is less and not greater when unjustified assumptions are made.

The difference between the standard deviation 0·035 Å and that obtained by Carpenter, 0·017 Å, must be attributed mainly to the different method of calculation used. The accuracy of the determinations is approximately equal; in the present work more structure amplitudes (87 compared with 62) were used and more independent values for each observation were obtained; on the other hand the value of R is larger, being 0·142 compared with Carpenter's 0·110 for the same planes. Choice of weighting factor can provide only a partial explanation for the discrepancy; the ratio between the standard deviation obtained by the approximate Fourier method and by the method of least squares with Carpenter's weighting factor is 1:0·92. It seems likely that the larger value of the standard deviation gives a true picture of the accuracy obtainable in this structure analysis; this view is confirmed by Carpenter's statement that movement of the nitrogen atom by 0·05 Å produced a barely perceptible change in the agreement index.

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The Crystal Structure of TiB

By B. F. Decker and J. S. Kasper

General Electric Research Laboratory, The Knolls, Schenectady, N.Y., U.S.A.

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The structure of titanium monoboride has been determined by single-crystal and powder methods to be of the FeB-type. The dimensions of the orthorhombic unit cell are $a_0 = 6{\cdot}12$, $b_0 = 3{\cdot}06$ and $c_0 = 4{\cdot}56$ Å. As in other borides of composition MB, the boron atoms form zigzag chains through the lattice. Short interatomic distances indicate a higher-than-normal valence for the titanium atoms, when calculated by application of the Pauling equation, $D(n) = D(1) - 0{\cdot}6 \log n$.

Introduction

Two borides of titanium have been reported by Ehrlich (1949) as a result of his examination of the titanium–boron system: TiB_2, a hexagonal phase with the AlB_2 structure, and TiB, a cubic phase of the zincblende type. The latter structure appears unlikely, as pointed out by Andersson & Kiessling (1950), who have suggested instead a NaCl-type structure. A more reasonable explanation (Brewer, Sawyer, Templeton & Dauben, 1951) of the cubic pattern obtained by Ehrlich is that it represents TiN. Consequently, there exists doubt as to the existence of the compound TiB. In any event, it has been concluded (Kiessling, 1950) that titanium does not form a boride wherein there occur chains of boron atoms, such as is characteristic of other transition metal borides of formula MB.

We have found that a boride of composition TiB exists and that, furthermore, it is of the FeB type (Bjurström, 1933) containing boron chains.

Experimental

The material used in this investigation was obtained from Dr F. H. Horn of the Physics Division of this laboratory, who prepared it by arc-melting a mixture of powdered boron and titanium of high purity. An excess of titanium was used (77 atomic %) and the TiB formed by reaction occurred as needles embedded in the excess titanium. Preferential solution of the titanium by hot sulfuric acid allowed the needles to be collected and examined. Many of the needles were found to be single crystals.

The empirical formula from chemical analysis was $TiB_{1.1}$. No reliable experimental density could be obtained from the small amount of material available.

The X-ray data were obtained with Cu $K\alpha$ (nickel filtered) radiation both from a single crystal (approximately 0·1 mm. in diameter and 1 mm. in length) and from powdered specimens. Weissenberg photographs were obtained for the equator and first layer

Table 1. *Observed and calculated structure factors for hOl data*

hOl	F_o	F_c
002	7	4
004	38	46
101	12	13
102	47	54
103	12	12
104	4	2
105	5	6
200	27	31
201	36	33
202	0	1
203	26	24
204	18	19
205	18	18
301	43	43
302	7	6
303	30	31
304	0	1
305	34	29
400	10	7
401	34	35
402	0	1
403	31	32
404	2	6
405	16	20
501	23	19
502	24	22
503	18	17
504	0	1
600	39	38
601	2	7
602	0	2
603	2	5
701	0	0
702	39	37

$$R = \Sigma||F_o|-|F_c||\div\Sigma|F_o| = 0{\cdot}13.$$

Table 2. *Powder pattern*

$$I_c = p\cdot\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\cdot F^2\times10^{-3}$$

hkl	I_c	I_o	*d* (Å)
101	30	21	3·633
200	55	50	3·053
201	83	167	2·543
011	112		
111	181	150	2·346
002	1	0	—
210	128	117	2·161
102	146	167	2·140
211	66	71	1·956
301	69	83	1·863
202	0	0	—
112	60	71	1·755
311	5	0	—
212	0	0	—
400	1	37	1·528
020	35		
302	1	0	—
103	3	0	—
401	24	33	1·461
121	3	0	—
220	8	83 *B*	1·362
410	26		
312	52		
203	10		
013	12		
113	24	28	1·331
411	4	25	1·310
221	17		
402	0	0	—
022	0		
122	43	67	1·244
213	17		
303	12	17	1·219
501	5	37	1·181
321	29		
222	0	0	—
412	0		
004	13	< 17	1·141
313	1	0	—
104	0	0	—
511	12	< 17	1·101
420	0	0	—
502	5	23	1·079
322	1		
403	12		
204	4	0	—
123	2	0	—
421	19	21	1·051
114	0		
600	8	0	—
512	23	37	1·017
413	3		
223	9		
214	23	25	1·008
601	1	$\leqslant 17$	0·994
031	6		
304	0		
131	12	< 17	0·981
422	0	0	—
610	4	< 17	0·966
230	11		
503	3	21	0·953
323	15		
611	11	21	0·945
231	8		
314	0		
521	7	$\leqslant 17$	0·934
602	0	0	—
132	11	< 17	0·920
404	0	17	0·914
024	19		
513	7	0	—
124	0	0	—
105	1	0	—
331	1	0	—
612	0	0	—
232	0		
522	9	25	0·881
423	21		
414	25	25 *B*	0·876
224	8		
205	4		
015	7		
115	14	< 17	0·866
701	0	0	—
620	19	25 *B*	0·847
430	14		
332	26		
603	0		
033	6		
215	7	0	—
133	14	< 17	0·839
621	1	0	—
431	3		
504	0		
324	0		
305	15	< 17	0·833
711	14	< 17	0·827
702	30	60	0·816
233	16		
613	17		
523	11	0	—
514	0	0	—
315	3	0	—
622	0	0	—
432	0		
712	1	0	—
424	2	0	—
405	17	0	—
333	2	0	—
125	3	0	—

B denotes considerable broadening of the line.

with the needle axis as rotation axis. Intensity measurements were made by visual comparison with calibrated intensities on a strip of film for both Weissenberg and powder data.

Unit cell and space group

By means of Laue photographs it was established that the Laue symmetry was *mmm*. Preliminary cell dimensions were obtained from the Weissenberg and rotation photographs and then were refined with the use of powder data. These were determined to be:

$$a_0 = 6{\cdot}12\pm0{\cdot}01,\quad b_0 = 3{\cdot}06\pm0{\cdot}01,\quad c_0 = 4{\cdot}56\pm0{\cdot}01\ \text{Å}\,.$$

The needle axis is *b*.

The selection rules governing systematic absences were found to be:

$0kl$: absent for $k+l = 2n+1$;
$h0l$: no systematic absences;
$hk0$: absent for $h = 2n+1$;
hkl: no systematic absences.

Accordingly, the possible space groups are *Pnma*–D_{2h}^{16} or, with a transformation of axes, *Pna*–C_{2v}^{9}, the former being considered as more probable from this investigation.

It was assumed that $Z = 4$ to conform to the space-group requirements. The volume per titanium atom (21·5 Å^3) then is reasonable when compared with the corresponding values for TiB_2 (25·5 Å^3) and Ti (17·5 Å^3). The calculated density for TiB is 4·56 g.cm.$^{-3}$.

Determination of the structure

Assuming the centrosymmetric space group *Pnma*, the four titanium atoms are required to be in the special positions

$$4(c):\ x, \tfrac{1}{4}, z;\ \bar{x}, \tfrac{3}{4}, \bar{z};\ \tfrac{1}{2}-x, \tfrac{3}{4}, \tfrac{1}{2}+z;\ \tfrac{1}{2}+x, \tfrac{1}{4}, \tfrac{1}{2}-z\,.$$

(Note that the same positions for Ti atoms would hold in the space group *Pna*.) Consequently, the location of titanium atoms could be obtained from $h0l$ data alone.

Approximate x and z parameters for the titanium atoms were obtained from a Patterson projection on (010) followed by a Fourier projection on (010), both effected with an optical synthesizer. Packing considerations on the basis of probable atomic radii indicated that there was only one set of four positions where boron atoms could be placed without making absurdly short interatomic distances. These positions are the centers of trigonal prisms formed by six titanium atoms. They also would be in 4(c) locations of *Pnma*.

A Fourier projection on (010) was then computed with Beevers–Lipson strips and is shown in Fig. 1. Considerable diffraction effects are evident, as would be expected from using data only to the Cu $K\alpha$ limit, but the second highest peak is of the appropriate height relative to the titanium peak for a boron atom. It is in the position predicted.

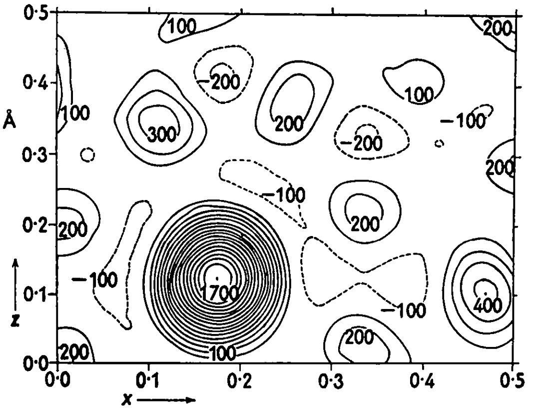

Fig. 1. Projection of electron density on (010) for TiB.

The parameters from the calculated projection, uncorrected for lack of convergence, are:

$$\text{for Ti: } x = 0{\cdot}177,\ z = 0{\cdot}123;$$
$$\text{for B: } x = 0{\cdot}029,\ z = 0{\cdot}603\,.$$

Structure factors calculated from these parameters were in good agreement with the observed values, as shown in Table 1. The boron contribution is significant for about one-third of the reflections.

Since the x and z parameters of the boron atoms correspond to the values for projections of the centers of trigonal prisms of neighboring titanium atoms, it appears very likely that the boron atoms are at these centers, with $y = \frac{1}{4}$, as has been inferred for FeB (Bjurström, 1933) and similar borides (Kiessling, 1950). No attempt was made to refine the y parameter for possible small deviations from the value of $\frac{1}{4}$. However, measured intensities of a powder photograph were compared with those calculated assuming the space group of higher symmetry *Pnma*, for which $y = \frac{1}{4}$ for boron (see Table 2). The agreement is judged satisfactory for indicating the essential correctness of the parameters proposed, despite limitations on the accuracy of the measured intensities. The extreme hardness and needle-like nature of the crystallites made it difficult to avoid slight orientation effects. Also, no absorption correction was applied, since it did not seem warranted for measurements made by comparison with a calibrated film strip.

Discussion of the structure

TiB is another boride of the FeB-type, characterized by zigzag chains of boron atoms parallel to the b direction, each boron atom lying at the center of a trigonal prism of six titanium atoms. The arrangement is shown in Fig. 2, and nearest neighbors for both the titanium and boron atoms, with interatomic distances listed, are shown in Fig. 3.

Comparison of TiB with monoborides of the same type reveals that the expansion of the lattice to accommodate the larger titanium atoms is less than one would expect from a consideration of the radii of the metal atoms. For example, ratios of axial lengths of TiB to those of FeB are:

$$a_{TiB}/a_{FeB} = c_{TiB}/c_{FeB} = 1{\cdot}12,\ b_{TiB}/b_{FeB} = 1{\cdot}04\,.$$

While the expansion along the a and c axes is almost as large as one would predict ($\sim 1{\cdot}14$) from atomic sizes, along the b axis (the boron chain direction) it is much less. Consequently, there are abnormally short Ti–Ti and Ti–B distances. This is reflected in the results obtained when an application of Pauling's (1947) theory of metal bonding is made to all of the known monoborides. Values of boron and metal valences obtained using the formula

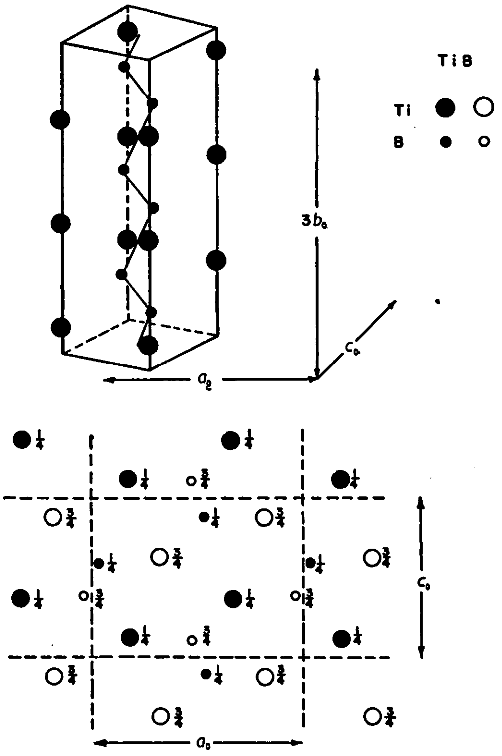

Fig. 2.

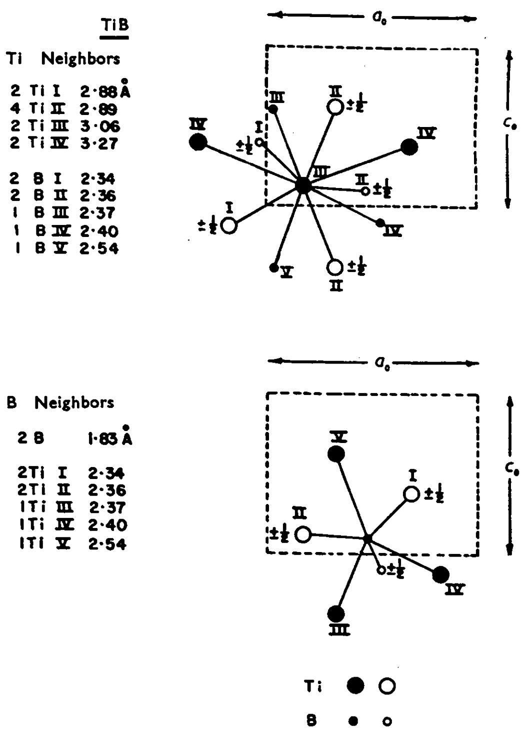

Fig. 3.

Fig. 2. The arrangement of atoms in TiB.
Fig. 3. Nearest neighbors for Ti and B atoms, and interatomic distances in the crystal TiB.

$$D(n) = D(1) - 0{\cdot}6 \log n$$

are given in Table 3. Although the boron valence is high in some cases, the metal valence is in essential agreement with or less than the Pauling valence for all compounds except TiB, where the value of 5·6 is much higher than the normal valence of 4. Such a value can hardly be taken literally as the true valence for titanium and this result may represent the inadequacy of the Pauling theory for this compound. Empirically, however, it can be interpreted as a reflection of the much tighter binding in TiB than for the other borides.

Table 3. *Calculated values of valence for monoborides, using Pauling's theory*

*M*B	B	*M*	Pauling valence for *M*
CbB	3·0	4·9	5
TaB	3·1	5·4	5
MoB	4·0	5·4	5·78
WB	4·0	5·6	5·78
FeB	4·3	5·5	5·78
CoB	4·3	6·1	5·78
MnB	3·9	4·9	5·78 (also 4·16)
CrB	4·0	4·9	5·78
TiB	3·4	5·6	4

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