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The Crystal Structure of Thorium and Zirconium Dihydrides by X-ray and Neutron Diffraction*

By R. E. Rundle

Institute for Atomic Research, and Department of Chemistry, Iowa State College, Ames, Iowa, U.S.A.

C. G. Shull and E. O. Wollan

Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

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Thorium forms a tetragonal lower hydride of composition ThH_2. The hydrides ThH_2, ThD_2 and ZrD_2 have been studied by neutron diffraction in order that hydrogen positions could be determined. The hydrides are isomorphous, and have a deformed fluorite structure. Metal–hydrogen distances in thorium hydride are unusually large, as in UH_3.

Thorium and zirconium scattering amplitudes and a revised scattering amplitude for deuterium are reported.

Introduction

ThH_2, discovered during X-ray study of the thorium–hydrogen system, and ZrH_2 (Hägg, 1930) have axes which suggest that they are isomorphous with the reported tetragonal structure of ThC_2 (Stackelberg, 1930). Though ThC_2 is now known to be monoclinic (Hunt & Rundle, 1951) the tetragonal lattices might be interpreted as suggesting H_2 groups for these hydrides, making their structure a matter of considerable interest.

This paper† presents X-ray evidence for the existence of ThH_2, the lattice constants and metal arrangement obtained by X-ray diffraction, and hydrogen positions as determined for both ZrH_2 and ThH_2 by neutron diffraction. In addition, the magnetic susceptibility of ThH_2, which has a bearing on the presence of H_2 groups, was examined.

Phase determination

Thorium has been reported to react with hydrogen to form a phase or phases varying in composition from about ThH_2 to ThH_4 (Winkler, 1891; Matignon & Delepine, 1901; Sieverts & Roell, 1926). However, the earlier evidence for any distinct hydride or hydrides was slight, and most of the earlier investigators favored the concept that the system was of the solid-solution type. No structural information was available in the older literature. Zachariasen (1944) found a higher hydride having a cubic structure unrelated to that of thorium metal. Shortly afterwards, during a systematic X-ray study of the thorium–hydrogen system, we found a lower hydride. It appeared tetragonal, and isomorphous with ZrH_2, and hence was presumed to be ThH_2. The composition study reported in Table 1 confirms this formula.

The limits of solubility of thorium and hydrogen in the hydride are uncertain, since, owing to the small particle size of the hydride, precise determinations of the lattice constant as a function of composition are impossible. However, it appears that large changes in the lattice constants do not occur, and presumably neither solubility is great. ThH_2 may be regarded as a distinct compound.

Table 1. *Thorium–hydrogen system*

Composition	Phases and intensity
$ThH_{0\cdot 92}$	Th (medium)—Tetragonal (medium)
$ThH_{1\cdot 24}$	Th (weak)—Tetragonal (medium)
$ThH_{1\cdot 59}$	Th (weak)—Tetragonal (strong)
$ThH_{1\cdot 78}$	Tetragonal
$ThH_{1\cdot 98}$	Tetragonal
$ThH_{2\cdot 11}$	Tetragonal (strong)—Cubic (very weak)*
$ThH_{2\cdot 49}$	Tetragonal (medium)—Cubic (medium)
$ThH_{2\cdot 56}$	Tetragonal (medium)—Cubic (medium)
$ThH_{2\cdot 96}$	Tetragonal (weak)—Cubic (strong)
$ThH_{3\cdot 12}$	Tetragonal (weak)—Cubic (strong)
$ThH_{3\cdot 53}$	Cubic
$ThH_{3\cdot 62}$	Cubic

* Zachariasen found that the higher hydride was a cubic phase.

Preparation of samples

The thorium hydrides are quite sensitive to oxidation. To prepare samples for X-ray study a known quantity of pure thorium metal was reacted with carefully purified hydrogen within a glass bulb equipped with attached thin-walled glass capillaries. A measured volume of hydrogen was admitted to the system at known pressure and temperature, the reaction initiated by heating to 400–450° C., and the excess hydrogen measured and evacuated.

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* Work performed under contract with Atomic Energy Commission.

† The publication of the data and conclusions in this paper have been delayed considerably because of declassification problems. All of the data were obtained and most of the analysis performed during the middle of 1948 or earlier.

Thorium metal forms a powder when reacted with hydrogen. The powdered hydride of known composition was shaken into the capillaries which were then sealed off the bulb and used for the X-ray studies.

The hydrides of lower compositions were made by removing hydrogen from the higher hydride at about 575° C. in a high vacuum. The hydrogen removed was measured by water displacement from a Mariotte bottle.

Because of the higher coherent scattering amplitude and lower spin diffuse scattering for deuterium, deuterides rather than hydrides are preferred for the neutron-diffraction studies. A sample of ThH_2 was studied, however, and this provided an interesting check on the ThD_2 conclusions, even though the two diffraction patterns were completely different. The deuterides were prepared and used in quite large amounts, so that slight surface oxidation was not so important as in the X-ray studies. They were prepared from thorium and zirconium metals in a vacuum system but were transferred to sample holders in a dry box under carbon dioxide. The thorium metal was pure Ames metal turnings, while the zirconium was Foote Mineral Co. metal reduced to fine turnings (the massive metal would not react under the conditions of the experiment).

The deuterium for the thorium deuteride was prepared by passing the vapor from 99·3 % D_2O, obtained from the A.E.C., over uranium turnings at 700°. The method is due to Newton (Spedding, Newton, Warf, Johnson, Nottorf, Johns & Daane, 1949). In the preparation of zirconium deuteride, 99·5 % deuterium gas supplied by the Stuart Oxygen Company was used. In both preparations the purity of the deuterium was assured by reacting it with uranium turnings at 250° C. and subsequently releasing it by heating the UD_3 thus formed to 500° C.

Structure determination

Lattice constants

X-ray powder diagrams of ThH_2 indicate it to be body-centered tetragonal,

$$a_0 = 4{\cdot}10 \pm 0{\cdot}03, \quad c_0 = 5{\cdot}03 \pm 0{\cdot}03\ \text{Å},$$
$$Z = 2, \quad \rho = 9{\cdot}20\ \text{g.cm.}^{-3}.$$

Our lattice constants for ZrH_2 are

$$a_0 = 3{\cdot}520 \pm 0{\cdot}003, \quad c_0 = 4{\cdot}449 \pm 0{\cdot}003\ \text{Å},$$

in good agreement with those of Hägg (1930), if his axes are transformed from face-centered to body-centered, and changed from kX. to Ångström units.

A few very weak maxima not explained by the above unit were noted in the ThH_2 X-ray pattern, and some of these have not been explained in terms of impurities. Since ThC_2 was found to be only pseudo-tetragonal, it was feared that this might also be the case for ThH_2. However, the extra reflections on the ThH_2 diagram were not related to the more numerous extra reflections of ThC_2. Moreover, the neutron-diffraction data leave no doubt that ZrH_2 and ThH_2 are isomorphous or very nearly isomorphous with respect to both metal and hydrogen positions. There is neither X-ray nor neutron-diffraction evidence to indicate anything other than the above body-centered lattice for ZrH_2. We presume that the extra lines in the ThH_2 pattern are due to unidentified impurities.

Magnetic susceptibilities

As noted above, the possibility must be considered that ThH_2 and ZrH_2 contain H_2 groups. Metal distances are materially greater in the hydrides than in the metals, and the metal arrangements are different in the metals and hydrides. It seemed unlikely that such large changes could be produced by the solution of H_2 molecules in the metals. Consequently, if H_2 groups were to exist, it seemed likely that they would do so as H_2^+ or H_2^- ions. In either case the ion would contain an unpaired electron, and should lead to paramagnetic dihydrides.

ThH_2 was examined and found to be diamagnetic. Our zirconium metal contained sufficient iron to render susceptibility measurements valueless. We have not examined the susceptibility of ZrH_2 further, but it appears likely that ZrH_2 is also diamagnetic.

Hydrogen positions in the hydrides

ThH_2, ThD_2 and ZrD_2 have been studied by neutron diffraction using the apparatus described by Wollan & Shull (1948). A monochromatic beam of neutrons of wave-length 1·057 Å was diffracted by the polycrystalline samples. The resulting diffraction patterns are shown in Figs. 1 and 2. A pronounced difference is to be seen in the patterns for ThH_2 and ThD_2, and this is a consequence of the reversed phase of scattering for hydrogen relative to that for deuterium and thorium. The very high diffuse scattering in the ThH_2 pattern is to be noted, and this is caused by the very large nuclear spin incoherence which characterizes hydrogen scattering. This is very much less in the case of the deuteride. The ZrD_2 pattern is very similar to that of ThD_2, aside from some intensity differences caused by scattering-amplitude differences.

All reflections observed are accounted for by the body-centered, tetragonal lattices obtained by X-ray diffraction. It is to be noted that without the neutron-diffraction data it would be unsafe to assume a body-centered set of positions for the hydrogen atoms.

The metal atoms can be placed at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ without loss of generality. There are then five possible sets of body-centered positions for hydrogen atoms. These are:

$$\begin{array}{rl}
\text{I} & 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\ +\ 0, \tfrac{1}{2}, \tfrac{1}{4};\ \tfrac{1}{2}, 0, \tfrac{1}{4}, \\
\text{II} & 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\ +\ 0, \tfrac{1}{2}, 0;\ \tfrac{1}{2}, 0, 0, \\
\text{III} & 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\ \pm\ 0, 0, z, \\
\text{IV} & 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\ +\ 0, \tfrac{1}{2}, z;\ \tfrac{1}{2}, 0, z, \\
\text{V} & 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\ +\ 0, \tfrac{1}{2}, z;\ \tfrac{1}{2}, 0, \bar{z}.
\end{array}$$

The structure proposed by Stackelberg (1930) for ThC_2 is not body-centered, but a similar structure with H_2 groups at random along [110] and [1$\bar{1}$0] is body-centered, and has been considered. This structure is eliminated by consideration of (002) alone, irrespective of the H_2 distance assumed, since it makes this reflection far more intense than observed.

Structure II is easily eliminated; e.g. it makes (002) strong and (112) very weak, contrary to observation. Likewise, III can be eliminated irrespective of z since it makes (110) strong. A somewhat more detailed examination of V eliminates it for all possible values of z.

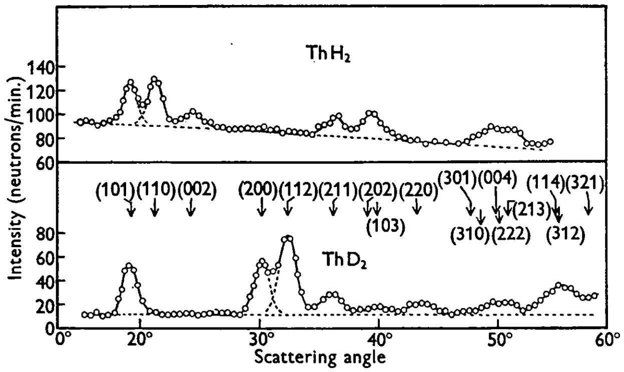

Fig. 1. Neutron-diffraction patterns taken for polycrystalline samples of ThD_2 and ThH_2. The difference in the two patterns is caused by the reversed phase of hydrogen scattering relative to that of deuterium.

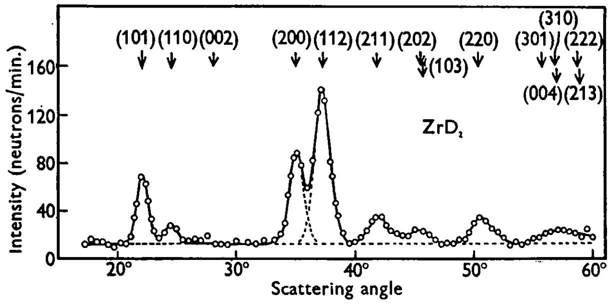

Fig. 2. Neutron-diffraction pattern taken for a polycrystalline sample of ZrD_2.

Structure I provides very satisfactory agreement between observed and calculated intensities (Tables 2–4), and structure IV is satisfactory in the neighborhood of $z=\frac{1}{4}$, where it becomes identical with structure I. The allowed variation of z from $\frac{1}{4}$ in structure IV is about 0·03 (Table 5). Since agreement becomes somewhat worse for any appreciable deviation of z from $\frac{1}{4}$, and since there is no obvious reason for any deviation, we presume that structure I is correct.

Neutron intensities

The observed neutron intensities, recorded in Tables 2–4, are integrated intensities on an absolute scale determined with a BF_3, B^{10} enriched, proportional counter by methods previously described. The calculated absolute neutron intensities were obtained from the equation

$$P_{hkl}=\frac{k}{L(\theta)}j_{hkl}F^2{}_{hkl}\exp\left[-\beta\sin^2\theta/\lambda^2\right],$$

where k, determined independently for this instrument, equals 0·066, j is the multiplicity factor, R is the structure factor and L is the Lorentz factor. For the powder-block method employed for the ThD_2 data, L is $\sin^2 2\theta$, and for the ThH_2 and ZrD_2 data, taken with cylindrical samples, it is $\sin 2\theta \sin\theta$. The exponential term is a temperature factor of the usual form, where β is determined empirically. Note that k is a known constant determined from studies with materials of

Table 2. *Calculated and observed intensities for* ThD_2

hkl	P_c*	$P_c\exp[-\frac{1}{2}\beta\sin^2\theta]$†		P_o (neutrons/ 4 min.)
101	332	320		322
110	7	7		<10
002	4	4		10
200	368	339		344
112	649	588		586
211	207	183		191
202	8	7	82	74
103	87	75		
220	196	166		125
301	65	52	213	181
310	4	3		
004	78	62		
222	4	3		
213	117	93		
114	4	3	416	429
312	538	413		
321	98	—		—

$R=\Sigma\,|\,P_o-P_c\,|\div\Sigma\,P_o=0{\cdot}05.$

* Using $f_D=0{\cdot}64$, $f_{Th}=1{\cdot}01\times10^{-24}$ cm.^{2}
† $\beta=1{\cdot}41\times10^{-16}$ cm.^{2}

Table 3. *Calculated and observed intensities for* ThH_2

hkl	P_c		$P_c\exp[-\frac{1}{2}\beta\sin^2\theta]$		P_o (neutrons/ 4 min.)
101	146		140		172
110	185		178		195
002	74		70		86
200	2		2		—
112	3		3		—
211	89		79		110
202	122	159	106	138	150
103	37		32		
220	1		1		—

Table 4. *Calculated and observed intensities for* ZrD_2

hkl	P_c*		P_o (neutrons/4 min.)
101	164		187
110	56		57
002	21		—
200	292		294
112	512		543
211	100		117
202	36	79	62
103	43		
220	154		121

* $f_D=0{\cdot}64$, $f_{Zr}=0{\cdot}67\times10^{-12}$ cm.; not corrected by temperature factor.

known cross-section, so the absolute intensity agreement is significant.

The coherent scattering amplitude for deuterium was determined previously, but if the parameterless positions for the deuterium atoms are assumed, the value can be improved somewhat by the present work, and for the calculation of Tables 2 and 4 a value, $f_D = +0{\cdot}64 \times 10^{-12}$ cm., has been used.

Table 5. *Calculated versus observed intensities for* ThD_2, *based on structure IV*

	$P_c \exp [-\frac{1}{2}\beta \sin^2 \theta]$								
hkl	$z = 0{\cdot}25$		0·27		0·29		0·31		P_o
101	320		320		320		320		322
110	7		7		7		7		< 10
002	4		8		22		43		10
200	339		339		339		339		344
112	588		580		553		510		586
211	183		183		183		183		191
202	7	82	15	90	38	113	76	151	74
103	75		75		75		75		
220	166		166		166		166		125
301	52	213	52	212	52	212	52	213	181
310	3		3		3		3		
004	62		58		48		33		
222	3		6		16		32		
213	93		93		93		93		
114	3	416	16	422	52	440	103	463	429
312	413		406		388		369		
R	0·052		0·054		0·078		0·124		

$R = \Sigma \mid P_o - P_c \mid \div \Sigma P_o$

Coherent scattering factors were available for neither zirconium nor thorium, and these were determined from ZrN, ZrO_2, Th and ThO_2. The scattering amplitudes* for zirconium and thorium thus determined are respectively $+0{\cdot}67$ and $+1{\cdot}01 \times 10^{-12}$ cm., whereas that for hydrogen has been taken as $-0{\cdot}39 \times 10^{-12}$ cm.

Discussion of the structures

The nearest neighbors of hydrogen and metal atoms are listed in Table 6. The four metal atoms about hydrogen are arranged tetrahedrally. One twofold axis of the tetrahedron has the direction [001], and the tetrahedron is flattened slightly in this direction. The hydride has a distorted fluorite structure, tetragonal rather than cubic because of compression along [001].

These hydrides are black and metallic (or interstitial) rather than saline in character. It seems clear from the metal distances, which are much larger for the hydrides than the pure metals, that metal–hydrogen interactions are quite important in the structure.

If one assumes that the bonds between metal and hydrogen are essentially covalent the H–*M* bonds are expected to be of bond number 0·25, or quarter bonds, since hydrogen can share at most one electron pair with its four neighbors. Using Pauling's metallic radii (H = 0·27, Zr = 1·454, Th = 1·652 Å) and rule (Pauling, 1947), one would predict for Th–H a distance of 2·28 Å versus 2·41 Å observed. Similarly, the predicted and observed ZrH bonds are 2·08 and 2·09 Å respectively. Though the agreement is satisfactory for ZrH_2, the observed value for ThH_2 is much too long, and would suggest very poor Th–H bonding. (Application of Pauling's rule gives a bond number for Th–H of 0·14.) In thorium hydride the metal–metal distances are relatively long, so that application of Pauling's rule would lead to the conclusion that in ThH_2 the number of electrons used by thorium in forming bonds (the metallic valence) is only 2·37, while for ZrH_2 the calculated valence is 3·94, versus 4 expected in both cases. There is no obvious explanation for the very long interatomic distances and apparent low metallic valence in the thorium hydride.

Table 6. *Interatomic distances in* ThD_2 *and* ZrD_2

ThD_2		ZrD_2
	About D	
4 Th at 2·41 Å		4 Zr at 2·09 Å
	About *M*	
8 H at 2·41 Å		8 H at 2·09 Å
8 Th at 3·83 Å		8 Zr at 3·33 Å
4 Th at 4·09 Å		4 Zr at 3·51 Å

It seems likely that the compression of the structure along c_0 (c_0 of ThD_2 is shorter than the corresponding distance, a_0, in thorium metal), leading to the distortion of the fluorite structure, occurs to provide for shorter metal–metal bonds. Unfortunately, quantitative rules, such as Pauling's, concerning bond distances are apparently too rough to be of help in understanding how large such a distortion should be. Neither are such rules of help in guessing hydrogen positions from metal positions. On the basis of Pauling's rule the distances of structure II, which is ruled out according to the neutron intensities, are at least as satisfactory as those of I, and, indeed, lead to a metal valence somewhat nearer the expected value. A similar situation has been noted in the case of UD_3, where hydrogen was again found in distorted tetrahedral positions with abnormally large U–H distances (Rundle, 1951), and again ordinary considerations of bond distances would seem to favor another structure (Rundle, 1947; Pauling & Ewing, 1948).

The authors are indebted to a number of people. Dr R. F. Raeuchle prepared the deuterides and hydride used in the neutron-diffraction studies and made the magnetic-susceptibility measurements on ThH_2. Dr R. Nottorf prepared the thorium hydrides of varying composition used in the X-ray studies, and Dr A. S. Wilson prepared most of the X-ray powder diagrams.

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* See Shull & Wollan (1951) for a more complete tabulation of neutron scattering amplitudes. The value used here for the zirconium scattering amplitude differs somewhat from that in the tabulation but is not outside the limits of error on either. The present value was suggested from consistency within the ZrD_2 data.

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The Crystal Structure of Tricalcium Silicate*

BY J. W. JEFFERY

Birkbeck College Research Laboratory, 21 Torrington Square, London W.C. 1, England

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Three polymorphic forms of tricalcium silicate, $3CaO.SiO_2$, the most important constituent of Portland cement clinker, have been studied. All three are strongly pseudo-rhombohedral, with hexagonal axes $a = 7{\cdot}0$, $c = 25{\cdot}0$ Å approximately. The pseudo-structure, which is a good approximation to the true structures of all three forms, has been determined. The space group is $R3m$ and $Z = 9$ for the hexagonal cell. The true symmetry, cell size and space group have been determined for the form known as alite, which has a composition $54CaO.16SiO_2.Al_2O_3.MgO$, i.e. in 18 molecules of $3CaO.SiO_2$, two silicon atoms have been replaced by aluminium, with one magnesium atom entering the structure to balance the charges. This form is monoclinic, Cm, with

$$a = 33{\cdot}08,\quad b = 7{\cdot}07,\quad c = 18{\cdot}56\ \text{Å},\quad \beta = 94^\circ\ 10',$$

and has two 'molecules' per unit cell.

Some preliminary deductions are made about the position of the aluminium and magnesium atoms in the unit cell and also about the type of distortion of the pseudo-structure which would account for the diffraction effects.

Introduction

The importance of tricalcium silicate, $3CaO.SiO_2$, arises from its occurrence in Portland cement. The main cementing material found in Portland cement clinker was called 'alite' by Tornebohm, who, with Le Chatelier, laid the basis for the modern theories of the composition of cement clinker. This occurred towards the end of the last century, and the problem of the composition and structure of alite has been the subject of controversy and speculation up to the present time.

A critical review of pre-war work has been given by Jeffery (1950), together with results obtained during the course of the present investigation. The accumulated evidence shows that alite is tricalcium silicate modified by slight 'solid solution'.

Polymorphism of tricalcium silicate

At least three forms of tricalcium silicate have been shown to exist. All three give, on rotation photographs with normal exposures, almost identical patterns, typified by the strong reflexions of Fig. 1, with row lines indicating rhombohedral symmetry. Laue photographs along the c axis (Fig. 2) also show the pseudo-trigonal character of all three forms. The approximate pseudo-hexagonal cell dimensions are

$$a = 7{\cdot}0,\quad c = 25{\cdot}0\ \text{Å}.$$

On rotation photographs with long exposures the lack of complete rhombohedral symmetry is shown by the complex character of high-angle reflexions and the occurrence of 'extra' reflexions. All three forms show these effects, but in different ways.

The characteristics of the three forms of tricalcium silicate which have been investigated

(a) *Pure tricalcium silicate*

The rotation photograph (Fig. 3) and the Laue photograph along the pseudo-hexagonal c axis (Fig. 2) show that this form is triclinic, with three unequal pseudo-hexagonal a axes. Powder photographs show many doublets where the other forms give single lines. The most clearly resolved doublet occurs at $d = 1{\cdot}466$

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* This paper is an abridged and amended version of part of a thesis approved by the University of London for the degree of Ph.D.