The Crystal Structure of Re₃B

B. ARONSSON, (MISS) MAGGIE BÄCKMAN and S. RUNDQVIST

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of Re₃B has been determined by powder and single crystal methods. The dimensions of the orthorhombic unit cell are \( a = 2.890 \, \text{Å}, b = 9.313 \, \text{Å} \) and \( c = 7.258 \, \text{Å} \) (± 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 \((y \approx 0.744)\).

It was reported in an earlier communication\(^1\) that three intermediate phases had been identified in arc-melted rhenium-boron alloys. Two of the phases, Re₂B₃ and ReB₂, were characterized by crystal structure data and the lattice parameters (l.p.) of the third phase, having the approximate composition Re₃B, were also given. As it was possible to obtain single crystals of Re₃B we decided to try to solve its structure with the principal aim of determining interatomic distances with moderate accuracy.

EXPERIMENTAL

Alloys were prepared by arc-melting 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 CuK\(\alpha\) and CrK\(\alpha\) radiation were taken with cameras of the Guinier type (the internal standard was silicon, \( a = 5.4306 \, \text{Å} \)) and single crystal photographs around the \( a \)-axis with an ordinary Weissenberg camera using MoK\(\alpha\) 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. Edström and Åsbrink \textit{et al.}\(^3\) In the structure factor calculations the atomic scattering factors were approximated to the following expression:

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

\textit{Acta Chem. Scand.} 14 (1960) No. 5
Appel  has calculated the following constants on the basis of the scattering factor tables by Tomas and Umetsu  (rhenium) and Ibers  (boron)

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhenium</td>
<td>25.854</td>
<td>28.303</td>
<td>19.925</td>
<td>0.170</td>
<td>1.885</td>
<td>15.175</td>
</tr>
<tr>
<td>Boron</td>
<td>1.644</td>
<td>0.406</td>
<td>2.878</td>
<td>0.6069</td>
<td>4.5832</td>
<td>33.019</td>
</tr>
</tbody>
</table>

The real part of the dispersion correction, \( D_r \) in the above expression, for rhenium was taken from the table of Dauben and Templeton .

RESULTS

The powder photographs of alloys in the composition range \( \text{ReB}_{2.2} - \text{ReB}_{0.4} \) indicated the existence of the two-phase regions \( \text{Re} + \text{Re}_2\text{B} \) and \( \text{Re}_3\text{B} + \text{Re}_2\text{B}_2 \). The powder photograph of an alloy with the nominal composition \( \text{Re}_3\text{B} \) is given in Table 1. It may be seen in the table that nearly all lines can be indexed with a centred orthorhombic cell (\( a = 2.890 \text{ Å} \), \( b = 9.313 \text{ Å} \), \( c = 7.258 \text{ Å} \), \( \pm 0.05 \% \)). The origin of the three non-indexed weak lines is unknown. No l.p. variations greater than 0.1 % for \( \text{Re}_3\text{B} \) 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 \( \text{Re}_3\text{B} \) is 19.4 g/cm³.

Single crystal photographs confirmed that \( \text{Re}_3\text{B} \) is orthorhombic and since \( hkl \) reflexions only appeared for \( h + k = 2n \) and \( h0l \) reflexions for \( l = 2n \), the most probable space groups are \( \text{Cmcm}, \text{C2cm} \) and \( \text{Cmc2} \). Apart from the normal decrease the distribution of intensities in the 0kl and 2kl zones was

Table 1. X-ray powder data of an arc-melted alloy with the nominal composition \( \text{Re}_3\text{B} \) (CrKα1 radiation, \( \lambda = 2.2896 \text{ Å} \), internal standard: silicon, \( a = 5.4306 \text{ Å} \)).

<table>
<thead>
<tr>
<th>( h ) ( k ) ( l ) for ( \text{Re}_3\text{B} )</th>
<th>( \sin \theta_{obs} )</th>
<th>( \sin \theta_{calc} ) for ( \text{Re}_3\text{B} )</th>
<th>( I_{obs} )</th>
<th>( I_{calc} ) for ( \text{Re}_3\text{B} )</th>
<th>( p/F^2 \cdot 10^{-3} ) for ( \text{Re}_3\text{B} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0464</td>
<td>w</td>
<td>27</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.0605</td>
<td>0.0604</td>
<td>w</td>
<td>19</td>
<td>25.4</td>
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<tr>
<td>002</td>
<td>0.0994</td>
<td>0.0995</td>
<td>w</td>
<td>19</td>
<td>25.4</td>
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<td>w</td>
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<td>19.8</td>
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<tr>
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<td>27</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>022</td>
<td>0.1601</td>
<td>0.1600</td>
<td>m</td>
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<td>152.9</td>
</tr>
<tr>
<td>110</td>
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<td>0.1720</td>
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<tr>
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<td>0.1968</td>
<td>0.1969</td>
<td>st</td>
<td>207</td>
<td>504.8</td>
</tr>
<tr>
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<td>0.2418</td>
<td>0.2418</td>
<td>st</td>
<td>205</td>
<td>569.0</td>
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<tr>
<td>041</td>
<td>0.2665</td>
<td>0.2667</td>
<td>m</td>
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<tr>
<td>122</td>
<td>0.2714</td>
<td>0.2715</td>
<td>vst</td>
<td>510</td>
<td>1499.2</td>
</tr>
<tr>
<td>023</td>
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<td>0.2844</td>
<td>vst</td>
<td>497</td>
<td>1505.5</td>
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<tr>
<td>130</td>
<td>0.2930</td>
<td>0.2929</td>
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<td>237</td>
<td>716.7</td>
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<tr>
<td>131</td>
<td>0.3177</td>
<td>0.3178</td>
<td>st</td>
<td>277</td>
<td>840.8</td>
</tr>
<tr>
<td>042</td>
<td>0.3413</td>
<td>0.3413</td>
<td>w</td>
<td>82</td>
<td>247.8</td>
</tr>
<tr>
<td>132</td>
<td>0.3924</td>
<td>0.3924</td>
<td>m</td>
<td>140</td>
<td>375.4</td>
</tr>
<tr>
<td>113</td>
<td>0.3959</td>
<td>0.3959</td>
<td>m</td>
<td>123</td>
<td>331.9</td>
</tr>
<tr>
<td>004</td>
<td>0.3982</td>
<td>0.3981</td>
<td>w</td>
<td>38</td>
<td>100.7</td>
</tr>
<tr>
<td>024</td>
<td>0.4585</td>
<td>0.4585</td>
<td>vw</td>
<td>29</td>
<td>64.3</td>
</tr>
</tbody>
</table>

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 $g_s(yz)$ and $g_c(yz)$ 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 ($B = 0.078$ 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 formula and given below.

From space considerations it is evident that the boron atoms must be located in a 4(c) position with $y = 0.744$. 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: 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) and the atomic radius of rhenium for coordination number 12 (1.37 Å). In Re₂B, as

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

in the borides of the Th$_7$Fe$_8$ and cementite structures\textsuperscript{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.

\textit{Table 2. Interatomic distances in Re$_8$B (in Å).}

\begin{tabular}{|c|c|}
\hline
 & Average \\
\hline
Re$_I$ in 8 (f) & \{$2.66, 2.73, 2.74 (2), 2.89 (2)$\} \hspace{0.5cm} 2.79 \\
- 5 Re$_{II}$: & 2.74 (3), 2.78 (2), 3.04. \\
- 3 B : & 2.23 (2), 2.54. \\
\hline
Re$_{II}$ in 4 (c) & \{$2.74 (4), 2.78 (4), 3.04 (2)$\} \hspace{0.5cm} 2.83 \\
- 2 Re$_I$ : & 2.89 (2). \\
- 3 B : & 2.23 (2), 2.95. \\
\hline
B 4 (c) & \{$2.23 (4), 2.54 (2)$\} \hspace{0.5cm} 2.23 \\
- 6 Re$_I$ : & (six first) \\
- 3 Re$_{II}$: & 2.23 (2), 2.95 \\
(- 2 B : & 2.89 (2)). \\
\hline
\end{tabular}

\textit{Acknowledgements.} The authors wish to thank Professor G. Hägg for his encouraging interest and many valuable comments on the manuscript. Financial support is gratefully

\textit{Acta Chem. Scand.} 14 (1960) No. 5
acknowledged from the Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force, through its European Office under Contract No. AF 61(052)-40 and from the Swedish Technical Science Research Council.

REFERENCES

3. Appel, K. "Technical Note from the Quantum Chemistry Group, University of Uppsala".

Received January 25, 1960.