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THE CRYSTAL STRUCTURES OF  $CeB_4$ ,  $ThB_4$ , AND  $UB_4$

Allan Zalkin and D. H. Templeton

November 22, 1949

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The Crystal Structures of  $CeB_4$ ,  $ThB_4$ , and  $UB_4$

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Department of Chemistry and Radiation Laboratory  
University of California, Berkeley, California

The compounds  $CeB_4$ ,  $ThB_4$ , and  $UB_4$  have been shown to crystallize in a new structure, which has been worked out from x-ray diffraction patterns. This structure is designated as the " $ThB_4$ -type structure", since that was the compound first observed. These borides were prepared by D. L. Sawyer and L. Brewer of this laboratory, who heated the metals and boron together in vacuum at about  $1500^\circ C$ . Powder diffraction patterns were obtained of the three compounds. Rotation and Weissenberg patterns were obtained for  $[110]$  and  $[001]$  axes of a small single crystal of  $ThB_4$ . The patterns were indexed on tetragonal lattices whose dimensions are listed in Table I.

Table I

Lattice Parameters

	$CeB_4$	$ThB_4$	$UB_4$
$a$	$7.205 \pm .008 \text{ \AA}$	$7.256 \pm .004 \text{ \AA}$	$7.075 \pm .004 \text{ \AA}$
$c$	$4.090 \pm .005 \text{ \AA}$	$4.113 \pm .002 \text{ \AA}$	$3.979 \pm .002 \text{ \AA}$
$c/a$	0.568	0.567	0.562
x-ray density	$5.74 \text{ g/cm}^3$	$8.45 \text{ g/cm}^3$	$9.38 \text{ g/cm}^3$

Consideration of the intensities leads to the following structure for the metal atoms:

$$\text{Space group } D_{4h}^5 = P4/m\bar{b}m$$

$$4 \text{ Ce, Th, U in } 4 (g): \pm(u, 1/2+u, 0; 1/2-u, u, 0)$$

$$u = 0.31$$

These metal atoms are coplanar, with each having five nearly equidistant neighbors in the plane. Each metal atom has two neighbors in adjacent planes, but these are at a greater distance. This structure has holes, between the layers, which are

best filled by boron atoms as follows:

$$4 \text{ BI in } 4(e): \pm(0, 0, \underline{v}; 1/2, 1/2, \underline{v})$$

$$\underline{v} = 0.2$$

$$4 \text{ BII in } 4(h): \pm(\underline{w}, 1/2+\underline{w}, 1/2; 1/2-\underline{w}, \underline{w}, 1/2)$$

$$\underline{w} = 0.1$$

$$8 \text{ BIII in } 8(j): \pm(\underline{x}, \underline{y}, 1/2; 1/2+\underline{x}, 1/2-\underline{y}, 1/2; \underline{y}, \underline{x}, 1/2; 1/2+\underline{y}, 1/2+\underline{x}, 1/2)$$

$$\underline{x} = 0.2$$

$$\underline{y} = 0.04$$

Thus the compounds were assigned formulas of the type  $\text{MB}_4$ , in agreement with the deduction, from the phases observed in various preparations, that the composition is between  $\text{MB}_2$  and  $\text{MB}_6$ .

This structure can be considered as a combination of two other more simple structures. Each atom BII is in a hole bounded by six metal atoms at corners of a triangular prism, as is the case with boron in the isostructural compounds  $\text{AlB}_2^1$ ,  $\text{ZrB}_2^2$ ,  $\text{TiB}_2^3$ ,  $\text{CrB}_2$ ,  $\text{NbB}_2$ ,  $\text{TaB}_2^4$ ,  $\text{VB}_2^5$ , and  $\text{UB}_2^6$ . The atoms BI and BIII are grouped together as octahedra in holes bounded by metals at the corners of square prisms, analogous to the arrangement in the compounds  $\text{CaB}_6$ ,  $\text{CeB}_6$ ,  $\text{ThB}_6$ , and others<sup>7</sup>, in which a simple cubic array of metal atoms is interpenetrated by boron octahedra. The distances in the  $\text{MB}_4$  compounds are in reasonable agreement with the corresponding ones in the  $\text{MB}_2$  and  $\text{MB}_6$  compounds.

A more detailed account of this work will be published subsequently. This research was supported by the United States Atomic Energy Commission.

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