

The Borides of Manganese

ROLAND KIESSLING

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

This investigation is part of a study on binary alloys between transition elements and boron.

Only a few investigations of the manganese-boron system have been reported. Previous investigations¹⁻⁶ report the existence of borides of the composition MnB and MnB₂. MnB has been investigated by X-ray methods⁷, but the results reported here are not consistent with these findings as will be discussed below.

GENERAL METHODS

The manganese, used as starting material, was purified by distillation in a high frequency vacuum induction furnace and had a purity of 99.6%. The boron was prepared by reducing boron tribromide with hydrogen⁸ and had a purity of 98—99%. The alloys were prepared in evacuated silica tubes by sintering mixtures for 48—72 hours at 1100—1200°C. Single crystals of the intermediary phases were obtained by prolonged heating at this temperature usually for 7—10 days. Analyses of selected alloys were carried out according to the methods, given in³.

The structure of the phases was determined by single crystal methods as described elsewhere⁹. The axes of the three orthorhombic phases were chosen so that the International tables could be used directly.

GENERAL SURVEY OF THE SYSTEM

Four intermediary phases, δ , ϵ , ζ , and η were observed. For preparations with boron content of more than about 70 atomic % some weak interferences were observed, which did not belong to the η -phase. It was not possible to decide whether these interferences belonged to a new phase or to impurities.

Single crystals were obtained from all the phases. They were metallic, hard and brittle and often had a reddish-brown colour.

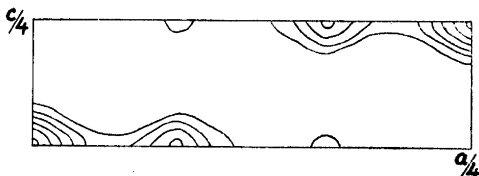


Fig. 1. δ -phase. Projection of the Patterson function on (010). ((400) and (004) are symmetry planes in the projection.)

The δ -phase probably had an extended homogeneity range with a boron content of about 20 atomic %. The ϵ -phase had the composition Mn_2B , the ζ -phase MnB and the η -phase Mn_3B_4 .

The δ -phase

This phase appeared pure in photographs of material with a boron content of about 20 atomic %. Only very small single crystals were obtained. Laue photographs showed the Laue symmetry to be mmm . Rotation and Weissenberg photographs were taken around [010], using Mo-K-radiation. Accurate cell dimensions were obtained from powder photographs, giving the axes of the orthorhombic cell (for a boron content of 20 atomic %):

$$a = 14.53 \text{ \AA}, \quad b = 7.293 \text{ \AA}, \quad c = 4.209 \text{ \AA}, \quad V = 446.0 \text{ \AA}^3.$$

The density found was 6.60, most closely corresponding to a cell content of $8 \text{ Mn}_4\text{B}$ (calculated density 6.87).

Reflections hkl were observed only for $h+k=2n$ and $k+l=2n$, $0kl$ only for $k=2n$, $l=2n$ and $k+l=4n$, $h0l$ only for $h=2n$, $l=2n$ and $h+l=4n$ and $hk0$ only for $h=2n$, $k=2n$ and $h+k=4n$. The probable space group thus is $Fddd$.

Manganese positions. There are several possible ways of placing 32 metal atoms in $Fddd$. $16(c) + 16(d)$ may be excluded, because 642 and 624 are strong reflections. For the same reason a combination of (c) or (d) with (e), (f) or (g) is less probable. From space considerations (length of c -axis only 4.2 \AA) (g) and the combination (a) + (b) are excluded. The projection of the Patterson function on the ac -plane $p(wv)$ (Fig. 1) showed only one strong maximum on the w -axis, giving a vector with a length of $c/2$ in the [0 1] direction. If the metal atoms were situated in $32:(h)$, then only the value $\frac{1}{4}$ for the z -parameter would be possible. With this z -coordinate, however, only two vectors with a projected length less than $a/2$ in the [1 0 0] direction would exist, whereas the Patterson projection showed the existence of four such vectors. The remaining possible positions for the 32 atoms are thus

Table 1. δ -phase. Weissenberg photographs with Mo-K radiation. Comparison between observed and calculated $|F|^2$ values.

$h k l$	$ F ^2$		$h k l$	$ F ^2$		$h k l$	$ F ^2$	
	obs.	calc.		obs.	calc.		obs.	calc.
0 0 4	181	136	9 1 3	—	4	9 3 3	20	15
0 0 8	68	41	11 1 3	—	2	11 3 3	54	47
2 0 2	163	148	2 2 0	—	1	13 3 3	36	40
2 0 6	50	39	6 2 0	134	145	1 3 5	38	40
4 0 0	21	26	10 2 0	—	0	4 4 0	54	54
4 0 4	—	8	14 2 0	—	0	8 4 0	41	42
6 0 2	—	0	18 2 0	41	48	12 4 0	9	8
8 0 0	14	15	0 2 2	23	15	2 4 2	—	0
10 0 2	80	87	4 2 2	57	54	6 4 2	111	87
12 0 0	154	154	8 2 2	36	43	10 4 2	—	0
12 0 4	88	89	12 2 2	—	7	0 4 4	—	7
14 0 2	65	63	2 2 4	—	0	4 4 4	32	27
16 0 0	11	7	6 2 4	61	65	1 5 1	—	3
24 0 0	59	51	10 2 4	—	0	3 5 1	—	6
1 1 1	9	7	1 3 1	109	115	5 5 1	35	38
3 1 1	7	11	3 3 1	30	31	7 5 1	35	35
5 1 1	54	65	5 3 1	—	6	9 5 1	—	4
7 1 1	45	55	7 3 1	—	5	11 5 1	—	2
9 1 1	9	6	9 3 1	20	12	13 5 1	—	2
11 1 1	—	3	11 3 1	38	62	1 5 3	—	2
13 1 1	—	2	13 3 1	46	53	3 5 3	—	4
1 1 3	—	3	1 3 3	66	68	5 5 3	30	28
3 1 3	—	6	3 3 3	27	19	7 5 3	30	26
5 1 3	36	38	5 3 3	—	3	9 5 3	—	3
7 1 3	39	35	7 3 3	—	3	11 5 3	—	2

16(e) and 16(f). The possibility that the 32 atoms occupy two 16:(f) positions may further be excluded as vectors appear in $p(uv)$ with u -components different from $\frac{1}{2}$ and $\frac{1}{4}$. The Patterson function along the line $u 0 0$ showed maxima at $u = 0$, $u = 0.165$ and $u = 0.500$. Only one maximum thus appears in the interval $0 < u < \frac{1}{2}$ and for this maximum $u \neq \frac{1}{4}$. The possibility of placing the 32 atoms in two 16:(e) positions may thus be excluded and the remaining possibility is 16:(e) + 16:(f) for the manganese atoms.

$$\begin{aligned}
 &(000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2} 0 \frac{1}{2}; \frac{1}{2} \frac{1}{2} 0) + \\
 &16:(e) x00; \bar{x}00; \frac{1}{4} + x \frac{1}{4} \frac{1}{4}; \frac{1}{4} - x \frac{1}{4} \frac{1}{4} \\
 &16:(f) 0y0; 0\bar{y}0; \frac{1}{4} \frac{1}{4} + y \frac{1}{4}; \frac{1}{4} \frac{1}{4} - y \frac{1}{4}
 \end{aligned}$$

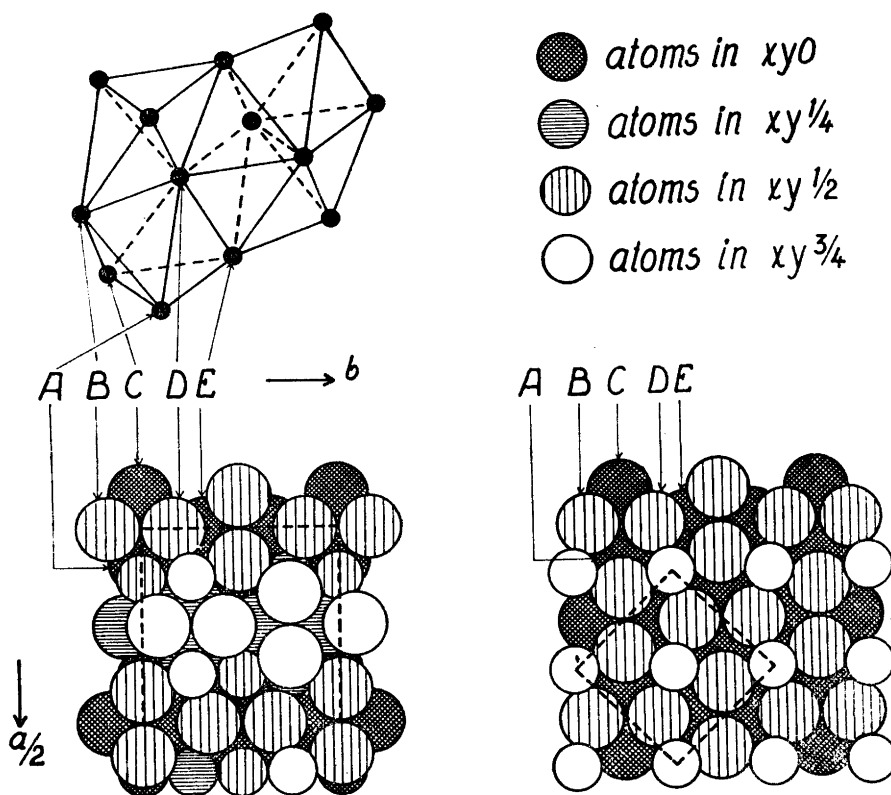


Fig. 2. δ - and ϵ -phases. Projections of the structures of the ideal δ -phase (left) and the ϵ -phase (right). The unit cells are indicated. Large circles represent manganese atoms, small circles boron atoms. The packing of the tetrahedra of manganese atoms in a sheet is shown separately.

The Patterson function along the line $0v0$ showed a maximum at $v = 0.35$ (of bad quality). Considering the maximum for $u = 0.165$ in $P(u00)$ a probable pair of parameters thus is $x = 0.165/2$, $y = (1 - 0.35)/2$ (the pair $x = 0.165/2$, $y = 0.35/2$ must be excluded from space considerations). A more accurate determination of y was made from intensity calculations, giving $y = 0.333 \pm 0.004$. A comparison between observed and calculated $|F|^2$ values using these parameters is given in Table 1 (the influence of boron is neglected). The agreement is good. The maximum in $P(u00)$ for $u = 0.500$ may be explained if the vectors with the component $a = \frac{1}{2}$, which are nearly parallel to the a -axis, are considered. The metal lattice may be regarded as built of parallel sheets of tetrahedra of manganese atoms (Fig. 2). In the

tetrahedron ABCD, the edges AC and BD have a length of 2.41 and 2.44 Å resp. whereas the edges AB, BC, CD, and AD all have the length 2.71 Å. In the tetrahedron ACED, the two shorter edges AC and ED have a length of 2.41 and 2.43 Å resp. and the four longer edges each 2.71 Å. The two tetrahedra are thus nearly equal. Each metal atom in 16:(f) is surrounded by two neighbours at 2.43 Å one at 2.44 Å and six at 2.71 Å, all in the same tetrahedron sheet and two at 2.71 Å, one from each neighbour sheet. Each metal atom in 16:(e) is surrounded by one neighbour at 2.41 Å and six at 2.71 Å, all in the same tetrahedron sheet, and two at 2.43 Å and two at 2.71 Å, all in the same neighbouring sheet. The structure may be compared with the Me_2B -borides of the CuAl_2 -type (C 16), to which the ϵ -phase Mn_2B also belongs. The metal lattice of these borides also consists of sheets of tetrahedra, as pointed out by Hägg¹⁰. The sheets are arranged in a different manner, forming two sheet systems at right angles. For Mn_2B each manganese atom is surrounded by one neighbour at 2.37 Å, two at 2.46 Å, four at 2.69 Å and four at 2.73 Å. The distances from a manganese atom to its metal neighbours thus are nearly the same for both lattice types.

Boron positions. The largest holes in the lattice are in the position 16:(e) with a value of the parameter $x = 0.375$. They are thus situated between adjacent sheets of manganese tetrahedra, forming strings in the [011] direction. An atom, placed in such a hole, would be surrounded by eight metal atoms, all at a distance of 2.19 Å from its centre. Additional holes of the lattice are situated in the tetrahedra of metal atoms. An atom, placed in such a hole, would be surrounded by four manganese atoms at a distance of 1.61 Å. The first type of holes thus has space for atoms with a radius of up to about 0.98 Å, compared with 0.40 Å for atoms in the last type of holes. The first possibility is thus the only possible for boron with its radius of about 0.87 Å. The metal lattice has space for 16 boron atoms per cell in these holes, giving an upper limit of 33.3 atomic % boron for the δ -phase. The reflections 840 and 931, which appear at nearly the same angle in the powder photographs, appeared at slightly varying positions in preparations with different boron contents. This indicates an extended homogeneity range. It was not possible to determine the limits, however, because of the small variations. The δ -phase appeared pure in preparations with a boron content of about 20 atomic %. About 50 % of the holes of the manganese lattice are thus occupied by boron atoms, and the number may possibly vary. The distance boron-boron, if two adjacent holes are occupied, is 2.11 Å.

The δ -phase, with a boron content of about 20 atomic %, thus crystallizes in *Fddd*. The orthorhombic unit cell contains 32 manganese atoms, occupying the positions 16:(e) and 16:(f). The parameters are $x = 0.083$ and $y = 0.333$.

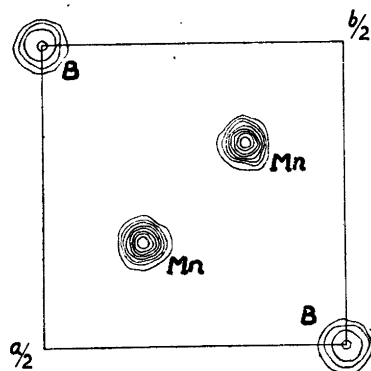


Fig. 3. ϵ -phase. Projection of the electron density on (001).

The boron atoms are placed in $16:(e)$ with $x = 0.375$. About 50 % of the boron sites are occupied by boron atoms.

The ϵ -phase

This phase was found homogeneous in preparations with a content of 33.3 atomic% boron. The hard and brittle crystals were often plate-like with a reddish-brown lustre. No displacements of the interferences were observed in the range between the δ - and ζ -phases, indicating a definite composition Me_2B . Laue photographs showed the Laue symmetry to be $4/mmm$. Rotation and Weissenberg photographs were taken around $[001]$ using Mo- K radiation. Accurate cell dimensions were obtained from powder photographs, giving the axes of the tetragonal cell:

$$a = 5.148 \text{ \AA}, c = 4.208 \text{ \AA}, c/a = 0.817, V = 111.5 \text{ \AA}^3.$$

The value of the length of the axes indicated an isomorphism between this boride and the borides of $CuAl_2$ -type ($C 16$)¹⁰⁻¹³, which was verified by further structure analysis. With a cell content of 4 Me_2B the calculated density is 7.19, in good agreement with the observed value 7.20. Reflections $h k l$ were observed only for $h + k + l = 2n$, $h k 0$ for $h + k = 2n$, $h h l$ for $l = 2n$ and $0 k l$ for $k = 2n$ and $l = 2n$, showing that space group $I4/mcm$ is possible. The metal atoms of the Me_2B -borides mentioned are situated in $8:(h)$ in $I4/mcm$. The section $P(uw0)$ of the Patterson space was investigated in order to determine the parameter x of $8:(h)$. The value $x = 0.163$ was obtained. This value is slightly less than the value $x = 0.167$ reported for Fe_2B ¹⁰. The axial ratio, however, is slightly different. Each manganese atom is surrounded

Table 2. ϵ -phase. Weissenberg photographs with Mo-K radiation. Comparison between observed and calculated $|F|$ -values.

$h k l$	$ F $		$h k l$	$ F $		$h k l$	$ F $	
	obs.	calc.		obs.	calc.		obs.	calc.
2 0 0	45	55	9 1 4	31	28	6 3 3	—	1
2 0 2	51	63	10 1 1	24	29	7 3 0	44	47
2 0 4	34	33	10 1 3	21	28	7 3 2	35	35
4 0 0	44	54	2 2 0	32	33	7 3 4	37	40
4 0 2	57	62	2 2 2	14	14	8 3 1	—	1
4 0 4	39	55	2 2 4	20	21	8 3 3	—	1
6 0 0	65	85	3 2 1	—	8	9 3 0	44	46
6 0 2	54	69	3 2 3	—	7	9 3 2	51	53
6 0 4	71	68	4 2 0	36	32	9 3 4	44	41
8 0 0	—	14	4 2 2	20	18	10 3 1	—	3
8 0 2	—	23	4 2 4	21	25	10 3 3	—	3
10 0 0	29	31	5 2 1	64	69	11 3 0	—	14
10 0 2	40	39	5 2 3	49	61	11 3 2	—	6
10 0 4	20	29	5 2 5	41	49	12 3 1	—	0
12 0 0	37	43	6 2 0	29	29	12 3 3	—	0
12 0 2	35	34	6 2 2	32	38	4 4 0	41	35
12 0 4	37	41	6 2 4	24	23	4 4 2	23	22
1 1 0	35	33	7 2 1	45	45	4 4 4	24	28
1 1 2	38	43	7 2 3	38	41	5 4 1	51	56
1 1 4	16	19	7 2 5	33	35	5 4 3	49	50
2 1 1	73	98	8 2 0	18	13	5 4 5	38	42
2 1 3	65	76	8 2 2	—	3	6 4 0	36	35
2 1 5	59	57	9 2 1	—	11	6 4 2	37	43
3 1 0	70	69	9 2 3	—	10	6 4 4	29	29
3 1 2	42	48	10 2 0	—	20	7 4 1	42	37
3 1 4	41	48	10 2 2	—	11	7 4 3	35	34
4 1 1	60	68	11 2 1	44	38	7 4 5	31	30
4 1 3	51	59	11 2 3	40	36	8 4 0	—	14
4 1 5	43	46	11 2 5	29	34	8 4 2	—	6
5 1 0	—	11	12 2 0	—	14	9 4 1	—	9
5 1 2	22	22	12 2 2	—	21	9 4 3	—	9
6 1 1	—	10	3 3 0	75	94	10 4 0	19	22
6 1 3	—	9	3 3 2	79	97	10 4 2	—	15
7 1 0	—	18	3 3 4	50	70	11 4 1	35	33
7 1 2	26	27	4 3 1	—	6	11 4 3	26	32
8 1 1	47	49	4 3 3	—	5	11 4 5	18	30
8 1 3	46	46	5 3 0	40	36	12 4 0	21	18
8 1 5	34	40	5 3 2	23	23	12 4 2	24	25
9 1 0	26	32	5 3 4	24	28	12 4 4	13	17
9 1 2	26	22	6 3 1	—	1	5 5 0	—	9

by three neighbours at 2.37, 2.46 and 2.46 Å, four at 2.69 and four at 2.73 Å. To verify the position of the boron atoms, obtained from space considerations (4:(a) in $I4/mcm$), the projection of the electron density on (001) was calculated (Fig. 3). (The signs of the observed $|F|$ -values could be calculated since the position of the heavy manganese atoms was determined from the Patterson section.) The boron atoms may thus be situated in 4:(a) or 4:(c). In 4:(a) the distance boron-manganese would be 2.20 Å, in 4:(c) 1.93 Å. The first possibility is thus the more probable one, giving a radius of the boron atom of 1.02 Å. In Table 2 a comparison between observed and calculated $|F|$ -values for several reflections is given. The lattice (Fig. 2) is similar to that of the δ -phase and is discussed above.

The ε -phase, Mn_2B , thus is of the $CuAl_2$ -type ($C 16$). The value of the parameter for the metal atoms is 0.163.

The ζ -phase

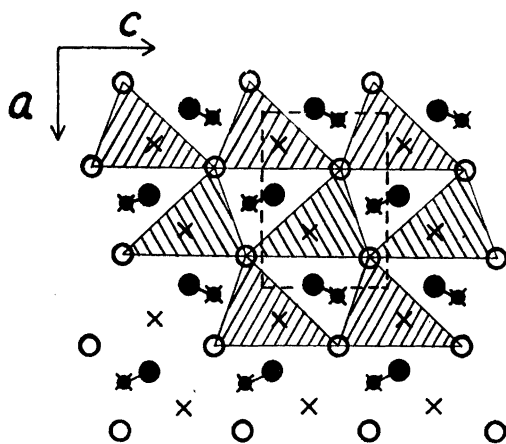
This phase crystallized homogeneously in preparations with a boron content of 50 atomic%. The interferences always appeared at fixed angles for preparations with boron content between the ε - and the η -phases. The homogeneity range thus is narrow. Rod-shaped single crystals with a reddish-brown lustre were obtained. Laue photographs showed the Laue symmetry to be mmm . Rotation and Weissenberg photographs were taken around [010] using Mo- K radiation. Accurate cell dimensions were obtained from powder photographs, giving the axes of the orthorhombic cell:

$$a = 5.560 \text{ \AA}, b = 2.977 \text{ \AA}, c = 4.145 \text{ \AA}, V = 68.61 \text{ \AA}^3.$$

The values of the length of the axes indicated isomorphism between this boride and the borides of FeB-type ($B 27$)¹¹, which was verified by further structure analysis.

With a cell content of 4 MnB the calculated density (6.37) most closely corresponds to the measured density (6.45).

Reflections $0 k l$ were observed only for $k + l = 2n$ and $h k 0$ only for $h = 2n$ showing that space group $Pnma$ is possible. The further structure analysis showed the ζ -phase to be isomorphous with FeB and with the metal atoms in 4(c) of $Pnma$. Bjurström's values of the parameters, $x = 0.180$ and $z = 0.125$ were in accordance with the results from a Patterson function projection on (010). The only holes, large enough for boron atoms, have their centres in 4:(c) with parameters $x = 0.031$ and $z = 0.614$ (compared with



- × = metal atoms in $x\frac{1}{4}z$
- = metal atoms in $x\frac{3}{4}z$
- = boron atoms in $x\frac{1}{4}z$
- = boron atoms in $x\frac{3}{4}z$

Fig. 4. ζ -phase. The lattice, projected on (010). The unit cell, chains of boron atoms and some prisms of metal atoms are indicated.

$x = 0.036$ and $z = 0.61$ for FeB). In Table 3 a comparison between observed and calculated $|F|$ -values for several reflections is given. In Fig. 4 the lattice is projected on (010). The lattice may be regarded as consisting of trigonal prisms of iron atoms with boron chains in the channels between them. Each metal atom is surrounded by four metal neighbours at 2.67 Å, two at 2.70 Å, two at 2.97 Å and two at 2.98 Å. Each boron atom is surrounded by six metal atoms at about 2.19 Å and the boron-boron distance is 1.80 Å. In Fig. 4 the prisms are indicated in order to point out the similarity between this phase and the two types represented by CrB⁹ and the δ -phase in the molybdenum-boron system¹². Both these types may be regarded as consisting of trigonal metal prisms with boron chains in the channels. For CrB all chains are parallel, for the molybdenum boride they extend in two directions. The similarity between MnB and Cr₃C₂¹⁴ may also be noted.

According to previous investigations⁷, MnB is orthorhombic with axes 2.95 kX, 11.5 kX and 4.10 kX. As will be observed two of these reported axes are nearly the same as for the ζ -phase above, whereas the third is doubled. No signs of this doubling was observed in this investigation, however. The structure suggested is not at all in accordance with the results obtained for the ζ -phase or any other intermediary phase observed in this investigation. The shortest distance manganese-manganese reported, 2.3 Å, seems too small. The parameters for boron are only roughly indicated and it is not possible to discuss the proposed structure from the data given.

The ζ -phase, MnB, thus is of the FeB-type (B 27).

Table 3. ζ -phase, Weissenberg photographs with Mo-K radiation. Comparison between observed and calculated $|F|$ -values.

$h k l$	$ F $		$h k l$	$ F $		$h k l$	$ F $	
	obs.	calc.		obs.	calc.		obs.	calc.
2 0 0	29	37	6 1 0	23	25	2 2 0	25	28
4 0 0	—	5	8 1 0	19	17	4 2 0	—	4
6 0 0	35	38	10 1 0	22	22	6 2 0	33	33
8 0 0	32	32	0 1 1	35	42	8 2 0	25	30
10 0 0	—	7	1 1 1	40	43	1 2 1	11	11
0 0 4	54	51	2 1 1	29	33	2 2 1	28	26
0 0 8	30	28	3 1 1	11	10	3 2 1	33	37
1 0 1	17	15	4 1 1	12	9	4 2 1	27	33
2 0 1	34	34	5 1 1	23	23	5 2 1	19	22
3 0 1	47	46	6 1 1	25	24	1 2 2	52	46
4 0 1	39	40	7 1 1	20	19	3 2 2	—	8
5 0 1	24	25	1 1 2	31	32	5 2 2	15	17
1 0 2	60	60	3 1 2	38	44	7 2 2	28	36
3 0 2	—	10	5 1 2	29	37	1 2 3	—	11
5 0 2	22	20	7 1 2	—	3	2 2 3	24	22
7 0 2	39	40	9 1 2	24	22	3 2 3	30	30
1 0 3	17	13	0 1 3	27	30	4 2 3	32	30
2 0 3	28	25	1 1 3	28	32	0 2 4	52	45
3 0 3	30	35	2 1 3	28	27	2 2 4	15	20
4 0 3	33	34	3 1 3	—	10	4 2 4	—	3
5 0 3	22	22	4 1 3	—	8	6 2 4	26	27
6 0 3	—	9	5 1 3	19	18	1 2 5	—	6
7 0 3	—	2	6 1 3	20	21	2 2 5	—	18
8 0 3	—	3	7 1 3	—	20	3 2 5	24	26
9 0 3	—	13	8 1 3	21	19	4 2 5	19	23
10 0 3	22	20	2 1 4	34	35	1 2 6	24	28
2 0 4	23	23	4 1 4	32	33	1 2 7	—	7
4 0 4	—	3	0 1 5	27	25	0 2 8	29	27
6 0 4	32	29	1 1 5	27	23	2 3 0	35	35
8 0 4	30	27	2 1 5	—	18	4 3 0	36	33
1 0 5	—	7	3 1 5	—	9	6 3 0	22	21
2 0 5	17	20	4 1 5	—	4	8 3 0	19	14
3 0 5	30	28	5 1 5	22	17	0 3 1	28	27
4 0 5	23	25	1 1 6	—	17	1 3 1	31	27
1 0 6	32	31	3 1 6	31	26	2 3 1	25	22
3 0 6	—	6	5 1 6	22	24	3 3 1	—	10
5 0 6	—	13	0 1 7	—	16	4 3 1	—	7
7 0 6	27	29	1 1 7	—	18	5 3 1	21	17
2 1 0	41	51	2 1 7	—	16	6 3 1	20	19
4 1 0	38	44	2 1 8	17	20	7 3 1	19	17

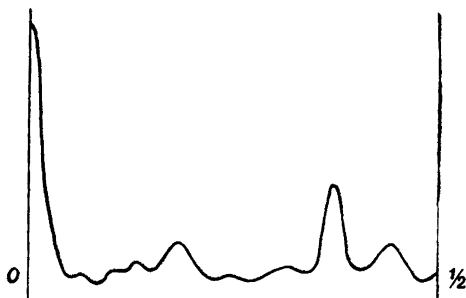


Fig. 5. η -phase. The Patterson function along the line $0v0$.

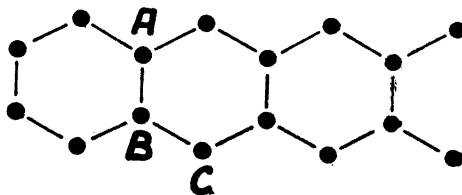


Fig. 6. η -phase. Double chain of boron atoms.

The η -phase

A fourth intermediary phase was obtained in a pure state with a content of 57 atomic% boron. It probably had the definite composition Mn_3B_4 . Well defined single crystals were obtained, needle- or plate-shaped with a reddish-brown, metallic colour. Laue photographs showed the Laue symmetry to be mmm . Rotation- and Weissenberg photographs were taken around $[001]$ and $[100]$, using Mo- K radiation. Accurate cell dimensions were obtained from powder photographs, giving the axes of the orthorhombic cell:

$$a = 3.032 \text{ \AA}, b = 12.86 \text{ \AA}, c = 2.960 \text{ \AA}, V = 115.4 \text{ \AA}^3.$$

The density found was 5.90, in close agreement with the density calculated for $2 \text{ Mn}_3\text{B}_4$ (5.99). Reflections hkl only appeared for $h+k+l=2n$, $0kl$ for $k+l=2n$, $h0l$ for $h+l=2n$ and $h k 0$ for $h+k=2n$. Probable space groups are thus $Immm$, $I222$, $I2_12_12_1$, and Imm . The length of the axes and the space group indicated isomorphism between this phase and the δ -phase in the tantalum-boron system¹³. This was verified by further structure analysis. The Patterson function was investigated along the line $0v0$ (Fig. 5). In addition to the maximum at $v=0$, three major peaks appeared, one strong at $v=0.372$, due to a manganese-manganese vector and two at $v=0.183$ and 0.442 resp., each due to two manganese-boron vectors (compare the δ -phase of the tantalum-boron system). The values of the parameters thus are $y=0.186$ for manganese in $4:(g)$, $y=0.369$ for boron in $4:(g)$ and $y=0.442$ for boron in $4:(h)$. The corresponding values for the tantalum boride were $y=0.180$ for tantalum and $y=0.375$ and 0.445 for boron, the value for tantalum determined from powder line intensities and values for boron from space considerations. From space considerations the

Table 4. η -phase, Weissenberg photographs with Mo-K radiation. Comparison between observed and calculated $|F|$ values.

$h k l$	$ F $		$h k l$	$ F $		$h k l$	$ F $	
	obs.	calc.		obs.	calc.		obs.	calc.
2 0 0	95	100	1 5 0	85	97	2 9 3	35	31
4 0 0	54	63	3 5 0	65	65	0 10 0	49	53
6 0 0	47	46	0 5 1	24	33	2 10 0	41	45
1 0 1	53	50	2 5 1	18	26	4 10 0	38	32
3 0 1	29	33	1 5 2	62	75	1 10 1	—	13
0 0 2	105	98	3 5 2	60	58	0 10 2	41	44
2 0 2	72	81	5 5 2	46	41	2 10 2	34	39
4 0 2	56	60	0 5 3	—	22	4 10 2	28	29
6 0 2	47	43	0 6 0	70	77	1 11 0	59	77
1 0 3	29	33	2 6 0	61	60	3 11 0	54	60
0 0 4	70	64	4 6 0	40	40	5 11 0	42	44
0 0 6	50	44	1 6 1	25	18	0 11 1	24	31
1 1 0	59	51	0 6 2	50	59	2 11 1	16	27
3 1 0	31	29	2 6 2	49	51	1 11 2	54	68
1 1 2	32	36	4 6 2	41	36	3 11 2	56	54
3 1 2	32	27	1 6 3	—	12	5 11 2	30	42
0 1 3	—	14	1 7 0	—	10	0 11 3	20	24
1 2 1	76	70	0 7 1	47	48	0 12 0	—	19
3 2 1	48	47	2 7 1	43	39	1 12 1	—	24
5 2 1	33	30	4 7 1	30	27	0 12 2	—	16
0 2 2	—	5	1 7 2	—	7	1 13 0	—	11
1 2 3	59	57	0 7 3	36	33	0 13 1	49	54
3 2 3	51	44	2 7 3	32	29	2 13 1	46	48
1 3 0	26	28	4 7 3	28	23	4 13 1	34	35
3 3 0	—	18	0 8 0	26	28	1 13 2	—	10
0 3 1	71	96	2 8 0	29	23	0 13 3	51	42
2 3 1	61	73	1 8 1	56	78	2 13 3	36	38
4 3 1	42	48	3 8 1	38	57	0 14 0	—	11
6 3 1	23	33	5 8 1	32	40	1 14 1	45	49
1 3 2	19	21	0 8 2	25	23	3 14 1	31	37
3 3 2	14	16	2 8 2	19	20	5 14 1	23	28
0 3 3	57	61	1 8 3	51	57	0 14 2	—	10
2 3 3	49	54	3 8 3	41	47	1 14 3	39	39
4 3 3	38	40	5 8 3	30	35	3 14 3	29	34
0 4 0	22	29	1 9 0	—	4	0 15 0	—	16
2 4 0	22	19	0 9 1	47	48	1 15 1	—	22
1 4 1	37	39	2 9 1	41	40	0 16 0	51	66
0 4 2	17	19	4 9 1	31	29	2 16 0	43	58
2 4 2	17	16	1 9 2	—	3	4 16 0	42	47
1 4 3	25	27	0 9 3	41	35	1 16 1	—	25

values of the parameters of boron in Mn_3B_4 would be 0.371 and 0.443 in close agreement with the values obtained from $P(0v0)$. In Table 4 a comparison between several observed and calculated $|F|$ -values are given, using the parameters obtained for manganese from $P(0v0)$ and for boron from space considerations. The agreement is good. The manganese atoms in $4:(g)$ are surrounded by four neighbours at 2.68 Å, two at 2.81, two at 2.96 and two at 3.03 Å. The atoms in $2:(c)$ are surrounded by four neighbours at 2.81 Å, two at 2.96 Å and two at 3.03 Å.

The boron atoms are connected to double chains, running through the metal lattice, with a distance boron-boron of 1.75 Å in the same half and 1.47 Å between different halves of a double chain.

If the value 0.87 Å, obtained from earlier investigations, is used as an approximate value for the radius of the boron atom, the distance 1.47 Å is less than $2r_B$ (1.74 Å). It thus seems as if adjacent boron atoms from different halves of a double chain (A and B in Fig. 6) have a tendency to form boron pairs with strong boron-boron bonds. For Ta_3B_4 , the same tendency was observed (distances $AB = 1.54$ Å, $BC = 1.85$ Å). The metal atoms of Ta_3B_4 , however, have a greater radius, making possible a more symmetrical arrangement of the boron atoms with distances $AB = BC = 2r_B$.

The η -phase, Mn_3B_4 , thus crystallizes in *Immm*, isomorphous with Ta_3B_4 . The parameters are $y = 0.186$ for manganese and $y = 0.371$ and 0.443 for boron

GENERAL DISCUSSION

The system manganese-boron belongs to the group, discussed by Hägg^{15,16}. The value of the ratio r_B/r_{Mc} is > 0.59 and the structures of the intermediary phases do not belong to the simple types. They are, however, all metallic. Especially for the phases with isolated boron atoms the structures are complicated. The system is similar to the other binary systems between transition metals and boron. The general tendency for the boron atoms to form chains or nets through the metal lattice is also found for this system. The δ - and ϵ -phases have isolated boron atoms, but with a tendency to form strings. The ζ -phase has boron chains and the η -phase double chains.

SUMMARY

The binary system manganese-boron has been investigated by X-ray methods. Four intermediary phases all with metallic properties have been found to exist and their structures have been determined. The δ -phase with a boron content of about 20 atomic% and probably with an extended homo-

geneity range, and the ε -phase Mn_2B with $CuAl_2$ -structure (*C* 16), are closely related.

The ζ -phase, MnB , is of the FeB type (*B* 27) and the η -phase, Mn_3B_4 , isomorphous to Ta_3B_4 ¹³.

As in the other binary systems between transition metals and boron there is a tendency for the boron atoms to form chains or nets.

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REFERENCES

1. Binet du Jassonaix, A. *Compt. rend.* **139** (1904) 1209.
2. Wedekind, E. *Ber.* **38** (1905) 1228.
3. Wedekind, E. *Ibid.* **40** (1907) 1259.
4. Hoffman, J. *Z. anorg. Chem.* **66** (1910) 361.
5. Heusler, F. and Take, E. *Trans. Faraday Soc.* **8** (1912) 169.
6. Ochsenfeld, R. *Ann. Physik* **12** (1932) 354.
7. Hocart, R., and Fallot, M. *Compt. rend.* **203** (1936) 1062.
8. Kiessling, R. *Acta Chem. Scand.* **2** (1948) 707.
9. Kiessling, R. *Ibid.* **3** (1949) 595.
10. Hägg, G. *Z. physik. Chem.* **B 11** (1930) 152.
11. Bjurström, T. *Arkiv Kemi, Mineral. Geol.* **A 11** (1933) no. 5.
12. Kiessling, R. *Acta Chem. Scand.* **1** (1947) 893.
13. Kiessling, R. *Ibid.* **3** (1949) 603.
14. Hellbom, K., and Westgren, A. *Svensk Kem. Tid.* **45** (1933) 141.
15. Hägg, G. *Z. physik. Chem.* **B 6** (1929) 221.
16. Hägg, G. *Ibid.* **12** (1931) 33.

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