

## Neutron Diffraction Studies of Hafnium-Hydrogen and Titanium-Hydrogen Systems\*

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Results of neutron and X-ray diffraction studies on Hf and Ti hydrogen systems are reported. It is shown that the first single-phase hydride formed is a non-stoichiometric compound with a  $\text{CaF}_2$ -type structure. It deforms to a face-centered tetragonal structure as the composition approaches  $\text{MX}_2$ . From the crystal-structure data of these hydrides the positions of hydrogen atoms, the nearest-neighbor atoms and their interatomic distances are determined. It is indicated that the size of the 'hole' for the hydrogen atom in the hydride is such that it must enter as an ion. The effect of metal-hydrogen bonds on the physical properties of hydrides, such as characteristic temperature and vibration frequency, is given. Evidence and explanation for the embrittlement of metals by hydrogen are offered.

### Introduction

Studies of metal-hydrogen systems by thermal, metallographic and X-ray diffraction methods usually reveal the formation of metal-hydride phases, the dimensions of the unit cell and the positions of the metal atoms. The positions of hydrogen atoms in general, however, are determined either by high precision and relatively laborious methods, or are just inferred. This difficulty or inability to locate the positions of hydrogen atoms with respect to one another and to the metal atoms prevents precise determination of crystal structures of the phases and, thereby, the type of bonding formed between metal and gas atoms. This has led to qualitative explanations and hypotheses (e.g. Smith, 1951) regarding the state of hydrogen in metals that are in some instances ambiguous and difficult to justify.

Neutron diffraction effects make it possible to locate metal and hydrogen atoms, at least in simple systems, with equal accuracy. This is due to the fact that the neutrons are scattered by the nuclei, except of course for the magnetic materials; and the nuclear coherent scattering amplitudes for both the light and the heavy atoms are of the same magnitude. Typical metal-hydrogen systems were studied. The objects were: (1) to determine the positions of hydrogen atoms, the nearest-neighbor atoms and the interatomic distances in each lattice; and (2) to obtain quantitative structure data which would form a basis for the explanation of the state of hydrogen, not only in these systems but other similar systems as well.

### Experimental procedure

In order to make use of the higher coherent scattering amplitude and lower spin-diffuse scattering of deu-

terium as compared with those of hydrogen, the samples of hydrogen-containing polycrystalline materials were deuterated for the present studies. Rolled metal strip about 5 mil. thick was cut into approximately  $\frac{1}{2}$  in.  $\times$   $\frac{1}{2}$  in. pieces. Each piece was dipped in an acid solution of 40%  $\text{HNO}_3$ , 5%  $\text{HF}$  and 55%  $\text{H}_2\text{O}$ , and removed when it became bright, then rubbed with a brush while under running water, rinsed in acetone and air dried. The samples were weighed, then heated and outgassed in a quartz tube evacuated to a pressure of  $10^{-6}$  mm. Hg at about  $1160^\circ\text{C}$ . for 16-48 hr. At  $1000^\circ\text{C}$ . a measured volume of deuterium gas was introduced into the tube at a known pressure. Most of the absorption of gas took place at  $700$ - $800^\circ\text{C}$ . To assure a thoroughly reacted sample it was cycled several times between temperatures approximately  $500$  and  $1000^\circ\text{C}$ ., corresponding to deuterium pressures of 140 and 573 mm. respectively. Usually the sample was held for several hours at the lower temperature and finally cooled slowly to room temperature. The composition of the sample was calculated from the weight of the metal and the volume of absorbed deuterium. The metals used were of crystal bar purity.

In contrast to the ductile metals, their deuterides were brittle, the ductility decreasing with increasing concentration of deuterium. The deuterides with compositions  $\text{MD}_{1.7-1.97}$ ,  $M$  being the metal atoms, were so brittle that they could be easily pulverized by crushing in mortar and pestle. All the samples studied in these investigations, however, were stable at room temperature and were handled without any special precautions.

The specimens were annealed at  $350^\circ\text{C}$ . for 24 hr. or longer. X-ray diffraction data were obtained for each phase for identification and for aid in structure determination. Neutron diffraction patterns were made from cylindrical samples consisting of about 10-15 g. of powdered specimen contained in a  $\frac{7}{16}$  in. diameter

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vanadium tube, 2 in. long and 5 mil. wall thickness with cadmium end plugs. These patterns were very nearly comparable to those obtained with X-ray diffraction techniques both in intensity and resolution. This was made possible by the high-intensity neutron beams, now available from the new heavy water Argonne reactor, that were made monoenergetic by diffracting from a  $2\frac{1}{2}$  in.  $\times$  5 in. and  $\frac{1}{2}$  in. thick copper single crystal cut parallel to (111) plane, and by a neutron diffraction spectrometer which has a  $2\theta$  Bragg angle range from  $-44^\circ$  to  $+136^\circ$ .

The operation of the spectrometer provides automatic recording of neutron diffraction patterns. The spectrometer arm moves with constant angular speeds of  $1\frac{1}{2}$ , 3, 6, 12, or  $24^\circ$  per hour, and the neutron diffraction pattern is recorded on a chart which travels at compatible speeds for convenience of angular measurement. A fission chamber placed between the copper crystal and the sample is employed as a monitor of the incident beam, and a  $\text{BF}_3$  counter mounted on the spectrometer arm serves as a detector of the diffracted neutrons. The monitor serves as a timer, in that the pulses received from the detector during a preset number of monitor counts are stored in an electronic computer system. At the end of the preset monitor count, the monitor and the detector circuits are gated out for a 2 sec. interval while the stored detector counts are first recorded and then cleared from the computer circuit. Therefore, each point recorded on the chart corresponds to the ratio of the diffracted intensity to the incident intensity over the increment of angle which the spectrometer arm has moved during the counting period. In practice this angular increment of  $2\theta$  is about  $0.1^\circ$ , insuring a sufficient number of counts for good statistics and still maintaining adequate resolution.

A provision is made for a systematic sampling of the background at the same time that a diffraction pattern is being obtained. A cadmium shutter is electronically inserted in the path of the incident beam every second, third, fourth, . . . , or tenth counting period. The cadmium shutter prevents the incident beam from striking the sample and the recorded value, therefore, is the background intensity.

## Results

### *Hafnium-hydrogen system*

This system at room temperature consists of at least three phases (Sidhu & McGuire, 1952): a deformed cubic or a tetragonal phase, a cubic phase and another tetragonal phase. The deformed cubic phase coexists with  $\alpha$ -hafnium and extends up to  $\text{HfH}_{1.53}$ . It converts into the face-centered cubic phase above  $\text{HfH}_{1.53}$ . The single cubic phase exists within a narrow range of compositions and transforms into the tetragonal phase between  $\text{HfH}_{1.80}$  and  $\text{HfH}_{1.87}$ . The tetragonal phase then extends up to  $\text{HfH}_{2.0}$ . The range of compositions just before the system becomes a single

cubic phase is quite sensitive to conditions under which the samples are prepared. Under certain conditions a transition phase is formed between the deformed cubic and the single cubic phases.\*

*Crystal structure of cubic phase—HfD<sub>1.628</sub>.*—X-ray and neutron diffraction patterns of  $\text{HfD}_{1.628}$  are shown in Fig. 1(A) and the diffraction data in Table 1. The value of the lattice parameter,  $a_0$ , as determined from X-ray data is  $4.681 \pm 0.005$  Å. This value is slightly smaller than the value  $4.708 \pm 0.002$  Å previously reported for the cubic hafnium hydride. The decrease is ascribed at least in part to the lattice contraction (Sidhu, 1954b) when hydrogen atoms are replaced by deuterium atoms in this system.

Since a face-centered cubic structure was suggested by X-ray diffraction data, the intensities were calculated by assuming both  $MX$ - and  $MX_2$ -type cubic structures. The structure factors,  $|F|$ , that gave the best agreement with the observed intensities were computed for the  $\text{CaF}_2$ -type structure, with:

$$4 \text{ Hf at: } (0, 0, 0); (\frac{1}{2}, \frac{1}{2}, 0); (\frac{1}{2}, 0, \frac{1}{2}); (0, \frac{1}{2}, \frac{1}{2})$$

$$\text{and } 8 \text{ D at: } \pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}); (\frac{3}{4}, \frac{3}{4}, \frac{1}{4}); (\frac{3}{4}, \frac{1}{4}, \frac{3}{4}); (\frac{1}{4}, \frac{3}{4}, \frac{3}{4}),$$

where the normal deuterium atom sites are only partially filled by  $1.628/2$  fraction of atoms. The calculated relative intensities were computed from the following equations:

$$\text{for X-rays, } I \propto |F|^2 m \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}; \quad (1)$$

$$\text{for neutrons, } I \propto |F|^2 m \frac{1}{\sin^2 \theta \cos \theta}$$

$$\times (\exp[-2B \sin^2 \theta / \lambda^2]), \quad (2)$$

where

$$|F_{hkl}| = \{1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\}$$

$$\times \{f_{\text{Hf}} + 1.628 f_{\text{D}} \cos \frac{1}{2} \pi (h+k+l)\}$$

and  $\exp[-2B \sin^2 \theta / \lambda^2]$  is the 'Debye-Waller' factor.

The value of  $2B$  was determined from the slope of the plot of logarithm of  $(I_o/I_c)$  versus  $\sin \theta / \lambda$ . The value of  $\bar{\mu}$ , the root-mean-square displacement of the atom perpendicular to the reflecting planes, and of  $\Theta$ , the characteristic temperature, were calculated by substituting  $B$  in the expression

$$B \frac{\sin^2 \theta}{\lambda^2} = 8\pi \bar{\mu}^2 \frac{\sin^2 \theta}{\lambda^2} = \frac{6h^2 T}{M_a k \Theta^2} \left\{ \varphi(x) + \frac{x}{4} \right\} \frac{\sin \theta}{\lambda^2}, \quad (3)$$

in which  $h$  is Plank constant,  $k$  Boltzmann's constant,  $T$  is absolute temperature,  $x = \Theta/T$ , and  $M_a$  is the

\* F. H. Ellinger of Los Alamos Scientific Laboratory, communicated to us that in their studies of the hafnium-hydrogen system, they observe a single cubic phase at about  $\text{HfH}_{1.75}$  which gradually deforms to an orthorhombic phase with a decrease in hydrogen content, reaching maximum deformation at about  $\text{HfH}_{1.5}$ . At this composition a tetragonal phase appears which coexists with the orthorhombic phase to about  $\text{HfH}_{1.25}$ , and then with continued decrease in hydrogen content the orthorhombic and tetragonal phases coexist with  $\alpha$ -hafnium.

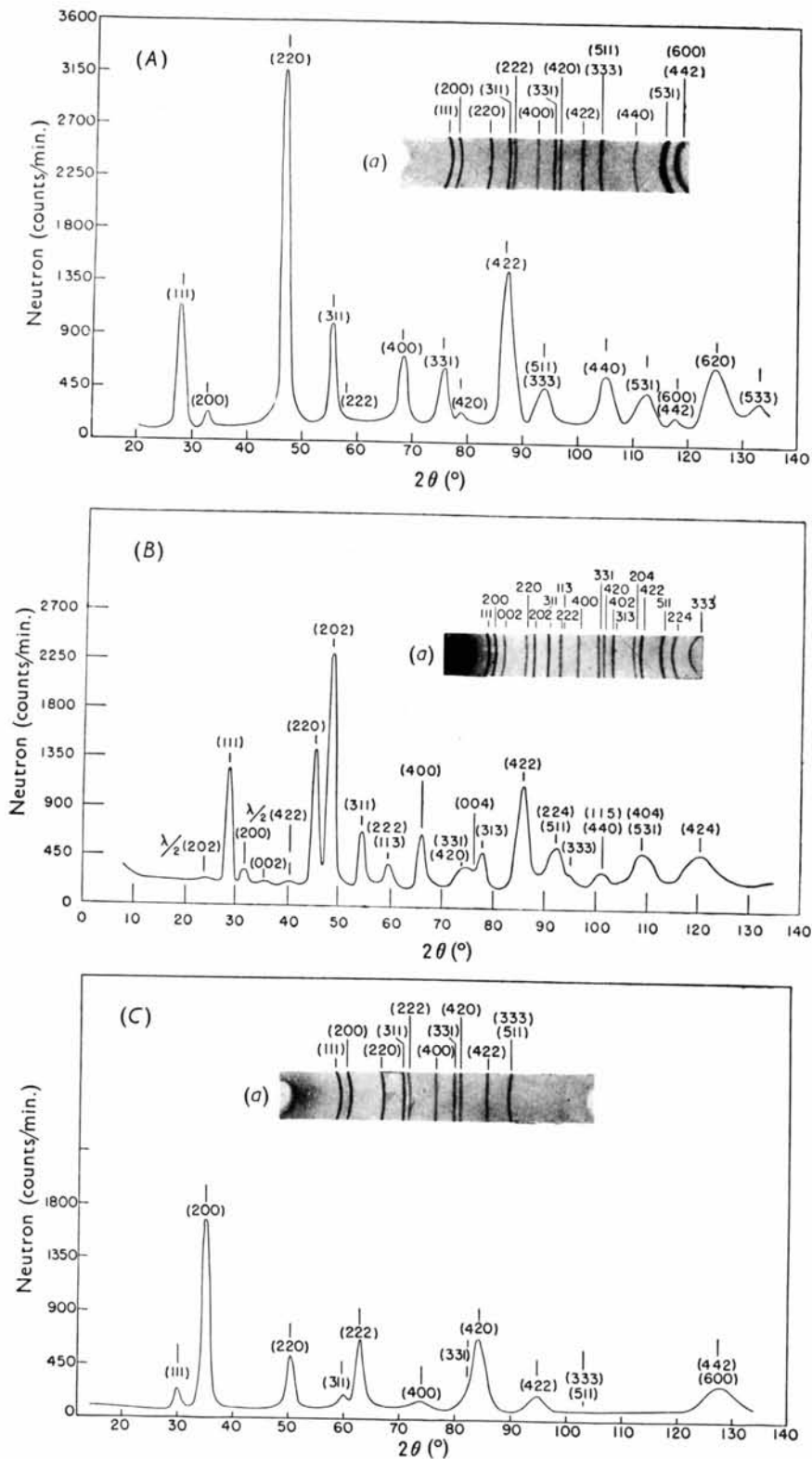


Fig. 1. (A) Diffraction patterns of HfD<sub>1.628</sub>. (a) X-ray filtered Cu K $\alpha$  radiation; camera diameter 114.6 mm. (b) Neutron,  $\lambda = 1.330$  Å. (B) Diffraction patterns of HfD<sub>1.983</sub>. (a) X-ray filtered Cu K $\alpha$  radiation; camera diameter 114.6 mm. (b) Neutron,  $\lambda = 1.330$  Å. (C) Diffraction patterns of TiD<sub>1.971</sub>. (a) X-ray filtered Co K $\alpha$  radiation; camera diameter 114.6 mm. (b) Neutron,  $\lambda = 1.337$  Å.

Table 1. *Interplanar spacings (d), calculated and observed X-ray and neutron diffraction relative intensities (I/I<sub>0</sub>) for HfD<sub>1.628</sub>*

| <i>hkl</i> | <i>d</i> (Å) | X-rays                          |                                | Neutrons                        |                                |
|------------|--------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|
|            |              | <i>I/I</i> <sub>0</sub> (calc.) | <i>I/I</i> <sub>0</sub> (obs.) | <i>I/I</i> <sub>0</sub> (calc.) | <i>I/I</i> <sub>0</sub> (obs.) |
| 111        | 2.702        | 100.0                           | <i>vs</i>                      | 38.3                            | 33.2                           |
| 200        | 2.334        | 48.9                            | <i>s</i>                       | 0.7                             | 2.5                            |
| 220        | 1.652        | 34.5                            | <i>s</i> —                     | 100.0                           | 100.0                          |
| 311        | 1.409        | 39.9                            | <i>s</i>                       | 29.3                            | 26.6                           |
| 222        | 1.351        | 10.9                            | <i>w</i>                       | 0.4                             | 2.1                            |
| 400        | 1.170        | 5.5                             | <i>vw</i>                      | 23.9                            | 20.3                           |
| 331        | 1.073        | 17.9                            | <i>m</i>                       | 16.3                            | 15.7                           |
| 420        | 1.047        | 17.1                            | <i>m</i>                       | 0.6                             | 1.6                            |
| 422        | 0.956        | 16.0                            | <i>m</i> —                     | 62.3                            | 61.9                           |
| 333, 511   | 0.901        | 17.0                            | <i>m</i>                       | 15.3                            | 17.3                           |
| 440        | 0.829        | 11.9                            | <i>w</i>                       | 24.1                            | 25.3                           |
| 531        | 0.793        | 71.9                            | <i>s</i>                       | 18.6                            | 17.9                           |
| 442, 600   | 0.781        | 13.4                            | <i>w</i> +                     | 0.5                             | 1.5                            |
| 620        | 0.744        | —                               | —                              | 43.7                            | 40.4                           |

*v* = very*s* = strong*m* = medium*w* = weak

$$*f_{\text{Hf}} = 0.88 \times 10^{-12} \text{ cm.}; \quad f_{\text{D}} = 0.65 \times 10^{-12} \text{ cm.}$$

$$R = \sum |I_o - I_c| \div \sum I_o = 0.069.$$

\* The value used here for the hafnium scattering amplitude was calculated from diffraction patterns of both HfD<sub>1.628</sub> and HfD<sub>1.983</sub> containing many more peaks than used before, and is, therefore, more precise than the approximate value reported previously (Sidhu, 1954a).

Table 2. *Interplanar spacings (d), calculated and observed X-ray and neutron diffraction relative intensities (I/I<sub>0</sub>) for HfD<sub>1.983</sub>*

| <i>hkl</i><br>(f.c.t.) | <i>d</i> (Å) | X-rays                          |                                | Neutrons                        |                                |
|------------------------|--------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|
|                        |              | <i>I/I</i> <sub>0</sub> (calc.) | <i>I/I</i> <sub>0</sub> (obs.) | <i>I/I</i> <sub>0</sub> (calc.) | <i>I/I</i> <sub>0</sub> (obs.) |
| 111                    | 2.70         | 100.0                           | <i>vs</i>                      | 39.3                            | 39.3                           |
| 200                    | 2.45         | 37.4                            | <i>s</i>                       | 3.6                             | 3.7                            |
| 002                    | 2.173        | 13.1                            | <i>m</i>                       | 1.5                             | —                              |
| 220                    | 1.728        | 12.8                            | <i>m</i>                       | 61.7                            | 63.0                           |
| 202                    | 1.624        | 20.7                            | <i>m</i> +                     | 100.0                           | 100.0                          |
| 311                    | 1.457        | 29.3                            | <i>s</i>                       | 23.4                            | 24.4                           |
| 222                    | 1.354        | 11.8                            | <i>m</i>                       | 2.1                             | 14.8                           |
| 113                    | 1.336        | 11.5                            | <i>m</i>                       | 9.9                             |                                |
| 400                    | 1.221        | 4.7                             | <i>w</i>                       | 25.0                            | 24.4                           |
| 331                    | 1.114        | 8.7                             | <i>m</i> —                     | 6.7                             | 14.8                           |
| 420                    | 1.093        | 8.7                             | <i>m</i> —                     | 1.5                             |                                |
| 004                    | 1.086        | 2.2                             | <i>vw</i>                      | 10.0                            |                                |
| 402                    | 1.065        | 8.9                             | <i>w</i> +                     | 1.4                             | 14.1                           |
| 313                    | 1.058        | 18.3                            | <i>m</i> +                     | 12.5                            |                                |
| 204                    | 0.993        | 10.7                            | <i>m</i>                       | 1.3                             | 68.9                           |
| 422                    | 0.978        | 22.8                            | <i>m</i> +                     | 66.2                            |                                |
| 511                    | 0.937        | 15.6                            | <i>m</i>                       | 10.2                            | 58.2                           |
| 224                    | 0.921        | 20.0                            | <i>m</i> +                     | 30.1                            |                                |
| 333                    | 0.903        | 35.6                            | <i>s</i>                       | 4.8                             |                                |
| 440                    | 0.863        | —                               | —                              | 14.0                            | 15.1                           |
| 115                    | 0.853        | —                               | —                              | 4.5                             |                                |
| 531                    | 0.822        | —                               | —                              | 8.6                             | 37.0                           |
| 404                    | 0.817        | —                               | —                              | 25.9                            |                                |
| 424                    | 0.766        | —                               | —                              | 50.5                            | 58.7                           |

$$R = 0.072.$$

Table 3. Structure constants of Hf, HfD<sub>1.628</sub>, and HfD<sub>1.983</sub>

| Composition          | Structure                | Lattice parameters  | Interatomic distances (Å)   | Volume of unit cell (10 <sup>-24</sup> cm. <sup>3</sup> ) | Calculated density (g.cm. <sup>-3</sup> ) |
|----------------------|--------------------------|---|---|---|---|
| Hf                   | Hexagonal                | $a_0 = 3.198 \pm 0.003 \text{ \AA}$<br>$c_0 = 5.055 \pm 0.003 \text{ \AA}$<br>$c_0/a_0 = 1.581$ | About Hf:<br>6 Hf at $3.131 \pm 0.003$<br>6 Hf at $3.198 \pm 0.003$<br>6 Hf at $4.475 \pm 0.003$  | 44.77   | 13.25                                     |
| HfD <sub>1.628</sub> | Face-centered cubic      | $a_0 = 4.680 \pm 0.003 \text{ \AA}$   | About Hf:<br>8 D at $2.026 \pm 0.003$<br>12 Hf at $3.309 \pm 0.003$<br>24 D at $3.880 \pm 0.003$<br><br>About D:<br>4 Hf at $2.026 \pm 0.003$<br>6 D at $2.340 \pm 0.003$<br>12 D at $3.309 \pm 0.003$<br>12 Hf at $3.880 \pm 0.003$<br>8 D at $4.053 \pm 0.003$  | 102.50  | 11.78                                     |
| HfD <sub>1.983</sub> | Face-centered tetragonal | $a_0 = 4.887 \pm 0.003 \text{ \AA}$<br>$c_0 = 4.345 \pm 0.003 \text{ \AA}$<br>$c_0/a_0 = 0.889$ | About Hf:<br>8 D at $2.041 \pm 0.003$<br>8 Hf at $3.270 \pm 0.003$<br>4 Hf at $3.456 \pm 0.003$<br>8 D at $3.688 \pm 0.003$<br>16 D at $4.013 \pm 0.003$<br><br>About D:<br>4 Hf at $2.041 \pm 0.003$<br>2 D at $2.173 \pm 0.003$<br>4 D at $2.444 \pm 0.003$<br>8 D at $3.270 \pm 0.003$<br>4 D at $3.456 \pm 0.003$<br>4 Hf at $3.688 \pm 0.003$<br>8 Hf at $4.013 \pm 0.003$ | 103.77  | 11.69                                     |

mass of the 'crystal atom' or the weighted average mass\* of two types of atoms expressed in atomic mass units.

The specific heat was calculated from the expression

$$C_v = 3R(x)^2 e^x / (e^x - 1)^2, \quad (4)$$

and the vibration frequency from

$$\nu_m = (k/h)\Theta. \quad (5)$$

$R$  in equation (4) is the gas constant.

*Crystal structure of tetragonal phase—HfD<sub>1.983</sub>.*—Positions of hafnium and hydrogen atoms in a body-centered tetragonal unit cell of this phase were determined from X-ray diffraction and low-angle portions of neutron diffraction patterns of the phase, and were employed in explaining the effect on metal-metal bonds of increased concentration of hydrogen in its structure (Sidhu, 1954a). In the present study a complete crystal structure has been determined. To

\* It is realized that to use an 'average mass' in expression (3), the masses of different atoms, in general, should be nearly the same. However, the  $(hkl)$  reflections, for which  $h$ ,  $k$ , and  $l$  are all odd, have contributions from only the Hf atoms, whereas the reflections for which  $h$ ,  $k$  and  $l$  are all even have contributions from both the Hf and D atoms. The values of  $2B$  determined from both sets of reflections agree within experimental error, giving some justification to the use of an 'average mass' for computation purposes and for at least qualitative interpretations.

visualize its relation to face-centered cubic structure of HfD<sub>1.628</sub> more readily, it is described by face-centered tetragonal unit cell and Miller indices.

X-ray and neutron diffraction patterns are given in Fig. 1(B) and the diffraction data in Table 2. The relative intensities were calculated by equations (1) and (2) and the structure factors by the expression

$$|F_{hkl}| = \{1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\} \times \{f_{\text{Hf}} + 1.983 f_{\text{D}} \cos \frac{1}{2}\pi(h+k+l)\}.$$

The structure constants for HfD<sub>1.628</sub> and HfD<sub>1.983</sub>, including lattice parameters, interatomic distances, volume of unit cell and calculated density are tabulated in Table 3. The constants of hafnium are included for comparison.

#### Titanium-hydrogen system

X-ray diffraction studies of titanium-hydrogen system have shown that at room temperature the system consists of at least three regions of concentration of hydrogen:  $\alpha$ -titanium, followed by a transformation region, in which  $\alpha$ -titanium transforms to a face-centered cubic hydride as additional hydrogen is added to the system, and a single face-centered cubic phase. The composition range of the single homogeneous cubic phase is approximately 60–66 atomic % hydrogen or deuterium (TiD<sub>1.50–1.94</sub>). With

Table 4. *Interplanar spacings (d), calculated and observed X-ray and neutron diffraction relative intensities (I/I<sub>0</sub>) for TiD<sub>1.971</sub>*

| hkl      | d (Å) | X-rays                   |                         | Neutrons                 |                         |
|----------|-------|--------------------------|-------------------------|--------------------------|-------------------------|
|          |       | I/I <sub>0</sub> (calc.) | I/I <sub>0</sub> (obs.) | I/I <sub>0</sub> (calc.) | I/I <sub>0</sub> (obs.) |
| 111      | 2.563 | 100.0                    | vs                      | 9.5                      | 9.2                     |
| 200      | 2.221 | 43.0                     | s                       | 100.0                    | 100.0                   |
| 220      | 1.569 | 29.1                     | m+                      | 27.9                     | 24.0                    |
| 311      | 1.339 | 29.3                     | m+                      | 6.9                      | 6.3                     |
| 222      | 1.281 | 7.9                      | w                       | 39.6                     | 40.0                    |
| 400      | 1.112 | 4.0                      | vw                      | 6.3                      | 4.0                     |
| 331      | 1.019 | 13.0                     | m                       | 3.6                      | 80.0                    |
| 420      | 0.993 | 12.3                     | m                       | 65.3                     |                         |
| 422      | 0.906 | 13.5                     | m                       | 15.6                     |                         |
| 333, 511 | 0.854 | 21.1                     | m+                      | 3.2                      | 1.4                     |
| 442, 600 | —     | —                        | —                       | 49.0                     | 40.0                    |

$$f_{\text{Ti}} = -0.38 \times 10^{-12} \text{ cm.}; f_{\text{D}} = 0.65 \times 10^{-12} \text{ cm.}$$

$$R = 0.098.$$

Table 5. *Structure constants of Ti and TiD<sub>1.971</sub>*

| Composition          | Structure           | Lattice parameters  | Interatomic distances (Å)  | Volume of unit cell (10 <sup>-24</sup> cm. <sup>3</sup> ) | Calculated density (g.cm. <sup>-3</sup> ) |
|----------------------|---------------------|---|--|---|---|
| Ti                   | Hexagonal           | $a_0 = 2.952 \pm 0.002 \text{ Å}$<br>$c_0 = 4.689 \pm 0.002 \text{ Å}$<br>$c_0/a_0 = 1.588$ | About Ti:<br>6 Ti at $2.899 \pm 0.002$<br>6 Ti at $2.952 \pm 0.002$<br>6 Ti at $4.137 \pm 0.002$   | 35.39   | 4.50                                      |
| TiD <sub>1.971</sub> | Face-centered cubic | $a_0 = 4.440 \pm 0.003 \text{ Å}$   | About Ti:<br>8 D at $1.923 \pm 0.003$<br>12 Ti at $3.140 \pm 0.003$<br>24 D at $3.681 \pm 0.003$<br><br>About D:<br>4 Ti at $1.923 \pm 0.003$<br>6 D at $2.220 \pm 0.003$<br>12 D at $3.140 \pm 0.003$<br>12 Ti at $3.681 \pm 0.003$<br>8 D at $3.845 \pm 0.003$ | 87.53   | 3.94                                      |

Table 6. *Some physical constants of hafnium deuterides*

| Composition          | 2B (Å <sup>2</sup> ) | $\bar{\mu}$ (Å) | $M_a$ (a.m.u.) | $\Theta$ (°K.) | $C_v$ (cal./mole °C.) | $\nu_m$ (vibrations/sec.) |
|----------------------|----------------------|-----------------|----------------|----------------|-----------------------|---------------------------|
| HfD <sub>1.628</sub> | 1.68                 | 0.103           | 69.21          | 244            | 5.64                  | $5.08 \times 10^{12}$     |
| HfD <sub>1.993</sub> | 1.06                 | 0.082           | 61.21          | 329            | 5.40                  | $6.86 \times 10^{12}$     |

increasing concentration of gas in this phase, however, there is a definite broadening of diffraction lines originating from (200), (220), (311), (400) etc. planes, while (111) and (222) reflections remain sharp. Hence, as the composition approaches TiD<sub>2</sub>, the cubic unit cell deforms to a face-centered tetragonal cell.

*Crystal structure of TiD<sub>1.971</sub>.*—X-ray and neutron diffraction patterns of titanium dideuteride are given in Fig. 1(C) and the diffraction data in Table 4. The structure of this phase is face-centered cubic, again of the CaF<sub>2</sub>-type, which confirms the structure reported by Hägg for the β-phase of the Ti-H system. Relative intensities and structure factors were calculated similarly as for HfD<sub>1.628</sub>. The structure constants for Ti and TiD<sub>1.971</sub> are given in Table 5.

## Discussion

The structure of the cubic phase of hafnium-deuterium system (Fig. 2) as derived from neutron and X-ray diffraction data is of the CaF<sub>2</sub> type. The shortest metal-metal atom distance in it is  $a_0/\sqrt{2}$  or  $3.309 \pm 0.003 \text{ Å}$ , and as shown in Table 3, this distance is larger by 3.5–5.7% than the interatomic distances in the pure metal. The nearest neighbors of each metal, however, are the deuterium atoms that are at a distance of  $a_0 \cdot \sqrt{3}/4$  or  $2.026 \pm 0.003 \text{ Å}$ . If all normal sites for deuterium atoms were occupied each metal atom would be surrounded by eight deuterium atoms. Since the transformation of the cubic phase to the tetragonal phase of this system takes place in the region of 64–65

atomic % deuterium (HfD<sub>1.78-1.86</sub>) it is apparent that the normal deuterium sites in the cubic phase are never filled. The structure, therefore, is typically a defect structure.

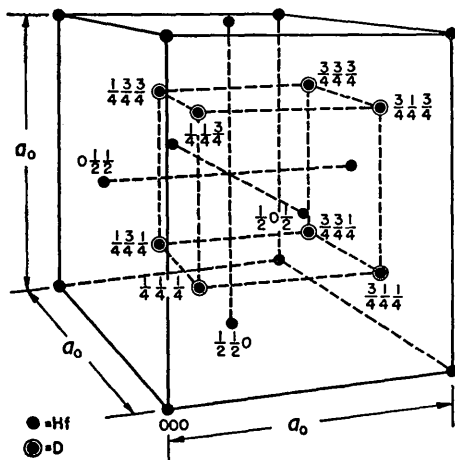


Fig. 2. Face-centered cubic unit cell of HfD<sub>1.628</sub> structure.

In the composition range of the cubic phase, 62–64.5 atomic % deuterium (HfD<sub>1.63-1.81</sub>) the lattice parameter  $a_0$  appears to remain constant. At the transformation point, however, there is a first-order change. The fluorite structure of the cubic phase transforms to a face-centered tetragonal structure with compression along one axis and expansion along the other two. This provides for shorter metal-metal atom bonds. As shown in Table 3, the distance of nearest approach of metal-metal atoms decreases from  $3.309 \pm 0.003$  Å in the cubic phase to  $3.270 \pm 0.003$  Å in the tetragonal phase. The strengthening of atomic bonds in the tetragonal structure on the whole is evidenced from the changes produced in some of the physical properties of the two structures, as given in Table 6. For example, both the Debye characteristic temperature and the vibrational frequency of atoms in the tetragonal structure are higher than those in the cubic structure.

As additional deuterium is absorbed by the sample in the tetragonal phase and the composition approaches HfD<sub>2</sub>, there is a further distortion of the tetragonal unit cell, causing a decrease in  $c_0$  and an increase in  $a_0$ . This has been ascribed to formation of additional hafnium-deuterium bonds (Sidhu, 1954a) that strengthen the short bonds,  $\frac{1}{2}(a_0^2 + c_0^2)$ , along the [101] direction and weaken the metal-metal bonds in the (001) plane. The volume of the unit cell of the distorted fluorite structure is larger than that of the cubic cell. The number of atom sites per each cell, however, is the same.

X-ray diffraction studies of the zirconium-hydrogen system have shown that the phases formed in this system are analogous to those in the hafnium-hydrogen system. The crystal structure of ZrD<sub>2</sub> determined by X-ray and neutron diffraction techniques is similar to

that of HfD<sub>1.983</sub> (Rundle, Shull & Wollan, 1952). The crystal structures of other corresponding hydrides in the two systems are also similar (Sidhu, 1954c). It may be inferred, therefore, that the conclusions drawn from the study of the hafnium-hydrogen system apply equally to the zirconium-hydrogen system.

The titanium-hydrides and deuterides\*, prepared under identical conditions as for those of hafnium and zirconium, show that the face-centered cubic phase in this system extends over a wider range of compositions and does not seem to transform to the tetragonal phase as readily as in the other two systems†. Some of the physical properties of TiD<sub>1.971</sub>, analogous to those of HfD<sub>1.628</sub>, are as follows: the root-mean-square displacement,  $\bar{\mu}$ , is 0.120 Å; the mass of the 'crystal atom',  $M_w$ , is 17.46 a.m.u.; the characteristic temperature,  $\Theta$ , is 428° K., and the vibrational frequency,  $\nu_m$ , is  $8.92 \times 10^{12}$  vibrations/sec. If high characteristic temperature and vibration frequency are taken as an indication of a strongly bound substance, it would appear that the TiD<sub>1.971</sub> cubic structure is more strongly bound than that of HfD<sub>1.628</sub>, as the values of these physical properties are greater than can be accounted for by mass differences alone. This may account for the lack of ready transformation to the tetragonal structure.

### Summary and conclusions

Studies of typical metal-hydrogen systems have been made by combined methods of neutron and X-ray diffraction. An increased intensity of neutron flux from the heavy water reactor, a wide range  $2\theta$  Bragg angle covered by the present Argonne Neutron Diffraction Spectrometer and an automatic recording of neutron diffraction patterns made it possible to obtain quantitative data that led to comprehensive interpretations. By reducing the size of the incident beam and consequently the amount of the specimen used, the resolution of the neutron diffraction peaks was improved. The exposure time to obtain a complete neutron pattern was comparable to that for the X-ray diffraction pattern. Although the neutron diffraction patterns presented here were obtained with wavelength,  $\lambda = 1.315$  Å, it could be reduced to 1 Å and thus many additional diffraction peaks could be observed. The main features of the techniques employed, the results obtained, and the interpretations made may be summarized as follows:

1. It was found necessary to use only pure metals and purified gas. The metal had to be rolled into thin

\* The titanium hydrides and deuterides were prepared with due knowledge of the difficulties that previous investigators had experienced (Gibb & Kruschwitz, 1950). For the study made here, well reacted homogeneous samples were prepared from pure metal and purified gas.

† It is reported that this deformation is much more pronounced below room temperature (private communication, C. G. Shull, Brookhaven National Laboratory).

sheets to obtain well reacted homogeneous samples. In the thick metal samples a gradient of gas concentration was observed, the greatest concentration being at the surface. The same sample contained hydrides and unreacted metal. Long annealing and degassing of thin metal strips at approximately 1100° C. in no way affected the absorption of hydrogen by the metal. The concept that in order to establish an entirely normal solubility equilibrium with hydrogen, a metal must be strained rather than thoroughly annealed (Smith, 1951) seems to be untenable in this case.

2. Vanadium has a coherent scattering amplitude (Bacon, 1955)  $f = -0.053 \times 10^{-12}$  cm. and essentially gives no diffraction peaks. The polycrystalline samples studied here with neutron diffraction, therefore, were contained in thin vanadium tube holders machined from solid metal rods. As an improvement over vanadium specimen holders, however, an alloy containing 62 atomic % titanium and 38 atomic % zirconium was developed, the scattering lengths of the two metals being such that the resultant coherent scattering amplitude is practically zero.

3. In the solid-state conversion of the metal to the hydride, the bonds formed between hydrogen and metal atoms readily displace the metal atoms from their normal positions in the lattice without impairment of the metal structure, the metal-hydrogen bonds being stronger than metal-metal atom bonds. In the transformation of a metal into a hydride or of one metal hydride into another, both kinds of phase transitions are observed. The first kind or the first order, in which energy, volume, and crystal structure change discontinuously, is evidenced by the abrupt change that takes place when face-centered cubic structure in hafnium- and zirconium-hydrogen systems transforms to face-centered tetragonal structure; the second kind or the continuous transitions, in which energy and volume change continuously, is the change observed when deformed cubic structure in hafnium-hydrogen system deforms to a single face-centered cubic phase (Sidhu & McGuire, 1952) and face-centered cubic phase of titanium-hydrogen system deforms to face-centered tetragonal structure.

4. In the formation of these hydrides the hexagonal structure of metals is completely changed, first to a cubic and then to a tetragonal structure with unit cells of different dimensions, volumes, densities, and containing larger number of atoms in them. In every respect these structures are of new compounds. However, as in the case of the cubic phase, all atom sites in the unit cell are seldom filled, and as a result the compounds formed are non-stoichiometric. Even the tetragonal phases in the hafnium- and the zirconium-hydrogen systems are formed below the stoichiometric ratios of  $\text{HfH}_2$  and  $\text{ZrH}_2$ , and they approach these compositions only when additional hydrogen is added to the systems. The range of variable compositions is considerable.

5. As given in Tables 3 and 5, hydrogen or deuterium atoms occupy definite positions in the lattice with respect to one another and to the metal atoms. The nearest neighbors of each atom, metal or gas, are the unlike atoms. The distances between metal-metal atoms in the hydrides are longer than those in the pure metals, and those between hydrogen-hydrogen or deuterium-deuterium atoms are longer than nuclear distances (Mark, 1940) of diatomic molecules of  $\text{H}\cdot\text{H}$  or  $\text{D}\cdot\text{D}$  ( $d = 0.75$  Å). For the size of site available to a gas atom to occupy in these hydrides, an indication of a smaller size hydrogen (loss of electron) is evident. It must enter, apparently, as an ion rather than an atom (Isenberg, 1950).

6. Another striking characteristic of these hydrides is that the first pure hydride phase formed in the three systems favors the  $\text{CaF}_2$ -type structure with a fraction of the atom sites unfilled. The metal-hydrogen bonds in this structure are anisotropic, and their directional nature becomes pronounced when the face-centered cubic structure transforms to the face-centered tetragonal structure with contraction along one axis and expansion along the other two. The brittleness observed in these hydrides may be ascribed to these directional bonds rather than to the mechanical defects, such as the presence of pores, microcracks, fissures, intergranular holes, etc., so often mentioned in the literature (Gibb & Kruschwitz, 1950; *Metals Handbook*, 1948). It seems that the causes of embrittlement of metals by gases in general lie in the type of bonds formed (Rundle, 1948) in a given metal-gas system rather than in its macroscopic appearance.

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