The Crystal Structure of CrB$_4$

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The crystal structure of CrB$_4$, previously denoted CrB$_6$, has been determined, the intensities being measured with a powder diffractometer. The symmetry is orthorhombic, space group *Immm*, with

$$a = 4.744 \text{ Å}, \quad b = 5.477 \text{ Å}, \quad c = 2.866 \text{ Å}$$

The unit cell contains two chromium atoms in position 2(a) and eight boron atoms in 8(n).

The boron atoms form a three-dimensional network, intersected by channels along the c-direction. The chromium atoms are situated in these channels.

The existence of a phase in the Cr—B system corresponding to the composition CrB$_6$ was reported by Epel'baum *et al.* in 1960,[1] and according to their work this was the only intermediate phase in the system between CrB$_2$ and pure boron.

An investigation was started somewhat later at this Institute in order to obtain more information about boron-rich chromium borides. The present paper reports X-ray powder data and results from a structure determination of a chromium boride of composition CrB$_4$. This phase is most probably the same as that earlier reported.

PREPARATION, X-RAY WORK AND NUMERICAL COMPUTATIONS

Samples with the initial compositions CrB$_{4.0}$, CrB$_{5.8}$, CrB$_{12.0}$, and CrB$_{30.0}$ were prepared by arc-melting pieces of electrolytic chromium (from Gesellschaft für Elektrometallurgie m.b.H., Werk Nuremberg, purity 99.97 %, as analyzed at the Department of Analytical Chemistry, Uppsala University) and crystalline boron (from Borax Consolidated, Ltd., claimed purity 99.8 %) on a water-cooled copper hearth under a purified argon atmosphere. The samples were then heat-treated in a high vacuum resistance furnace in crucibles of CrB$_2$ at temperatures between 1350°C and 1400°C for one week (sometimes for up to three weeks) and at 1600°C for three days at a pressure of 2×10^{-6} mm Hg. Single crystals of CrB$_4$ suitable for X-ray work were not obtained.

The reaction products were examined in Guinier-Hägg focussing cameras with strictly monochromatic CrKα_1 or CuKα_1 radiation. An aluminium foil was used to reduce the fluorescence radiation in the latter case. Unit cell dimensions were measured using

silicon ($a = 5.43054$ Å) as internal calibration standard and the accuracy of the measurements was estimated to be better than ± 0.04 %.

The intensities of the reflexions were recorded using a Philips Powder Diffractometer PW 1050. The intensities were measured up to $2\theta = 161°$, using Cu$K\alpha$ radiation with a single crystal lithium fluoride monochromator [reflecting planes (200)] between the specimen and the counter, and alternatively, using Cr$K\alpha$ radiation up to $2\theta = 126°$, hence increasing the resolution at low diffraction angles. Special care was taken in charging the specimen holder to avoid orientation effects. Measurements on rotating and fixed specimen gave no significant differences in the intensities. When using chromium radiation each reflexion was measured twice.

The sample, used for the intensity measurements, had the initial composition CrB$_{5.8}$ and contained small amounts of "boron". No chemical analysis was undertaken.

Numerical computations were made on a CD 3600 computer employing programs as follows (all programs are 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.

Atomic scattering factors were interpolated from Table 3.3.1A in Ref. 2 and the real part of the dispersion correction was taken from Cromer.[3]

RESULTS

The X-ray investigation of the annealed samples showed the following two-phase equilibria. The sample with an initial composition CrB$_{4.0}$ contained CrB$_2$+CrB$_4$ after annealing at 1350°C—1400°C. The other specimens contained CrB$_4$ and a boron-rich phase. The sample used for the structure determination was of nominal composition CrB$_{5.8}$. However, allowing for an observed weight loss of 2.5 % during melting and the difficulty of estimating the amount of the weakly scattering boron-rich phase also present, the phase-analytical evidence for the composition CrB$_4$ of the phase investigated was considered as satisfactory. The boron-rich phase ("boron") shows a diffraction pattern similar to that of β-rhombohedral boron but contains measurable amounts of chromium (2—4 at.-% as indicated by micro-probe analysis). A further investigation of this phase is now being undertaken at this Institute. When heated at 1600°C all specimens gave CrB$_2$+"boron".

Table 1. Powder diffraction data for CrB$_4$. Observed intensities were measured with CuKα radiation ($\lambda=1.54178$ Å). Sin$^2\theta$-values refer to CuKα_1 radiation ($\lambda=1.54051$ 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[a]	4616	4614	7168	7272	33.40	33.69
0 2 0[a]	7918	7910	1040	1387	25.30	29.22
0 1 1[a]	9203	9201	1362	1490	23.25	24.34
1 0 1[a]	9857	9859	6124	5785	46.80	45.48
2 0 0[a]	10547	10544	424	575	20.15	23.45
1 2 1[a]	17764	17770	2094	1974	29.23	28.35
2 2 0[a]	18454	18455	1473	1468	34.18	34.16
2 1 1[a]	19741	19745	3260	2981	36.95	35.31
1 3 0[a]	20433	20435	1079	1575	30.29	36.61
0 3 1[a]	25023	25022	1634	1893	38.55	41.50
3 1 0[a]	25705	25702	1200	1295	33.84	35.10
0 0 2[a]	28893	28894	886	868	39.86	39.44
3 0 1[a,b]	30948	30948	—	89	—	12.02
0 4 0[a]	31639	31642	110	91	16.56	15.25
1 1 2[a]	33504	33507	970	942	21.56	21.24
2 3 1[a]	35560	35566	539	572	16.31	16.76
0 2 2	36801	36804	430	435	19.11	19.23
3 2 1	38855	38858	1645	1729	27.07	27.75
2 0 2	39444	39438	279	280	15.85	15.89
1 4 1[b]	41505	41501	847	735	—	18.59
3 3 0[b]		41523		128	—	10.96
4 0 0[b]	42180	42178	921	186	—	18.79
2 4 0[b]		42186		808	—	27.74
2 2 2	47347	47348	1414	1100	26.99	23.81
1 3 2	49337	49328	1141	1282	24.53	26.00
4 2 0	—	50088	406	458	20.77	22.05
4 1 1	—	51379	1004	942	23.23	22.50
1 5 0	—	52076	232	359	15.85	19.69
3 1 2	—	54596	1487	1246	28.59	26.17
0 5 1	—	56663	258	294	16.93	18.07
0 4 2	—	60535	182	111	14.26	11.12
3 4 1	—	62590	976	1257	23.30	26.45
0 1 3[b]	—	66989		139	—	12.31
4 3 1[b]	—	67199		416	—	15.05
2 5 1[b]	—	67208	2522	662	—	18.99
1 0 3[b]	—	67647		476	—	22.74
5 1 0[b]	—	67880		179	—	13.91
3 3 2[b]	—	70417		120	—	7.96
4 0 2[b]	—	71072		201	—	14.55
2 4 2[b]	—	71080	1679	924	—	22.04
0 6 0[b]	—	71193		339	—	26.70
5 0 1[b]	—	73126		586	—	24.51
3 5 0[b]	—	73165	1287	345	—	18.81
4 4 0[b]	—	73819		377	—	19.58
1·2 3	—	75558	667	487	18.16	15.52
2 1 3[b]	—	77533	—	853	—	20.18
4 2 2	—	78982	457	688	14.55	17.86
1 5 2[b]	—	80970		576	—	15.97
5 2 1[b]	—	81036		450	—	14.11
1 6 1[b]	—	81053	1636	949	—	20.48
2 6 0[b]	—	81738		151	—	11.47
0 3 3[b]	—	82810	1318	779	—	25.65
5 3 0[b]	—	83701		635	—	22.86
3 0 3[c]	—	88736	—	68	—	6.82
2 3 3[c]	—	93354	—	417	—	10.40
6 0 0[c]	—	94899	—	631	—	23.86
3 2 3[b]	—	96647	2376	1886	—	18.45
5 1 2[b]	—	96774		783	—	11.76

[a] I_o and I_c refer to CrKα radiation but F_o and F_c to CuKα radiation (see text under RESULTS).
[b] Not used in the refinement. [c] Not observed.

The powder pattern of CrB_4 could not be indexed in terms of the tetragonal unit cell given by Epel'baum et al.[1] with sufficient agreement between observed and calculated theta values but it could be very well accounted for in terms of an orthorhombic cell with $a=4.7441$ Å, $b=5.4773$ Å, and $c=2.8659$ Å (for values of $\sin^2\theta_{obs}$ and $\sin^2\theta_{calc}$ see Table 1). This symmetry and unit cell is also supported by electron diffraction data from crystals of approximate size 10^{-4} cm. No significant changes in the cell dimensions were observed. A few reflexions, for instance (200) and (120), overlap as a consequence of the axial ratio $a{:}b$ being nearly $\sqrt{3}{:}2$. Allowing for this limitation, reflexions with $h+k+l=2n+1$ were not observed, which indicated a body centered unit cell.

The following facts suggest that CrB_4 is the same phase as that reported by Epel'baum et al.[1]

1. There is very good agreement between the intensities and d-values reported in the present and in the earlier investigation.

2. CrB_4 is stable up to a temperature between 1400°C and 1600°C while "CrB_6" formed at 1300°C but not at 1900°C. Thus the stability region is roughly the same in both investigations.

3. Both investigations indicate that the phase forms equilibrium with CrB_2 as well as "boron" at low temperature. The discrepancy between the compositions reported is small considering the uncertainty of the phase-analytical method used by Epel'baum et al.[1]

After correcting the intensities for Lorentz-polarization and multiplicity factors, it was observed that the ratio $F_o(hk0)/F_o(hk2)$ was constant within the experimental errors. This observation and the fact that the c-axis was only 2.866 Å strongly indicates that all atoms are situated in two planes parallel to (001) and spaced $c/2$ apart. The two Patterson sections $P(uv0)$ and $P(uv\frac{1}{2})$ were calculated using the copper data only. Two computations of each section were made. In one calculation the overlap reflexions (see above) were given indices according to the condition of body centering, in the other these reflexions were excluded. In spite of marked series termination errors the two calculations were very similar and it was concluded that the unit cell is body centered. Three space groups were possible: $Immm$, $Imm2$ and $I222$ ($I2_12_12_1$ could be eliminated through space considerations and incompatibility with the Patterson function). It was found possible to interpret the Patterson function in terms of a cell content of two chromium atoms and eight boron atoms. Assuming the space group $Immm$ the atomic positions occupied should be $8(n)$ for boron and $2(a)$ for chromium while $Imm2$ would require $8(e)$ and $2(a)$ and $I222$ would require $8(k)$ and $2(a)$.

Observed structure factors for 29 resolved reflexions were used to refine atomic parameters and isotropic individual temperature factors by the least squares method, assuming the space group with the highest symmetry, $Immm$. Among the F_o values used in the refinement fifteen were measured with chromium radiation because of better resolution and smaller orientation effects. Since the dispersion correction for chromium radiation is very much larger than that for copper radiation and since the least squares program used could not incorporate different atomic scattering factor values for different reflexions, the chromium data ($F_{o,CrK\alpha}$) were transferred to copper data ($F_{o,CuK\alpha}$) by an iterative application of the formula:

$$F_{o,\mathrm{Cu}K\alpha} = F_{o,\mathrm{Cr}K\alpha} \times F_{c,\mathrm{Cu}K\alpha}/F_{c,\mathrm{Cr}K\alpha}$$

Initially F_c values, calculated from the preliminary atomic parameters, were used and this procedure was repeated until the changes in the $F_{o,\mathrm{Cu}K\alpha}$ values of the fifteen reflexions were negligible.

The least squares program used minimizes the function $\sum w \cdot (|F_c| - |F_o|)^2$. The weighting factor, w, was put equal to $1/\sigma_F^2$ for the F_o values, calculated from chromium data, and put equal to $1/3\sigma_F^2$ for the rest. The standard deviations of the structure factors were calculated using a formula given by Evans [4] for single crystal data, modified by including the multiplicity factors. The full-matrix refinement of two scale factors together with atomic and thermal parameters converged rapidly and after the last cycle the shifts were less than 0.5 % of the calculated standard deviations. The final R value, defined as $\sum ||F_o| - |F_c||/\sum |F_o|$, was 0.071.

Difference Fourier sections were finally calculated for $z=0$ and $z=\frac{1}{2}$. The largest maxima (or minima) in these maps were less than 15 % of the boron peaks in the final electron density map. At the position $2(b)$, of interest in connection with the subsequent discussion, the deviation from zero in the difference maps was less than 8 % of the boron maxima in the electron density synthesis.

Refinements assuming the space groups $Imm2$ and $I222$ gave shifts in the atomic positions which were less than the calculated standard deviations. Thus the structure appears to be described satisfactorily with $Immm$ symmetry.

Final structure data for CrB₄ were obtained as follows:

Space group $Immm$ $Z=2$;

a =	4.7441 Å	σ =	0.0003 Å
b =	5.4773 Å	σ =	0.0003 Å
c =	2.8659 Å	σ =	0.0001 Å
V =	74.47 Å³		

	x	$\sigma(x)$	y	$\sigma(y)$	B (Å²)	$\sigma(B)$ (Å²)
2 Cr in 2(a)					0.18	0.31
8 B in 8(n)	0.1751	0.0037	0.3455	0.0040	0.51	0.65

The good agreement between observed and calculated structure factors for resolved reflexions as well as between observed intensities and the corresponding sum of calculated intensities for overlapping reflexions (see Table 1) is taken as proof that the structure determination is correct. It is, however, somewhat difficult to estimate the accuracy of the results. It must be remembered that the standard deviations obtained are based on a moderate number of reflexions only.

X-Ray powder data for CrB₄ are given in Table 1 and interatomic distances are listed in Table 2.

DISCUSSION

The crystal structure of CrB₄ is shown in projection along the c-axis in Fig. 1. The boron atoms form a three-dimensional network, intersected by

Table 2. Interatomic distances and their standard deviations (Å units) in CrB_4. Distances shorter than 3.0 Å are listed.

	Dist.	S.d.
Cr — 4B	2.067	0.021
— 8B	2.268	0.014
— 2Cr	2.866	0.000
B — B	1.662	0.035
— B	1.693	0.044
— 2B	1.911	0.027
— Cr	2.067	0.021
— 2Cr	2.268	0.014
— B	2.372	0.040
— 2B	2.866	0.000
— 4B	2.962	0.016

channels along the [001] direction through 0,0,0 and 1/2,1/2,0. The chromium atoms are situated in these channels.

The boron network may be described as follows. Within planes parallel to (001), the boron atoms are linked into groups of four in a rectangular, nearly square, arrangement. The two edges of the rectangles are not significantly different in length, the average being 1.68 Å. Successive planes of boron squares are connected through boron-boron contacts of 1.91 Å, forming zig-zag chains running in the c-direction. In addition to the four boron neighbours each boron atom also coordinates three chromium atoms, two at a distance of 2.27 Å and one at 2.07 Å.

Each chromium atom is surrounded by an irregular polyhedron, consisting of twelve boron and two chromium atoms.

The tetrahedral radius of boron [5] is 0.88 Å and the Goldschmidt radius for 12-coordination of Cr is 1.28 Å. Using these values the expected boron-boron distance is 1.76 Å while a chromium-boron distance ought to be 2.16 Å. Consequently the B—B distance of the zig-zag chain is larger than the radius sum while the B—B distances in the plane perpendicular to the direction of the c-axis are possibly somewhat smaller than the radius sum. The average
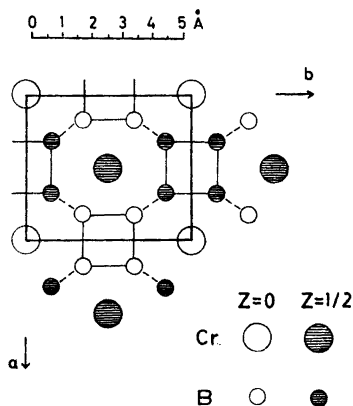

Fig. 1. The crystal structure of CrB_4 as viewed along the c-axis.

chromium-boron distance is close to the radius sum. The Cr—Cr distance in the [001] direction is 2.87 Å, which exceeds the radius sum by 0.3 Å and indicates a rather weak interaction. The distance between chromium atoms in adjacent channels is large (3.90 Å).

An interesting and characteristic feature of the CrB_4 structure is the existence of voids in the position 2(b) (coordinates 0,1/2,1/2 and 1/2,0,0). An atom in this position would be surrounded by eight boron neighbours at a distance of 1.86 Å, these neighbours being situated at the corners of a distorted cube elongated in the c-direction. Thus the size of this void is sufficient to contain atoms with radii less than 1.0 Å without seriously distorting the lattice. However, the present investigation gives no support for the occurrence of boron in position 2(b), since the final difference synthesis showed no appreciable electron density in this position. Furthermore no variations of the cell dimensions with composition were observed. It should also be noted that a boron atom in the 2(b) position would coordinate as many as eight close boron neighbours, but such a high coordination has never been observed in the structures of other borides with similar compositions. In the UB_4 type structure the boron atoms coordinate three or five other boron atoms and in the CaB_6 type structure five other boron atoms. Also in the less boron rich "W_2B_5" type structure the proposed existence of six boron neighbours to each boron atom in the puckered layers has not been experimentally confirmed. In fact, a recent investigation has shown that these boron layers are defect [6] and the coordination number hardly exceeds three.

In many cases borides and silicides crystallize with the same structure type.[7] Several examples are found among the monosilicides and monoborides as well as among the disilicides and diborides. In this respect it is interesting to observe a relationship between the structure of CrB_4 and that of $ThSi_2$. In both structures the non-metal atoms are connected in a three-dimensional network. However, in $ThSi_2$ there are three close non-metal atoms to each non-metal atom while in CrB_4 there are four.

A phase of the composition MnB_4 was reported by Fruchart and Michel in 1960.[8] The published powder pattern of this phase is very similar to that of CrB_4. A closer investigation of MnB_4 is now being undertaken at this Institute.

REFERENCES

1. Epel'baum, V. A., Sevast'yanov, N. G., Gurevich, M. A. and Zhdanov, G. S. *J. Struct. Chem. (USSR) (Eng. Transl.)* **1** (1960) 55.
2. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
3. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
4. Evans, Jr., H. T. *Acta Cryst.* **14** (1961) 689.

5. Pauling, L. *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York 1960.
6. Lundström, T. *Arkiv Kemi* **30** (1968) 115.
7. Aronsson, B., Lundström, T. and Rundqvist, S. *Borides, Silicides and Phosphides*, Methuen, London 1965.
8. Fruchart, R. and Michel, A. *Compt. Rend.* **251** (1960) 2953.