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Single-crystal x-ray diffraction of n-H_2 at high pressure

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X-ray diffraction from a single crystal of solid n-H_2 has been obtained at high pressure in a diamond-anvil cell, and the crystal structure has been determined. Nineteen diffraction maxima, corresponding to the hexagonal-close-packed structure ($P6_3/mmc$, $Z=2$), were observed. Unit-cell dimensions at 5.40 ± 0.03 GPa and 300 ± 1 K are $a = 2.659 \pm 0.002$ Å, $c = 4.334 \pm 0.003$ Å, and $V = 26.55 \pm 0.05$ Å^3. The structure determination and volume measurement provide the most accurate checks to date on the equation of state and phase diagram of hydrogen in this pressure range.

The properties of compressed hydrogen are of fundamental interest in condensed-matter and planetary physics; of particular importance are the structure and equation of state of the molecular solid at high pressure.[1,2] Although well studied at low temperature by x-ray diffraction (see Ref. 1), structural properties of hydrogen at high pressure, including atomic structure and unit-cell parameters, have not previously been measured. Progress has been hindered because of the dual difficulty of first obtaining a hydrogen single crystal and then detecting x-ray diffraction from this extremely low-Z molecular solid. Structural information on the solid at high pressure has therefore been limited to inferences based on spectroscopic measurements,[3,4] which provide only an indirect structural probe. Knowledge of the equation of state of the molecular solid at high pressure is especially important for estimating the pressure of the insulator-metal transition in compressed hydrogen. The pressure-volume equation of state has been a subject of controversy, because recent experimental determinations are inconsistent.[5–7] In this Brief Report we report the first single-crystal x-ray diffraction measurements on solid hydrogen in the GPa pressure range. The structure is found to be hexagonal close-packed at 5.4 GPa (54 kbar). From the measured intensities, the structure has been refined with a term for isotropic rms thermal displacement of the H_2 molecule. Our well-constrained measurement of molar volume at this pressure lies between less precise recent experimental determinations, and is smaller than the results of recent theoretical models.

The experiment was performed using a diamond-anvil pressure cell designed for x-ray diffraction.[8] The cell was loaded in a pressure vessel containing fluid hydrogen at 0.2 GPa and 300 K.[9] The sample was confined by a stainless-steel gasket with hole 150 μm in diameter and 50 μm thick. The pressure in the diamond cell was increased to 5.40 ± 0.03 GPa, a pressure just above the 300-K freezing point.[10] It was hoped that a single crystal of hydrogen would form, as in previous high-pressure experiments on condensed gases.[11] Pressure was determined using the ruby-fluorescence method.[12] The shift of the ruby R_1 band was determined by extrapolating the position of the R_1 band at different laser intensities below 5 mW to zero, to eliminate possible heating effects on the pressure determination. During these experiments it was found that at low laser power (≈ 5 mW of 488.0-nm Ar^+ excitation) a ruby chip shifted position slightly as a result of melting next to the grain. This observation confirms the proximity of the sample pressure to the melting line of n-H_2.[10]

X-ray diffraction experiments were performed on an automated four-circle diffractometer with graphite-monochromatized molybdenum $K\alpha$ radiation ($\lambda = 0.70930$ Å). A conventional fine-focus x-ray tube was employed with a loading of 1.38 kW (46 kV and 30 mA). Initial orientation of the n-H_2 sample was attempted with conventional x-ray film techniques. Precession-type x-ray orientation photographs revealed strong diffraction effects from diamond and beryllium components of the pressure cell, as well as several weak ruby maxima, but no hydrogen diffraction effects were visible on film. Film-orientation methods, which can detect diffraction maxima of 75–100 counts/sec above background, have been used for all previous high-pressure single-crystal studies at this laboratory. An alternative orientation strategy was thus required.

In order to orient the weakly diffracting hydrogen sample without benefit of films, we made two assumptions: First, the structure of n-H_2 was assumed to be either hexagonal close-packed (hcp) or cubic close-packed (ccp),[13] and second, the density at 5.4 GPa and 300 K was assumed to be between 0.24 and 0.27 g/cm^3.[5–7,14] The (111) reflection of the ccp and the (002) reflection of the hcp structure are both strong and both would lie in the 2θ range 18.5°–19.3°, given the assumed structures and density range. A systematic diffractometer search over this 2θ range was conducted.

After approximately 80 h of automated searching, one weak diffraction maximum of 50 counts/sec, compared to a background of 15 counts/sec, was observed at a 2θ of 18.84°. This peak was centered in eight equivalent positions following the method of Hamilton[15] and was found to originate from the gasket hole. A systematic search was then conducted for other reflections at known fixed angles from the presumed hydrogen (002) hcp or (111) ccp reflection. No cubic-type diffractions [for example, a second (111)-type reflection at 70.54° from the first reflection] were observed. However, at 90° from the first reflection a second reflection at $2\theta = 17.76°$, consistent with a (100) hcp reflection, was found with an intensity of 35 counts/sec. These two suspected hydrogen diffraction effects defined an hcp orientation matrix that led to 17 additional weak diffraction maxima, ranging in intensity from 25 counts/sec to less than 5 counts/sec above background. The typical 25-min scans, through the (002) and (110) diffraction peaks, are shown in Fig. 1. Reflections of class (hhl) with $l = 2n$ (n integer), which are extinct in hcp structures, were all unobserved, but all other classes were present.

Unit-cell dimensions were determined from the angular positions of the five strongest reflections to be $a = 2.659 \pm 0.002$ Å and $c = 4.334 \pm 0.003$ Å, with a unit-cell volume of 26.55 ± 0.05 Å^3. Initial unit-cell refinements were made without symmetry constraints (i.e., as triclinic), and the resultant values conformed within the estimated standard deviation to hexagonal dimensionality. Final unit-cell refinement, as reported above, was made with hexagonal constraints.[16] The axial ratio c/a is 1.630 ± 0.003, consistent with the ideal value of 1.633. The orientation of the hydrogen crystal was such that close-packed H_2 layers were approximately perpendicular to the diamond-anvil faces (i.e., the c axis was subparallel to the anvils). This preferred orientation is similar to that observed in low-temperature structural studies of solid D_2 at 0.1 MPa (1 bar).[17] No systematic relationship between the n-H_2 and diamond lattices was observed.

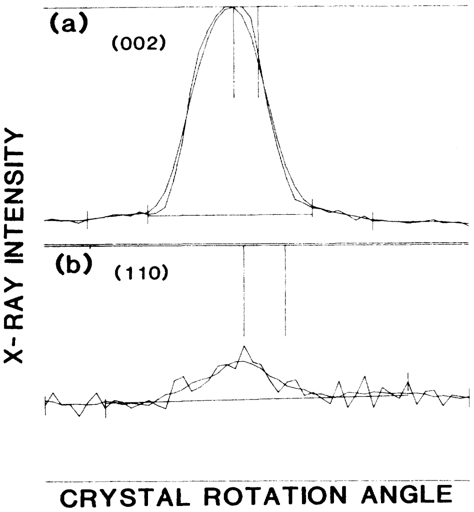

FIG. 1. Diffractometer scans of (a) the (002) peak and (b) the (110) peak of solid n-H_2 at 5.4 GPa. The scans were made with 30-sec counts at each of 51 ω steps of 0.02°. The horizontal line at the bottom of each scan is a fitted background; the two vertical lines at the top of each scan represent the ideal separation of Mo $K\alpha_1$ and Mo $K\alpha_2$ lines; peak scans are drawn with both individual step intensities (jagged lines) and a five-point smoothing function (smoother curves). Maximum observed intensity for the (002) reflection is 68 counts/sec vs a background of 9 counts/sec. For the (110) reflection maximum intensity is 13 vs a background of 8 counts/sec.

Relative intensities of hydrogen reflections were measured by an automated step-scan procedure.[18] The profile of each accessible reflection in the region $\sin\theta/\lambda < 0.50$ was determined with ω scans of 51 0.02°-step increments. An unusually long counting time of 30 sec per step was used to resolve the very weak reflections. Resulting integrated intensities ranged from 300 ± 100 to $18\,000 \pm 400$ counts. Integrated intensities were corrected for diamond-cell absorption and gasket-shadowing effects, and symmetrically equivalent reflections were averaged to yield eight structure factors.

The structure of hexagonal n-H_2 (space group $P6_3/mmc$, $Z = 2$) was refined using program RFINE.[19] The molecules were assumed to rotate freely on the basis of Raman spectra that indicate nearly pure rotational transitions at this pressure,[20] in agreement with theoretical considerations.[21] Freely rotating H_2 molecules were modeled with a scattering factor for orientationally disordered H_2 computed from wave functions determined with the GAUSSIAN-82 program.[22] Only two variable parameters, a scale factor and a term for isotropic thermal motion of the H molecule, were required. All H_2 molecules are centered on fixed positions in the hcp structure; intermolecular distances are thus defined by unit-cell dimensions alone. The refinement converged after three cycles to a residual of 7.7%. Calculated and observed structure factors are given in Table I. The refined value of isotropic thermal parameter B is 4.8 ± 1.8 Å^2. This parameter is related to the isotropic rms displacement μ of the H_2 molecule by the following relation:

$$\mu = \sqrt{B}/2\sqrt{2}\pi \; .$$

The resulting rms thermal displacement for H_2 is thus 0.25 ± 0.03 Å.

One inference from the crystal structure refinement is that one dominant hydrogen single crystal filled most of the sample chamber. Structure refinement based on reflections corrected for gasket shielding was significantly better than that for uncorrected data; thus, the crystal extended close to gasket walls. Experiments on crystalline hydrogen at higher pressure, now in progress, indicate

TABLE I. Observed and calculated structure factors for n-H_2 at 5.4 GPa and 300 K. Structure factors were calculated on the basis of a hexagonal close-packing arrangement of orientationally disordered H_2 molecules: space group $P6_3/mmc$, $Z = 2$, unit-cell dimensions $a = 2.659$ and $c = 4.334$ Å.

(hkl)	d (Å)	$10^4 F_{\text{obs}}$	$10^4 F_{\text{calc}}$
(100)	2.303	23	25
(002)	2.167	51	45
(101)	2.034	35	34
(102)	1.578	12	11
(110)	1.330	12	13
(103)	1.224	8	9
(112)	1.133	4	8
(004)	1.084	7	7

that one single crystal may not always form. Twinning or multiple crystals have been observed to cause loss of diffraction intensity in one experiment at about 6.0 GPa, for example.

The present single-crystal x-ray data provide the most accurate test to date of previous estimates of the hydrogen equation of state. We calculate a volume of 7.994 ± 0.015 cm^3/mol ($\rho = 0.252 \pm 0.001$ g/cm^3) at 5.4 GPa. This volume is about 2% larger than that predicted by the Shimizu, Brody, Mao, and Bell[5] equation of state, which is based on Brillouin scattering data to 20 GPa. This equation yields a volume of 8.0 cm^3/mol at about 5.1 GPa. On the other hand, our observed value is significantly smaller than that suggested by the equation of state of van Straaten, Wijngaarden, and Silvera,[6] which was determined to 37.1 GPa at 5 K by optical methods. van Straaten *et al.* report a pressure of about 5.4 GPa at a volume of 8.0 cm^3/mol at 5 K, but thermal corrections from 5 K to room temperature will increase the calculated pressure significantly at this volume.

The thermal pressure P_{th} at 300 K and 8.0 cm^3/mol must be included for direct comparison of our experimental data with the results of van Straaten *et al.*[6] as well as theoretical (static-lattice) calculations. Hemmes, Driessen, and Griessen[23] have calculated this contribution for the equation-of-state data of van Straaten *et al.*[6] using a Mie-Grüneisen model with parameters constrained by spectroscopic data. In addition, Ross, Ree, and Young[7] have calculated P_{th} using lattice dynamics with pair potentials fit to the data of Shimizu *et al.*[5] Both approaches give $P_{\text{th}} \approx 0.6$ GPa at $T = 300$ K and $V = 8.0$ cm^3/mol, despite the differences in input data (i.e., independent of the effective potentials used). Adding P_{th} to the 5-K result listed by van Straaten *et al.*,[6] gives 6.0 GPa, which is significantly larger than our measured pressure. A thermal pressure shift applied to the theoretical results of Ross *et al.*[7] at 8.0 cm^3/mol also gives higher pressures (6.2 and 5.7 GPa for the Young-Ross and exp-6 potentials, respectively).

The present results demonstrate for the first time that x-ray diffraction can be used to determine directly structural and equation-of-state information on this weak-scattering solid at high pressure. The new volume data serve as a useful fixed point with which to refine potentials in theoretical equation-of-state calculations. It should also be pointed out that the present pressure-volume data appear to be close to the equation of state determined recently by adiabatic compression by Matveev *et al.*,[24] although a quantitative comparison cannot be made because numerical results were not reported. It is believed that experiments on n-H_2 and n-D_2 now in progress at higher pressure will provide accurate information on the pressure-volume relations of the hydrogen isotopes. Higher-pressure x-ray diffraction data on molecular hydrogen also provide the best prospect for direct observation of high-pressure phase transitions, such as orientational ordering.[1]

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