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The Crystal Structure of MnB_4

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The crystal structure of MnB_4 has been determined by X-ray methods using intensities measured with a powder diffractometer. The symmetry is monoclinic with space group $C2/m$ and

$$a=5.503 \text{ Å}, b=5.367 \text{ Å}, c=2.949 \text{ Å}, \beta=122.71°$$

The unit cell contains two manganese atoms in position 2(*a*) and eight boron atoms in position 8(*j*).

The MnB_4 structure is a slightly distorted form of the CrB_4 structure. A three-dimensional network is formed by the boron atoms. The manganese atoms are situated in channels along the *c* direction in the boron network.

The MnB_4 phase was first reported by Fruchart and Michel in 1960,[1] who found that MnB_2 decomposed into Mn_3B_4 and MnB_4 at lower temperatures. In 1967 the X-ray powder pattern of MnB_4 was indexed on a tetragonal unit cell by Markovskii and Bezruk.[2] However, their choice of unit cell was not very plausible since the agreement between observed and calculated *d* values was poor and many reflexions observed by Fruchart and Michel could not be accounted for. A phase diagram for the system Mn-B was also published by Markovskii and Bezruk in 1967 [3] according to which MnB_4 melts congruently in contrast to the results published by Fruchart and Michel, who found that MnB_4 decomposed into MnB_2 and boron at higher temperatures. Andersson [4] found in 1969 that MnB_4 was monoclinic, and at the same time gave preliminary results from a crystal structure determination. In this paper final results of the structure determination and some phase analytical observations in the region MnB_2-B are presented.

PREPARATION, X-RAY WORK AND NUMERICAL COMPUTATIONS

To supplement the preliminary phase analysis reported previously by Andersson [4] samples with the initial compositions $MnB_{2.1}$, $MnB_{3.4}$, $MnB_{6.4}$, and $MnB_{9.7}$ were prepared by arc-melting pieces of manganese (from Koch-Light Laboratories, Ltd., claimed purity 99.99 %) and crystalline boron (from Borax Consolidated, Ltd., claimed purity 99.8 %) under an atmosphere

of purified argon. The samples, resting on a bed of MnB_2 fragments, were then annealed in a high vacuum resistance furnace under an atmosphere of about 350 mm Hg of purified argon gas at temperatures ranging from 1050°C up to 1400°C and times varying between one and two weeks. Heat treatments were made at 50°C intervals within this temperature range. The temperature measurements were made using a pyrometer calibrated against a tungsten lamp secondary standard and the accuracy of the measurements was estimated to be better than ± 25°C.

The reaction products were examined by X-ray powder diffraction using Guinier-Hägg type focussing cameras with strictly monochromatic $CrK\alpha_1$ radiation ($\lambda_{CrK\alpha_1} = 2.28962$ Å). Unit cell dimensions were measured using silicon ($a = 5.43054$ Å) as internal calibration standard. The very small standard deviations for the cell dimensions are those calculated during the least squares refinement, and thus do not take account of any systematic errors in the measurements.

Single crystals of MnB_4 suitable for X-ray investigation were not obtained. X-Ray powder diffraction methods were therefore used in the crystal structure determination of MnB_4. The intensities of the reflexions were recorded by the $\theta - 2\theta$ scanning method up to $2\theta = 154°$ using a Philips Powder Diffractometer PW 1050 with $CrK\alpha$ radiation. To obtain a better peak to background ratio a single crystal lithium fluoride monochromator [reflecting planes (200)] was used between the specimen and the proportional counter. To reduce the statistical errors, the recordings of weaker reflexions were repeated until the intensities of all reflexions were known with about the same accuracy.

In the preparation of specimens for the intensity measurements great care was taken to avoid preferred orientation among the crystallites in the samples, since preferred orientation was earlier observed in a MnB_4 powder specimen.[4] Complete intensity measurements were made on two specimens prepared in two different ways. One was prepared by filling the specimen holder with powder and carefully levelling the surface without application of pressure to give the plane configuration required by the diffraction geometry. The other was made by mixing the MnB_4 powder with about its own volume of finely powdered gum-arabic and then pressing the mixture into the specimen holder to obtain the required plane surface.

The sample used for the intensity measurements had the initial composition $MnB_{4.0}$ (prepared by Andersson [4]) and contained small amounts of MnB_2. No chemical analysis was undertaken.

Numerical computations were made on a CD 3600 computer using the following programs all written in FORTRAN IV:

Least squares refinement of unit cell dimensions	CELSIUS: J. Tegenfeldt, Uppsala, Sweden.
Calculation of 2θ for all possible reflexions	DIFFUS: N.-O. Ersson, Uppsala, Sweden.
Lorentz-polarization and multiplicity factor correction	PULVER LP: R. Liminga, Uppsala, Sweden; modified by N.-O. Ersson, Uppsala, Sweden.

Fourier summations and structure factor calculations	DRF: A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
Least squares refinement of positional parameters and temperature factors	LALS: P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
Calculation of interatomic distances	DISTAN: A. Zalkin, Berkeley, U.S.A.
Crystal structure illustrations	OR TEP: C. K. Johnsson, Oak Ridge, U.S.A.

Atomic scattering factors were interpolated from Table 3.3.1A in Ref. 5 and the real part of the dispersion correction was taken from Cromer.[6]

RESULTS

The X-ray examination of the reaction products from the annealed samples gave the following results. The samples with the initial compositions $MnB_{2.1}$ and $MnB_{3.4}$ both showed a two-phase equilibrium between Mn_3B_4 and MnB_4 when heat-treated at 1050°C. After annealing at 1100°C and higher temperatures the $MnB_{2.1}$ sample contained only MnB_2. The $MnB_{3.4}$ sample contained MnB_2 and MnB_4 when annealed at temperatures from 1100°C up to 1350°C. When annealed at 1400°C the same sample contained MnB_2 together with another phase, here denoted MnB_x, which is probably very boron-rich. The samples with the initial compositions $MnB_{6.4}$ and $MnB_{9.7}$ both showed the same two-phase equilibria. After annealing at temperatures up to 1350°C they contained MnB_4 plus MnB_x and when heat-treated at 1400°C they contained MnB_2 and MnB_x. After melting the $MnB_{2.1}$ sample contained MnB_2 and the other samples MnB_2 and MnB_x.

These results show that an eutectoid decomposition of MnB_2 into Mn_3B_4 and MnB_4 occurs between 1050°C and 1100°C and that a peritectoid decomposition of MnB_4 into MnB_2 and MnB_x occurs between 1350°C and 1400°C. This is in complete agreement with the results by Fruchart and Michel[1] and by Andersson,[4] but conflicts with the phase diagram given by Markovskii and Bezruk.[3]

The powder pattern of MnB_4 could be indexed[4] to give very good agreement between observed and calculated $\sin^2\theta$ values in terms of a monoclinic unit cell with $a = 5.503$ Å, $b = 5.367$ Å, $c = 2.949$ Å, and $\beta = 122.71°$. The absence of reflexions with $h + k = 2n + 1$ indicated a C-centered unit cell. No significant changes in the cell dimensions were observed (for values of $\sin^2\theta_o$ and $\sin^2\theta_c$ see Table 1). The d values corresponding to the observed $\sin^2\theta$ values are in very good agreement with those given by Fruchart and Michel.[1] The tetragonal unit cell proposed by Markovskii and Bezruk[2] cannot explain the MnB_4 powder pattern satisfactorily because the agreement between observed and calculated $\sin^2\theta$ values is unsatisfactory and many observed reflexions cannot be explained.

The X-ray diffraction powder pattern of MnB_x is similar to that of β-rhombohedral boron and could be indexed in terms of a hexagonal unit cell with $a = 10.99$ Å and $c = 24.00$ Å. This unit cell was confirmed by a single-crystal investigation. The unit cell of MnB_x is slightly larger than that of β-rhombohedral boron and the intensities of the reflexions are somewhat different. Presumably MnB_x is similar to a phase in the Cr-B system with the composition $CrB_{\sim 41}$, the crystal structure of which has been recently determined.[7] The structure of $CrB_{\sim 41}$ is closely related to that of β-rhombohedral boron.

The unit cell dimensions observed for Mn_3B_4 and MnB_2 are in good agreement with those given by Aronsson *et al.*[8]

The intensities of the recorded MnB_4 reflexions were corrected for the Lorentz-polarization and multiplicity factors. The expression for the Lorentz-polarization factor for X-rays rendered monochromatic by a crystal has been treated by Azaroff.[9] A modification of this treatment gives the following angle-depending factor for the Lorentz-polarization correction using a monochromator crystal between the specimen and the counter:

$$\frac{1 + \cos^2 2\theta_1 \cdot \cos^2 2\theta_2}{\sin^2 \theta_1 \cdot \cos \theta_1}$$

where $2\theta_1$ is the diffraction angle in the specimen and $2\theta_2$ is the diffraction angle in the monochromator crystal.

The crystal structure was determined using the intensity material from the sample prepared without gum-arabic. However, of the 29 recorded reflexions only 19 were sufficiently well resolved to be used. A three-dimensional Patterson synthesis was calculated using these reflexions. In spite of the marked series termination effects, the Patterson function could be interpreted in terms of space group $C2/m$ symmetry by placing two manganese atoms in position $2(a)$ and eight boron atoms in $8(j)$. The same space group symmetry was assumed in the least squares refinement of atomic positional parameters and isotropic individual temperature factors. The program used minimizes the function $\sum w \cdot (|F_o| - |F_c|)^2$. The weighting factor, w, was put equal to unity for all reflexions, since they all were recorded with the same accuracy as mentioned earlier. The refinement converged rapidly and after the last cycle the shifts were less than 0.1 % of the calculated standard deviations. The final discrepancy index, defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$, was 0.052.

Finally a three-dimensional difference Fourier synthesis was calculated. The largest deviations from zero in this were less than 19 % of the boron peaks in the final electron density map. At the position $2(d)$, of interest in the subsequent discussion, the deviation from zero in the difference maps was less than 3 % of the boron maxima in the electron density synthesis.

A refinement using the F_o values for the 19 resolved reflexions obtained from the specimen prepared by mixing the MnB_4 powder with gum-arabic gave the final discrepancy index 0.063. The results of the two refinements did not differ significantly as can be seen in Table 2 where structure data for MnB_4 are given.

There were no features of the electron density and difference maps which would indicate that the $C2/m$ symmetry adopted was incorrect. With the very limited intensity material available, further refinements based on the

lower space groups *Cm* or *C*2 would hardly provide any conclusive evidence as regards the true symmetry. The structure of MnB_4 is accordingly described with $C2/m$ symmetry.

X-Ray powder data for MnB_4 are given in Table 1. The *F* and *I* values refer to the specimen prepared without gum-arabic. Interatomic distances are listed in Table 3. In the calculation of the distances the mean values of the positional parameters given in Table 2 were used. The calculation of the standard deviations of the distances were based upon the largest standard deviation of each positional parameter.

The very good agreement between observed and calculated structure factors for resolved reflexions as well as between observed and calculated intensities for overlapping reflexions (see Table 1) is taken as proof that the structure is correctly determined. However, it is difficult to estimate the accuracy of the results. It must be remembered that the standard deviations obtained are based on a small number of reflexions only.

Table 1. Powder diffraction data for MnB_4. $\sin^2\theta$ values refer to $CrK\alpha_1$ radiation ($\lambda = 2.28962$ Å). Observed intensities were measured with $CrK\alpha$ radiation ($\lambda = 2.29092$ Å).

h k l	$\sin^2\theta_o \times 10^5$	$\sin^2\theta_c \times 10^5$	I_o	I_c	F_o	F_c
1 1 0	10668	10663	4662	4632	32.55	32.45
0 2 0	18199	18200	681	796	23.33	25.23
1 1 $\bar{1}$	19622	19624	863	1077	19.32	21.59
2 0 $\bar{1}$	21084	21083	1642	1685	39.14	39.65
0 0 1	21285	21290	1595	1620	38.77	39.07
2 0 0	24444	24452	379	255	20.29	16.66
2 2 $\bar{1}$	39282	39284	701	704	24.44	24.49
0 2 1	39495	39491	810	706	26.32	24.57
2 2 0	42655	42653	1115	994	31.82	30.04
3 1 $\bar{1}$	43872	43869	1102	1061	31.95	31.35
1 1 1	44286	44283	1223	1053	33.78	31.34
1 3 0	47060	47064	749	879	26.96	29.20
1 3 $\bar{1}$	—	56024	1103	1169	33.98	34.98
3 1 0	—	59568	843	722	29.86	27.63
2 0 $\bar{2}$	—	60295	489	541	32.18	33.85
4 0 $\bar{1}$[a]	—	69781		49	—	10.00
2 0 1[a]	—	70402	700	50	—	10.07
3 1 $\bar{2}$[a]	—	70751		302	—	17.46
1 1 $\bar{2}$[a]	—	71165		310	—	17.68
0 4 0	—	72801	63	69	11.13	11.66
2 2 $\bar{2}$	—	78495	194	224	13.28	14.26
3 3 $\bar{1}$[a]	—	80270	293	120	—	10.26
1 3 1[a]	—	80684		117	—	10.06
4 0 $\bar{2}$	—	84332	49	61	8.77	9.83
0 0 2	—	85162	59	58	9.52	9.42
4 2 $\bar{1}$[a]	—	87981	1267	607	—	20.53
2 2 1[a]	—	88603		614	—	20.38
2 4 $\bar{1}$[a]	—	93885	791	391	—	13.89
0 4 1[a]	—	94092		405	—	14.02

[a] Not used in the refinement.

Table 2. Structure data for MnB_4. Standard deviations are given in parenthesis and refer to the last decimal place of the respective values. Space group $C2/m$ (No. 12). $Z=2$. 2 Mn in 2(*a*) and 8 B in 8(*j*). Cell dimensions: $a=5.5029(3)$ Å, $b=5.3669(3)$ Å, $c=2.9487(2)$ Å, and $\beta=122.710(5)°$. Cell volume 73.28 Å^3.

	Specimen without gum-arabic	Specimen with gum-arabic
R-value (%)	5.2	6.3
B_{Mn}(Å^2)	1.52(41)	1.68(52)
x_B	0.1948(57)	0.1994(71)
y_B	0.3429(40)	0.3460(49)
z_B	0.1967(95)	0.2033(119)
B_B (Å^2)	1.67(64)	1.31(77)

Table 3. Interatomic distances in MnB_4 (Å units). Distances shorter than 3.0 Å are listed. Standard deviations are given in parenthesis and refer to the last decimal place of the respective values.

	Dist.		Dist.
Mn—4B	2.062(28)	B—Mn	2.062(28)
—4B	2.189(30)	—Mn	2.189(30)
—4B	2.210(32)	—Mn	2.210(32)
—2Mn	2.949(00)	—B	2.474(60)
B—B	1.669(53)	—B	2.805(66)
—B	1.825(66)	—2B	2.920(18)
—B	1.839(57)	—2B	2.932(18)
—B	1.871(59)	—2B	2.949(00)

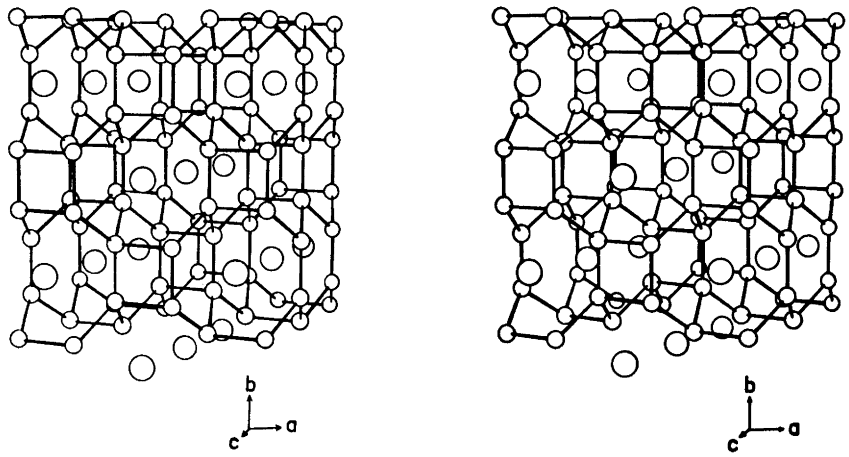

Fig. 1. Stereoscopic pair of drawings showing the atomic arrangement in MnB_4 as viewed almost perpendicular to the (001) plane. The small connected circles represent boron atoms and the larger isolated circles represent manganese atoms.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A stereoscopic pair of drawings illustrating the atomic arrangement in MnB_4 as viewed almost perpendicular to the (001) plane are shown in Fig. 1.

The crystal structure of MnB_4 is a distortion of that of CrB_4.[10] The relationship between the crystal structures of MnB_4 and CrB_4 is easily seen if the C-centered MnB_4 unit cell is transformed to an I-centered one with $a = 4.630$ Å, $b = 5.367$ Å, $c = 2.949$ Å, and $\beta = 90.31°$. These values are close to the values for the orthorhombic CrB_4 cell, $a = 4.774$ Å, $b = 5.477$ Å, and $c = 2.866$ Å. The close relationship between MnB_4 and CrB_4 raises the question of whether CrB_4 is also monoclinic. The structure determination,[10] however, gave no reason to suspect a lower symmetry. Furthermore the resolution of the powder cameras used in the determination of the unit cell dimensions is so high that a deviation in any of the unit cell angles from 90° by more than 0.05° would have been easily observed.

The conventional C-centered unit cell will be used in the following description of the MnB_4 structure.

The boron atoms form a three-dimensional network which may be described as built up of groups of four boron atoms forming planar rectangles all parallel to each other and almost perpendicular to the c axis. The lengths of the edges of these rectangles, 1.67 Å and 1.83 Å, are not significantly different and the angle between a rectangle and the c axis is not significantly separated from 90°. Each boron atom in such a rectangle is connected to two boron atoms in other rectangles, one in a rectangle $c/2$ above and one in a rectangle $c/2$ below as viewed in the direction of the c axis. These interrectangular distances are 1.84 Å and 1.87 Å. The fact that the rectangles are not quite perpendicular to the c axis results in two different distances. The interrectangular linkages form zig-zag chains of boron atoms running in the c direction. The three-dimensional boron network may also be described on the basis of these chains. Each boron atom in a chain is connected to two boron atoms in adjacent chains, the angle between these boron-boron connections being 90° and all linkages between the chains being perpendicular or almost perpendicular to the c axis.

The boron network is intersected by channels in the direction of the c axis through 0,0,0 and 1/2,1/2,0. The manganese atoms are situated in these channels.

Each boron atom is surrounded by four boron atoms, forming a very distorted tetrahedron, and three manganese atoms. Each manganese atom is surrounded by an irregular polyhedron of twelve boron atoms and two manganese atoms.

The average distance from a boron atom to its four boron neighbours is 1.80 Å. This distance is slightly longer than twice the tetrahedral boron radius,[11] 1.76 Å, and almost the same as the corresponding average in the CrB_4 structure which is 1.79 Å. The sum of the tetrahedral boron radius, 0.88 Å, and the Goldschmidt radius for 12-coordination of manganese, 1.31 Å, is 2.19 Å. The distances from a boron atom to its three coordinated manganese atoms, 2.06 Å, 2.19 Å, and 2.21 Å, give an average of 2.15 Å which is insignificantly shorter than the radius sum. For the CrB_4 structure the average of the

chromium-boron distances is 2.20 Å while the radius sum is 2.16 Å. The average of the Mn–B distances is shorter than the average of the Cr–B distances, which is contrary to what would be expected from the radius sums but is in agreement with what is often observed for Me–B distances, namely that the Me–B distances become shorter in comparison with the radius sums as the group number of the metal atom increases.

The shortest Mn–Mn distance, 2.95 Å, is between adjoining manganese atoms in the *c* direction. This distance exceeds the radius sum with more than 0.3 Å which indicates only a weak Mn–Mn interaction. The shortest distance between manganese atoms in adjacent channels is 3.83 Å.

Voids of appreciable size exist in the MnB_4 structure just as in CrB_4. These voids are in the position 2(*d*) (coordinates 0,1/2,1/2 and 1/2,0,1/2) and an atom in this position would have eight boron neighbours, four at a distance of 1.92 Å and four at a distance of 1.93 Å at the corners of a somewhat distorted quadratic prism, and two manganese neighbours at a distance of 2.32 Å. Accordingly, atoms with radii less than one Ångström can occupy position 2(*d*) without distorting the lattice. Though the size of the voids is sufficient to accommodate boron atoms (radius 0.88 Å), the present investigation indicates that the voids are unfilled, since the final difference synthesis showed no perceptible electron density in position 2(*d*). Furthermore no variations of the unit cell dimensions with composition were observed. The absence of boron atoms in this position is consistent with earlier observations in boride structures. Lundström [12] found that there is strong experimental evidence to show that boron atoms in borides containing less boron than MeB_{12} never coordinate more than five other boron atoms. A boron atom in position 2(*d*) in the MnB_4 structure would, as already mentioned, have as many as eight close boron neighbours.

A dominating feature in the structures of MnB_4 and CrB_4 is the three-dimensional network of boron atoms, and it seems that the chemical bonding between the boron atoms may to a large extent be responsible for the cohesion in these structures. From a purely geometrical point of view it appears that the channels in the boron network cannot be expanded beyond a certain critical limit without disruption of some boron-boron bonds. Accordingly, the size of metal atoms capable of being accommodated in the channels is strictly limited. Efforts by the present authors to prepare a CrB_4-type phase in the V–B system have been unsuccessful. The fact that VB_4 does not occur may indicate that the size of the vanadium atom exceeds the critical limit. The Goldschmidt radius for 12-coordination of vanadium is 1.36 Å as compared with the chromium radius of 1.28 Å. However, no CrB_4- or MnB_4-type phases have been reported for iron, cobalt, and nickel, which have radii slightly smaller than those of chromium and manganese. Evidently, size-factor effects alone do not provide reliable stability criteria. A more fundamental approach must be based on an analysis of the electronic requirements for bond formation within the boron framework. As an example of this type of treatment may be mentioned the studies by Lipscomb and Britton.[13] In a molecular-orbital calculation for borides with the AlB_2, ThB_4, CaB_6, and UB_{12} structures they found that it was necessary to assume an electron transfer from metal to boron in order to obtain a stable bond configuration. Even if these results

are rather approximate, the importance of the electronic state of the transition metal atoms is clearly indicated. It seems likely that the deformation of the CrB_4-type boron network in MnB_4 depends on the difference in electronic states between the chromium and manganese atoms rather than on simple geometrical size effects.

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