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The Crystal Structures of CeB_4, ThB_4 and UB_4

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The isostructural compounds CeB_4, ThB_4 and UB_4 are tetragonal with $a = 7{\cdot}205$, $c = 4{\cdot}090$; $a = 7{\cdot}256$, $c = 4{\cdot}113$; and $a = 7{\cdot}075$, $c = 3{\cdot}979$ Å, respectively, and with space group $P4/mbm$. The metal locations are determined by X-rays and the boron locations by geometrical considerations. The structure is a combination of the AlB_2- and CaB_6-type structures, with the boron atoms forming a three-dimensional network among the metal atoms. The B–B bond lengths range from 1·69 to 1·80 Å.

A method for making absorption corrections for highly absorbing crystals of prismatic form is described.

Introduction

In an investigation of refractory borides (Brewer, Sawyer, Templeton & Dauben, 1951) it was found that cerium, thorium and uranium form isostructural tetraborides. The determination of this structure is described in the present paper. The existence and composition of the compound UB_4 were established by Andrieux (1929). Bertaut & Blum (1949) found the unit-cell dimensions, space group, and uranium positions of UB_4, in independent agreement with our results. They also agree with our boron positions, found by steric considerations (Bertaut, 1950). A brief account of our results has appeared elsewhere (Zalkin & Templeton, 1950).

These borides were synthesized by heating the elements together in vacuum at about 1500° C. Most of the products were microcrystalline powders, but some thorium preparations contained clusters of single crystals a few tenths millimetre in size. These crystals were rectangular parallelepipeds, nearly cubic in habit, with very flat faces and sharp edges, and with black metallic luster.

Rotation, oscillation, and Weissenberg diffraction patterns, taken with copper $K\alpha$ X-rays, revealed the structure of these crystals to be tetragonal with the symmetry of the space group D_{4h}^{5}–$P4/mbm$ or of one of its subgroups. The powder patterns of CeB_4, ThB_4 and UB_4 were then indexed. The resulting lattice parameters (based on chromium $K\alpha_1 = 2{\cdot}2896$ Å) are listed in Table 1. The unit cell contains four molecules.

The faces of the ThB_4 crystals were of the forms {110} and {001}. The diffraction patterns were taken with rotation about the [110] and [001] axes, which are parallel to crystal edges.

Patterson projections

The intensities of the spots on the zero-layer Weissenberg photographs were estimated by visual comparison with a set of standard spots made by variable exposure time. The resulting data, with no correction for absorption, were used to compute projections of the Patterson function. It was apparent from the [110] projection that the thorium atoms lie in a plane of constant z, since all the peaks in the Patterson function appeared at $z = 0$. We have chosen the origin so that $z = 0$ for these atoms. The same conclusion follows from the fact that the intensity of the reflection (hkl) is nearly independent of l, though this fact was at first obscured by the large absorption effects.

Only one arrangement of four thorium atoms in a plane was found to be congruous with the largest peaks in the [001] Patterson projection. This arrangement is represented by:

$$4\ \mathrm{Th}\ \text{in}\ 4(g)\ \text{of}\ P4/mbm\colon\ \pm(u,\ \tfrac{1}{2}+u,\ 0;\ \tfrac{1}{2}-u,\ u,\ 0),\quad u \simeq 5/16\ .$$

A choice of $u \simeq 3/16$ gives the same structure, but with different origin. If the parameter u is exactly 5/16 (0·3125), then the contribution of thorium to the

Table 1. *Lattice parameters*

	a	c	c/a	X-ray density (g.cm.$^{-3}$)
CeB_4	7·205±0·004 Å	4·090±0·004 Å	0·568	5·74
ThB_4	7·256±0·004	4·113±0·002	0·567	8·45
UB_4	7·075±0·004	3·979±0·002	0·562	9·38*
UB_4†	7·066	3·97	0·562	

* Andrieux (1929) reports 9·32 g.cm.$^{-3}$ as the experimental density.

† Bertaut & Blum (1949).

reflection (hkl) is zero if $4h-k = 8n+4$ or if $4k-h = 8n+4$. No such reflection was observed with copper $K\alpha$ X-rays. It is estimated from a consideration of the variation of calculated structure factors with u that the parameter must be $0{\cdot}313 \pm 0{\cdot}002$.

Correction for absorption

The half-thickness for absorption of copper $K\alpha$ X-rays in ThB_4 is estimated to be 3×10^{-4} cm., or one or two per cent of the dimensions of the crystals used. Thus diffraction is observed only for those surfaces which are exposed to the incident beam. If we neglect edge and end effects, for the moment, then the diffracted beam is zero unless it emerges from the same surface.

In Fig. 1 only face AB is effective for diffraction toward M, while both faces AB and AD are effective toward N. The diffraction intensity from one face for an equatorial reflection is

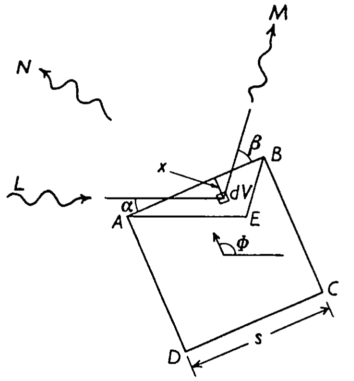

Fig. 1. Geometry for absorption correction.

$$I = Q \int \exp\left[-\sigma x\,(\operatorname{cosec}\alpha + \operatorname{cosec}\beta)\right] dV\ ,$$

where Q includes all factors except absorption and volume, σ is the linear absorption coefficient of the crystal, x is the distance of the volume element dV from the surface, and angles α and β are related to the Bragg angle θ and the rotation coordinate of the crystal Φ by

$$\alpha = \Phi - \tfrac{1}{2}m\pi\ ,$$
$$\beta = 2\theta - \alpha\ ,$$
$$m = 0, 1, 2, \text{ or } 3\ ,$$

and the integral is taken over the volume ABE. For a cube of side s large compared with $1/\sigma$, the result of the integration is

$$I = Qs^2/(\operatorname{cosec}\alpha + \operatorname{cosec}\beta)\ .$$

The function $G = \Sigma\,(\operatorname{cosec}\alpha + \operatorname{cosec}\beta)^{-1}$, where all contributing faces are considered, is plotted as a function of Φ and θ in Fig. 2. To this function must be added the effect of edges and ends, which is difficult to calculate because it depends on the perfection of the form of the crystal. The sharper the edges, the less their contribution. We arbitrarily added 0·07 to G (10% of its maximum value) and found satisfactory agreement with the observed intensities. The constant factors s^2 and σ were omitted from the calculations.

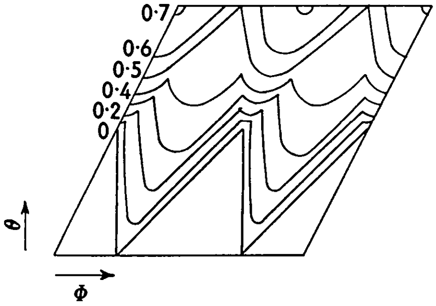

Fig. 2. The function G for a square prism, drawn to fit the zero-layer Weissenberg photographs.

This method, with trivial modifications, can be applied to any highly absorbing prismatic crystal rotated about the prism axis.

Signs were calculated for F values, corresponding to the above structure for the thorium atoms. Projections of the electron density along [001] are shown in Figs. 3 and 4, which illustrate the effect of the correction for absorption. The accuracy of the data is not sufficient to resolve peaks due to boron, but the thorium parameter is well verified. Consequently, the boron atoms were located by space considerations.

Boron positions

A large number of metallic borides are known in which a metallic lattice is interpenetrated by chains or nets

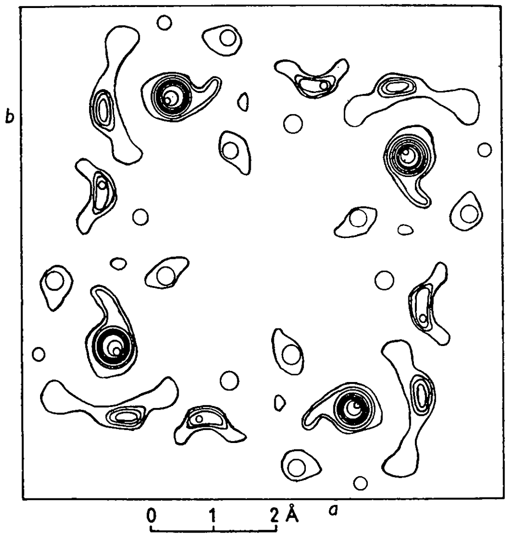

Fig. 3. Projection of ThB_4 on (001), data not corrected for absorption. Contours are on an arbitrary scale, commencing at 100 with intervals of 100.

of boron atoms. Each boron atom has from two to five boron neighbors, situated at a distance of 1·7–1·8 Å; this distance is independent of the coordination number. Of particular interest to us here are the compounds AlB_2 (Hofmann & Jäniche, 1936), ZrB_2 (McKenna, 1936), TiB_2 (Ehrlich, 1947), CrB_2, NbB_2, TaB_2 (Kiessling, 1949), VB_2 (Norton, Blumenthal & Sindeband, 1949), UB_2 (Daane & Baenziger, 1949) and MoB_2 (Bertaut & Blum, 1951), in which a simple hexagonal metallic lattice is interpenetrated by boron sheets, and the compounds CaB_6, CeB_6, ThB_6 and others (Allard, 1932; v. Stackelberg & Neumann, 1932), in which a simple cubic lattice of metal atoms is interpenetrated by a three-dimensional net of boron atoms.

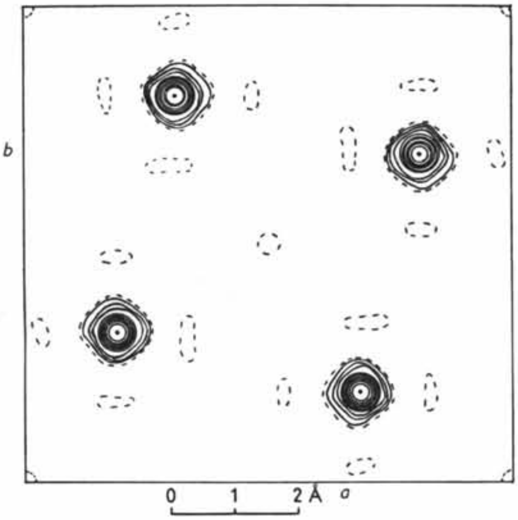

Fig. 4. Projection of ThB_4 on (001), data corrected for absorption. Solid contours on an arbitrary scale, commencing at 100 with intervals of 100. The broken contours are at 50. The small peaks are not considered significant.

If the atoms are assigned radii consistent with those found in other borides, there is just room in ThB_4 for 16 boron atoms per unit cell, and these can be arranged in only one way. The thorium lattice consists of layers of the kind shown in Fig. 5(*b*), each thorium having five thorium neighbors in the same layer. Between the layers are holes each bounded by six thorium atoms arranged at the corners of a triangular prism, just as in UB_2, Fig. 5(*a*). There are other holes each bounded by eight thorium atoms at the corners of a square prism nearly the same size as the simple cube of ThB_6, one layer of which is shown in Fig. 5(*c*). One boron (called B II) fits into each triangular hole, just as in the MB_2 compounds, and there are four such holes per unit cell. There is room for an octahedron of six boron atoms (B I and B III) in each square hole, just as in ThB_6, and there are two of these holes per unit cell. The boron atoms in adjacent holes are in contact and form a continuous three-dimensional network. A layer of this network is shown in Fig. 6. The octahedra are in contact with similar octahedra in adjacent layers.

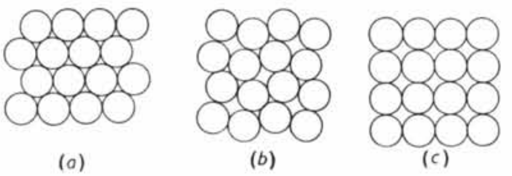
(*a*) (*b*) (*c*)

Fig. 5. Arrangement of metal atoms within a layer of (*a*) UB_2, (*b*) UB_4 or ThB_4, and (*c*) ThB_6.

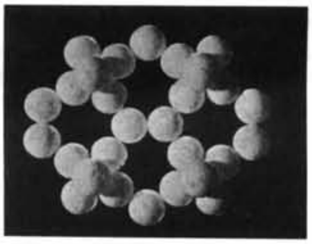

Fig. 6. The boron arrangement in ThB_4.

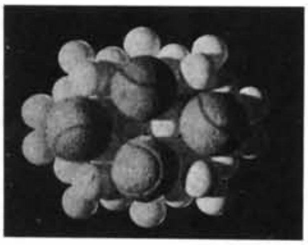

Fig. 7. The structure of ThB_4.

The parameters of the boron atoms were calculated by trial and error to make the borons as nearly equidistant as possible and as far from thorium atoms as possible. The results are:

$$4\,\mathrm{B\,I}\quad \text{in } 4(e)\text{:}\quad \pm(0, 0, v;\ \tfrac{1}{2}, \tfrac{1}{2}, v)\,,\quad v = 0{\cdot}212\,.$$

$$4\,\mathrm{B\,II}\quad \text{in } 4(h)\text{:}\quad \pm(w, \tfrac{1}{2}+w, \tfrac{1}{2};\ \tfrac{1}{2}-w, w, \tfrac{1}{2}),\quad w = 0{\cdot}087\,.$$

$$8\,\mathrm{B\,III}\quad \text{in } 8(j)\text{:}\quad \pm(x, y, \tfrac{1}{2};\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2};\ \bar{y}, x, \tfrac{1}{2};\ \tfrac{1}{2}+y, \tfrac{1}{2}+x, \tfrac{1}{2}),\quad x = 0{\cdot}170,\ y = 0{\cdot}042\,.$$

The distances of nearest neighbors are:

	ThB_4	CeB_4	UB_4
B I–B I	1·74 Å	1·73 Å	1·69 Å
–4 B III	1·74	1·73	1·69
B II–B II	1·79	1·77	1·74
–2 B III	1·79	1·78	1·75
B III–2 B I	1·74	1·73	1·69
–B II	1·79	1·78	1·75
–2 B III	1·80	1·78	1·75
M–4 B I	2·78	2·77	2·71
–4 B II	2·96	2·94	2·87
–2 B II	3·10	3·08	3·01
–8 B III	2·84	2·83	2·76
–4 *M*	3·74	3·71	3·65
–*M*	3·85	3·82	3·75
–2 *M*	4·11	4·09	3·98

Powder diffraction intensities

The intensities of the diffraction lines of a powder of UB_4 were recorded with a Norelco diffraction apparatus equipped with a Geiger counter. These are tabulated in Table 2, together with intensities calculated using the above parameters. The geometry of the spectrometer is such that a perfectly smooth sample has an absorption factor which is independent of θ. The systematic deviation between observed and calculated intensities for small θ which is shown in Table 2 is explained by roughness of the sample. No temperature factors have been introduced. The intensities calculated with or without the boron atoms are in reasonable agreement with those observed. Therefore the diffraction data do not determine the boron positions.

Table 2. *Intensity calculations on* UB_4

		Calculated intensities		
hkl	$\sin^2\theta$* calc.	not including borons	including borons	Observed† intensities
110	0·0237	12	6	<10
001	0·0375	165	119	57
200	0·0475	126	106	56
210	0·0594	167	148	88
111	0·0613	7	7	3
201	0·0850	122	124	86
220	0·0950	26	25	9
211	0·0969	171	181	121
310	0·1187	19	21	23
221	0·1325	31	36	33
002	0·1501	18	29	23
320	0·1543	7	8	3
311	0·1562	25	26	29
112	0·1739	2	2	3
400	0·1900	0	0	0
321	0·1918	11	8	13
202	0·1976	35	36	32
410	0·2018	58	61	59
212	0·2095	54	48	49
330	0·2137	23	23	22
401	0·2275	0	0	0
420	0·2374	0	0	0
411	0·2393	69	73	74
222	0·2451	12	9	11
331	0·2512	35	32	23
312	0·2689	11	7	10
421	0·2749	0	0	0
430	0·2968	5^+	5^-	5
322	0·3045	5^-	5^+	6
510	0·3087	4	3	4
431	0·3343	9	10	11
003	0·3378	7	6	
402	0·3401	0	0	0
520	0·3443	2	2	< 6
511	0·3462	7	18	13
412	0·3520	35	36	47
113	0·3616	9	7	< 7
332	0·3638	19	22	20
440	0·3800	0	0	0
521	0·3818	4	3	3
203	0·3853	12	12	19
422	0·3876	0	0	0
213	0·3972	19	20	19
530	0·4036	16	17	17
441	0·4174	0	0	0
600	0·4274	5	5	10
223	0·4328	5	5	7
610	0·4393	8	8	<12
531	0·4411	28	26	34
432	0·4469	6	5	9
512	0·4558	5	5	< 7
313	0·4565	5	5	10
601	0·4649	9	9	9
620	0·4749	4	4	3
611	0·4767	15	15	11

* Cu $K\alpha$ λ = 1·5418 Å.

† The intensity is given as 0 when the reflection was not observed in the Weissenberg or powder photographs. It is given as < 7, etc., when it was observed in photographs but was too weak to measure with the spectrometer.

The effect of boron on the intensities would be more significant in the case of CeB_4, but we did not have any pure samples of this compound large enough for a spectrometer measurement.

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