

## The Solubility of Chromium in $\beta$ -Rhombohedral Boron as Determined in $\text{CrB}_{\sim 41}$ by Single-Crystal Diffractometry†

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The structure of a crystal with the composition  $\text{CrB}_{\sim 41}$  has been investigated using single-crystal diffractometry. The composition represents the maximum solubility of chromium in  $\beta$ -rhombohedral boron. The space group is  $R\bar{3}m$  and the hexagonal axes are  $a = 10.964 \text{ \AA}$  and  $c = 23.848 \text{ \AA}$ . The three-dimensional boron network is essentially equivalent to that in  $\beta$ -rhombohedral boron. The chromium atoms occupy two crystallographic positions, both of which are only partially occupied. The two chromium atoms coordinate twelve and fourteen boron atoms respectively. The result of an investigation of holes in the  $\beta$ -rhombohedral structure is reported. There are at least eight crystallographic positions, which represent holes of sufficient size to accommodate boron or metal atoms in the structure.

During an investigation of the boron-rich range of the Cr-B system (1) the present authors observed that strikingly well-crystallized single crystals were easily obtained by arc-melting very boron-rich samples. These crystals were much more perfect than those obtained from a pure boron melt. It appeared interesting to investigate in detail the crystal structure of this phase in order to clarify whether it represents a solid solution of chromium in  $\beta$ -rhombohedral boron or if it is an entirely new structure type. The former alternative proved to be the correct one, and the study has thus provided knowledge of the exact positions of the chromium atoms in the  $\beta$ -boron structure.

In the meantime similar solid solutions were discovered for manganese (2) and for the remaining  $3d$  transition metals (3). A particularly large increase in the unit cell was observed for scandium and manganese. The influence of the  $3d$  elements on the microhardness of  $\beta$ -boron crystals was also investigated (3).

### Experiments

Samples with the initial compositions  $\text{CrB}_{9.0}$ ,  $\text{CrB}_{30.0}$  and  $\text{CrB}_{100.0}$  were prepared by arc-melting electrolytic chromium (from Gesellschaft für Elektrometallurgie m.b.H., Werk Nuremberg; 99.97%

Cr as analyzed at the Department of Analytical Chemistry, University of Uppsala) and crystalline boron (from Borax Consolidated, claimed purity 99.8%) using an atmosphere of purified argon.

Cell dimensions of powders were determined with Guinier-Hägg cameras using pure  $\text{CrK}_{\alpha_1}$  radiation ( $\lambda = 2.28962 \text{ \AA}$ ) and zone-refined silicon ( $a = 5.43054 \text{ \AA}$ ) as internal calibration standard. The cell dimensions of the single crystal, used for the collection of the intensity data, were obtained from the measurements of the  $2\theta$  angles of 44 reflexions on a manual General Electric single-crystal orienter, using  $\text{CuK}_{\alpha_1}$  radiation ( $\lambda = 1.54051 \text{ \AA}$ ) according to a procedure described elsewhere (4). The zero-point correction of the  $2\theta$  scale was determined using a basic beryllium acetate crystal. All cell dimensions were refined with the least-squares program CELSIUS (the reader will find the names of the authors and a brief characterization of the programs in Ref. (2)).

The intensities were measured with a General Electric four-circle automatic diffractometer using nickel filtered  $\text{CuK}_{\alpha}$  radiation and a scintillation detector with pulse height discrimination. The moving crystal-moving counter technique was used. The background was measured at each side of the scanning interval, which was monotonically increased with  $2\theta$  according to

$$2\theta_1 - 2\theta_2 = 1.5 + (0.5) \text{tg } \theta.$$

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The stability of the X-ray generator and counter circuitry was checked by examining a standard reflexion after every fiftieth reflexion measured. The calculation of the setting angles was made on the Uppsala CD 3600 Computer with the program GIP (5). The output data were transferred from tape to punched cards with the program GONDATA (5).

Crystals from the sample of the nominal composition  $\text{CrB}_{9.0}$  were preliminarily investigated by oscillation and Weissenberg techniques. Invariably they displayed a monoclinic symmetry and, consequently, the reflexions within one quarter of the reciprocal space were measured on the diffractometer (1483 independent reflexions with  $2\theta$  less than  $130^\circ$ ). The crystal chosen for these measurements had a triangular prismatic shape with base  $40 \times 40 \times 60 \mu\text{m}$ , and height, along  $\phi$  axis,  $100 \mu\text{m}$ . The calculated linear absorption coefficient was  $73 \text{ cm}^{-1}$  for copper radiation. No absorption correction was thus considered necessary.

One of the crystals, giving a Weissenberg photograph identical to that of the "diffractometer" crystal, was analyzed with an electron probe micro-analyzer, using a pure chromium standard and 15 kV accelerating voltage. Measurements on twelve points of the crystal surface gave very good agreement between the values. The chromium content obtained was 11.9 wt% (2.7 at. %), corrected for absorption according to the procedure described by Philibert (6). The atomic number effect is estimated to change this value by less than 0.3 percentage units.

### Phase Analysis and Crystal Data

The samples  $\text{CrB}_{9.0}$  and  $\text{CrB}_{30.0}$  were two-phase specimens, containing  $\text{CrB}_2$  and a phase closely related to  $\beta$ -rhombohedral boron. The latter phase is here denoted  $\text{CrB}_{\sim 41}$ , which is the composition obtained from the crystal structure refinement to be described below. Since the crystal was picked from a two-phase specimen, its composition represents the maximum solid solubility of chromium in  $\beta$ -rhombohedral boron. Initially the unit cell was described by us as monoclinic belonging to the space group  $C2/m$ ,  $C2$  or  $Cm$  and with the cell dimensions  $a = 17.11 \text{ \AA}$ ,  $b = 10.96 \text{ \AA}$ ,  $c = 14.95 \text{ \AA}$ , and  $\beta = 143.83^\circ$ . The intensity measurements, however, showed that the symmetry is rhombohedral with space group  $R\bar{3}m$  (No 166). The hexagonal unit cell of the single crystal is given in Table I, which also contains further cell dimensions measured with powder techniques. The standard deviations given in Table I are very small and the accuracy may be lower than indicated by these values by influence

TABLE I  
UNIT-CELL DIMENSIONS OF  $\text{CrB}_{\sim 41}$ ,  $\text{CrB}_{\sim 100}$  AND  
PURE BORON ( $\text{\AA}$  UNITS)<sup>a</sup>

	<i>a</i>	<i>c</i>
$\text{CrB}_{\sim 41}$ (powder)	10.9666(3)	23.8514(8)
$\text{CrB}_{\sim 41}$ (single crystal)	10.9637(2)	23.8477(4)
$\text{CrB}_{\sim 100}$ (powder)	10.9528(6)	23.8330(14)
Boron (arc melted, powder)	10.9253(5)	23.8103(16)
Boron (not melted, powder)	10.9265(3)	23.8164(13)

<sup>a</sup> Standard deviations are given in parenthesis and refer to the last decimal place of the respective values.

from systematic errors. However, the accuracy is estimated to be higher than 0.04% in all cases. Thus, the cell dimensions of the single crystal do not necessarily deviate significantly from those of the  $\text{CrB}_{\sim 41}$  powder, while the increase in the size of the unit cell in passing from pure boron via  $\text{CrB}_{\sim 100}$  (as measured in a single-phase sample) to  $\text{CrB}_{\sim 41}$  undoubtedly is significant.

The X-ray powder data for  $\text{CrB}_{\sim 41}$  are given in Table II. The intensities display significant changes as compared to those of pure  $\beta$ -boron.

### Structure Determination and Refinement

The intensities were corrected for the Lorentz and polarization effects, using the program DATAP 2 (7), and a Patterson synthesis was calculated using the Fourier summation program DRF (2). At this point Prof. R. E. Hughes of Cornell University became aware of our work in Uppsala. He kindly put at our disposal at that time unpublished atomic coordinates from the structure determination of  $\beta$ -rhombohedral boron (8), which much facilitated our further work. These coordinates were transformed to the space group  $C2/m$  and a three-dimensional  $F_0$  synthesis was calculated. From this synthesis positional and occupational parameters for the chromium atoms were obtained.

The structure was refined with the program LALS (2) and the function minimized was

$$\sum w(|F_o| - |F_c|)^2.$$

The atomic scattering factors were taken from "International Tables for X-Ray Crystallography" (9) and were corrected for the real part of the anomalous dispersion as calculated by Cromer (10).

After a few refinement cycles it was obvious that no deviations from trigonal symmetry occur.

TABLE II  
X-RAY POWDER DATA FOR  $\text{CrB}_{\sim 41}$  UP TO  $\sin^2 \theta = 0.50$ — $\text{CrK}_{\alpha_1}$  RADIATION ( $\lambda = 2.28962 \text{ \AA}$ )

$h k l$	$\sin^2 \theta_o$	$\sin^2 \theta_c$	$I_o$	$h k l$	$\sin^2 \theta_o$	$\sin^2 \theta_c$	$I_o$
0 1 2	$2371 \times 10^{-5}$	$2375 \times 10^{-5}$	<i>m</i>	0 4 2	$24172 \times 10^{-5}$	$24169 \times 10^{-5}$	<i>m</i>
1 1 0	4355	4359	<i>m</i>	1 2 8	24912	24915	<i>w</i>
1 0 4	5136	5139	<i>st</i>	4 0 4	26926	26934	<i>m</i>
0 2 1	6045	6042	<i>m</i>	0 2 10	28846	28850	<i>vw</i>
1 1 3	6431	6432	<i>vw</i>	0 1 11	29332	29329	<i>w</i>
2 0 2	6731	6734	<i>w</i>	4 1 0	30499	30513	<i>vw</i>
0 1 5	7212	7212	<i>w</i>	3 2 4	31294	31293	<i>w</i>
0 0 6	8298	8294	<i>m</i>	3 0 9}	31734	31737	<i>w</i>
0 2 4	9502	9498	<i>vw</i>	0 3 9}			
2 1 1	10402	10401	<i>st</i>	4 1 3}	32587	32586	<i>w</i>
1 2 2	11089	11093	<i>vw</i>	1 4 3}			
1 1 6	12646	12653	<i>vw</i>	4 1 6}	38811	38806	<i>vw</i>
3 0 3}	15153	15150	<i>m</i>	1 4 6}			
0 3 3}							
1 2 5	15929	15930	<i>m</i>	3 3 0	39237	39231	<i>w</i>
0 2 7	17095	17100	<i>m</i>	2 4 1	40916	40914	<i>vw</i>
0 0 9	18661	18661	<i>w</i>	3 3 3	41308	41304	<i>w</i>
1 3 1	19119	19119	<i>w</i>	1 3 10	41923	41927	<i>vw</i>
2 0 8	20550	20556	<i>vw</i>	5 0 5	42089	42084	<i>w</i>
3 0 6}	21374	21371	<i>m</i>	2 3 8	42353	42351	<i>m</i>
0 3 6}				2 4 4	44373	44370	<i>vw</i>
1 3 4	22574	22575	<i>m</i>	0 2 13	44741	44746	<i>w</i>
1 1 9	23024	23020	<i>w</i>	4 0 10	46286	46286	<i>w</i>
4 0 1	23471	23478	<i>w</i>	3 1 11	46772	46765	<i>w</i>

Accordingly, the atomic coordinates and indices were transformed from the monoclinic space group  $C2/m$  to the rhombohedral  $R\bar{3}m$ , using hexagonal axes. The matrix used for the monoclinic to hexagonal transformation of indices was

$$\frac{1}{2} \begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

This procedure reduced the 1483 independent reflexions to 553 independent hexagonal reflexions. For further refinement average structure factors were used except for the weakest structure factors, which were calculated from the averaged intensities to avoid unnecessary errors.

No cutting procedure was applied for the weak reflexions. However, the 12 weakest structure factors were given the standard value 2.6, which is one-third of the observed structure factor for reflexions with  $F_o \approx 3\sigma$ .

Using this reduced structure factor material the atomic coordinates, isotropic temperature factors, and one scale factor were refined with LALS (2). Refinements of the scale factor, temperature factors and occupational parameters of the atoms B(13),

Cr(1) and Cr(2) were performed with the program ORFLS (11). The final  $R$  index, defined as

$$\frac{\sum | |F_o| - |F_c| |}{\sum |F_o|}$$

was 4.7%, including all 553 reflexions. All shifts in the parameters were at this stage less than 5% of the estimated standard deviations. Since the weight analysis for weights based on counter statistics was less satisfactory, it was decided to use the empirical weighting scheme

$$w = \frac{1}{(a + |F_o| + c|F_o|^2)}$$

The constants found to give the best weighting analysis were  $a = 270$  and  $c = 0.008$ .

The observed and calculated structure factors are listed in Table III. Atomic and thermal parameters, including estimated standard deviations and fractional occupations of atomic positions, are presented in Table IV. Hoard et al. (8) reported a sixteenth boron atom at 18( $h$ ) with  $x = 0.0546$  and  $z = 0.1166$ . A refinement of the present material

TABLE III  
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  $\text{CrB}_{41}$ 

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>						
3	0	0	66.4	66.0	3	2	2	55.8	47.8	4	2	8	52.1	52.3	7	4	12	41.2	40.5	1	5	17	18.9	18.8	
0	0	0	41.1	41.9	6	6	9	29.0	26.1	4	2	8	46.6	45.4	5	5	12	47.4	48.4	4	5	17	37.6	38.9	
9	0	0	39.5	38.3	9	2	3	22.1	19.1	2	2	3	201.5	200.9	5	5	12	2.6	2.8	2	6	17	7.9	0.9	
6	9	1	119.0	118.4	1	4	4	159.0	156.9	8	8	8	37.3	34.4	3	6	12	66.6	69.0	0	7	17	22.3	22.4	
1	1	1	65.8	67.1	4	3	4	82.9	82.5	2	3	8	14.7	13.5	6	6	12	106.6	109.0	0	7	17	6.3	2.6	
4	7	1	39.8	37.6	7	3	4	40.5	41.2	0	0	3	34.9	39.2	1	7	12	66.9	69.4	0	0	18	5.0	4.5	
10	2	2	52.0	53.0	2	2	4	75.9	73.7	3	4	8	175.1	181.4	4	7	12	25.7	25.3	3	0	18	49.2	52.8	
0	0	0	9.7	4.4	5	4	4	50.1	46.0	6	4	8	61.4	59.0	2	8	12	92.4	92.2	6	0	18	102.3	101.8	
3	8	3	14.6	11.4	8	0	4	54.1	55.6	1	4	5	11.7	10.5	0	9	12	53.1	55.1	1	1	18	44.5	47.2	
3	2	0	172.5	174.7	9	4	4	78.3	78.3	4	1	5	53.7	53.3	1	0	13	64.9	64.4	4	1	18	67.1	67.7	
3	6	3	37.8	36.2	4	5	4	99.5	90.5	8	8	8	61.0	58.1	4	7	0	136.3	200.6	7	7	18	15.2	15.2	
3	6	3	33.6	30.9	1	6	4	20.2	19.5	7	5	6	30.7	26.7	2	2	1	13	9.4	8.6	5	2	18	21.0	15.0
4	5	0	166.6	173.4	4	6	4	10.1	6.2	3	7	8	51.6	53.1	5	1	13	43.5	42.1	0	3	18	73.4	76.6	
5	4	0	137.4	139.7	2	7	4	87.6	86.8	0	7	8	46.6	46.7	8	0	13	37.7	33.0	3	3	18	15.1	15.3	
5	6	0	218.9	229.3	0	0	8	75.3	76.5	0	7	8	85.2	86.9	0	2	13	154.0	151.2	6	3	18	22.0	22.4	
1	4	4	41.1	41.8	4	4	4	10.2	7.4	4	8	8	9.9	9.4	6	2	13	11.1	6.6	1	4	18	19.6	20.0	
4	7	0	52.2	41.0	1	9	4	64.9	66.7	0	9	8	64.9	65.1	4	3	13	20.4	4.4	4	4	18	65.6	63.0	
10	0	0	29.6	28.3	11	4	4	80.4	76.3	0	10	0	112.5	106.8	1	3	13	12.5	10.2	2	5	18	87.7	88.7	
0	0	1	89.5	88.3	2	2	0	16.4	8.6	2	0	0	65.7	58.1	4	3	13	23.5	24.9	0	6	18	28.6	27.6	
0	0	1	146.6	142.9	10	0	0	58.1	57.5	3	6	0	94.3	97.1	2	2	4	13	28.2	25.6	3	6	18	48.0	47.1
0	0	1	8.0	8.1	8	0	1	126.1	120.7	9	0	1	65.7	58.1	5	5	13	30.5	31.3	1	0	19	97.6	102.7	
2	2	1	49.0	44.0	3	3	1	12.6	10.9	1	1	9	48.0	40.1	3	5	13	43.4	39.2	4	4	0	76.9	75.3	
3	6	3	24.9	23.1	3	6	1	110.8	114.6	1	1	9	12.6	6.9	6	5	13	64.4	61.6	7	7	0	99.7	98.1	
3	6	3	15.3	13.0	9	1	2	35.8	35.5	10	1	9	12.6	6.9	6	5	13	2.8	2.9	2	1	19	36.4	35.7	
3	6	3	37.4	29.6	1	7	2	89.0	85.0	7	1	9	80.0	79.8	4	6	13	22.5	21.4	5	1	19	64.0	63.8	
4	4	4	74.7	73.6	4	7	2	74.2	72.9	2	2	2	13.0	9.8	4	6	13	55.8	56.9	0	2	19	5.8	4.7	
7	2	2	58.5	59.0	1	7	2	81.8	83.9	8	8	2	21.0	16.9	0	8	13	13.5	9.9	3	2	19	66.1	65.2	
7	2	2	70.8	70.4	2	3	3	44.9	39.9	3	3	9	124.2	122.4	3	8	13	5.6	8.9	6	2	19	14.4	3.0	
0	0	1	22.3	19.2	8	0	4	78.5	77.2	6	3	9	33.0	9.8	2	2	0	14	11.0	11.8	2	4	19	39.3	36.9
0	0	1	19.1	17.1	4	4	4	43.9	44.7	1	4	4	27.1	27.2	5	6	14	46.5	55.4	5	4	19	58.3	58.3	
3	3	6	63.9	64.0	3	6	2	29.3	28.2	7	4	9	48.3	51.8	8	0	14	52.6	52.4	0	5	19	45.6	46.7	
3	3	6	27.7	23.6	4	4	2	20.6	20.5	4	4	9	50.4	47.2	8	0	14	11.1	7.9	3	5	19	16.1	19.4	
4	6	6	99.9	104.7	1	4	2	20.6	23.9	2	2	5	75.8	77.4	6	1	14	125.2	131.6	1	6	19	72.0	72.0	
4	6	6	41.7	43.8	5	5	2	15.5	14.9	2	2	6	23.3	21.0	9	1	14	35.2	35.7	0	8	19	89.0	87.9	
5	2	2	13.8	12.6	2	6	6	44.9	42.2	3	6	9	37.8	36.9	1	2	14	12.8	10.6	2	0	20	40.0	38.5	
7	8	1	26.3	22.7	3	7	2	64.4	63.8	6	6	9	8.0	5.5	4	2	14	32.5	28.5	5	0	20	71.5	71.1	
3	3	1	13.6	7.2	0	7	2	126.0	132.7	1	7	9	9.3	10.7	2	14	72.9	71.7	0	1	20	23.8	19.6		
2	0	10	6.1	2.5	4	8	5	30.4	30.4	2	8	9	35.5	35.2	5	3	14	67.5	69.3	6	2	20	29.1	27.6	
2	0	10	12.3	9.7	2	9	6	41.4	41.9	0	9	9	2.6	0.6	0	4	14	116.0	117.5	1	2	20	33.6	34.2	
8	0	0	51.9	48.1	0	10	0	82.5	83.4	4	0	10	11.3	8.7	6	4	14	11.3	7.1	2	3	20	9.8	10.1	
8	0	0	8.5	4.9	10	0	6	212.1	213.2	4	0	10	116.7	120.3	1	5	14	7.5	4.9	5	3	20	29.0	28.0	
11	0	2	18.1	14.4	6	0	6	133.5	130.8	7	0	10	136.2	133.5	4	2	14	52.3	53.4	4	0	20	18.7	25.3	
1	0	2	54.3	49.9	9	0	6	32.0	32.6	10	0	10	136.2	133.5	5	6	14	67.5	62.6	3	0	20	51.8	51.3	
1	1	1	57.3	51.8	1	1	6	38.3	35.6	8	1	10	67.9	60.7	0	7	14	64.4	64.9	4	5	20	4.0	2.3	
3	6	3	43.3	45.4	4	1	6	2.6	0.6	5	1	10	37.9	36.4	3	7	14	53.2	49.8	2	6	20	24.4	24.9	
1	1	2	21.8	16.9	10	1	6	56.9	54.7	0	2	10	98.5	102.7	1	8	14	55.1	53.7	0	7	20	84.0	82.1	
4	2	2	19.4	16.3	1	6	6	18.7	18.3	3	2	10	2.6	5.2	0	0	15	20.8	18.7	0	0	21	46.9	48.8	
4	2	2	29.8	27.9	5	2	6	53.9	53.5	6	2	10	23.8	23.2	3	6	0	15	62.4	60.1	2	0	21	12.2	16.0
7	2	2	12.0	12.0	8	2	6	23.5	25.4	1	3	10	8.2	79.8	9	0	15	10.4	8.3	1	1	21	38.7	39.0	
8	0	4	100.6	104.2	0	3	6	97.3	89.8	4	3	10	43.1	44.3	4	1	15	72.1	74.2	4	1	21	76.0	75.2	
8	0	4	23.8	20.3	3	6	3	11.5	9.1	7	3	10	64.0	63.3	4	1	15	21.1	20.1	2	2	21	24.9	25.4	
3	6	4	148.1	140.8	3	6	3	65.1	66.5	2	4	10	149.1	153.0	7	7	15	12.8	6.4	5	2	21	48.2	49.2	
3	6	4	11.0	12.7	9	3	6	62.6	63.4	5	4	10	8.2	13.9	5	2	15	16.7	16.1	0	3	21	80.5	80.0	
3	6	4	52.7	50.4	7	4	4	43.5	44.6	0	5	10	15.1	13.8	8	2	15	42.3	41.0	3	4	21	16.2	9.4	
1	1	4	2.6	2.6	7	4	4	8.1	1.4	3	6	5	10.3	9.5	0	3	15	218.6	224.8	4	4	21	22.0	20.1	
7	2	2	21.6	20.0	2	5	5	42.0	44.9	1	6	10	2.9	1.0	3	3	15	36.7	37.2	2	5	21	27.9	24.5	
7	2	2	14.6	11.6	5	6	6	57.5	55.9	4	6	10	40.2	41.3	6	3	15	56.9	54.8	0	6	21	10.0	4.7	
0	3	7	31.6	32.8	3	6	6	38.8	32.7	2	7	10	8.9	3.7	1	4	15	65.3	44.9	0	22	21	67.3	66.0	
0	3	7	15.9	15.5	6	6	6	20.5	21.9	0	8	10	27.8	27.9	2	5	15	77.3	76.4	2	0	22	66.6	66.1	
4	8	2	11.8	12.6	1	7	6	33.7	33.7	1	9	10	25.9	21.5	5	5	15	16.2	15.4	5	1	22	33.2	36.0	
4	8	2	60.4	60.4	4	7	6	80.5	79.7	2	0	11	90.2	90.2	0	6	15	22.7	17.6	0	2	22	9.2	5.5	
0	0	10	39.4	38.1	2	8	6	7.6	4.6	5	0	11	46.8	48.8	3	6	15	125.9	126.5	3	2	22	21.3	19.5	
0	0	10	28.1	27.9	4	8	6	2.1	12.2	8	0	11	38.9	38.1	1	7	15	14.0	2.0	1	3	22	37.1	37.5	
3	0	3	113.5	105.5	1	10	6	15.0	17.7	3	1	11	125.2	122.7	2	8	15	18.6	21.1	4	3	22	35.0	31.4	
3	0	3																							

with a boron atom inserted at this position resulted in an occupational parameter of 0.1, which deviates from zero with less than two standard deviations. Furthermore, a final three-dimensional  $F_o-F_c$  synthesis displayed no electron density at the position mentioned. This Fourier synthesis had no positive or negative peak exceeding 6% of a boron maximum in the final  $F_o$  synthesis.

It should be noted from Table IV that the 18% occupation of position 18(*h*) by Cr(2) atoms is very closely equivalent to almost a full occupation of that position by boron atoms. There are, however, several reasons for believing that the electron density at the position 18(*h*) with  $x = 0.20547$  and  $z = 0.17364$  is to be ascribed to a chromium atom, Cr(2). As discussed below, this assumption is supported by the observed interatomic distances between Cr(2) and its neighbours, and by the result of a least-squares refinement, replacing chromium with boron. Further support is also provided by the electron probe microanalysis mentioned above.

The Cr(2) atom has one boron neighbour at 2.01 Å (in a partially filled position) and a further 14 boron neighbours at 2.3–2.5 Å (Table V). These

distances are in better agreement with the Cr–B radius sum, 2.16 Å, than with the B–B radius sum, 1.76 Å, using the tetrahedral boron radius and the twelve coordinated chromium radius (12). The distance Cr(2)–Cr(2), which is 5% shorter than the radius sum, should not be considered as disturbingly short, since the position is only partially filled.

During one of the refinements the scattering factor of the Cr(2) atom was replaced by that of boron, which resulted in a temperature factor of 0.05 for this boron atom. Since all other boron atoms have temperature factors larger than 0.3, the low value of 0.05 is most probably a compensation for the fact that the scattering factor of boron has a more rapid “fall-off” with  $\theta$  than has the scattering factor of chromium. In general one should not expect an atom in a “large hole” to have a very small temperature factor.

### Description and Discussion of the Structure

A comparison of the positional parameters of the boron atoms in  $\text{CrB}_{\sim 41}$  (Table IV) with those in  $\beta$ -rhombohedral boron (8) shows that the boron

TABLE IV  
STRUCTURE DATA FOR  $\text{CrB}_{\sim 41}^{ab}$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
B(1)	36( <i>i</i> )	0.17779(29)	0.17576(29)	0.17683(10)	0.499(47)
B(2)	36( <i>i</i> )	0.31909(28)	0.29596(28)	0.12884(10)	0.504(47)
B(3)	36( <i>i</i> )	0.26123(28)	0.21692(28)	0.41987(11)	0.470(46)
B(4)	36( <i>i</i> )	0.23635(28)	0.25163(28)	0.34685(10)	0.426(46)
B(5)	18( <i>h</i> )	0.05543(20)	0.11086(20)	0.94409(15)	0.469(64)
B(6)	18( <i>h</i> )	0.08635(20)	0.17271(20)	0.01332(15)	0.316(61)
B(7)	18( <i>h</i> )	0.11075(20)	0.22150(20)	0.88660(15)	0.415(62)
B(8)	18( <i>h</i> )	0.16993(20)	0.33986(20)	0.02782(15)	0.454(63)
B(9)	18( <i>h</i> )	0.12991(21)	0.25981(21)	0.76627(15)	0.527(64)
B(10)	18( <i>h</i> )	0.10239(20)	0.20477(20)	0.69813(15)	0.432(63)
B(11)	18( <i>h</i> )	0.05641(20)	0.11283(20)	0.32673(16)	0.473(65)
B(12)	18( <i>h</i> )	0.09018(21)	0.18036(21)	0.39859(15)	0.501(63)
B(13) <sup>c</sup>	18( <i>h</i> )	0.05642(31)	0.11284(31)	0.55495(23)	0.88(10)
B(14)	6( <i>c</i> )	0	0	0.38517(28)	0.51(11)
B(15)	3( <i>b</i> )	0	0	1/2	0.79(17)
Cr(1) <sup>d</sup>	6( <i>c</i> )	0	0	0.13451(6)	0.146(31)
Cr(2) <sup>e</sup>	18( <i>h</i> )	0.20547(19)	0.41095(19)	0.17364(14)	0.944(61)

<sup>a</sup> Space group  $R\bar{3}m$  (No. 166). Hexagonal unit-cell dimensions:  $a = 10.9637(2)$  Å,  $c = 23.8477(4)$  Å. Cell volume:  $2482.5$  Å<sup>3</sup>. (Rhombohedral unit cell:  $a = 10.162$  Å,  $\alpha = 65.295^\circ$ ,  $V = 827.5$  Å<sup>3</sup>.)

<sup>b</sup> Standard deviations are given in parenthesis and refer to the last decimal place of the respective values.

<sup>c</sup> Occupancy 71.7(18)%.

<sup>d</sup> Occupancy 71.9(6)%.

<sup>e</sup> Occupancy 18.0(3)%.

atoms form a three-dimensional network, which is essentially the same in the two substances. The chromium atoms of  $\text{CrB}_{\sim 41}$  are situated in holes in the boron network. Since the atomic arrangement in  $\beta$ -rhombohedral boron has been described in detail by Hoard, Hughes et al. (8, 13) only a brief recapitulation will be given here as a background for the following discussion.

The  $\beta$ -rhombohedral structure is conveniently described using a complex  $\text{B}_{84}$  unit. This structural unit consists of one central boron icosahedron and twelve half-icosahedra. The vertex atom of each half-icosahedron is bonded along the quasifivefold axis to one of the vertex atoms in the central icosahedron. The linking is such that, assuming idealized, regular icosahedra, there is a mirror plane between the two vertex atoms. The hexagonal unit cell contains three  $\text{B}_{84}$  units, centred at (000),  $(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$  and  $(\frac{2}{3}, \frac{1}{3}, \frac{2}{3})$  and oriented with their threefold axes parallel to the  $c$  axis. With respect to the type of linking to other  $\text{B}_{84}$  units the half-icosahedra can be divided into two types. The first type is represented by those oriented along the rhombohedral axes (i.e., the six half-icosahedra closest to the  $c$  axis). They are linked to half-icosahedra of the same type in other  $\text{B}_{84}$  units, forming new complete icosahedra. The other type of half-icosahedra in the  $\text{B}_{84}$  unit are those lying nearly in the same  $xy$  plane as the center and with their quasifivefold axes only slightly inclined (about  $5^\circ$ ) to that plane. Three such half-icosahedra from three different  $\text{B}_{84}$  units, already linked together with the first type of icosahedra, are linked together with a  $\text{B}_{10}$  unit, consisting of a condensate of three half-icosahedra. In the  $\text{B}_{10}$  unit the vertex atom of the three half-icosahedra is common to all three while the half-icosahedra further share one triangular face in pairs. The linkage of the  $\text{B}_{84}$  and  $\text{B}_{10}$  units results in a three-dimensional network of boron atoms, in which all boron atoms are part of an icosahedron. However, the hexagonal cell contains three further boron atoms (in a threefold position), which do not belong to any icosahedral unit. Each of these boron atoms is situated between two  $\text{B}_{10}$  units, being octahedrally surrounded by six boron atoms, three from each  $\text{B}_{10}$  unit. The ideal boron content of the hexagonal cell is  $3 \times 84 + 6 \times 10 + 3 = 315$  boron atoms.

The boron network of  $\text{CrB}_{\sim 41}$  agrees closely with that of  $\beta$ -rhombohedral boron. However, the boron atom B(16), which is situated in a partially occupied position in  $\beta$ -boron, is not present in the structure of  $\text{CrB}_{\sim 41}$ . Furthermore, as can be seen from Table V, many of the interatomic distances display significant shifts as compared to the equivalent distances of

TABLE V  
INTERATOMIC DISTANCES IN  $\text{CrB}_{\sim 41}$  (Å UNITS)<sup>ab</sup>

B(1)-B(2)	1.825(4)	B(8)-2B(3)	1.801(4)
B(1)-B(9)	1.832(4)	B(8)-B(10)	1.828(4)
B(1)-B(7)	1.835(4)	B(9)-B(10)	1.707(5)
B(1)-B(2)	1.845(4)	B(9)-B(7)	1.790(3)
B(1)-B(1)	1.905(5)	B(9)-2B(1)	1.832(4)
B(1)-B(1)	1.972(5)	B(9)-2B(2)	1.849(3)
B(1)-Cr(1)	2.185(3)	B(10)-B(9)	1.707(5)
B(1)-Cr(2)	2.442(3)	B(10)-2B(11)	1.788(3)
B(2)-B(3)	1.721(4)	B(10)-B(8)	1.828(4)
B(2)-B(7)	1.798(3)	B(10)-2B(4)	1.839(4)
B(2)-B(2)	1.824(5)	B(11)-B(14)	1.758(6)
B(2)-B(1)	1.825(4)	B(11)-2B(10)	1.788(3)
B(2)-B(1)	1.845(4)	B(11)-B(12)	1.830(5)
B(2)-B(9)	1.849(3)	B(11)-2B(4)	1.854(3)
B(2)-Cr(2)	2.419(3)	B(11)-2B(11)	1.855(3)
B(2)-Cr(2)	2.431(3)	B(12)-B(14)	1.742(2)
B(3)-B(2)	1.721(4)	B(12)-2B(3)	1.784(3)
B(3)-B(12)	1.784(3)	B(12)-B(11)	1.830(5)
B(3)-B(13)	1.800(4)	B(12)-2B(4)	1.857(4)
B(3)-B(8)	1.801(4)	B(12)-2B(13)	1.864(5)
B(3)-B(4)	1.832(3)	B(12)-Cr(2)	2.363(5)
B(3)-B(3)	1.892(5)	B(13)-B(15)	1.693(5)
B(3)-Cr(2)	2.283(4)	B(13)-B(14)	1.785(7)
B(3)-Cr(2)	2.446(4)	B(13)-2B(3)	1.800(4)
B(4)-B(4)	1.680(5)	B(13)-2B(13)	1.856(5)
B(4)-B(8)	1.731(3)	B(13)-2B(12)	1.864(5)
B(4)-B(3)	1.832(3)	B(13)-Cr(2)	2.005(5)
B(4)-B(10)	1.839(4)	B(13)-2Cr(2)	2.398(4)
B(4)-B(11)	1.854(3)	B(14)-3B(12)	1.742(2)
B(4)-B(12)	1.857(4)	B(14)-3B(11)	1.758(6)
B(4)-B(4)	2.424(5)	B(14)-3B(13)	1.785(7)
B(5)-B(7)	1.727(4)	B(15)-6B(13)	1.693(5)
B(5)-B(6)	1.752(5)	B(15)-6Cr(2)	2.434(2)
B(5)-2B(6)	1.761(4)	Cr(1)-3B(5)	2.150(3)
B(5)-2B(5)	1.823(3)	Cr(1)-3B(7)	2.163(2)
B(5)-Cr(1)	2.150(3)	Cr(1)-6B(1)	2.185(3)
B(6)-B(8)	1.624(3)	Cr(2)-B(13)	2.005(5)
B(6)-B(5)	1.752(5)	Cr(2)-2B(3)	2.283(4)
B(6)-2B(6)	1.759(3)	Cr(2)-B(12)	2.363(5)
B(6)-2B(5)	1.761(4)	Cr(2)-2B(13)	2.398(4)
B(7)-B(5)	1.727(4)	Cr(2)-2B(2)	2.419(3)
B(7)-B(9)	1.790(3)	Cr(2)-2B(2)	2.431(3)
B(7)-2B(2)	1.798(3)	Cr(2)-B(15)	2.434(2)
B(7)-2B(1)	1.835(4)	Cr(2)-2B(1)	2.442(3)
B(7)-Cr(1)	2.163(2)	Cr(2)-2B(3)	2.446(4)
B(8)-B(6)	1.624(3)	Cr(2)-2Cr(2)	2.451(2)
B(8)-2B(4)	1.731(3)		

<sup>a</sup> Distances listed are Cr-Cr < 4.0 Å, Cr-B < 3.0 Å and B-B < 2.7 Å.

<sup>b</sup> Standard deviations are given in parenthesis and refer to the last decimal place of the respective values.

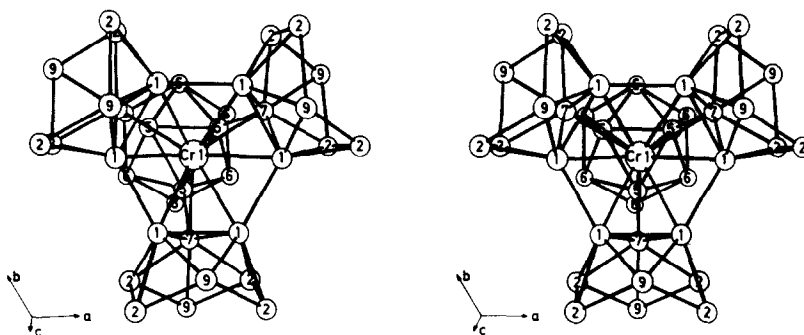


FIG. 1. Stereoscopic pair of drawings showing the environment of the Cr(1) atom, as seen almost parallel to the  $c$  axis.

$\beta$ -boron. Two-thirds of the independent distances in the boron network are unchanged at the 99.95% level of confidence, while one-third has increased or decreased by 0.015–0.057 Å. The largest alterations are the decrease in the B(7)–B(9) distance from 1.847 to 1.790 Å and the increase in the B(1)–B(1) distance from 1.919 to 1.972 Å. The atomic position 18( $h$ ) with B(13) atoms is occupied to 72% (Table IV) in close agreement with the occupancy factor of two-thirds obtained for  $\beta$ -boron (8).

The environments of the chromium atoms in  $\text{CrB}_{\sim 41}$  are demonstrated stereoscopically in Figs. 1 and 2, which have been drawn with the aid of the program ORTEP (2). The two crystallographic positions, which contain chromium atoms, are only partially occupied. Cr(1) is surrounded by 12 boron atoms at the average distance 2.16 Å, which is equal to the radius sum. As can be seen from Fig. 1 the environment is symmetrical. Cr(1) is situated on the threefold axis and within the  $\text{B}_{84}$  unit. All neighbours are at approximately the same distance and form a truncated tetrahedron.

The Cr(2) atom has 15 adjacent boron neighbours, 14 at an average distance of 2.40 Å and one at

2.01 Å (this is one of the three B(13) neighbours). However, the occupancy of the B(13) position is 72% and that of the Cr(2) position is only 18%. Consequently, a simultaneous occupation of the two positions, yielding the short distance 2.01 Å, is very improbable. This further implies, that a Cr(2) atom actually has 14 boron neighbours. The partial occupancy of the B(13) position is, on the other hand, not a consequence of the short Cr(2)–B(13) distance since it was also observed in pure  $\beta$ -boron (8). Moreover, each Cr(2) atom has two Cr(2) neighbours at the very short distance 2.45 Å. The low occupancy of the Cr(2) position, 18%, renders the occurrence of such close Cr–Cr contacts less probable.

In discussing the positions of the chromium atoms in  $\text{CrB}_{\sim 41}$  it seems appropriate to investigate a little more in detail the size and properties of the holes which occur in the  $\beta$ -boron structure. The structure is a very open one and the degree of space filling is only 36%, assuming  $r_{\text{B}} = 0.88$  Å. Accordingly, the structure contains many holes. The present authors have found that many of these holes are sufficiently large to accommodate atoms. The approximate positions of the holes are collected in Table VI. The

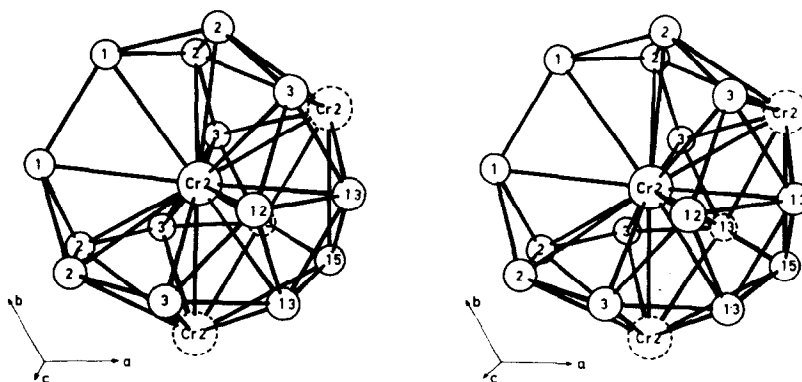


FIG. 2. Stereoscopic pair of figures illustrating the coordination of the Cr(2) atom, as viewed almost parallel to the  $c$  axis. Dashed circles denote atomic positions, probably unoccupied. See text.

TABLE VI  
APPROXIMATE COORDINATES FOR HOLES IN THE BORON  
NETWORK OF CrB<sub>~41</sub> (HEXAGONAL UNIT CELL)

Hole	Position	Coordinates	Occupied by
A(1)	6(c)	0; 0; 0.135	Cr(1)
A(2)	18(h)	0.108; 0.216; 0.100	—
A(3)	36(i)	0.279; 0.248; 0.046	—
D	18(h)	0.205; 0.411; 0.174	Cr(2)
E	6(c)	0; 0; 0.245	—
F(1)	18(h)	0.065; 0.130; 0.245	—
F(2)	18(h)	0.117; 0.233; 0.252	—
G	18(h)	0.055; 0.109; 0.117	—

distances from the center of the holes to the neighbouring atoms in CrB<sub>~41</sub> are given in Table VII. It should be noted, however, that the positions of the holes for obvious reasons are only approximate and that the "interatomic" distances, given in Table VII, may change appreciably if the hole positions are actually occupied by atoms.

Holes of the type A(1), A(2), and A(3) are situated outside the triangular faces of the central icosahedron of the B<sub>84</sub> unit. Position A(1), is situated on the hexagonal axis and accordingly has a high symmetry, while the positions A(2) and A(3) have a lower symmetry. All three holes are surrounded by 12 boron atoms. As can be seen from Table VII, A(1) is the largest of them.

The D and E positions have as many as 15 close boron neighbours. The E hole has a radius of 1.35 Å while the D hole is smaller, one of its neighbours being only 2.01 Å from its center.

The positions F(1) and F(2) are closely related to each other. They cannot be occupied by atoms simultaneously, since the distance between the centers is only 0.99 Å. The two holes are possibly better described as one single elongated hole. Position F(1) has seven boron neighbours at distances between 1.95 and 2.18 Å, involving low compatibility of the hole for boron atoms as well as for metal atoms. This position also interferes with position E. It is possible for small metal atoms ( $r_{Me} = 1.24$  Å) to occupy position F(2) but they would coordinate only three close boron atoms. Thirteen further boron atoms are, however, found at 2.39–2.66 Å. The great diversity in neighbouring distances may be one reason for the fact that this hole is empty.

Position G has eight boron neighbours and is of suitable size for a boron atom. In pure β-boron the electron density indicated a partial occupation of the hole by boron (8). In the present investigation of CrB<sub>~41</sub> no significant electron density was observed at this position, which probably is a consequence of the short distance to the Cr(1) atoms in position A(1).

This survey of the holes in the β-rhombohedral boron structure has shown that in addition to positions A(1) and D there is at least one further position, which can accommodate metal atoms, namely the E position. Since this hole has a radius of 1.35 Å, it is surprising that chromium prefers the D position. Single-crystal studies of other metals dissolved in β-boron may, however, cast some further light on this question.

During the preparation of this paper, Mattes et al. (14) reported the results of a single-crystal investiga-

TABLE VII  
ENVIRONMENT OF HOLES IN CrB<sub>~41</sub><sup>a</sup>

Hole	Boron Neighbours	Further Possible Neighbours
A(1)	12B, 2.15–2.19	3G, 1.12; 3A(2), 2.21; 1E, 2.63
A(2)	12B, 2.06–2.14	1G, 1.09; 2A(3), 2.15; 1A(1), 2.21; 1D, 2.55; 2G, 2.75
A(3)	12B, 1.91–2.20	1A(2), 2.15; 1A(3), 2.27; 1A(3), 2.38; 1G, 2.73
D	1B, 2.01; 14B, 2.28–2.45	2D, 2.45; 1F(2), 2.52; 1A(2), 2.55
E	15B, 2.23–2.53	3F(1), 1.24; 3F(2), 2.22; 1A(1), 2.63
F(1)	7B, 1.95–2.18; 2B, 2.79	1F(2), 0.99; 1E, 1.24; 2F(1), 2.14
F(2)	3B, 2.12; 13B, 2.39–2.66	1F(1), 0.99; 1E, 2.22; 1D, 2.52
G	8B, 1.79–1.85; 6B, 2.54–2.62	1A(2), 1.09; 1A(1), 1.12; 2A(3), 2.73; 2A(2), 2.75

<sup>a</sup> Distances are given in Ångström units. All neighbours within 2.8 Å are given.



tion of  $\text{Cu}_2\text{Al}_{2.7}\text{B}_{10.4}$ . The metal atoms of this compound are situated at the same positions as in  $\text{CrB}_{\sim 41}$ , although the position *D* has significantly different coordinates.

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