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Crystal Structure of Tetragonal Boron Related to α-AlB_{12}

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Single crystals of the so-called β-tetragonal (or tetragonal II or III) boron modification have been obtained from boron deposits prepared by hydrogen reduction of BBr_3 on tantalum filaments at 1200°C. Chemical analysis of the samples shows that this phase can be regarded as a true modification of pure elemental boron in contrast to α-tetragonal phases which require small amounts of foreign atoms to stabilize their boron framework.

The lattice parameters ($a = 10.14(1)$ Å; $c = 14.17(1)$ Å) were obtained and refined from single crystal data. The unit cell contains four chemical units, $B_{21} \cdot 2B_{12} \cdot B_{2.5}$ resulting in $d_c = 2.34$ g cm^{-3} ($d_m = 2.36(2)$ g cm^{-3}). The systematic extinctions are compatible with space group $P4_1$ or $P4_3$.

The structure was determined from 1009 independent reflexions using a model derived from the recently solved structure of α − AlB_{12} ($a = 10.161$ Å; $c = 14.283$ Å; space group $P4_12_12$ or $P4_32_12$). The final R value (unweighted data) is 9.6%.

Basically, the structure of this tetragonal form of boron consists of the same three-dimensional boron skeleton, built upon simple and twinned icosahedra, as that of α-AlB_{12}. However, the defective twinned icosahedral B_{19} units in α-AlB_{12} are now completed (B_{21} units) in the related tetragonal boron. A number of interstitial sites, located at positions different from those occupied by aluminum in α-AlB_{12}, are totally or partially filled by boron atoms and very probably increase the stability of the boron framework.

Introduction

Two tetragonal forms of boron have been reported in the past. Their existence as true modifications of pure elemental boron has remained a subject of controversy for many years and has been recently discussed in detail (*1*).

The first one, called α-tetragonal (or tetragonal I) boron, was claimed to be, a long time ago, a true modification of pure boron by A. W. Laubengayer *et al.* and its structure was solved, on single crystal, by J. L. Hoard *et al.* in 1958 (*2–4*). More recently, E. Amberger, K. Ploog *et al.* have shown that it corresponds, in fact, to tetragonal boron-rich phases with a three-dimensional network of B_{12} icosahedra stabilized by small amounts of foreign atoms such as carbon ($B_{48}B_2C_2$), nitrogen ($B_{48}B_2N_2$) or/and transition elements ($B_{48}B_2Ti_{1.3\text{-}2.0}$ or $B_{48}C_{1.68}Ti_{1.78}$), rather than to a true modification of pure elemental boron (*5–18*).

The second tetragonal form (referred to variously as β-tetragonal, tetragonal II or tetragonal III) was first reported by C. P. Talley *et al.* in 1960. It was obtained as a polycrystalline material by hydrogen reduction of pure BBr_3 on tungsten or rhenium filaments heated at 1270°C. The cell

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parameters ($a = 10.12$ Å; $c = 14.14$ Å), established from a powder pattern, were found to be very similar to those of α-AlB_{12}(*19*). Later on, these results were confirmed, independently, by E. Amberger and K. Ploog and by M. Botret (*5, 6, 20*). Approximately at the same time, D. B. Sullenger *et al.* also reported the presence of crystals of this second tetragonal phase in products resulting from passing boron powder through an argon plasma at very high temperatures; the main component being β-rhomobohedral boron (*22*). All these experiments seemed to support the existence of a second tetrahedral form of boron. However, the existence of several boron-rich borides (α-AlB_{12}, BeB_6 and $LiB_{\sim 10.8}$) with very similar cell parameters casts some doubt on its occurrence as a true modification of pure boron (*15–18*).

We have been able to prepare, in a reproducible manner, single crystals of this second tetragonal phase and to establish that this material does not contain significant amounts of impurities, As was expected by earlier investigators, its structure, which we have studied by conventional single crystal X-ray analysis, is closely related to the recently published structure of α-AlB_{12} (*23–24*).

Experimental

(1) Preparation and Analysis of the Samples

The crystals that we have studied were picked up, after crushing, from samples obtained independently by K. Ploog, and M. Boiret by chemical vapor deposition on a tantalum filament according to techniques described elsewhere (*1, 20, 21*). In both cases, the boron source (BBr_3) and the reducing agent (H_2) were highly purified materials. The tantulum filaments ($\varnothing = 200$ to 750 μ) were heated for 1 to 4 hr, at a temperature of 1200°C, in a BBr_3-H_2 gas flow. The resulting boron deposits had a thickness of 1 to 2 mm.

Since the deposition of boron was made from very pure reagents and in carefully cleaned apparatus, the only possible contamination could come from the substrate. It has been, indeed, established that diffusion phenomena occur at the boron–substrate interface during the boron deposition process at high temperature on refractory metals (*1, 25, 26, 27*). For tantalum, they result in the formation of a TaB_2 layer and in a slow diffusion of tantalum into the boron deposit (Fig. 1).

An electron microprobe analysis has been made, for tantalum, on polished sections, along a diameter of the deposit. As shown in Fig. 2, the limit of solubility of tantalum in boron is small and of the order of 0.025 at.% at the TaB_2/B interface, corresponding to a B/Ta atomic ratio of 3600. Depending on the deposition duration, the percentage of tantalum in the boron deposits falls, radially, more or less rapidly. In the less favorable case (sample 1), it is only 0.007 at.% (B/Ta at.ratio = 15 000) at 50 μ from the TaB_2/B interface. Thus, the contamination of boron by the substrate, although it does exist, remains very slight. Moreover, in the boron deposits where the crystals used for the structure analysis were picked up, the tantalum filaments had been first covered with a 100–200 μ layer of β-rhombohedral boron prior to the deposition of the tetragonal form. As a consequence, the tantalum diffusion in the boron deposit was practically limited to the β-rhombohedral phase (*21*).

A common impurity in boron samples prepared from BBr_3 is carbon(1). The analysis for carbon could not be easily made on our filament deposit. However, it has been performed on large size α-rhombohedral microcristalline boron samples deposited at 800°C on the inner wall of a silica tube *from the same* BBr_3 *sources*, with the result of a carbon content of 200 ppm (*28*).

Furthermore, it has been observed by both K. Ploog and M. Boiret that doping the

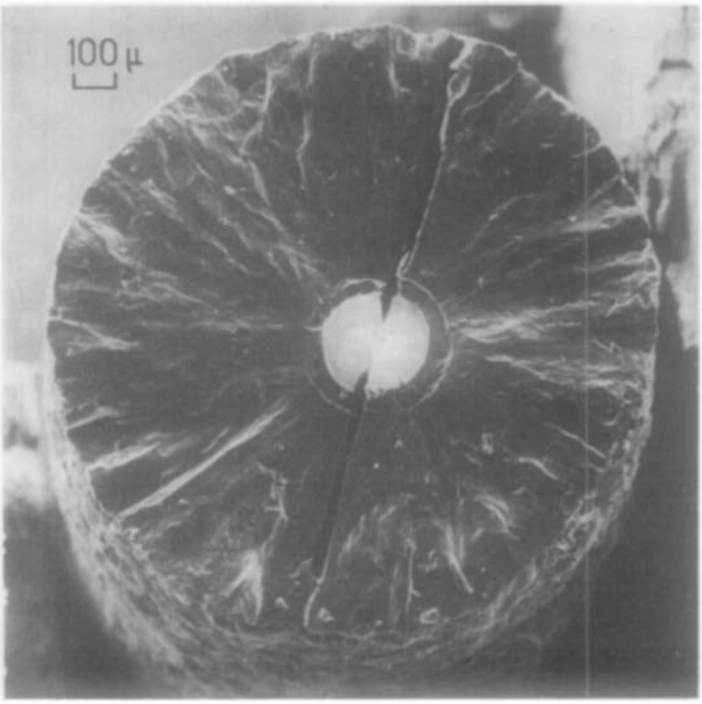

FIG. 1. Section of a rod of tetragonal boron obtained by CVD (BBr_3–H_2 mixture; 1200°C; 1.atm.; 1 h) on a tantalum filament. The tantalum substrate is surrounded by a layer of TaB_2 (according to *20*).

BBr_3-H_2 gas mixture, with trace amounts of carbon inhibited the deposition of tetragonal boron and instead induced that of the α-tetragonal boride phase in a reproducible manner (*5, 6, 7, 20*).

From these results it appears that the tetragonal phase, obtained for the first time by C. P. Talley *et al.* (who already underlined its high purity), is indeed a true modification of boron. In fact it is the only tetragonal variety of *pure* boron that has been reported up to now.

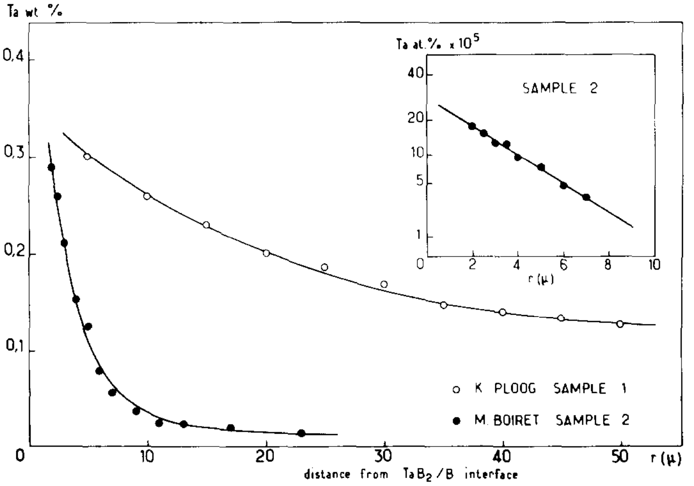

FIG. 2. Electron microprobe analysis of tantalum in a section of a tetragonal boron rod as a function of distance r, from the TaB_2/B interface. CVD conditions: (a) sample I: 1200°C; 2 h; (b) sample 2: 1200°C; 1 h. Insert gives Ta at.% as a function of r in a gaussian-arithmetic plot.

(2) Single Crystal Diffraction Data

A preliminary study of the zero—and upper—layer Weissenberg and precession photographs indicates a tetragonal Laue symmetry 4/m. The systematic extinctions are compatible with space group $P4_1$ or $P4_3$. The lattice parameters obtained and refined from single crystal data are: $a = 10.14(1)$ Å and $c = 14.17(1)$ Å. They are in good agreement with those previously reported for samples prepared by CVD, but somewhat different from those given by D. B. Sullenger *et al.* for their material, obtained by plasma melting and quenching (Table I).

The cell contains four chemical units $B_{21} \cdot 2B_{12} \cdot B_{2.5}$ established by the present structure analysis. The calculated density, $d = 2.341$ g/cm^3, is in good agreement with the measured values, $d = 2.36 \pm 0.02$ g/cm^3.

A single crystal, having a very irregular form and approximate dimensions $0.09 \times 0.09 \times 0.08$ mm, was mounted on its **c** axis. The intensities were collected on a three-cycle automatic diffractometer with CuKα radiation ($\lambda = 1.5418$ Å); a pyrolytic graphite monochromator (002) and a 4° take-off angle. A scintillation counter and a θ–2θ multiple scanning technique with a scan rate of 10° (2θ) per minute were used. In order to improve the counting statistics 10 independent scans were made. The background was measured at each end of the scan range for a time equal to the actual scan time. 1250 independent reflections were obtained after averaging the four equivalent reflections actually measured to a $\theta_{\max} = 67°$. 1009 has an intensity $I > 2\sigma(I)$, where $\sigma(I) = (\text{total counts} + \text{backgrounds})^{1/2}$, and were considered to be observed. These intensities were corrected for Lorentz and polarization effects. No absorption correction was applied ($\mu r \simeq 0.03$). An isotropic extinction correction was applied during refinement $g = 1.4 \times 10^{-6}$.

(3) Determination and Refinement of the Structure

The structure was solved by Fourier methods starting with a model derived from the α-AlB_{12} structure (*23, 24*). This model was chosen because of the close similarities between the cell dimensions and symmetry of the two phases (Table I). It consisted only of the B_{12} and B_{19} units of the α-AlB_{12} structure. This partial boron framework was fitted to the $P4_3$ space group taking into account the stereochemical requirements of the icosahedral units (the B_{12} units imply

TABLE I

CELL CONSTANTS α-AlB_{12} AND THE RELATED TETRAGONAL ELEMENTAL BORON MODIFICATION

References	Synthesis	Lattice parameters		Space groups	Density g/cm^3
		a (Å)	c (Å)		
(1) Tetragonal boron:					
Present work	CVD	10.14 ± 0.01	14.17 ± 0.01	$P4_1$ or $P4_3$	2.36 ± 0.02
C. P. Talley *et al.* (*19*)	*CVD*	10.12 ± 0.02	14.14 ± 0.02	—	2.364 ± 0.005
E. Amberger and K. Ploog (*6, 7*)	CVD	10.12	14.14	$P4_122$ or $P4_322$	2.360 ± 0.003
D. B. Sullenger *et al.* (*22*)	Plasma quenching	10.061 ± 0.005	14.210 ± 0.005	$P4_12_12$ or $P4_32_12$	2.367 ± 0.002
(2) α-AlB_{12}					
I. Higashi *et al.* (*23*)	Al flux	10.158(2)	14.270(5)	$P4_12_12$ or $P4_32_12$	2.55(*c*) 2.54(*m*)
J. S. Kasper *et al.* (*24*)	Al flux	10.161(7)	14.283(8)	$P4_12_12$ or $P4_32_12$	2.65 ± 0.08

TABLE II

Atomic Parameters ($\times 10^3$), Temperature Factors ($\times 10^2$) and Occupancy Factors

Atom	X	Y	Z	U (Å^2)[a]	O.F.
B(1)	-123(1)[b]	742(1)	128(1)	0.54(5)	1.0
B(1p)	238(1)	377(1)	871(1)	0.12(5)	1.0
B(2)	-40(1)	628(1)	208(1)	0.79(5)	1.0
B(2p)	131(1)	461(1)	790(1)	0.29(5)	1.0
B(3)	-44(1)	809(1)	225(1)	0.04(5)	1.0
B(3p)	313(1)	459(1)	770(1)	0.14(5)	1.0
B(4)	-44(1)	893(1)	116(1)	0.04(5)	1.0
B(4p)	394(1)	460(1)	883(1)	0.34(5)	1.0
B(5)	-33(1)	606(1)	78(1)	0.27(5)	1.0
B(5p)	106(1)	470(1)	920(1)	0.53(5)	1.0
B(6)	-37(1)	776(1)	28(1)	1.19(5)	1.0
B(6p)	271(1)	468(1)	969(1)	1.55(5)	1.0
B(7)	109(1)	721(1)	244(1)	0.58(5)	1.0
B(7p)	220(1)	607(1)	754(1)	1.25(5)	1.0
B(8)	105(1)	886(1)	191(1)	2.04(5)	1.0
B(8p)	388(1)	608(1)	806(1)	0.60(5)	1.0
B(9)	118(1)	600(1)	155(1)	0.65(5)	1.0
B(9p)	98(1)	622(1)	845(1)	1.79(5)	1.0
B(10)	113(1)	687(1)	47(1)	1.54(5)	1.0
B(10p)	194(1)	616(1)	932(1)	0.34(5)	1.0
B(11)	112(1)	864(1)	65(1)	0.71(5)	1.0
B(11p)	365(1)	613(1)	934(1)	1.39(5)	1.0
B(12)	204(1)	758(1)	144(1)	0.25(5)	1.0
B(12p)	260(1)	702(1)	860(1)	1.91(5)	1.0
B(13)	317(1)	554(1)	362(1)	0.29(5)	1.0
B(13p)	56(1)	814(1)	632(1)	1.15(5)	1.0
B(14)	389(1)	698(1)	325(1)	2.76(5)	1.0
B(14p)	197(1)	886(1)	675(1)	3.52(1)	1.0
B(15)	203(1)	696(1)	340(1)	0.62(5)	1.0
B(15p)	193(1)	706(1)	655(1)	0.30(5)	1.0
B(16)	468(1)	614(1)	413(1)	0.42(5)	1.0
B(16p)	113(1)	964(1)	589(1)	0.39(5)	1.0
B(17)	467(1)	792(1)	420(1)	1.07(5)	1.0
B(17p)	292(1)	955(1)	574(1)	1.23(5)	1.0
B(18)	187(1)	589(1)	449(1)	1.21(5)	1.0
B(18p)	91(1)	688(1)	552(1)	0.29(5)	1.0
B(19)	265(1)	675(1)	547(1)	0.39(5)	1.0
B(19p)	171(1)	767(1)	455(1)	0.70(5)	1.0
B(20)	346(1)	536(1)	496(1)	0.58(5)	1.0
B(20p)	40(1)	849(1)	503(1)	0.52(5)	1.0
B(21)	439(1)	685(1)	524(1)	0.72(5)	1.0
B(21p)	182(1)	940(1)	476(1)	0.11(5)	1.0
B(22)	334(1)	835(1)	497(1)	0.62(5)	1.0
B(23)	39(1)	534(1)	497(1)	0.85(5)	1.0
B(24)	290(1)	839(1)	384(1)	2.87(5)	1.0
B(24p)	332(1)	801(1)	629(1)	2.50(5)	1.0
B(25)	145(1)	433(1)	466(1)	2.02(5)	0.50(3)
B(25p)	61(1)	360(1)	35(1)	0.60(5)	0.50(3)
B(26)	225(1)	244(1)	732(1)	5.83(5)	0.47(3)

[a] The expression for the isotropic temperature factor is $\exp[-2\pi U((h^2+k^2)a^{*2}+1^2g^{*2})]$.

[b] The estimated standard deviations are averages taken over a number of least-squares cycles.

atoms B(1) to B(12*p*) and the B_{19} units, atoms B(13) to B(22) (see Table II).

A Fourier synthesis, calculated using the above hypothesis, showed a number of additonal maxima. The first three maxima were assumed to be fully occupied boron sites. One of them (atom B(23)) corresponds to the single boron atom in α-$A1B_{12}$ while the remaining (atoms B(24) and B(24*p*) complete the initial B_{19} units giving a B_{21} unit which is now a *new fully occupied twinned icosahedron*. A further Fourier synthesis was calculated showing three other density maxima, each of them corresponding to approximately half a boron atom (atoms B(25), B(25*p*) and B(26)).

The atomic positions and isotropic temperature factors, as well as, the occupancy factors of B(25), B(25*p*) and B(26) were refined using a full matrix least-squares program including the three partial boron atoms. The atomic scattering factors were those of D. I. Cromer and J. B. Mann (*29*). The resulting R value was 9.5%, where $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. All the isotropic temperature factors had, at this stage, very reasonable values. The relativity moderate R value certainly results from mediocre counting statistics due to the smallness and average quality of the crystal used for data collection. However, all attempts to obtain a better quality crystal from the CVD boron deposits were unsuccessful. A final difference synthesis revealed no further maxima greater than 6% of a boron atom.

Observed and calculated structure factors are compared in a separate table.[1] The atomic and thermal parameters are given in Table II and the interatomic distances presented in Table III.

Description and Discussion of the Structure

From a topological point of view, the structure of tetragonal boron is very closely related to that of α-AlB_{12} (*23, 24*). In fact, the three-dimensional boron skeletons are practically identical and only the completion of the twinned icosahedral units as well as the existence of interstitial boron atoms instead of aluminum being the major differences.

The crystal structure of tetragonal boron is basically a boron framework structure made up of B_{12} icosahedra and B_{21} completed twinned icosahedra having a common triangular face. The unit formula of tetragonal boron as was deduced from the present crystallographic study is $B_{21} \cdot 2B_{12} \cdot B_{2.5}$. This is corroborated by the agreement between the calculated and measured densities ($d_c = 2.34\ \mathrm{g/cm^3}$; $d_m = 2.36 \pm 0.02\ \mathrm{g/cm^3}$). The unit cell contains a total of 8 B_{12} icosahedra, 4 B_{21}-twinned icosahedra and 10 single boron atoms (six of them occupying partially their sites). Figure 3 and 4 show, respectively, projections of the B_{12} and B_{21} units on the (001) plane.

The three-dimensional boron skeleton obeys the general rules of the crystal chemistry of boron-rich phases (*1, 30, 31*). The B_{12} and B_{21} units are linked together by *direct* B–B bonds shared with *single boron atoms*. In the resulting three-dimensional boron skeleton, some of the intrerstitial sites are partially filled with *interstitial boron atoms* which play a role similar to that of aluminum in α-AlB_{12}.

The boron skeleton can be described as an arrangement of parallel *chains of B_{12} icosahedra* located in plane perpendicular to the **c** axis (Fig. 5). As a result of the existence of the fourfold screw axis, the distance between these planes is $c/4$ and the chains run alternately in the x and y directions (Figs. 5 and 6). In a given plane, the distance between two *adjacent* chains (10.141(1) Å) is equal to that existing *within* a chain between three adjacent icosahedra and determines the a

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[1] See NAPS document number for pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 305 East 46th Street, New York, N.Y. 10017. Remit in advance for each NAPS accession number \$1.50 for microfiche or \$5.00 for photocopies up to 30 pages. 15¢ for each additional page. Make checks payable to Microfiche Publications.

TABLE III

INTERATOMIC DISTANCES (BETWEEN 1.55 Å AND 2.10 Å)

B–B bonds in the B_{12} icosahedra					
B(1	–B(2)	1.826(9)	B(5)	–B(6)	1.858(9)
	–B(3)	1.738(9)		–B(9)	1.881(9)
	–B(4)	1.738(9)		–B(10)	1.750(9)
	–B(5)	1.796(9)	B(5*p*)	–B(6*p*)	1.807(9)
	–B(6)	1.691(9)		–B(9*p*)	1.877(9)
B(1*p*)	–B(2*p*)	1.796(9)		–B(10*p*)	1.786(9)
	–B(3*p*)	1.823(9)	B(6)	–B(10)	1.793(9)
	–B(4*p*)	1.800(9)		–B(11)	1.837(9)
	–B(5*p*)	1.777(9)	B(6*p*)	–B(10*p*)	1.709(9)
	–B(6*p*)	1.702(9)		–B(11*p*)	1.819(9)
B(2)	–B(3)	1.853(9)	B(7)	–B(8)	1.836(9)
	–B(5)	1.860(9)		–B(9)	1.769(9)
	–B(7)	1.847(9)		–B(12)	1.768(9)
	–B(9)	1.788(9)	B(7*p*)	–B(8*p*)	1.850(9)
B(2*p*)	–B(3*p*)	1.873(9)		–B(9*p*)	1.783(9)
	–B(5*p*)	1.858(9)		–B(12*p*)	1.835(9)
	–B(7*p*)	1.805(9)	B(8)	–B(11)	1.793(9)
	–B(9*p*)	1.830(9)		–B(12)	1.772(9)
B(3)	–B(4)	1.766(9)	B(8*p*)	–B(11*p*)	1.862(9)
	–B(7)	1.809(9)		–B(12*p*)	1.782(9)
	–B(8)	1.767(9)	B(9)	–B(10)	1.767(9)
B(3*p*)	–B(4*p*)	1.805(9)		–B(12)	1.832(9)
	–B(7*p*)	1.788(9)	B(9*p*)	–B(10*p*)	1.805(9)
	–B(8*p*)	1.777(9)		–B(12*p*)	1.852(9)
B(4)	–B(6)	1.724(9)	B(10)	–B(11)	1.811(9)
	–B(8)	1.855(9)		–B(12)	1.802(9)
	–B(11)	1.769(9)	B(10*p*)	–B(11*p*)	1.757(9)
B(4*p*)	–B(6*p*)	1.745(9)		–B(12*p*)	1.703(9)
	–B(8*p*)	1.867(9)	*B*(11)	–*B*(12)	1.802(9)
	–B(11*p*)	1.746(9)	*B*(11*p*)	–B(12*p*)	1.761(9)
B–B bonds in the B_{21} twinned icosahedra					
B(13)	–B(14)	1.725(9)	B(15)	–B(18)	1.897(9)
	–B(15)	1.872(9)		–B(19*p*)	1.822(9)
	–B(16)	1.796(9)		–B(24)	1.810(9)
	–B(18)	1.831(9)	B(15*p*)	–B(18*p*)	1.797(9)
	–B(20)	1.923(9)		–B(19)	1.736(9)
B(13*p*)	–B(14*p*)	1.722(9)		–B(24*p*)	1.751(9)
	–B(15*p*)	1.794(9)	B(16)	–B(17)	1.805(9)
	–B(16*p*)	1.748(9)		–B(20)	1.880(9)
	–B(18*p*)	1.739(9)		–B(21)	1.761(9)
	–B(20*p*)	1.865(9)	B(16*p*)	–B(17*p*)	1.822(9)
B(14)	–B(15)	1.894(9)		–B(20)	1.831(9)
	–B(16)	1.712(9)		–B(21*p*)	1.742(9)
	–B(17)	1.830(9)	B(17)	–B(21)	1.859(9)
	–B(24)	1.937(9)		–B(22)	1.792(9)
B(14*p*)	–B(15*p*)	1.845(0)		–B(24)	1.928(9)
	–B(16*p*)	1.698(9)	B(17*p*)	–B(21*p*)	1.789(9)
	–B(17*p*)	1.855(9)		–B(22)	1.692(9)
	–B(24*p*)	1.748(9)		–B(24*p*)	1.787(9)
B–B bonds in the B_{21} twinned icosahedra					
B(18)	–B(19)	1.820(9)	B(19*p*)	–B(20*p*)	1.710(9)
	–B(19*p*)	1.812(9)		–B(21*p*)	1.784(9)
	–B(20)	1.830(9)		–B(22)	1.887(9)
B(18*p*)	–B(19)	1.770(9)		–B(24)	1.735(9)
	–B(19*p*)	1.775(9)	B(20)	–B(21)	1.826(9)
	–B(20*p*)	1.848(9)	B(20*p*)	–B(21*p*)	1.751(9)
B(19)	–B(19*p*)	1.856(9)	B(21)	–B(22)	1.897(9)
	–B(20)	1.783(9)	B(21*p*)	–B(22)	1.896(9)
	–B(21)	1.790(9)		–B(24)	1.985(9)
	–B(22)	1.903(9)	B(22)	–B(24)	1.656(9)
	–B(24*p*)	1.859)9)		–B(24*p*)	1.899(9)
B–B in B_{12}–B_{12}, B_{12}–B_{21} and B_{21}–B_{21} linkages					
B(1)	–B(12*p*)	1.789(9)	B(7)	–B(15)	1.672(9)
B(1*p*)	–B(12)	1.779(9)	B(7*p*)	–B(15*p*)	1.753(9)
B(2)	–B(2*p*)	1.743(9)	B(8)	–B(20*p*)	1.850(9)
B(3)	–B(11)	1.775(9)	B(8*p*)	–B(20)	1.784(9)
B(3*p*)	–B(11*p*)	1.694(9)	B(9)	–B(17)	1.641(9)
B(4)	–B(16*p*)	1.654(9)	B(9*p*)	–B(17*p*)	1.721(9)
B(4*p*)	–B(16)	1.648(9)	B(10)	–B(10*p*)	1.728(9)
B(6)	–B(14*p*)	1.678(9)	B(13)	–B(21)	1.709(9)
B(6*p*)	–B(14)	1.728(9)	B(13*p*)	–B(21*p*)	1.784(9)
B–B in $B_{\text{interstitial}}$–$B_{\text{polyhedral}}$ and $B_{\text{interstitial}}$–$B_{\text{interstitial}}$ linkages					
B(1)	–B(26)	1.808(9)	B(18)	–B(23)	1.743(9)
B(3)	–B(26)	1.912(9)	B(18)	–B(25)	1.659(9)
B(5)	–B(23)	1.822(9)	B(18*p*)	–B(23)	1.827(9)
B(5)	–B(25)	1.986(9)	B(18*p*)	–B(25*p*)	1.640(9)
B(5*p*)	–B(23)	1.829(9)	B(21*p*)	–B(24)	1.985(9)
B(5*p*)	–B(25*p*)	2.022(9)	B(23)	–B(25)	1.553(9)
B(10)	–B(26)	1.845(9)	B(23)	–B(25*p*)	1.572(9)
B(10*p*)	–B(26)	1.746(9)	B(24)	–B(25*p*)	1.876(9)
B(11)	–B(26)	1.994(9)	B(24*p*)	–B(25)	1.694(9)
B(12*p*)	–B(26)	1.882(9)			

parameter of the lattice. Such chains also occur in the [111] direction, the diagonal of the unit cell being equal to four times the size of a B_{12} icosahedron regarded as a packing unit. As a consequence, the *c* parameter of the lattice is also determined by size considerations and approximately equal to $a\sqrt{2}$ ($a\sqrt{2} = 14.34(1)$ Å; $c = 14.17(1)$ Å). These features of the structure justified the similarities that exist between the *a* parameter of tetragonal boron and the *a* parameter of β-rhombohedral boron (10.139 Å) or the *c* parameter of

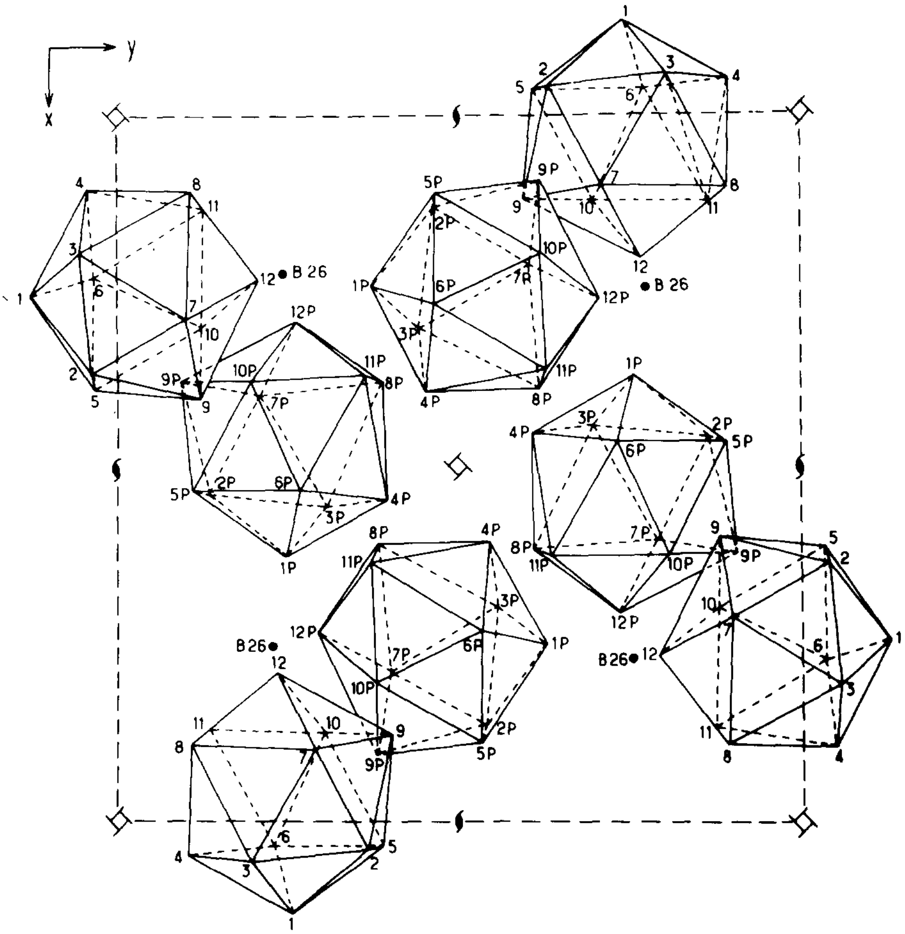

FIG. 3. Projection of the icosahedral B_{12} partial framework on the (001) plane, including the B(26) interstitial site.

$NaB_{0.84}B_{14}$(10.298 Å) where such chains of B_{12} icosahedra are also present (*31, 32*). They also partly support Matkovich's views according to which the cell parameters of boron-rich phases are mainly determined by packing consideration of icosahedral units (*33*).

The chains of B_{12} icosahedra located in adjacent planes are tightly linked together by *direct* B–B inter-icosahedron bonds (B_2–B_{2p}; B_3–B_{11}; B_{3p}–B_{11p}; B_{10}–B_{10p}) and by *additional B–B bonds* shared with the *interstitial* B(26) atoms. As shown in Figs. 5 and 6, the interstitial B(26) atom occupies an interstitial site formed by four icosahedra centered at the vertices of a tetrahedron and belonging to two B_{12} chains located in adjacent planes. Thus each B_{12} icosahedron is linked to six adjacent icosahedra. There remain, for each icoshedron, six outwardly directed unshared bonds in this partial bonding scheme.

The three-dimensional boron skeleton built upon the chains of B_{12} icosahedra contains *large holes*, as shown in Fig. 6. These holes are occupied by the B_{21} twinned icosahedron units. The centers of these B_{21} units taken at the centers of the common triangular faces B_{19}–B_{22}–B_{19p}, lie approximately at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$, $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ and $(\frac{3}{4}, \frac{1}{4}, 0)$ as illustrated in Fig. 4. Within each hole, a B_{21} unit is oriented in such a way that it

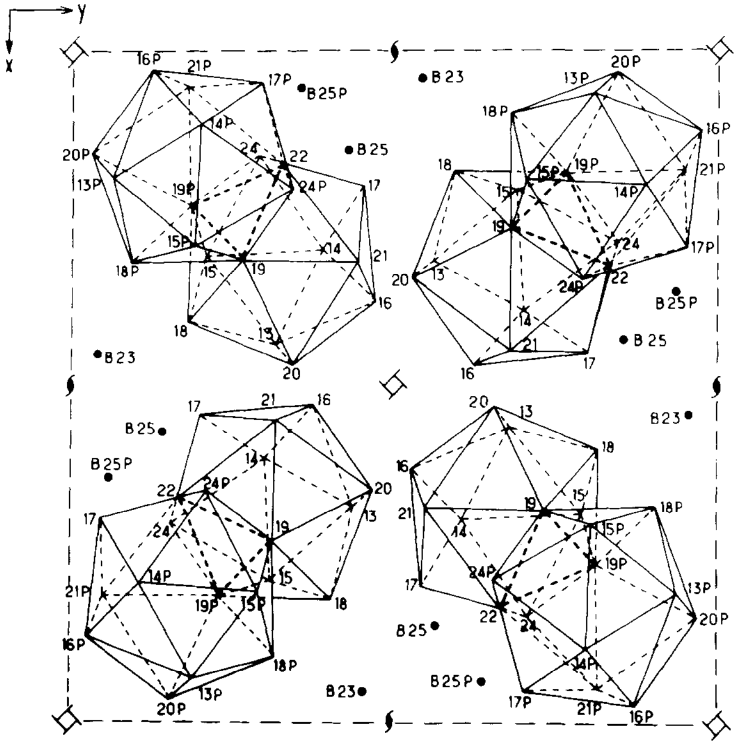

FIG. 4. Projection of the partial icosahedral (B_{21} units) framework, including the B(23), B(25) and B(25p) single boron atoms, on the (001) plane.

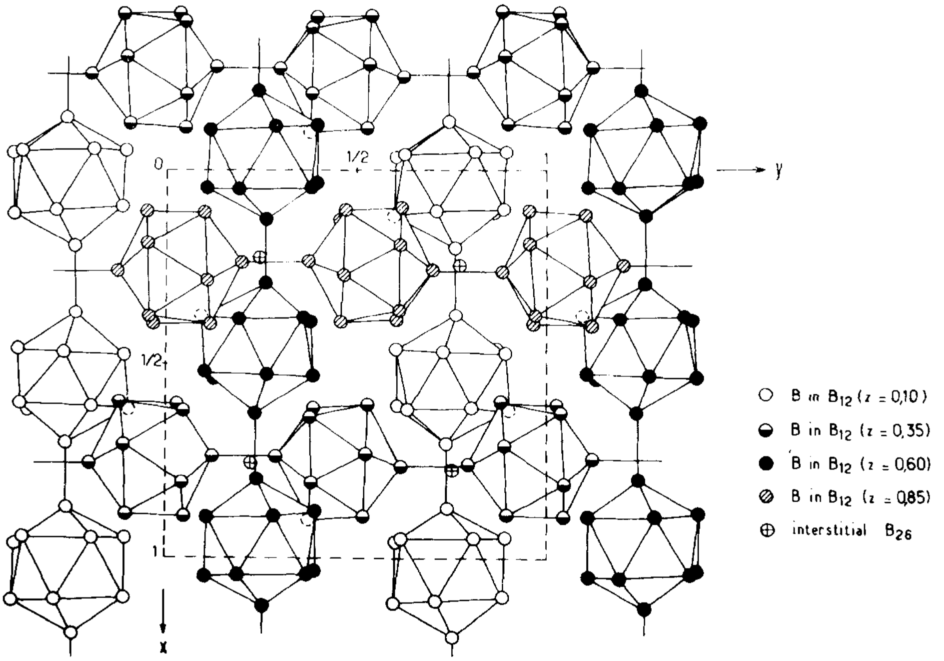

FIG. 5. The arrangement of the B_{12} units made up of chains of B_{12} icosahedra running alternately in the x and y directions.

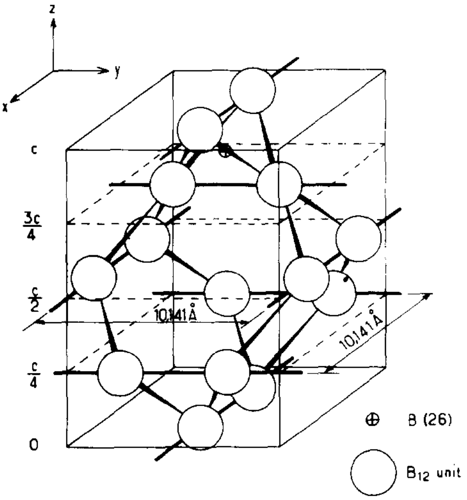

FIG. 6. Void of large size existing in the arrangement of the chains of B_{12} icosahedra. This void is occupied by a twinned iscosahedron unit B_{21}.

shares a maximum of direct inter-icosahedral bonds, oriented along the fivefold axes, with the adjacent B_{12} or B_{21} units. The remaining bonds are fulfilled with the single boron atoms.

In the resulting complex three-dimensional skeleton, each B_{12} icosahedron is linked to six adjacent B_{12} icosahedra, five B_{21} twinned icosahedra and one single boron atom B(23). As a consequence, the boron skeleton cannot be described with a $B_{12}(B_{12})_{12}$ or a $B_{12}(B_6)_{12}$ giant unit, since in both cases a B_{12} icosahedron has to be surrounded by 12 icosahedra (or by 12 half-icosahedra). This is in opposition with the earlier statement by V. I. Matkovich *et al.* according to which the α-AlB_{12}-type structure could be based on B_{84} units (*33*).

In a B_{21} unit, only 18 of the 21 apex atoms share B–B bonds outwardly directed, the three atoms (B(19), B(19*p*) and B(22)) of the common triangular face having only intra-icosahedral linkages. Each B_{21} unit is linked to 10 B_{12} icosahedra and to 4 B_{21} twinned icosahedra, this direct intericosahedron bonding scheme accounting for 14 to 18 outwardly directed bonds. The remaining four bonds, involving atoms B(18), B(18*p*), B(24) and B(24*p*), are shared with the single boron atoms B(23) (two bonds), B(25) and (B25*p*). Atom B(23), which is also present in the structure of α-AlB_{12}, fully occupies its site. On the contrary, atoms B(25) and B(25*p*), which are required to fulfill the sixth bond of the new B(24) and B(24*p*) atoms of the now completed B_{21} unit, only partially occupy their sites (occupancy: 0.50). This uncommon partial occupany, for such important atoms, could be related to the short B(23)–B(25) and B(23)–B(25*p*) distances (1.553 and 1.572 Å respectively). However, a similar feature has been already reported for the B(13) atoms (occupancy: 0.73) of the B_{28} condensed icosahedron unit in the highly refined structure of β-rhombohedral boron (*1, 32*).

As it can be observed from Table III, there is a much greater spread in the values of the B–B distances within a B_{21} unit in comparison to the B_{12} unit. This phenomenon, also found in α-AlB_{12}, has been already reported for the triply condensed B_{28} icosahedral unit in β-rhombohedral boron (where the icosahedra sharing triangular faces are more distorted than those occurring within the chains running along the edges of the rhombohedral unit cell).

The B–B bonds within, as well as between, the B_{12} units range from 1.692 to 1.877 Å and from 1.695 to 1.780 Å respectively, with an average length of 1.799 and 1.751 Å. These distances are comparable to those found in α-AlB_{12} (1.805 and 1.709 Å) and in various boron-rich phases having structures based on chains of B_{12} icosahedra such as β-rhombohedral boron (1.80 and 1.72 Å) or $NaB_{0.8}B_{14}$ (1.806 and 1.745 Å).

The B–B bonds within a B_{21} unit range from 1.657 to 1.938 Å with an average length of 1.813 Å and an exceptionally long distance of 1.986 Å between B(21*p*) and B(24) which is one of the new boron atoms completing the B_{21} unit. In α-AlB_{12} an average intra-B_{21} B–B bond of 1.814 Å was observed, as well as an extremely long distance of 1.979 Å between atoms B(18) and B(18*p*). Such long B–B distances (1.90 Å) have been already reported for the triply condensed B_{28} icosahedral unit in β-rhombohedral boron. The average B_{21}–B_{21} and B_{12}–B_{21} connecting bond distances are 1.785 and 1.724 Å respectively.

It appears from these results, that in tetragonal boron the average intericosahedral bonds (B_{12}–B_{12}: 1.751; B_{12}–B_{21}: 1.724 and B_{21}–B_{21}: 1.785 Å) are significantly shorter than the corresponding intraicosahedral bonds (1.799 Å for B_{12} and 1.813 Å for B_{21}), in agreement with the general rule of the crystal chemistry of boron-rich phases.

There seems to be a wide range of temperature factors which is probably due to the low data to parameter ratio. However, the high-temperature factors of atoms B(14), B(14*p*), B(24), B(24*p*), could indicate that these four sites are vulnerable. The U of B(26) is highly correlated to the O.F.

As is often the case in many boron-rich phases, the single atoms in tetragonal boron do not obey, in their coordination polyhedra, the general principles followed by boron atoms within the icosahedral units (*31*). There are two kinds of single boron atoms in the structure: B(23), B(25) and B(25*p*) on one hand, and B(26) on theother hand. The former complete the bonding scheme of the icosahedral boron atoms (sixth bond outwardly directed along the icosahedral fivefold axes) while the latter, B(26), is only an interstitial atom (Fig. 7).

Atom B(23), also found in α-AlB_{12}, is linked by regular B–B bonds to two B_{12} (atoms B(5) and B(5*p*)) and two B_{21} (atoms B(18) and B(18*p*)) icosahedral units. It also shares *very short bonds* (1.554 and 1.573 Å) with the neighboring single atoms B(25) and B(25*p*). The existence of such very short bonds may explain the fact that the occupancy for these atoms is only 0.50.

In the same way, atoms B(25) and B(25*p*), which do not exist in α-AlB_{12} since the twinned icosahedron unit is defective (19 atoms instead of 21), are necessary for the sixth outwardly directed bond of the new B(24) and B(24*p*) icosahedral boron atoms in the completed B_{21} units. Atom B(25), for example, is coordinated to four boron atoms: one from a B_{12} unit (B(5)), two from B_{21} units (B(18) and B(18*p*)) and one single atom B(23). As already stated, the very short B(23)–B(25) distance may be at the origin of the low occupancy factor for atom B(25). Atom B(25) is only very weakly bonded (1.987 Å) to the icosahedral boron atom B(5) which is in turn also linked to B(23) by a much stronger bond (1.823 Å). This kind of bonding scheme has been already found for atom B(6) in Na$B_{0.84}B_{14}$ (*31*).

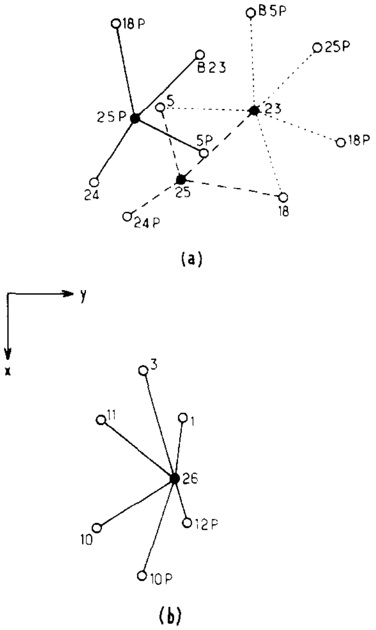

FIG. 7. Bonding arrangement of the four single boron atoms: (a): B(23) B(25) and B(25*p*); (b): B(26).

On the contrary, the single B(26) atoms, which is not present in α-AlB_{12} is typically an *interstitial boron atom* (as is, for example, the atom B(16) in β-rhombohedral boron). It lies in an interstitial void formed by four neighboring icosahedra, as shown in Fig. 6, where it is coordinated to six boron atoms and not to 12 as it could be expected from the nature of the site. Its low occupancy factor of 0.50, which is not in accord with the existence of very short bonds, clearly underlines its nature as an interstitial atom. Its presence, which is not strictly required by the bonding pattern of the icosahedral boron atoms, probably contributes to reinforce the cross-linking between two neighboring chains of B_{12} icosahedra running in adjacent planes.

It appears from the present study that the boron framework of tetragonal boron is practically that found in α-AlB_{12} with the exception of the completed twinned icosahedral B_{21} instead of the defective B_{19} unit. The full twinned B_{21} icosahedron is, therefore, a new polyhedral unit never observed up to now in any of the boron modifications or the boron-rich borides. As in α-AlB_{12}, all boron atoms of the icosahedral B_{12} and B_{21} units (including the new B(24) and B(24*p*) atoms), as well as the single B(23) atoms fully occupy their sites. However, the aluminum atom interstitial sites as found in α-AlB_{12} are not occupied. On the contrary, three new boron atoms B(25), B(25*p*) and B(26) occupy new positions with a fractional occupancy of 50%. The first two serve to fulfill the bonding requirement of the added B(24) and B(24*p*) icosahedral atoms and the last one contributes toward increasing the stability of the structure.

Steric considerations do not allow the simultaneous occurence of the completed twinned B_{21} units and of the Al(1) and Al(3) atoms, in α-AlB_{12}. The distances between the new boron atoms (B(24) and B(24*p*)) in tetragonal boron and the positions occupied by Al(1) and Al(3) in α-AlB_{12} would have been:

B(24) – Al(1): 1.801 Å
B(24) – Al(3): 0.842 Å
B(24*p*) – Al(1*p*): 1.631 Å
B(24*p*) – Al(3): 0.732 Å

These distances are obviously too short for a boron-aluminum bond ($r_B + r_{Al} = 0.88 + 1.43 = 2.31$ Å), even taking into account the fact that aluminum does not fully occupy its position (Al(1): 72%; Al(3): 24%). In α-AlB_{12}, the mean distance for the Al(1)–B bonds was found to be 2.305 Å with a short 2.081 Å bond) and 2.290 Å for the Al(3)–B bonds (with a short 2.044 Å bond). Thus, atomic size considerations could explain why the B_{21} units are defective in α-AlB_{12}.

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