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The Effect on Metal–Metal Bonds of Increased Concentration of Hydrogen in Hafnium Dihydride

BY S. S. SIDHU

Argonne National Laboratory, Lemont, Illinois, U.S.A.

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A tetragonal unit cell of hafnium dihydride is formed at a composition of $HfH_{1.87}$. Each metal atom has 12 Hf atoms as its neighbors, 8 at a distance 3·289±0·002 Å and 4 at 3·461±0·002 Å; they constitute short and long metal–metal bonds respectively. As the concentration of hydrogen atoms is increased, the dihydride structure exhibits anisotropic changes; a_0 increases and c_0 decreases. It is shown that the anisotropy arises from the additional metal–gas bonding, which strengthens the short and weakens the long metal–metal bonds.

Introduction

Hafnium dihydrides formed in the composition range of $HfH_{1.87-2.10}$ crystallize in a deformed fluorite-type tetragonal structure contracted along the *c* axis. As the concentration of hydrogen increases, the symmetry of the face-centered tetragonal unit cell remains the same but its lattice parameters change; a_0 increases and c_0 decreases. The volume of the unit cell also increases. This paper presents experimental evidence of these changes and their relation to metal–metal bonds in the dihydride.

Experimental procedure

The samples were prepared by heating and outgassing the metal in an evacuated quartz tube at 1100° C. The temperature was then lowered to 1000° C. and a measured volume of purified gas was admitted into the tube at a known pressure. The volume of gas was in excess of the theoretical absorption for the dihydride. Most of the absorption of gas took place at 700–800° C. The sample $HfH_{1.98}$ was cooled from 750° to 350° C. at a rate of 2·5° C. per min., annealed at 350° C. for 24 hr. at a decomposition pressure of the dihydride, and then cooled to room temperature in the furnace in 1½ hr.

The sample $HfH_{2.10}$ was cooled from 750° to 350° C. at a slow rate of about 0·4° C. per min., annealed at 350° C. for 48 hr., cooled further to 225° C. at the above rate and then cooled in the furnace in 1½hr. The gas pressure in the tube during cooling from 350° C. to room temperature varied from 170 to 150 mm. The hafnium deuteride sample was prepared the same way as $HfH_{2.10}$. The deuterium gas used was 99·5% pure and was obtained from Stuart Oxygen Company. Compositions of the samples were calculated from the weight of the metal and the volume of the observed hydrogen.

Results

The tetragonal structure of hafnium dihydride, as reported previously (Sidhu & McGuire, 1952), is isomorphous with that of zirconium dihydride (Rundle, Shull & Wollan, 1952*a*, *b*; Hägg, 1930). When the axes of the face-centered tetragonal cell are transformed to body-centered tetragonal, the unit cell (Fig. 1) contains 2 HfH_2 with:

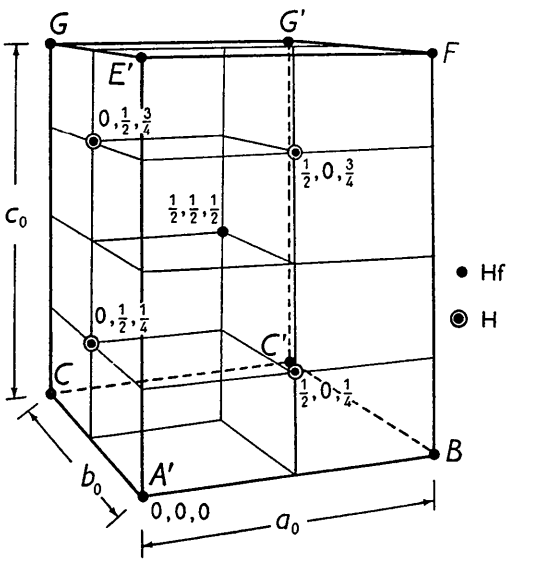

Fig. 1. Body-centered tetragonal unit cell of HfH_2 structure.

Hf: 0, 0, 0; ½, ½, ½.
H: 0, ½, ¼; 0, ½, ¾; ½, 0, ¼; ½, 0, ¾.

The positions of hafnium atoms were determined from X-ray powdered patterns, and those of deuterium or hydrogen from neutron diffraction patterns (Fig. 2). The calculated and the observed relative intensities for X-ray and neutron scattering are given in Table 1.

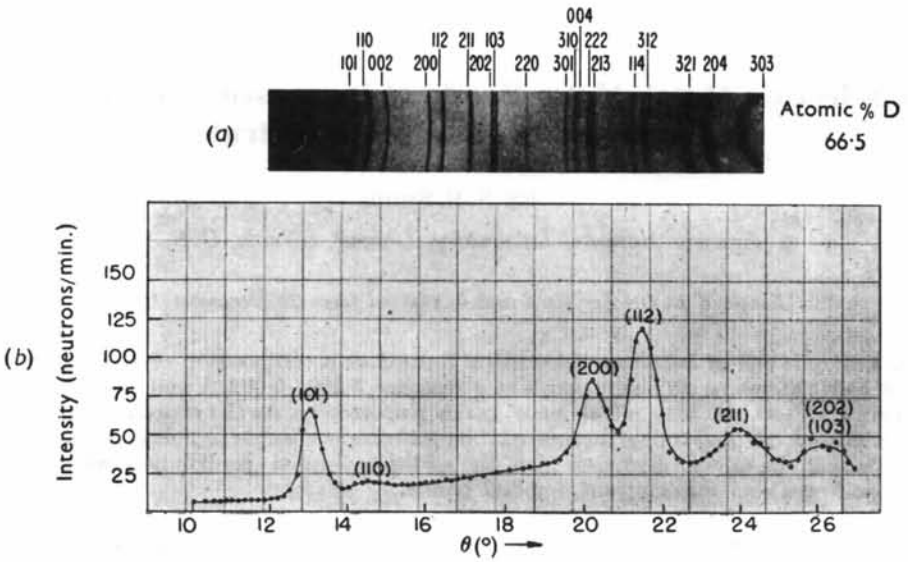

Fig. 2. (*a*) X-ray diffraction pattern of HfD_2 (Co $K\alpha$ radiation; camera diameter 114·6 mm.). (*b*) Low-angle portion of neutron diffraction pattern of HfD_2.

Table 1. *Calculated and observed X-ray and neutron diffraction relative intensities (I/I_0) for* HfD_2

	X-rays		Neutrons	
hkl (B.-c.t.)	I/I_0* (Calc.)	I/I_0 (Obs.)	I/I_0 (Calc.)	I/I_0 (Obs.)
101	100·0	*vs*	47·4	45
110	37·4	*s*	0·6	—
002	13·1	*m*	0·2	—
200	12·8	*m*	56·0	56
112	20·7	*m*+	100·0	100
211	29·3	*s*	30·2	34
202	11·8	*m*	13·6	12
103	11·5	*m*		
220	4·7	*w*		
301	8·7	*m*−		
310	8·7	*m*−		
004	2·2	*vw*		
222	8·9	*w*+		
213	18·3	*m*+		
114	10·7	*m*		
312	22·8	*m*+		
321	15·6	*m*		
204	20·0	*m*+		
303	35·6	*s*		

v = very; *s* = strong; *m* = medium; *w* = weak.
B.-c.t. = body-centered tetragonal.

* X-ray diffraction intensities were calculated by using atomic scattering factors of Hf only; neutron diffraction intensities were calculated by using scattering amplitudes of both Hf and D; the intensities were not corrected by temperature factor.

For a cylindrical sample the intensities were calculated from the following equations:

$$\text{For X-rays, } I \propto |F|^2 m \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}.$$

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

The neutron scattering amplitude for hafnium was calculated from the observed intensities of diffraction peaks and was found to be approximately $+0{\cdot}97\times10^{-12}$ cm. It was based on the scattering amplitude of deuterium as $0{\cdot}65\times10^{-12}$ cm.

X-ray diffraction patterns of $HfH_{1\cdot98}$ and $HfH_{2\cdot10}$, (Fig. 3) show a marked contrast. The interplanar spacings (Table 2) of planes of high *l* indices, such as

Table 2. *Diffraction data for* $HfH_{1\cdot98}$ *and* $HfH_{2\cdot10}$

	$HfH_{1\cdot98}$		$HfH_{2\cdot10}$	
hkl (B.-c.t.)	*d* (Å)	I/I_0	*d* (Å)	I/I_0
101	2·72	*vs*	2·71	*vs*
110	2·45	*s*	2·46	*s*
002	2·199	*m*	2·181	*m*
200	1·732	*m*	1·737	*m*
112	1·637	*m*+	1·633	*s*
211	1·460	*s*	1·466	*s*
202	1·361	*m*	1·359	*m*
103	1·351	*w*+	1·344	*m*−
220	1·223	*w*	1·230	*w*
301	1·116	*m*	1·121	*m*
310	1·093	*m*−	1·102	*m*−
004	—	—	1·091	*vw*
222	1·069	*vw*	1·072	*w*+
213	1·065	*m*+	1·062	*m*
114	1·004	*w*	0·997	*w*
312	0·979	*m*+	0·982	*m*
321	0·937	*m*	0·941	*m*
204	0·928	*m*	0·924	*m*+
303	0·906	*s*	0·906	*s*

(002), (103), (004), (204), etc. are considerably decreased and those of high *hk* indices are generally increased. The structure constants calculated from the diffraction data of the two hydrides and of hafnium metal are given in Table 3.

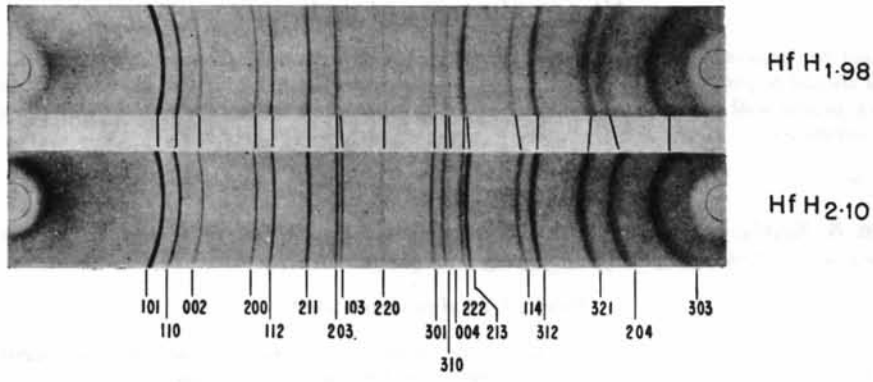

Fig. 3. X-ray diffraction pattern of hafnium dihydrides (Co $K\alpha$ radiation; camera diameter 114·6 mm.).

Table 3. *Structure constants of* Hf, $HfH_{1.98}$ *and* $HfH_{2.10}$

Composition	Structure	Lattice parameters	Interatomic distances (Å)	Volume of unit cell (10^{-24} cm.^{3})	Calculated density (g.cm.$^{-3}$)
Hf	Hexagonal	$a_0 = 3{\cdot}198 \pm 0{\cdot}003$ Å $c_0 = 5{\cdot}055 \pm 0{\cdot}003$ Å $c_0/a_0 = 1{\cdot}581$	About Hf: 6 Hf at $3{\cdot}198 \pm 0{\cdot}003$ 6 Hf at $3{\cdot}131 \pm 0{\cdot}003$	44·77	13·25
$HfH_{1.98}$	Tetragonal	$a_0 = 3{\cdot}461 \pm 0{\cdot}002$ Å $c_0 = 4{\cdot}395 \pm 0{\cdot}002$ Å $c_0/a_0 = 1{\cdot}270$	About H: 4 Hf at $2{\cdot}050 \pm 0{\cdot}002$ About Hf: 8 H at $2{\cdot}050 \pm 0{\cdot}002$ 8 Hf at $3{\cdot}289 \pm 0{\cdot}002$ 4 Hf at $3{\cdot}461 \pm 0{\cdot}002$	52·65	11·39
$HfH_{2.10}$	Tetragonal	$a_0 = 3{\cdot}478 \pm 0{\cdot}002$ Å $c_0 = 4{\cdot}361 \pm 0{\cdot}002$ Å $c_0/a_0 = 1{\cdot}254$	About H: 4 Hf at $2{\cdot}053 \pm 0{\cdot}002$ About Hf: 8 H at $2{\cdot}053 \pm 0{\cdot}002$ 8 Hf at $3{\cdot}287 \pm 0{\cdot}002$ 4 Hf at $3{\cdot}478 \pm 0{\cdot}002$	52·75	11·37

Discussion

In the crystal structure of hafnium metal (Table 3) each atom is surrounded by 12 like atoms, 6 at a distance 3·198 Å and the other 6 at 3·131 Å. The metal–metal bonds are essentially of the same length. In the lattice of hafnium dihydride, each metal atom is also surrounded by 12 like atoms, but in this case 8 hafnium atoms are at 3·289 Å, the distance of nearest approach of metal–metal atoms, and 4 hafnium atoms at 3·461 Å or a_0 in the (001) plane. These give rise to short and long metal–metal bonds respectively in the HfH_2 structure. In addition each metal atom is surrounded by 8 hydrogen atoms that are located in the flattened tetrahedra of metal atoms equidistant from 4 hafnium.

As the unit cell is formed at $HfH_{1.87}$, all normal sites for hydrogen atoms do not seem to be occupied. Absorption of additional hydrogen in samples prepared by long annealing and slow cooling at sufficient gas pressure forms additional Hf–H bonds. These bonds apparently drain electrons from the metal–metal bonds in the (001) plane, thus weakening the latter and causing an increase in a_0. On the other hand there is general strengthening of the short bonds; they either decrease or remain practically the same in length. As a result there is a further compression of the structure along the c axis, causing a decrease in c_0. The increase Δa_0 and the decrease Δc_0 are related by the expression: $\Delta a_0 = \frac{1}{2}(c_0/a_0)|-\Delta c_0|$.

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