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Synthesis and crystal structure of $Mg_2B_{24}C$, a new boron-rich boride related to "tetragonal boron *I*"

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Abstract

Single crystals of $Mg_2B_{24}C$, a new boron-rich boridecarbide of magnesium, were synthesized as black needles and columns by reaction of the elements in Ta ampoules and BN crucibles at 1300 °C. The crystal structure was determined by X-ray diffraction (P-4n2, $a = 8.9391(13)$ Å, $c = 5.0745(10)$ Å, $Z = 2$, 713 reflections, 64 variables, $R_1(F) = 0.0235$, $wR_2(I) = 0.0591$). It is closely related to "tetragonal boron *I*" and can be described as a tetragonal rod packing of corner-linked B_{12} icosahedra with C and Mg atoms in the voids. Each B_{12} icosahedron has 2 B–C bonds and 10 exohedral bonds to other icosahedra, 2 within the rod and 4×2 to neighbouring rods. The isolated C atoms are 4-fold coordinated forming distorted tetrahedra. Mg is placed on two crystallographically independent positions within the three-dimensional $B_{12}C$ network. $Mg_2B_{24}C$ is the first example for a compound related to "tetragonal boron *I*" with a stoichiometric composition.

Keywords: Synthesis; Single crystals; Structure analysis; Magnesium boride; Boron-rich boride; WDX measurements

1. Introduction

The chemistry of boron-rich borides is ruled by the dominance of icosahedral units and the frequent occurrence of partial and/or mixed occupations. All these features are characteristic for boron as an element with electron deficiency [1,2]. Problems arising from this are the real and postulated structures of elementary boron. A nice example is the so-called "tetragonal boron *I*" which was first published in 1943 as a modification of elementary boron [3–5]. The crystal structure is remarkably simple and bases on a framework of B_{12} icosahedra which are linked by exohedral boron–boron bonds and additional isolated boron atoms with tetrahedral coordination (Fig. 1). Because the unit cell contains four icosahedra and two isolated boron atoms, the formula $(B_{12})_4(B)_2 = B_{50}$ is used. Later on it was shown that there are additional isolated boron atoms and the formation of "tetragonal boron *I*" is connected to the presence of small amounts of carbon and nitrogen. Therefore, a formulation as boron-rich boride is more correct: $B_{25}C$ and $B_{25}N$, respectively [6,7]. The reason for the pronounced tendency to the incorporation of foreign atoms can be seen in the special requests of boron polyhedra. According to Wade's rules, B_{12} icosahedra with 12 exohedral bonds form very stable closo-clusters as B_{12}^{2-} units. This favours the incorporation of more electron-rich elements like carbon or nitrogen and/or the uptake of metal atoms which can transfer their electrons to the boron polyhedra by formation of cations. In the case of "tetragonal boron *I*," this is a very common phenomenon. Table 1 gives an overview on boron-rich borides derived from "tetragonal boron *I*".

A closer view to the published investigations shows sometimes contradicting results. The uncertainties result

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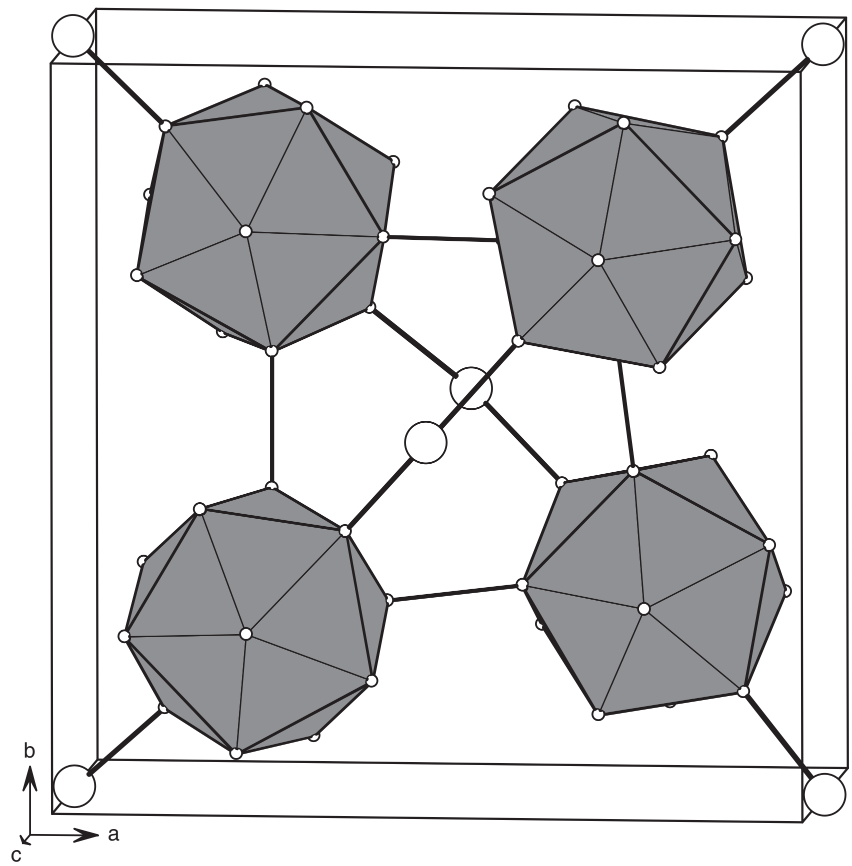

Fig. 1. Crystal structure (unit cell) of "tetragonal boron I".

Table 1
Overview of compounds related to "tetragonal boron I" and "β-AlB_{12}"

Compound	Space group	Lattice constants *a* and *c* (Å)		References	Remarks
Tetrag. boron *I*	$P4_2/nnm$	8.75	5.06	[4,5]	s.c. (single crystal)
$B_{25}C$	P-42m	8.753	5.093	[6–9]	s.c., CVD
$B_{25}N$	P-42m	8.634	5.128	[6–9]	s.c., CVD
BeB_{12}	Tetrag. boron *I*	8.80	5.08	[10a]	s.c.
BeB_{12}	$P4_2/nnm$	8.856	5.116	[10b]	s.c.
$AlBeB_{24}$	$P4_2/nnm$	8.82	5.08	[11]	s.c., Be not labelled
$B_{25}Ti_{0.94}$	$P4_2/nnm$	8.830	5.072	[12a]	s.c., CVD, twinned
$B_{25}V_{0.65}$	$P4_2/nnm$	8.824	5.072	[12b]	s.c., CVD, twinned
$B_{25}Ni$	$P4_2/nnm$	8.986	5.078	[13]	s.c.
$B_{25}Zn$	$P4_2/nnm$	9.006	5.06	[14]	Powder
$B_{25}AlCu_{0.8}$	P-4n2	9.002	5.069	[15]	s.c.
$B_{48}Al_3Si$	Tetragonal	8.91	5.05	[16]	Powder, film data
$B_{24}CTi_{0.93}$	$P4_2/nnm$	8.876	5.062	[17]	s.c., CVD
$B_{24}CV_{0.65}$	$P4_2/nnm$	8.857	5.070	[17]	s.c., CVD
$B_{48}Al_{2.7}C_2$	Orthorhombic distortion, super structure			[18,19]	s.c., phase transition

from two reasons. Firstly, the identity of the "isolated" atoms is not always clear. From many investigations it is known that commercially available boron usually contains small amounts of carbon. If no special care is taken, there is always some carbon in the system that occupies the "tetrahedral" positions between the icosahedra. In several cases the carbon content was confirmed if suitable analytical methods were used (exceptions: $B_{25}N$ [8,9], $B_{25}Ti$ [12a], $B_{25}V$ [12b], BeB_{12} [10b].

Secondly, boron-rich borides are compounds where the three-dimensional framework of icosahedra is stabilized by additional electrons which come from metal atoms incorporated into the crystal structure. These metal atoms usually show partial occupation and/or disorder. The separation between these two subjects is very difficult because of synthetic, crystallographic and analytical reasons.

Besides a complex crystal chemistry, boron-rich borides also show interesting material properties. High hardness (according to Mohs 9–9.5), high melting points (2000–2500 °C), low density (2.5 g/cm^3), stability in air up to about 700 °C and low chemical reactivity (stable against hot acids and bases) allow the application in metallic and ceramic composite materials (metal matrix composites, ceramic matrix composites [20]), as high-temperature material, as abrasives and in cutting tools [21] as well. Furthermore, applications as thermoelectrics [22] and HT semiconductors [23] are very promising.

Now we have synthesized the new compound $Mg_2B_{24}C$ by reacting the elements in a copper melt. Its crystals structure is related to "tetragonal boron I". Within this structure family, $Mg_2B_{24}C$ is the first stoichiometric compound free from mixed and/or partial occupations and disordered atoms.

2. Synthesis

Single crystals of $Mg_2B_{24}C$ were synthesized from the elements in a Cu/Mg melt. Cu, Mg, B and C were mixed in a molar ratio of 300:100:75:3 and pressed into a pellet (ca. 2 g). The pellet was put into a h-BN crucible and the crucible into a tantalum ampoule, which was sealed by welding with an electric arc. The ampoule was heated under an argon atmosphere up to 1300 °C and held for 25 h, cooled with 10 K/h to 500 °C and with 100 K/h to room temperature. The ampoule was opened and the excess melt dissolved in conc. nitric acid. As a residue, black needles and columns with tetragonal cross-section were yielded (max. length: 0.4 mm; max. diameter: 0.15 mm).

Qualitative and quantitative analyses on selected single crystals were conducted by EDX and WDX measurement. Several single crystals were checked by EDX (Jeol, JSM 6400 with Ge detector, sample fixed with conducting glue on a graphite platelet mounted on an Al sample holder). It confirmed magnesium as the only heavy element ($Z>10$). By WDX (Jeol, JXA 8200), a more detailed analysis with special consideration of light elements ($4<Z<11$) was done to confirm the carbon content and to exclude the incorporation of nitrogen and oxygen. For the WDX measurements, single crystals were fixed in a matrix with Cu/epoxy resin and polished to get a clear surface and to assure the measurement of the interior of the crystal [24] and not the surface which may be influenced by contact to the melt. Boron, carbon and magnesium were confirmed as the only elements with $Z>4$. The molar ratio B:C:Mg was found to be 88.9:4.1:7.0 in excellent agreement with the ideal composition of a stoichiometric compound $Mg_2B_{24}C$ determined by X-ray methods (88.9:3.7:7.4).

3. Structure solution and refinement

Investigations with a single crystal diffractometer equipped with Mo$K\alpha$ radiation and an image plate detector (Fa. Stoe, IPDS I) revealed a primitive tetragonal unit cell with $a = 8.9660(13)$ Å and $c = 5.0898(10)$ Å, indicating a similarity to "tetragonal boron I" ($P4_2/nnm$, $a = 8.75$ Å, $c = 5.06$ Å). Measurement of 5255 intensities gave a data set of 713 independent reflections (661 with $I>2\sigma(I)$). The reflection condition $h+l=2n$ for reflections hhl was fulfilled but not the condition $h+k=2n$ for reflections $hk0$. Therefore, the structure solution was started in space group P-4n2. Direct Methods (SHELXL [25]) revealed the position of the Mg atoms, carbon and most of B atoms. Missing atoms were localized by subsequent difference Fourier syntheses. The labelling B/C was done according to bonding distances and electron densities. Refinements of the occupation factors revealed that all positions were fully occupied within the very small standard deviations. Because of the low absorption coefficient (0.25 mm^{-1}), no correction of absorption effects was done. Finally, R-values of $R_1(F) = 0.0235$ and $wR_2(I) = 0.0591$ were yielded for 713 reflections and 63 free variables. All atoms were refined with anisotropic thermal displacement parameters. Despite the low electron number of boron and carbon, the values U_{equ} and U_{ij} are small and nearly equal confirming correct assignment, full occupation and a well-ordered structure. The different values of the thermal displacement parameters for the two Mg atoms result from the different surroundings (see below). Details of the refinement are listed in Table 2. Coordinates and thermal displacement parameters are given in Tables 3 and 4. Selected distances are shown in Table 5. Further details of the structure refinement (complete list of distances and angles, F_o/F_c list) may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Zusammenarbeit, D-76344 Eggenstein-Leopoldshafen (Germany) (fax: +49 724 808 666: e-mail: crysdata @fiz-karlsruhe.de) on quoting the registry number CSD-416341, the name of the authors and this journal.

4. Results and discussion

4.1. Crystal structure of $Mg_2B_{24}C$

The crystal structure of $Mg_2B_{24}C$ (Fig. 2) can directly be derived from "tetragonal boron I".

B_{12} icosahedra and isolated carbon atoms form a three-dimensional framework with covalent bonds. All boron atoms of the icosahedron perform one exohedral bond, 10 to a neighbouring icosahedron, two to the isolated carbon atoms. Each C atom connects four B_{12} icosahedra by single bonds with a bond length of 1.669(1) Å. The B–C–B bonding angles of 98.2° and 135.5° describe a strongly compressed tetrahedron. The exohedral B–B distances are between 1.678(2) and 1.777(2) Å (average: 1.756 Å) and shorter than the endohedral bonds (1.737(2)–2.079(2) Å,

Table 2
Crystallographic data and refinement of $Mg_2B_{24}C$

Compound	$Mg_2B_{24}C$
Temperature	293(2) K
Crystal size	Black column $0.1 \times 0.1 \times 0.3\,mm^3$
Crystal system	Tetragonal
Space group	*P*-4*n*2 (No. 118)
Unit cell	$a = 8.9391(13)$ Å $c = 5.0745(10)$ Å $V = 405.5(1)$ Å^3 $Z = 4$
$d_{calc.}$	$2.621\,g/cm^3$
Data collection	STOE IPDS I, Mo$K\alpha$; $\lambda = 0.71073$ Å (graphite monochromated) $0° \leqslant \omega \leqslant 180°, \Psi = 0°, \Delta\omega = 2°$ 360 s exposure time $3° < 2\theta < 65.8°$ $-13 < h < 13$; $-13 < k < 13$; $-7 < l < 7$
μ	$0.25\,mm^{-1}$
Absorption correction	None
$R_{int.}/R_{sigma}$	0.0694/0.0329
Refinement	SHELXL [25]; full-matrix least-squares refinement on F^2
$N(hkl)$ meas.; unique	5255; 713
$N'(hkl)$ $(I > 2\sigma(I))$	661
Parameters refined	63
R values	$R_1 = 0.0235$, w$R_2 = 0.0591$
All data	$R_1 = 0.0267$, w$R_2 = 0.0591$
Weighting scheme	0.0395/0.0 (SHELXL [25])
Extinction correction	0.000(19) (SHELXL [25])
Goodness of fit	1.046
Residual electron density (max., min., sigma)	$+0.26/-0.20/0.06\,e^-/$Å^3

Table 3
Atomic coordinates, isotropic displacement parameters (in (Å^2)) and site occupation factors of $Mg_2B_{24}C$, e.s.d.'s in parentheses

Atom	Site	x	y	z	sof	U_{eq}
Mg1	2*a*/−4	0.0	0.0	0.0	0.993(6)	0.0089(2)
Mg2	2*d*/2 2 2	0.0	0.5	0.75	0.993(6)	0.0125(2)
C	2*b*/−4	0.0	0.0	0.5	0.97(2)	0.0060(3)
B1	8*i*	0.7642(1)	0.2516(1)	0.5855(2)	1.00(1)	0.0067(2)
B2	8*i*	0.1281(1)	0.1159(1)	0.6245(2)	0.98(1)	0.0068(2)
B3	8*i*	0.2691(1)	0.4076(1)	0.5877(3)	1.00(1)	0.0067(2)
B4	8*i*	0.4227(1)	0.2591(1)	0.5845(3)	0.99(1)	0.0070(2)
B5	8*i*	0.3252(1)	0.0791(1)	0.5984(3)	1.01(1)	0.0072(2)
B6	8*i*	0.0982(1)	0.3065(1)	0.5830(3)	1.02(1)	0.0071(2)

Table 4
Anisotropic displacement parameters (in (Å^2)) of $Mg_2B_{24}C$, e.s.d.'s in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg1	0.0066(2)	0.0066(2)	0.0135(4)	0	0	0
Mg2	0.0127(2)	0.0127(2)	0.0122(4)	0.0067(2)	0	0
C	0.0060(5)	0.0060(5)	0.0062(9)	0	0	0
B1	0.0070(4)	0.0069(4)	0.0062(5)	0.0010(3)	−0.0006(3)	−0.0004(4)
B2	0.0072(4)	0.0066(4)	0.0065(5)	0.0004(3)	0.0001(3)	−0.0005(3)
B3	0.0067(4)	0.0072(4)	0.0063(5)	0.0004(3)	−0.0009(4)	0.0001(3)
B4	0.0065(4)	0.0071(4)	0.0073(6)	0.0000(3)	0.0007(3)	0.0000(4)
B5	0.0069(4)	0.0072(4)	0.0074(6)	0.0000(3)	0.0009(4)	0.0001(4)
B6	0.0074(4)	0.0064(4)	0.0073(6)	0.0002(3)	−0.0011(4)	−0.0002(4)

(average: 1.832 Å). These relations are typical for boron-rich borides [26]. B1 plays a special role because it has no B–Mg contacts and shows a quite short exohedral distance B1–B1 of 1.678(2) Å. Remarkable is the unusual long distance B4–B4 with 2.079(3) Å which is the longest ever found for a boron-rich boride. This can be explained because this edge of the icosahedron is strongly involved in the Mg–B interaction (see below). A similar situation is observed in $B_{24}AlCu_{0.8}$ (2.026 Å) [15] and in $B_{48}Al_{2.7}C_2$ (2.03 Å) [18]. This enlargement is obviously related to the metal atom interaction because it is not observed in $B_{25}C$ [12a], $B_{25}N$ [12b], $B_{24}CTi_{0.92}$ [17], $B_{24}CV_{0.65}$ [17] and α-rhombohedral boron [27] where the longest endohedral distances are 1.86–1.89 Å.

Table 5
Selected distances (in (Å)) and angles (in (deg)) in $Mg_2B_{24}C$

B1–B1 *1.678(2)*	B2–C *1.669(1)*	B3–B4 *1.753(1)*
B1–B6 1.737(2)	B2–B6 1.738(1)	B3–B 1.775(1)
B1–B4 1.769(2)	B2–B5 1.797(1)	B3–B1 1.781(1)
B1–B3 1.781(2)	B2–B3 1.814(2)	B3–B6 1.803(1)
B1–B5 1.803(1)	B2–B4 1.821(2)	B3–B2 1.814(1)
B1–B2 1.868(1)	B2–B1 1.868(2)	B3–B4 1.910(1)
B1–B 1.792[a]	B2–B 1.808[a]	B3–B 1.817[a]
B4–B3 *1.753(1)*	B5–B4 1.777(2)	B6–B1 1.737(2)
B4–B1 1.769(2)	B5–B2 1.797(1)	B6–B2 1.738(1)
B4–B5 1.777(2)	B5–B1 1.803(1)	B6–B3 1.775(1)
B4–B2 1.821(2)	B5–B4 1.831(1)	B6–B3 1.803(2)
B4–B5 1.831(1)	B5–B6 *1.841(1)*	B6–B5 *1.841(1)*
B4–B3 1.910(1)	B5–B5 1.957(2)	B6–B6 2.079(3)
B4–B 1.842[a]	B5–B 1.833[a]	B6–B 1.826[a]
C–B2 1.669(1) 4*x*	Mg1–B3 2.267(1) 4*x*	Mg2–B6 2.117(1) 4*x*
B2–C–B2 135.50(7) 2*x*	Mg1–B4 2.302(1) 4*x*	Mg2–B5 2.463(1) 4*x*
B2–C–B2 98.24(2) 4*x*	Mg1–B2 2.453(1) 4*x*	Mg2–B3 2.673(1) 4*x*
	Mg1–C 2.545(1) 2*x*	

Italics: Exohedral B–B distances.
[a]Averaged values.

The two Mg sites are not only different by site symmetry but also by its position within the framework of B_{12} icosahedra and carbon atoms (Fig. 3). Mg1 with site symmetry -4 is located above and below the carbon atom and coordinated by four triangles of four icosahedra, resulting in a 8+4 pattern with Mg–B distances of 2.267(1), 2.302(1) and 2.453(1) Å. The coordination is completed by two carbon atoms (2.545(1) Å). Mg2 is also 12-fold coordinated by boron with distances of 2.117(1), 2.463(1) and 2.673(1) Å according to a 4+8 pattern, but the differences are much more pronounced. The coordinating boron atoms can be assigned to the vertices of six icosahedra. Despite of the significantly different Mg–B distances, the effective coordination numbers are comparable for both Mg atoms. Following a suggestion of Pauling [28], bond orders can be estimated from the sum of

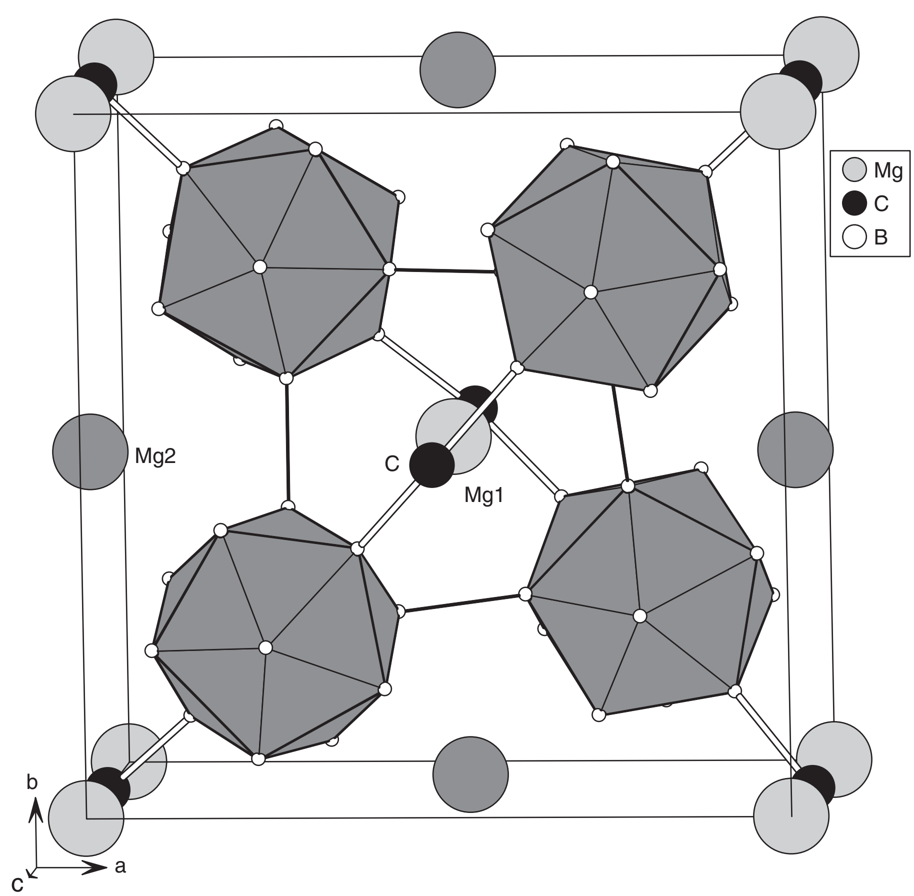

Fig. 2. Crystal structure (unit cell) of $Mg_2B_{24}C$.

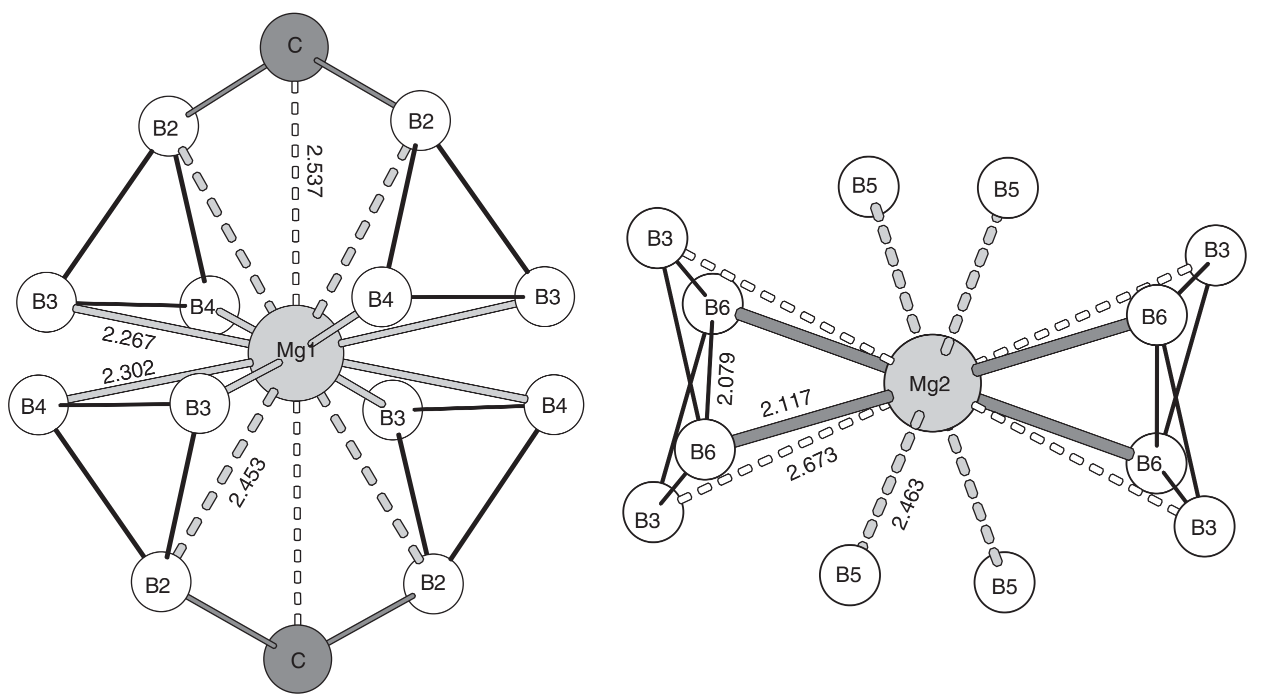

Fig. 3. Coordination of Mg1 (left) and Mg2 (right).

the single bond radii. Using the equation $d_n = d_1 - 0.71\,\text{Å}\log n$ (n: bond order; d_1: sum of single bond radii; d_n: observed distance) and single bond radii of $r_B = 0.88\,\text{Å}$ and $r_{Mg} = 1.40\,\text{Å}$ bond orders of 10.16 are yielded for Mg1 and of 10.12 for Mg2.

4.2. Description by rod packing

A clearly arranged survey on the compounds related to "tetragonal boron *I*" is possible using the concept of rod packing developed by O'Keeffe and Andersson [29]. In the crystal structure of "tetragonal boron *I*," the icosahedra form linear rods by connection via apices in *trans* position. These rods are arranged as tetragonal bodycentred packing, i.e. with respect to the centres of the icosahedra the four neighboured rods are shifted by $c/2$ against each other. In this rod packing (Fig. 4) the isolated boron, carbon or nitrogen atoms occupy positions coordinated by the apices of four icosahedra with distorted tetrahedral geometry. The voids occupied by Mg1 are also surrounded by four icosahedra but according to the arrangement of the icosahedra these voids are coordinated by four triangles. The resulting polyhedron can be described as a truncated tetrahedron (Friauf-polyhedron). In total, 1/2 of the channels between the rods are occupied by C and Mg1. The distance between pseudo-tetrahedral voids amounts to $c/2$. The second half of the channels is filled by Mg2. With respect to the icosahedra centres, Mg2 is in pseudo-octahedral voids with two shorter distances to icosahedra in the same height and four longer distances. The orientation of the icosahedra is in a way that two edges and four apices point to the Mg2 atom. Therefore it results in a 12-fold coordination with four quite short (2.12 Å) and eight significantly longer distances (2.46−2.67 Å). Because of the very short distances, Mg2–B6 the boron atoms neighboured to B6 (B3) contribute as the longest distances to the Mg2 coordination. A closer view shows that two pseudo-octahedral voids with site symmetry 2 2 2 alternate in c-direction in a distance of $c/2$ (sites 2c and 2d). The differences between the two positions are the short distances to the edges of the icosahedra which are rotated by 90° against each other (Fig. 4).

Compared to the structure of "tetragonal boron *I*" and the other related compounds, the ordered occupation of the octahedral voids leads to a symmetry reduction from $P4_2/nnm$ to $P\text{-}4n2$. An explanation for the ordered occupation may be that a distance of $c/2$ between neighboured Mg atoms is too short. A similar distribution of the metal atoms is observed for $B_{25}AlCu_{0.8}$ [15] where Al occupies the site of Mg1 and Cu partially (80%) the site of Mg2. An unanswered question is why the minimum distances observed are 2.26 Å for Al–B and 2.05 Å for Cu–B. This is in contradiction to the radii.

In $B_{24}CTi_{0.93}$ and $B_{24}CV_{0.65}$, the metal atoms occupy partially only the "tetrahedral" position (site 2a in $P\text{-}4n2$, site 2b in $P4_2/nnm$), so no symmetry reduction takes place.

Furthermore, the symmetry reduction from $P4_2/nnm$ to $P\text{-}4n2$ allows a shift of the icosahedra in direction of the diagonals (110) and (−110) of about 0.1 Å. This is also related to the short Mg2–B4 distances because it enables relaxation. The full occupation of the 2c site allows to maintain the tetragonal symmetry, in contrast to $B_{48}Al_{2.7}C_2$ where the partial occupation leads to an orthorhombic super structure and twinning, which is

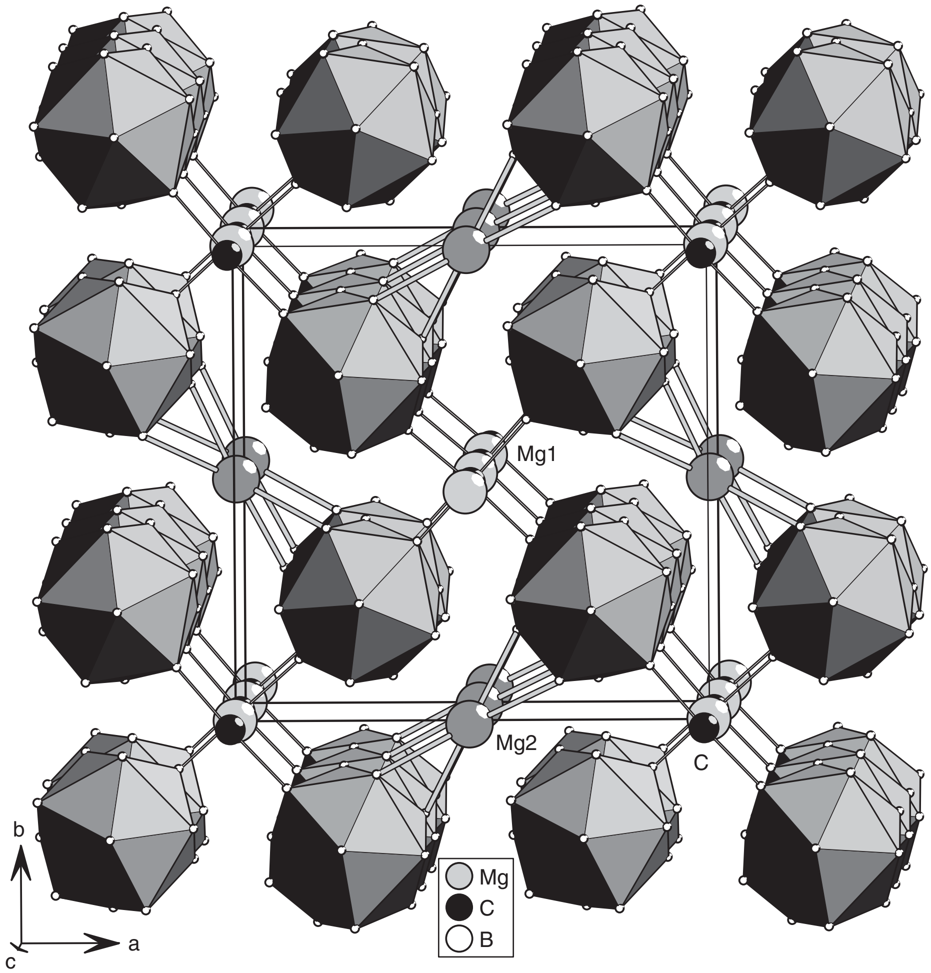

Fig. 4. Rod packing in $Mg_2B_{24}C$, exohedral B–B bonds omitted for clarity.

combined with a phase transition at 650 °C [18]. The close correlation of the Mg2 positions to the symmetry of the crystal structure is shown by ignoring the violation of the reflection condition $h+k=2n$. The data set of $Mg_2B_{24}C$ can also be refined in space group $P4_2/nnm$ (389 reflections, 39 parameters, $R_1(F)=0.13$, $wR_2(I)=0.33$), but the site of Mg2 has only an occupation of 0.5 and the distance Mg2–B is shortened to 1.998(8) Å.

In $AlBeB_{24}$ [11], $B_{25}AlCu_{0.8}$ [15] and $B_{48}Al_{2.7}C_2$ [18], the Al atoms on the position of Mg1 are disordered leading to a shift of about ±0.3 Å in the direction of the C atoms. This disorder is not observed for $Mg_2B_{24}C$ probably because magnesium is bigger than aluminium and can fill the void.

$Mg_2B_{24}C$ is the first stoichiometric member of its structural family and one of the few examples of a boron-rich boride with stoichiometric composition. An explanation for this may be that $Mg_2B_{24}C$ fits perfectly the rules of Wade [30] and Longuet-Higgins and Roberts [31] which give the number of electrons needed for the stabilization of boron polyhedra. According to these rules, a closo-cluster of n atoms has $n+1$ binding molecular orbitals. If every atom of the polyhedron performs one regular exohedral $2e$–$2c$ bond, it will need $2n+2$ electrons to fill the bonding MO's at its best. In the case of $Mg_2B_{24}C$, each B_{12} icosahedron has 12 "normal" exohedral $2e$–$2c$ bonds. The two electrons needed for the highest stability as a B_{12}^{2-} unit are provided by magnesium. The carbon atom with its tetrahedral coordination has four regular B–C bonds and will neither give nor need additional electrons. In recent times, validity and reliability of the electron counting rules of Wade and Longuet-Higgins have been proven for other boron-rich borides like $MgB_{12}C_2$ [24,32], $MgB_{12}Si_2$ [33], $LiB_{13}C_2$ [34] and $Li_2B_{12}C_2$ [34].

5. Conclusions

The structure of $Mg_2B_{24}C$ represents a missing link between "tetragonal boron I" and the metal-containing compounds listed in Table 1. It explains a number of problems (symmetry, occupation factors, etc.) observed for compounds related to "tetragonal boron I". All structural features of $Mg_2B_{24}C$ can be explained by the typical properties of boron-rich boridecarbides of magnesium. The analytical results by EDX and WDX are in perfect agreement with the X-ray results and the structure chemistry of boron-rich compounds.

Further investigations on physical properties like hardness, conductivity [35], vibrational spectra, UV–Vis spectra, thermoelectric power and band structure calculations are in progress.

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