CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200601002

Synthesis, Crystal Structure, and Properties of Two Modifications of $MgB_{12}C_2$

Volker Adasch,[a] Kai-Uwe Hess,[b] Thilo Ludwig,[c] Natascha Vojteer,[c] and Harald Hillebrecht*[c]

Abstract: Single crystals of two modifications of the new magnesium boride carbide $MgB_{12}C_2$ were synthesized from the elements in a metallic melt by using tantalum ampoules. Crystals were characterized by single-crystal X-ray diffraction and electron microprobe analysis (energy-dispersive (EDX) and wavelength-dispersive (WDX) X-ray spectroscopy). Orthorhombic $MgB_{12}C_2$ is formed in a Cu/Mg melt at 1873 K. The crystal structure of o-$MgB_{12}C_2$ ($Imma$, $Z=4$, $a=5.6133(10)$, $b=9.828(2)$, $c=7.9329(15)$ Å, 574 reflections, 42 variables, $R_1(F)=0.0208$, $wR_2(I)=0.0540$) consists of a hexagonal primitive array of B_{12} icosahedra with Mg atoms and C_2 units in trigonal-prismatic voids. Each icosahedron has six exohedral B–B and six B–C bonds. Carbon is tetrahedrally coordinated by three boron atoms and one carbon atom with a remarkably long C–C distance of 1.727 Å. Monoclinic $MgB_{12}C_2$ is formed in an Al/Mg melt at 1573 K. The structure of m-$MgB_{12}C_2$ ($C2/c$, $Z=4$, $a=7.2736(11)$, $b=8.7768(13)$, $c=7.2817(11)$ Å, $\beta=105.33(3)$°, 1585 reflections, 71 variables, $R_1(F)=0.0228$, $wR_2(I)=0.0610$) may be described as a distorted cubic close arrangement of B_{12} icosahedra. Tetrahedral voids are filled by C atoms and octahedral voids are occupied by Mg atoms. The icosahedra are interconnected by four exohedral B–B bonds to linear chains and by eight interstitial C atoms to form a three-dimensional covalent network. Both compounds fulfill the electron-counting rules of Wade and Longuet-Higgins.

Keywords: boron · crystal growth · magnesium boride carbide · structure elucidation · WDX measurements · X-ray diffraction

Introduction

Because boron-rich borides and boride carbides contain a great variety of boron polyhedra, they form their own class of compounds and show unique structure chemistry[1] and physical properties.[2] Furthermore, they are of growing interest in a number of applications in material sciences, for example as high-temperature materials,[3] abrasives,[4] composites,[5] high-T_c superconductors,[6] high-temperature semiconductors,[7] and high-temperature thermoelectrics.[8] Our previous investigations have shown that the use of molten metals allows synthetic access to new borides and boride carbides not available by conventional high-temperature methods.[9–11] Motivated by the discovery of superconductivity in MgB_2[12] and the excellent material properties of Mg alloys[13] we extended this method to compounds containing Li[14] and Mg[15–17] by using h-BN crucibles and tantalum ampoules.

MgB_2C_2[18] was the only ternary compound reported for the system Mg/B/C.[19,20] The crystal structure of MgB_2C_2 can be described as a heterographite, in which boron and carbon form hexagonal layers and magnesium is intercalated between the layers.

Recently we reported on $Mg_2B_{24}C$, the first boron-rich boride carbide of magnesium,[17] which is related to "tetragonal boron I". Herein, we report on the synthesis and crystal growth of two modifications of $MgB_{12}C_2$ by the use of Cu/Mg or Al/Mg melts. On the basis of single-crystal data the crystal structures were solved and refined. Compositions

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[a] Dr. V. Adasch
DRONCO AG
Wiesenmühle 1
95632 Wunsiedel (Germany)

[b] Dr. K.-U. Hess
Ludwig-Maximilians-Universität München
Institut für Mineralogie, Petrologie und Geochemie
Theresienstrasse 41/III, 80333 München (Germany)

[c] Dr. T. Ludwig, Dipl.-Chem. N. Vojteer, Prof. Dr. H. Hillebrecht
Albert-Ludwigs-Universität Freiburg
Institut für Anorganische und Analytische Chemie
Albertstrasse 21, 79104 Freiburg (Germany)
and
Freiburger Materialforschungszentrum FMF
Stefan-Maier-Strasse 25, 79104 Freiburg (Germany)
Fax: (+49) 761-203-6102
E-mail: harald.hillebrecht@ac.uni-freiburg.de

were confirmed by energy-dispersive X-ray (EDX) and wavelength-dispersive (WDX) X-ray spectroscopy measurements on single crystals. Thermal behavior and Vickers hardness H_V were measured for m-$MgB_{12}C_2$.

Results and Discussion

o-$MgB_{12}C_2$: The crystal structure of o-$MgB_{12}C_2$ (Figure 1a) is characterized by B_{12} icosahedra in a hexagonal primitive array. o-$MgB_{12}C_2$ is closely related to MgB_7.[21] One half of the trigonal-prismatic voids are filled by Mg atoms, the other by C_2 units. The occupation of the trigonal prisms alternates in the direction of the b axis, however, prisms with the same occupation form zigzag chains in the [100] direction (Figure 1a).

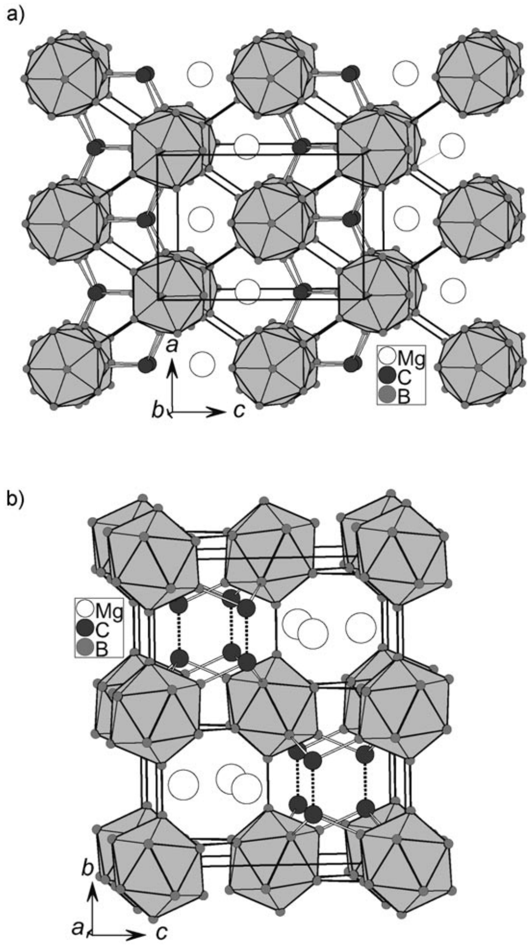

Figure 1. Crystal structure of o-$MgB_{12}C_2$; a) view in the [010] direction; b) view in the [100] direction.

Within the hexagonal layer, each B_{12} icosahedron is coordinated by six icosahedra and forms exohedral B–B bonds to four of them with a bond length of 1.731 Å. This explains the pseudohexagonal metric of the a–c plane and its significant deviation from the ideal value ($c/a = 1.41 \neq \sqrt{3}$). One fivefold axis of the icosahedron is orientated parallel to the b axis. Because the neighboring layers are congruent, two additional exohedral B–B bonds are formed with remarkably short distances of 1.626 Å. Therefore the framework of icosahedra can also be described as a hexagonal rod packing[27] of linear chains of B_{12} icosahedra. The B_{12} icosahedra are very regular, the endohedral B–B distances range from 1.755 to 1.862 Å (av 1.788 Å), which is comparable to other boron-rich borides.[1,14–17] The exohedral bonds of the B_{12} icosahedra are completed by six B–C bonds. Bonding distances of between 1.645 and 1.660 Å are comparable to those in other boron-rich boride carbides with similar structures, such as $Mg_2B_{24}C$ (1.669 Å[17]) or $LiB_{13}C_2$ (1.625 Å[14]) and correspond to the expected values for a single bond.

The C atoms are tetrahedrally coordinated by three boron atoms with nearly equal distances (1.646–1.660 Å) and one carbon atom with a remarkably long distance of 1.727 Å (Figure 2). The bonding angles show a slight deviation from the ideal values (98.7–117.2°). The unusually long C–C distance is to our knowledge one of the longest ever found.[28] Following a suggestion of Pauling,[29] bond orders can be estimated from the sum of the single-bond radii. By using the equation $d_n = d_1 - 0.71$ Å $\log n$ (n: bond order; d_1: sum of single bond radii; d_n: observed distance) and a single bond radius of $r_C = 0.77$ Å, the bond order is calculated to be $n = 0.55$. An additional contribution may result from a Mg–C interaction. The Mg–C distance of 2.29 Å amounts to a bond order of 0.5.

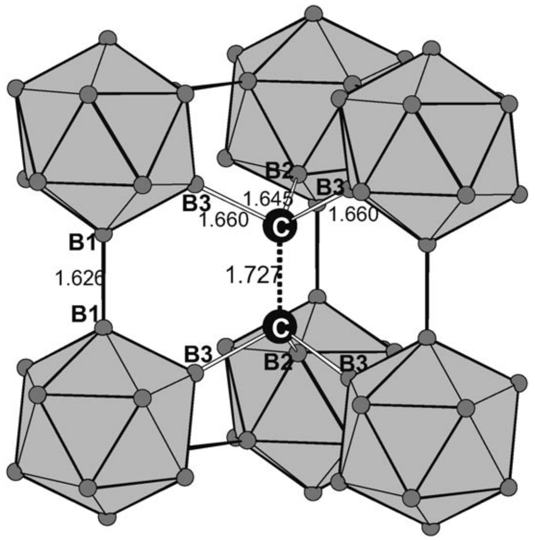

Figure 2. Coordination of C_2 units in o-$MgB_{12}C_2$.

The Mg atoms are coordinated by two C atoms (2.290 Å) and 14 B atoms with Mg–B distances of between 2.590 and 2.841 Å (Figure 3). With respect to the packing of icosahedra, the trigonal-prismatic void comprises four vertices and two faces. The sides of the trigonal prism are capped by two Mg atoms (3.321 Å) and one C_2 unit. The Mg–B distances

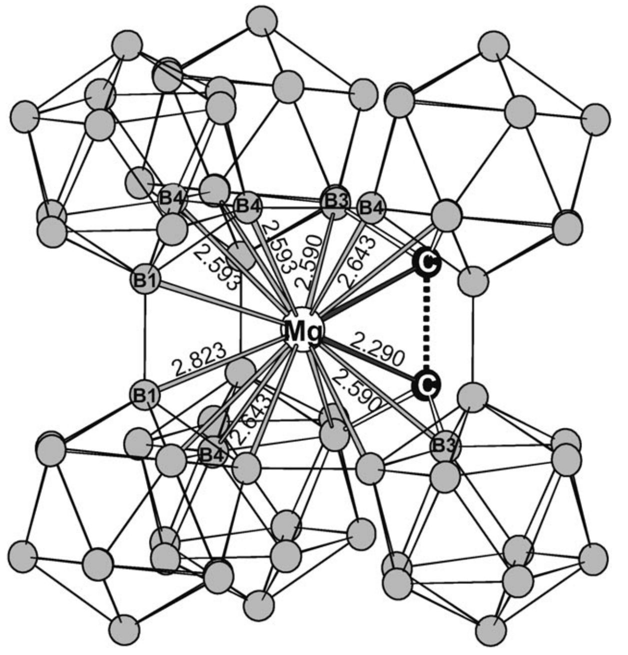

Figure 3. Mg coordination in o-$MgB_{12}C_2$; ellipsoids represent a probability of 99 %.

of o-$MgB_{12}C_2$ are significantly longer than in m-$MgB_{12}C_2$, which agrees well with the higher coordination number.

The crystal structure of o-$MgB_{12}C_2$ is closely related to those of MgB_7[21] and $LiB_{13}C_2$[14] both in terms of the same space group (*Imma*) and similar unit-cell dimensions. The B_{12} icosahedra show the same arrangement and orientation. In MgB_7, which can be written as $(Mg)_2(B_{12})(B_2)$, the trigonal-prismatic voids of the packing of the icosahedra are occupied by one of the Mg atoms and B_2 units, which are similar to the C_2 units in o-$MgB_{12}C_2$. The second Mg atom is located at the center of the rectangular faces that connect the trigonal-prismatic voids occupied by the B_2 units. Compared to o-$MgB_{12}C_2$, the only differences are the additional Mg atom, the significantly longer B–B distance of 2.282 Å for the B_2 unit, and exohedral B–B distances between the layers of 1.763 Å.

The crystal structure and stoichiometry of o-$MgB_{12}C_2$ are in perfect agreement with the qualitative predictions of Wade[30] and Longuet-Higgins.[31] According to Wade's electron-counting rules for boron polyhedra[30] a *closo* cluster with n atoms and one exohedral 2e–2c bond for each cluster atom (usually a B–H bond) will need $2n+2$ electrons to fill the bonding molecular orbitals at best. Longuet-Higgins[31] showed that Wade's rules can be transferred to solid-state compounds. In o-$MgB_{12}C_2$ the two electrons needed for the highest stability as a $B_{12}{}^{2-}$ unit or more realistically to the three-dimensional framework of B_{12} icosahedra and carbon atoms are provided by magnesium. In this quite simple model the carbon atoms are considered as fourfold bonded, and therefore, as giving no contribution to the stabilization of the B_{12} icosahedra. So the formula of o-$MgB_{12}C_2$ can be written as $Mg^{2+}[B_{12}]^{2-}(C_2)$ considering the building units or $Mg^{2+}[B_{12}C_2]^{2-}$, if the three-dimensional character of the framework of mainly covalent bonds is emphasized.

The simple electron-counting rules that fit for many boron-rich borides of electropositive metals[11,14–17] suggest a C–C single bond for the C_2 unit, despite the long distance. This long distance has not necessarily to be the result of a weak C–C bond, but may be caused by the framework of the B_{12} icosahedra and can be seen as similar to steric effects in molecular compounds. The size of the trigonal prismatic void for the C_2 unit is given by the orientation of the icosahedra. Every C atom is connected to three different icosahedra by an exohedral 2e–2c B–C bond. A shortening of the C–C distance demands the elongation of the three B–C bonds. Alternatively the layers of the icosahedra can come closer, but the exohedral distances between the layers are already very short (B1–B1: 1.626 Å) compared to other exohedral B–B distances (e.g. in $Mg_2B_{24}C$ 1.68–1.77 Å).[17] Therefore the minimum of the C–C distance is limited by the three B–C bonds and the exohedral B–B bond between the layers (or within the rods, respectively). This explanation is supported by a comparison to $LiB_{13}C_2$ ($\equiv LiB_{12}(CBC)$).[14] The structure of $LiB_{13}C_2$ shows the same array of icosahedra as o-$MgB_{12}C_2$, but the Mg atom is substituted by a Li atom and the C_2 unit by a linear CBC group. In $LiB_{13}C_2$ the exohedral B–B bonds between the layers are quite long (1.796 Å), which can be caused by the "longer" CBC group (2.83 Å) leading to an expansion of the interlayer distances.

More detailed investigations concerning the electronic structure of o-$MgB_{12}C_2$ and the role of the C–C interaction are in progress.

***m*-$MgB_{12}C_2$**: The structure of m-$MgB_{12}C_2$ (Figure 4) is characterized by the presence of slightly distorted, crystallographically equivalent B_{12} icosahedra. The arrangement of the B_{12} units can be considered as a distorted cubic close packing with the tetrahedral interstitials completely occupied by C atoms and the octahedral vacancies fully filled by Mg atoms, whereas the Mg site is split. Thus, m-$MgB_{12}C_2$ can formally be described as a modified $MnCu_2Al$ structure type[32] (or Li_3Bi type[33]), with B_{12} units substituting for Al, C for Cu, and Mg for Mn.

In m-$MgB_{12}C_2$, each B_{12} icosahedron is linked to eight neighboring B_{12} units by covalent bonds to isolated C atoms with B–C distances of between 1.634 and 1.673 Å and to two adjacent B_{12} units by four exohedral B–B bonds (B5–B6 1.734 Å). The result is a three-dimensional covalent network. The B–B bonds within the B_{12} units range from 1.757 to 1.910 Å (average length approximately 1.816 Å), whereas the length of the B–B bonds between the B_{12} icosahedra is 1.734 Å. Thus, the average intericosahedral bonds are shorter than the corresponding intraicosahedral bonds, which is in good agreement with the general rules of crystal chemistry of boron-rich phases.[1]

The B–C bonds coincide with the quasi-fivefold axes, whereas the B–B bonds are aligned parallel to the twofold axis of the icosahedron to form infinite chains of B_{12} units running parallel to the [010] direction. This type of linkage

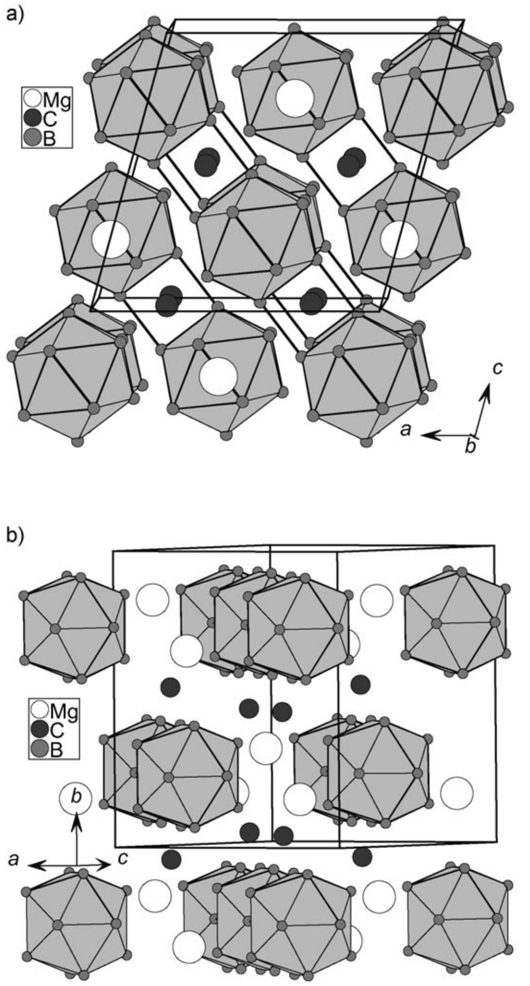

Figure 4. Crystal structure of m-$MgB_{12}C_2$; a) view in the [010] direction; b) view in [101] direction; Mg′ omitted for clarity (see text).

between icosahedra by B−B bonds, leading to the formation of an approximate square is rather unusual (Figure 5).

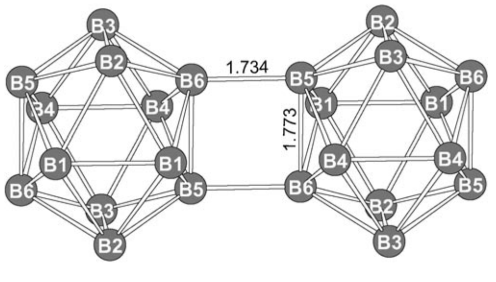

Figure 5. Linkage of B_{12} icosahedra in m-$MgB_{12}C_2$.

The interstitial C atoms in the tetrahedral voids of the B_{12} icosahedra packing link four icosahedra, three of them located in the same plane and one located in a neighboring plane (Figure 6). Two of the three icosahedra located in the same plane belong to the same chain of B_{12} units. The tetrahedral coordination of the C atom is almost regular with B-C-B angles ranging from 108.4–114.9°. The B−C distances, ranging from 1.634 to 1.673 Å (average length approximately 1.654 Å), are slightly longer than those found in boron carbide $B_{13}C_2$ (1.617 Å),[34] but similar to those in o-$MgB_{12}C_2$.

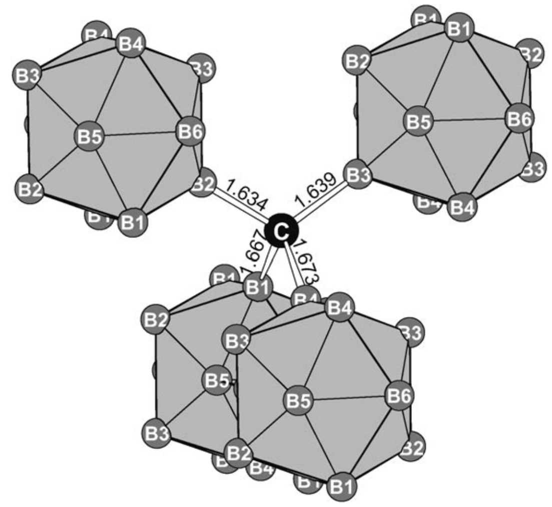

Figure 6. Coordination of C atoms in m-$MgB_{12}C_2$.

Difference Fourier synthesis and anisotropic refinement clearly showed that in m-$MgB_{12}C_2$, the Mg atoms located in the octahedral interstitials (4e site) are disordered by ± 0.703 Å from the center of the two split-positions in the y direction (Figure 7). Taking this into account, Mg is coordinated by ten boron atoms with Mg−B distances ranging from 2.295 to 2.618 Å and by two carbon atoms (2.467 Å). This is in good agreement with the Mg−B distances observed in MgB_7 (2.16–2.89 Å)[10,11,21] and similar to o-$MgB_{12}C_2$. With reference to the icosahedra, the coordination of Mg consists of four edges, each of one of the four icosahedra at the same height and one edge of one icosahedra above (Figure 7) and below, respectively. Assuming the Mg atom is in the center of the two split positions (i.e., $y=0$), the theoretical distances Mg−B2, Mg−B3, Mg−B5, Mg−B6 would be in the range of approximately 2.19–2.79 Å, whereas the Mg−B4 distance would increase to approximately 3.06 Å. Therefore the reason for the partial disorder seems to be an ordering process that occurs on cooling and transforms the 8+4 coordination to an energetically more favorable 2+4+4 (+2)-type. The driving force for this is the desire to shorten the distances Mg−B4 and to avoid a nearly planar coordination. The disorder is statistical. There was no evidence for superstructure formation or twinning. Investigations of additional single crystals always showed this type of disorder. Typical occupation factors for Mg′ were in the range from 8 to 14%. A similar coordination of Al (and therefore the same type of disorder) is also found in the boron-rich borides $Al_{2.7}B_{48}C_2$,[25] $B_{24}AlBe$,[35] and $B_{25}AlCu_{0.8}$.[36]

The icosahedra linked through exohedral bonds of a vertex are a remarkable structural feature of m-$MgB_{12}C_2$. Up to now this type of bonding has only been reported in

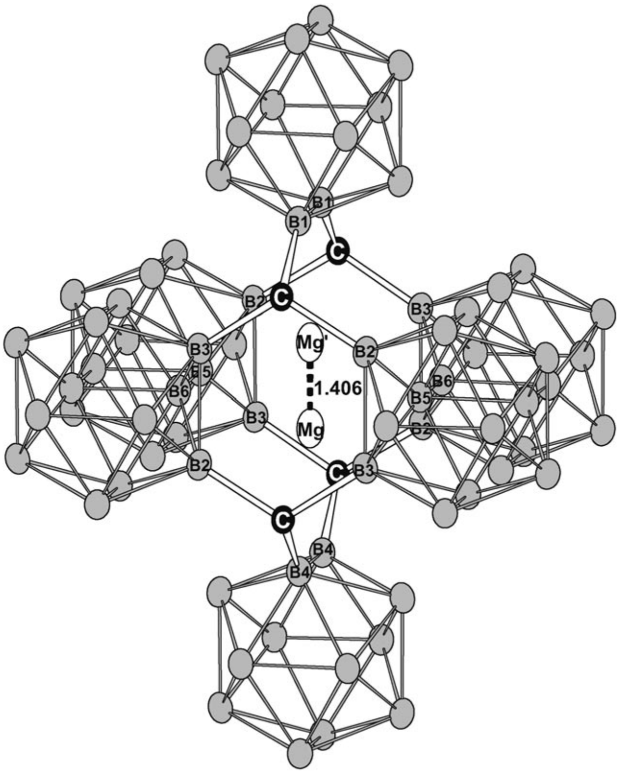

Figure 7. Coordination of Mg in m-$MgB_{12}C_2$ with partial occupations (Mg: 87.2 %, Mg′: 12.8 %); ellipsoids represent a probability of 99 %.

$YB_{41}Si_{1.2}$ by Higashi and co-workers[37] and very recently in $Li_2B_{12}C_2$,[14] and $Mg_{1.13}B_{12}Si_2$,[38] by our group. It is of interest to point out that the centers of neighboring icosahedra within the chains are unusually close together (4.415 Å). This distance is significantly shorter than the distance between icosahedra linked along their quasi-fivefold axis ($\geq$5 Å) in numerous boron-rich phases[39,14–17] and even shorter than the corresponding distance in $YB_{41}Si_{1.2}$ (4.756 Å), $Mg_{1.13}B_{12}Si_2$ (4.660 Å), and $Li_2B_{12}C_2$ (4.706 Å). The reasons for the differences are the exohedral B−B distances. Although for m-$MgB_{12}C_2$ the exohedral distances of 1.733 Å are in the normal range, they are significantly longer in the other examples ($Li_2B_{12}C_2$, $Mg_{1.13}B_{12}Si_2$, $YB_{41}Si_{1.2}$: 1.821, 1.818, 1.798 Å, respectively). The deviation from the cubic close packing of B_{12} icosahedra in $MgB_{12}C_2$ is manifested in shorter a and c axes as well as in an enlarged angle β (90→105.3°) resulting from the unusual linkage of the B_{12} units by B−B bonds (Figure 5).

The crystal structure of m-$MgB_{12}C_2$ contains a high pseudosymmetry. The projection in Figure 4a shows a nearly perfect orthorhombic symmetry with a smaller I-centered unit cell for the covalent framework of B_{12} icosahedra and C atoms. Indeed a refinement is possible with a body-centered orthorhombic unit cell with $a=4.4238(9)$, $b=8.800(2)$, $c=5.8062(12)$ Å and space group *Immm*,[40] but in this structure the Mg atoms are equally distributed on both positions denoted as Mg and Mg′ in Figure 7. The symmetry reduction is only caused by the (nearly) ordered Mg atoms. The relation between both structures can be described with a group–subgroup relation[41,42] as given in Scheme 1

Immm	*t2*	*I2/m*	*k2*	*C2/c*
$a = 4.424$ Å	$\longrightarrow$	$a' = a$	$\longrightarrow$	$a'' = a' - c'$
$b = 8.800$ Å		$b' = b$, ß ≈ 90°		$b'' = b'$, ß ≈105°
$c = 5.806$ Å		$c' = c$		$c'' = a' + c'$

Scheme 1.

The crystal structure of m-$MgB_{12}C_2$ shows once again the validity of the simple electron-counting rules of Wade and Longuet-Higgins. Each boron atom of the B_{12} icosahedron participates in one exohedral 2e–2c bond (eight to carbon atoms, four to neighbored icosahedra), carbon coordinates fourfold to the icosahedra, and Mg supplies the two electrons needed for the stability of the *closo* cluster (B_{12}^{2-}). m-$MgB_{12}C_2$ can be written as $Mg^{2+}[B_{12}]^{2-}(C)_2$ considering the building units or $Mg^{2+}[B_{12}C_2]^{2-}$, if the three-dimensional character of the framework of mainly covalent bonds is emphasized.

Similar to other structure determinations of comparable compounds, such as o-$MgB_{12}C_2$, $Mg_2B_{24}C$,[17] $LiB_{13}C_2$,[14] $Li_2B_{12}C_2$[14], the distinction between boron and carbon atoms is easy. With the correct labeling, all thermal displacement parameters have nearly the same value. The ellipsoids show only small deviations from ideal spheres. The very small absolute values of U_{eq} indicate the high hardness of boron-rich boride carbides. Although the data collection for m-$MgB_{12}C_2$ was done at room temperature a complete data set was collected up to $2\theta=85°$. Therefore, and because of the interesting bonding properties of boron-rich boride carbides, electron density measurements by using high-angle data are planned for this class of compounds.

Hardness measurements: Measurements of the Vickers hardness H_V (DIN EN 6507) were conducted to check the potential of m-$MgB_{12}C_2$ as an abrasive.[42] A single crystal was fixed in a ceramic paste (Demotec 200, Demotec) and epoxy resin (Demotec 200, Demotec). The sample was cut and polished. The indentation was measured under a load of 5 N (Type M-400-G2, Leco). To compare the obtained values, the hardnesses of two samples of boron carbide B_4C were measured in the same way.

The indentation experiments gave values of between 26.0 and 33.8 GPa for m-$MgB_{12}C_2$. The results for B_4C were 27.0 GPa for a polycrystalline sample (source: Ortwin Rave) and 30.2 GPa for a crystalline standard FEPA 36 (diameter 0.4–0.6 mm[43]). The results for B_4C were in good agreement with published values for H_V (28–32 GPa).[3c,44] Furthermore, the hardness of m-$MgB_{12}C_2$ is comparable to that of other boron-rich borides such as $B_{48}Al_{2.7}C_2$[45] or $MgAlB_{14}$,[45] which give values about 30 GPa. Obviously, the hardness of boron-rich borides is limited by the mechanical properties of the three-dimensional network of B_{12} icosahedra.

Thermal properties: Because of the interesting material properties of boron-rich borides, differential thermal analysis/thermogravimetric (DTA/TG) measurements were made on *m*-$MgB_{12}C_2$ (Al_2O_3 crucibles, DTA/TG-type L81/1550, Linseis). In argon, *m*-$MgB_{12}C_2$ was stable up to 1673 K and showed no phase-transition to *o*-$MgB_{12}C_2$. Investigations in air showed an increase in weight above 893 K, which was explained by the oxidation of *m*-$MgB_{12}C_2$ to B_2O_3. Above 1173 K, a loss of weight was observed because of the sublimation of B_2O_3.[46] In summary, the stability of *m*-$MgB_{12}C_2$ in air is similar to boron carbide B_4C, which was investigated for comparison under the same conditions.

Conclusion

Molten metals are useful tools for the synthesis and crystal growth of boron-rich borides. The two modifications of $MgB_{12}C_2$ are good examples of a class of stoichiometric boron-rich borides in which the crystal structures are ruled by a quite simple principle. The boron atoms form a highly symmetrical arrangement of B_{12} icosahedra, which are connected by exohedral 2e–2c B–B bonds and additional 2e–2c bonds to the carbon atoms to build up a three-dimensional framework. Different crystal structures are realized by different topological arrays of the building units. The magnesium atoms are placed in the voids of the framework.

In the case of *m*-$MgB_{12}C_2$, the icosahedra form a cubic closest packing with isolated C atoms in tetrahedral voids. Each B_{12} icosahedron has eight B–C bonds and four exohedral B–B bonds. The linkage of the icosahedra through edges is very unusual and leads to the formation of linear chains. In *o*-$MgB_{12}C_2$, the B_{12} icosahedra follow a hexagonal primitive packing with C_2 units in trigonal-prismatic voids. Each icosahedron has six exohedral B–B bonds and six B–B bonds. The carbon atoms are tetrahedrally coordinated by three boron and one carbon atom, but the C–C distance is remarkably long (1.727 Å). *m*-$MgB_{12}C_2$, which is obtained at lower temperature (1573 K), shows no phase-transition up to 1673 K.

Both modifications of $MgB_{12}C_2$ confirm the possibility to apply Wade's electron-counting rules for the stability of boron polyhedra to solid compounds with a three-dimensional framework. Each Mg atom supplies two additional electrons for the $(n+1)$ bonding molecular orbitals of the icosahedra. This results in a stoichiometric compound that can be described as $Mg^{2+}[B_{12}C_2]^{2-}$ or $Mg^{2+}B_{12}{}^{2-}C_2$, respectively. A clear distinction between boron and carbon atoms is possible on the basis of the refinement of X-ray data. The compositions were confirmed by EDX and WDX measurements of single crystals.

Hardness and thermal stability of *m*-$MgB_{12}C_2$ are characteristic for a boron-rich boride.

Further investigations on the physical properties (conductivity, magnetism, optical and vibrational spectra, thermoelectricity) are in progress. According to preliminary results, single-crystalline samples of both compounds are non-superconducting.[47]

Experimental Section

Synthesis of *o*-$MgB_{12}C_2$: Single crystals of *o*-$MgB_{12}C_2$ were synthesized from the elements in a Cu/Mg melt. Cu (powder, >250 mesh, p.A., Merck), Mg (powder, 325 mesh, 99.8 %, Riedel-de Haën), C (graphite powder, <100 micron, 99.9 %, Heraeus), and B (crystalline, ≈325 mesh, 99.7 %, Alfa Aesar) were mixed in a molar ratio of 300:100:2:9 and pressed into a pellet (ca. 2 g). The pellet was put into a h-BN crucible and the crucible was placed into a tantalum ampoule, which was sealed by welding with an electric arc. The ampoule was heated under an argon atmosphere up to 1873 K, kept at this temperature for 40 h, cooled at $10\,K\,h^{-1}$ to 1073 K, then at $100\,K\,h^{-1}$ to room temperature. The ampoule was opened and the excess melt was dissolved in concentrated nitric acid. Single crystals of *o*-$MgB_{12}C_2$ were black and were irregular in shape with sizes of up to 0.5 mm. Single crystals of dark red MgB_7[10,11,21] and dark green $Mg_3B_{50}C_8$[10,11,22] were obtained as by-products (ca. 5 %).

Synthesis of *m*-$MgB_{12}C_2$: For *m*-$MgB_{12}C_2$ an Al/Mg melt was used with a ratio Al:Mg:C:B of 300:100:3:75 (Al: powder, 40—325 mesh, 99.8 %, Alfa Aesar). The ampoule was heated under an argon atmosphere up to 1573 K, kept at this temperature for 25 h, then cooled at $10\,K\,h^{-1}$ to 773 °C, followed by cooling at $100\,K\,h^{-1}$ to room temperature. The ampoule was opened and the excess melt was dissolved in 6 N hydrochloric acid. Besides powdered by-products, gray-brown single crystals of *m*-$MgB_{12}C_2$ were obtained. The single crystals represented about 50 % of the residue and were of irregular shape with a size of up to 0.8 mm. Defects on the crystal surface were probably due to the reaction with the hydrochloric acid.

Analyses: Qualitative and quantitative analyses on selected single crystals were conducted by EDX and WDX measurements. Several single crystals of *o*-$MgB_{12}C_2$ and *m*-$MgB_{12}C_2$ were checked by EDX (Jeol, JSM 6400 with Ge detector, sample fixed with conducting glue on a graphite platelet mounted on an aluminum sample holder). It was confirmed that magnesium is the only heavy element ($Z > 10$).

A more-detailed analysis, especially in terms of light elements ($4 < Z < 11$), was performed by WDX (Jeol, JXA 8200) to exclude their incorporation (oxygen, nitrogen) or to assure their presence (carbon), respectively, because these problems frequently occur in boron-rich boride analysis. For the WDX measurement the single crystals used for the structure determinations by X-ray methods were fixed in a matrix with Ag/epoxy resin. They were polished to get a clear surface and to ensure the measurement of the interior of the crystal[11] and not of the surface that may be influenced by the contact to the melt or the single-crystal-isolation process. Boron, carbon, and magnesium were detected as the only elements with $Z > 4$. The molar ratios B:C:Mg were found to be 77.6.15.7:6.6 for *o*-$MgB_{12}C_2$ and 78.9:14.4:6.7 for *m*-$MgB_{12}C_2$. Calculated values for the composition $MgB_{12}C_2$ are 80:13.3:6.7.

The special properties of boron-rich borides require a detailed quantitative analysis and special care with the refinement of single-crystal data (for example, NaB_{15}/Na_2B_{29};[23] NaB_5C/KB_5C/KB_6[24]). In some previous contributions we have shown that the combination of high-quality single-crystal data and WDX/EDX measurements of single crystals yielded reliable results for this special class of compounds ($Al_{2.7}B_{48}C_2$,[25] MgB_{17},[15a] MgB_{12},[15b,c] $MgB_{12}Si_2$,[16] $Mg_2B_{24}C$[17]).

Structure solution and refinement: Single-crystal investigations of *o*-$MgB_{12}C_2$ were performed by using a diffractometer equipped with $Mo_{K\alpha}$ radiation and an image-plate detector (IPDS II, Stoe). They revealed a body-centered orthorhombic unit cell with $a = 5.6133(10)$, $b = 9.828(2)$, and $c = 7.9329(15)$ Å. The measurement of 3580 intensities gave a data set of 574 independent reflections (541 with $I > 2\sigma(I)$) for Laue class *mmm*. Because of the low absorption coefficient ($0.24\,mm^{-1}$) no correction of absorption effects was done. The additional reflection condition *hk*0 with $h = 2n$ led to the space group *Imma* and the non-centrosymmetric space group *Ima*2, respectively. The structure solution by direct methods (SHELXTL[26]) was started in *Imma* and revealed a structure model with six independent atoms. The labeling of the atoms was done according to electron densities and bonding distances. All atoms were refined with anisotropic thermal parameters. Because partial and mixed occupations are well-known for boron-rich borides, all occupation factors were refined separately as a free variable. Because no deviations from full occupation were observed, *o*-$MgB_{12}C_2$ has to be regarded as an ordered structure with a stoichiometric composition. Finally R values of $R_1(F) = 0.0208$ and $wR_2(I) = 0.0540$ resulted for 574 reflections and 42 free variables. Several single crystals from different batches were measured. Details for the best refinement are listed in Table 1. Coordinates and thermal-displacement parameters are given in Tables 2 and 3. Selected distances and angles are shown in Table 4.

Table 2. Atomic coordinates, isotropic displacement parameters [Å^2], and site occupation factors of *o*-$MgB_{12}C_2$, esds in parentheses.

Atom	Site	x	y	z	sof	$U_{eq.}$
Mg	4e/mm2	0.0	0.25	0.36187(4)	1.003(4)	0.0087(1)
C	8h/m	0.0	0.33785(5)	0.62929(7)	0.987(6)	0.0036(1)
B1	8h/m	0.0	0.33274(6)	0.02107(7)	1.006(6)	0.0038(1)
B2	8h/m	0.0	0.40606(6)	0.81860(8)	0.998(6)	0.0039(1)
B3	16j	0.26069(7)	0.41504(4)	0.94807(5)	1.002(4)	0.0040(1)
B4	16j	0.16176(7)	0.43614(4)	0.16054(5)	1.003(4)	0.0038(1)

Table 3. Anisotropic displacement parameters [Å^2] of *o*-$MgB_{12}C_2$, esds in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg	0.0112(2)	0.0085(2)	0.0064(2)	0	0	0
C	0.0029(2)	0.0041(2)	0.0038(2)	0	0	−0.0002(1)
B1	0.0034(2)	0.0038(2)	0.0043(2)	0	0	0.0001(1)
B2	0.0035(2)	0.0042(2)	0.0038(2)	0	0	−0.0003(1)
B3	0.0031(2)	0.0043(2)	0.0043(2)	0.0002(1)	0.0002(1)	−0.0001(1)
B4	0.0034(2)	0.0045(2)	0.0038(2)	0.0000(1)	−0.0002(2)	0.0001(1)

Table 1. Crystallographic data and refinement for *o*-$MgB_{12}C_2$ and *m*-$MgB_{12}C_2$.

Compound	*o*-$MgB_{12}C_2$	*m*-$MgB_{12}C_2$
temperature [K]	293(2)	293(2)
crystal shape	irregular polyhedron	irregular polyhedron
colour	black	gray-brown
size [mm^3]	$0.04 \times 0.04 \times 0.04$	$0.03 \times 0.03 \times 0.03$
crystal system	orthorhombic	monoclinic
space group	*Imma* (no 74)	*C*2/*c* (no. 15)
a [Å]	5.6133(10)	7.2736(11)
b [Å]	9.828(2)	8.7768(13)
c [Å]	7.9329(15)	7.2817(11)
β [°]		105.33(3)
V [Å^3]	437.62(8)	448.32(7)
Z	4	4
ρ_{calcd} [g cm^{-3}]	2.702	2.638
data collection[a]	STOE IPDS II	Siemens P4
	$0° \leq \omega \leq 180°$	$\omega/2\theta$ scan
	$\psi = 0°$, 111;	scan width
	$\Delta\omega = 2°$	$0.60 \pm 0.40 \tan\theta$
exposure time	300s	60s/scan
θ range	$3° < 2\theta < 72°$	$3° < 2\theta < 85°$
	$-9 < h < 9$	$-13 < h < 13$
	$-16 < k < 16$	$-16 < k < 1$
	$-13 < l < 13$	$-13 < l < 13$
μ [mm^{-1}]	0.24	0.24
absorption correction	none	none
R_{int}/R_{sigma}	0.070/0.039	0.0278/0.0182
refinement	SHELXTL;[26] full-matrix least-squares refinement on F^2	
$N(hkl)$ measured; unique	3580, 574	3328, 1585
$N'(hkl)$ ($I > 2\sigma I$))	541	1491
parameters refined	42	71
R values		
R_1	0.0208	0.0233
wR_2	0.0540	0.0597
all data R_1	0.0228	0.0269
weighting scheme[26]	0.0255/0.0521	0.0385/0.0
extinction correction[26]	0.030(9)	0.00108(12)
goodness-of-fit	1.145	1.130
residual electron density [e Å^{-3}] (max, min, sigma)	+0.46/−0.23/0.07	+0.37/−0.49/0.08

[a] $Mo_{K\alpha}$; $\lambda = 0.71073$ Å (graphite-monochromated.

Table 4. Selected distances [Å] and angles [°] in *o*-$MgB_{12}C_2$, exohedral B−B distances in italics.

Mg−B3 (4×)	2.5901(5)		
Mg−B4 (4×)	2.5926(6)		
Mg−B4 (4×)	2.6425(6)		
Mg−B2 (2×)	2.8411(7)		
Mg−C (2×)	2.2904(7)		
C−B2	1.6446(8)	B2-C-B3 (2×)	98.70(3)
C−B3 (2×)	1.6603(5)	B3-C-B3	108.01(4)
C−C	1.7266(11)	B2-C-C	114.05(3)
C−Mg	2.2904(7)	B3-C-C (2×)	117.19(2)
B1−B1	*1.6262(12)*	B2−C	1.6446(8)
B1−B4 (2×)	1.7554(6)	B2−B1	1.7604(9)
B1−B2	1.7604(9)	B2−B6 (2×)	1.7899(6)
B1−B3 (2×)	1.7694(6)	B2−B1 (2×)	1.8046(7)
B3−C	1.6603(5)	B4−B4	*1.7309(8)*
B3−B1	1.7694(6)	B4−B1	1.7554(6)
B3−B4	1.7859(6)	B4−B3	1.7859(6)
B3−B4	1.7867(6)	B4−B3	1.7867(6)
B3−B2	1.7899(6)	B4−B2	1.8046(7)
B3−B3	1.8621(9)	B4−B4	1.8160(9)

Single crystals of *m*-$MgB_{12}C_2$ were investigated with a four-circle diffractometer (P4, Siemens). The C-centered monoclinic unit cell with $a = 7.2736(11)$, $b = 8.7768(13)$, $c = 7.2817(11)$ Å and $\beta = 105.33(3)°$ was determined from 25 high-angle reflections. The measurement of half an Ewald sphere up to $2\theta = 85°$ gave 3328 intensities. The merging without absorption correction (0.24 mm^{-1}) in Laue class 2/*m* yielded a data set of 1585 independent reflections (1491 with $I > 2\sigma(I)$). The additional reflection condition $h0l$ with $l = 2n$ led to space group *C*2/*c* and the non-centrosymmetric space group *Cc*, respectively. The structure solution by direct methods (SHELXTL[26]) was started in *C*2/*c*. The labeling of the eight independent atoms was done according to electron densities and bonding distances. All atoms were refined with anisotropic thermal parameters. It turned out that Mg is displaced 0.7 Å from the center of its coordination sphere and disordered on two positions (sof: 0.87/0.13). All occupation factors were refined separately as a free variable to check for partial and mixed occupations. Because no deviations from full occupation were observed, *m*-$MgB_{12}C_2$ was regarded as a stoichiometric compound. Finally R values of $R_1(F) = 0.0228$ and $wR_2(I) = 0.0612$ were yielded for 1585 reflections and 71 free variables. Similar to *o*-$MgB_{12}C_2$, data from different single crystals were recorded. Details of structure solution and refinement of the best data set are listed in Tables 1, 5, and 6. Selected distances and angles are shown in Table 7. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum, Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (fax: +49)724-808-666: e-mail:

Table 5. Atomic coordinates, isotropic displacement parameters [Å^2] and site occupation factors of *m*-$MgB_{12}C_2$, esds in parentheses.

Atom	site	*x*	*y*	*z*	sof	$U_{eq.}$
Mg	4e/2	0.0	0.16990(2)[a]	0.75	0.4361(11)[a]	0.0072(1)[a]
Mg′	4e/2	0.0	0.83010(2)[a]	0.75	0.0639(11)[a]	0.0072(1)[a]
C	8f	0.25197(3)	0.45914(3)	0.00153(2)	1.000(4)	0.0038(1)
B1	8f	0.10276(4)	0.57624(3)	0.85326(3)	0.997(3)	0.0044(1)
B2	8f	0.13031(4)	0.36075(3)	0.11976(3)	1.002(3)	0.0044(1)
B3	8f	0.36870(4)	0.35685(3)	0.88129(3)	1.000(3)	0.0044(1)
B4	8f	0.39689(4)	0.58148(3)	0.14738(3)	1.003(3)	0.0043(1)
B5	8f	0.57515(4)	0.24778(3)	0.97845(3)	1.000(4)	0.0041(1)
B6	8f	0.27158(4)	0.24973(3)	0.67475(4)	0.990(4)	0.0042(1)

[a] Coupled refinement.

Table 6. Anisotropic displacement parameters [Å^2] of *m*-$MgB_{12}C_2$, esds in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg*	0.0070(1)	0.0090(1)	0.0070(1)	0	0.0041(1)	0
Mg′*	0.0070(1)	0.0090(1)	0.0070(1)	0.0	0.0041(1)	0
C	0.0036(1)	0.0044(1)	0.0036(1)	0.0000(1)	0.0014(1)	0.0000(1)
B1	0.0039(1)	0.0052(1)	0.0041(1)	0.0002(1)	0.0014(1)	0.0003(1)
B2	0.0038(1)	0.0055(1)	0.0041(1)	−0.0004(1)	0.0015(1)	0.0002(1)
B3	0.0040(1)	0.0054(1)	0.0041(1)	0.0004(1)	0.0015(1)	−0.0001(1)
B4	0.0040(1)	0.0051(1)	0.0040(1)	−0.0001(1)	0.0015(1)	−0.0001(1)
B5	0.0037(1)	0.0052(1)	0.0036(1)	0.0000(1)	0.0012(1)	−0.0001(1)
B6	0.0036(1)	0.0055(1)	0.0038(1)	−0.0001(1)	0.0011(1)	0.0000(1)

Table 7. Selected distances [Å] and angles [°] in *m*-$MgB_{12}C_2$, exohedral B−B lengths in italics.

Mg−Mg′	1.4060(4)[a]	Mg′−Mg	1.4060(4)[a]		
Mg−B6 (2×)	2.2948(5)	Mg′−B5 (2×)	2.2907(5)		
Mg−B5 (2×)	2.3026(5)	Mg′−B6 (2×)	2.2962(5)		
Mg−B4 (2×)	2.3859(5)	Mg′−B1 (2×)	2.3440(5)		
Mg−B3 (2×)	2.6115(7)	Mg′−B3 (2×)	2.6088(7)		
Mg−B2 (2×)	2.6181(7)	Mg′−B2 (2×)	2.6206(7)		
Mg−C (2×)	2.4669(7)	Mg′−C (2×)	2.4943(7)		
C−B2	1.6344(4)	B2-C-B3	114.88(3)		
C−B3	1.6391(4)	B2-C-B1	108.43(2)		
C−B1	1.6673(5)	B2-C-B4	110.05(2)		
C−B4	1.6733(5)	B3-C-B1	109.41(2)		
C−Mg	2.4669(7)	B3-C-B4	111.23(2)		
C−Mg′	2.4943(7)	B1-C-B4	102.03(3)		
B1−C	1.6673(5)	B2−C	1.6344(4)	B3−C	1.6391(4)
B1−B5	1.7985(4)	B2−B5	1.7569(5)	B3−B6	1.7560(5)
B1−B6	1.8149(4)	B2−B6	1.7682(5)	B3−B5	1.7635(5)
B1−B6	1.8189(8)	B2−B1	1.8426(5)	B3−B4	1.8496(5)
B1−B1	1.8426(5)	B2−B1	1.8493(5)	B3−B4	1.8525(5)
B1−B2	1.8493(4)	B2−B3	1.9099(6)	B3−B2	1.9099(6)
B4−C	1.6733(5)	B5−B6	*1.7335(7)*	B6−B5	*1.7335(7)*
B4−B6	1.7779(4)	B5−B2	1.7569(5)	B6−B3	1.7560(5)
B4−B5	1.7958(4)	B5−B3	1.7635(5)	B6−B2	1.7682(5)
B4−B4	1.8163(8)	B5−B6	1.7733(6)	B6−B5	1.7733(6)
B4−B3	1.8496(5)	B5−B4	1.7958(4)	B6−B4	1.7779(4)
B4−B3	1.8525(5)	B5−B1	1.7985(4)	B6−B1	1.8149(4)

[a] Refinement with disorder and partial occupation.

crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-416800 (*m*-$MgB_{12}C_2$) and CSD-416801 (*o*-$MgB_{12}C_2$).

Acknowledgements

Thanks are due to the Bayerisches Geo-Institut (BGI, Universität Bayreuth) for the access to WDX measurements and to Detlev Krauße for his support. This work was supported by the program "Neue Werkstoffe in Bayern", project B21092.

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Received: July 13, 2006