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The lattice constants of thorium dihydride.*

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Thorium dihydride has been reported by Rundle, Shull & Wollan (1952) to be body-centered tetragonal with

$$a_0 = 4{\cdot}10 \pm 0{\cdot}03 \text{ and } c_0 = 5{\cdot}03 \pm 0{\cdot}03 \text{ Å} .$$

Some unaccounted-for lines were observed in the X-ray pattern, and were attributed to unidentified impurities. The X-ray data are tabulated in a report by Rundle, Wilson, Nottorf & Raeuchle (1948). This tabulation indicates that the value of a_0 should have been reported as 4·06 Å, and does not list the 220, 310 and 114 maxima.

In order to obtain more accurate values of the lattice constants, and to check on the unidentified and unlisted lines, a series of five samples of thorium hydride have been prepared, in the overall composition range $ThH_{1\cdot 93}$ to $ThH_{1\cdot 73}$. Although a body-centered tetragonal (b.c.t.) unit cell conforms to standard crystallographic usage, the thorium dihydride phase will be considered here to be face-centered tetragonal (f.c.t.) since there is also a face-centered cubic (f.c.c.) phase, and the relationship between the two phases is thus made more evident.

Crystal-bar thorium was used, containing 0·02 wt.% (*w*/*o*) oxygen, as indicated by each of two vacuum-fusion determinations. This corresponds to 0·16 *w*/*o* ThO_2. Hydrogen was obtained from the dissociation of uranium hydride, or was purified by being passed over hot uranium metal. The hydrides were prepared on a vacuum line, with the amount of hydrogen absorption or removal measured volumetrically. After a preliminary outgassing at 600 °C., the thorium sample reacted with hydrogen at 350 °C., and was heated to about 530 °C. and allowed to cool. X-ray samples were prepared by transferring about 5 mg. of the powdered hydride to thin-walled pyrex capillaries having an I.D. of about 0·5 mm. in an argon-filled dry-box, with subsequent evacuation and sealing of the capillaries. Samples less rich in hydrogen were prepared by returning the hydride sample, contained in the closed reaction vessel, to the vacuum line, and heating it to 700 °C. or higher to remove the desired amount of hydrogen. The duration of heating amounted to 1 hour for the 2nd and 3rd samples, 5 hours for the 4th sample, and 7 hours for the 5th sample. This last sample was heated as high as 750 °C. Cooling to room temperature required 5 or 6 hours, and the samples were usually allowed to stand over-night while this occurred. In each step about 3% of the hydrogen contained in the sample was removed, and approximately the same amount of gas was reabsorbed by the sample from the reaction vessel volume on cooling.

Table 1. *Lattice constants of the face-centered tetragonal thorium dihydride phase*

H : Th	a_0	c_0
1·93 ± 0·02	5·7348 ± 0·0003 Å	4·9706 ± 0·0004 Å
1·88 ± 0·02	5·7248 ± 0·0003	4·9946 ± 0·0004
1·84	5·7240 ± 0·0008	5·0052 ± 0·0010
1·79	5·7188 ± 0·0003	5·0007 ± 0·0003
1·73	5·7154 ± 0·0008	5·0096 ± 0·0010

Table 2. *Diffraction data for the face-centered tetragonal thorium dihydride phase of composition* $ThH_{1\cdot 93}$

hk	$1/d^2$ (calc.)(1)	$1/d^2$ (obs.)	*v*(2)	*I* (obs.)(3)	*I* (calc.)
111	0·1013	0·1035		*vs*	100·0
200	0·1216	0·1249		*m*	39·2
002	0·1619	0·1641		*vw*	13·6
220	0·2432	0·2466		*w*	15·2
202	0·2835	0·2865		*m* +	24·1
311	0·3445	0·3479		*s*	35·6
222	0·4051	0·4082		*m*	13·6
113	0·4251	0·4285		*m* −	12·6
400	0·4865	0·4923		*vvw*	5·0
331	0·5878	0·5913	+ 0·00003	*w*	7·4
420	0·6081	0·6128	− 0·0006	*vw*	7·0
004	0·6476	0·6508		*w*	1·6
402	0·6484				6·3
313	0·6683	0·6709	+ 0·0006	*m*	12·1
204	0·7692	0·7729		*s*	5·0
422	0·7700				9·9
511	0·8310	0·8335	+ 0·0005	*m*	9·0
224	0·8908	0·8936	+ 0·0002	*w*	4·2
333	0·9116	0·9149	− 0·0002	*w*	4·1
440	0·9730	0·9768	− 0·0005	*vvw*	2·0
115(4)	1·0727	1·0773		*m* +	3·9
531	1·0743				7·9
600	1·0946	. . .		. . .	1·9
404	1·1341	1·1379		*m* −	3·9
442	1·1349				3·9
513	1·1548	1·1580	− 0·0006	*w*	7·9
620	1·2163	1·2192	− 0·0005	*vvw*	4·1
424	1·2557	1·2584		*s*	8·4
602	1·2565				4·2
315	1·3159	1·3177	− 0·00007	*m* −	8·9
622	1·3782	1·3775	+ 0·0013	*m* −	9·7
533	1·3981	1·3984	+ 0·0006	*m* +	10·0
006	1·4571	. . .		. . .	1·4
335(5)	1·5592	1·5639		*vs*	7·9
551	1·5608				7·9
711	1·5608				15·8
206	1·5787	Not read		. . .	8·6
640	1·5811				8·6
444	1·6206	1·6210	− 0·0007	*s*	11·1

(1) Calc. using least-squares cell constants before rounding-off:

$$1/d^2 = (h^2 + k^2)/(5{\cdot}7348)^2 + l^2/(4{\cdot}9706)^2 .$$

(2) $v = \sin^2\theta(\text{calc.}) - \sin^2\theta(\text{obs.}) + 0{\cdot}000717(1/\sin\theta + 1/\theta)\sin^2 2\theta$, from the least-squares computation.

(3) *s* = strong, *m* = moderate, *w* = weak, *v* = very.

(4) Lines beyond this point become increasingly diffuse.

(5) Lines beyond this point are Cu $K\alpha_1$ lines; prior lines read as Cu $K\alpha$ lines.

A vacuum-fusion analysis of the final hydride sample of composition $ThH_{1\cdot 73}$ was carried out after the sample had been stored in a screw-capped vial for about 5 months and had undergone considerable exposure to the atmosphere. This analysis showed 0·20 and 0·19 *w*/*o* oxygen in two determinations, corresponding to about 1·6 *w*/*o* ThO_2. However, the oxygen content of the hydride

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samples used for preparation of the X-ray powder patterns is considered to be more nearly that given above for the metal itself, since the hydride was not exposed to the air during the process of preparation of the samples.

Debye–Scherrer patterns were prepared using a 114·6-mm. diameter Straumanis-type camera, with Ni-filtered Cu radiation (λ for Cu $K\alpha = 1{\cdot}5418$ Å, λ for Cu $K\alpha_1 = 1{\cdot}54051$ Å). Corrections were made for film shrinkage, and line intensities were estimated visually.

The two samples richest in hydrogen gave X-ray diffraction patterns corresponding to the dihydride phase reported by Rundle, Shull & Wollan (1952). The other three samples also gave patterns showing this phase to be present, but in addition displayed two sets of lines characteristic of f.c.c. lattices. The cell constants corresponding to the f.c.t. thorium dihydride patterns are listed in Table 1. These were obtained by using a least-squares computational method described by Mueller, Heaton & Miller (1960), with application of the Nelson–Riley correction function, using 13 lines lying between values of θ of 36 and 79°. Table 2 contains the observed and calculated X-ray diffraction data for the f.c.t. thorium dihydride sample of composition $ThH_{1{\cdot}93}$. Only lines which are characteristic of the f.c.t. lattice were observed. The lines not listed by Rundle, Wilson, Nottorf & Raeuchle (1948) do appear. The relative intensities were calculated using the usual expression:

$$I \propto F^2p(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)\ .$$

The most reliable values for the cell constants of the f.c.c. phases were obtained for the sample least rich in hydrogen, $ThH_{1{\cdot}73}$, where the most lines were available for a computation similar to that employed for the f.c.t. hydride phase. For this sample the cell constants of the cubic phases were found to be $5{\cdot}4893 \pm 0{\cdot}0002$, and $5{\cdot}0843 \pm 0{\cdot}0007$ Å.* The former cell constant is believed to be that of a f.c.c. thorium hydride, previously reported by Peterson, Westlake & Rexer (1959), who give a value of 5·492 Å. The latter cell constant is characteristic of f.c.c. thorium metal, in which a small proportion of hydrogen is probably dissolved. The intensities of these cubic patterns were relatively weak compared to the f.c.t. dihydride pattern, except for the $ThH_{1{\cdot}73}$ sample, for which the f.c.c. hydride pattern was of comparable intensity to the f.c.t. dihydride pattern. The presence of these other phases of course means that the overall compositions are not an accurate measurement of the actual composition of the f.c.t. hydride phases present in the last three samples, and is also indicative of a non-equilibrium situation.

Peterson, Westlake & Rexer (1959) observed only the pattern of the tetragonal hydride in X-ray diagrams of samples prepared using thorium containing 0·16 and 1·1 *w/o* ThO_2, while hydride samples prepared using metal containing 4·0 and 6·0 *w/o* ThO_2 displayed only the pattern of the cubic hydride. Since these samples were obtained from dissociation pressure experiments in which constancy of pressure was used as a measure of equilibrium, they are certainly more representative of equilibrium conditions than the last three samples prepared here. However, the observation of the pattern of the cubic hydride for samples relatively low in oxygen content in the present work seems to be at variance with the findings of these authors.

If the b.c.t. lattice constants of the dihydride phase reported by Rundle, Shull & Wollan (1952) are converted to f.c.t. lattice constants, they become: $a_0 = 5{\cdot}80$ and $c_0 = 5{\cdot}03$ Å. These values may be compared with the lattice constants found here for the $ThH_{1{\cdot}93}$ sample, which become, after rounding-off: $a_0 = 5{\cdot}735$ and $c_0 = 4{\cdot}971$ Å. There is seen to be a significant difference. Peterson, Westlake & Rexer (1959) have reported lattice constants of $a_0 = 5{\cdot}73$ and $c_0 = 4{\cdot}99$ Å for the f.c.t. unit cell. However, the actual compositions of the samples of thorium hydride used by both these sets of authors may not have exactly corresponded to the composition ThH_2, and it has been demonstrated here that the lattice constants vary with hydrogen content. A further basis for discrepancy between lattice constants reported by different authors, especially when more than one lattice constant is involved, is the method of arriving at the best values of the constants from the observed data. Extrapolation techniques, least-squares methods, systematic error corrections and other factors are of significance, and the lattice constants finally arrived at are dependent upon which methods are used.

The crystal structure of the higher hydride of thorium has been derived by Zachariasen (1953), who assigned to it the formula Th_4H_{15} on the basis of X-ray diffraction data and of the highest composition reported attained, namely, a hydrogen: thorium atomic ratio of 3·62. In the course of the present work two separate preparations of the higher thorium hydride were carried out, on different vacuum lines. In the first preparation the maximum absorption was calculated volumetrically to have reached a hydrogen: thorium atomic ratio of $3{\cdot}76 \pm 0{\cdot}03$, and in the second a ratio of $3{\cdot}73 \pm 0{\cdot}02$. These compositions may be considered to constitute supporting evidence for the correctness of the formula Th_4H_{15} for the higher hydride of thorium. One of these samples was used to prepare an X-ray powder pattern, which was found to be similar to that reported by Zachariasen (1953) for Th_4H_{15}.

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* The precisions expressed here and in Table 1 are standard errors as defined in the computational program. An accuracy of $\pm 0{\cdot}005$ Å for the cell constants is more realistic.