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Structural Investigation of Cr_2B_3, Cr_3B_4, and CrB by Single-Crystal Diffractometry

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The crystal structures of Cr_2B_3, Cr_3B_4, and CrB, of which Cr_2B_3 is a new compound, were investigated by single-crystal X-ray diffractometry. Cr_2B_3 crystallizes in the orthorhombic space group *Cmcm* with $a = 3.0264(5)$, $b = 18.115(4)$, $c = 2.9542(4)$ Å, $Z = 4$. The intensity data were collected on a four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation. The structure was solved by the Patterson method and refined with a full-matrix least-squares program to an R value ($= \Sigma|\Delta F|/\Sigma|F_o|$) of 0.021 for 1310 reflections. The structures of Cr_3B_4 and CrB were refined starting from published data; the R values were 0.032 (Cr_3B_4) and 0.022 (CrB). The structure of Cr_2B_3 can be described by stacking sheets of the AlB_2 structure type in the same manner as in the cases of Cr_3B_4 and CrB. The fusion of two neighboring sheets is performed by a 5Cr tetragonal pyramid and a Cr–B direct bond at their boundary. The essential difference between the structures of these compounds is only in the widths of the sheets. The relations of the widths of the sheets to the bond distances and angles of boron atoms are discussed.

1. Introduction

Recently we prepared crystals of a new boride, Cr_2B_3, from high-temperature Al–Cr–B melts and examined the optimum conditions to obtain single crystals in pure form containing no extra phase (*1*). In this paper we report the results of the structure analysis of this compound by single-crystal X-ray diffractometry. Structure refinements for Cr_3B_4 and CrB prepared by the same technique (*2*) as Cr_2B_3 were performed and the structural details are compared with those of Cr_2B_3.

2. Experimental

i. Cr_2B_3

A vertical alumina tube furnace equipped with silicon carbide resistors and alumina crucibles was used. The claimed purities of boron, chromium, and aluminum were 99.8, 99.9, and 99.99%, respectively. The growth conditions to obtain the present single crystal were as follows: 32.6 g of a mixture in which the atomic ratio of Cr : B : Al was 1 : 1.55 : 28.9 was heated to 1500°C, kept for 10 hr, cooled down to 1000°C at the rate of 50°C/hr, and then allowed to cool to

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TABLE I

CRYSTAL DATA AND CHEMICAL ANALYSIS

Crystal system	Orthorhombic
a (Å)	3.0264(5)
b (Å)	18.115(4)
c (Å)	2.9542(4)
Space group	*Cmcm*
Formula unit	Cr_2B_3
D_m[a] (g cm^{-3})	5.55(3)
D_x (g cm^{-3})	5.593
Z	4
Cr	72.4 wt%
B	23.8
Al	3.2
Fe	0.03
In total	99.43
Chemical composition	$CrB_{1.58}$ ($Cr_{1.89}B_3$)

[a] Pycnometer method with distilled water.

room temperature. The crystals grown in the reaction mixture were separated by dissolving the excess of aluminum in hydrochloric acid.

The crystals obtained were examined by X-ray diffraction. The X-ray diffraction patterns, as observed on oscillation and Weissenberg or precession photographs, revealed the Laue symmetry *mmm*. The systematic absences $h + k \neq 2n$ for hkl and $l \neq 2n$ for $h0l$ were consistent with the space groups *Cmcm*, *C2cm*, or *Cmc*2_1. The basic crystal data and the results of the chemical analysis are given in Table I. The lattice constants were determined by use of a single-crystal diffractometer; the wavelength employed was 0.71073 Å for Mo$K\alpha$ radiation. The density was measured by a pycnometer using distilled water.

For the intensity measurement a well-formed columnar crystal with dimensions 0.1 × 0.1 × 0.17 mm was used. The reflections ($0 \leqq h \leqq 7$, $-44 \leqq k \leqq 44$, $0 \leqq l \leqq 7$; $2\theta < 120°$) were measured by a Rigaku automated four-circle diffractometer, with graphite-monochromatized Mo$K\alpha$ radiation. The ω ($2\theta \leqq 40°$) or 2θ–ω ($40° < 2\theta < 120°$) scan modes were used at a rate of 2° min^{-1} in ω. Background counts of 10 sec were measured on each side of the scanning width ($\Delta\omega = 1.2 + 0.5 \tan \theta$). Three standard reflections were monitored and no noticeable variations were observed. A total of 1310 reflections with F_o values greater than 2.5 times the standard deviations were collected. They were corrected for the Lorentz, polarization, and absorption effects. Anisotropic secondary extinction effects were corrected in the course of the last least-squares refinement of the structure.

ii. Cr_3B_4 and CrB

The crystals were obtained by growth from high-temperature aluminum solutions (*2*). Approximately spherical crystal fragments with average diameters of 0.075 mm (Cr_3B_4) or 0.08 mm (CrB) were selected for intensity measurements. The reflections within the range of $2\theta < 120°$ ($0 \leqq h \leqq 7$, $0 \leqq k \leqq 31$, $-7 \leqq l \leqq 7$ for Cr_3B_4; $0 \leqq h \leqq 7$, $0 \leqq k \leqq 19$, $-7 \leqq l \leqq 7$ for CrB) were collected in the same manner as for the Cr_2B_3 single crystal. A total of 937 (Cr_3B_4) or 554 (CrB) reflections were used for the structure analysis. Absorption and secondary extinction corrections were made as in the case of Cr_2B_3. The crystal data for these materials are as follows: Cr_3B_4, space group *Immm*; $a = 3.0004(8)$, $b = 13.018(3)$, $c = 2.9516(8)$ Å; $Z = 2$. CrB, space group *Cmcm*; $a = 2.9782(7)$, $b = 7.870(1)$, $c = 2.9346(7)$ Å; $z = 4$.

3. Structure Determination and Refinement

i. Cr_2B_3

A noticeable amount of aluminum impurity was found in the Cr_2B_3 crystals by chemical analysis (Table I). Electron-probe microanalysis (EPMA) on the crystals, however, indicated that most of the impu-

TABLE II

FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS[a] OF Cr_2B_3

Atom	Site	x	y	z	B_{eq} (Å^2)[b]	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(1)	4c	0	0.42766(1)	$\frac{1}{4}$	0.30	40(1)	37(1)	37(1)	0	0	0
Cr(2)	4c	0	−0.29630(1)	$\frac{1}{4}$	0.29	37(1)	35(1)	40(1)	0	0	0
B(1)	4c	0	0.0236(1)	$\frac{1}{4}$	0.31	47(5)	38(4)	33(5)	0	0	0
B(2)	4c	0	0.1186(1)	$\frac{1}{4}$	0.30	42(5)	38(5)	34(5)	0	0	0
B(3)	4c	0	−0.1713(1)	$\frac{1}{4}$	0.34	47(5)	51(5)	33(5)	0	0	0

[a] The expression for anisotropic temperature factors is $\exp\{-10^{-4} \cdot 2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$.

[b] The equivalent isotropic temperature factor is defined by $B_{eq} = \frac{8}{3}\pi^2\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathrm{a}_i \cdot \mathrm{a}_j$.

rity came from aluminum inclusions in small pores inside the crystals and from minute fragments of the Al_2O_3 crucible sticking to the single crystals; the spectrum from aluminum was strongly detected at local spots but only faintly on the general surfaces of the crystals (*1*). Accordingly, the solution of Al to Cr_2B_3 was considered to be about the detection limit of the EPMA, ca. 0.05 wt%. Therefore, the replacement of chromium by impurity aluminum atoms at their crystallographic sites was neglected in the structure determination.

The positions of the Cr atoms were determined by examination of a Patterson map; the prominent peaks of the Patterson map were consistent with 2(4Cr) atoms in 2(4c) sites (0, 0.43, $\frac{1}{4}$; 0, −0.30, $\frac{1}{4}$) of the space group *Cmcm*. The boron sites were solved from a difference ($F_o - F_{Cr}$) Fourier map. The structure thus obtained was refined with the full-matrix least-squares program RADIEL (*3*). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The final reliability factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ or $Rw = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, calculated with anisotropic thermal and secondary extinction parameters, was 0.021 or 0.032. A refinement of the occupancy of the Cr sites did not result in a significant deviation from a full occupation. At this stage a difference Fourier map was featureless. The atomic coordinates and temperature factors are given in Table II.

ii. Cr_3B_4 and CrB

The structures of Cr_3B_4 (*4*) and CrB (*5*) were refined starting from published structural data. The final reliability factors R(Rw) obtained for Cr_3B_4 and CrB were 0.032(0.045) and 0.022(0.028), respectively. Since the intensity data of CrB showed very strong secondary extinction effects within the lower reflection angle range, the refinement was made by using the data with $\sin \theta/\lambda > 0.5$; the reduced number of 513 reflections was sufficient for the refinement of the much smaller number of structural parameters. The refined structural parameters of Cr_3B_4 and CrB are presented in Tables III and IV, respectively. The atomic scattering factors and anomalous dispersion correction factors were taken from Ref. (*6*). Most of the calculations for the structure analysis, other than the least-squares refinement, were performed using the program UNICS-III (*7*).

4. Description of the Structure and Discussion

As discussed in our previous paper (*1*), Cr_2B_3 is the only well-characterized boride compound designated M_2B_3 (M = metal). It

TABLE III

FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS[a] OF Cr_3B_4

Atom	Site	*x*	*y*	*z*	B_{eq} (Å^2)[a]	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(1)	4*g*	0	0.18624(3)	0	0.24	33(1)	23(1)	34(1)	0	0	0
Cr(2)	2*c*	$\frac{1}{2}$	$\frac{1}{2}$	0	0.25	37(2)	26(2)	31(2)	0	0	0
B(1)	4*g*	0	0.3611(2)	0	0.30	45(9)	43(9)	27(8)	0	0	0
B(2)	4*h*	0	0.4336(2)	$\frac{1}{2}$	0.29	43(9)	21(8)	46(9)	0	0	0

[a] The expression for anisotropic temperature factors or the equivalent temperature factor is the same as that used in Table II.

should be noted here, however, that the structure of Cr_2B_3 is essentially the same as the proposed structure for V_2B_3 (*8*). V_2B_3 was assumed to exist from an X-ray powder diagram of a mixture with V_3B_4 and VB_2, and the structure was proposed from space consideration.

The structure of Cr_2B_3 can be described by stacking sheets of the AlB_2 structure; the sheet is prepared by slicing the structure of the AlB_2 type in parallel to the (010) plane. The stacking is performed by translation $\frac{1}{2}$, $\frac{1}{2}$, 0 of the sheet according to the orthorhombic *C*-face-centered space group to which the structure of Cr_2B_3 belongs. The sheet has the width of half of the *b* axis length, lying parallel to the (010) plane (Figs. 1a and 1b). Since the outermost surface of each sheet is covered by a rectangular network of Cr atoms, the fusion between the sheets is effected by a direct bonding of Cr atoms. Thus in the bond between the sheets each 4Cr rectangle is capped by a Cr atom of the neighboring sheet so that they form a 5Cr tetragonal pyramid (Fig. 1b).

The interatomic distances are given in Table V. The Cr–Cr and B–B distances in a sheet of AlB_2 structure are compatible with those in CrB_2 (hexagonal, AlB_2 type: a = 2.973(1), c = 3.074(1) Å; Cr–Cr: 2.973(1), 3.074(1) Å; Cr–B: 2.304(1) Å; B–B: 1.716(1) Å) (*2*).

In Fig. 2, the central part of Fig. 1 is described with atom numbering. In addition to the direct Cr–Cr linkage, a Cr–B direct linkage is formed between adjacent sheets; the bond length of the former is 2.699(3) Å (Table V) and that of the latter is 2.263(2) Å (Table V, Fig. 2). The Cr–Cr bond length is approximately equal to the Cr metallic radius sum, 2.60 Å, of coordination number 12 (*9*), and the Cr–B bond length is the usual one compatible with those present within the sheet of AlB_2 structure. The Cr–Cr distances (2.801(3)–3.0264(5) Å) within the sheet are significantly longer than the sum of their metallic radii. Thus in each of

TABLE IV

FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS[a] OF CrB

Atom	Site	*x*	*y*	*z*	B_{eq} (Å^2)[a]	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	4c	0	0.14525(3)	$\frac{1}{4}$	0.28	33(1)	36(1)	38(1)	0	0	0
B	4c	0	0.4360(2)	$\frac{1}{4}$	0.36	39(4)	57(4)	41(4)	0	0	0

[a] The expression for anisotropic temperature factors or the equivalent temperature factor is the same as that used in Table II.

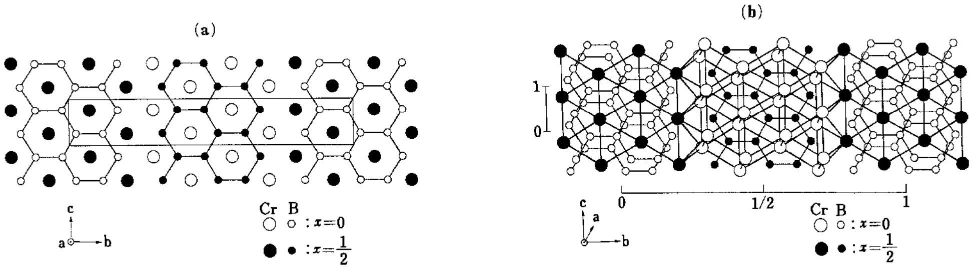

FIG. 1. The crystal structure of Cr_2B_3: (a) projection along the *a* axis; (b) a perspective drawing illustrating the boundary structure of the sheets of AlB_2 type.

the sheets, the strong connection between atoms may not occur through a Cr–Cr interaction but through Cr–B and B–B linkages.

The structures of Cr_3B_4 and CrB can be described in the same way as in the case of Cr_2B_3, by stacking sheets of AlB_2 structure. In the structure of Cr_2B_3, the width of the sheets corresponds to $3 \times d_{(010)}$ (Å) of the AlB_2-type structure (Fig. 1). On the other hand, in Cr_3B_4 and CrB, the widths of the sheets are $2 \times d_{(010)}$ (Å) and $1 \times d_{(010)}$ (Å), respectively (Figs. 3 and 4). In both crystal structures the structures of the boundaries of the sheets are the same as that in Cr_2B_3; fusion of the layers is performed by forming 5Cr tetragonal pyramids. The Cr–Cr bond lengths between the sheets are 2.6804(5) Å for Cr_3B_4 and 2.6625(4) Å for CrB; the Cr–B bond lengths between the sheets are 2.276(3) Å and 2.288(2) Å, for Cr_3B_4 and CrB, respectively.

The similarity of the structures in these compounds is significant; the only noticeable difference is in the width of the sheet of the AlB_2 structure. This common structural feature may account for the approximately equal microhardness of these very hard materials, including CrB_2 (*1*, *2*). On the other hand, as the structure of CrB_2 does not have the boundary structure seen in the other three, the similarity of the microhardness indicates that the Cr–Cr and Cr–B bonds in the boundary should be as

TABLE V

INTERATOMIC DISTANCES[a] IN Cr_2B_3 (Å)

$Cr(1)-2Cr(1)^{1,2}$	3.0264(5)	$Cr(2)^{9}-4B(3)^{14-17}$	2.194(4)
$-2Cr(1)^{3,4}$	2.954(5)	$B(1)^{19}-2Cr(1)^{0,1}$	2.305(1)
$-2Cr(1)^{5,6}$	3.008(3)	$-4Cr(1)^{5,6,20,21}$	2.291(1)
$-2Cr(2)^{7,8}$	2.801(3)	$B(2)^{19}-4Cr(1)^{5,6,20,21}$	2.275(4)
$Cr(2)^{9}-2Cr(1)^{5,6}$	2.801(3)	$-2Cr(2)^{9,11}$	2.160(1)
$-2Cr(2)^{10,11}$	3.0264(5)	$B(3)^{15}-2Cr(1)^{5,20}$	2.347(2)
$-2Cr(2)^{12,13}$	2.954(6)	$-4Cr(2)^{9,11,12,23}$	2.194(2)
$-4Cr(2)^{14-17}$	2.699(3)[b]	$-Cr(2)^{15}$	2.263(2)[b]
$Cr(1)-2B(1)^{18,19}$	2.305(1)	$B(1)^{19}-2B(1)^{15,17}$	1.707(6)
$-2B(1)^{14-17}$	2.291(1)	$-B(2)^{19}$	1.721(3)
$-2B(2)^{14-17}$	2.275(4)	$B(2)^{19}-B(1)^{19}$	1.721(3)
$-2B(3)^{18,19}$	2.347(2)	$-2B(3)^{15,17}$	1.759(6)
$Cr(2)^{9}-2B(2)^{18,19}$	2.160(1)	$B(3)^{15}-2B(2)^{19,22}$	1.759(6)
$-B(3)^{9}$	2.263(2)[b]		

[a] Those between every atom and its neighboring Cr and B atoms are listed. The atoms are designated with following symmetry codes: none or 0, $(0,y,\frac{1}{4})$; 1, $(1,y,\frac{1}{4})$; 2, $(-1,y,\frac{1}{4})$; 3, $(0,y,\frac{5}{4})$; 4, $(0,y,-\frac{3}{4})$; 5, $(0,1-y,-\frac{1}{4})$; 6, $(0,1-y,\frac{3}{4})$; 7, $(0,-y,-\frac{1}{4})$; 8, $(0,-y,\frac{3}{4})$; 9, $(0,1+y,\frac{1}{4})$; 10, $(-1,1+y,\frac{1}{4})$; 11, $(1,1+y,\frac{1}{4})$; 12, $(0,1+y,-\frac{3}{4})$; 13, $(0,1+y,\frac{5}{4})$; 14, $(-\frac{1}{2},\frac{1}{2}-y,-\frac{1}{4})$; 15, $(\frac{1}{2},\frac{1}{2}-y,-\frac{1}{4})$; 16, $(-\frac{1}{2},\frac{1}{2}-y,\frac{3}{4})$; 17, $(\frac{1}{2},\frac{1}{2}-y,\frac{3}{4})$; 18, $(-\frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$; 19, $(\frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$; 20, $(1,1-y,-\frac{1}{4})$; 21, $(1,1-y,\frac{3}{4})$; 22, $(\frac{1}{2},\frac{1}{2}+y,-\frac{3}{4})$; 23, $(1,1+y,-\frac{3}{4})$.

[b] Cr–Cr or Cr–B bond length between layers.

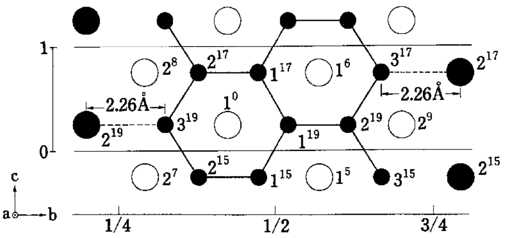

FIG. 2. A partial structure of Cr_2B_3 viewed along the *a* axis, illustrating the Cr–B bond between the sheets of AlB_2-type structure.

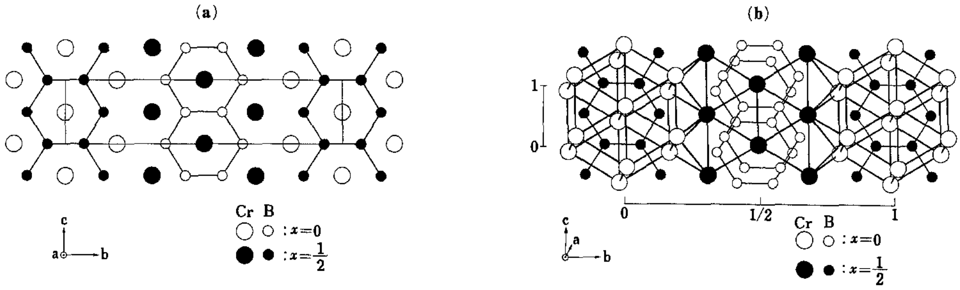

FIG. 3. The crystal structure of Cr_3B_4: (a) projection along the *a* axis; (b) a perspective drawing illustrating the boundary structure of the sheets of AlB_2 type.

strong as the Cr–B bond within the AlB_2-type structure.

In Table VI, the bond lengths and angles of the B atoms and the volumes of the 6Cr trigonal prisms in CrB, Cr_3B_4, Cr_2B_3, and CrB_2 are compared. The B–B bond length, for which an average is taken for Cr_3B_4 or Cr_2B_3, decreases with increasing boron content. The volume of the 6Cr trigonal prism, on the other hand, increases with increasing boron content. Considering that all the boron atoms in each compound are contained in 6Cr trigonal prisms, this might seem unreasonable. The superficial contradiction is, however, solved by acknowledging that the Cr atoms at the surface of the neighboring sheet interact strongly with the boron atoms in the sheet considered (for example, $Cr(2)^{19}$–$B(3)^{19}$ or $Cr(2)^{17}$–$B(3)^{17}$ in Fig. 2), and this interaction occurs with much greater frequency as the boron content decreases. As a result, the B–B bond having the B atom combined strongly with a Cr atom in the neighboring sheet elongates to a certain extent. In the case of Cr_2B_3, such a bond is $B(3)^{19}$–$B(2)^{17}$ or $B(2)^{19}$–$B(3)^{17}$ in Fig. 2; the bond length is 1.759(6) Å (Table V) and is noticeably longer than the bond length in the central zigzag chain, 1.707(6) Å ($B(1)^{17}$–$B(1)^{19}$ (Fig. 2 or Table V). A similar tendency is seen for Cr_3B_4. The B–B bond length in the zigzag chains which is elongated by the Cr–B interaction (Fig. 3) is 1.752(2) Å, and the length of the B–B bond between the chains is 1.729(4) Å. In the case of CrB, all the boron atoms in the single zigzag chain strongly interact with the Cr atoms of neighboring sheets, and the bond length is the longest (1.780(1) Å).

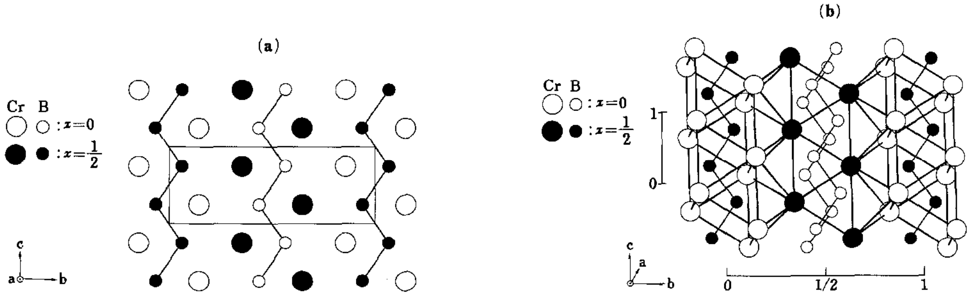

FIG. 4. The crystal structure of CrB: (a) projection along the *a* axis; (b) a perspective drawing illustrating the boundary structure of the sheets of AlB_2 type.

TABLE VI

COMPARISON OF BOND LENGTHS AND ANGLES OF B–B CHAINS, AND VOLUMES OF 6Cr TRIGONAL PRISMS AS OBSERVED IN Cr_2B_3, Cr_3B_4, AND CrB

Compound	B–B bond lengths[a] (Å)	Bond angle in B–B zigzag chains (Å)	Volume of 6Cr trigonal prism ($Å^3$)
CrB	1.780(1)	111.4(2)	9.991
Cr_3B_4	1.744(3)	114.8(2) 114.8(2)	10.736
Cr_2B_3	1.731(4)	114.2(2) 119.8(2)[b] 114.2(2)	10.637 11.716 (10.997) av.[b]
(CrB_2)	1.716(1)	120	11.765

[a] For Cr_3B_4 and Cr_2B_3 average bond lengths are presented, and the average values are calculated by taking account of the multiplicity of the bond length.

[b] The bond angle of the central zigzag chain.

The B–B bond angles (Table VI) in the B–B zigzag chains also suggest a strong Cr–B interaction between the sheets of AlB_2 structure. In the triple chains in Cr_2B_3, the bond angle of the central chain remains unchanged from that in the usual boron hexagonal network of AlB_2 structure. On the other hand, the bond angles of the chains on the outer side of the triple chains are reduced to the same extent as the angles of the chains in Cr_3B_4. The bond angle in CrB appears even more reduced. The boron atom which directly contacts the Cr atom of a neighboring sheet necessarily shifts toward the Cr atom from the center of the 6Cr trigonal prism which contains the boron atom. The distances of shift are 0.205(3), 0.192(3), and 0.123(2) Å for Cr_2B_3, Cr_3B_4, and CrB, respectively. The size of the shift increases as the width of the sheet of AlB_2 structure increases. This seems reasonable because the attraction by the Cr atom from the neighboring sheet of the opposite side through its combined B atom should decrease with the increased width of the sheet (Figs. 2–4).

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