The Crystal Structure of the Molybdenum Boride $Mo_{1-x}B_3$*

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The structure of $Mo_{1-x}B_3$, with x close to 0.20, has been investigated using powder diffractometry, in conjunction with the electron microprobe and chemical analysis. The range of homogeneity of the compound is very small and does not include the stoichiometric composition. The structure is described in the hexagonal space group $P6_3/mmc$ with the axes $a = 5.2026$ (2) Å and $c = 6.3489$ (3) Å. No significant variations in cell dimensions were observed. There are four formula units per unit cell with molybdenum at 2(b) (occupancy 60 %) and 2(c) and boron at 12(i) with x= 0.333. The refinement was performed with least-squares and Fourier difference techniques. The final R value, based on intensities, was 8.8 %.

The structure may be described as a stacking of two-dimensional boron nets and highly defect metal layers. The molybdenum–boron distance exceeds the radius sum by 3 %, while the Mo–Mo distances are 7 and 13 % longer than the radius sum. There are holes in the structure, which are large enough to accommodate boron atoms. However, there is no evidence that these holes are even partially filled.

During investigations of the Mo–B and W–B systems Chrétien and Helgorsky (*1*) found a boron-rich phase of the claimed composition MeB₄. Later Rudy, Benesovsky and Toth (*2*) reported in these systems a boride, which they denoted MeB₁₂. There is sufficient similarity in the powder data, given in the two papers, to make it highly probable that the phases that were studied in these investigations, were identical. In subsequent papers (*3–6*) it was established that the correct unit cell of the compound is hexagonal with the approximate axial lengths $a = 5.20$ Å and $c = 6.34$ Å. Two structure proposals for WB₄ have also been presented (*3, 7*) but they disagree fundamentally as regards the boron skeleton. Therefore, the present authors decided to undertake a more accurate redetermination of the structure.

The presence of heavy metal atoms in the structure restricts the accuracy to which the boron atoms can be located by X-ray methods. In this respect the molybdenum boride offers considerably better experimental conditions and consequently, was chosen for the structure analysis. The result of this structure investigation has been *briefly* presented and discussed in a previous

paper (*8*). The present paper provides a full account of the experimental work. As a result of the structure investigation it was found that the correct crystallographic formula is $Mo_{1-x}B_3$ with $x \approx 0.20$.

Experimental Methods

Preparation. Pressed pellets of molybdenum powder (purity by assay 98.7 %) and crushed crystalline boron (Borax Consolidated Ltd., claimed purity 99.8 %) were arc-melted under purified argon. The specimens were then heat-treated for extended periods in a high-vacuum furnace at 1400°C and 1800°C. Single crystals of sufficient size for X-ray intensity measurements were, however, not obtained and consequently, powder specimens had to be used for the intensity measurements. The samples used in these measurements were obtained by a solid state reaction between the elements at 1800°C for 72 hr. The nominal compositions of the samples were MoB₄ and MoB₆.

It was observed that a surface layer was formed on the pellets during the heat-treatments mentioned. It consisted mainly of the molybdenum boride "Mo₂B₅." The rate of formation of this layer could be diminished, although not com-

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pletely suppressed, by using purified argon as an inert atmosphere.

X-Ray methods. The cell dimensions reported in this paper were measured in a Guinier-Hägg focusing camera using $CuK\alpha_1$, radiation (wavelength 1.54051 Å) and silicon as internal standard ($a = 5.43054$ Å). The standard deviations given include no allowance for possible systematic errors. The absolute error is, however, estimated to be less than 0.03 % in all measurements.

The X-ray intensities were measured by direct summation on the read-out scaler, using a Philips powder diffractometer PW 1050 with rotating specimen and a LiF monochromator between the sample and the proportional counter. With this geometry and under the assumption of an ideally imperfect monochromator crystal the formula for the Lorentz-polarization correction is

$$\frac{1 + \cos^2 2\theta \cdot \cos^2 2\theta_M}{\sin^2 \theta \cdot \cos \theta},$$

where θ is the Bragg angle of the specimen and θ_M that of the monochromator. This correction has been used in the calculation of the intensities in Table IV. Measurements were performed with copper radiation up to $2\theta = 155°$. A set of intensities using chromium radiation was also recorded and used to facilitate the resolution of overlapping reflexions. In order to investigate the influence of possible preferred orientation in the sample complete intensity measurements were performed on specimens prepared in two different ways. One specimen was prepared by filling the sample holder with pure boride powder with the application of only moderate pressure, while the second was prepared by using equal amounts by volume of boride powder and finely crushed gum arabic powder.

Chemical analysis. Samples used for intensity measurements were analyzed for boron and molybdenum at the Analytical Department of this Institute. The samples were treated in a boiling mixture of HNO_3 and HCl. From this treatment a small residue was left, which was combusted in oxygen gas and subsequently dissolved in $HCl + H_2SO_4$. The residual solution contained about 1 % of the total boron content and only traces of molybdenum. An emission spectroscopic investigation of the residue from the $HNO_3 + HCl$ treatment showed that the residue mainly consists of SiO_2 and Al in addition to boron established chemically. The content of boron and molybdenum in the solutions were

determined titrimetrically. The sample of nominal composition MoB_4 was found to contain 62.74 % Mo and 34.43 % B while that of nominal composition MoB_6 contained 55.90 % Mo and 41.81 % B. Accordingly the as-analyzed compositions are $MoB_{4.75\pm0.03}$ and $MoB_{6.60\pm0.04}$.

Electron microprobe analysis. The sample of nominal composition MoB_4 was investigated, using a Geoscan microprobe, at the Institute of Mineralogy and Geology, University of Uppsala. The molybdenum content was determined using MoL radiation (accelerating voltage 15 kV) and Mo_2B as a standard substance. The result was corrected for the absorption and atomic number effects according to a procedure given by Philibert (9). The average value obtained from several grains of the main phase in the sample was 70.5 % Mo. This corresponds to a formula $MoB_{3.7\pm0.4}$, assuming the sum of the boron and molybdenum contents to be 1.0. The estimated error is larger than the observed variations from one grain to another considering the uncertainty in the above-mentioned correction term. It may also be mentioned that the application of the empirical correction of Moll (10) results in a composition $MoB_{3.7}$ in good agreement with that given above.

Calculations. The numerical computations were performed on a CDC 3600 computer in Uppsala. The least-squares refinement of temperature and occupancy factors, using the well resolved reflexions, were made with the program ORFLS (11). The final least-squares refinement, using all observed reflexions, was performed with the program POWOW (12). A list of remaining programs used is to be found elsewhere (13). The atomic scattering factors and the real part of the dispersion correction were taken from Ref. (14). The imaginary part of the dispersion correction was not included since it was known, from the experiences of a powder refinement of a tungsten boride (the correction being larger than in this case), that this correction does not influence the final results significantly.

Structure Determination and Refinement

The dimensions of the hexagonal unit cell were measured in both of the two-phase regions on either side of $Mo_{1-x}B_3$. The measurements refer to specimens of nominal compositions MoB_6 and MoB_4. The former sample contained solely β-rhombohedral boron and $Mo_{1-x}B_3$, while the latter contained traces of β-rhombohedral boron

TABLE I

UNIT CELL DIMENSIONS WITH STANDARD DEVIATIONS
(Å UNITS)

Phase	Nominal composition	Two-phase region	a	c
$Mo_{1-x}B_3$	MoB_6	$Mo_{1-x}B_3 + \beta$-rhombohedral boron	5.2026(2)	6.3489(3)
$Mo_{1-x}B_3$	MoB_4	$Mo_{1-x}B_3 +$ "Mo_2B_5"	5.2033(4)	6.3498 (8)
"Mo_2B_5"	MoB_4	$Mo_{1-x}B_3 +$ "Mo_2B_5"	3.0118(2)	20.936(2)

in addition to $Mo_{1-x}B_3$ and Mo_2B_5. The results are given in Table I, which also includes the cell dimensions of boron-rich "Mo_2B_5."

Among the reflexions not affected by overlaps zero intensities were observed for hhl reflexions with l odd and for hkl reflexions with $h - k = 3n$ and l odd. If these extinctions are systematic the intensity data are consistent with the space groups $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$. Of these $P6_3/mmc$ was chosen for the description of the structure.

An initial Patterson synthesis indicated that the metal atoms are situated in positions 2(b) and 2(c) and that position 2(b) has an occupancy of about 80% of that in 2(c). The synthesis was furthermore consistent with the occurrence of boron atoms in position 12(i) with the x parameter close to 0.33. Refinement of the structure was undertaken using least-squares method as well as difference syntheses. The latter technique was necessary in order to investigate the possible occurrence of further boron atoms. The results from the ORFLS least-squares refinement of the

two data sets (denoted A and B) previously described are collected in Table II. These calculations were based on about 20 nonoverlapped reflexions or reflexions resolved with the data using chromium radiation. The R value given in Table II is defined as $\sum ||F_0| - k|F_c||/\sum|F_0|$ and was calculated only for the nonoverlapped reflexions. The reflexions were given equal weight in the refinement procedure with ORFLS. A comparison was also made of observed and calculated intensities for nonoverlapped reflexions as well as for overlapped reflexions. The discrepancies were very similar for the two groups of reflexions, which is revealed by the index $\sum ||\sqrt{I_0}| - k|\sqrt{I_c}||/\sum |\sqrt{I_0}|$. For data set A this index was 0.061 for nonoverlapped and 0.059 for all reflexions, including the overlapped ones. The results from the two refinements (Table II) indicate that the two data sets, obtained from boron-poor and boron-rich sample composition, represent the same structure in all its details. Although separate reflexions may differ

TABLE II

STRUCTURE DATA FOR $Mo_{1-x}B_3$[a,b] FROM ORFLS REFINEMENT
OF NONOVERLAPPED DATA

	Data A[c]		Data B[d]	
	B (Å^2)	Occupancy	B (Å^2)	Occupancy
Mo(1) in 2(b)	2.1(5)	0.73(7)	2.9(7)	0.67(8)
Mo(2) in 2(c)	0.7(2)	1.00	0.4(2)	1.00
B in 12(i)[e]	1.3(8)	1.00	0.6(5)	1.00
R value	0.044		0.061	

[a] Space group $P6_3/mmc$ (No. 194). Unit cell: see Table I.
[b] Standard deviations in parentheses refer to the last decimal place.
[c] From sample of nominal composition MoB_4.
[d] From sample of nominal composition MoB_6.
[e] With x parameter 1/3.

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appreciably (up to 15σ), the above-mentioned conclusion is further supported by the agreement index, defined as $\sum |I_A - kI_B|/\sum I_A$, in which k was calculated from the scale factors of the refinements. This index has the value 0.14. Accordingly, a final refinement was undertaken using the average values of the intensities from both recordings.

In this stage of the investigation the powder least-squares program POWOW (12) was made available to the authors. This program has the advantage to utilize in the refinement procedure the nonresolved overlapped reflexions as well. POWOW was used for checking the ORFLS refinements as well as for the final refinement using the average intensities. More appropriate statistical weights were used in these refinements and the R value as given in Table III, was defined by $\sum w||I_0| - k|I_c||/\sum |I_0|$, where I_0 and I_c denote values for separate, resolved reflexions or sums for unresolved, overlapping reflexions. The final R value as defined above was 8.8%. Final structure data are presented in Table III, where the x parameter of position 12(i) is assumed to be 0.333, an assumption which means that the boron–boron distances within each boron layer are equal. This x parameter was also used in Table IV, which gives the observed and calculated intensities. A least-squares refinement of the x parameter only yielded the value 0.341 with the standard deviation 0.036 after 5 cycles and a last shift of 0.002. This is not a significant deviation from 0.333.

A three-dimensional Fourier difference synthesis was finally calculated using the parameters obtained in the least-squares refinement. The difference sections were computed with grid points ~ 0.1 Å from each other. A careful

TABLE III

FINAL STRUCTURE DATA FOR $Mo_{1-x}B_3$ (x=0.20) OBTAINED FROM POWOW REFINEMENT OF AVERAGE INTENSITIES FROM TWO MEASUREMENTS[a]

	B (Å²)	Occupancy
Mo(1) in 2(b)	1.3(4)[b]	0.60(4)
Mo(2) in 2(c)	0.4(1)	1.00
B in 12(i), x = 0.333	2.7(7)	1.00
R value (%)	8.8	

[a] Space group $P6_3/mmc$. Unit cell: see Table I.
[b] Standard deviations in parentheses refer to the last decimal place.

TABLE IV

OBSERVED AND CALCULATED INTENSITIES FOR $Mo_{1-x}B_3$ (x = 0.20, Cu$K\alpha$ RADIATION)[a]

$h\,k\,l$	I_{obs}	I_{calc}
1 0 1	50 478	50 293
0 0 2	10 419	8564
1 1 0, 1 1 2	25 674	24 170
2 0 1	13 026	11 165
1 1 2	35 613	39 139
1 0 3	8139	8170
2 1 1	8855	10 097
0 0 4	3950	3550
2 0 3	4885	4101
3 0 0, 2 1 2, 1 0 4	8601	8754
3 0 2, 1 1 4	11 156	12 019
2 1 3	4754	5002
2 2 0, 2 0 4	3325	2929
3 1 1, 1 0 5	6165	5811
2 2 2	6867	6695
4 0 1, 2 0 5	3186	2899
3 0 4	6170	5757
3 1 3	3086	2686
3 2 1, 2 1 5	5122	4714
2 2 4	2526	2787
4 0 3	966	1123
4 1 0, 3 2 2, 3 1 4, 1 1 6	6995	6387
4 1 2	7327	6918
3 2 3	1544	2064
5 0 1, 3 1 5, 1 0 7	4397	4086
3 3 0, 5 0 2, 3 2 4, 3 0 6	4955	4011
4 2 1, 4 0 5, 2 0 7	4966	4395
3 3 2, 4 1 4	7193	7551
5 0 3	1123	1163
2 2 6	3674	3794
5 1 1, 3 2 5, 2 1 7	8501	8783
4 2 3	2899	3583

[a] The observed intensities are average values of the two measurements described in the text.

inspection of the Fourier sections showed that the largest positive peak (at 0.82, 0.64, 0.25) is 17% and the largest negative peak (at 0.82, 0.90, 0.25) is 19% of a boron maximum in the corresponding F_0 syntheses. In the latter a molybdenum atom displayed a maximum of 115 e/Å³ and a boron atom 9 e/Å³. The observed background level in the difference map is normal and there is, accordingly, no indication of the occurrence of further boron atoms in the structure. In particular there were no indications of extra electron density in the positions (1/3, 2/3, 0.61), (0.666, 0.141, 0.427) and (0.472, 0.141, 0.202) as proposed for the corresponding tungsten compound by previous authors (3, 7).
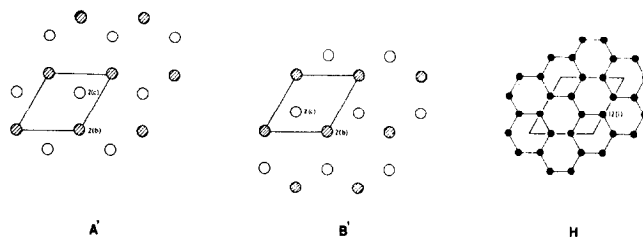
FIG 1. The structure of $Mo_{1-x}B_3$ may be described as a stacking of defect metal layers (A', B') and boron layers (H). Stacking sequence A'HB'H . . ..
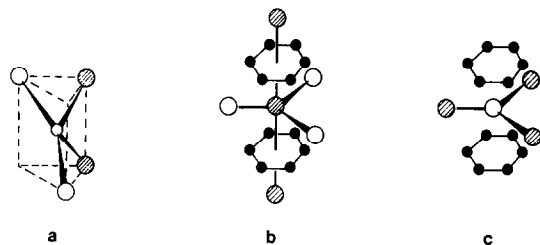

FIG. 2. The environment of (a) B; (b) Mo(1); (c) Mo(2).

Attempts to obtain better agreement between observed and calculated structure factors using model structures with puckered boron layers were not successful.

Description of the Structure

The crystal structure of $Mo_{1-x}B_3$ may be described in terms of defect metal layers (A', B') and planar boron layers (H) of the type occurring in the normal transition metal diborides. The A' and B' layers can be regarded as close-packed metal layers with one third of the metal atoms removed. Furthermore, one of the two remaining metal positions is occupied only to 60%. The layers, which are shown in Fig. 1, are stacked in the c direction according to the sequence A'HB'HA'H .... The stacking is such that no direct boron–boron contacts occur in the c direction. Furthermore, there are dumbbell-like holes in the structure centered at (2/3, 1/3, 1/4) and extending in the c direction.

The coordination of the various atoms is shown in Fig. 2. The boron atom has four close molybdenum neighbors at four of the six corners of a triangular prism. It has furthermore three close boron neighbors within the boron layer. The molybdenum atoms are surrounded by 12 boron atoms arranged in two regular hexagons (Fig. 2). The molybdenum atoms differ as

TABLE V

INTERATOMIC DISTANCES IN $Mo_{1-x}B_3{}^a$

Mo(1)[b]–12 B	2.351[c]
3 Mo(2)	3.004
2 Mo(1)	3.174
Mo(2) –12 B	2.351
3 Mo(1)	3.004
B – 3 B	1.734
2 Mo(1)	2.351
2 Mo(2)	2.351
6 B	3.004
2 B	3.174
3 B	3.468
6 B	3.617

[a] All distances less than 3.80 Å are listed.
[b] Mo(1) occupies 0.60 of position 2(b).
[c] The estimated standard deviations of Mo–Mo distances are determined by those of the cell dimensions. For Mo–B and B–B distances they depend on the correctness of the assumption that the x parameter of boron is 0.333.

regards metal environment, since Mo(1) has five metal neighbors in a bipyramidal arrangement and Mo(2) has only three close metal neighbors belonging to the same metal layer (A' or B').

The interatomic distances are shown in Table V. As shown, the Mo–B distances are slightly longer (3%) than the sum of the boron radius (0.88 Å) and the 12-coordinated Goldschmidt radius of molybdenum. The observed Mo–Mo distances exceed the radius sum much more, for instance in the c direction by as much as 13%.

Discussion

Since greater confidence is in general attached to data obtained from single crystal experiments, it seems appropriate to start with a discussion of the quality of this powder diffraction investiga-

tion. The structure determination of $Mo_{1-x}B_3$ has given x close to 0.20, which implies a composition in full agreement with that obtained from electron microprobe analysis. The chemical analysis on the other hand gave a higher boron content in the two specimens. This fact is, however, explained by the occurrence of free boron (β-rhombohedral boron according to X-ray diffraction results), which was detected in both specimens with diffraction as well as electron microprobe techniques. As mentioned earlier, there are only traces of free boron in MoB_4, which however also contained Mo_2B_5. Furthermore, there is no reason to suspect any significant preferred orientation effect in the intensity data, since the two refinements agree excellently and the final difference map displays a low residual level of electron density. The relatively small number of reflexions used in the least-squares refinement suggests, however, that little physical significance should be attached to the temperature factors (Tables II and III). These facts together indicate that the conclusions as regards the occupation of the metal and boron positions are based on sound experimental evidence. The cell dimensions as seen in Table I do not vary significantly and, accordingly, $Mo_{1-x}B_3$ has a very narrow homogeneity range. Thus the composition of the investigated compound is invariant at $Mo_{1-x}B_3$ with x close to 0.20.

The most conspicuous structural features of $Mo_{1-x}B_3$ are the large amount of defects in the structure and the occurrence of boron–boron bonds solely in two dimensions.

The present structure determination has shown that there are no further boron atoms in the structure in addition to the boron atoms in position $12(i)$ and, accordingly, the structure contains a dumbbell-shaped hole at $(2/3, 1/3, 1/4)$. It is interesting to note that the holes are large enough to accommodate at least two boron atoms. However, these boron atoms would then have as many as seven boron neighbors at a distance of 1.75–1.87 Å, which has never been observed in transition metal borides containing less boron than $MeB_{12}(8)$. A more comprehensive discussion of borides containing holes is found in a recent review by Lundström (8).

It is supposed that some diborides and hexaborides contain metal vacancies but the experimental ground for this is rather scanty. The present investigation involves clear experimental evidence for the occurrence of vacancies among the Mo(1) atoms in position $2(b)$.

It has been proposed that in the corresponding tungsten compound the holes mentioned should accommodate pairs of boron atoms (3) or even octahedra of boron atoms (7). However, since no further boron atoms were found in $Mo_{1-x}B_3$, it seems unlikely that the configurations mentioned occur in the iso-structural $W_{1-x}B_3$.

The crystal structure of $Mo_{1-x}B_3$ is closely related to those belonging to the structure types of AlB_2, "Mo_2B_5" and $WB_{2.0}$ insofar as these compounds also contain boron in planar networks. The metal coordination of these boron atoms is triangular prismatic. However, there are also other types of boron atoms, which coordinate four metal atoms tetrahedrally in "Mo_2B_5," $WB_{2.0}$, Ru_2B_3 as well as ReB_2. The boron atoms of $Mo_{1-x}B_3$ evidently assume an intermediate position as regards the metal coordination, since they coordinate four metal atoms situated at four of the corners of a trigonal prism (Fig. 2). It is furthermore interesting to note that $Mo_{1-x}B_3$ up till now is the most boron-rich boride structure in which there is no three-dimensional linking of the boron atoms. Such a network, however, occurs in all known MeB_4 structures, namely in the structure of ThB_4 (8), CrB_4 (13) as well as the recently determined MnB_4 (15).

Acknowledgments

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