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Comment on *Struktur des tetragonalen* $(B_{12})_4B_2Ti_{1\cdot3-2\cdot0}$, by E. Amberger and K. Polborn.*

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A re-interpretation of the structure of a boron-rich Ti boride strongly confirmed the idea that the 2(*b*) positions are occupied by carbon and not by boron atoms. Thus, these single carbon atoms in 2(*b*) stabilize the tetragonal arrangement of B_{12} icosahedra and the Ti atoms in position 2(*a*) merely fill interstitial holes.

In the course of their structure determination of a boron-rich Ti boride, Amberger & Polborn (1975) found in a difference Fourier synthesis an electron density of about 5·9 electrons per site for the 2(*b*) position. According to Amberger & Polborn, this 2(*b*) position should be occupied by boron atoms, each with 5 electrons. Although the population parameter of position 2(*b*) was not varied later during the refinement, the excess electron density at these sites still seemed to be present. The authors explained this fact by an electron transfer from Ti atoms in 2(*a*) to the B atoms in 2(*b*).

However, the Ti atoms in the 2(*a*) positions merely fill interstitial holes, since they cannot have any bonding functions with the surrounding atoms for the following reasons. According to our Raman investigations of α-boron (Richter & Ploog, 1975) and the lattice dynamical model of B_{12} icosahedra of Weber & Thorpe (1975), the bonds pointing outward from the B_{12} units are strongly directed two electron σ bonds. The atoms in the 2(*b*) position, while acting as bridges with covalent σ bonds between four icosahedra, require 4 nearly tetrahedrally directed orbitals suitable to form σ bonds. Thus, second row atoms in 2(*b*), such as B, C or N with only four low-lying orbitals, cannot accept additional electron density from a fifth ligand in 2(*a*) (*e.g.* Ti), since there are no orbitals available. An electron transfer from 2(*a*) to 2(*b*) *via* the nearest neighbouring icosahedral atoms B(2) and/or B(3) can also be excluded, since the atoms B(2) form strong intericosahedral σ bonds to adjacent icosahedra, and the atoms B(3) form the σ bonds to the 2(*b*) atoms. Thus, for an interaction with the 2(*a*) atom there are definitely no extra orbitals existing on these atoms. So, in 2(*a*), the Ti atoms are not suitable for stabilizing the tetragonal icosahedral framework. The unique holes in the framework, where the Ti atoms could interact with icosahedral B atoms, are the positions 4(*c*) $(0\tfrac{1}{2}0, \tfrac{1}{2}00, 0\tfrac{1}{2}\tfrac{1}{2}, \tfrac{1}{2}0\tfrac{1}{2})$. However, these holes are not occupied by any atom in the tetragonal Ti boride.

Finally, to account for the increased electron density in 2(*b*) we believe that this position is occupied by carbon atoms with 6 electrons each and not by boron atoms. This idea is strongly supported by the fact that carbon was not strictly excluded during the synthesis of the crystals (graphite disc coated by BN layers as substrate, which is carried by a graphite stick), and that a carbon analysis of the *investigated* crystals was not carried out (which, in fact, is rather difficult in the presence of Ti).

Therefore, we recalculated the crystal structure of the Ti boride using the $F_{\rm obs}$ values and the x,y,z coordinates given by Amberger & Polborn. We checked model I with carbon in position 2(*b*) [ideal composition: $(B_{12})_4C_2Ti_2$] and model II with boron in position 2(*b*) [ideal composition: $(B_{12})_4B_2Ti_2$]. All calculations were carried out with programs of the X-RAY system–version of June 1972 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The atomic scattering factors used were those of Cromer & Mann (1968). The computations were made on the UNIVAC 1108 computer at the Computer Centre of the University of Stuttgart. Refinement of all parameters, of the population parameters of positions 2(*a*) and 2(*b*), and of the isotropic temperature factors converged after three cycles at $R=0{\cdot}063$ (based on F with unit weights).

In Tables 1 and 2, only the population parameters and the isotropic temperature factors of the two models are listed, since the coordinates and their standard deviations show only marginal differences from those already published. The population parameters of 2(*a*) and 2(*b*) refer to fully occupied icosahedral positions, *i.e.*, five electrons per site. As can be seen from Tables 1 and 2, model I with carbon in position 2(*b*) is favoured for two reasons:

(i) the population parameter for position 2(*b*) in model II is greater than unity, which would involve a non-existing 'super' boron atom at this position;

(ii) the temperature factor U for position 2(*b*) in model I is much lower.

The somewhat lower population parameter of position 2(*b*) in model I is in accordance with the results of our

Table 1. *Population parameters, isotropic temperature factors* ($B=78{\cdot}96\times U$) *and standard deviations of model* I [C *in* 2(*b*)]

Structure chemical composition as derived from refinement procedures: $(B_{12})_4C_{1\cdot68}Ti_{1\cdot78}$.

Atom	Population parameter	U (×100)
B(1)	1·00	0·81 (17)
B(2)	1·00	1·34 (18)
B(3)	1·00	2·37 (28)
B(4)	1·00	1·36 (21)
C	0·84 (7)	1·78 (76)
Ti	0·89 (2)	0·75 (12)

Table 2. *Population parameters, isotropic temperature factors* ($B=78{\cdot}96\times U$) *and standard deviations of model* II [B *in* 2(*b*)]

Structure chemical composition as derived from refinement procedures: $(B_{12})_4B_{2\cdot20}Ti_{1\cdot78}$.

Atom	Population parameter	U (×100)
B(1)	1·00	0·82 (17)
B(2)	1·00	1·35 (18)
B(3)	1·00	2·41 (28)
B(4)	1·00	1·36 (21)
B(5)	1·10 (9)	2·53 (76)
Ti	0·89 (2)	0·75 (12)

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* A reply by Amberger & Polborn to this comment will appear in *Acta Cryst.* Vol. B32, part 4.

structure determination of $B_{48}B_2C_2$ and $B_{48}B_2N_2$ (Ploog, Schmidt, Amberger, Will & Kossobutzki, 1972; Ploog, 1974). It can be explained by the fact that the 2(*b*) sites are not fully occupied in these crystals, all of which were prepared as thermodynamically unstable compounds far below their melting point by chemical vapour deposition. The bond distance of 1·67 Å between the carbon atom in 2(*b*) and the icosahedral boron atom B(2) is comparable to that found in $B_{48}B_2C_2$ (1·63 Å) and in the rhombohedral boron carbide $B_{13}C_2$ (1·61 Å, Ploog, Kossobutzki & Will, 1973).

Since conclusions regarding transfer of charge, as derived from even the best X-ray data, must be regarded with reserve, the interpretation of the data of Amberger & Polborn on the basis of an occupation of position 2(*b*) by carbon atoms is much more straightforward. Thus, the tetragonal icosahedral framework of this boron-rich Ti boride again is stabilized by the atoms in 2(*b*), namely carbon, and the Ti atoms in 2(*a*) merely fill interstitials. The structure chemical composition of this tetragonal Ti boride, derived from the refinement procedure, is then given by $(B_{12})_4C_{1\cdot68}Ti_{1\cdot78}$.

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Crystal structure of β-Li_2SO_4.

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The crystal structure of β-Li_2SO_4 ($P2_1/a$) has been refined to $R=0\cdot039$ on the basis of 2027 independent diffractometer-measured reflexions corrected for absorption. The sulphate tetrahedra are nearly regular with S–O distances in the region 1·470 (1)–1·478 (1) Å.

The present work was undertaken as part of a programme to determine the dimensions of the suplhate ion as accurately as possible (*e.g.* Nord, 1974). The results here are almost consistent with an independent investigation by Alcock, Evans & Jenkins (1973). Since they reported an *R* value of 0·081 and approximately four times greater values for the estimated standard deviations of the atomic parameters, interatomic distances, and angles, the publication of the present study seems worthwhile.

Crystals of β-Li_2SO_4 were grown from the melt. The lattice parameters, based on a refinement of 32 single-indexed reflexions measured from a Guinier powder photograph (Cu $K\alpha_1$ radiation, 25°C), are: $a=8\cdot239$ (1), $b=4\cdot954$ (1), $c=8\cdot474$ (1) Å, $\beta=107\cdot98$ (3)°, $V=328\cdot9$ Å^3, $Z=4$, $d_{calc}=2\cdot220$ g cm^{-3}. The space group is $P2_1/a$ (No. 14). A small irregularly shaped single crystal, covered with a thin layer of shellac to prevent hygroscopic decomposition, was used for the collection of single-crystal data on a Siemens AED diffractometer (Mo $K\alpha$ radiation, graphite monochromator, θ–2θ scan up to $\theta=50°$). Corrections for *Lp* and absorption effects [μ(Mo $K\alpha$) = 7·92 cm^{-1}] were applied to the 2027 independent non-extinct reflexions.

The final refinements were carried out on an IBM 360/75 computer by means of the full-matrix least-squares program *LALS*. Hughes's (1941) weighting function was used. However, zero weights were assigned to 320 reflexions for which $\sigma(I)/I>\frac{1}{2}$; these were nevertheless included in all other calculations. The atomic scattering factors for Li^+, S^0, and O^- were taken from *International Tables for X-ray Crystallography* (1968). The final atomic parameters are given in Table 1. *R*(unweighted) = 0·039. It is evident upon inspection of the structure factor list* that extinction effects are quite negligible.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31494 (5 pp.). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and temperature factors* ($\times 10^4$) *for* β-Li_2SO_4 ($P2_1/a$)

General equivalent positions 4(*e*): $\pm(x,y,z)$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,z)$. Estimated standard deviations are given in parentheses. The anisotropic temperature factors are of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Li(1)	1986 (3)	5693 (4)	3806 (3)	58 (3)	117 (6)	47 (3)	−7 (4)	36 (4)	3 (3)
Li(2)	4356 (3)	5755 (4)	1287 (3)	58 (3)	151 (6)	49 (3)	−4 (4)	45 (4)	−32 (4)
S	3110 (1)	640 (1)	2516 (1)	31 (1)	71 (1)	28 (1)	−5 (1)	19 (1)	−5 (1)
O(1)	4636 (1)	−644 (2)	2299 (1)	37 (2)	121 (2)	60 (2)	19 (2)	34 (2)	−36 (2)
O(2)	1636 (1)	58 (2)	1053 (1)	37 (2)	201 (2)	34 (2)	−34 (2)	2 (2)	−3 (2)
O(3)	2747 (1)	−507 (2)	3981 (1)	78 (2)	117 (2)	33 (2)	−45 (2)	51 (2)	−2 (2)
O(4)	3389 (1)	3572 (2)	2739 (1)	64 (2)	69 (2)	63 (2)	−11 (2)	66 (2)	−11 (2)