

## Lattice Parameter and Coefficient of Thermal Expansion of Thorium

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Values of the lattice parameter of 99.86% pure thorium were determined by the asymmetric method over the temperature range +10 to +60° C., using copper radiation. A value of  $5.0741 \pm 0.0001$  kX. ( $5.0843 \text{ \AA}$ ) at 25° C., corrected for refraction, was obtained. The precision of the determination was better than 1:60,000. The computed closest atom-to-atom distance was  $3.5952 \text{ \AA}$ . The linear expansion coefficient was  $11.6 \times 10^{-6} (\text{°C.})^{-1}$  for 10–60° C. The expansivity curve suggested some transition in the region of 38° C. but no definite conclusion could be drawn. The calculated X-ray density at 25° C. was  $11.724 \pm 0.004 \text{ g.cm.}^{-3}$ .

### Introduction

The importance of thorium as a reactor material has prompted more detailed studies of its fundamental properties. A survey of the lattice parameters, expansion coefficients, and other physical constants reported in Table 2 suggested the need for a further study of these constants. Accordingly a precision determination of the lattice parameter, which may be of theoretical and practical importance in further investigations of the solid state, was undertaken.

### Material used

The thorium was prepared at the Battelle Memorial Institute by the van Arkel method (1934), in which thorium is deposited on a heated wire by the thermal dissociation of the tetraiodide. The sample was in the shape of a small cylinder containing quasi-crystalline

aggregates (thorium chips) of fairly uniform size oriented radially (Fig. 1). The thorium, according to Dr B. W. Gonser, contained approximately 0.1% total metallic impurities and the following non-metals in weight percents:

C, 0.020; O, 0.01; N, 0.01.

As the metal was appreciably malleable, no powder mount could be prepared. Therefore, the X-ray mounts were made by carefully separating the thorium chips with a probe and mounting suitable specimens, on the basis of size and surface characteristics, on fine glass fibers, as in single-crystal work (Straumanis & Ieviņš, 1940). The powder patterns obtained showed that the chips were polycrystalline, although they sometimes resembled single crystals.

Considerable difficulty arose in finding thorium chips of a size to produce sharp X-ray spectra. While attempting to reduce the size of the chips in dilute hydrochloric acid, the formation of a black brittle solid, insoluble in the acid, was observed on the surface of the metal. A small amount was collected, washed, dried, and powdered by grinding in an agate mortar. An X-ray pattern of the powder, using unfiltered copper radiation, though exhibiting diffuse lines, revealed the substance to be thorium dihydride (Rundle, Shull & Wollan, 1952). Further attempts to reduce the size of the thorium chips in this manner were abandoned, and eventually a chip was obtained from the sample (Fig. 1) which yielded back-reflection lines deemed sharp enough to attain the precision reported.

Other thorium chips were flattened on a small anvil, and strips were cut and placed in a silica glass tube, which was sealed and evacuated. The thorium strips were annealed at approximately 800° C. in a helium atmosphere, and air quenched. Unfortunately the X-ray patterns of these strips could not be used for precision work because the  $\alpha_1$  and  $\alpha_2$  (533) lines were diffuse and not clearly resolved. Furthermore, other

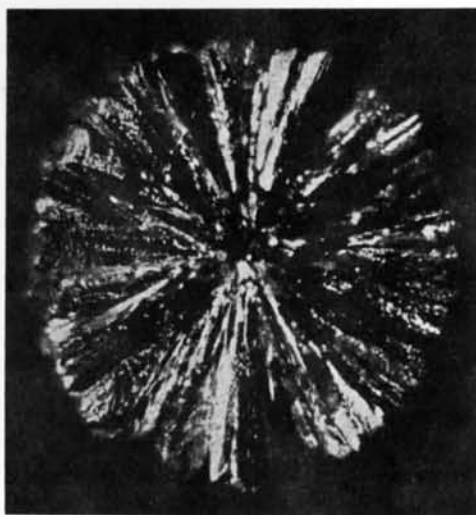


Fig. 1. Sample of Th prepared by thermal decomposition of  $\text{ThI}_4$ .  $12\times$ .

lines, which were identified as belonging to black thorium oxide, appeared on the films and therefore only the chip selected directly from the sample could be utilized.

### Experimental procedure

The values of the lattice parameter were determined at intervals of five or ten degrees between +10 and +60° C., using the asymmetric method (Straumanis & Ieviņš, 1940; Klug & Alexander, 1954, p. 454). The portion of thorium chip bathed by the beam had an average diameter of less than 0.2 mm. The 6 cm.-long collimator had a bore of 0.8 mm. The lines were measured from peak to peak intensity. A graphical method (Straumanis, 1952) was used to index the patterns.

Unfiltered copper radiation ( $\lambda K\alpha_1 = 1.537395$  kX.) was used at all temperatures with exposure times of  $1\frac{1}{2}$  hr. The lattice constant was calculated using the strong  $\alpha_1$  (533) line with  $\theta \cong 84^\circ$ . Although the doublet  $\alpha_1, \alpha_2$  (533) was clearly resolved, only the  $\alpha_1$  line could be considered sufficiently strong and uniform in texture to allow accurate measurements. Two sets of lines in the front-reflection region,  $\alpha$  (111) and  $\alpha$  (200), together with  $\alpha_1$  (533) in the back-reflection region, were measured to determine the effective film circumferences and conversion factors. No extrapolation methods nor corrections except that for refraction were used to obtain the final value of the constant.

### Experimental results

Table I shows the values of the lattice parameter obtained at different temperatures and the variations in value at any one temperature between +10 and 60° C. In some instances more than two photographs were taken.

From the data of column 4, assuming a linear expansion between 10 and 60° C., the average lattice

Table I. Variation of lattice parameter of 99.86% pure thorium with temperature; final values at 25° C.

Line  $\alpha_1$  (533); Cu radiation ( $K\alpha_1 = 1.537395$  kX.);  $\varphi$ , back-reflection angle;  $\alpha = 11.6 \times 10^{-6}$  (°C.)<sup>-1</sup>

Temp. (°C.)	$\varphi$ (°)	$a$ (kX.)	$a_{\text{average}}$ (kX.)	$a_{\text{reduced to 25° C.}}$ (kX.)
10.0	6.485	5.07316	5.07320	5.07408
	6.493	5.07323		
20.0	6.525	5.07356	5.07365	394
	6.542	5.07373		
30.0	6.583	5.07415	5.07415	386
	6.582	5.07415		
35.0	6.611	5.07443	5.07443	384
40.0	6.620	5.07455	5.07456	368
	6.620	5.07453		
	6.628	5.07461		
45.0	6.679	5.07514	5.07510	392
	6.670	5.07505		
50.0	6.705	5.07540	5.07537	386
	6.703	5.07538		
	6.696	5.07532		
60.0	6.773	5.07613	5.07606	400
	6.765	5.07604		
	6.761	5.07600		

Average  $\left\{ \begin{array}{l} 5.07390 \pm 0.00008 \text{ kX. or} \\ 5.08415 \text{ \AA} \end{array} \right.$

Final value corrected for refraction  $\left\{ \begin{array}{l} 5.0741 \pm 0.0001 \text{ kX. or} \\ 5.0843 \text{ \AA at 25° C.} \end{array} \right.$

Closest atom-to-atom spacing 3.5952 Å at 25° C.

expansion coefficient  $\alpha$  was calculated to be  $11.6 \times 10^{-6}$  (°C.)<sup>-1</sup>. However, when a more accurate plot of lattice parameter versus temperature was prepared, a break was suggested in the region of 38° C. (broken lines, Fig. 2).

The expansivity curve could then be described by two expansion coefficients  $\alpha = 9.55 \times 10^{-6}$  (°C.)<sup>-1</sup> below, and  $\alpha = 13.9 \times 10^{-6}$  (°C.)<sup>-1</sup> above the break. Alternatively, a smooth curve also could be drawn through the points (solid line, Fig. 2) as to make the

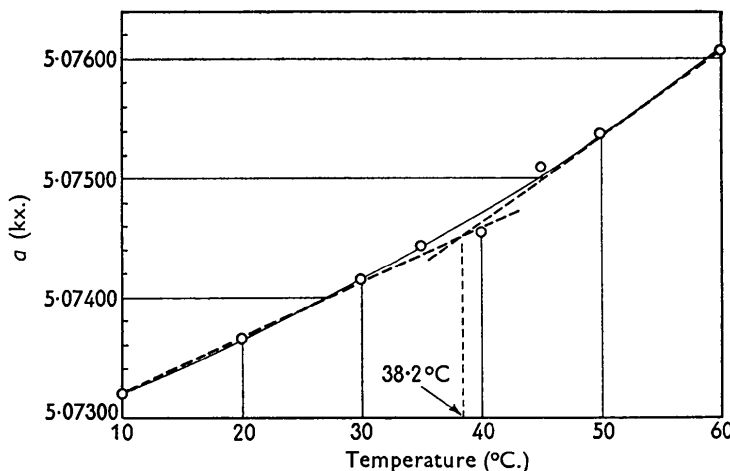


Fig. 2. Expansivity curve of Th.

Table 2. *Physical constants of thorium*

	$\alpha$ ( $^{\circ}\text{C.})^{-1} \times 10^6$ )	Density ( $\text{g.cm.}^{-3}$ )		Reference
		Obs.	Calc.	
5.12 kX.	—	—	—	Bohlin, 1920
5.04 kX.	—	—	11.7	Hull, 1921
—	11.7–12.3 (0–100° C.)	11.3–11.7	—	Marden <i>et al.</i> , 1927
5.074 ± 0.002 kX.	—	—	11.71	Burgers <i>et al.</i> , 1930
5.091 ± 0.004 kX.	11.1 (20–60° C.)	11.1–11.5	11.61	Thompson, 1933
—	11.1 (20–60° C.)	—	—	Hidnert <i>et al.</i> , 1933
5.089 ± 0.001 Å	—	—	—	Chiotti, 1954
5.0741 ± 0.0001 kX. or 5.0843 Å at 25° C.	11.6 (10–60° C.)	—	11.724	Present work

expansion coefficient temperature dependent. The analytical expression for this curve was then given ( $a_t$  not corrected for refraction) by:

$$a_t = 5.07282 + 3.67037 \times 10^{-5}t + 2.51853 \times 10^{-7}t^2 + 4.93827 \times 10^{-10}t^3$$

( $a_t$  in kX.,  $t$  in  $^{\circ}\text{C.}$ ).

The value computed for  $\alpha$  at 35° C., corresponding to the mid-point of the temperature interval, was  $11.1 \times 10^{-6}$ ; at 10° C. it was  $8.26 \times 10^{-6}$  and at 60° C.  $14.2 \times 10^{-6}$  ( $^{\circ}\text{C.})^{-1}$ .

By means of  $\alpha = 11.6 \times 10^{-6}$  ( $^{\circ}\text{C.})^{-1}$ , the average parameters of Table 1 (column 4) were reduced to a standard temperature of 25° C. (Table 1, column 5). The refraction correction applied was 0.00016 kX. (Wilson, 1940; Klug & Alexander, 1954, p. 98), and the error mentioned in Table 1 is the probable error. The precision is therefore 1 part in 63,000. A higher precision could not be attained because the average expansion coefficient of  $\alpha = 11.6 \times 10^{-6}$  ( $^{\circ}\text{C.})^{-1}$  was used for the reduction of the constants, and because of the considerable width of the last  $\alpha_1$  line.

Using the final value of the parameter, and the newest atomic weight of thorium (232.05), the calculated X-ray density for four atoms per unit cell is  $11.724 \pm 0.004$   $\text{g.cm.}^{-3}$  (Straumanis, 1953, 1954; Cohen & DuMond, 1955).

### Discussion

A glance at Table 2 suffices to show the widely divergent values of physical data reported for thorium. Apparently the discrepancies arose mainly from use of materials of unknown purity.

The van Arkel method of preparing thorium was very desirable for this work, where low oxygen or nitrogen content is required. Yet some traces of thoria were apparent on the surface of the chips and were indicated on some films by the presence of a few very faint lines. As reported by Chiotti (1954, 1955) and concluded in this study, no solid solutions were formed. Thus the effect of surface thoria on the precision of the reported lattice parameter is felt to be negligible in the temperature interval covered. The lattice parameter expressed in kX. obtained by Burgers & van Liempt (1930) agrees very well with that found in this investigation.

The average linear expansion coefficient of  $11.6 \times 10^{-6}$  ( $^{\circ}\text{C.})^{-1}$  varies little from those reported in Table 2. The apparent break in the expansivity curve is similar to that observed with chromium (Straumanis & Weng, 1955). As with chromium, no signs of abnormal broadening of lines, nor of other alterations, were noted over the range of temperatures studied. Owing to the difficulty of reproducing the expansion coefficient accurately, even for the same sample, it is hard to draw any definite conclusion. However, it does appear that the expansion coefficient is temperature dependent in this small interval, while those of other metals, such as aluminum (Ieviš & Straumanis, 1936), are not in the same interval.

The density computed was higher than all those reported in the literature, but was less than the observed value of 11.75  $\text{g.cm.}^{-3}$  reported for thorium produced by the iodide method (de Boer, 1943); van Arkel suggested that the most likely value for the experimental density is  $11.7 \pm 0.1$   $\text{g.cm.}^{-3}$ .

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## The Crystal Structure of the Monoclinic Form of *n*-Hexatriacontane

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The unit cell of the monoclinic form of *n*-hexatriacontane,  $C_{36}H_{74}$ , was determined by X-rays. It is  $a = 5.57$ ,  $b = 7.42$ ,  $c = 48.35$  Å,  $\beta = 119^\circ 6'$ , with two molecules per cell and space group  $C_{2h}^2-P2_1/a$ . Fourier projections were prepared and atomic co-ordinates determined with the aid of the subcell theory. The chains pack essentially in an orthorhombic subcell with  $a_0 = 4.945$ ,  $b_0 = 7.42$ ,  $c_0 = 2.546$  Å, space group  $D_{2h}^{16}-Pbnm$ , but a monoclinic subcell is needed for structure-factor computations. The chain is regular and periodic within experimental error, with an average single C-C bond length  $1.534 \pm 0.006$  Å and the zigzag bond angle  $112^\circ 1' \pm 21'$ .

### Introduction

The interest in accurate crystal-structure determination of *n*-paraffins is twofold: the effect of environment on the bond lengths and angles of carbon deserves study and the details of polymorphism need elucidation. Considerable advance has recently been made by Smith (1953), who showed that the space group of the odd orthorhombic hydrocarbons described by Müller (1928) is  $D_{2h}^{11}-Pbcm$  instead of  $D_{2h}^{16}-Pnam$ . Smith has also shown that for even orthorhombic hydrocarbons the  $(00l)$  long spacings are halved, a point also confirmed by Bunn (private communication), so that the  $c$  axis of the orthorhombic  $n-C_{36}H_{74}$ , obtained by Vand (1953) from powder data, needs to be doubled. Smith also found that pure even paraffins above  $n-C_{26}$  normally crystallize as monoclinic at room temperature, whereas about 2% impurity of neighbouring homologues changes them to the orthorhombic form, the amount of impurity decreasing with increasing chain length. As our monoclinic crystals were obtained by recrystallization of the orthorhombic material used by Vand (1953) for density determination, one can infer from Smith's data that during recrystallization some purification took place and that the original orthorhombic material was probably less than about 98–99% pure, whereas the monoclinic crystals used in the present work were of a higher purity. However, it proved impossible to check this in a mass spectrograph owing to the experimental difficulties.

Monoclinic crystals of *n*-hexatriacontane,  $C_{36}H_{74}$ , were grown slowly from light petroleum solution by evaporation at room temperature. They were flat lozenge-shaped plates with an inter-edge angle of about  $75^\circ$ , with the  $\{001\}$  and  $\{110\}$  faces well developed. Most of the crystals were twinned about  $(001)$ , but it was possible to select under polarized light a few untwinned crystals.

### Determination of the unit cell

Rotation, oscillation and zero- and first-layer Weissenberg photographs were taken about the  $a$  and  $b$  axes using Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.542$  Å). The axial lengths  $a$  and  $b$  were measured from rotation photographs, carefully calibrated by powder lines of copper. The Weissenberg photographs were calibrated by powder lines of NaCl, so that cell dimensions so obtained should be free of systematic camera and film-shrinkage errors.

The long spacing was obtained by measuring Bragg angles  $\theta$  of all the observable  $00l$  reflexions and by taking the weighted average of its reciprocal  $c^*$ ,

$$c^* = 2 \sum \sin \theta_{00l} / \sum l,$$

and calculating the standard deviation from the residuals. The value  $c^* = 0.03650 \pm 0.00006$  was obtained, from which

$$c \sin \beta = \lambda / c^* = 42.25 \pm 0.07 \text{ Å}.$$

The best value of the monoclinic angle  $\beta$  has been evaluated by least squares from Weissenberg photo-

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