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The Crystal Structure of Rhenium Diboride*

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The crystal structure of ReB_2 has been determined from powder data. The unit cell is hexagonal; $a = 2{\cdot}900$ and $c = 7{\cdot}478$ Å; there are two ReB_2 units per unit cell. The structure may be described in terms of alternating layers of rhenium and boron atoms; the former are planar, the latter are puckered. The two boron atoms show up clearly in difference maps ($\varrho_{x,2x,z_{\text{obs.}}} - \varrho_{x,2x,z_{\text{Re}}}$). B–B bond lengths are 1·82 Å; shortest Re–B distance are 2·23 and 2·26 Å.

The transition metals react with boron to form a large number of simple binary phases. The diboride phases have been most extensively studied, mainly because of their simple crystal structures and interesting physical and chemical properties.

Most of the transition metals form a series of isomorphous diborides (Post, Glaser & Moskowitz, 1954); the unit cells are hexagonal, the space group is $P6/mmm$ and there is one formula weight per unit cell, with the metal atoms at 0, 0, 0 and the boron atoms at $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$. This structure is most simply described in terms of alternating planar metal and boron atom layers perpendicular to the c axis.

The stability of this phase decreases as we proceed from Group IV to V and VI. It is formed, for example, by Zr and Nb but the isomorphous MoB_2 phase is stable only above 1600 °C. and can be retained at room temperature only by quenching. Hf and Ta also form 'normal' diborides, but no WB_2 phase has yet been reported. Both Mo and W form compounds analogous to the diborides which are stable at room temperature; Kiessling (1947) has assigned the formula Me_2B_5 to these phases. In these compounds the boron layers are puckered and the arrangement of metal atoms is more complicated than in the simple 'normal' diborides.

It was felt that it would be of some interest to investigate the Re/B system to determine whether a stable diboride phase exists and, if so, to establish its crystal structure.

The Re–B system has been investigated on only a few occasions. Heyne & Moers (1931) first reported the existence of a rhenium-boron alloy but gave no further details. Recently, Nesphor (1958) investigated the rhenium-boron system; specimens of various compositions were prepared by heating the metal with the appropriate amounts of boron at 2,000 °C. They describe a tetragonal phase, Re_2B, and reported an additional phase in the range from 40 to 80 atomic percent of boron; the latter was simply identified on powder photographs but was not characterized further. Aronsson (1960) has reported that three stable phases exist in the rhenium–boron system: Re_3B, orthorhombic; Re_7B_3, hexagonal; and ReB_3, hexagonal. He did not detect the tetragonal ReB_2 which Neshpor had reported.

The powder pattern of the ReB_3 phase reported by Aronsson is virtually indistinguishable from that of the compound which we are describing in this paper and which we have identified as ReB_2.

Experimental

Spectroscopically pure rhenium was heated with two parts of amorphous boron by two methods: in sealed, evacuated silica tubes at 1200 °C. for 12 hours, and by induction heating under an atmosphere of helium in vitrified alumina crucibles at 1500 °C. Both procedures yielded the same product; the material prepared at the higher temperature was somewhat more crystalline. The X-ray powder pattern indicated that only one phase (our ReB_2) was present. Chemical analysis indicated the empirical formula $ReB_{1{\cdot}94}$ (total Re plus B analysis equalled 98.78% by weight).

All lines of the powder diffraction patterns of the reaction product were indexed on the basis of a hexagonal unit cell with $a = 2{\cdot}900 \pm {\cdot}001$ and $c = 7{\cdot}478 \pm {\cdot}002$ Å. There are two molecules per unit cell. The calculated density is 12·68 g.cm.$^{-3}$. Reflections of the type $h,h,\overline{2h},l$ were systematically absent. Three space groups are consistent with these absences: $P6_3mc$, $P\overline{6}2c$ and $P6/mmc$. All three are equivalent with respect to the necessary twofold and fourfold positions if the structure is assumed to be centrosymmetric. The centrosymmetric $P6/mmc$ was considered to be a reasonable choice in view of the simplicity of the structure; this choice was confirmed during the course of the analysis.

If the unit cell contains two ReB_2, the Re atoms will be at $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$; the boron atoms will be at $\pm(\frac{1}{3}, \frac{2}{3}, z)$; $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z)$.

Single crystals could not be obtained, but it was felt that, in spite of the swamping effect of the rhenium contributions to all reflections, a satisfactory

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determination of the one variable position parameter could be made if reflection intensities from carefully prepared powder specimens were measured precisely. Comparisons of diffractometer traces and films, as well as the reproducibility of relative intensities on diffractometer traces taken with different specimens, prepared in different ways, indicated that preferred orientation effects were negligible. Reflection intensities were recorded with a scintillation counter in conjunction with pulse height discrimination to reduce unwanted background. Filtered Cu *K* radiation was used. Integrated intensities were determined by measuring peak areas obtained when the diffractometer was run at a scanning rate of $\frac{1}{8}°$ (2θ) per minute (Table 1). These were converted in the usual way to relative values of $|F|^2$. Thomas–Fermi atomic form factors for rhenium, corrected for dispersion effects (Dauben & Templeton, 1955), and boron form factors computed by Ibers (1957) were used in the calculation of structure factors.

Table 1. *Powder diffraction data:*
ReB_2, Cu $K\alpha$, Ni filter

I/I_0*	d (Å)	hkl	F_o	F_o (corr.)†	F_c‡
65	2·74	002	44·4	53·9	−55·2
30	2·51	100	27·4	31·2	−30·6
100	2·38	101	40·5	45·7	−46·2
20	2·08	102	22·3	24·7	24·3
11	1·868	004	47·6	51·6	51·9
40	1·768	103	41·7	44·9	45·4
7	1·499	104	22·2	23·2	−23·5
14	1·449	110	46·5	48·4	48·3
15	1·351	112	39·7	40·7	−40·1
9	1·284	105	32·5	33·1	−33·3
3	1·255	200	21·4	21·8	−22·4
2	1·246	006	41·0	41·4	−42·0
9	1·238	201	34·7	35·1	34·7
3	1·190	202	18·8	18·9	18·6
9	1·145	114	39·6	39·9	40·2
7	1·121	203	34·8	35·0	−35·5
2	1·116	106	19·4	19·4	19·6
2	1·042	204	19·3	19·3	−18·9
4	0·983	107	33·0	33·0	32·8
3	0·961	205	27·6	27·6	27·5
2	0·949	210	18·3	18·3	−18·8
5	0·945	116	33·0	33·0	−35·1
8	0·942	211	29·3	29·3	−29·0
1	0·935	005	30·7	30·7	32·0
2	0·9201	212	15·9	15·9	15·8
7	0·8871	213	30·2	30·2	30·7
5	0·8847	206	—	—	16·9
1	0·8760	108	14·6	14·6	−15·4
2	0·8465	214	17·1	17·1	−16·6
3	0·8374	300	34·8	34·8	34·8
4	0·8171	302	30·2	30·2	−29·3
4	0·8139	207	28·5	28·5	−29·3
5	0·8017	215	24·5	24·5	−24·7
3	0·7889	109	24·2	24·2	−25·7
4	0·7858	118	27·1	27·1	28·7

* Peak height.

† F_o corrected for surface roughness and extinction (see text).

‡ For $Z_{\text{boron}} = 0·548$.

In the 'normal' transition metal diboride structure (Post, Glaser & Moskowitz, 1954) formed by most transition metals, the boron nets are strictly planar and there is only one MeB_2 unit per unit cell. Simple geometrical considerations rule out the possibility of such planar boron nets in ReB_2. The boron–boron separation in the transition metal diborides with planar boron nets ranges from 1·73 to 1·81 Å. In ReB_2. however, a planar arrangement of boron atoms would lead to boron–boron separtions of only 1·67 Å. Such an arrangement would be based on a z parameter (z_B) of 0·500; this would also lead to closest Re–B approaches of $c/4$, or $1·87_0$ Å. If we assign to boron and to rhenium the radii 0·87 and 1·37 Å we would expect a minimum distance of close approach of 2·24 Å rather than 1·87 Å. These geometrical difficulties would disappear if the boron coordinate is changed to approximately 0·55.

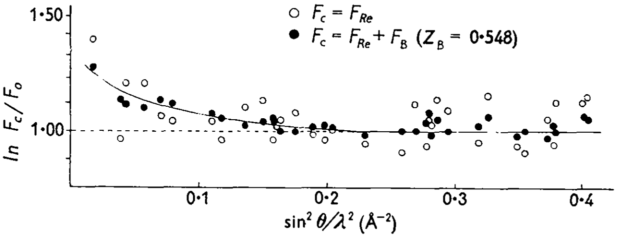

Fig. 1. $\ln F_{\text{Re}}/F_o$ versus $\sin^2\theta/\lambda^2$.

The parameter was determined by locating the minima in plots of the discrepancy factor, R, vs. z_B. As a check on the validity of the procedure, a preliminary calculation of R was made for the case where only the contributions from rhenium atoms were included in F_c. It was noted that values of $\ln F_{\text{Re}}/F_o$ plotted against $\sin^2\theta/\lambda^2$ showed a uniform scatter about 1·0 for Bragg angles greater than about 30°, but rose to higher values at smaller angles (Fig. 1). It appeared likely that this effect was caused by a combination of surface roughness and extinction effects in the powdered specimens, and an empirical correction was applied by multiplying values of F_o in this angular region by factors which brought the *smoothed* curve to 1·0 (Fig. 1). The plot shown in Fig. 1 also indicated that the temperature factors were very small and that their omission from structure factor calculations could not lead to serious errors. When only rhenium contributions were included in F_c, R was equal to 6·2% for all reflections (including the low angle corrected ones). When boron contributions were also included in F_c, the plot of R vs. z_B showed a minimum of 1·9% at $z = 0·548$.

Another calculation was then made in which the computed contributions of the rhenium atoms were omitted from the F_c and also subtracted from the F_o. This showed a minimum of $R = 31·5\%$ for values of z

between 0·546 and 0·550. The 31.5% figure was considered satisfactory in view of the fact that in general the rhenium contributions which had been subtracted amounted to more than 90% of the total diffracted intensities.

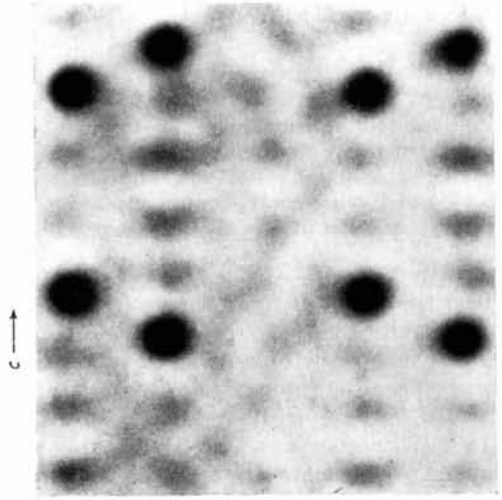

Fig. 2. $\varrho_{x,\,2x,\,z\,\mathrm{obs.}}-\varrho_{x,\,2x,\,z\,\mathrm{Re}}$.

Electron density difference maps ($\varrho_D x$, z and $\varrho_D x$, $2x$, z) were computed with the von Eller photosummateur (von Eller, 1955), using F_o-F_{Re} as the coefficients of the Fourier series. The $\varrho_D(x, 2x, z)$ map is shown in Fig. 2. The two boron atoms are clearly resolved on both maps and the best estimate of their positions on the $[\varrho_D(x, 2x, z)]$ map indicates that z is very close to 0·550. There is no indication of a boron atom at 0, 0, 0 as postulated by Aronsson for $\mathrm{ReB_3}$.

Discussion

It is clear that the value of z_B lies in the range $0{\cdot}548\pm{\cdot}003$. The $\mathrm{ReB_2}$ structure may be described in terms of planar layers of rhenium atoms separated by puckered layers of boron atoms. Interatomic distances are:

Re–Re: 2·900 (6); Re–B: 2·26 (6), 2·23 (2)
B–Re: 2·26 (3), 2·23 (1); B–B: 1·82 (3)

The shortest boron to boron distances equal 1·822 Å; the B–B–B angle is 105·5°. Rhenium to boron distances are of two types: the distance from a rhenium atom to a boron atom directly 'above' or 'below' it (i.e. with the same x and y coordinates) is 2·23 Å; the other Re–B is 2.26 Å.

The boron coordination around each rhenium atom consists of two trigonal bipyramids joined at a common apex, with their three-fold axes collinear and parallel to the c axis (Fig. 3). Rhenium is at the common apex and the eight boron atoms are at the remaining vertices.

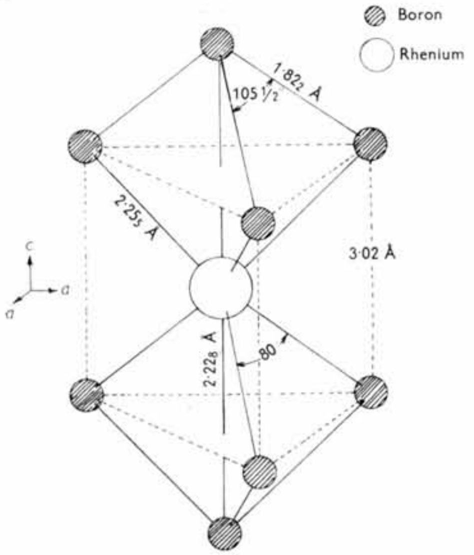

Fig. 3. Environment of Re atom in $\mathrm{ReB_2}$.

The structural relations among the closely related $Me\mathrm{B_2}$, $\mathrm{ReB_2}$, $\mathrm{W_2B_5}$ and $\mathrm{Mo_2B_5}$ structures are represented most clearly in terms of a notation due to Kiessling (1947). The sequence of approximately close-packed, planar, layers of metal atoms in the c direction is:

('normal') $Me\mathrm{B_2}$: $A-A-A-A$ ...
$\mathrm{ReB_2}$: $AB\ AB\ AB$ ...
$\mathrm{W_2B_5}$: $AA\ BB\ AA\ BB$ ...
$\mathrm{Mo_2B_5}$: $AA\ BB\ CC\ AA\ BB\ CC$ ...

Kiessling denoted puckered boron sheets by K and planar sheets by H. The complete stacking sequence in the c direction is then:

$Me\mathrm{B_2}$: $AH\ AH\ AH$ ...
$\mathrm{ReB_2}$: $AK\ BK\ AK\ BK$ ...
$\mathrm{W_2B_5}$: $AH\ AK\ BH\ BK\ AH$ ...
$\mathrm{Mo_2B_5}$: $AH\ AK\ BH\ BK\ CH\ CK\ AH$ ...

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