the ideal value for an hcp lattice and depends only weakly on the pressure.

TABLE I.

P, GPa	6,17	15,5	16,5	18,5	20,5	25,5	30,9
a, Å	2,6274	2,38	2,36	2,32	2,29	2,24	2,19
c, Å	4,293	3,854	3,808	3,768	3,714	3,640	3,542
c/a	1,634	1,62	1,62	1,62	1,62	1,62	1,62
V, cm^3/mole	7,729	5,69	5,55	5,31	5,11	4,72	4,43

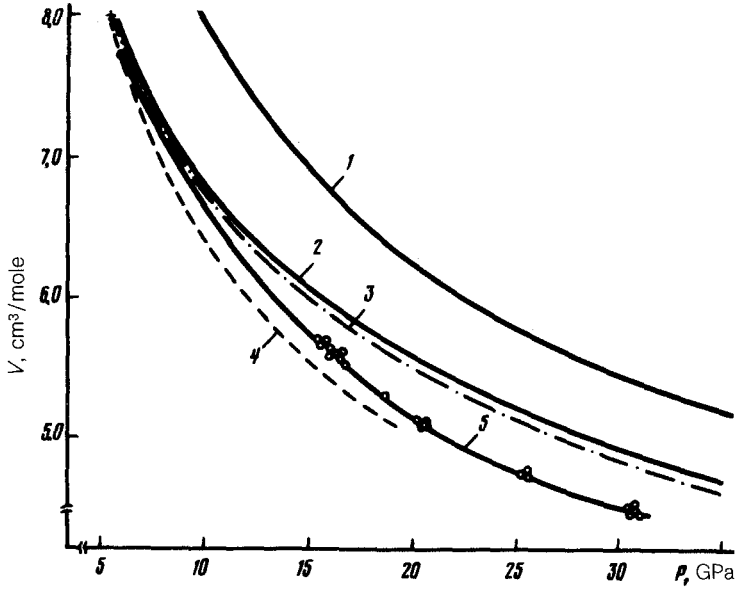

FIG. 3. Molar volume of deuterium versus the pressure. 1—Ceperley, Alder (theoretical)[9]; 2—Anisimov, Petrov (theoretical)[8]; van Straaten *et al.* (experimental)[10]; 4—Shimizu *et al.* (experimental)[11]; 5—present study; + — Hazen *et al.*[16]

Comparison of our data with the experimental results of Refs. 10 and 11 reveals some substantial differences, which go considerably beyond the limits on the errors declared by the authors. At $P > 10$ GPa, the data of Ref. 10 ($T = 5$ K) lie considerably higher than our own results. Incorporating the thermal pressure would evidently aggravate this discrepancy. The discrepancy between our data and the results of Ref. 11 is smaller, but still appreciable ($\sim 4\%$).

Figure 3 also shows results of theoretical calculations of the equation of state of the molecular phase of hydrogen (the isotope effect can be ignored in the comparison).[10,11] Three-particle interactions were taken into account systematically in Refs. 7 and 8. Ceperley and Alder made one of the first applications of the quantum-mechanical Monte Carlo method to problems of a real substance. It can be seen from Fig. 3 that the agreement between the theoretical results and the experimental results is still far from perfect, so at the moment there is no reason to believe that the theoretical estimates of the the pressure at which hydrogen would turn metallic are realistic.

We note in conclusion that Hazen *et al.*[16] have recently reported data on the parameters of the unit cell of hydrogen at a pressure of 5.4 GPa, found by x-ray diffraction with a four-circle diffractometer and diamond anvils. Their results agree well with our own data.

We wish to thank B. K. Vaĭnshteĭn and N. A. Chernoplekov for support of this study, Yu. N. Kagan and V. V. Pushkarev for useful discussions, and Yu. A. Bulanovskiĭ and Yu.O. Stankevich for assistance in the experiments.

[1)]Deuterium has a coherent neutron scattering cross section three times as large as that of hydrogen.

[1]E. Wigner and H. B. Hantington, J. Chem. Phys. **3**, 764 (1935).
[2]S. K. Sharma, H. K. Mao, and P. M. Bell, Phys. Rev. Lett. **44**, 886 (1980).
[3]H. K. Mao, P. M. Bell, and R. J. Hemley, Phys. Rev. Lett. **55**, 99 (1985).
[4]A. A. Abrikosov, Astron. Zh. **31**, 112 (1954). [Sic.]
[5]Yu. Kagan, A. Kholas, and V. V. Pushkarev, Zh. Eksp. Teor. Fiz. **73**, 968 (1977) [Sic.]
[6]M. Ross, Rep. Prog. Phys. **48**, 1 (1985).
[7]S. I. Anisimov and Yu. V. Petrov, Zh. Eksp. Teor. Fiz. **74**, 778 (1978) [Sov. Phys. JETP **47**, 407 (1978)].
[8]Yu. V. Petrov, Zh. Eksp. Teor. Fiz. **84**, 776 (1983) [Sic.]
[9]D. M. Ceperley and B. J. Alder, Phys. Rev. **B36**, 2092 (1987).
[10]J. van Straaten, R. J. Wijngaarden, and I. F. Silvera, Phys. Rev. Lett. **48**, 97 (1982).
[11]H. Shimizu, E. M. Brody, H. K. Mao, and P. M. Bell, Phys. Rev. Lett. **47**, 128 (1981).
[12]M. Ross, F. H. Ree, and D. A. Young, J. Chem. Phys. **74**, 1487 (1983).
[13]S. Ch. Shil'shteĭn, V. P. Glazkov, I. N. Makarenko *et al.*, Fiz. Tverd. Tela (Leningrad) **25**, 3309 (1983) [Sov. Phys. Solid State **25**, 1907 (1983)].
[14]V. P. Blazkov, A. V. Irodova, V. A. Somenkov *et al.*, J. Less-Common Met. **129**, 165 (1987).
[15]H. K. Mao, P. M. Bell, J. Shaner, and D. Steinberg, J. Appl. Phys. **49**, 3276 (1978).
[16]R. M. Hazen, H. K. Mao, L. W. Finger, and R. J. Hemley, Phys. Rev. **B36**, 3944 (1987).

Translated by Dave Parsons