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The Crystal Structure of Re_3B

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The crystal structure of Re_3B has been determined by powder and single crystal methods. The dimensions of the orthorhombic unit cell are $a = 2.890$ Å, $b = 9.313$ Å and $c = 7.258$ Å ($\pm$ 0.05 %). There are four formula units in the elementary cell, and the space-group is *Cmcm*. The twelve rhenium atoms are situated in an eightfold position 8 (*f*) ($y = 0.1345$, $z = 0.0620$) and a fourfold position 4 (*c*) ($y = 0.4262$). From space considerations it has been concluded that the boron atoms are also situated in a 4 (*c*) position ($y \simeq 0.744$).

It was reported in an earlier communication [1] that three intermediate phases had been identified in arcmelted rhenium-boron alloys. Two of the phases, Re_7B_3 and ReB_3, were characterized by crystal structure data and the lattice parameters (l.p.) of the third phase, having the approximate composition Re_3B, were also given. As it was possible to obtain single crystals of Re_3B we decided to try to solve its structure with the principal aim of determining interatomic distances with moderate accuracy.

EXPERIMENTAL

Alloys were prepared by arcmelting rhenium (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 reported compositions are nominal.

Powder photographs using Cu$K\alpha$- and Cr$K\alpha_1$-radiation were taken with cameras of the Guinier type (the internal standard was silicon, $a = 5.4306$ Å) and single crystal photographs around the *a*-axis with an ordinary Weissenberg camera using Mo$K\alpha$ radiation. The multiple film technique was employed with thin iron foil between the films. Intensities were estimated by comparison with an intensity scale. Fourier series and structure factor calculations were made on the electronic digital computer BESK with programs (available at BESK) devised by M. Edstrand and Åsbrink *et al.*[2] In the structure factor calculations the atomic scattering factors were approximated to the following expression:

$$f_i = A_i.\exp\left(-\frac{a_i}{\lambda^2}\sin^2\Theta\right) + B_i.\exp\left(-\frac{b_i}{\lambda^2}\sin^2\Theta\right) + C_i.\exp\left(-\frac{c_i}{\lambda^2}\sin^2\Theta\right) + D_i$$

Appel [3] has calculated the following constants on the basis of the scattering factor tables by Tomas and Umeda [4] (rhenium) and Ibers [5] (boron)

	A	B	C	a	b	c
Rhenium	25.854	28.303	19.925	0.170	1.885	15.175
Boron	1.644	0.406	2.878	0.6069	4.5832	33.019

The real part of the dispersion correction, (D_i in the above expression), for rhenium was taken from the table of Dauben and Templeton[6].

RESULTS

The powder photographs of alloys in the composition range $ReB_{0.2}$—$ReB_{0.4}$ indicated the existence of the two-phase regions Re + Re_3B and Re_3B + Re_7B_3. The powder photograph of an alloy with the nominal composition Re_3B is given in Table 1. It may be seen in the table that nearly all lines can be indexed with a centred orthorhombic cell (a = 2.890 Å, b = 9.313 Å, c = 7.258 Å, ± 0.05 %). The origin of the three non-indexed weak lines is unknown. No l.p. variations greater than 0.1 % for Re_3B have been observed indicating that its range of homogeneity is narrow. It is concluded from the unit cell dimensions that there are twelve rhenium atoms in the elementary cell. The calculated X-ray density of Re_3B is 19.4 g/cm³.

Single crystal photographs confirmed that Re_3B is orthorhombic and since *hkl* reflexions only appeared for $h + k = 2n$ and *h0l* reflexions for $l = 2n$, the most probable space groups are *Cmcm*, *C2cm* and $Cmc2_1$. Apart from the normal decrease the distribution of intensities in the 0*kl* and 2*kl* zones was

Table 1. X-ray powder data of an arcmelted alloy with the nominal composition Re_3B ($CrKa_1$ radiation, λ = 2.2896 Å, internal standard: silicon, a = 5.4306 Å).

h k l for Re_3B	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$ for Re_3B	I_{obs}	I_{calc} for Re_3B	$p\|F\|^2 \cdot 10^{-3}$ for Re_3B
?	0.0464		w		
020	0.0605	0.0604	w	27	19.8
002	0.0994	0.0995	w	19	25.4
?	0.1079		w		
?	0.1174		w		
022	0.1601	0.1600	m	76	152.9
110	0.1719	0.1720	w	22	47.6
111	0.1968	0.1969	st	207	504.8
040	0.2418	0.2418	st	205	569.0
041	0.2665	0.2667	m	101	289.4
112	0.2714	0.2715	vst	510	1499.2
023	0.2844	0.2844	vst	497	1505.5
130	0.2930	0.2929	st	237	716.7
131	0.3177	0.3178	st	277	840.8
042	0.3413	0.3413	w	82	247.8
132	0.3924	0.3924	m	140	378.4
113	0.3959	0.3959	m	123	331.9
004	0.3982	0.3981	w	38	100.7
024	0.4585	0.4585	vw	29	64.3

similar indicating that the rhenium atoms are situated in planes perpendicular to the a-axis with a spacing of $a/2$. With this distribution of atoms the $|F|^2$ values for $0kl$ and $1kl$ reflexions were sufficient for the evaluation of the Patterson section $P(0yz)$. The position and heights of all peaks in $P(0yz)$ could be explained if the rhenium atoms were assumed to occupy one 8(f) and one 4(c) position in the space group *Cmcm*. This space-group was thus chosen and during the refinement of the structure nothing was found to contradict this choice.

The y and z coordinates of the rhenium atoms were refined from successive $\varrho_o(yz)$ and $\varrho_c(yz)$ electron density projections. In the final stages of refinement the F_o values of the four strongest reflexions, which were obviously weakened because of extinction, were replaced by the corresponding F_c values. Using an empirical isotropic temperature factor ($B = 0.07_8$ Å^2) the final R value of 96 observed $0kl$ reflexions (omitting the four strongest reflexions) was 12.4 % *. This relatively high value for the discrepancy index results from no corrections having been made for absorption, and that extinction has been only partly, and extremely crudely, corrected for. It should be noted that because of these errors the uncertainty of the atomic parameters is probably greater than as indicated by the standard deviations calculated from Cruickshank's [7] formula and given below.

From space considerations it is evident that the boron atoms must be located in a 4(c) position with $y \simeq 0.744$. As no boron parameter can be obtained from the experimental data we have chosen it so that the six shortest rhenium-boron atomic distances are equal.

The resulting atomic parameters are:

8 Re_I in 8(f) : $y = 0.1345 \pm 0.0003$, $z = 0.0620 \pm 0.0003$
4 Re_{II} in 4(c) : $y = 0.4262 \pm 0.0003$
4 B in 4(c) : $y = 0.744$

A projection of the structure on the bc-plane is shown in Fig. 1. The structure is very simple and may be described as being built up of triangular prisms of rhenium atoms at the centres of which are boron atoms. The rhenium skeleton is densely packed and the average values of the shortest rhenium-rhenium distances (see Table 2) are only just greater than the shortest rhenium-rhenium distance in elementary rhenium, *i.e.* 2.74 Å. Parallel to {023} the rhenium atoms form slightly corrugated densely packed planes which consist of interconnected triangles and squares.

The boron atoms have the same environment as in a number of other borides [8]: *i.e.* six neighbours at the corners of a triangular prism and three more remote neighbours outside the rectangular faces of the prism. (The two boron neighbours outside the triangular faces of the prism are probably too distant (2.89 Å) for consideration). The average of the six shortest metal-boron distances is 2.23 Å in good agreement with the value of 2.24 Å which is the sum of the normal atomic radius of boron (0.87 Å according to Kiessling [9]) and the atomic radius of rhenium for coordination number 12 (1.37 Å). In Re_3B, as

* A list of calculated and observed structure factors can be obtained from this Institute on request.

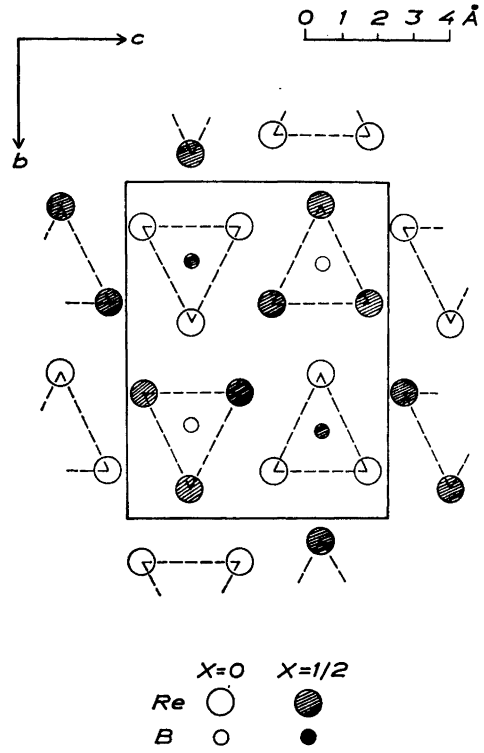

Fig. 1. The structure of Re_3B projected on (100).

in the borides of the Th_7Fe_3 and cementite structures [1,9], all the nine neighbours of boron are metal atoms. The coordinations around the metal atoms are also similar in these three closely related structures.

Table 2. Interatomic distances in Re_3B (in Å).

			Average
Re_I in 8 (*f*)	— 6 Re_I :	2.66, 2.73, 2.74 (2), 2.89 (2)	2.79
	— 5 Re_{II}:	2.74 (2), 2.78 (2), 3.04.	
	— 3 B :	2.23 (2), 2.54.	
Re_{II} in 4 (*c*)	— 10 Re_I :	2.74 (4), 2.78 (4), 3.04 (2)	2.83
	— 2 Re_{II}:	2.89 (2).	
	— 3 B :	2.23 (2), 2.95.	
B 4 (*c*)	— 6 Re_I :	2.23 (4), 2.54 (2)	2.23
	— 3 Re_{II}:	2.23 (2), 2.95	(six first)
	(— 2 B :	2.89 (2)).	

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