Synthesis, crystal growth and structure of Mg containing β-rhombohedral boron: $MgB_{17.4}$

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

[a]*DRONCO AG, Wiesenmühle 1, D-95632 Wunsiedel, Germany*
[b]*Ludwig-Maximilians-Universität München, Institut für Mineralogie, Petrologie und Geochemie, Theresienstr. 41/III, D-80333 München, Germany*
[c]*Albert-Ludwigs-Universität Freiburg, Institut für Anorganische und Analytische Chemie, Albertstr. 21, D-79104 Freiburg, Germany*
[d]*Freiburger Materialforschungszentrum FMF, Stefan-Maier-Str. 25, D-79104 Freiburg, Germany*

Abstract

For the first time, single crystals of Mg containing β-rhombohedral boron $MgB_{17.4}$ were synthesised from the elements in a Mg/Cu melt at $1600\,°C$. The crystal structure determined by the refinement of single crystal data (space group $R\text{-}3m$, $a = 10.991(2)\,Å$, $c = 24.161(4)\,Å$, 890 reflections, 123 variables, $R_1(F) = 0.049$, $wR_2(I) = 0.122$) improves and modifies the former structure model derived from earlier investigations on powder samples. Mg is located on four different positions with partial occupation. While the occupation of the sites D (53.3%), E (91%) and F (7.2%) is already known from other boron-rich borides related to β-rhombohedral boron, the occupation of the fourth position ($18h$, 6.7%) is observed for the first time. Two boron positions show partial occupation. The summation reveals the composition $MgB_{17.4}$ and $Mg_{5.85}B_{101.9}$, respectively, confirmed by WDX measurements. The single crystals of $MgB_{17.4}$ show the highest Mg content ever found. Preliminary measurements indicate no superconductivity.
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1. Introduction

Boron-rich borides exhibit interesting and unique properties [1] like high hardness, high melting points and chemical inertness. Owing to their physical properties as well boron-rich borides are important materials for thermoelectrics [2], high temperature semiconductors [3] and possible high-T_c superconductors [4,5]. Most of the work on boron-rich borides was done with β-rhombohedral boron and related compounds [6].

The structure of elemental β-rhombohedral boron is known to take up different metals. The acceptor levels of the boron polyhedra are filled up by the electrons of the metal atoms and the cations occupy a variety of large interstitial voids between the boron icosahedra and the B_{28}-units. Binary borides related to β-rhombohedral boron are known for Al, Cr, Cu, Fe, Ge, Li, Mn, Ni, Sc, Si, V, Zn and Zr [7]. Recently, boron-rich borides of Li [8] and Mg [9,10] were in the focus because theoretical investigations predicted superconductivity [5]. The observation of superconductivity for MgB_2 with $T_c = 39\,K$ [11] additionally increased the interest in Mg borides.

Several investigations are reported for the binary system Mg/B [12] and the compounds MgB_2, MgB_4, MgB_7 and $MgB_{\sim 20}$ are well established. Very recently, synthesis and characterisation of MgB_{12} was reported [13]. But still there are uncertainties, which arise mainly from the special properties of boron-rich borides of magnesium. First the melting points are very different leading to difficulties for the growth of single crystals. Additional problems are caused by the high reactivity of Mg and the tendency of boron-rich borides to incorporate impurities.

*Corresponding author. Albert-Ludwigs-Universität Freiburg, Institut für Anorganische und Analytische Chemie, Albertstr. 21, D-79104 Freiburg, Germany. Fax: +49 761 203 6102.
E-mail address: harald.hillebrecht@ac.uni-freiburg.de (H. Hillebrecht).

These aspects can be taken from the work on Mg containing β-rhombohedral boron published up to now. Brutti et al. [9] yielded powder samples by heating the elements in a Ta-crucible at 1150 °C. MgB_7 was formed as a by-product and "removed" by annealing in vacuum at 1000 °C. The structure refinement was done with Rietveld methods using conventional X-ray and synchrotron data. The expected framework of boron polyhedra was confirmed and three different partially occupied Mg sites (Table 7) were found. The Mg positions were localised by checking the possible metal positions as they were proposed by Anderson and Lundstrom [14].

Soga et al. [10] doped β-rhombohedral boron with Mg via the gas phase at 1200 °C. Boron and magnesium were put into tantalum or boron nitride containers and sealed in a quartz tube. The highest Mg content and the smallest Si contamination, which were monitored by EDX measurements, were achieved by twofold heating for 10 h. A repeated exposure or increased reaction time resulted in higher Si and/or lower Mg contents. The refinement (X-ray data, Rietveld method) based on the model given by Brutti et al. [9] with three partially filled Mg positions. Si was found to occupy the A1 site and to substitute the B1 position. Because no single crystals were obtained all structure determinations and measurements of physical properties were done on powder samples.

In this contribution, we report on the first crystal growth of Mg containing β-rhombohedral boron by use of a Cu/Mg melt. On the basis of single crystal data the crystal structure was refined and some features were specified. The sum of the occupation factors of 15 boron atoms and four magnesium atoms revealed the composition $MgB_{17.4}$.

2. Synthesis

Single crystals of Mg containing β-rhombohedral boron were synthesised from the elements in a Cu/Mg melt. Cu, Mg and B (crystalline, ~325 mesh, 99.7%, Alfa Aesar) were mixed in a molar ratio of 12:4:3 and pressed to a pellet (ca. 2 g). The pellet was put into an h-BN crucible and the crucible into a tantalum ampoule, which was sealed by welding with an electric arc. The ampoule was heated under argon atmosphere up to 1600 °C held for 40 h, cooled with 10 K/h to 800 °C and with 100 K/h to room temperature. The ampoule was opened and the excess melt was dissolved in conc. nitric acid. Single crystals of $MgB_{17.4}$ were of dark brown colour and irregular shape with a size of up to 0.5 mm. As by-products single crystal of MgB_{12} [13] and $Mg_3B_{50}C_8$ [15] were found. The latter can be explained by the carbon content of "elemental" boron. Qualitative and quantitative analyses on selected single crystals were done 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 aluminium sample holder). It was confirmed that magnesium is the only heavy element ($Z > 10$). By WDX (Jeol, JXA 8200) a more

detailed analysis especially in consideration of light elements ($4 < Z < 11$) was done to exclude their incorporation (especially carbon), which occur frequently in boron-rich borides. For the WDX measurement the single crystal used for the structure determination by X-rays (composition $MgB_{17.4}$) was fixed in a matrix with Ag/epoxy resin. It was polished to get a clear surface and to assure the measurement of the interior of the crystal [15] and not of the surface that may be influenced by the contact to the melt. Boron and magnesium were detected as the only elements with $Z > 4$. The molar ratio B:Mg was found to be 93.3:6.7 leading to the composition $MgB_{14.0}$ in good agreement with the composition determined by X-ray methods. A similar procedure was applied for MgB_{12} (X-ray: $MgB_{12.41}$; WDX: $MgB_{12.35}$) [13a].

3. Structure refinement

Investigations with a single crystal diffractometer equipped with $MoK\alpha$ radiation and an image plate detector (Fa. Stoe, IPDS II) revealed a rhombohedral unit cell with $a = 10.991(2)$ Å and $c = 24.161(2)$ Å in hexagonal setting (rhombohedral setting: $a = 10.139(2)$ Å, $\alpha = 65.20(2)°$). The measurement of 18,288 intensities gave a data set of 890 independent reflections (555 with $I > 2\sigma(I)$). Because of the low absorption coefficient (0.21 mm^{-1}) no correction of absorption effects was done. According to dimension and symmetry of the unit cell a structure of the β-rhombohedral boron type was assumed. The refinement was started with the structure model derived from powder data by Rietveld methods [9]. The evaluation of thermal displacement parameters, occupation factors, difference Fourier maps and of the bond distances found in other boron-rich borides of Mg (MgB_{12} [13], MgB_7 [15,16]) led to a structure model with four partially occupied sites for Mg and 15 independent B positions. Two of the boron positions are partially occupied as well. The thermal displacement parameter of B1 is unusual high but is also observed in most of the compounds of the β-rhombohedral B type [7]. For $MgB_{17.4}$, this high value did not change with a free occupation factor. The refinement with a shift (disorder) in the x–y plane is possible with an isotropic thermal displacement parameter. According to the difference Fourier syntheses no additional boron atoms between the boron polyhedra as they were observed in β-rhombohedral boron [17] and some other related compounds [7] were found in $MgB_{17.4}$. We have measured data sets for six crystals from different batches and refined the crystal structures. Within the standard deviations Mg-occupations were the same.

Finally, R-values of $R_1(F) = 0.049$ and $wR_2(I) = 0.122$ were yielded for 890 reflections and 123 free variables. All atoms were refined with anisotropic thermal displacement parameters.

Details for the best refinement of a single crystal are listed in Table 1. Coordinates and thermal displacement parameters are given in Tables 2 and 3. Selected distances

Table 1

Details of the crystal structure determination of $MgB_{17.4}$

Crystal shape and colour	Irregular polyhedron, dark brown
Crystal dimensions	$0.6 \times 0.4 \times 0.5$ mm
Crystal system	Rhombohedral
Space group	$R\text{-}3m$
Lattice constants	$a = 10.992(2)$ Å, $c = 24.161(4)$ Å
	[rhomb. setting: $a = 10.139(2)$ Å,
	$\alpha = 65.29(2)°$]
Cell volume	2527.5 Å^3
No. of formula units	3
Composition in unit cell	$Mg_{17.55}B_{305.6}$
Density calculated	2.557 g/cm^3
Radiation	$MoK\alpha$ (IPDS II), graphite
	monochromator
Range (hkl)	$-15 \leqslant h \leqslant 15$, $-15 \leqslant k \leqslant 15$, $-32 \leqslant l \leqslant 32$
Range (2Θ)	5–$59°$
Temperature of measurement	$21 °C$
Scan modus/measurement	90 frames, 14 min with $2°\varphi$ increment
Reflections measured	18,288
Unique reflections	890 (555 with $I > 2\sigma$)
Internal R-value	0.1444 ($\sigma = 0.0605$)
Absorption coefficient	0.21 mm^{-1}
Absorption correction	None
Structure solution	Direct methods/SHELXTL [18]
Refinement	SHELXTL [18]
Residual electron density	$+0.47$ e$^-$/Å^3, -0.36 e$^-$/Å^3
	($\sigma = 0.07$ e$^-$/Å^3)
Weighting function	$1/[\sigma^2(F_0^2) + (0.0850P)^2 + 0.00P]$ with
	$P = (F_0^2 + 2F_c^2)/3$
Number of parameters	123
R-values	$R_1(F) = 0.049$, $wR_2(I) = 0.122$

Table 2

Coordinates, thermal displacement parameters (in [Å^2]) and site occupation factors

Atom	Site	x	y	z	U_{eq}	Occupation
B1[a]	3b	0[a]	0	0.5	0.044(3)[a]	1
B2	6c	0	0	0.3849(2)	0.0238(11)	1
B3	18h	0.0541(2)	0.9459(2)	0.9434(1)	0.0234(6)	1
B4	18h	0.0850(2)	0.9150(2)	0.0130(1)	0.0228(6)	1
B5	18h	0.1080(2)	0.8920(2)	0.8887(1)	0.0241(7)	1
B6	18h	0.1683(2)	0.8317(2)	0.0276(1)	0.0248(7)	1
B7	18h	0.1301(2)	0.8699(2)	0.7674(1)	0.0242(7)	1
B8	18h	0.1017(2)	0.8983(2)	0.6986(1)	0.0243(7)	1
B9	18h	0.0580(2)	0.9420(2)	0.3279(1)	0.0257(7)	1
B10	18h	0.0898(2)	0.9102(2)	0.3971(1)	0.0244(7)	1
B11	18h	0.0556(3)	0.9444(3)	0.5569(2)	0.0281(17)	0.639(18)
B12	36i	0.1742(2)	0.1726(3)	0.1741(1)	0.0246(5)	1
B13	36i	0.3183(2)	0.2929(2)	0.1281(1)	0.0242(5)	1
B14	36i	0.2625(2)	0.2180(3)	0.4182(1)	0.0259(5)	1
B15	36i	0.2387(4)	0.2531(6)	0.3468(1)	0.0239(12)	0.92(2)
Mg1	6c	0	0	0.2342(1)	0.0230(7)	0.910(11)
Mg2	18h	0.1990(1)	0.8010(1)	0.1777(1)	0.0336(8)	0.533(7)
Mg3	18f	0.2876(15)	0.3333	0.3333	0.034(9)	0.072(12)
Mg4	18h	0.2080(12)	0.7920(12)	0.4121(9)	0.049(8)	0.067(7)

[a]Refinement with disorder model: site 18g; $x = 0.0243(12)$; $U_{iso} = 0.0150(34)$.

are shown in Tables 4–6. Further details on the structure refinement (complete list of distances and angles, F_o/F_c-list) may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (fax: +49 724 808 666: e-mail: crysdata@fiz-karlsruhe.de) on quoting the registry number CSD-416332.

Compared to other single crystals of boron-rich borides and boridecarbides obtained from molten metals the quality of $MgB_{17.4}$ single crystals is remarkably lower. Therefore we assume the single crystals were formed by diffusion of Mg into the β-rhombohedral boron crystals. Furthermore, the "interstitial" boron atoms (B16, site 18h, $x = 0.0546$, $z = 0.1176$, occupation 27% [17]) of β-rhombohedral boron, which are needed for electronic reasons in the structure of elemental boron cannot be detected in the crystal structure of $MgB_{17.4}$, so the exchange of these boron atoms has to be assumed as well.

Similar observations were made for Li containing β-rhombohedral boron, LiB_{10}. On single crystal growth and structure refinement of LiB_{10} we will report elsewhere [19].

Our results obtained from single crystal investigations confirm and improve the data published by Brutti et al. [9] and by Soga et al. [10] but reveal also some new observations. The lattice constants in [9] are slightly smaller ($a = 10.9830(4)$ Å, $c = 24.1561(15)$ Å) and the

composition is given as $MgB_{19.6}$. Although synchrotron data were used, no anisotropic refinement could be done, the values of the thermal parameters differ by a factor of 2.6, and the standard deviations of the atom positions are not completely consistent. The occupation factors were not refined as free parameters, but determined according to a trial and error strategy for assumed positions [14].

The samples investigated by Soga and coworkers [10] contained varying amounts of silicon because of the method of preparation. While the a lattice constant is nearly the same ($a = 10.9880(8)$ Å), the c lattice constant with a value of $24.084(2)$ Å is distinctly smaller and according to the work of Soga et al. [10] correlated to the lower Mg content ($MgSi_{0.06}B_{23.7}$). The lower Mg content results from a smaller occupation factor on the E-site and the empty position of Mg4. The occupation factors of all atoms were refined, but no positional parameters and thermal displacement parameters are given. In a very recent contribution, the same group presented results on powder samples without silicon and a higher Mg content after an improvement of the synthesis [20].

4. Results and discussion

The crystal structure of $MgB_{17.4}$ is closely related to β-rhombohedral B. It contains B_{12}-icosahedra and B_{28}-units in a ratio of 2:1. The B_{28}-unit can be constructed by connecting three icosahedra via common triangle planes. The unit cell with a rhombohedral setting is shown in Fig. 1. Four B_{12} icosahedra in a ratio of 1:3 occupy the corners (icosahedron 1; B3, B4) and the middle of the

Table 3
Anisotropic thermal displacement parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.060(4)	0.060(4)	0.013(4)	0	0	0.030(2)
B2	0.0240(15)	0.0240(15)	0.023(3)	0	0	0.0120(8)
B3	0.0232(10)	0.0232(10)	0.0223(15)	0.0004(6)	−0.0004(6)	0.0105(12)
B4	0.0239(10)	0.0239(10)	0.0214(14)	−0.0006(6)	0.0006(6)	0.0125(12)
B5	0.0237(10)	0.0237(10)	0.0240(16)	0.0016(6)	−0.0016(6)	0.0113(12)
B6	0.0252(11)	0.0252(11)	0.0227(14)	−0.0002(6)	0.0002(6)	0.0116(12)
B7	0.0243(10)	0.0243(10)	0.0224(14)	0.0000(6)	−0.0000(6)	0.0111(12)
B8	0.0252(11)	0.0252(11)	0.0235(16)	0.0010(6)	−0.0010(6)	0.0133(12)
B9	0.0252(11)	0.0252(11)	0.0272(17)	−0.0003(6)	0.0003(6)	0.0131(13)
B10	0.0255(11)	0.0255(11)	0.0242(15)	−0.0003(6)	0.0003(6)	0.0143(12)
B11	0.033(2)	0.033(2)	0.022(3)	−0.0016(10)	0.0016(10)	0.019(2)
B12	0.0243(10)	0.0256(10)	0.0232(11)	−0.0001(8)	0.0009(8)	0.0119(8)
B13	0.0240(11)	0.0230(10)	0.0245(11)	−0.0010(8)	−0.0002(8)	0.0108(8)
B14	0.0262(11)	0.0249(10)	0.0276(11)	0.0002(8)	−0.0004(9)	0.0136(9)
B15	0.0259(16)	0.023(2)	0.0239(15)	−0.0001(13)	0.0003(11)	0.0131(17)
Mg1	0.0240(8)	0.0240(8)	0.0212(11)	0	0	0.0120(4)
Mg2	0.0341(10)	0.0341(10)	0.0306(12)	0.0046(5)	−0.0046(5)	0.0156(10)
Mg3	0.031(9)	0.024(20)	0.044(11)	0.013(11)	0.007(5)	0.012(11)
Mg4	0.050(11)	0.050(11)	0.044(13)	0.002(5)	−0.002(5)	0.024(11)

Table 4
B–B distances (Å), *exohedral distances in italics*, icosahedron 1: B3, B4; icosahedron 2: B5, B7, B12, B13; B$_{28}$-unit: B2, B6, B8, B9, B10, B11, B14, B15

B1–B11 (6x)	1.736(6)[a]	B8–*B7*	*1.749(5)*	B13–*B14*	*1.757(3)*
B2–B10 (3x)	1.735(3)	B8–B9 (2x)	1.800(3)	B13–B5	1.810(3)
B2–B11 (3x)	1.759(7)	B8–B15 (2x)	1.864(4)	B13–B7	1.817(3)
B2–B9 (3x)	1.767(6)	B8–B6	1.875(5)	B13–B12	1.844(3)
B3–*B5*	*1.673(5)*	B9–B2	1.767(6)	B13–B13	1.886(5)
B3–B4 (2x)	1.767(4)	B9–B10	1.779(5)	B13–B12	1.896(3)
B3–B4	1.781(5)	B9–B8 (2x)	1.800(3)	B14–*B13*	*1.757(3)*
B3–B3 (2x)	1.783(6)	B9–B15 (2x)	1.851(5)	B14–B6	1.800(4)
B4–*B6*	*1.624(5*	B9–B9 (2x)	1.914(6)	B14–B10	1.800(3)
B4–B4 (2x)	1.735(4)	B10–B2	1.735(3)	B14–B15	1.815(5)
B4–B3 (2x)	1.767(3)	B10–B9	1.779(5)	B14–B11	1.829(6)
B4–B3	1.781(5)	B10–B14 (2x)	1.800(3)	B14–B14	1.907(5)
B5–*B3*	*1.673(5)*	B10–B11 (2x)	1.863(4)	B15–*B15*	*1.659(12)*
B5–B13 (2x)	1.810(3)	B10–B15 (2x)	1.867(5)	B15–B6	1.742(4)
B5–B12 (2x)	1.829(4)	*B11–B1*	*1.736(6)*	B15–B14	1.815(5)
B5–B7	1.831(5)	B11–B2	1.759(7)	B15–B9	1.851(5)
B6–*B4*	*1.624(5)*	B11–B14 (2x)	1.829(5)	B15–B8	1.864(4)
B6–B15 (2x)	1.743(4)	B11–B11 (2x)	1.835(9)	B15–B10	1.867(5)
B6–B14 (2x)	1.800(4)	B11–B10 (2x)	1.863(4)		
B6–B8	1.875(5)	B12–B5	1.829(4)		
B7–*B8*	*1.749(5)*	B12–B13	1.844(3)		
B7–B13 (2x)	1.817(3)	B12–B12	1.878(5)		
B7–B5	1.831(5)	B12–B7	1.883(4)		
B7–B12 (2x)	1.883(4)	B12–B13	1.896(3)		
		B12–B12	*1.933(5)*		

[a] Refinement with disorder (see above): B1–B11: 1.610(8) (2x), 1.756(6) (2x), 1.900(10) (2x), B1···B1: 0.534(27).

Table 5
Mg–B distances (Å) in MgB$_{17.4}$

Mg1–B12 (6x)	2.396(3)	Mg3–B15 (2x)	0.835(6)	Mg4–B9	2.19(2)
Mg1–B7 (3x)	2.477(3)	Mg3–B6 (2x)	2.224(10)	Mg4–B10	2.28(2)
Mg1–B9 (3x)	2.518(4)	Mg3–B14 (2x)	2.352(4)	Mg4–B12 (2x)	2.29(2)
Mg1–B8 (2x)	2.527(4)	Mg3–B8 (2x)	2.361(3)	Mg4–B8 (2x)	2.471(17)
Mg2–B11	2.221(6)	Mg3–B9 (2x)	2.462(9)	Mg4–B7 (2x)	2.490(11)
Mg2–B12 (2x)	2.355(3)	Mg3–B10 (2x)	2.506(9)	Mg4–B13 (2x)	2.506(12)
Mg2–B10	2.377(4)	Mg3–B15 (2x)	2.693(16)	Mg4–B14 (2x)	2.534(18)
Mg2–B13 (4x)	2.397(3)	Mg3–B4 (2x)	2.897(16)	Mg4–B15 (4x)	2.546(19)
Mg2–B14 (4x)	2.438(2)				
Mg2–B11 (2x)	2.486(3)				
Mg2–B1	2.571(2)				

Table 6
Mg–Mg distances (Å) and occupation factors in MgB$_{17.4}$

	Distance	Occupation
Mg1–Mg4 (3x)	2.44(2)	0.910(11)/0.067(7)
Mg2–Mg2 (2x)	2.611(3)	0.533(7)/0.533(7)
Mg2–Mg4	2.33(2)	0.533(7)/0.067(7)
Mg3–Mg3	2.66(3)	0.072(12)/0.072(12)
Mg2–Mg4 (2x)	2.45(2)	0.072(12)/0.067(7)
Mg4–Mg1	2.44(2)	0.067(7)/0.910(11)
Mg2–Mg2	2.33(2)	0.067(7)/0.533(7)
Mg2–Mg3 (2x)	2.45(2)	0.067(7)/0.072(12)

vertices of the unit cell (icosahedron 2; B5, B7, B12, B13). Two B$_{28}$-units are placed on the main body diagonal and connected by a single boron atom (B1). The Mg atoms are in voids between the boron polyhedra.
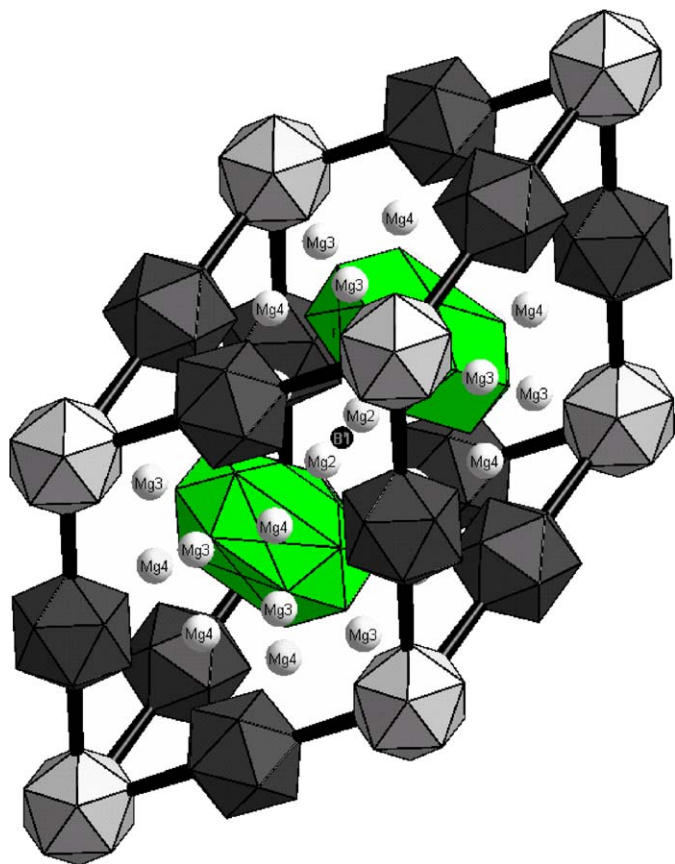
Fig. 1. Unit cell of $MgB_{17.4}$ (rhombohedral setting).

The coordination of the boron atoms reflects the bonding mode of the boron polyhedra. All boron atoms which form the icosahedra have one short exohedral bond and five longer endohedral bonds. The same pattern (one short exohedral and five long endohedral bonds) is found for those B atoms of the B_{28}-unit (B6, B8, B14, B15) which form the 12 half-icosahedra of the B_{84}-units (see below). The remaining boron atoms of the B_{28}-unit (B2, B9, B10, B11) have no exohedral bonds to other boron polyhedra. B2 belongs to all of the three icosahedra and has nine neighbours (or eight, respectively, if the 2/3 occupation of B11 is considered). B9 and B10 with eight boron neighbours are part of the common triangles and belong to two icosahedra. The shorter distances of B10 may result from the lower coordination number because of the B11 deficit. B11 has eight (or seven) endohedral bonds, five within the icosahedron, two (or one) to a B11 atom of the icosahedron condensed at it and one to the connecting B1 atom. The bonds of B1 are a special case. With a full occupation of B11 the coordination would be an elongated trigonal antiprism, but the 2/3 occupation results in a fourfold coordination which might be described as a more or less distorted tetrahedron and is obviously correlated with the "suspicious" thermal displacement parameter of B1. The refinement with a disorder model in x-direction (site 18g) results in a shift of 0.267(13) Å. The initially large value for U_{eq} is reduced to a value of U_{iso} as it is common

for boron-rich borides. Furthermore, the coordination of B1 changes to a situation as it is found for other boron-rich borides with additional exohedral boron atoms like MgB_{12} [13] and α-AlB_{12} [22]. Although this model is quite plausible the refinement with anisotropic thermal parameters led to large standard deviations for the site parameter x and the U_{ij}-values. Therefore, a clear decision for $MgB_{17.4}$ is not possible on the basis of our data.

The boron–boron distances up to 2.0 Å are listed in Table 4. It is well known for boron-rich borides that B–B distances within the polyhedra are in general longer than in between but there are significant differences for the different polyhedra. The endohedral B–B distances in icosahedron 1 are between 1.735 and 1.783 Å ($\varnothing$: 1.764 Å). In icosahedron 2 they are significantly longer with values between 1.810 and 1.896 Å ($\varnothing$: 1.857 Å). The same tendency is found for the exohedral bonds. For icosahedron 1 they range from 1.624 Å (to the B_{28}-unit) up to 1.673 Å (to icosahedron 2). The values for icosahedron 2 cover a larger range from 1.673 Å (to icosahedron 1) and 1.749/1.757 Å (to the B_{28}-unit) to 1.933 Å (to icosahedron 2) ($\varnothing$: 1.800 Å). The endohedral B–B distances of the B_{28}-unit are between 1.735 and 1.914 Å ($\varnothing$: 1.824 Å), the exohedral distances between 1.624 and 1.757 Å ($\varnothing$: 1.706 Å). According to these values the polyhedra show a different "volume" in the order icosahedron 1 < B_{28}-unit < icosahedron 2. This may be explained by different effective charges for the polyhedra. The "isolated" boron atom (B1) connects two B_{28}-units via bonds to B11 (1.736 Å). Because the position of B11 is only partially occupied (about 2/3), the effective coordination of B1 is reduced from 6 to 4. If the partial occupation of B15 is taken into consideration, too, the real composition of the B_{28}-unit is about $B_{26.5}$.

The surroundings of Mg are shown in Fig. 2. Coordination numbers between 12 and 16 are found. Mg–B distances range from 2.19 to 2.90 Å (Table 5) as it is known for other boron-rich borides [MgB_7, MgB_{12}] and boridecarbides ($MgB_{12}C_2$, $Mg_2B_{24}C$, [15]). The only exception is the short distance Mg3–B15 (0.84 Å), but the site of B15 is only partially occupied and the deficit corresponds to the occupation factor of Mg3. This observation was also reported in earlier investigations [9,10] and is confirmed by our results. The shortest Mg–Mg distances are between 2.33 and 2.66 Å but they are combined with the occupation factors in a way that a sum of 1 is not significantly exceeded (Table 6).

There are several ways for the description of the 3D structure of β-rhombohedral boron. Callmer [21] used a cubic closest packing of B_{84}-units and B_{10}-units in trigonal voids. The B_{84}-units are formed by a central B_{12} icosahedron (icosahedron 1) and 12 half-icosahedra (six from icosahedron 2, six from the B_{28}-units): $B_{84} = B_{12}(B_6)_{12}$. The B_{10}-fragment is the "rest" of the B_{28}-units. The deviation of the rhombohedral angle of $\alpha = 65.2°$ from 60° represents the distortion of the cubic closest packing (Table 7). A second way of description shows the

similarity to MgB_{12} [13a], α-AlB_{12} and γ-AlB_{12} [22]. According to this a 3.6.3.6.-net (Kagomé-net) is formed by icosahedra 2 (Fig. 3). The nets are stacked in a sequence ABC in direction (001) of the unit cell (hexagonal setting). The orientation of the nets is in a way that in c-direction two triangles of the Kagomé-net (rotated by 180°) and a hexagon are alternating. Icosahedron 1 is placed between the two triangles and connects the nets. The B_{28}-units are located in the voids above and below the hexagons and are connected by the B1 atom. Icosahedron 1 and the B_{28}-unit form layers (Fig. 4) that are placed between the Kagomé-nets. Fig. 5 shows the rhombohedral unit cell as a fragment of the layers with the hexagon in the middle, above and below the B_{28}-units and two other triangles of the Kagomé-net, connected by the icosahedra 1.

In MgB_{12} there are also 3.6.3.6.-nets of icosahedra which are connected by the second kind of icosahedra, but the stacking sequence is ABAB and the B_{28}-units are replaced by B_{21}-units. In γ-AlB_{12} there is the same arrangement of boron polyhedra as in MgB_{12}, but instead of B_{21}-units there are two different types of B_{20}-units leading to a symmetry reduction and a different electron demand.

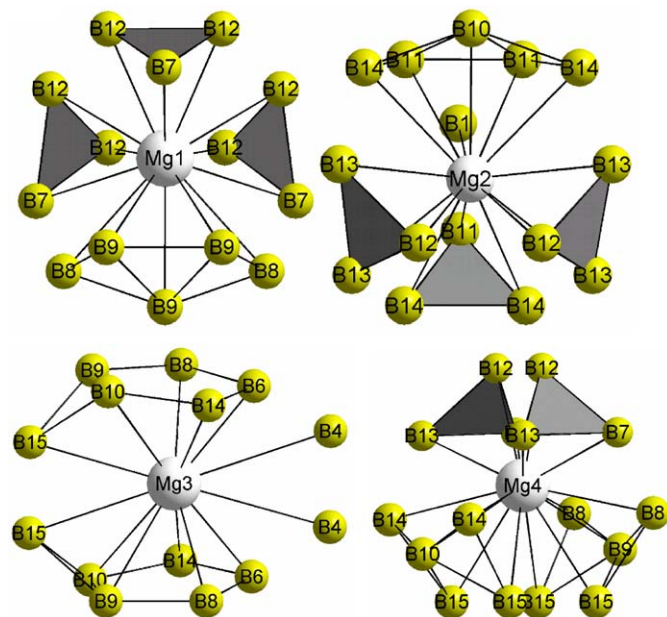A comparison to other binary boron-rich borides derived from β-rhombohedral boron [7] reveals that $MgB_{17.4}$ shows the highest metal content ever found, except the Li compound LiB_{10} [19]/$LiB_{\sim13}$ [8]. This high metal content originates mainly from the high occupation factor for the D site (53%) with a multiplicity of 18, but also the nearly full occupation of the E site (91%) makes a considerable contribution. The closest similarity is found to ScB_{28} [23]. This is easy to understand because Mg and Sc have nearly the same atomic radii and are both very electropositive metals. The main difference is the charge of the cation leading to the corresponding compositions. In ScB_{28} scandium occupies three sites (site D: 31.4(3)%; site E: 72.7(5)%; site F: 5.7(3)%), the position of Mg4 remains empty. Furthermore the same partial occupation of boron sites was observed (61.3(4)% and 92.5(10)%). Also, the structure of ZnB_{25} is related [24]. In ZnB_{25} nearly the same positions are occupied as in ScB_{28} (site D: 28(1)%; site E: 34(1)%; site G 13(1)%, very close to site F), additionally the A1-site (6c; 0,0,0.136) is occupied with 49(1)%.

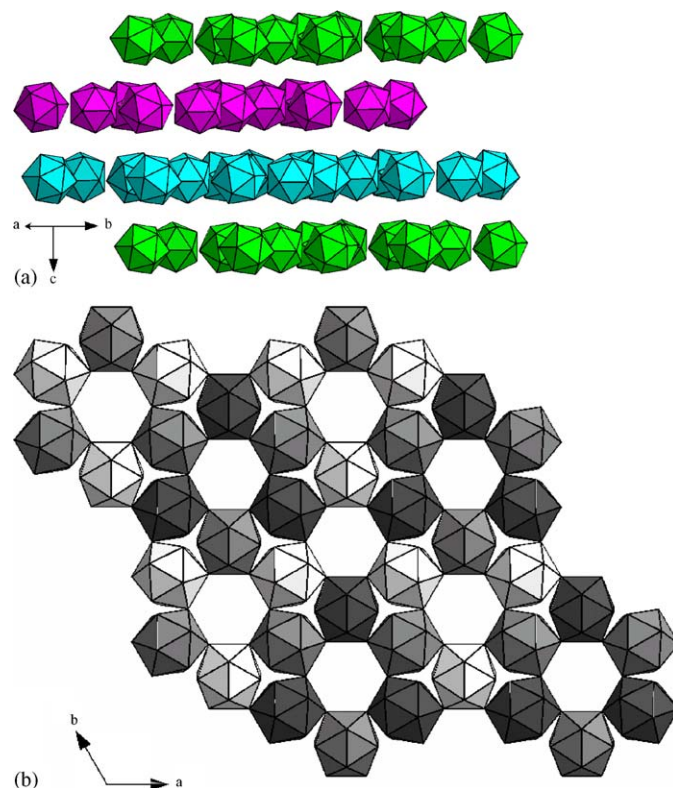Fig. 2. Coordinations of Mg atoms in $MgB_{17.4}$.

Fig. 3. 3.6.3.6.-nets (Kagomé-nets) of icosahedra 2: (a) sequence ABCA, view in a–b plane, (b) sequence ABC as projection along (001).

Table 7
Comparison of structure models and occupation factors (%) for $MgB_{17.4}$

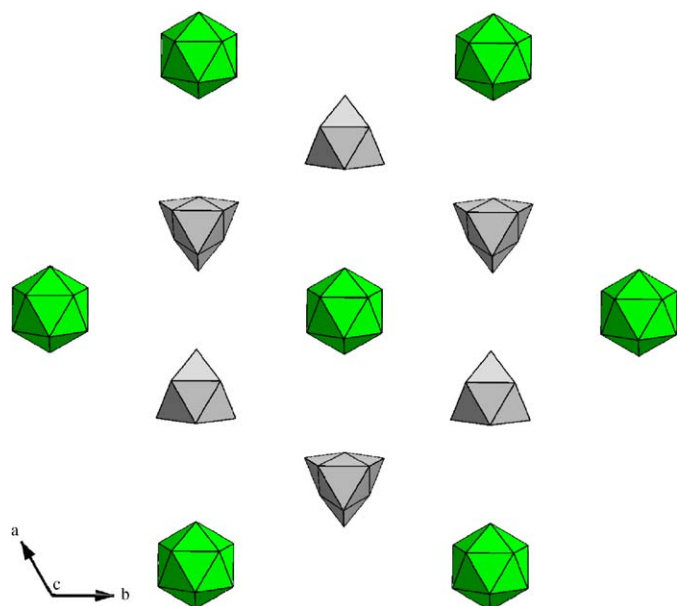|	B15	B11	Mg1	Mg2	Mg3	Mg4	Si (A$_1$)	Composition	
Brutti et al.	92	59	88	49	8	—	—	$Mg_{5.18}B_{101.6}$	$MgB_{19.6}$
Soga et al.	92(1)	67(1)	68(1)	44.2(4)	4.8(7)	—	11.9(5)	$Mg_{4.3}Si_{0.24}B_{102.1}$	$MgSi_{0.06}B_{23.7}$
This work	92(2)	64(2)	91(1)	53.3(2)	7.2(12)	6.7(7)	—	$Mg_{5.85}B_{101.9}$	$MgB_{17.4}$

Atom numbers referred in Table 2.

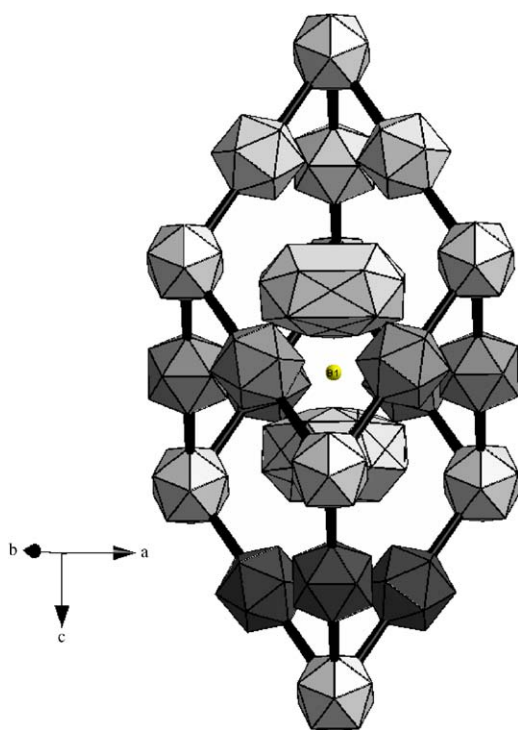Fig. 4. Layers of icosahedra 1 and B_{10}-fragments of the B_{28}-units.

Fig. 5. Rhombohedral unit cell of $MgB_{17.4}$ as a part of the layers, Mg atoms omitted (see text).

in this range are known (for example 2.117 Å in $Mg_2B_{24}C$ [15]), it seems to be more favourable to occupy another position, i.e. the site of Mg4, if a higher metal content is realised. To increase the occupation of Mg2 or Mg3 may be impossible because of the necessity of additional defects in the boron polyhedra (B11/Mg3) or short Mg–Mg contacts (Mg2). The latter may be important because it was predicted, that the occurrence of superconductivity is correlated to the occupation of the D site [10]. A second interesting point is the extent of Mg-doping in $MgB_{17.4}$. It is generally acknowledged, that the intrinsic acceptor level of β-rhombohedral boron can take up 8 electrons [10] and the incorporation of metal atoms takes place to fill up these levels. Up to now all compounds of the β-rhombohedral boron type are semiconductors. The Mg-content of 5.85 atoms corresponds to 11.7 electrons, the highest value ever found for a compound of the β-rhombohedral boron type. Because band structure calculations are still in progress, a rough estimation can be made by the Wade rules [25], which can also be applied to solid state compounds [26]. It is well known that a nido-cluster needs two electrons more than a closo-cluster with the same number of atoms. Therefore a missing boron atom in an icosahedron increases the uptake of electrons. This may explain the deficit for B11 and especially B15, which was only observed for $MgB_{17.4}$, ScB_{28} and LiB_{10}. Also in the case of ScB_{28} the metal atoms can transfer 11 electrons to the boron polyhedra, significantly more than the expected 8 electrons. Similar observations were made for LiB_{10} [19].

5. Conclusions

The use of a mixture of Mg and Cu as a solvent enables the formation of single crystals of Mg containing β-rhombohedral boron. The crystal structure determination is based on single crystal data and reveals the composition $MgB_{17.4}$, as determined from the sum of the occupation factors and confirmed by WDX measurements. The evaluation of the difference Fourier map reveals that Mg atoms partially occupy four different positions. One of them was observed for the first time for a compound related to β-rhombohedral boron and not detected in the earlier investigations on powder samples. Two of the boron positions have partial occupation factors as well.

According to preliminary results the single crystalline samples are also non superconducting as it was already observed for the powder samples.

On the first sight the structure of $MgB_{17.4}$ just seems to extend the series of binary borides related to β-rhombohedral boron, but a closer view shows several details, which improve the understanding of this class of compounds. Together with ScB_{28} it is the only compound without occupation of the A1 site. Obviously Mg^{2+} is too big for this site. A virtual occupation would lead to Mg–B distances of about 2.12–2.14 Å. Although Mg–B distances

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