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On the existence of tetragonal boron and the crystal structures of $B_{50}C_2$ and $B_{50}N_2$: an x-ray diffraction analysis

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Auszug

Das sog. „I-tetragonale Bor“ aus der Literatur ist in Realität ein höheres Borkarbid oder Bornitrid. Wir haben jetzt zwei solcher Kristalle mit der Zusammensetzung $B_{50}C_2$ und $B_{50}N_2$ mit Röntgenbeugungsmethoden untersucht und die Kristallstrukturen bis $R = 5{,}4\%$ verfeinert. Vier B_{12}-Ikosaeder in der Elementarzelle sind durch zwei Kohlenstoff- bzw. Stickstoffatome in $2b = 0 0 \frac{1}{2}$; $\frac{1}{2} \frac{1}{2} 0$ verbunden. Aus Präzessions-Elektronendichtebestimmungen wurden die restlichen zwei Boratome in den Lücken zwischen den Bor-Ikosaedern festgelegt, wo sie statistisch über mehrere Punktlagen verteilt sind und so optimal die Ikosaeder verknüpfen und gleichzeitig die quantenmechanische Bedingung für eine stabile Elektronenstruktur erfüllen.

Abstract

"I-tetragonal boron" of the literature is in fact a higher boron carbide or boron nitride. We have studied two crystals of composition $B_{50}C_2$ and $B_{50}N_2$ by x-ray diffraction analysis and determined the precise electron densities to $R = 5.4\%$. Four icosahedra in the unit cell are bridged by two carbon or nitrogen atoms respectively at $2b$ in $0 0 \frac{1}{2}$; $\frac{1}{2} \frac{1}{2} 0$. Two boron atoms fill the large holes between the icosahedra in a statistical way providing connections between two icosahedra.

I. Introduction

1943 Laubengayer *et al.*[1] reported the preparation of crystals believed to be a new form of elementary boron.

Laubengayer's crystals were subsequently studied by Hoard, Hughes and Sands[2] with x-ray methods and their crystal structures were

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[1] A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, Boron. I. Preparation and properties of pure crystalline boron. J. Amer. Chem. Soc. **65** (1943) 1924—1931.

[2] J. L. Hoard, R. E. Hughes and D. E. Sands, The structure of tetragonal boron. J. Amer. Chem. Soc. **80** (1958) 4507—4515.

published. They are commonly known as "tetragonal boron" or "*I*-tetragonal boron". The following "typical" crystallographic data were given to

$$a = 8.740 \pm 0.015\ \text{Å}, \qquad c = 5.068 \pm 0.010\ \text{Å}$$

$$\text{space group } P4_2/nnm{-}D_{4h}^{12} \qquad \text{with 50 atoms/unit cell}$$

$$\text{density} = 2.29{-}2.33\ \text{g/cm}^3.$$

The crystal structure was described to be constituted of four B_{12} boron icosahedra in the unit cell, which should be linked by two boron atoms.

There are severe doubts about the existence of such a structure of elementary boron. LONGUET-HIGGINS and ROBERTS[3] in a theoretical paper on the bonding mechanism in boron icosahedra and their application to boron-rich crystals immediately pointed out that a structure as reported by HOARD und HUGHES does not have a stable electronic configuration and therefore cannot be correct. However the crystals are extremely stable with extreme hardness and a high melting point.

Further chemical evidence has been accumulated in the last years by BECHER and coworkers[4] in Münster and by AMBERGER and coworkers[5] in Munich. These studies have shown that while it is possible to induce the *I*-tetragonal lattice by introducing electron donor atoms, especially C, N or Be, and also Al, it is impossible to crystallize elementary, *e.g.* pure boron with the above described unit cell.

The two crystal specimens studied by HOARD and HUGHES, which were described as a "needle-like" and a "plate-like" one, yielded different results in their density, lattice parameters and diffraction intensities. There is only one reasonable explanation for this discrepan-

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[3] H. C. LONGUET-HIGGINS and M. DE V. ROBERTS, The electronic structure of an icosahedron of boron atoms. Proc. Roy. Soc. [London] A **230** (1955) 110—119.

[4] H. J. BECHER and A. SCHÄFER, Über die Modifikationen des Bors. Versuche zur Einlagerung von Beryllium in das Borgitter. Z. anorg. allg. Chem. **306** (1960) 260—265. — K. KROGMANN and H. J. BECHER, Strukturbestimmung eines aluminium- und berylliumhaltigen tetragonalen Bors der Formel $AlBe_{0.8}B_{24.2}$. Z. anorg. allg. Chem. **392** (1972) 197—208.

[5] K. PLOOG, H. SCHMIDT, E. AMBERGER, G. WILL, and K. H. KOSSOBUTZKI, $B_{48}B_2C_2$ und $B_{48}B_2N_2$, zwei Nichtmetallboride mit der Struktur des sog. *I*-tetragonalen Bors. J. Less-Common Metals **29** (1972) 161—169. — E. AMBERGER and H. SCHMIDT, Stickstoffinduziertes Gitter beim Bor: *I*-tetragonales Bornitrid $(B_{12})_4B_2N_{1-2}$. Z. Naturforsch. **26b** (1971) 641—646. — K. PLOOG and E. AMBERGER, Kohlenstoff-induzierte Gitter beim Bor: *I*-tetragonales $(B_{12})_4B_2C$ und $(B_{12})_4B_2C_2$. J. Less-Common Metals **23** (1971) 33—42.

cy. Since no chemical analysis was performed, the chemical composition is not known and additional non-boron atoms must have been present in the two crystals. All efforts to clarify this puzzle have therefore to concentrate on additional atoms between the icosahedra. X-ray diffraction with its possibility to locate atoms through their electron densities is an appropriate tool.

We have studied boron rich compounds previously, AlB_{10} [6] and C_4AlB_{24} [7] and found that carbon and/or aluminium is distributed in a statistical way between the icosahedra, however at well defined distances and angles. These atoms are needed in the crystal structure to give the required closed shell electronic configuration to the B_{12} icosahedra as postulated by LONGUET-HIGGINS and ROBERTS[3]. We have now done x-ray diffraction work to clarify the problem of "tetragonal boron". Careful preparative work has been done by AMBERGER and his coworkers, yielding two compounds of known composition $B_{50}C_2$ and $B_{50}N_2$ both crystallizing with the I-tetragonal lattice. We have studied both crystals by x-ray diffraction methods with extreme care and precision, and the results of this study are reported in this paper.

II. Crystal data

For preparation and analysis of the crystals we refer to reference[4]. The crystals studied were of irregular shape with the approximate

Table 1. *Crystal data of* $B_{50}C_2$ *and* $B_{50}N_2$

Composition		$B_{50}C_2$	$B_{50}N_2$
Temperature of preparation		1200	1400 °C
Lattice constants with standard deviations			
	$a =$	8.753(4)	8.634(4) Å
	$c =$	5.093(15)	5.128(3) Å
Density	observed	2.43	2.46 g cm^{-3}
	calculated	2.426	2.463 g cm^{-3}
Chemical analysis		$B_{50}C_{1.9}$	$B_{50}N_{1.8}$
Weight % of C or N	observed	4.1	4.5
	calculated	4.25	4.93

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[6] G. WILL, Crystal structure analysis of AlB_{10} by the convolution molecule method. Acta Crystallogr. **23** (1967) 1071—1079.

[7] G. WILL, Die Kristallstruktur von C_4AlB_{24}. Acta Crystallogr. B **25** (1969) 1219—1222.

dimensions

$B_{50}C_2$: 80 × 80 × 100 microns

$B_{50}N_2$: 80 × 80 × 260 microns.

The unit-cell data derived from diffractometer least-squares evaluation, and other crystal-chemical data are summarized in Table 1.

III. Experimental

Diffraction data were collected on a Philips Pailred diffractometer, which is essentially an automatic two-circle diffractometer with Weissenberg geometry. θ-2θ scan technique at a rate of 0.15°/min over 3° scan range was used, and background counts were collected for 60 sec at both the upper and lower scan limits. This leads to 21 min for each reflection. We have chosen this low scan speed in order to achieve the required statistics and accuracy on the small crystals available. We have measured all equivalent reflections, including forbidden ones, resulting in a total of 797 for $B_{50}C_2$ and 783 for $B_{50}N_2$ respectively (the radiation was Cu$K\alpha$). Their counting statistics are analyzed in Table 2.

Table 2. *Distribution of the observed reflection intensities according to their standard deviations σ*

number of reflections in $B_{50}C_2$	standard deviations of the measured intensities	number of reflections in $B_{50}N_2$
323	$\sigma < 2\%$	299
197	2%– 4%	215
112	4%– 6%	112
77	6%– 8%	63
42	8%–10%	39
46	$\sigma > 10\%$	55
797		783

The crystals were mounted along their c axis and data were collected up to the fourth layer line. The crystal orientations were checked by rotating around the scattering vectors $[00l]$. The maximum intensity deviation is 3%, the standard deviations σ for rotations around [001], [002], [003], and [004] range between 0.26% and 0.76%. Absorption is negligible in these crystals, extinction was checked during the refinement and found to be negligible.

IV. Space group

The space group is given as $P4_2/nnm$ by HOARD and HUGHES[2] from the conditions of the observed reflections:

hkl	no conditions
$hk0$	$h + k = 2n$
$0kl$	$k + l = 2n$
hhl	no conditions .

We felt it necessary to check these conditions and to measure *all* reciprocal lattice points including the forbidden ones. From a total of 797 measured reflections, 145 should be forbidden by the above extinction rules.

In both crystals we did measure significant intensities for forbidden reflections. With $B_{50}C_2$ at least eight reflections showed intensities well above the limit of detection, and for $B_{50}N_2$ we observed at least 41 "forbidden" reflections. For $B_{50}N_2$ we definitely must reject $P4_2/nnm$ as the proper space group, and we propose $P\bar{4}2m$ instead, which is a subgroup of $P4_2/nnm$. $P\bar{4}$ is of still lower symmetry and can be safely rejected. A detailed discussion is given in the next sections.

V. The crystal structure of $B_{50}C_2$

The crystal structures of the compounds studied are closely related to the structure proposed by HOARD and HUGHES[2]. We have taken their model as a starting basis and then used Fourier, difference Fourier and least-squares calculations to locate all atoms in the unit cell and to determine the precise electron-density distribution (Fig. 1).

Already in the first difference Fourier maps it became clear that the atoms at $2b$, bridging four icosahedra, are carbon atoms and not boron as assumed by HOARD and HUGHES. Further strong electron densities appeared in the positions $2a = (000)$ and $8i = x00$. Least-squares calculations at that stage resulted in $R = 7.7\,\%$ with 5.76e = carbon in $2b$, 0.65e = statistical boron in $2a$, and 0.57e = statistical boron in $8i$. The ensuing difference Fourier maps revealed now new electron densities at $8h = 0\,\frac{1}{2}\,z$ indicating boron atoms statistically distributed over the large holes between the icosahedra (Fig. 2).

The final full-matrix least-squares calculations, including isotropic and anisotropic temperature factors, and verified by difference Fourier calculations gave the detailed electronic distribution tabulated in Table 3. The final R value is $5.4\,\%$. Table 3 lists isotropic temperature

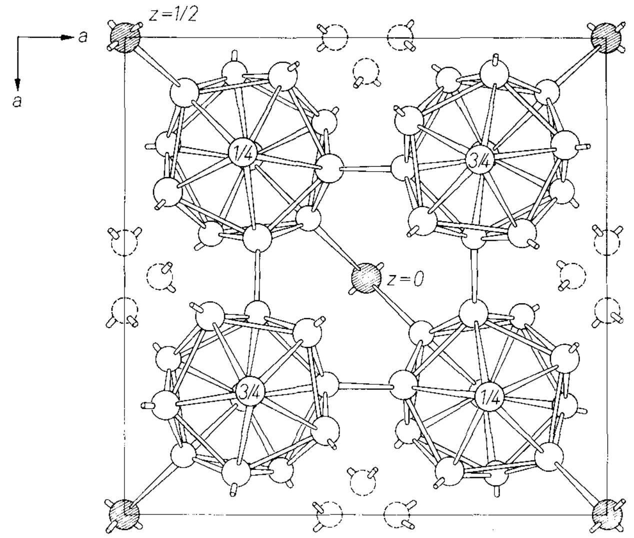

Fig. 1. Projection of the structure along the *c* axis

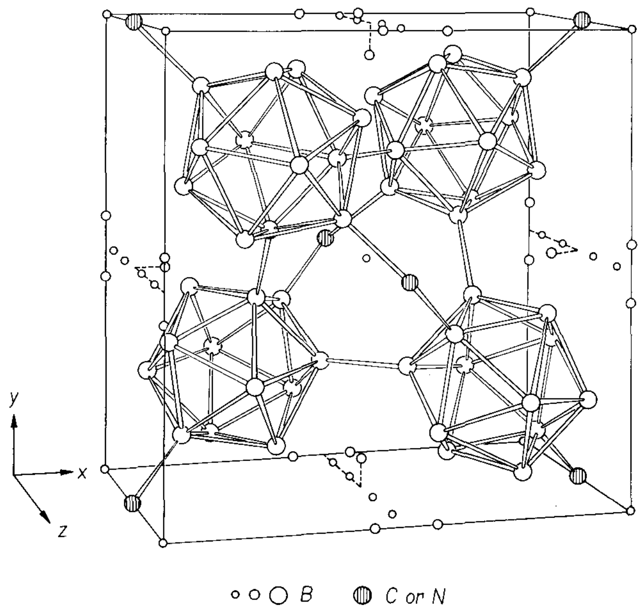

Fig. 2. Crystal structure of $B_{50}C_2$ (respectively $B_{50}N_2$) depicting one unit cell

factors, since the anisotropic refinement yielded no deviation from spherical symmetry. The occupation numbers of the icosahedral boron atoms were kept constant $= 5$ and served as an internal

Table 3. *Coordinates, isotropic temperature factors and electron densities in* $B_{50}C_2$ *from the least-squares calculations*

Table 3a, space group $P4_2/nnm$, 186 reflections, $R = 5.4\%$

		position	electrons /site	coordinates			temperature factor B
				x	y	z	
icosahedron	B(1)	16*n*	5	.3259(2)	.0890(2)	.3990(6)	1.06(4) Å^2
	B(2)	16*n*	5	.2260(2)	.0806(2)	.0873(6)	0.97(4)
	B(3)	8*m*	5	.1227(5)	.1227(5)	.3798(8)	1.16(5)
	B(4)	8*m*	5	.2474(6)	.2474(6)	.5849(7)	1.00(5)
atoms between the icosahedra	B(5)	2*a*	0.64	.0	.0	.0	1.00(5)
	B(6)	8*i*	0.49	$.43_3(4)$	.0	.0	1.00(5)
	B(7)	8*h*	0.56	.0	.5	.856(6)	1.00(5)
	C(8)	2*b*	5.45	.0	.0	.5	0.54(9)

Table 3b, space group $P\bar{4}2m$, 228 reflections, $R = 6.5\%$

		position	electrons /site	coordinates			temperature factor B
				x	y	z	
icosahedron	B(1)	8*o*	5	.3260(4)	.0889(4)	.3995(12)	0.82(7) Å^2
	B(1′)	8*o*	5	.8260(4)	.5892(4)	.1019(13)	1.28(8)
	B(2)	8*o*	5	.2268(4)	.0809(4)	.0878(10)	0.92(7)
	B(2′)	8*o*	5	.7252(4)	.5802(4)	.4135(11)	1.02(8)
	B(3)	4*n*	5	.1241(9)	.1241(9)	.3803(18)	1.22(10)
	B(3′)	4*n*	5	.6183(9)	.6183(9)	.1207(17)	1.04(10)
	B(4)	4*n*	5	.2473(8)	.2473(8)	.5849(15)	0.81(12)
	B(4′)	4*n*	5	.7443(9)	.7443(9)	.9150(16)	1.18(13)
atoms between the icosahedra	B(5)	1*a*	0.73	.0	.0	.0	1.00
	B(5′)	1*b*	0.62	.5	.5	.5	1.00
	B(6)	4*i*	0.41	.4345(9)	.0	.0	1.00
	B(6′)	4*j*	0.56	.9273(7)	.5	.5	1.00
	B(7)	4*m*	0.59	.0	.5	.839(9)	1.00
	B(7′)	4*m*	0.53	.0	.5	.393(15)	1.00
	C(8)	1*c*	5.50	.0	.0	.5	0.4(2)
	C(8′)	1*d*	5.44	.5	.5	.0	0.8(2)

calibration. This gave us a possibility to determine the electronic occupancies of the non-icosahedral atoms by least-squares refinement with high reliability and accuracy. For a test we additionally allowed the parameter for the icosahedral boron atoms to vary (with the

Table 4

Comparison of atomic positions in the two space groups $P4_2/nnm$ and $P\bar{4}2m$

	$P4_2/nnm$			$P\bar{4}2m$		
icosahedral atoms	B(1)	$16n$	xyz	B(1), B(1′)	$8o$	xyz and $x'+\frac{1}{2}; y'+\frac{1}{2}; \frac{1}{2}-z'$
	B(2)	$16n$	xyz	B(2), B(2′)	$8o$	xyz and $x'+\frac{1}{2}; y'+\frac{1}{2}; \frac{1}{2}-z'$
	B(3)	$8m$	xxz	B(3), B(3′)	$4n$	xxz and $x'+\frac{1}{2}; x'+\frac{1}{2}; \frac{1}{2}-z'$
	B(4)	$8m$	xxz	B(4), B(4′)	$4n$	xxz and $x'+\frac{1}{2}; x'+\frac{1}{2}; \frac{1}{2}-z'$
non-icosahedral atoms	B(5)	$2a$	000	B(5), B(5′)	$1a$	000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
	B(6)	$8i$	$x00$	B(6), B(6′)	$4i$	$x00$ and $x'+\frac{1}{2}\frac{1}{2}\frac{1}{2}$
	B(7)	$8h$	$0\frac{1}{2}z$	B(7), B(7′)	$4m$	$0\frac{1}{2}z$ and $\frac{1}{2}0\frac{1}{2}+z'$
	C(8)	$2b$	$00\frac{1}{2}$	C(8), C(8′)	$1c$	$00\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$

scale factor as a constant) resulting in values of respectively 5.01, 4.93, 4.98 and 5.00, corraborating our model and our approach.

Summation of all electrons in $B_{50}C_2$ gives a total of 20.7 electrons distributed between the B_{12} icosahedra. This is only 1.3 electrons less than the 22 electrons expected. Refering to the chemical analysis of Table 1 with $B_{50}C_{1.9}$ the difference between the x-ray analysis and the chemical analysis leaves a deficit of merely 0.7 electrons.

The earlier least-squares calculations were carried out in the original space group $P4_2/nnm$. Since we did observe significant intensities for at least eight reflections forbidden in this space group (all in the zone $[hk0]$), refinement was also done in the space group $P\bar{4}2m$. This allows atomic pairs previously fixed by symmetry to move now independently (Table 4). The R value of this least-squares calculation in $P\bar{4}2m$ reached $R = 6.5\,^0/_0$. The new coordinates are within the limits of the standard deviation of the first set, Table 3a. On the basis of only 8 additional reflections showing significant intensities it is difficult to decide between the two space groups, and at least for $B_{50}C_2$ x-ray diffraction does not give sufficient evidence to decide between space group $P4_2/nnm$ proposed originally, or $P\bar{4}2m$.

VI. The crystal structure of $B_{50}N_2$

In $B_{50}N_2$ we proceeded along the same lines as in $B_{50}C_2$ with Fourier, difference Fourier and least-squares calculations and obtained finally the coordinates and electron-distribution values listed in Table 5a (using $P4_2/nnm$). The bridge $2b$ between the icosahedra is now nitrogen. The final R value was $5.4\,^0/_0$ (space group $P4_2/nnm$).

The total number of non-icosahedral electrons detected in $B_{50}N_2$ is 23.32, compared to 22.6 electrons expected from the chemical

Table 5. *Coordinates, isotropic temperature factors and electron densities in* $B_{50}N_2$ *from the least-squares calculations*

Table 5*a*, space group $P4_2/nnm$, 182 reflections, $R = 5.4\,^0/_0$

		position	electrons /site	coordinates			temperature factor
				x	y	z	B
icosahedron	B(1)	16*n*	5	.3242(2)	.0871(2)	.3993(5)	0.88(4) Å^2
	B(2)	16*n*	5	.2278(2)	.0811(2)	.0863(5)	0.72(4)
	B(3)	8*m*	5	.1197(5)	.1197(5)	.3710(7)	0.80(5)
	B(4)	8*m*	5	.2457(5)	.2457(5)	.5853(7)	0.81(5)
atoms between the icosahedra	B(5)	2*a*	0.07	.0	.0	.0	1.00
	B(6)	8*i*	1.15	.431(2)	.0	.0	1.00
	B(7)	8*h*	0.13	.0	.5	$.86_5$(.03)	1.00
	N(8)	2*b*	6.50	.0	.0	.5	0.37(4)

Table 5*b*, space group $P\bar{4}2m$, 223 reflections, $R = 5.8\,^0/_0$

		position	electrons /site	coordinates			temperature factor
				x	y	z	B
icosahedron	B(1)	8*o*	5	.3209(5)	.0908(5)	.3978(11)	1.14(7) Å^2
	B(1′)	8*o*	5	.8273(4)	.5836(4)	.0998(11)	0.58(6)
	B(2)	8*o*	5	.2276(4)	.8223(4)	.0873(9)	0.63(6)
	B(2′)	8*o*	5	.7276(5)	.5801(5)	.4145(9)	0.79(7)
	B(3)	4*n*	5	.1185(10)	.1185(10)	.3742(16)	0.87(9)
	B(3′)	4*n*	5	.6193(9)	.6193(9)	.1322(16)	0.72(9)
	B(4)	4*n*	5	.2444(9)	.2444(9)	.5772(12)	0.70(10)
	B(4′)	4*n*	5	.7449(9)	.7449(9)	.9060(13)	0.82(10)
atoms between the icosahedra	B(5)		0	.0	.0	.0	
	B(5′)		0	5	5	.5	
	B(6)	4*i*	1 22	.436(3)	0	.0	1.00
	B(6′)	4*j*	1.11	.927(3)	.5	.5	1.00
	B(7)	4*m*	0.24	.0	.5	.85(3)	1.00
	B(7′)		0				
	N(8)	1*c*	6.44	.0	.0	.5	0.3(1)
	N(8′)	1*d*	6.66	.5	.5	.0	0.7(1)

composition. We can therefore claim to have located all electrons in the crystal. In contrast to $B_{50}C_2$ we have now few, or even no electrons at all on the sites 2*a* and 8*h*. However in both crystals there is some electron transfer from the nitrogen and carbon atoms at $2b$ (6.5 electrons instead of 7 for N).

In $B_{50}N_2$ we observed some rather strong reflections forbidden in $P4_2/nnm$. Hence this space group must be rejected and $P\bar{4}2m$ is assumed to be the proper space group. We have performed least-squares calculations in $P\bar{4}2m$ with all 223 reflections. The results are included in Table 5*b*. The final *R* value was 5.8⁰/₀.

Table 4 shows the relation between the two space groups. For example, the position $8h$ is split into two groups $4m$.

Comparing Tables 3*a* and 3*b* ($B_{50}C_2$) and 5*a* and 5*b* ($B_{50}N_2$) we observe that in $B_{50}C_2$ the electrons are almost equally distributed over the two split sites. In $B_{50}N_2$ however we observe now in $P\bar{4}2m$ no electrons in site B(7′), which means a loss in symmetry and may be responsible for the lower symmetry of that compound.

A further difference between $B_{50}C_2$ and $B_{50}N_2$ is the occupation of $2a$, where we find no electrons in $B_{50}N_2$ in contrast to 0.64 electrons in $B_{50}C_2$.

VII. Discussion of the theory of LONGUET-HIGGINS and ROBERTS

Let us first give some quantum mechanical considerations using the concept of closed shell-type boron icosahedra, as postulated by LONGUET-HIGGINS and ROBERTS[3]. Each boron atom possesses four valence orbitals, one $2s$ and three $2p$. In the LCAO approach the unhybridized set of 48 atomic orbitals of one B_{12} icosahedron can be combined into 12 equivalent outward pointing *sp*-hybrid orbitals and a set of 13 bonding and 23 antibonding molecular orbitals separated by a substantial energy gap. The latter 13 orbitals lie on the surface of the icosahedron with strong bonding forces to the next boron atoms. The 12 *sp*-hybrid orbitals must be perpendicular to the nearly spherical icosahedral surface providing single radial *sp*-hybrid orbitals, each of which can form a strong σ-bond between the icosahedron and the next icosahedron or any other atom.

In order to obtain a stable crystal configuration two conditions have to be fulfilled:

i) To achieve a closed shell configuration 38 valence electrons are required for each icosahedron, 26 for the inner icosahedral bonding orbitals, and 12 for the outward pointing *sp*-hybrid orbitals. The 12 boron atoms can, however, contribute only 36 electrons leaving a deficit of two electrons, which has to be compensated by additional inter-icosahedral atoms.

ii) The twelve *sp*-hybrid bonds must find atomic orbitals close enough and in the proper directions in order to form covalent bonds.

It is obvious, that the original structure proposed by HOARD *et al.* together with the given composition $B_{50} = (B_{12})_4B_2$ cannot fulfill either of the two requirements. It also explains convincingly the failure of preparing *elementary* boron in the *I*-tetragonal form.

The structures reported here satisfy both requirements to a very high degree. Before discussing the crystal structure we want to emphasize that distance *and* directions have to be satisfied. Especially the latter condition explains the statistical distribution of the boron atoms in the large holes.

VIII. Discussion of the crystal structures

The crystal structures (Fig. 1) of $B_{50}C_2 = B_{48}B_2C_2$ and $B_{50}N_2 = B_{48}B_2N_2$ are determined by the icosahedral framework of four B_{12} units, as already found by HOARD and HUGHES. They are centered in the positions $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}$.

The B—B distances within the icosahedra are tabulated in Table 6. They range from 1.750 to 1.891 Å, with an average B—B distance of 1.80 ± 0.004 Å for both $B_{50}C_2$ and $B_{50}N_2$. These values are in good agreement with values found previously in elementary boron[8], AlB_{10} [6], C_4AlB_{24} [7] and $B_{13}C_2$ [9].

The "coordination polyhedron" for one boron atom *in* the icosahedron is a pentagonal pyramide consisting of five boron atoms and one σ orbital perpendicular to the pentagonal plane. Three boron atoms on the surface of an icosahedron form a triangle with angles between 58° and 63° and an average value of 60.02 ± 0.18° (for both compounds), compared to 60° for the ideal case of an equilateral triangle.

Each icosahedral boron atom has one σ bond pointing outward perpendicular to the pseudospherical icosahedral surface. Of the twelve icosahedral boron atoms, six form bonds with the next icosahedra to atoms B′(2) and B′(4) (Table 7), four with B—B distances of 1.668 Å ($B_{48}B_2C_2$) and 1.656 Å ($B_{48}B_2N_2$) respectively, and two with

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[8] J. L. HOARD, D. B. SULLENGER, C. H. L. KENNARD and R. E. HUGHES, The structure analysis of β rhombohedral boron. J. Solid State Chem. **1** (1970) 268—277. — D. GEIST, R. KLOSS und H. FOLLNER, Verfeinerung des β-rhomboedrischen Bors. Acta Crystallogr. **B 26** (1970) 1800—1802.

[9] G. WILL and K. H. KOSSOBUTZKI, An x-ray structure analysis of boron carbide $B_{13}C_2$. J. Less-Common Metals **44** (1975) 87—97.

Table 6. *B—B bond distances within the boron icosahedron*

atoms	$B_{50}C_2$	$B_{50}N_2$
1—1	1.848(6) Å	1.875(6) Å
1—2	1.814(4)	1.809(4)
1—2′	1.816(3)	1.797(3)
1—3	1.805(5)	1.794(5)
1—4	1.815(4)	1.802(4)
2—2′	1.800(4)	1.791(4)
2—3	1.781(5)	1.764(5)
2—4′	1.758(3)	1.750(3)
3—4	1.864(5)	1.891(5)

Table 7

	number of bonds	$B_{50}C_2$		$B_{50}N_2$	
		bond distance	angle α	bond distance	angle α
a) bonds between icosahedra					
B(2)—B′(2)	4	1.668(5) Å	7.67(13)°	1.656(5) Å	6.93(12)°
B(4)—B′(4)	2	1.682(8)	$3.2_2(.4)$	1.693(8)	$5.2_6(.4)$
b) bonds to non-icosahedral atoms					
B(3)—C, resp. N (2*a*)	2	1.638(4)	$0.8_1(.3)$°	1.604(4)	$3.0_6(.3)$°
B(1)—B(6) (8*i*)	4	1.620(5)	53°	1.610(3)	55°
or B(1)—B(7) (8*h*)	4	1.726(5)	49°	1.702(2)	49°

1.682 Å and 1.693 Å respectively. Since for a stable electronic configuration the icosahedral *sp*-hybrid orbitals pointing perpendicular to the icosahedral surface must form covalent bonds, the directions of the bonds are of importance. We have included in Table 7 the angle α between the bond direction and the normal defined by two atoms lying on opposite sites of an icosahedron. This angle therefore defines the deviation from the quantum mechanically ideal direction normal to the icosahedron. The values found are between 3° and 7°. The B—B bonds between icosahedra have a mean value of 1.670 Å and are therefore considerably shorter than B—B distances within the icosahedra.

Of the remaining six icosahedral boron atoms two are bonded to carbon or nitrogen respectively in positions 2*b* $(0 0 \frac{1}{2}, \frac{1}{2} \frac{1}{2} 0)$ with a B—C distance of 1.638 Å and a B—N distance of 1.604 Å, and four are bonded to single boron atoms in the statistically occupied positions $8i$ and $8h$. The B—B distances to the atoms in $8i$ and $8h$ are 1.620 Å and 1.726 Å for $B_{48}B_2C_2$ and 1.610 Å and 1.702 Å for $B_{48}B_2N_2$.

The atoms in the positions $2b$ deserve attention. They form bridges with covalent bonding between four icosahedra. In contrast to the proposal of HOARD *et al.*[2] these bridges are however occupied by carbon or nitrogen and *not* by boron atoms. The four icosahedra surrounding the C or N atoms form a flattened bisphenoid due to the tetrahedral c/a ratio $= 0.58$ and 0.59 respectively.

The attachment of carbon, nitrogen and boron atoms to the listed intericosahedral sites is unequivocal. If, for example, carbon in $[0 0 \frac{1}{2}]$ is replaced by boron, the R value increases from 5.8 to 7.5 per cent. The quantitative occupations given in Table 3 and 5 were derived from least-squares calculations. The standard deviation is about 0.1 electron.

The main difference to the former structure proposal and the improvement of the electronic properties is found in the two single boron atoms per unit cell, which are statistically distributed in the large tetrahedral holes around the positions $4c$ $(0\frac{1}{2}0, \frac{1}{2}00, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2})$. We believe that we have here the key for the understanding of the structure. These tetrahedral holes measure about 3.4 Å in diameter and are therefore too large to accept just one bonding boron atom in the center close enough to all icosahedra to serve as a link. The boron atoms are therefore found displaced towards two icosahedra, which finally yields a statistical distribution over 16 positions, namely $8i$ and $8h$ (see Table 3). The displacement from the center is 0.60 Å and 0.68 Å, respectively. The spatial situation easily permits such a displacement from the central position. The geometric bonding conditions in the icosahedral framework in fact force the boron atoms to such displacements. These additional atoms, however, permit the fulfillment of the conditions (*i*) and (*ii*) for stable structures to a very high degree. These bonding conditions are depicted in Fig. 3. The third intericosahedral site $2a$ obviously accepts boron atoms just by chance since there is sufficient space between two carbon or nitrogen atoms. These boron atoms do not seem to have any bonding function, which is also expressed by the fact, that in $B_{50}N_2$ these holes are practically empty.

From the electron balance we learn, that only 50% of the large holes around $4c$ are occupied by boron. This leads us to the conclusion that a compound of $B_{50}C_2X_2$ should be possible or even more stable.

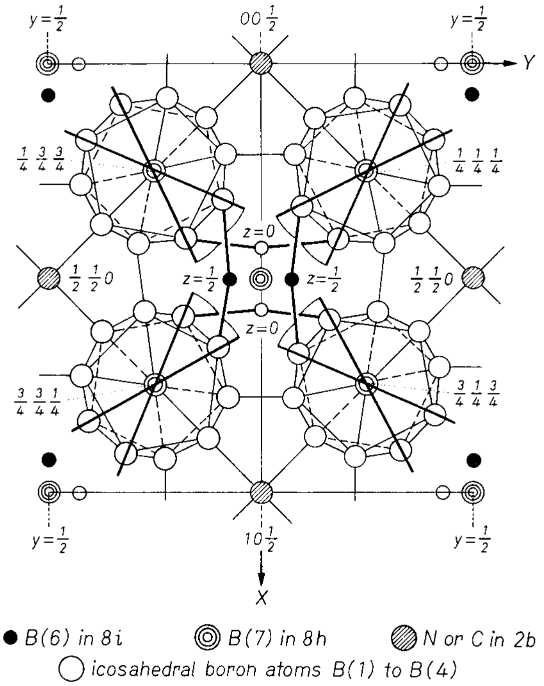

Fig. 3. Bonding relation between two icosahedra via shifted boron atoms B(6) at 8*i* or B(7) at 8*h* (referring to Table 3 and 5, space group $P4_2/nnm$). The atoms are shifted by, respectively, 0.59 Å and 0.73 Å in $B_{50}C_2$, and 0.60 Å and 0.68 Å in $B_{50}N_2$ from the center of the hole between the icosahedra at 4*c*

If we wish to fill the holes at 2*a* too, the composition could be as high as $B_{50}C_2X_3$. X could be boron, perhaps also Be or Al.

The distances between positions 8*i* and 8*h* range from 0.9 Å to 1.47 Å, so in general there is space for only one boron atom. It can be imagined however, that through distortion of the tetragonal lattice these holes can be widened enough to accept two boron atoms thus yielding the perfect quantum-mechanical condition.

In conclusion we find, that the quantum-mechanically unstable B_{48} lattice is stabilized by boron and carbon or nitrogen atoms yielding the compositions $B_{48}B_2C_2$ and $B_{48}B_2N_2$. The extra atoms fill holes in the tetragonal icosahedral framework.

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