

## The Solubilities of Copper and Manganese in $\beta$ -Rhombohedral Boron as Determined in $\text{CuB}_{\sim 28}$ and $\text{MnB}_{\sim 23}$ by Single-Crystal Diffractometry

SVEN ANDERSSON AND BENGT CALLMER

*Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden*

Received July 24, 1973

The structures of two crystals with the compositions  $\text{CuB}_{\sim 28}$  and  $\text{MnB}_{\sim 23}$  have been determined using single-crystal diffractometry. The compositions probably represent the maximum solubility of copper and manganese in  $\beta$ -rhombohedral boron. The space group is  $R\bar{3}m$ , and the hexagonal axes are  $a = 10.970 \text{ \AA}$  and  $c = 23.890 \text{ \AA}$  for  $\text{CuB}_{\sim 28}$ , and  $a = 10.988 \text{ \AA}$  and  $c = 23.994 \text{ \AA}$  for  $\text{MnB}_{\sim 23}$ . The three-dimensional boron network of  $\beta$ -rhombohedral boron is retained almost unchanged in the two compounds and the metal atoms are situated in holes in this network. In  $\text{MnB}_{\sim 23}$  the manganese atoms partly occupy three crystallographic positions. In  $\text{CuB}_{\sim 28}$  one of these positions is split up into two and the copper atoms consequently occupy four crystallographic positions.

### Introduction

In 1970 Andersson and Lundström (1) determined the maximum solubility of chromium in  $\beta$ -rhombohedral boron as well as the positions of the chromium atoms in the  $\beta$ -boron structure by using single-crystal diffractometry. The solubility found was 2.4 atm% corresponding to the composition  $\text{CrB}_{\sim 41}$  with the chromium atoms partly occupying two sets of holes in the  $\beta$ -boron network. In the meantime, similar solid solutions for manganese (2) and for the remaining 3d elements (3) were discovered from X-ray powder data. The powder reflexions of these solid solutions are characterized by significant changes in intensity as compared with those of  $\beta$ -rhombohedral boron and the unit-cell volumes are enlarged.

The partial occupation of two sets of holes by chromium atoms in  $\text{CrB}_{\sim 41}$  and a third nonoccupied set, which is large enough to accommodate such atoms, made it interesting to investigate solutions with other metals as solutes. Furthermore, Mössbauer studies of solid solutions of iron in  $\beta$ -rhombohedral boron indicated three crystallographically different metal positions (4).

The solutions of copper and manganese were chosen for a first investigation for two reasons, these metals have about the same radii as chromium and large solution hardening effects were obtained with these solutes (3).

### Experiments

The crystals investigated were taken from samples with the initial compositions  $\text{CuB}_{21.0}$  and  $\text{MnB}_{9.2}$  prepared by arc-melting crystalline boron (from Borax Consolidated, claimed purity 99.8%) and copper (from Johnson, Matthey & Co., claimed purity 99.99%) or manganese (from Koch-Light Laboratories, Ltd., claimed purity 99.99%) under an atmosphere of purified argon.

The arc-melted samples were examined by X-ray powder diffraction using Guinier-Hägg cameras with pure  $\text{CrK}\alpha_1$  radiation ( $\lambda = 2.28962 \text{ \AA}$ ). Unit-cell dimensions of powders were determined using silicon ( $a = 5.43054 \text{ \AA}$ ) as internal calibration standard. The cell dimensions of the two crystals used for the collection of the intensity data sets, were obtained from the measurements of the  $2\theta$  angles of 13 reflexions from the  $\text{CuB}_{\sim 28}$

crystal and 11 reflexions from the  $\text{MnB}_{\sim 23}$  crystal on a manual General Electric single-crystal orienter, using  $\text{CuK}\alpha$  radiation. The  $2\theta$  value of a reflexion was defined as the average of the  $2\theta$  angles at one third of the maximum of the peak intensity. The wavelength used in the calculations of the unit-cell parameters was 1.54242 Å, which represents the average of  $\lambda_{\text{CuK}\alpha_1}$  and  $\lambda_{\text{CuK}\alpha_2}$ . The zero-point correction of the  $2\theta$  scale was determined using a basic beryllium acetate crystal. All unit-cell dimensions were refined using a least-squares program.

The two intensity data sets were collected using an automatic Stoe-Philips four-circle diffractometer controlled by a PDP8/I computer. The  $\omega/2\theta$  scan technique and  $\text{MoK}\alpha$  radiation monochromatized by a graphite single crystal were used. The background was measured by stationary counting at each side of the scanning interval, which was chosen to be  $1.60^\circ$ . The reflexions with  $h \geq 0$ ,  $k \leq 0$ , and  $l \geq 0$  (hexagonal indices) were measured up to  $2\theta = 60^\circ$  for both crystals. To check the setting of the crystal and the stability of the diffractometer system three standard reflexions were measured every 50 reflexions.

The crystals used for the intensity measurements both had a largest cross-section less than 0.13 mm. The calculated linear absorption coefficients for  $\text{MoK}\alpha$  radiation were  $25 \text{ cm}^{-1}$  for  $\text{CuB}_{\sim 28}$  and  $18 \text{ cm}^{-1}$  for  $\text{MnB}_{\sim 23}$ . Absorption corrections were thus considered unnecessary.

The crystals were also investigated by oscillation and Weissenberg techniques in order to check their quality and the symmetry, and to ascertain that no superstructure had been formed.

### Numerical Computations

The major calculations were performed using the CD 3600 Computer in Uppsala employing the following programs:

Lorentz- and polarization factor corrections

DATAPH: P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel; modified by P.-G. Jönsson, Uppsala, Sweden.

Sorting and averaging of equivalent reflexions

SORTA: J.-O. Lundgren, Uppsala, Sweden.

Fourier calculations

DRF: A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden.

Least-squares refinements of positional parameters, occupancy and temperature factors

LALS: P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; modified considerably by J.-O. Lundgren, Uppsala, Sweden.

Calculations of interatomic distances

DISTAN: A. Zalkin, Berkeley, U.S.A.

Crystal structure graphics

ORTEP: ORNL-3794, C. K. Johnson, Oak Ridge, U.S.A.

Smaller calculations were performed using the departmental IBM 1800 computer.

The atomic scattering factors used in the calculations were taken from Table 3.3.1A in Ref. (5) and were corrected for anomalous dispersion as given by Cromer (6).

### Phase Analysis and Crystal Data

Examination of the X-ray powder patterns of the two samples showed them to be two-phase specimens. The  $\text{CuB}_{21.0}$  sample contained copper, probably with a small amount of dissolved boron (7, 8), and a phase closely related to  $\beta$ -rhombohedral boron, in agreement with the results of Carlsson and Lundström (3). The  $\text{MnB}_{9.2}$  sample contained  $\text{MnB}_2$  and a " $\beta$ -boron" phase in complete agreement with the results of Andersson and Carlsson (2). The " $\beta$ -boron" phases are here denoted  $\text{CuB}_{\sim 28}$  and  $\text{MnB}_{\sim 23}$ , which are the compositions obtained from the crystal-structure refinements to be described below. The intensities of the powder lines of these phases were markedly different from those of pure  $\beta$ -rhombohedral boron.

The hexagonal unit-cell dimensions of the single crystals and those measured with powder techniques are given in Table I. The standard

TABLE I  
UNIT-CELL DIMENSIONS OF  $\text{MnB}_{\sim 23}$ ,  $\text{CuB}_{\sim 28}$  AND PURE BORON  
( $\text{\AA}$  UNITS)<sup>a</sup>

	<i>a</i>	<i>c</i>
$\text{MnB}_{\sim 23}$ (powder) <sup>b</sup>	10.9907(8)	23.9964(24)
$\text{MnB}_{\sim 23}$ (single-crystal)	10.9875(5)	23.9937(28)
$\text{CuB}_{\sim 28}$ (powder)	10.9723(10)	23.8894(23)
$\text{CuB}_{\sim 28}$ (single-crystal)	10.9703(4)	23.8898(12)
Boron (arc melted, powder) <sup>c</sup>	10.9253(5)	23.8103(16)

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

<sup>b</sup> From Ref. (3).

<sup>c</sup> From Ref. (1).

deviations given are those obtained from the least-squares refinements and the accuracy may thus be somewhat lower than indicated by these values due to the influence of systematic errors. Accordingly, the cell dimensions found for the single crystal and those obtained from the powder determination do not deviate significantly from each other. This fact, together with the occurrence of a more metal-rich phase in the alloys from which the single crystals were picked, ensures that the compositions of the crystals, as obtained from the crystal-structure determination, very probably represent the maximum solubility of copper (3.5 atm%; 17.4 wt%) and manganese (4.1 atm%; 17.9 wt%) in  $\beta$ -rhombohedral boron at very high temperatures.

#### Determination and Refinement of the Structures

The intensities were corrected for the Lorentz and polarization effects. The indices of the reflexions were transformed to  $h, k, l \geq 0$ , and by averaging the  $F_0^2$  values for equivalent reflexions the sets of intensity data were reduced to 938 and 922 independent reflexions for  $\text{MnB}_{\sim 23}$  and  $\text{CuB}_{\sim 28}$ , respectively. Reflexions with  $\overline{F_0^2} < 2\sigma_{\overline{F_0^2}}$  were considered as not significantly different from the background and were thus omitted in the following calculations. This reduced the number of inde-

pendent reflexions used to 728 for  $\text{MnB}_{\sim 23}$  and 701 for  $\text{CuB}_{\sim 28}$ .

Assuming that the three-dimensional boron networks were the same in  $\text{MnB}_{\sim 23}$  and  $\text{CuB}_{\sim 28}$  as in  $\text{CrB}_{\sim 41}$  (1) and  $\beta$ -rhombohedral boron (9), three-dimensional  $F_0$  syntheses were calculated using the coordinates of the boron atoms in  $\text{CrB}_{\sim 41}$ . From these syntheses approximate values of the positional and occupational parameters of the manganese and copper positions were obtained. Peaks assigned to metal atoms were in both compounds found in three positions, 6(c) (0 0 0.13), 18(h) (0.20 0.40 0.17), and 6(c) (0 0 0.23). These are the positions denoted A(1), D, and E by Andersson and Lundström (1).

Atomic coordinates, isotropic temperature factors, occupational parameters for the metal atoms and one boron atom, B(13), and one scale factor were then refined for each compound using the method of least-squares. The function minimized was  $\sum w(|F_0| - |F_c|)$ . The refinements converged rapidly and the final discrepancy index, defined as  $\sum \|F_0| - |F_c| / \sum |F_0|$ , was 5.1% for  $\text{MnB}_{\sim 23}$  and 11.4% for  $\text{CuB}_{\sim 28}$ . For both compounds the last shifts were less than 5% of the standard deviations for the 58 parameters refined. Weights were assigned according to the formula  $w = 1/(a + |F_0| + c|F_0|^2)$ . The values of *a* and *c* found to give the best

weighting analyses were 160 and 0.005 for  $\text{MnB}_{\sim 23}$  and 120 and 0.007 for  $\text{CuB}_{\sim 28}$ .

When examining the results of the refinement of  $\text{CuB}_{\sim 28}$ , it was observed that the temperature factor of the copper atom in position  $D$  was very large,  $B = 2.9$ : A difference synthesis around this position resulted in three maxima, one in position  $18(h)$  with the coordinates (0.19 0.38 0.18) and two in a position  $36(i)$  with the coordinates (0.20 0.43 0.17). It was therefore assumed that a particular copper atom in the  $D$  hole could be either in a position  $18(h)$ ,  $\text{Cu}(2')$ , or in a position  $36(i)$   $\text{Cu}(2'')$ . When introducing this splitting in a least-squares refinement the  $R$  value decreased from 11.4% to 6.4%. At this stage difference syntheses around the metal positions indicated marked anisotropic thermal motion of the metal atoms in hole  $D$ ,  $\text{Cu}(2')$  and  $\text{Cu}(2'')$ , and hole  $E$ ,  $\text{Cu}(3)$ . A refinement using anisotropic temperature factors for these three metal atoms lowered the  $R$  value to 5.3%. A complete three-dimensional difference synthesis was now calculated, and a peak, about 10% of a boron maximum in the  $F_0$  synthesis, was found in position  $18(h)$  with the coordinates (0.055 0.110 0.115). This is the position found to be partially occupied by a boron atom,  $\text{B}(16)$ , by Hoard et al. (9). A further refinement was therefore carried out including positional parameters, an isotropic temperature factor, and an occupancy parameter for  $\text{B}(16)$ . The final  $R$  value was 4.8%, and the last shifts were less than 5% of the standard deviations for all the 76 parameters refined. In the final difference synthesis the largest deviations from zero were less than 5% of a boron maximum in the  $F_0$  synthesis.

Observed and calculated structure factors for  $\text{CuB}_{\sim 28}$  are given in Table II, structure data in Table IV, and copper-boron and copper-copper distances in Table VI. The temperature factor obtained for  $\text{Cu}(1)$  is slightly negative, but this is not serious since the standard deviation is large and since the temperature factor is strongly correlated to the occupancy factor for the copper position. The large temperature factor value for the  $\text{B}(16)$  atom can be disregarded for the same reasons. The large standard deviations of the

$\text{Cu}(2')$  and  $\text{Cu}(2'')$  parameters are due to the very short distance between these positions, which makes the refinement insensitive to the distribution of the atoms on the two positions as well as to their coordinates. In a refinement with only one copper position in the  $D$  hole the standard deviation of the occupancy factor was only 2% of the obtained occupancy. Thus, the total copper content of the  $D$  hole is known with a better accuracy than indicated by the standard deviations of the  $\text{Cu}(2')$  and  $\text{Cu}(2'')$  occupational parameters in Table IV.

For  $\text{MnB}_{\sim 23}$  the largest deviations from zero in a three-dimensional difference synthesis were less than 6% of the boron maxima in the  $F_0$  synthesis. In the synthesis features were observed which might possibly indicate a splitting of the  $\text{Mn}(2)$  position, as well as a very small occupation of the  $\text{B}(16)$  position. For these reasons, refinements including a split-up  $\text{Mn}(2)$  position and a  $\text{B}(16)$  atom were performed. These gave no significant proof, however, for a splitting of the  $\text{Mn}(2)$  position or the occurrence of  $\text{B}(16)$ . The occupancy factor for the Mn atom in position  $36(i)$ , 5.4%, was less than two standard deviations and the occupancy factor for the  $\text{B}(16)$  atom, 2.5%, was about one standard deviation. Accordingly, the structure of  $\text{MnB}_{\sim 23}$  is described with one manganese position in hole  $D$  and without any  $\text{B}(16)$  atom. No indications of anisotropic thermal motion of the atoms were observed.

Observed and calculated structure factors for  $\text{MnB}_{\sim 23}$  are given in Table III, structure data in Table V, and manganese-boron and manganese-manganese distances in Table VII.

### Description and Discussion of the Structures

The boron networks of  $\text{MnB}_{\sim 23}$  and  $\text{CuB}_{\sim 28}$  are almost identical to that of  $\beta$ -rhombohedral boron (9). As in  $\text{CrB}_{\sim 41}$  (1) the metal atoms are situated in holes in the boron network.

The structure of  $\beta$ -rhombohedral boron has been described in detail by Hoard et al. (9, 10). This structure is conveniently described using a complex  $\text{B}_{84}$  unit, consisting



TABLE III  
OBSERVED AND CALCULATED STRUCTURE FACTORS ( $\times 10$ ) FOR MnB<sub>2</sub>

	h	k	l	F <sub>o</sub>	F <sub>c</sub>
	0	0	0	100	100
	1	0	0	100	100
	2	0	0	100	100
	3	0	0	100	100
	4	0	0	100	100
	5	0	0	100	100
	6	0	0	100	100
	7	0	0	100	100
	8	0	0	100	100
	9	0	0	100	100
	10	0	0	100	100
	11	0	0	100	100
	12	0	0	100	100
	13	0	0	100	100
	14	0	0	100	100
	15	0	0	100	100
	16	0	0	100	100
	17	0	0	100	100
	18	0	0	100	100
	19	0	0	100	100
	20	0	0	100	100
	21	0	0	100	100
	22	0	0	100	100
	23	0	0	100	100
	24	0	0	100	100
	25	0	0	100	100
	26	0	0	100	100
	27	0	0	100	100
	28	0	0	100	100
	29	0	0	100	100
	30	0	0	100	100
	31	0	0	100	100
	32	0	0	100	100
	33	0	0	100	100
	34	0	0	100	100
	35	0	0	100	100
	36	0	0	100	100
	37	0	0	100	100
	38	0	0	100	100
	39	0	0	100	100
	40	0	0	100	100
	41	0	0	100	100
	42	0	0	100	100
	43	0	0	100	100
	44	0	0	100	100
	45	0	0	100	100
	46	0	0	100	100
	47	0	0	100	100
	48	0	0	100	100
	49	0	0	100	100
	50	0	0	100	100
	51	0	0	100	100
	52	0	0	100	100
	53	0	0	100	100
	54	0	0	100	100
	55	0	0	100	100
	56	0	0	100	100
	57	0	0	100	100
	58	0	0	100	100
	59	0	0	100	100
	60	0	0	100	100
	61	0	0	100	100
	62	0	0	100	100
	63	0	0	100	100
	64	0	0	100	100
	65	0	0	100	100
	66	0	0	100	100
	67	0	0	100	100
	68	0	0	100	100
	69	0	0	100	100
	70	0	0	100	100
	71	0	0	100	100
	72	0	0	100	100
	73	0	0	100	100
	74	0	0	100	100
	75	0	0	100	100
	76	0	0	100	100
	77	0	0	100	100
	78	0	0	100	100
	79	0	0	100	100
	80	0	0	100	100
	81	0	0	100	100
	82	0	0	100	100
	83	0	0	100	100
	84	0	0	100	100
	85	0	0	100	100
	86	0	0	100	100
	87	0	0	100	100
	88	0	0	100	100
	89	0	0	100	100
	90	0	0	100	100
	91	0	0	100	100
	92	0	0	100	100
	93	0	0	100	100
	94	0	0	100	100
	95	0	0	100	100
	96	0	0	100	100
	97	0	0	100	100
	98	0	0	100	100
	99	0	0	100	100
	100	0	0	100	100

TABLE IV  
STRUCTURE DATA FOR CuB<sub>28</sub><sup>a</sup>

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
B(1)	36( <i>i</i> )	0.17406(28)	0.17401(28)	0.17597(11)	0.504(40)
B(2)	36( <i>i</i> )	0.31940(28)	0.29442(27)	0.12863(11)	0.492(40)
B(3)	36( <i>i</i> )	0.26251(28)	0.21851(27)	0.41905(11)	0.515(40)
B(4)	36( <i>i</i> )	0.23636(27)	0.25166(28)	0.34668(10)	0.496(40)
B(5)	18( <i>h</i> )	0.05408(20)	0.10816(20)	0.94372(15)	0.443(50)
B(6)	18( <i>h</i> )	0.08557(20)	0.17113(20)	0.01323(15)	0.439(51)
B(7)	18( <i>h</i> )	0.10940(20)	0.21879(20)	0.88691(15)	0.465(52)
B(8)	18( <i>h</i> )	0.16955(20)	0.33909(20)	0.02799(15)	0.487(52)
B(9)	18( <i>h</i> )	0.12956(20)	0.25912(20)	0.76667(15)	0.516(53)
B(10)	18( <i>h</i> )	0.10228(20)	0.20456(20)	0.69845(14)	0.395(51)
B(11)	18( <i>h</i> )	0.05680(20)	0.11360(20)	0.32642(15)	0.469(52)
B(12)	18( <i>h</i> )	0.09043(20)	0.18086(20)	0.39781(15)	0.457(52)
B(13) <sup>b</sup>	18( <i>h</i> )	0.05650(34)	0.11301(34)	0.55595(24)	0.53(14)
B(14)	6( <i>c</i> )	0	0	0.38560(27)	0.426(86)
B(15)	3( <i>b</i> )	0	0	1/2	0.60(13)
B(16) <sup>c</sup>	18( <i>h</i> )	0.0546(16)	0.1092(16)	0.1171(12)	2.42(62)
Cu(1) <sup>d</sup>	6( <i>c</i> )	0	0	0.13654(13)	-0.08(26)
Cu(2') <sup>e</sup>	18( <i>h</i> )	0.19638(92)	0.39277(92)	0.17791(45)	anisot. <sup>h</sup>
Cu(2'') <sup>f</sup>	36( <i>i</i> )	0.2043(20)	0.4317(18)	0.16996(42)	anisot. <sup>h</sup>
Cu(3) <sup>g</sup>	6( <i>c</i> )	0	0	0.22554(8)	anisot. <sup>h</sup>

<sup>a</sup> Standard deviations are given in parentheses and refer to the last decimal place of the respective values. Space group  $R\bar{3}m$  (No. 166). Hexagonal unit-cell dimensions:  $a = 10.9703(4)$  Å,  $c = 23.8898(12)$  Å. Cell volume:  $2489.9$  Å<sup>3</sup>. (Rhombohedral unit cell:  $a = 10.175$  Å,  $\alpha = 65.243^\circ$ ,  $V = 830.0$  Å<sup>3</sup>.)

<sup>b</sup> Occupancy 61.1(19)%.

<sup>c</sup> Occupancy 20.9(22)%.

<sup>d</sup> Occupancy 6.1(5)%.

<sup>e</sup> Occupancy 22.1(20)%.

<sup>f</sup> Occupancy 10.5(10)%.

<sup>g</sup> Occupancy 50.5(6)%.

<sup>h</sup> Atom	$\beta_{11} \cdot 10^5$	$\beta_{22} \cdot 10^5$	$\beta_{33} \cdot 10^5$	$\beta_{12} \cdot 10^5$	$\beta_{13} \cdot 10^5$	$\beta_{23} \cdot 10^5$
Cu(2')	321(58)	321(58)	74(8)	40(41)	-6(11)	6(11)
Cu(2'')	892(141)	398(88)	29(9)	-446(87)	145(29)	-44(19)
Cu(3)	303(15)	303(15)	79(4)	151(8)	0	0

of one central icosahedron and twelve half-icosahedra. Each atom of the central icosahedron is bonded along a fivefold axis to the vertex atom of a half-icosahedron. In the hexagonal unit cell the B<sub>84</sub> units are centered at (000), ( $\frac{1}{3}$   $\frac{2}{3}$   $\frac{2}{3}$ ), and ( $\frac{2}{3}$   $\frac{1}{3}$   $\frac{1}{3}$ ) and oriented with their threefold axes parallel to the *c* axis. According to the function they have in the interconnection of B<sub>84</sub> units the half-icosahedra can be divided into two types. One type comprises those oriented along the rhombohedral axes, i.e., the six half-icosahedra

closest to the *c* axis. These are connected to half-icosahedra of the same type in neighboring B<sub>84</sub> units, forming new complete icosahedra. The other type of half-icosahedra in the B<sub>84</sub> unit are those lying almost in the same *xy* plane as the center. Three such half-icosahedra from different B<sub>84</sub> units, which are also linked together with the first-mentioned type of icosahedra, are linked together through a B<sub>10</sub> unit, consisting of a condensate of three half-icosahedra. The linkage of the B<sub>84</sub> and B<sub>10</sub> units results in a three-dimensional net-

TABLE V  
STRUCTURE DATA FOR  $\text{MnB}_{\sim 23}$ <sup>a</sup>

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
B(1)	36( <i>i</i> )	0.17538(35)	0.17375(35)	0.17526(13)	0.472(47)
B(2)	36( <i>i</i> )	0.31901(35)	0.29428(34)	0.12845(14)	0.456(48)
B(3)	36( <i>i</i> )	0.26193(35)	0.21789(35)	0.41905(13)	0.524(49)
B(4)	36( <i>i</i> )	0.23780(35)	0.25253(35)	0.34698(13)	0.455(47)
B(5)	18( <i>h</i> )	0.05412(25)	0.10823(25)	0.94386(18)	0.362(62)
B(6)	18( <i>h</i> )	0.08527(24)	0.17054(24)	0.01318(18)	0.322(60)
B(7)	18( <i>h</i> )	0.10940(24)	0.21879(24)	0.88790(19)	0.355(63)
B(8)	18( <i>h</i> )	0.16841(25)	0.33682(25)	0.02804(18)	0.503(69)
B(9)	18( <i>h</i> )	0.12981(25)	0.25961(25)	0.76670(19)	0.417(63)
B(10)	18( <i>h</i> )	0.10211(26)	0.20421(26)	0.69820(19)	0.522(67)
B(11)	18( <i>h</i> )	0.05752(25)	0.11504(25)	0.32738(19)	0.436(63)
B(12)	18( <i>h</i> )	0.09019(24)	0.18038(24)	0.39796(19)	0.461(65)
B(13) <sup>b</sup>	18( <i>h</i> )	0.05582(39)	0.11165(39)	0.55613(28)	0.40(15)
B(14)	6( <i>c</i> )	0	0	0.38577(36)	0.53(12)
B(15)	3( <i>b</i> )	0	0	1/2	0.96(19)
Mn(1) <sup>c</sup>	6( <i>c</i> )	0	0	0.13368(18)	0.29(11)
Mn(2) <sup>d</sup>	18( <i>h</i> )	0.20199(10)	0.40398(10)	0.17460(7)	0.889(39)
Mn(3) <sup>e</sup>	6( <i>c</i> )	0	0	0.23304(7)	0.397(41)

<sup>a</sup> Standard deviations are given in parentheses and refer to the last decimal place of the respective values. Space group  $R\bar{3}m$  (No. 166). Hexagonal unit-cell dimensions:  $a = 10.9875(5)$  Å,  $c = 23.9937(28)$  Å. Cell volume:  $2508.6$  Å<sup>3</sup>. (Rhombohedral unit cell:  $a = 10.208$  Å,  $\alpha = 65.118^\circ$ ,  $V = 836.2$  Å<sup>3</sup>.)

<sup>b</sup> Occupancy 65.0(23) %.

<sup>c</sup> Occupancy 25.6(7) %.

<sup>d</sup> Occupancy 43.1(5) %.

<sup>e</sup> Occupancy 66.2(8) %.

work of boron atoms, where all atoms are part of an icosahedron. Furthermore, the hexagonal unit cell contains three boron atoms, which are integral parts of the three-dimensional network without being parts of any icosahedron. Each of these atoms is situated between two  $B_{10}$  units, being octahedrally linked to six boron atoms, three from each  $B_{10}$  unit. The ideal boron content of the hexagonal unit cell is 315 boron atoms. The structure refinement of  $\beta$ -boron (9) indicates, however, that at least two of the boron positions are less than fully occupied. The boron atoms B(16) occupy the position denoted by *G* in Ref. (2) to only 33 %, and the B(13) positions are occupied to only 67 %.

The alterations in the network of  $\beta$ -rhombohedral boron induced by the dissolved metal atoms are small. No changes in the distances

between neighboring boron atoms are greater than 0.06 Å. As can be expected from the expansion of the unit cell (Table I), the changes are on an average greater in  $\text{MnB}_{\sim 28}$  than in  $\text{CuB}_{\sim 23}$ . The largest alterations are the decrease in the B(13)–B(14) distance from 1.812 Å in  $\beta$ -boron to 1.753 Å in  $\text{MnB}_{\sim 23}$  and to 1.761 Å in  $\text{CuB}_{\sim 28}$  and the increase in the B(11)–B(11) distance from 1.846 Å in  $\beta$ -boron to 1.896 Å in  $\text{MnB}_{\sim 23}$ . While the occupancy of the B(13) position as obtained in  $\text{MnB}_{\sim 23}$  (65 %) and in  $\text{CuB}_{\sim 28}$  (61 %) does not deviate significantly from that in  $\beta$ -boron, the occupancy of the B(16) position has decreased to 21 % in  $\text{CuB}_{\sim 28}$ . In  $\text{MnB}_{\sim 23}$  as well as in  $\text{CrB}_{\sim 41}$  (1), the B(16) position is empty.

The metal atoms in  $\text{MnB}_{\sim 23}$  and  $\text{CuB}_{\sim 28}$  occupy the various crystallographic positions to a fractional extent only. It appears that the



TABLE VI

COPPER-BORON AND COPPER-COPPER DISTANCES IN  $\text{CuB}_{12}$   
(Å UNITS)<sup>a</sup>

Cu(1)-3B(16)	1.136(19)	-B(15)	2.237(16)
-Cu(3)	2.126(10)	-2Cu(2'')	2.241(16)
-6B(1)	2.129(5)	-B(13)	2.259(15)
-3B(7)	2.153(3)	-B(3)	2.301(13)
-3B(5)	2.176(9)	-Cu(2')	2.348(20)
-3Cu(2')	3.860(9)	-B(13)	2.361(16)
		-B(2)	2.405(17)
Cu(2')-2Cu(2'')	0.435(18)	-B(12)	2.421(11)
-B(13)	2.217(11)	-B(3)	2.426(14)
-2B(1)	2.288(9)	-B(2)	2.456(18)
-B(12)	2.346(11)	-Cu(2'')	2.456(37)
-2Cu(2'')	2.348(20)	-Cu(2')	2.579(20)
-2B(2)	2.354(9)	-B(1)	2.589(17)
-2B(3)	2.404(11)	-B(3)	2.595(15)
-2B(2)	2.414(10)	-B(2)	2.596(17)
-2B(3)	2.424(10)	-B(2)	2.665(17)
-2B(13)	2.504(10)	-B(1)	2.680(16)
-2Cu(2'')	2.579(20)	-Cu(2'')	3.740(33)
-B(15)	2.616(9)	-2Cu(2'')	3.872(28)
-2Cu(2')	2.657(10)	-Cu(2')	3.993(35)
-Cu(1)	3.860(9)		
-Cu(3)	3.901(9)	Cu(3)-Cu(1)	2.126(10)
		-6B(1)	2.247(3)
Cu(2'')-Cu(2')	0.253(37)	-3B(9)	2.469(2)
-Cu(2')	0.435(18)	-3B(11)	2.641(4)
-B(13)	1.833(14)	-3B(10)	2.660(3)
-Cu(2'')	2.019(35)	-3B(16)	2.790(27)
-B(3)	2.193(12)	-3Cu(2')	3.901(9)

<sup>a</sup> Standard deviations in parentheses. Distances listed are Cu-B < 3.0 Å and Cu-Cu < 4.0 Å.

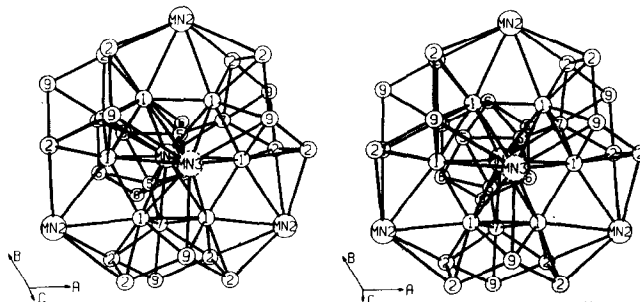


FIG. 1. Stereoscopic pair of drawings showing the environment of an Me(1) atom, as seen almost in the direction of the *c* axis. The dashed circle denotes an atomic position, which is presumably nonoccupied. See text.

TABLE VII  
MANGANESE-BORON AND MANGANESE-MANGANESE  
DISTANCES IN  $MnB_{\sim 23}$  (Å UNITS)<sup>a</sup>

Mn(1)-3B(5)	2.127(5)	-2B(13)	2.461(5)
-3B(7)	2.145(3)	-2B(3)	2.465(3)
-6B(1)	2.162(4)	-B(15)	2.507(1)
-Mn(3)	2.384(5)	-2Mn(2)	2.528(1)
-3Mn(2)	3.967(1)	-Mn(1)	3.967(1)
Mn(2)-B(13)	2.104(6)	Mn(3)-6B(1)	2.367(3)
-2B(3)	2.337(4)	-Mn(1)	2.384(5)
-B(12)	2.390(5)	-3B(9)	2.470(2)
-2B(1)	2.397(3)	-3B(11)	2.515(4)
-2B(2)	2.422(3)	-3B(10)	2.549(4)
-2B(2)	2.425(3)		

<sup>a</sup> Standard deviations in parentheses. Distances listed are Mn-B < 3.0 Å and Mn-Mn < 4.0 Å.

partial occupation of these positions (and also the B(13) and B(16) positions) may at least to some extent depend on spatial restrictions. While fully occupied positions would inevitably lead to abnormally short interatomic distances, such anomalous contacts can be avoided if the positions are only partially occupied and the vacancies distributed in a suitable manner. This feature becomes more evident in the following detailed discussion.

The environments of the metal atoms in  $MnB_{\sim 23}$  and  $CuB_{\sim 28}$  are shown stereoscopically in Figs. 1-3. The Me(1) atoms partly occupy the A(1) position, thus lying on the *c* axis and having 12 boron neighbors

at the corners of a truncated tetrahedron (see Fig. 1). In  $MnB_{\sim 23}$  the average Mn(1)-B distance is 2.15 Å, which is slightly shorter than the radius sum, 2.19 Å. The corresponding average in  $CuB_{\sim 28}$  is also 2.15 Å, while the radius sum is 2.16 Å. The very short distance of 1.14 Å between Cu(1) and the B(16) atoms occupying the *G* position renders a simultaneous filling of the two positions impossible. However, the low occupancies of the two positions, 6% for Cu(1) and 21% for B(16), permit a distribution of the atoms without any abnormally short contacts occurring. In  $MnB_{\sim 23}$ , where the A(1) position is occupied to 26%, the *G* position is nonoccupied, as in  $CrB_{\sim 41}$  where the A(1)

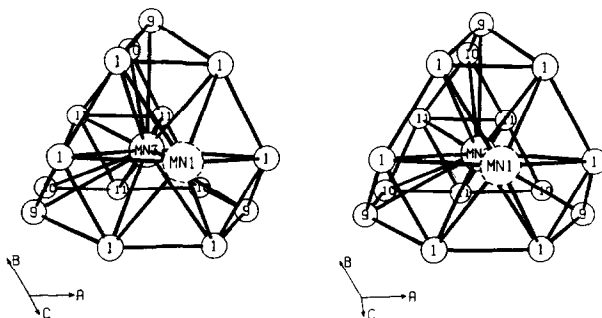


FIG. 2. Stereoscopic pair of figures showing the environment of an Me(3) atom, as seen almost parallel to the *c* axis. The dashed circle denotes an atomic position, which is presumably nonoccupied. See text.

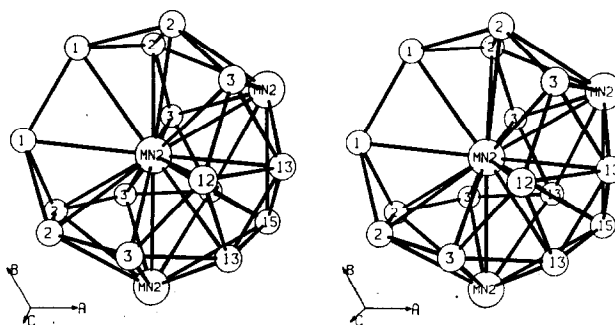


FIG. 3. Stereoscopic pair of drawings illustrating the coordination of an Me(2) atom, as viewed almost parallel to the  $c$  axis.

occupancy is 72% (1). Since the occupation of the B(16) position in  $\beta$ -rhombohedral boron is approximately 33% (9), the presence of metal atoms in position A(1) seems to cause a greater decrease in the occupancy of the B(16) position than that required to avoid the formation of very short B(16)–Me distances.

In  $\text{MnB}_{\sim 23}$  and  $\text{CuB}_{\sim 28}$  the  $E$  hole is partly occupied by metal atoms, Me(3). Like the A(1) hole, this hole is also situated on the  $c$  axis. The shortest distance between metal atoms occupying the A(1) and  $E$  holes is 2.38 Å in  $\text{MnB}_{\sim 23}$  and 2.13 Å in  $\text{CuB}_{\sim 28}$ . These distances are both considerably shorter than the corresponding metal–metal radius sum, 2.62 Å and 2.56 Å. Since the sum of the Me(3) and Me(1) occupancies is only 66% + 26% = 92% in  $\text{MnB}_{\sim 23}$  and 51% + 6% = 57% in  $\text{CuB}_{\sim 28}$  the atoms and vacancies are most likely distributed in such a way that all Me(1)–Me(3) distances have normal values. A metal atom in the  $E$  hole has 15–18 boron neighbors depending on the actual number of B(16) atoms present. The environment of the Me(3) atoms excluding B(16) is shown in Fig. 2. In  $\text{MnB}_{\sim 23}$  where the B(16) position is non-occupied, the fifteen Mn(3)–B distances vary between 2.37 Å and 2.55 Å, the average distance being 2.45 Å. In  $\text{CuB}_{\sim 28}$  the variation in the fifteen Cu(3)–B distances is greater, ranging from 2.25 Å to 2.66 Å. The average distance is 2.45 Å. However, the B(16) occupancy of 21% in  $\text{CuB}_{\sim 28}$  provides additional Cu(3)–B(16) contacts the distance being

2.79 Å. Thus, the Cu(3) atom may have between 15 and 18 boron neighbors.

The environment of a metal atom Me(2) in the  $D$  hole is shown in Fig. 3. In  $\text{MnB}_{\sim 23}$  this position is occupied to 43%. An Mn(2) atom has a maximum of 15 boron neighbors. The distances to 14 of these are between 2.34 Å and 2.51 Å, the distance to the fifteenth, one of three B(13) neighbors, is only 2.10 Å, which is 4% shorter than the radius sum, 2.19 Å. However, this distance is not to be considered as disturbingly short. The fact that the B(13) position is occupied to only 65% implies that an Mn(2) atom may have less than 15 boron neighbors. A consequence of this is that the short 2.10 Å distance may be less frequent. Furthermore, an Mn(2) atom has two Mn(2) neighbors at the short distance of 2.53 Å. The occupancy of the Mn(2) position being only 43% makes the occurrence of such close Mn–Mn distances less probable.

In  $\text{CuB}_{\sim 28}$  the metal atoms in the  $D$  hole are distributed on two crystallographically different positions. One position, Cu(2'), in 18(h) occupied to 22% and one, Cu(2''), in position 36(i) occupied to 11%. Of the three possible sites in a single  $D$  hole, one for Cu(2') and two for Cu(2'') (one on each side of the mirror plane), only one can be occupied per hole, the Cu(2')–Cu(2'') and Cu(2'')–Cu(2'') distances being only 0.44 Å and 0.25 Å, respectively. On an average, only 43% of the  $D$  holes accommodate copper atoms.

Although it cannot be excluded that some thermal anisotropy may occur for the copper

TABLE VIII  
OCCUPANCY FACTORS OF PARTIALLY OCCUPIED POSITIONS  
IN  $\text{MeB}_x$  AND  $\beta$ -RHOMBOHEDRAL BORON<sup>a</sup>

Atom	Occupation (%)			
	$\text{CrB}_{\sim 41}$ ( <i>I</i> )	$\text{MnB}_{\sim 23}$	$\text{CuB}_{\sim 28}$	$\beta$ -boron ( <i>9</i> )
Me(1)	71.9(6)	25.6(7)	6.1(5)	—
Me(2)	18.0(3)	43.1(5)	43.1(8) <sup>b</sup>	—
Me(3)	0	66.2(8)	50.5(6)	—
B(13)	71.7(18)	65.0(23)	61.1(19)	67
B(16)	0	0	20.9(22)	33

<sup>a</sup> Standard deviations are given in parentheses.

<sup>b</sup> The occupancy is the sum of that of Cu(2') in 18(*h*) and that of Cu(2'') in 36(*i*). The standard deviation is that obtained in a refinement with only one copper position in the *D* hole.

atoms in the *D* hole, the smoothness of the final difference synthesis may be taken as clear evidence for the correctness of the disordered distribution proposed for the Cu(2) atoms.

A copper atom in the Cu(2') position has as a maximum 15 boron neighbors at distances ranging from 2.22 Å to 2.62 Å. The number of neighbors may be less than 15 since three of them are B(13) atoms, the occupancy of this position being only 61%. The very short distance, 1.83 Å, between a copper atom in the Cu(2'') position and one of its three B(13) neighbors reduces the maximum number of boron neighbors of a Cu(2'') atom to 14. The corresponding distances vary between 2.19 Å and 2.68 Å.

The distances from a copper atom in a *D* hole to copper atoms situated in adjacent *D* holes range from 2.02 Å to 2.66 Å. It is in fact possible for a Cu(2') or a Cu(2'') atom to have two copper neighbors at normal Cu–Cu distances, the radius sum being 2.56 Å. However the occupancy of *D* holes by copper atoms is only 43%, and thus copper–copper contacts do not necessarily exist.

In  $\text{MnB}_{\sim 23}$  and  $\text{CuB}_{\sim 28}$  the metal atoms enter three sets of holes, *A*(1), *D*, and *E*, while in  $\text{CrB}_{\sim 41}$  only the *A*(1) and *D* holes accommodate metal atoms. This, as well as the differences in occupation of the holes by the three metals, see Table VIII, cannot be explained

as size-factor effects, since their Goldschmidt radii are almost equal. Nor can the alterations in the B(16) occupancy be entirely accounted for by spatial reasons. The explanations must be sought in the electronic structure of the metal atoms and the electronic requirements of the  $\beta$ -boron network. In a Mössbauer investigation of iron in  $\beta$ -rhombohedral boron (4) the isomer shifts obtained indicate the occurrence of iron atoms in both the ferric and ferrous state. Thus, iron seems to act as a donor of electrons in  $\beta$ -rhombohedral boron. Further measurements of the physical properties of transition-metal solutions in  $\beta$ -rhombohedral boron may provide more conclusive evidence concerning the nature of the chemical bonding in these materials.

#### Acknowledgments

The authors thank Professor I. Olovsson for all facilities put at their disposal. We are also deeply grateful to Professor S. Rundqvist and Dr. T. Lundström for their active interest in our work. Thanks are also due to Dr. J.-O. Carlsson and Mr. H. Karlsson for skillful assistance. This work has been financially supported by the *Swedish Natural Research Council*.

#### References

1. S. ANDERSSON AND T. LUNDSTRÖM, *J. Solid State Chem.* **2**, 603 (1970).

2. S. ANDERSSON AND J.-O. CARLSSON, *Acta Chem. Scand.* **24**, 1791 (1970).
3. J.-O. CARLSSON AND T. LUNDSTRÖM, *J. Less Common Metals* **22**, 317 (1970).
4. R. WÄPPLING, L. HÄGGSTRÖM, AND S. DEVANARAYANAN, *Phys. Scripta* **5**, 97 (1972).
5. "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962.
6. D. T. CROMER, *Acta Crystallogr.* **18**, 17 (1965).
7. M. HANSEN AND K. ANDERKO, in "Constitution of Binary Alloys," p. 248, McGraw-Hill, New York, 1958.
8. M. V. RAO AND R. N. ANDERSON, *J. Less Common Metals* **25**, 427 (1971).
9. J. L. HOARD, D. B. SULLENGER, C. H. L. KENNARD, AND R. E. HUGHES, *J. Solid State Chem.* **1**, 268 (1970).
10. J. L. HOARD AND R. E. HUGHES, in "The Chemistry of Boron and Its Compounds" (E. L. Muetterties, Ed.), p. 25, John Wiley, New York, 1967.