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The Crystal Structure of $Ru_{11}B_8$

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The crystal structure of $Ru_{11}B_8$ has been determined by single crystal methods.

The orthorhombic unit cell has the following dimensions: $a = 11.60_9$ Å, $b = 11.34_2$ Å and $c = 2.83_8$ Å.

There are two formula units in the elementary cell and the space-group is $Pbam-(D_{2h}^9)$ No. 55.

The twentytwo ruthenium atoms are situated in one twofold position and five fourfold positions with two ruthenium atoms in 2(*a*), twelve ruthenium atoms in three fourfold positions 4(*g*): $x_{II} = 0.2844$ $y_{II} = 0.3913$, $x_{III} = 0.0429$ $y_{III} = 0.3952$, $x_{IV} = 0.1686$ $y_{IV} = 0.1740$ and eight ruthenium atoms in two fourfold positions 4(*h*): $x_V = 0.4636$ $y_V = 0.2962$, $x_{VI} = 0.3404$ $y_{VI} = 0.0616$.

The sixteen boron atoms are also situated in fourfold positions with four in 4(*g*): $x_{II} = 0.34_{79}$ $y_{II} = 0.21_{56}$, and twelve in 4(*h*): $x_I = 0.13_{98}$ $y_I = 0.01_{81}$, $x_{III} = 0.15_{23}$ $y_{III} = 0.32_{65}$, $x_{IV} = 0.27_{99}$ $y_{IV} = 0.25_{35}$.

Very little is known about the structures of the borides of the platinum metals.

Buddery and Welch [1] have prepared a number of such borides by direct combination of the elements.

Mooney and Welch [2] determined the crystal structure of Rh_2B from single crystal data. Later Aronsson [3] determined the crystal structures of Ru_7B_3 and Rh_7B_3 and Aronsson and co-workers [4] the crystal structures of RhB, PtB and IrB_{1-2}.

An X-ray investigation of the Ru—B system has been started at this Institute in order to establish the existence and compositions of the intermediate phases and to determine the crystal structures. In arc-melted ruthenium-boron alloys five intermediate phases can be identified, Ru_7B_3, $Ru_{11}B_8$, RuB, $RuB_{\sim 1.5}$, $RuB_{\sim 3}$.

The present paper gives an account of the crystal structure of the phase $Ru_{11}B_8$.

EXPERIMENTAL

Alloys were prepared by high frequency-melting ruthenium (claimed purity *ca.* 99.8 %, obtained from Heraeus, Hanau, Germany) and boron (claimed purity 99.0—99.7 %, kindly donated by Borax Consolidated, London). No chemical analyses were carried out and all compositions reported are nominal.

The reaction products were investigated with X-ray powder methods. Guinier-type cameras with Cu$K\alpha$-radiation were used. The unit cell dimensions were determined with CaF_2 as internal calibration standard, $a = 5.4630$ Å.

For the single-crystal work, a small, roughly spherical crystal fragment was selected from a crushed $Ru_{1.25}B$-alloy. Single crystal photographs were taken around the *c*-axis with an equi-inclination Weissenberg camera with niobium-filtered MoK radiation. The multiple film technique was employed with thin iron foil between successive films. The intensities were visually estimated with the aid of a standard intensity scale. The summation of the Fourier series and the structure factor calculations were made on the electronic digital computer BESK with programs (available at BESK) devised by M. Edstrand and Åsbrink *et al.*[5] In the structure factor calculations the atomic scattering factors were approximated to the following expression:

$$f_i = A_i \exp(-a_i/\lambda^2\sin^2\Theta) + B_i \exp(-b_i/\lambda^2\sin^2\Theta) + C_i \exp(-c_i/\lambda^2\sin^2\Theta) + D_i$$

The constants A_i, B_i, C_i and a_i, b_i, c_i have been calculated by Appel [6] on the basis of atomic scattering factor tables given by Tomas and Umeda [7] for ruthenium and by Ibers [8] for boron.

	A	*B*	*C*	*a*	*b*	*c*
Ruthenium	15.176	16.599	11.760	0.240	2.637	20.292
Boron	1.644	0.406	2.878	0.6069	4.5832	33.019

The real part of the dispersion correction for ruthenium (D_i in the expression above) was obtained from the table of Dauben and Templeton [9].

RESULTS

The powder photograph of the alloy from which the actual single-crystal specimen was selected, gave the following dimensions of the orthorhombic unit cell:

$$a = 11.60_9 \text{ Å}, \quad b = 11.34_2 \text{ Å}, \quad c = 2.83_6 \text{ Å and } U = 373.4 \text{ Å}^3.$$

Small variations of the lattice parameters (0.2 %) have been observed.

It is evident from powder and single-crystal data that $Ru_{11}B_8$ is orthorhombic. Since $0kl$ reflexions appear only for $k = 2n$, and $h0l$ reflexions only for $h = 2n$, and no limiting conditions are found for hkl,$hk0$ and $00l$ reflexions, the most probable space-groups are *Pbam* and *Pba*2. The distribution of intensities in the $hk0$ and $hk2$ zones are similar, apart from the normal decline. This distribution of intensities indicates that the ruthenium atoms are situated in planes perpendicular to the *c*-axis with a spacing of $c/2$. For that reason, only the $|F|^2$ values for $hk0$ and $hk1$ reflexions were necessary for evaluating the Patterson sections $P(UV0)$ and $P(UV\ 1/2)$. The analysis of these sections showed that the heights and positions of all large peaks in $P(UV0)$ and $P(UV\ 1/2)$ could be interpreted by assuming the space-group to be *Pbam* with twenty ruthenium atoms in five fourfold positions and two ruthenium atoms in a twofold position. If the twofold position 2(*a*) is chosen, twelve ruthenium atoms are situated in three fourfold positions 4(*g*) and eight ruthenium atoms in two

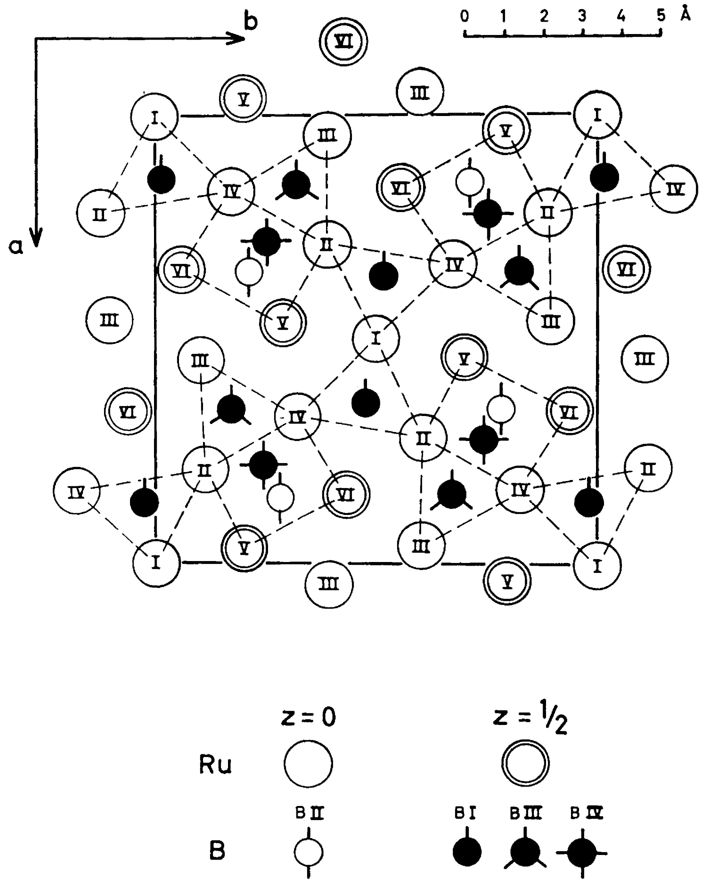


Fig. 1. The structure of $Ru_{11}B_8$ projected on the *ab*-plane.

fourfold positions 4(*h*). During the refinement of the structure nothing was found to contradict the choice of the space-group *Pbam*. (Small deviations from this symmetry for the boron positions cannot be excluded.)

Starting with the rough parameter values obtained from the Patterson maps, signs were calculated for the observed $F(hk0)$ values, and the electron density projection $\varrho\ (xy)$ was computed. The x and y coordinates of the ruthenium atoms were refined from successive difference syntheses. After the final refinement of the ruthenium coordinates, the R value 0.105 was obtained for the observed 310 independent *hk*0 reflexions when an empirical isotropic temperature factor with $B = 0.23_0$ Å^2 was applied. No corrections for absorption and extinction were made.

In the final difference synthesis map, in which all ruthenium atoms were subtracted, four rather well resolved boron maxima were visible. Three of

Table 1. Final atomic parameters of $Ru_{11}B_8$. Space-group *Pbam*. (The standard deviation for all Ru-coordinates is $\pm$ 0.0002.)

2 Ru_I	in 2(*a*)		
4 Ru_{II}	in 4(*g*)	x_{II} = 0.2844	y_{II} = 0.3913
4 Ru_{III}	in 4(*g*)	x_{III} = 0.0429	y_{III} = 0.3952
4 Ru_{IV}	in 4(*g*)	x_{IV} = 0.1686	y_{IV} = 0.1740
4 Ru_V	in 4(*h*)	x_V = 0.4636	y_V = 0.2962
4 Ru_{VI}	in 4(*h*)	x_{VI} = 0.3404	y_{VI} = 0.0616
4 B_I	in 4(*h*)	x_I = 0.13_{98}	y_I = 0.01_{81}
4 B_{II}	in 4(*g*)	x_{II} = 0.34_{79}	y_{II} = 0.21_{56}
4 B_{III}	in 4(*h*)	x_{III} = 0.15_{23}	y_{III} = 0.32_{65}
4 B_{IV}	in 4(*h*)	x_{IV} = 0.27_{99}	y_{IV} = 0.25_{35}

these maxima, corresponding to one 4(*g*) position and three 4(*h*) positions had about the same height, but the B_{IV} maxima was considerably lower and not symmetrical in shape. Only one other maximum of the same height as the boron maxima was found, but space considerations showed that this maximum could not be a boron maximum.

With the same temperature factor ($B = 0.23_0$ Å^2) and with all atoms subtracted, a final refinement cycle was made. The reliability index of the observed 310 independant *hk*0 reflexions was found to be 0.097. A list of calculated and observed structure factors can be obtained from this Institute on request.

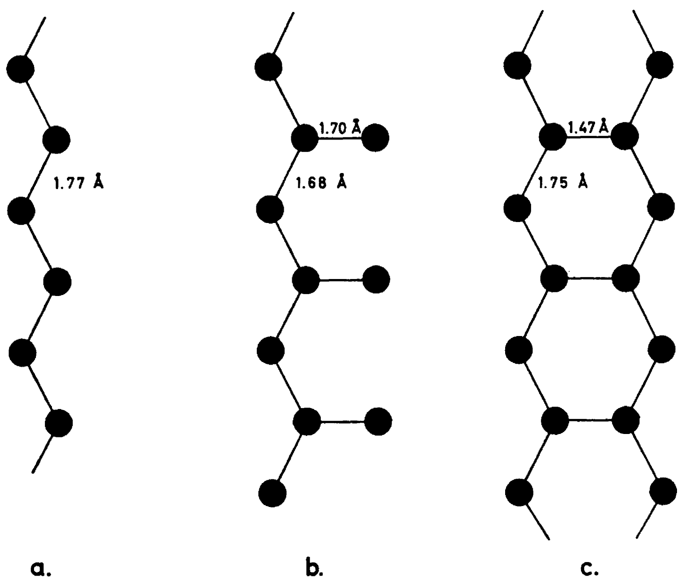


Fig. 2. Three different types of boron chains.

a. boron chain in FeB
b. boron chain in $Ru_{11}B_8$
c. boron chain in Mn_3B_4

Table 2. Interatomic distances (in Å) in $Ru_{11}B_8$. (Distances $\leq$ 3.25 Å listed. The standard deviations of Ru−Ru distances less than 0.01 Å.)

Atom	Neighbour	Distance	Average
Ru_{I}	− 2Ru_{I}	2.84(2)	2.78 Å
	− 2Ru_{II}	2.79(2)	
	− 2Ru_{IV}	2.78(2)	
	− 4Ru_{V}	2.74(4)	
	− 4B_{I}	2.16(4)	
Ru_{II}	− Ru_{I}	2.79	2.79 Å (nine shortest)
	− 2Ru_{II}	2.84(2)	
	− Ru_{III}	2.80	
	− 2Ru_{IV}	2.81; 3.25	
	− 2Ru_{V}	2.74(2)	
	− 2Ru_{VI}	2.80(2)	
	− 2B_{I}	2.20(2)	
	− B_{II}	2.12	
	− 2B_{III}	2.21(2)	
	− 2B_{IV}	2.11(2)	
Ru_{III}	− Ru_{II}	2.80	2.77 Å
	− 3Ru_{III}	2.58; 2.84(2)	
	− Ru_{IV}	2.90	
	− 2Ru_{V}	2.75(2)	
	− 4Ru_{VI}	2.72(2);2.79(2)	
	− B_{II}	2.59	
	− 2B_{III}	2.06(2)	
Ru_{IV}	− Ru_{I}	2.78	2.81 Å (nine shortest)
	− 2Ru_{II}	2.81; 3.25	
	− Ru_{III}	2.90	
	− 2Ru_{IV}	2.84(2)	
	− 4Ru_{VI}	2.76(2); 2.79(2)	
	− 2B_{I}	2.29(2)	
	− B_{II}	2.13	
	− 2B_{III}	2.24(2)	
	− 2B_{IV}	2.12(2)	
Ru_{V}	− 2Ru_{I}	2.74(2)	2.79 Å
	− 2Ru_{II}	2.74(2)	
	− 2Ru_{III}	2.75(2)	
	− 2Ru_{IV}	2.79(2)	
	− 2Ru_{V}	2.84(2)	
	− Ru_{VI}	3.02	
	− 2B_{I}	2.79; 2.94	
	− 2B_{II}	2.16(2)	
	− B_{III}	2.60	
	− B_{IV}	2.19	
Ru_{VI}	− 2Ru_{II}	2.80(2)	2.80 Å
	− 4Ru_{III}	2.72(2); 2.79(2)	
	− 2Ru_{IV}	2.76(2)	
	− Ru_{V}	3.02	
	− 2Ru_{VI}	2.84(2)	
	− B_{I}	2.38	
	− 2B_{II}	2.25(2)	
	− B_{III}	2.67	
	− B_{IV}	2.29	
B_{I}	− 2Ru_{I}	2.16(2)	2.22 Å (six shortest)
	− 2Ru_{II}	2.20(2)	
	− 2Ru_{III}	2.29(2)	
	− 2Ru_{V}	2.79; 2.94	
	− Ru_{VI}	2.38	
	− 2B_{I}	2.84(2)	
	− B_{III}	3.25	
	− 2B_{IV}	3.13; 3.14	
B_{II}	− Ru_{II}	2.12	2.18 Å (six shortest)
	− Ru_{III}	2.59	
	− Ru_{IV}	2.13	
	− 2Ru_{V}	2.16(2)	
	− 2Ru_{VI}	2.25(2)	
	− 2B_{II}	2.84(2)	
	− 2B_{III}	2.96(2)	
	− 2B_{IV}	1.68(2)	
B_{III}	− 2Ru_{II}	2.21(2)	2.17 Å (six shortest)
	− 2Ru_{III}	2.06(2)	
	− 2Ru_{IV}	2.24(2)	
	− Ru_{V}	2.60	
	− Ru_{VI}	2.67	
	− B_{I}	3.25	
	− 2B_{II}	2.96(2)	
	− 2B_{III}	2.84(2)	
	− B_{IV}	1.70	
B_{IV}	− 2Ru_{II}	2.11(2)	2.16 Å
	− 2Ru_{IV}	2.12(2)	
	− Ru_{V}	2.19	
	− Ru_{VI}	2.29	
	− 2B_{I}	3.13; 3.14	
	− 2B_{II}	1.68(2)	
	− B_{III}	1.70	
	− 2B_{IV}	2.84(2)	

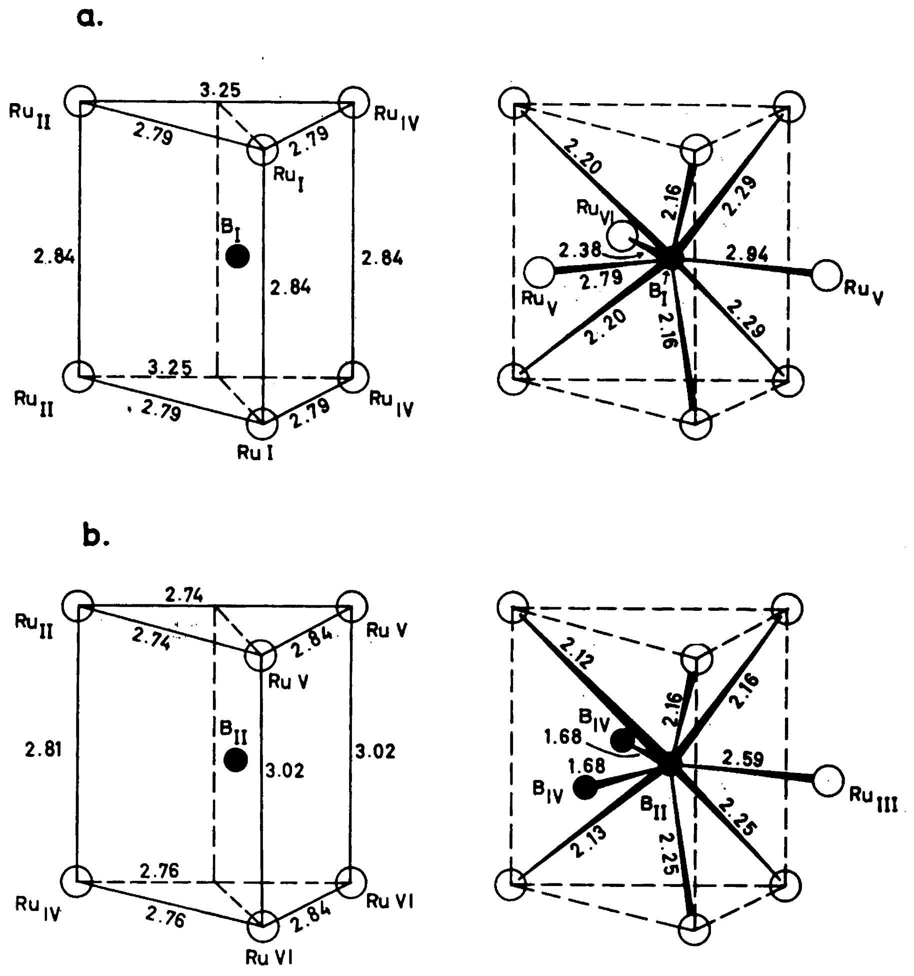


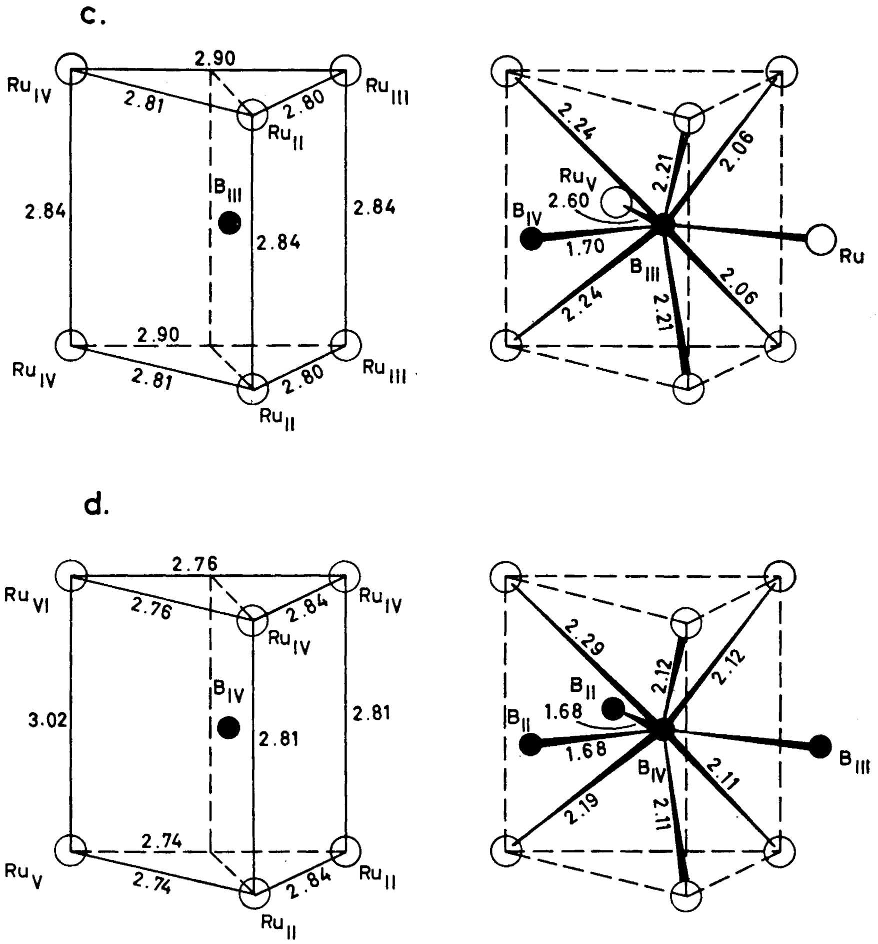
Fig. 3. The environment of the boron atoms in $Ru_{11}B_8$.
a. the environment of the B_I atoms
b. the environment of the B_{II} atoms

The final atomic parameters with standard deviations and interatomic distances are listed in Tables 1 and 2. (The standard deviations of the atomic parameters of ruthenium were estimated with Cruickshank's [10] formula.)

DESCRIPTION OF THE STRUCTURE

A projection of the structure on the *ab*-plane is shown in Fig. 1.

From the crystal-chemical point of view, the structure of $Ru_{11}B_8$ shows many resemblances to the orthorhombic Ni_4B_3 structure described by Rund-



c. the environment of the B_{III} atoms
d. the environment of the B_{IV} atoms

qvist [11]. Both structures can be described as built-up by interconnected trigonal prisms of metal atoms, with the boron atoms situated in the centers of these prisms. The metal atoms have ten or eleven neighbours of their own kind, and the boron atoms have the usual triangular prismatic environment.

In both the structures the boron atoms are partly isolated without close boron contacts, partly connected to infinite zig-zag chains running throughout the structure in the direction of the shortest axis.

The boron chains in orthorhombic Ni_4B_3 are single zig-zag chains of the same type as the chains in the MeB-borides of the FeB-, MoB- and CrB-types [12]. Every boron atom in the chains is in close contact with two other boron atoms.

In the boron zig-zag chains in $Ru_{11}B_8$ every second boron atom is in close contact with two other boron atoms and every second boron atom is in close contact with three other boron atoms (see Fig. 2 b). In the borides of composition Me_3B_4[12] the boron atoms form double chains.

The boron chain in $Ru_{11}B_8$ can be looked upon as a transition type between a single chain and a double chain.

For comparison a single chain in FeB[13] and a double chain in Mn_3B_4[14] are shown in Figs. 2 a and 2 c.

The four types of trigonal ruthenium atom prisms are shown in Figs. 3 a, b, c and d together with the environments of the B_I, B_{II}, B_{III} and B_{IV} atoms.

The coordination number of the boron atoms is nine, the B_I atoms have nine ruthenium neighbours, the B_{III} atoms have eight ruthenium neighbours and one boron neighbour, the B_{II} atoms have seven ruthenium neighbours and two boron neighbours and the B_{IV} atoms have six ruthenium neighbours and three boron neighbours.

The metal-metal distances are normal with an average distance of 2.79 Å. The average of the twentyfour shortest ruthenium-boron distances is 2.18 Å. This value is in good agreement with the sum, 2.21 Å, of the normal atomic radius of boron, 0.87 Å (Kiessling [12]) and the atomic radius of ruthenium for coordination number 12, 1.34 Å.

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