ACTA CHEMICA SCANDINAVICA 14 (1960) 1414–1418

A Note on the Compositions and Crystal Structures of MnB_2, Mn_3Si, Mn_5Si_3 and $FeSi_2$

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The existence of a manganese diboride, MnB_2, with the AlB_2-structure has been confirmed. Faint super-structure lines on the powder photographs of alloys containing Mn_3Si indicate that in this phase, as in Fe_3Si, some ordering of the silicon and metal atoms takes place at temperatures below 1 000°C. The reported crystal structures of Mn_5Si_3 and $FeSi_2$ have been confirmed and refined with single crystal data.

In connection with investigations on the Mn—Si—B and Fe—Si—B systems [1] some crystallographic studies of the binary phases MnB_2, Mn_3Si, Mn_5Si_3, and $FeSi_2$ were made. It was found appropriate to present the results (which are commented on in a recent review article [2]) in a separate paper.

EXPERIMENTAL

The alloys were prepared by arc-melting or sintering mixtures of the elements. The same chemicals were used as in the study [1] of the Mn—Si—B and Fe—Si—B systems, and the chemical analyses for silicon and boron were also carried out in the same way. Manganese was determined by the bismuthate method after the sample had been dissolved in HF + HNO_3, the hydrofluoric acid removed by evaporating with sulfuric acid, and the solution passed through a cadmium reductor. The accuracy of the manganese analyses is estimated to be ± 0.2 %.

Powder photographs were taken in cameras of the Guinier type with silicon (a = 5.4306 Å) as internal standard for the l.p. (lattice parameter) determinations. Single crystals of Mn_5Si_3 and $FeSi_2$ with cross-sections of about 0.02 mm were examined in a Weissenberg camera. The multiple film technique was used and the intensities were visually estimated. The atomic scattering factors were taken from the tables by Tomas and Umeda [3] (manganese, iron), Tomiie and Stam [4] (silicon) and Ibers [5] (boron). The final structure factors for Mn_5Si_3 were computed on the digital electronic computer BESK with a program devised by Åsbrink *et al.*[6] The scattering factors were approximated with the formula:

$$f_i = A_i \exp(-a_i/\lambda^2\sin^2\Theta) + B_i \exp(-b_i/\lambda^2\sin^2\Theta) + C_i \exp(-c_i/\lambda^2\sin^2\Theta) + D_i$$

On basis of the above mentioned structure factor tables, Appel [7] has calculated the following constants:

	A	B	C	a	b	c
Mn	8.630	9.427	6.744	0.345	3.724	26.541
Si	2.8315	6.8065	4.3870	0.3235	2.2965	51.770

The real part of the dispersion correction, (D_i in the above expression) for manganese was taken from the tables by Dauben and Templeton [8]. No corrections were made for extinction or absorption.

RESULTS

MnB_2. Arc-melted manganese-boron alloys with a boron content higher than 67 atom per cent gave a powder photograph that could be indexed with a small hexagonal cell. From the unit cell dimensions it was evident that the photograph originated from a phase isomorphous with AlB_2, and with this assumption excellent agreement between observed and calculated intensities was obtained (see Table 1). The l.p. of MnB_2, $a = 3.009$ Å, $c = 3.039$ Å, agree very well with those recently reported by Binder and Post [9] who found $a = 3.007$ Å and $c = 3.037$ Å. No variations greater than 0.05 % were observed for the l.p. of MnB_2 in alloys with compositions from $MnB_{1.7}$ to MnB_3, which indicates that the homogeneity range of MnB_2 is narrow. An alloy containing small amounts of Mn_3B_4 was analysed to contain 70.71 (± 0.15) % manganese and 28.12 (± 0.15) % boron most of the remainder very probably being oxygen. Thus, the atomic ratio B/Mn in this sample is 2.019/1.000, indicating that the composition of the manganese diboride is about $MnB_{2.05}$. However, if it is assumed that the oxygen present in the sample is bound to boron as B_2O_3, the composition of the manganese boride is found to correspond to the formula $MnB_{2.01}$, not significantly deviating from the stoichiometric formula $MnB_{2.00}$. Interatomic distances in MnB_2 are collected in Table 2.

Mn_3Si. The simple body-centered cubic structure of Mn_3Si was determined by Laves [10] who found the manganese and silicon atoms to be statistically distributed in the structure. The powder photographs of alloys sintered at 950°C and containing Mn_3Si and Mn_5Si_3 showed some faint lines the positions and intensities of which could be satisfactorily accounted for by assuming the atoms in Mn_3Si to be ordered. Thus, it seems very likely that, similar to the situation in Fe_3Si, the distribution of metal and silicon atoms in Mn_3Si becomes ordered at lower temperatures. The cube-edge of Mn_3Si as determined is this study is 5.722 Å (2 × 2.861) in reasonable agreement with the older values 2.85 Å[10] and 2.857 Å[11].

Mn_5Si_3. The approximate formula of Mn_5Si_3 was determined by Vogel and Bedarff [12] and was confirmed by Åmark *et al.*[11] who also solved the crystal

Table 1. Powder photograph (Cu$K\alpha$) of an arc-melted alloy with the nominal composition MnB_2.

hkl	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	I_{obs}	I_{calc}	$pF^2_{calc} \times 10^{-2}$
001	0.0646	0.0644	w	4.7	3.84
100	0.0876	0.0875	st	13.6	16.0
101	0.1519	0.1519	vst	24.1	45.4
002	0.2574	0.2574	vw	2.5	7.16
110	0.2625	0.2625	m	7.3	21.1
111	0.3270	0.3269	vw	4.3	13.4
102	0.3448	0.3449	w	5.9	17.5
200	0.3501	0.3501	vw	2.9	8.70
201	0.4145	0.4144	m	10.3	26.1

Table 2. Interatomic distances in MnB_2 (in Å).

Mn— 8Mn: 3.01(6), 3.04(2)	B—6Mn: 2.31(6)
—12B : 2.31(12)	—3B : 1.74(3)

structure of Mn_5Si_3. The chemical and X-ray analyses of two arc-melted alloys with compositions approximating to Mn_5Si_3 gave the following results

% Mn	% Si	Σ	atomic composition	observed phases	l.p. of Mn_5Si_3
76.61	22.15	98.76	$Mn_5Si_{2.83}$	Mn_5Si_3 and small amounts of Mn_3Si	$a = 6.910$ Å $c = 4.814$ Å
75.94	23.45	99.39	$Mn_5Si_{3.02}$	Mn_5Si_3 and traces (~ 1 %) of MnSi	$a = 6.910$ Å $c = 4.814$ Å

No l.p. variations could be observed for Mn_5Si_3, indicating that its homogeneity range is small. The results of the chemical analyses show that the composition closely corresponds to the stoichiometric formula.

The crystal structure of Mn_5Si_3 was refined from single crystal data. The space-group $P6_3/mcm$ derived by Åmark *et al.*[11] was confirmed and, starting with the atomic parameters given by these authors, the atomic parameters were refined from successive $\varrho_o(xz)$ and $\varrho_o(xz)$—$\varrho_c(xz)$ syntheses until the final back-shift corrections were less than half the standard deviation as estimated with Cruickshank's formula [18]. The final parameters are as follows:

4 Mn in 4(*d*)
6 Mn in 6(*g*) $x = 0.2358 \pm 0.0006$
6 Si in 6(*g*) $x = 0.5992 \pm 0.0015$

The final *R*-value for 51 observed *h*0*l*-reflexions was 8.0 % when an empirical isotropic temperature factor with $B = 0.34_0$ Å^2 had been applied. Observed and calculated structure factors are collected in Table 3 and interatomic distances are given in Table 4. In the last difference synthesis a negative region was observed at the silicon position, indicating that the scattering parameter of the atom in this position is slightly less (about 1 electron) than had been assumed. The experimental data, however, are hardly so accurate that this effect can be regarded as significant.

$FeSi_2$. Phragmén [14] has suggested a very simple structure for this phase, the homogeneity range of which does not include the stoichiometric composition. Phragmén's observations that $FeSi_2$ is tetragonal and that there is one formula unit in the elementary cell were corroborated. There are no systematic extinctions and thus the most symmetrical possible space-group is *P*4/*mmm*. During the refinement no evidence was found indicating that a space-group of lower symmetry should be chosen. The distribution of intensities showed that the structure proposed by Phragmén [13] was approximately correct and starting with his parameter for the silicon atom in 2(*h*) the $\varrho(xz)$ electron density projection was refined by successive F_o and F_o—F_c syntheses. The following atomic and scattering parameters were found for a crystal picked out of an alloy which contained $FeSi_2$ with the l.p. $a = 2.684$ and $c = 5.128$ Å.

	atomic par.	scattering par.
Fe(?) in 1(*a*)		24.0_5
2 Si in 2(*h*)	$z = 0.270_0$	14.0

Table 3. Observed and calculated structure factors for Mn_5Si_3. (A temperature factor with $B = 0.34_0$ Å^2 has been applied to the F_c-values.)

hkl	F_o	F_c	*hkl*	F_o	F_c
1 0 0		— 7.2	8 0 2	— 61.7	— 67.3
2 0 0	— 50.5	— 46.7	9 0 2		— 2.2
3 0 0	107.3	112.9	10 0 2	— 22.4	— 25.1
4 0 0	50.2	46.2	11 0 2		— 0.5
5 0 0	71.7	63.2	12 0 2		— 5.9
6 0 0	26.6	20.6	13 0 2	— 39.2	— 35.3
7 0 0		— 5.1	14 0 2		— 8.3
8 0 0	39.3	37.7	15 0 2		11.8
9 0 0	58.2	59.9	0 0 4	171.3	168.5
10 0 0		2.3	1 0 4		— 4.0
11 0 0	— 18.9	— 21.2	2 0 4	— 29.7	— 25.0
12 0 0	52.6	44.6	3 0 4	74.9	74.8
13 0 0	29.6	20.0	4 0 4	34.5	32.2
14 0 0		— 6.0	5 0 4	42.1	46.1
15 0 0	18.4	13.5	6 0 4		16.2
0 0 2	—107.1	— 93.4	7 0 4		— 5.1
1 0 2	— 80.2	— 67.7	8 0 4	29.9	30.4
2 0 2	— 32.8	— 28.8	9 0 4	51.8	50.7
3 0 2	22.5	21.3	10 0 4		0.0
4 0 2	— 95.8	— 94.1	11 0 4		— 18.4
5 0 2	— 94.7	—104.2	12 0 4	44.1	38.6
6 0 2	56.2	62.0	13 0 4		17.4
7 0 2	— 32.6	— 30.4	14 0 4		— 5.3
15 0 4		11.9	7 0 8		— 4.8
0 0 6	— 36.5	— 44.9	8 0 8	16.3	18.2
1 0 6	— 31.3	— 29.5	9 0 8	36.4	33.3
2 0 6	— 14.9	— 15.1	10 0 8		— 1.0
3 0 6		11.9	11 0 8		— 12.4
4 0 6	— 51.4	— 54.8	12 0 8	25.4	26.9
5 0 6	— 60.8	— 62.0	0 0 10		— 25.6
6 0 6	41.0	39.8	1 0 10	— 16.5	— 17.4
7 0 6	— 15.8	— 19.2	2 0 10		— 8.4
8 0 6	— 46.4	— 45.8	3 0 10		8.0
9 0 6		— 2.1	4 0 10	30.9	— 30.1
10 0 6	— 16.5	— 17.1	5 0 10	— 31.6	— 31.4
11 0 6		— 0.7	6 0 10	21.6	21.8
12 0 6		— 4.2	7 0 10		— 10.1
13 0 6	— 28.9	— 27.9	8 0 10	— 26.9	— 26.6
14 0 6		— 6.5	9 0 10		— 1.5
0 0 8	70.8	80.4	10 0 10		— 9.9
1 0 8		1.2	0 0 12	41.6	39.2
2 0 8		— 15.2	1 0 12		— 0.3
3 0 8	35.7	37.8	2 0 12		— 8.8
4 0 8		18.4	3 0 12		18.8
5 0 8		22.8	4 0 12		9.9
6 0 8		10.3	5 0 12		10.9

The final R-value for the 33 observed $h0l$-reflexions was 7.4 % after an empirical isotropic temperature factor with $B = 0.40_3$ Å^2 had been applied. Interatomic distances are collected in Table 5. The scattering parameter of the atom in 1(a) is (probably significantly) less than 26/14 of that of the atom in 2(h). This indicates that the former position is not completely occupied by

Table 4. Interatomic distances in Mn_5Si_3 (in Å).

			Average
Mn_I in 4(*d*)	— 2 Mn_I	: 2.41 (2)	
	— 6 Mn_{II}	: 2.96 (6)	2.82
	— 6 Si	: 2.43 (6)	
Mn_{II} in 6(*g*)	— 4 Mn_I	: 2.96 (4)	
	— 6 Mn_{II}	: 2.82 (2), 2.91 (4)	2.91
	— 5 Si	: 2.41 (2), 2.51, 2.66 (2)	2.53
Si in 6(*g*)	— 4 Mn_I	: 2.43 (4)	
	— 5 Mn_{II}	: 2.41 (2), 2.51, 2.66 (2)	2.49
	— 2 Si	: 2.77 (2)	

Table 5. Interatomic distances in $FeSi_2$ (in Å).

Fe — 4Fe:	2.68 (4)	Si — 4Fe:	2.35 (4)
— 8Si:	2.35 (8)	— 6Si:	2.36, 2.68(4), 2.77

iron atoms which is consistent with the observation that the iron content of $FeSi_2$ does not attain 33 atom per cent. Siborenko, *et al.*[15] have shovn that the deviation from stoichiometry is very likely associated with a fraction of the iron positions being vacant.

Acknowledgements. I want to express my gratitude to Professor Hägg for his kind interest in this work and for the facilities he has put at my disposal. The chemical analyses were carried out at the analytical department of this Institute and I wish to thank the Head of this department, Dr. F. Nydahl, as well as Dr. L. Gustafsson.

I sincerely acknowledge financial support from the *Air Force Office of Scientific Research and the Research and Development Command, United States Air Force* through its European Office under Contract No. AF 61(052)—40 and from the *Swedish State Council of Technical Research.* Facilities for use of the electronic digital computer BESK were given by the *Swedish Board for Computing Machinery.*

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Received July 1, 1960.