crystal forms follow, in general, the conditions imposed by the space group $P2_1/c$. From structural data, the ideal morphological sequence does not agree fully with the observed sequence of morphological importance (Table 3); only the {001} and {110} crystal forms do not follow the 'Donnay–Harker law'. These anomalies may be ascribed to other physical factors, not considered by this rule (bond energy, *etc.*).

The authors do not propose to carry out further work on this compound.

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*Acta Cryst.* (1969). B**25**, 698

# Determination of the Light-Atom Positions in $Mo_2BC$*

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(*Received* 26 *April* 1968)

A previous investigation of the crystal structure of $Mo_2BC$ by Jeitschko, Nowotny & Benesovsky (*Mh. Chem.* (1963) **94**, 565) resulted in the direct location of the Mo atoms; the light atoms were assigned probable positions on the basis of geometrical arguments. The authors reinvestigated the crystal structure using diffractometrically recorded intensities. The crystals are orthorhombic, $a=3{\cdot}086$, $b=17{\cdot}35$, $c=3{\cdot}047$ Å; space group, *Cmcm*. For four units of $Mo_2BC$ per unit cell, the calculated density is 8·74 g.cm$^{-3}$. Full-matrix, least-squares refinement resulted in an *R* index of 3·5%, and a confirmation of the structure model of Jeitschko *et. al., viz.* C atoms in octahedral sites (six Mo neighbors) and B atoms forming zigzag chains passing through the centers of trigonal prisms of Mo atoms. Bond distances are: Mo–C, 2·08–2·17; Mo–B, 2·31 and 2·77; B–B, 1·79; Mo–Mo, 2·93–3·10 Å. A number of other metal-B, C systems were examined in a search for additional examples of the $Mo_2BC$-type structure, but without success. The metals studied were: Ti, V, Cr, Nb, Ta and W; the authors were also unable to prepare $Mo_2BSi$.

## Introduction

In their investigation of the crystal structure of $Mo_2BC$, Jeitschko, Nowotny & Benesovsky (1963) (hereafter referred to as JNB) were able to determine only the metal-atom positions from their diffraction data. Using geometrical arguments, JNB placed the light atoms so that the boron atoms formed zigzag chains, as found frequently in monoborides and the carbon atoms occupied octahedral holes (six Mo neighbors) as found, for example, in NaCl-type monocarbides. The structure resulted in very reasonable interatomic distances. On the other hand, several metallic borocarbides of composition $MB_2C_2$, with M = a lanthanide element (Smith, 1964) or scandium (Smith, Johnson & Nordine, 1965), have exhibited novelly connected B, C networks. It therefore seemed of interest to establish directly the light-atom positions in $Mo_2BC$. Further interest is attached to this problem with the discovery (Johnston, 1964) that $Mo_2BC$ becomes superconductive below 5·4°K.

## Experimental

The compound was prepared by arc-melting appropriate amounts of Mo metal filings, boron and carbon (as graphite) in a gettered argon atmosphere. The fused button was turned over and remelted several times to improve the homogeneity. Parallelepiped-shaped single crystals were obtained by crushing the button.

An X-ray powder pattern was readily indexed on the basis of the *C*-centered orthorhombic cell ($a=3{\cdot}086$, $b=17{\cdot}35$, $c=3{\cdot}047$ Å) given by JNB. These lattice constants were used in subsequent calculations, our own values based on $\lambda_{Cu\ K\alpha}=1{\cdot}5418$ Å being insignificantly different. Probable errors in the lattice constants are estimated to be about 0·2%. No impurity lines were observed.

A chemical analysis of a portion of the button gave these percentages: Mo, $89{\cdot}0\pm0{\cdot}1$; B, $4{\cdot}97\pm0{\cdot}02$; C, $5{\cdot}43\pm0{\cdot}12$ (average of two analyses). Corresponding theoretical percentages for $Mo_2BC$ are 89·37, 5·04 and 5·59, respectively. The analysis corresponds to a Mo:B:C atomic ratio of $2{\cdot}000\pm0{\cdot}002:0{\cdot}991\pm0{\cdot}004:0{\cdot}971\pm0{\cdot}022$. JNB reported that the phase was possibly carbon-poor, but no quantitative figures were given.

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

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Single-crystal oscillation and Weissenberg photographs confirmed the orthorhombic symmetry. The systematic extinctions (*hkl* for $h+k$ odd; *h*0*l* for *l* odd) are characteristic of the space groups *Cmcm*, $Cmc2_1$ and *C*2*cm* (*International Tables for* X-*ray Crystallography*, 1952). Assuming four units of $Mo_2BC$ per unit cell, we obtain a calculated density of 8·74 $g.cm^{-3}$. JNB give the calculated density as 8·71 $g.cm^{-3}$. By way of comparison, the calculated density for tetragonal MoB is 8·77 $g.cm^{-3}$; for hexagonal MoC, 8·77 $g.cm^{-3}$.

Intensities were measured diffractometrically, using the stationary-crystal, stationary-counter technique (Furnas, 1957), Zr-filtered Mo $K\alpha$ and pulse-height discrimination. The crystal specimen was a parallelepiped, with dimensions $0{\cdot}14\times0{\cdot}11\times0{\cdot}10$ mm along **a**, **b**, and **c**, respectively. A total of 82 independent reflections were recorded up to a $2\theta$-cutoff of 45°. The intensities were converted to a set of relative $|F|$'s through the application of Lorentz–polarization factors and $2\theta$-dependent absorption correction (the crystal shape taken to be a sphere with $\mu R=0{\cdot}9$; $\mu=144 cm^{-1}$ for Mo $K\alpha$ radiation).

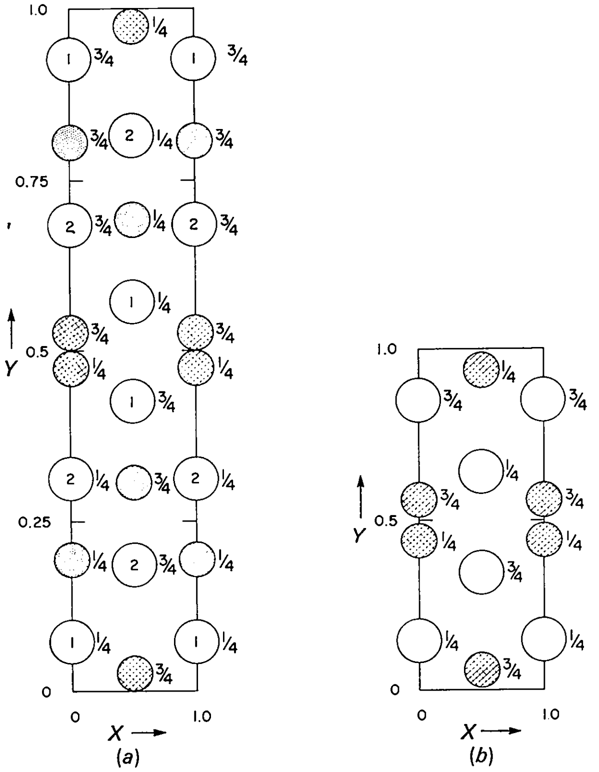

Fig. 1. Comparison of crystal structures of $Mo_2BC$ (*a*) and CrB-type MoB (*b*). Numerals within open circles identify type of Mo atom; cross-hatched and stippled circles represent B and C atoms, respectively. Elevations along *Z* are also indicated. In both drawings, the direction of the chains of boron atoms is perpendicular to the plane of the paper.

## Determination of structure

Positions of the Mo atoms were readily located from a Patterson map; the light atoms were found in an ensuing electron-density map. All atoms were found to occupy 4(*c*) positions of space group *Cmcm* $[\pm(0,y,\frac{1}{4})+C$-centering], and the structure model of JNB was confirmed. Refinement of the nine variable parameters was by means of the full-matrix, least-squares program of Gantzel, Sparks & Trueblood (ACA Program No. 319, unpublished). The quantity minimized was $\Sigma\, w[|F_o|-(1/K)|F_c|]^2$ where *K* is the scale factor relating $|F_o|$ and $|F_c|$ and the *w*'s are given by the following weighting scheme: $w=F_o^{1/4}, F_o<A$; $w=A^{5/4}F_o^{-1}$, $F_o>A$. When the structure factors were placed on an absolute scale, $A=105$. Atomic scattering factors for the neutral atoms were HFS values of Hanson, Herman, Lea & Skillman (1964); real and imaginary anomalous dispersions for the Mo atoms were those of Cromer (1965). Extinction corrections of the form $F_o$(corrected)$=KF_o(1+\beta I_o)$, where $\beta$ is the extinction parameter and $I_o$ is the raw intensity, were applied. A value of $1{\cdot}6\times10^{-5}$ for $\beta$ gave the lowest $R[=\Sigma\,(K|F_o|-|F_c|)/\Sigma\,K|F_o|]$ and was not further refined. Five cycles of least-squares refinement reduced *R* to 3·5% (all reflections); (without the extinction corrections, *R* was 5·2%). Changes in parameter values in the last cycle were < 0·01 times the standard deviations. A final difference map showed a maximum deviation from zero of < 0·5 e.Å$^{-3}$. A difference synthesis in which the Mo atoms were subtracted out gave these peak heights: for C, 4·2 e.Å$^{-3}$; for B, 3·8 e.Å$^{-3}$. Details of the refinement in *Cmcm* being satisfactory, no consideration was given to the noncentrosymmetric alternatives.* Neither was any attempt made to refine the occupancy factors of the light atoms.

Final parameters, along with those of JNB, are given in Table 1. Table 2 lists observed and calculated structure factors.

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* There exists a further consideration about the choice of space group, and this concerns the possibility of a lower point symmetry at any of the atomic sites. We note that the structure can also be described using the 4(*b*) positions of space group $C222_1$. These special positions are identical to the 4(*c*) positions of *Cmcm*, and extinctions based on these 4(*b*) positions match those observed (although extinctions based on the general positions do not). The point symmetry of the 4(*b*) positions in $C222_1$ is 2 *versus mm* for the 4(*c*) positions in *Cmcm*. In the present case where isotropic temperature parameters were employed, the atomic arrangement does, in fact, correspond to *mm* symmetry. However, were anisotropic thermal effects pronounced, the point symmetry could degenerate to only twofold symmetry. Thus, in carrying out an anisotropic temperature parameter refinement, both space groups should be considered (one more degree of freedom in the thermal ellipsoid tensor is permitted in $C222_1$). These same remarks apply also to the case of CrB-type compounds. In view of the numerous examples of this structure-type, it is not unreasonable to suppose that some of these compounds may require $C222_1$ as the proper space group for description of the thermal motion.

Table 1. *Parameters in* $Mo_2BC$

All atoms in 4(*c*) positions of space group *Cmcm*. Values of $y$ correspond to $0,y,\frac{1}{4}$ site (e.s.d.'s in parentheses).

| | This investigation | | JNB |
|---|---|---|---|
| | $y$ | $B$ | $y$ |
| Mo(1) | 0·0721 (1) | 0·3 ± 0·1 Å² | 0·0705 |
| Mo(2) | 0·3139 (1) | 0·5 ± 0·1 | 0·319 |
| C | 0·1920 (15) | 1·2 ± 0·5 | 0·192 |
| B | 0·4731 (18) | 1·1 ± 0·6 | 0·027* |

* On the basis of the structure model, we judge this should have been 0·473.

## Discussion

The present determination of the light-atom positions confirms the structure model of JNB for $Mo_2BC$. Parameter values (Table 1) compare, moreover, rather excellently with those deduced by JNB.

$Mo_2BC$ and CrB-type MoB have many common structural features. Both are orthorhombic, of space group *Cmcm*, with very similar *a* and *c* axis repeat distances; the translation along **b** in $Mo_2BC$ is about twice that of CrB-type MoB. In both materials the boron atoms form infinite chains. The crystal structure of $Mo_2BC$ can, in fact, be considered as a *rearrangement* of the CrB-type phase, as the placement of atoms in the region $0<y<\frac{1}{4}$ in $Mo_2BC$ (Fig. 1) is virtually identical with the section of structure in orthorhombic MoB for $0<y<\frac{1}{2}$. If now the section of structure in MoB for $\frac{1}{2}<y<1$ is inverted through $\frac{1}{2},\frac{3}{4},\frac{1}{2}$ and the boron atoms are renamed as carbon atoms, the structure closely resembles that of $Mo_2BC$ for $\frac{1}{4}<y<\frac{1}{2}$.

Interatomic distances of greatest chemical interest are (Table 3): Mo–C, 2·08, 2·11, 2·17 (4×) Å; Mo–B, 2·31 (2× and 4×) and 2·76 Å; B–B, 1·79 Å and Mo–Mo, 2·93–3·10 Å. Quite generally, the shortest Mo–X (X = Mo, B or C) distances are associated with Mo(1). For the sake of comparison, the sum of atomic radii (tetrahedral radii for B and C, metallic radius for Mo; values from Pauling, 1960) are: Mo–C, 2·16; Mo–B, 2·27; B–B, 1·76; Mo–Mo, 2·77 Å. Somewhat larger Mo–Mo distances are thus found in $Mo_2BC$ than in the metal. The shortest boron–carbon distance observed is 3·60 Å. Against this, there are several B···B and C···C distances which clearly correspond to nonbonding interactions and which are even shorter. For example, the short *a* and *c* axes necessarily place like atoms 3·0–3·1 Å apart. We conclude that there is no tendency for covalent-like bonding between boron and carbon in $Mo_2BC$.

Coordination polyhedra for the two types of Mo atoms are shown in Fig. 2. Mo(1) has 17 neighbors: 6B, 1C and 10Mo atoms; Mo(2) has 18 neighbors: 5C, 1B and 12Mo atoms. Thus, Mo(1) shows a preference for boron over carbon as neighbors, the converse being true for Mo(2). The coordination polyhedron around Mo(2) can be regarded as a cuboctahedron of 12 Mo atoms plus an octahedron of carbon and boron atoms. As such, the polyhedron closely resembles the complex ions $Nb_6Cl_{12}^{2+}$ and $Ta_6Cl_{12}^{2+}$ (Vaughan, Sturdivant & Pauling, 1950); the configuration about Mo(1), on the other hand, more closely resembles that of Mo in CrB-type MoB. Each C atom is surrounded by six Mo neighbors at the vertices of

Table 2. *Absolute values of observed and calculated structure factors for* $Mo_2BC$

| H | K | L | FO | FC | H | K | L | FO | FC | H | K | L | FO | FC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 2 | 0 | 12 | 12 | 0 | 2 | 1 | 14 | 16 | 0 | 2 | 2 | 10 | 6 |
| 0 | 4 | 0 | 28 | 26 | 0 | 4 | 1 | 212 | 226 | 0 | 4 | 2 | 19 | 20 |
| 0 | 6 | 0 | 9 | 7 | 0 | 6 | 1 | 29 | 28 | 0 | 6 | 2 | 10 | 9 |
| 0 | 8 | 0 | 237 | 236 | 0 | 8 | 1 | 65 | 68 | 0 | 8 | 2 | 163 | 167 |
| 0 | 10 | 0 | 57 | 56 | 0 | 10 | 1 | 33 | 33 | 0 | 10 | 2 | 38 | 41 |
| 0 | 12 | 0 | 71 | 68 | 0 | 12 | 1 | 150 | 153 | 0 | 12 | 2 | 52 | 55 |
| 0 | 14 | 0 | 18 | 13 | 0 | 14 | 1 | 46 | 45 | 0 | 14 | 2 | 12 | 12 |
| 0 | 16 | 0 | 122 | 121 | 0 | 16 | 1 | 72 | 73 | 0 | 2 | 3 | 9 | 9 |
| 0 | 18 | 0 | 71 | 71 | 0 | 0 | 2 | 216 | 212 | 0 | 4 | 3 | 134 | 134 |
| 0 | 20 | 0 | 73 | 74 | | | | | | | | | | |

| H | K | L | FO | FC | H | K | L | FO | FC | H | K | L | FO | FC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 6 | 3 | 20 | 16 | 1 | 17 | 0 | 20 | 21 | 1 | 1 | 2 | 45 | 44 |
| 1 | 1 | 0 | 68 | 62 | 1 | 1 | 1 | 176 | 175 | 1 | 3 | 2 | 88 | 90 |
| 1 | 3 | 0 | 131 | 124 | 1 | 3 | 1 | 69 | 72 | 1 | 5 | 2 | 130 | 132 |
| 1 | 5 | 0 | 185 | 183 | 1 | 5 | 1 | 42 | 42 | 1 | 7 | 2 | 61 | 64 |
| 1 | 7 | 0 | 91 | 87 | 1 | 7 | 1 | 106 | 107 | 1 | 9 | 2 | 12 | 13 |
| 1 | 9 | 0 | 18 | 16 | 1 | 9 | 1 | 156 | 162 | 1 | 11 | 2 | 43 | 44 |
| 1 | 11 | 0 | 60 | 55 | 1 | 11 | 1 | 50 | 50 | 1 | 13 | 2 | 123 | 123 |
| 1 | 13 | 0 | 159 | 150 | 1 | 13 | 1 | 11 | 12 | 1 | 1 | 3 | 102 | 100 |
| 1 | 15 | 0 | 62 | 57 | 1 | 15 | 1 | 36 | 34 | 1 | 3 | 3 | 46 | 45 |

| H | K | L | FO | FC | H | K | L | FO | FC | H | K | L | FO | FC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5 | 3 | 27 | 28 | 2 | 2 | 1 | 10 | 11 | 2 | 6 | 2 | 8 | 9 |
| 2 | 0 | 0 | 221 | 214 | 2 | 4 | 1 | 152 | 165 | 2 | 8 | 2 | 131 | 137 |
| 2 | 2 | 0 | 8 | 6 | 2 | 6 | 1 | 22 | 20 | 3 | 1 | 0 | 38 | 37 |
| 2 | 4 | 0 | 24 | 20 | 2 | 8 | 1 | 49 | 51 | 3 | 3 | 0 | 78 | 74 |
| 2 | 6 | 0 | 12 | 9 | 2 | 10 | 1 | 28 | 27 | 3 | 5 | 0 | 115 | 109 |
| 2 | 8 | 0 | 169 | 168 | 2 | 12 | 1 | 121 | 125 | 3 | 7 | 0 | 57 | 53 |
| 2 | 10 | 0 | 43 | 41 | 2 | 0 | 2 | 170 | 166 | 3 | 1 | 1 | 101 | 101 |
| 2 | 12 | 0 | 58 | 55 | 2 | 2 | 2 | 4 | 4 | 3 | 3 | 1 | 43 | 46 |
| 2 | 14 | 0 | 13 | 12 | 2 | 4 | 2 | 16 | 17 | 3 | 5 | 1 | 28 | 28 |

Table 3. *Bond data in* $Mo_2BC$ (*e.s.d.'s include only uncertainties in positional parameters*)

| Atom 1 | Atom 2 | Distance Å | E.s.d. Å | Atom 1 | Atom 2 | Distance Å | E.s.d. Å |
|---|---|---|---|---|---|---|---|
| Mo(1) | C | 2·081 | 0·026 | Mo(2) | C | 2·114 | 0·026 |
| | 4 B | 2·306 | 0·011 | | 4 C | 2·171 | 0·001 |
| | 2 B | 2·310 | 0·023 | | B | 2·761 | 0·031 |
| | 2 Mo(1) | 2·930 | 0·004 | | 4 Mo(1) | 2·935 | 0·002 |
| | 4 Mo(2) | 2·935 | 0·002 | | 2 Mo(2) | 3·047 | |
| | 2 Mo(1) | 3·047 | | | 2 Mo(2) | 3·086 | |
| | 2 Mo(1) | 3·086 | | | 4 Mo(2) | 3·102 | 0·003 |
| C | Mo(1) | 2·081 | 0·026 | B | 2 B | 1·787 | 0·033 |
| | Mo(2) | 2·114 | 0·026 | | 4 Mo(1) | 2·306 | 0·011 |
| | 4 Mo(2) | 2·171 | 0·001 | | 2 Mo(1) | 2·310 | 0·023 |
| | | | | | Mo(2) | 2·761 | 0·031 |

| | | |
|---|---|---|
| < Mo(1)–C–Mo(2) | 87·3 ± 0·7° | (4×) |
| < Mo(2)–C–Mo(2) | 92·7 ± 0·7 | (4×) |
| < Mo(2)–C–Mo(2) | 89·1 ± 0·1 | (2×) |
| < Mo(2)–C–Mo(2) | 90·6 ± 0·1 | (2×) |
| < B–B–B | 116·9 ± 3·4 | |

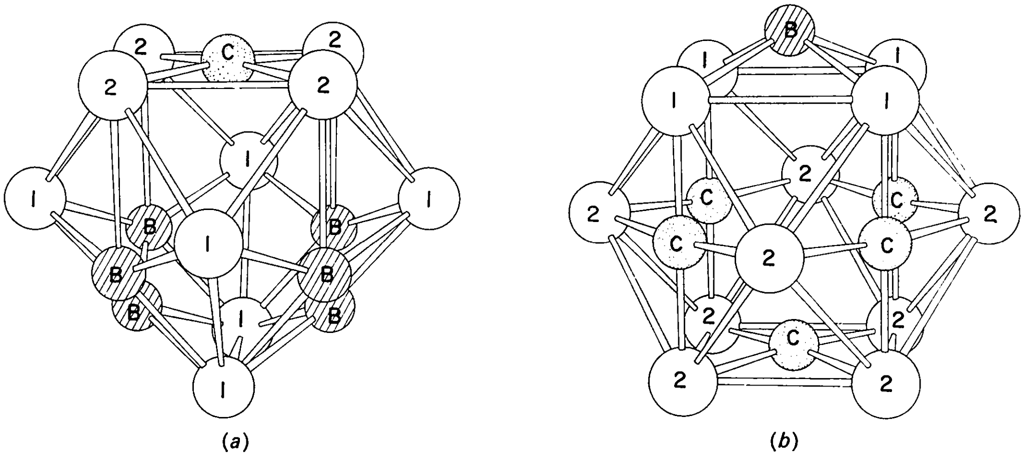

Fig. 2. Ball-and-stick drawings of coordination polyhedra for (*a*) Mo(1) and (*b*) Mo(2). The central atom is omitted for clarity. Numerals within open circles identify type of Mo atom. The orientation is approximately that of Fig. 1.

a nonregular octahedron (bond angles range from 87·3° to 92·7°). As is the case in CrB, each boron atom is coordinated to six Mo neighbors at the corners of a trigonal prism as well as to two boron atoms (within the chain) and another Mo atom which is more distant (2·76 Å) than the other Mo neighbors (2·31 Å).

Although the CrB structure-type occurs rather frequently in intermetallic systems (see, for example, the review by Schob & Parthé, 1965), the $Mo_2BC$-type structure apparently does not. An investigation by Rudy, Benesovsky & Toth (1963) indicated the only ternary borocarbide formed with the metals V, Nb, Ta, Mo and W is, in fact, $Mo_2BC$. We also have been unable to prepare the $Mo_2BC$-type phase (by arc-melting techniques) for the metals, Ti, V, Cr, Nb, Ta and W; similarly we were unable to synthesize $Mo_2BSi$.

We are indebted to Drs A. Zalkin and C. K. Johnson for furnishing copies of the several IBM 7094 programs used in the calculations. We thank L. Rigdon for the chemical analyses and V. Silveira for powder photography.

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