5. Concluding remarks

This paper concludes the study of the seminvariants for the non-centrosymmetric space groups which was initiated in a previous paper (Hauptman & Karle, 1956). The theory of the seminvariants provides a basis for specifying an origin and the enantiomorph or reference frame when required. Furthermore it demonstrates the existence of relationships between the measured intensities and the values of phases. It will be the purpose of future publications to elucidate the exact nature of these relationships and by these means to continue the unified program for phase determination in the non-centrosymmetric space groups which has already been completed for the centrosymmetric ones (Karle & Hauptman, 1961 ff.).

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Neutron Diffraction Investigation of Solid Solutions $AlTh_2D_n$

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Solid solutions of composition $AlTh_2D_n$, with $n=0, 2, 3, 4$, have been studied by means of neutron diffraction. For $n=4$ the deuterium atoms completely fill a set of equivalent Th-tetrahedra, quite similar to the arrangement in thorium hydride. For the other compositions these sites are partly occupied. No evidence for ordering has been found, even at a temperature of 82 °K.

The intermetallic compound $AlTh_2$ easily absorbs hydrogen. Apart from a two-phase region at room temperature between the compositions $AlTh_2H_0$ and $AlTh_2H_{\sim 1.5}$, the hydrogen is dissolved homogeneously until the ultimate composition $AlTh_2H_4$ is reached (van Vucht, 1960). X-ray investigation shows that the tetragonal symmetry of $AlTh_2$ is conserved in the solid solutions. When the lattice parameters are plotted against n, the number of hydrogen atoms per $AlTh_2$, a is found to increase up to $n=2$. There it shows a sharp break, followed by a decrease until saturation. On the other hand c increases monotonically.

As part of a larger program, a neutron-diffraction investigation was undertaken with the object of establishing the hydrogen positions. Only microcrystalline samples were available so that to avoid a large background of incoherent scattering the deuterides rather than hydrides were used. The relevant neutron scattering lengths (Shull & Wollan, 1956) are, in 10^{-12} cm., $b_{Al}=0{\cdot}35$, $b_{Th}=1{\cdot}01$ and $b_D=0{\cdot}65$.

Experimental procedure

The deuterides were prepared in exactly the same way as the hydrides (van Vucht, 1960). For the room-temperature neutron-diffraction measurements 10 mm. dia. cylindrical thin-walled aluminium sample holders were used. By means of a glass tube and a section of fernico tube these were connected to the apparatus in which the deuteride was prepared. Using a tilting arrangement the finished product could be transferred to the sample holder under vacuum after which the glass connecting tube was sealed off. The sample holder was then placed on the diffractometer described by Goedkoop (1957) and the diffraction pattern recorded with 1·026 Å neutrons. Resolution was mainly determined by Soller slits 0·25 mm. wide and 200 mm. long placed in front of the counter.

For measurements at low temperature a single-jacketed vacuum cryostat as shown in Fig. 1 was placed on the goniometer. Liquid air or liquid nitrogen was placed in the inner cylinder, to the bottom of which the sample holder was fixed. The glass-sealed sample holders were unsuited for this arrangement and so a shorter one closed by means of a screw-plug

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Table 1. *Observed and calculated neutron intensities*

	hkl	2θ	I_c		I_o
$AlTh_2$					
	110	10·9	2		—
	200	15·4	7		4
	211	20·1	130	149	149
	002	20·2	19		
	220	21·9	7		8
	112	22·9	15		21
	310	24·6	33		35
	202	25·6	24		26
	321	29·9	1	16	19
	222	30·0	0		
	400	31·3	4		
	312	32·0	11		
	330	33·2	14		16
	411	33·8	39		36
	420	35·2	8	52	46
	213	35·3	44		
	402	37·6	20		22
	332	39·3	43		37
$AlTh_2D_2$					
	110	10·8	31		25
	200	15·2	9		7
	002	18·8	21		26
	211	19·4	46		53
	220	21·6	6	25	21
	112	21·8	19		
	310	24·2	82	111	112
	202	24·4	29		
	222	28·8	0		—
	321	29·2	5		—
	400	30·8	27	39	54
	312	30·8	12		
	330	32·6	32	174	168
	411	33·2	35		
	213	33·4	99		
	420	34·4	9		
	402	36·4	21		25
	332	38·0	45	49	51
	004	38·2	4		
	510	39·6	2	13	—
	422	39·6	0		
	114	40·0	1		
	431	40·0	0		
	323	40·0	8		
	204	41·4	2		
	521	43·0	11	55	58
	413	43·2	27		
	440	44·0	17		
$AlTh_2D_3$					
	110	10·8	211		195
	200	15·3	38		28
	002	18·4	69		69
	211	19·4	67		115
	112	21·4	62	87	86
	220	21·6	25		
	202	24·0	108	510	481
	310	24·2	402		
	222	28·6	0	45	69
	321	29·2	45		
	312	30·6	37	205	185
	400	30·8	168		
	330	32·8	157	842	915
	213	32·8	531		
	411	33·2	119		
	420	34·6	35		
	402	36·2	66		58
	004	37·4	1	156	159
	332	37·8	155		
	114	39·0	13	103	83
	422	39·5	2		
	510	39·6	15		
	323	39·6	68		
	431	40·0	0		
	204	40·6	5		
$AlTh_2D_4$					
	110	10·9	334		320
	200	15·5	55		55
	002	18·1	52		51
	211	19·6	18		82
	112	21·2	50	77	80
	220	22·0	27		
	202	23·9	113	668	639
	310	24·6	555		
	222	28·6	0		36
	321	29·6	75		88
	312	30·7	23	280	270
	400	31·2	257		
	213	32·5	836	1162	1226
	330	33·2	220		
	411	33·6	106		
	420	35·0	45		51
	402	36·4	47	47	49
	004	36·7	0		
	332	38·1	141	167	103
	114	38·4	26		
	323	39·6	130	159	145
	422	39·7	3		
	204	40·0	3		
	510	40·1	23		
	431	40·4	0		
	413	42·8	140	345	353
	224	43·2	14		
	521	43·5	3		
	512	44·4	37		
	314	44·7	0		
	440	44·8	151		

had to be used. The sample was transferred to it in a glove box filled with dry nitrogen. The neutrons reached the sample through the outer aluminium cylinder, which in this region had been turned off to a wall-thickness of 1 mm., and through a thin thermal shield. During measurements the temperatures at top and bottom of the sample were recorded continuously.

Room temperature measurements were made for $n=0, 2, 3$ and 4. The diagrams, with instrumental background subtracted, are shown in Fig. 2. The intensities of the peaks appear in the last column of Table 1. For $n=2$ data were also taken at liquid-nitrogen temperature: they are shown in Fig. 3 and Table 2.

Determination of the crystal structures

The crystal structure of $AlTh_2$ has been determined previously, by means of X-rays, by Braun and van

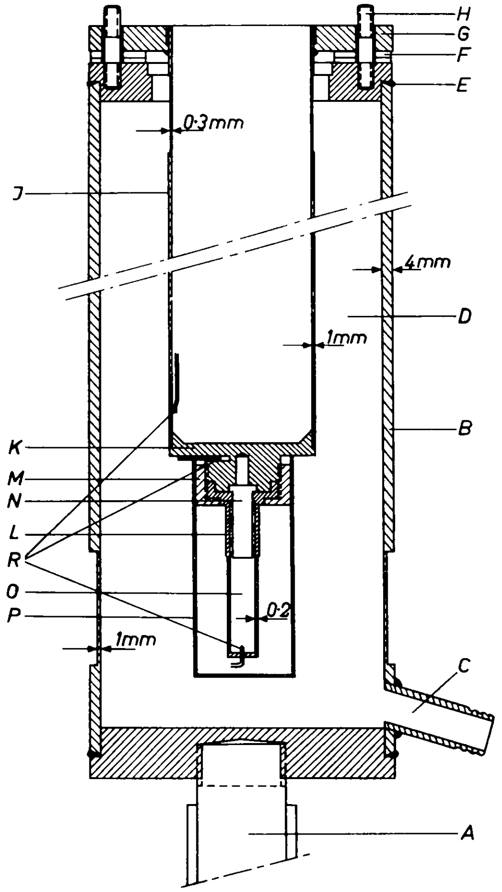

Fig. 1. Vertical section through cryostat. *A*. Support. *B*. Aluminium outer cryostat cylinder. *C*. Suction line. *D*. Vacuum jacket. *E*. Aluminium flange. *F*. Pair of rubber washers. *G*. Stainless steel flange. *H*. Stud. J. Stainless steel inner cryostat cylinder. *K*. Brass bottom of inner cylinder. *L*. Aluminium specimen holder. *M*. Specimen holder clamping nut. *N*. Aluminium specimen holder plug. *O*. Specimen. *P*. Thermal shield. *R*. Thermocouples.

Vucht (1955) and by Murray (1955). As reported by the former authors, it may be described as follows:

Space group $I4/mcm$, 4 units $AlTh_2$ per cell:

$$a = 7{\cdot}62,\ c = 5{\cdot}86\ \text{Å}\ .$$

Th in $8(h)$: $\pm(x_{Th}, \frac{1}{2}+x_{Th}, 0)$; $\pm(\frac{1}{2}+x_{Th}, \bar{x}_{Th}, 0)$; $\pm(\frac{1}{2}+x_{Th}, x_{Th}, \frac{1}{2})$; $\pm(x_{Th}, \frac{1}{2}-x_{Th}, \frac{1}{2})$ with $x_{Th} = 0{\cdot}162$.

Al in $4(a)$: $\pm(0, 0, \frac{1}{4})$; $\pm(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$.

Using these data the neutron intensities of $AlTh_2$ were calculated. They are listed in the third column of Table 1, where they are seen to be in quite good agreement with the observed values.

X-ray powder investigation of the hydrides resulted in diagrams which were identical with that of $AlTh_2$ except for the shifting of reflections due to the changing lattice constants. It was therefore concluded that, on the introduction of hydrogen, the space group, as far as the Al and Th atoms are concerned, remains the same. A careful study of the X-ray intensities showed that for all the best fit was obtained with the same thorium parameter, $x_{Th} = 0{\cdot}162$, as in the alloy containing no hydrogen.

Table 2. *Neutron diffraction intensities of* $AlTh_2D_2$ *powder at* $T = 82$ °K. *compared to those at* $T = 293$ °K.

hkl	θ	I_0 $T = 293$ °K.	I_0 $T = 82$ °K.
110	5·4	103	85
200	7·6	25	30
002	9·4	286	294
211	9·7		
220	10·8	88	110
112	10·9		
310	12·1	360	378
202	12·2		
222	14·4	69	85
321	14·6		
400	15·4	255	159
312	15·4		
330	16·3	554	575
411	16·6		
213	16·7		
420	17·2		
402	18·2	93	90
332	19·0	158	187
004	19·1		

It thus remained to place the deuterium atoms. In $AlTh_2D_4$, which apparently represents a maximum filling of positions, there are 16 deuterium atoms in the cell. Assuming that the space group is in fact the same as that of $AlTh_2$, there are four different 16-fold positions. These were tried, the only one giving satisfactory agreement with the neutron data being

D in $16(l)$: $\pm(x_D, \frac{1}{2}+x_D, \pm z_D)$; $\pm(\frac{1}{2}+x_D, \bar{x}_D, \pm z_D)$; $\pm(\frac{1}{2}+x_D, x_D, \frac{1}{2}\pm z_D)$; $\pm(x_D, \frac{1}{2}-x_D, \frac{1}{2}\pm z_D)$.

The parameter values were found by trial and error to be $x_D = 0{\cdot}368$ and $z_D = 0{\cdot}137$. Table 1 shows the intensities calculated for this configuration. They are seen to agree closely with the observed values with the notable exception of 211. As will be shown later, this arrangement places the deuterium atoms in the centers of the tetrahedral holes formed by the structure between sets of four Th atoms.

In the intermediate deuterides, $n < 4$, it is now to be expected that the deuterium atoms occupy the same sites, but only partially. If this is so, the question arises to what extent the distribution of the hydrogen atoms over the 16 sites is ordered.

The peculiar variation of the lattice constants with n would suggest that the hydrogen positions are in fact ordered to some extent. In particular, the fact that a is a maximum for $n = 2$, i.e. for half the total number of sites occupied, could be understood by assuming that up to that point at most one of a pair of two sites that differ in z-coordinate only is occupied. Such a pair of sites are the centers of two deformed

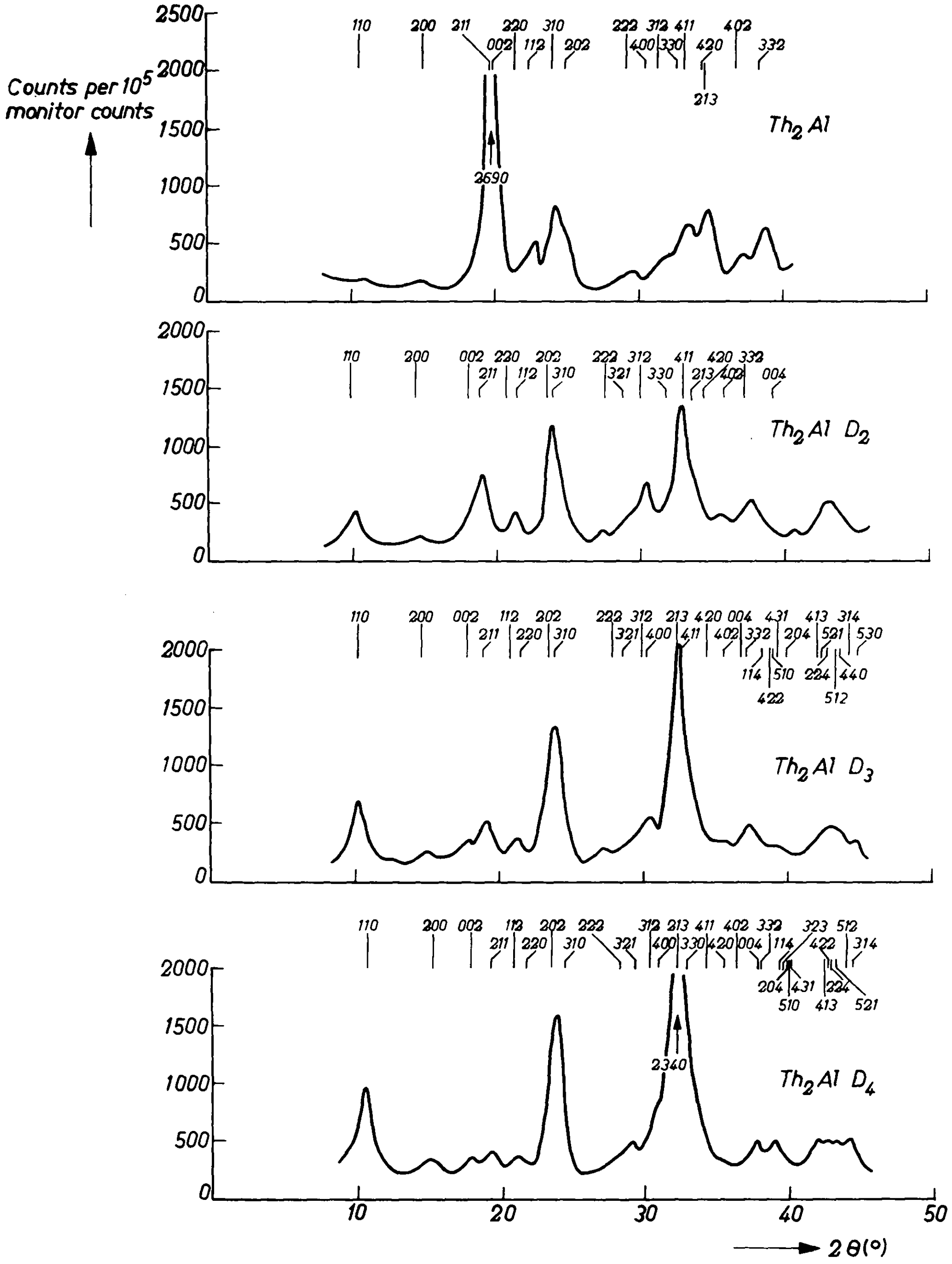

Fig. 2. Neutron diffraction diagrams of AlTh$_2$D$_n$ for $n=0$, $n=2$, $n=3$ and $n=4$ at room temperature.

Th-tetrahedra with common base (see Fig. 4).* Thus in AlTh$_2$D$_2$ each deuterium atom would have a choice between two positions.

There are, then, three possibilities:

(*a*) There is no correlation between the ways in which different pairs of sites are singly occupied.

(*b*) There is short-range order between the ways of occupation of the neighbouring pairs.

(*c*) There is long-range order.

Alternatives (*a*) and (*b*) would give rise to the same neutron intensities as for no order at all. The intensities for AlTh$_2$D$_2$ should then, apart from possible

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* The opposite arrangement, with always either none or both of the two paired sites occupied, may be ruled out on the basis of the proton magnetic resonance measurements mentioned later in this paper.

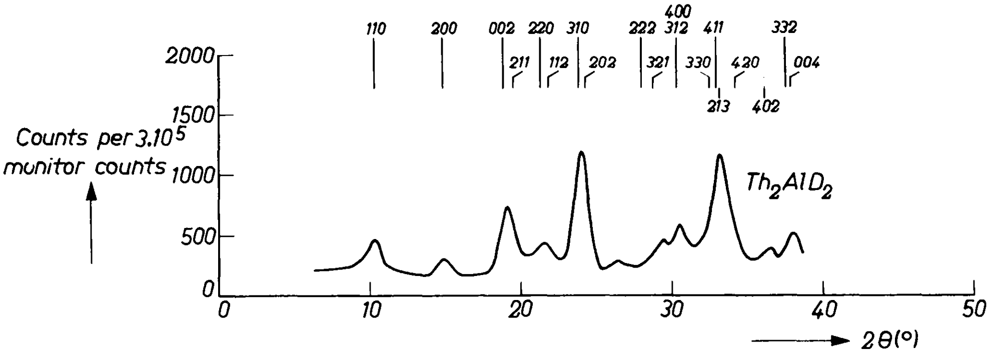

Fig. 3. Neutron diffraction diagram of $AlTh_2D_2$ at 82 °K.

variations in the parameters, be the same as those calculated for $AlTh_2D_4$ with the deuterium contribution to the structure factor counted half. The result is found to agree closely with the observed diagram and the arrangement may be improved still somewhat by adjusting the deuterium parameters to

$$x_D = 0{\cdot}370 \quad \text{and} \quad z_D = 0{\cdot}125\ .$$

The results are again shown in Table 1.

Alternative (*c*) leaves a large number of possible ordering schemes. Some of these require a change in space group, which should in principle cause extra lines in the X-ray and neutron diagrams. Such lines have not been observed. For those schemes of ordering which are compatible with the space group, the neutron intensities have been calculated. They all agree less well with the observed intensities than those calculated without long-range order. The differences are not sufficient to exclude the possibility of long-range order entirely, but they do make it unlikely.

A distinction between total disorder and the alternatives (*a*) and (*b*) could in theory be made from the shape of the neutron diffuse scattering. However, the Bragg peaks are so crowded together in the diagram that they do not allow an examination of the diffuse scattering which is sufficiently accurate to see the effect.

Further support for the absence of long-range order is provided by proton magnetic resonance measurements on $AlTh_2H_2$ by Kroon, Van der Stolpe and Van Vucht (1959). These indicate in fact a total absence of ordering at room temperature. Below 225 °K., however, they do find indications for ordering of the hydrogen atoms. To see whether any long-range order would appear in $AlTh_2D_2$ measurements were made at 82 °K. (Fig. 3). No significant difference from the diagram taken at room temperature was obtained: see Fig. 3 and Table 2.

The neutron data for the phase $AlTh_2D_3$ led to similar conclusions as for $AlTh_2D_2$. The intensities in the third column of Table 1 have again been calculated for a disordered structure, with

$$x_D = 0{\cdot}370 \quad \text{and} \quad z_D = 0{\cdot}130\ .$$

Agreement is seen to be good, again with exception of 211.

This last discrepancy, which was even more pronounced in the case of $AlTh_2D_4$, is almost certainly due to the presence of small amounts of unreacted $AlTh_2$ in the sample. As inspection of Table 1 shows 211 is by far the strongest peak in $AlTh_2$, where it occurs at 20·1°, which is quite close to its position in the other two samples. One easily verifies that an admixture of only 4·5% of $AlTh_2$ is sufficient to account for the discrepancy observed in $AlTh_2D_4$.

A feature less easily accounted for is the scattering which all the deuterides show between 27° and 29° scattering angle. It does not correspond to any peaks and its presence makes the observed intensities of the 222 reflections somewhat uncertain.

Discussion of the structures

The final parameter values are once more summarized in Table 3. A *c*-axis projection of the unit cell is shown in Fig. 4.

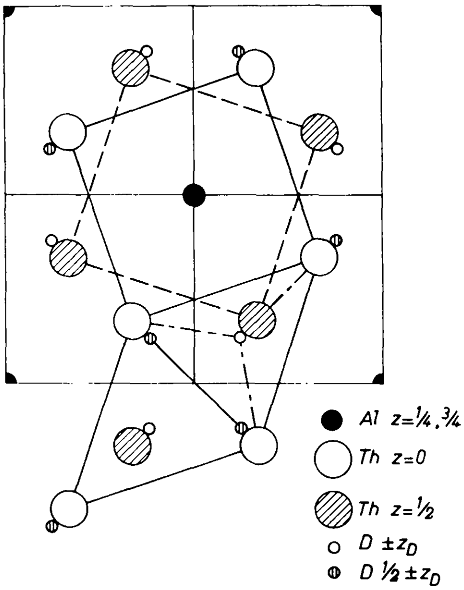

Fig. 4. A *c*-axis projection of the unit cell of $AlTh_2D_n$.

In $AlTh_2$ the thorium and aluminium atoms are in alternate layers, perpendicular to the c-axis. The thorium atoms form distorted tetrahedra, with three atoms in one layer and one in the next at a distance $c/2$.

Table 3. *X-ray-determined cell constants of a few deuterides of* $AlTh_2$

x_D and z_D are the experimentally obtained deuterium parameter values

Specimen	a (Å)	c (Å)	x_{Th}	x_D	z_D
$AlTh_2$	7·62	5·86	0·162	—	—
$AlTh_2D_2$	7·702	6·230	0·162	0·370	0·125
$AlTh_2D_3$	7·676	6·383	0·162	0·370	0·130
$AlTh_2D_4$	7·629	6·517	0·162	0·368	0·137

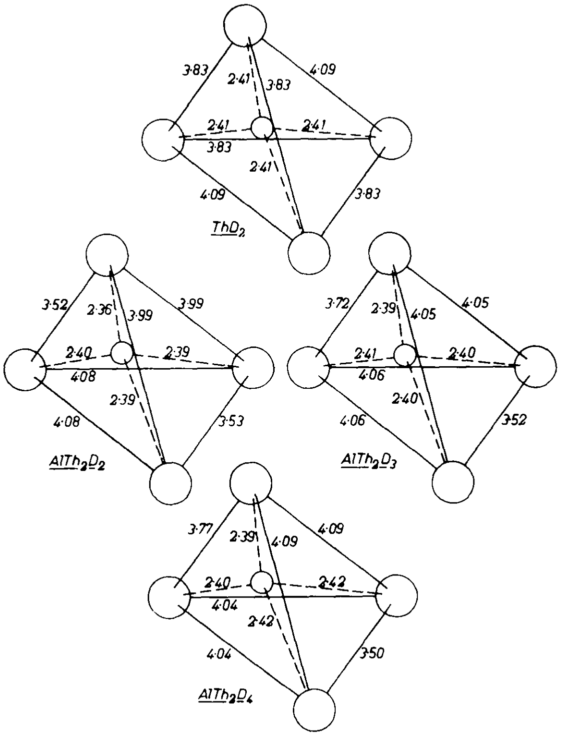

Fig. 5. Packing of thorium atoms around deuterium in $AlTh_2D_2$, $AlTh_2D_3$ and $AlTh_2D_4$ compared to that in ThD_2.

It is seen now that in the hydrides the hydrogen sites are roughly at the centers of these deformed tetrahedra, so that each hydrogen is surrounded by four thorium atoms. Conversely, each Th atom is surrounded by 8 hydrogen sites: roughly along the c-axis there is one to each side, whilst the six others are at the corners of a nearly trigonal prism. This configuration is quite similar to the one found in ThD_2 (Rundle *et al.*, 1952).

Interatomic distances between H and Th may be seen from Fig. 5, which shows the configuration around each hydrogen site for the various hydrides as well as for ThD_2. The parameter changes are seen to be such that, despite the changes in lattice constants, the interatomic distances are relatively constant.

In the intermediate hydrides only a fraction of the thorium tetrahedra are occupied. It is seen that the pairs of sites which have been referred to above are in fact the centers of two tetrahedra with a common base. The changes in lattice constant might then be taken to suggest that up to $n = 2$ only one of the two tetrahedra is filled. We have seen that if this is so, the neutron data suggest that the two positions are filled at random, without correlation between different pairs of tetrahedra.

The authors wish to express their thanks to Dr B. O. Loopstra, who originally took part in the work, and especially to Mr H. J. J. de Haan who designed and operated the cryostat.

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