

The Crystal Structure of Ru_7B_3

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The crystal structure of Ru_7B_3 has been determined from single crystal data. There are two formula units in the unit cell, which Åselius¹⁴ has determined to be hexagonal with $a = 7.467 \text{ \AA}$ and $c = 4.713 \text{ \AA}$. The space group is $P6_3mc$. The ruthenium atoms are situated in two six-fold positions 6 (c) with $x_{\text{I}} = 0.4563$, $z_{\text{I}} = 0.318$, and $x_{\text{II}} = 0.1219$, $z_{\text{II}} = 0.000$ and one two-fold position 2(b) with $z_{\text{III}} = 0.818$. The structure of Ru_7B_3 is very closely related to that of the trigonal chromium carbide Cr_7C_3 .

Very little is known about the borides of the platinum metals. Buddery and Welch¹ have shown that a number of such borides exists and are easily prepared by direct combination of the elements. These authors have given the approximate compositions of many borides of the platinum metals and, in some cases, also have established the unit cell dimensions. Later Mooney and Welch² determined the crystal structure of Rh_2B from single crystal data. Rh_2B seems to be the only noble metal boride with known crystal structure and, as Geller³ points out, it is isomorphous with Rh_2Ge^3 , $\delta\text{-Ni}_2\text{Si}^4$ and Co_2Si^5 .

Since a knowledge of the platinum metal borides is very essential for a better understanding of the transition metal borides, X-ray investigations in this group of compounds have been started at this institute. The borides of ruthenium were supposed to be those most related to the well-known molybdenum and iron borides and were therefore chosen as the first object of investigation. In an investigation of the Ru-B system, Åselius¹⁴, confirming the results of Buddery and Welch, has found that the most metal-rich intermediate phase in this system has the approximate composition Ru_2B . He was able to index the powder photograph, choosing a hexagonal unit cell with $a = 7.467 \text{ \AA}$, $c = 4.713 \text{ \AA}$ and $c/a = 0.631$. The density was found to be 10.7 g/cm^3 , showing that there are 14 ruthenium atoms in the unit cell and indicating that the formula should be written Ru_7B_3 rather than Ru_2B . Åselius¹⁴ has also found the isomorphous phase Rh_7B_3 with $a = 7.47 \text{ \AA}$, $c = 4.78 \text{ \AA}$ and $c/a = 0.640$.

The crystal structure of Ru_7B_3 has been determined with single crystals kindly donated by Åselius. The relation of this structure to that of the trigonal chromium carbide 6 , Cr_7C_3 , and to other transition metal borides will be discussed.

EXPERIMENTAL

Some small single crystals were picked out of an arc melted alloy. By use of $\text{MoK}\alpha$ -radiation, Weissenberg photographs around the a - and c -axes were taken of two crystals which were found to be free from satellites. The multiple film technique (with thin iron foils between the films) was used and the intensities were estimated visually. With the exception of a few low angle reflexions from the larger crystal (rotated around the a -axis), no serious influence from absorption or extinction could be detected. $\log I_o/I_c$ decreased linearly with $\sin^2\theta/\lambda^2$, and for both crystals the temperature constant B was found to be 0.42 \AA^2 . The $\rho_o(xy)$ and $\rho_c(xy)$ electron density projections were computed on the Hagg-Laurent 7 machine and with Beevers-Lipson strips. Twenty eight nonequivalent $hki0$ reflexions were used in these calculations.

DETERMINATION AND DESCRIPTION OF THE STRUCTURE

The Weissenberg photographs showed that the crystals were hexagonal. There was no evidence that the symmetry should be lower. The systematic extinctions of $h\bar{h}2hl$ reflexions for l odd gave the possible space groups $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$. The approximate positions of the 14 ruthenium atoms in the unit cell were deduced from the following two conditions:

(1). The ruthenium atoms cannot all have the z -parameters 0, $1/4$, $1/2$ and $3/4$. This is a consequence of the relation $|F|_{0008} < |F|_{0002} < |F|_{0004} < |F|_{0006}$ which was found from the intensities of the $000l$ -reflexions.

(2). No Ru-Ru contacts are shorter than 2.5 \AA . This seems a reasonable assumption since the shortest Ru-Ru distance in pure ruthenium is 2.65 \AA . In particular, this condition establishes that two ruthenium atoms cannot have the same x - and y -parameters but different z -parameters because such a situation would imply Ru-Ru contacts shorter than 2.36 \AA ($c/2 = 2.357 \text{ \AA}$).

These two conditions eliminate all the positions of space group $P6_3/mmc$. Condition (2) rules out $12(k)$, $12(i)$, $6(g)$, $4(f)$, $4(e)$, $2(b)$ and $2(a)$. Condition (1) rules out any combination of $12(j)$, $6(h)$ and the remaining two-fold positions. In the same way any combination of the positions of space group $P\bar{6}2c$ violates one or both of the above conditions. Only the space group $P6_3mc$ then remains. Of the positions in this space group condition (2) eliminates $12(d)$ and $2(a)$. The only alternative remaining is to put the 14 ruthenium atoms into two six-fold positions $6(c)$ and one two-fold $2(b)$ position. An evaluation of the threedimensional Patterson function in the section $P(xy0)$ and along $P(00z)$ showed that no Ru-Ru contacts shorter than 2.7 \AA exist in the basal plane or in the direction of the c -axis. This supports the correctness of condition (2). In addition, the Patterson function gave approximate x -parameters of the ruthenium atoms. Approximate z -parameters could be obtained from space considerations.

The x -parameters were refined from successive $\rho_o(xy)$ and $\rho_c(xy)$ syntheses until the final "backshift"-corrections were less than ± 0.001 . The final x -parameters (Table 1) are estimated to be reliable to within ± 0.002 . No

Table 1. Final atomic parameters of Ru₇B₃. Space group *P6₃mc*. (Estimated accuracy of *x*-parameters ± 0.002 , of *z*-parameters ± 0.003 .)

6 Ru _I	in 6(<i>c</i>)	$x_I = 0.456_3$	$z_I = 0.318$
6 Ru _{II}	in 6(<i>c</i>)	$x_{II} = 0.121_9$	$z_{II} = 0.000$
2 Ru _{III}	in 2(<i>c</i>)	$x_{III} = 1/3$	$z_{III} = 0.818$
6 B	in 6(<i>c</i>)	$x_B = 0.18_7$	$z_B = 0.58_0$

significant difference in the scattering parameters (number of electrons) of the different ruthenium atoms was revealed in the Fourier projections. The *z*-parameter of the Ru_{II} atom (Table 1) was chosen to be zero. The *z*-parameter of the Ru_I atom was obtained by comparison between calculated and observed $|F|$ values of $3n03n\bar{l}$ reflexions ($l = 5, 7, 9$), the contribution of the Ru_{III} atom to these reflexions being zero. In the same way the *z*-parameter of the latter was obtained from inspection of $20\bar{2}l$ reflexions ($l = 5, 7, 9$) since the contribution of the Ru_I atom to the intensities of these reflexions was found to be very small. A variation of ± 0.001 in the *z*-parameters changed the $|F|_{\text{calc}}$ values by 1–5 %, and the final *z*-parameters are estimated to be reliable to within ± 0.003 . With the final atomic parameters given in Table 1, the reliability index of the observed 28 nonequivalent $hki0$ reflexions was found to be 8.2 % while that of the observed 64 nonequivalent $h0\bar{h}l$ reflexions was 11.8 %.

As seen from Fig. 1 the ruthenium skeleton of Ru₇B₃ is fairly densely packed and is built up mainly of metal tetrahedra, some of which are outlined in the figure. Besides the tetrahedra there are metal octahedra with their centres in $0, 0, 1/4$ and $0, 0, 3/4$ and sharing faces in the *c*-direction. Between

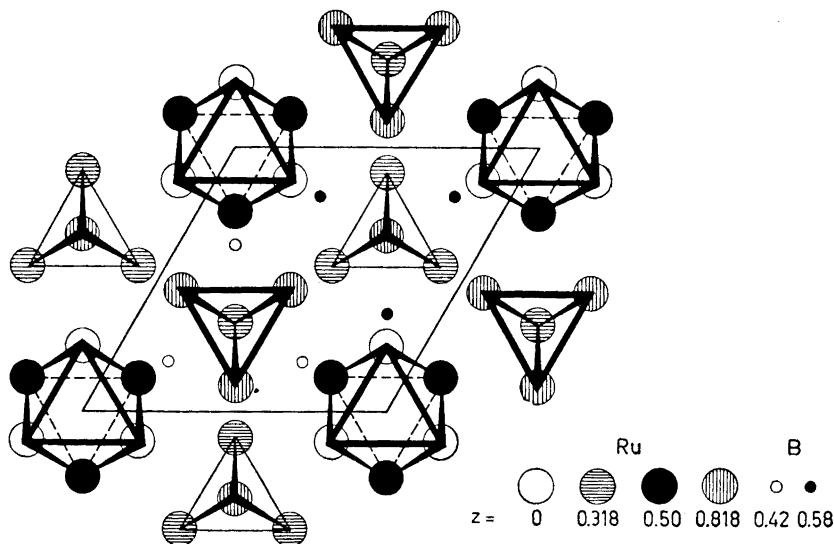


Fig. 1. The structure of Ru₇B₃ as seen along the hexagonal axis.

the octahedra and the tetrahedra there are two types of 'holes' whose centres in the mirror planes correspond to positions 6(c). The larger 'hole' has a roughly trigonal prismatic environment and the parameters of its centre are $x = 0.20$; $z = 0.58$. The smaller hole is more irregular and the parameters of its 'centre' are $x \sim 0.20$; $z \sim 0.42$. In addition to these two types of holes only the octahedral holes of the metal skeleton can possibly accommodate the boron atoms. (The tetrahedral interstices are much too small for a boron atom.)

The difference ($F_o - F_c$) synthesis (only the contribution from the ruthenium atoms was included in the F_c terms) was carried out in the xy -projection. No maximum was found in the origin, indicating that there are no boron atoms in the octahedral holes. The highest maximum of the difference synthesis (amounting to 5 % of the ruthenium maxima of the F_o synthesis) had the coordinates $x \sim 0.17$; $y \sim 0.83$, which indicates that one of the remaining 'holes' did contain boron atoms. An attempt has been made to obtain some experimental evidence showing which of the two holes is actually occupied. Since the x_B -parameter is about 0.20, the $50\bar{5}l$ ($l = 2, 4$) are the $h0\bar{h}l$ reflexions that are most likely to give some information about the z -parameter of the boron atom. Fortunately, these two reflexions are fairly weak and therefore a considerable influence of the boron atoms on their intensities can be anticipated. The $|F_o - F_c|/|F_o|$ values for the $50\bar{5}2$ and $50\bar{5}4$ reflexions are given below. The value of $|F_c|$ has been computed for the two alternative boron positions and also for the situation when the contribution from boron is neglected.

$|F_o - F_c|/|F_o|$ values for the $50\bar{5}2$ and $50\bar{5}4$ reflexions

	neglecting boron	with 6 boron atoms in 6(c) and $x_B = 0.20, z_B = 0.58; x_B = 0.20, z_B = 0.42$	
$50\bar{5}2$	0.21	0.11	0.31
$50\bar{5}4$	0.16	0.11	0.27

As seen from the table, a z_B value of 0.58 is strongly preferred over the value of 0.42. In fact, with $x_B = 0.20$ the only z_B parameters which will improve the agreement between observed and calculated structure factors for the above reflexions are $z_B \sim 0.1$ and $z_B \sim 0.6$, and the first of these is impossible since it would give a Ru-B distance of about 1 Å.

Thus, there is considerable experimental evidence that the boron atoms are situated in the largest hole of the ruthenium skeleton, corresponding to a position 6(c) with $x_B \sim 0.20$ and $z_B \sim 0.58$. Since the experimental material does not permit an accurate determination of the boron positions, the coordinates of the centre of the hole have been chosen as boron parameters. Aside from the experimental evidence, it is very unlikely from space considerations that boron atoms can occupy the 'smaller' holes of the metal skeleton since this would involve Ru-B distances shorter than 2.0 Å.

The final atomic parameters are given in Table 1. The interatomic distances (< 3.5 Å) are given in Table 2. A projection of the structure along the c -axis is shown in Fig. 1.

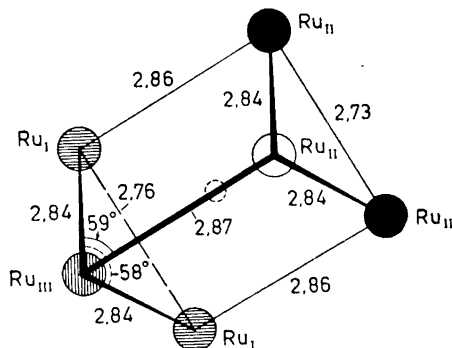


Fig. 2. The environment of the boron atoms in Ru₇B₃ as seen along the hexagonal axis.

DISCUSSION

The Ru-Ru contacts (Table 2) are on the average only 0.10 Å longer in Ru₇B₃ than in ruthenium where the average interatomic distance is 2.68 Å. There are also contacts shorter than those in pure ruthenium. The Ru_I atoms form zig-zag rows in the *c*-direction with an intermetallic distance of 2.61 Å. The boron atom has its six closest neighbours at an average distance of 2.16 Å. (With $r_{\text{Ru}} = 1.34$ Å, r_{B} will be 0.82 Å.) This value is rather small and is in accordance with the Me-B distances found in MoB (B-6 Mo 2.23 Å)⁸ and in the recently discovered borides of the cementite (Fe₃C) type⁹, e.g. in Ni₃B (B-6 Ni 2.04 Å). In these two phases the boron atoms have a trigonal prismatic environment as in Ru₇B₃. In Mo₂B⁸ and Rh₂B² where the boron atoms have more than six close neighbours, the Me-B distances are considerably larger. In Mo₂B the boron atoms have eight metal neighbours at 2.37 Å; in Rh₂B nine at distances between 2.38 Å and 2.63 Å with an average value of 2.50 Å.

The most remarkable feature of the structure of Ru₇B₃ is its close similarity to that of the trigonal chromium carbide⁶, Cr₇C₃. The formula and the unit cell of this carbide were determined by Westgren and Phragmén¹⁰, who found the unit cell to be hexagonal with $a = 13.87$ kX, $c = 4.53$ kX and $2c/a = 0.654$. Later Westgren *et al.*¹¹ found a small deviation from the hexagonal symmetry and concluded that Cr₇C₃ was indeed trigonal. In a more recent paper on this

Table 2. Interatomic distances (in Å) in Ru₇B₃. (Estimated accuracy ± 0.03 Å.)

		Average
Ru _I	— 11 Ru 2.61(2); 2.72; 2.76(2); 2.81(2); 2.84(2); 2.86(2).	2.77 Å.
	— 4 B 2.15(2); 2.66(2).	
Ru _{II}	— 11 Ru 2.73(2); 2.81(2); 2.84(4); 2.86(2); 2.87.	2.82 Å.
	— 4 B 2.15; 2.16(2); 2.86.	
Ru _{III}	— 12 Ru 2.72(3); 2.84(6); 2.87(3).	2.78 Å.
	— 3 B 2.20(3).	
B	— 9 Ru 2.15; 2.15(2); 2.16(2); 2.20; 2.66(2); 2.86.	2.16 Å.
	— 2 B 3.22(2).	(six first)

phase, Westgren⁶ gave its approximate crystal structure. As $hki0$ reflexions appeared only when h was even and k was even, a projection on the basal plane could be divided into four identical parts. The atomic arrangements projected on such a part were determined by Westgren. Using the space group $P6_3mc$ he found 6 Cr_I in 6(c) with $x_I = 0.455$, 6 Cr_{II} in 6(c) with $x_{II} = 0.125$ and 2 Cr in 2(b). The chromium parameters of Westgren agree within 0.001 and 0.003 with those reported here for the ruthenium atoms of Ru₇B₃. Westgren did not try to determine the z -parameters but he gave a description of the complete structure using the hexagonal space group $P6_3mc$. In particular, he pointed out the trigonal prismatic environment of the carbon atoms. It is evident from Westgren's proposed structure that the near environment of the atoms in Cr₇C₃ and Ru₇B₃ is practically the same. The structure of Cr₇C₃ can be described as a slightly distorted superstructure of Ru₇B₃, making the unit cell four times larger and causing the symmetry to decrease to trigonal.

Ru₇B₃ is another example of a boride with close similarities to the 'complicated' carbides of chromium, manganese and iron. Other recently discovered examples are Co₃B and Ni₃B⁹ which crystallize in the cementite (Fe₃C) structure. It has also been found that boron and carbon to a large extent can substitute for each other in the 'complicated' carbide structures, e.g. in Fe₃(C, B)¹² and in Fe₂₃(C, B)₆¹³. It does not seem unlikely that further studies on the platinum metal borides will reveal additional similarities between borides and carbides.

Acknowledgements. The research described in this paper was sponsored by the *European Commission of Air Research and Development Command* under Contract No. AF 61(052)–40. The financial support from this authority is gratefully acknowledged.

The author wishes to thank professor G. Hägg for his kind interest. Many thanks are also due to Dr S. Rundqvist for valuable suggestions and to Mr J. Åselius who has permitted me to quote unpublished results.

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Received October 6, 1958.