

Table 1. Comparison of the two possible indexings of layer lines for poly- γ -methyl-L-glutamate

ζ obs (\AA^{-1})*	29 residue/8 turn Bamford <i>et al.</i> (1956) $c=43.2 \text{ \AA}$, $P/p=3.625$		65 residue/18 turn Present study $c=97.26 \text{ \AA}$, $P/p=3.611$	
	l	ζ cal	l	ζ cal
0.070 ₇	3	0.069 ₄	7	0.072 ₀
0.112 ₂	5	0.115 ₇	11	0.113 ₁
0.185 ₈	8	0.185 ₁	18	0.185 ₁
0.299 ₀	13	0.300 ₈	29	0.298 ₁
0.668 ₉	29	0.671 ₁	65	0.668 ₃

* Bamford *et al.* (1956).

The $\zeta(n)-P/p$ diagram may be used in the study of helical polynucleotides as shown by Tsuboi (1964). In this case, the relation between the intensity and n is not always simple, especially for the multistranded helix owing to the exact or approximate extinction rules with respect to n . This fact, however, gives us a clue to infer the strandedness of the helix. Some of the results are shown in Fig. 4.

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Topotactic transition in C_4AlB_{24} . By R. F. GIESE, JR., J. ECONOMY and V. I. MATKOVICH, *Research Branch, Research and Development Division, The Carborundum Company, Niagara Falls, New York, U.S.A.*

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During the past 25 years considerable work has been carried out on determining the stoichiometry and structure of complex borides while properties and reactions of these materials have received little attention. Recently, a high temperature reversible disproportionation was reported for $C_2Al_3B_48$ (Matkovich, Economy & Giese, 1964). It was shown that $C_2Al_3B_48$ existed as a single phase only at elevated temperatures and that on cooling it disproportionated reversibly into two phases. The outer form of the high temperature crystal was retained, resulting in an intergrowth of the two low temperature phases. In the present work, an irreversible high temperature transformation of C_4AlB_{24} to a boron carbide type structure is described. In this case the morphology of the original single crystal is retained, yielding a single crystal of the new phase, even though significant changes occur in both the packing of the B_{12} icosahedra and placement of interstitial atoms. Several examples of similar rearrangements have recently been reported in the literature and are described as topotactic reactions (Lotgering, 1959; Shannon & Rossi, 1964).

Single crystals of C_4AlB_{24} prepared by a method reported earlier (Matkovich, Economy & Giese, 1964) were placed in a boron nitride crucible and fired in an argon atmosphere

at temperatures ranging from 1700°C to 2000°C. At temperatures exceeding 2000°C recrystallization takes place and crystals assume the form of slightly distorted octahedra. This paper is concerned only with samples obtained below recrystallization temperatures.

Under the microscope it appeared that the outer form of the crystals changed very little, although the faces lost some of their luster in reflected light. X-ray examination of the product revealed that each specimen was still a single crystal; however, the orthorhombic unit cell of C_4AlB_{24} ($a=8.88 \text{ \AA}$, $b=9.10 \text{ \AA}$, $c=5.69 \text{ \AA}$; space group $Bbmm$) could no longer be observed. Since the crystal retained its original outer form, the axis directions could be traced. It was found that there was no longer a crystallographic axis in the direction of the orthorhombic a and b axes. In the direction of the c axis, however, a period of about 5.63 \AA was observed. By use of Weissenberg X-ray photographs the unit cell was found to be rhombohedral ($a=5.23 \text{ \AA}$; $\alpha=65^\circ 10'$), B_4C type, with hexagonal dimensions of $a=5.63$, $c=12.29 \text{ \AA}$. It was established that one of the rhombohedral axes coincides with the [101] direction of the orthorhombic precursor crystal. (The transition of axes is illustrated in Fig. 1.) The density of crystals was

found to vary between 2.35 and 2.50 g.cm⁻³ (measured by heavy-liquid method). The above-listed cell dimensions correspond to the low density fraction, while the fraction corresponding to a density of 2.50 g.cm⁻³ was found to have $a=5.68$, $c=12.45$ Å. The variation in volume and density indicates a composition range from C₄Al_{0.5}B₂₄ to C₄Al_{1.5}B₂₄. This difference is in agreement with the observed variation in density of the original (orthorhombic) C₄AlB₂₄ crystals. In a few cases the transformation was accompanied by a slight decrease of aluminum content.

The structure of C₄AlB₂₄ is composed of boron icosahedra arranged in an approximately hexagonal closest packed array (Matkovich, Economy & Giese, 1964). The carbon atoms link icosahedra in pairs along the shortest axis. The icosahedra are cross-linked by direct boron-boron bonds in directions radial to the shortest axis. The aluminum atoms appear to be statistically distributed interstitially.

The structure of rhombohedral boron carbide consists of a cubic closest packed array of boron icosahedra slightly distorted along a direction perpendicular to the close-packed layers (Zhdanov & Sevastianov, 1941; Clark & Hoard, 1943). The rhombohedral unit cell has an icosahedron at each vertex and this arrangement provides three potential interstitial sites along the threefold axis.

From the above descriptions it is apparent that a transition from the orthorhombic to the rhombohedral unit cell involves a rearrangement from hexagonal closest packing

to cubic closest packing of B₁₂ icosahedral groups. These two types of packing are illustrated in Fig. 1. It can readily be seen that both types of packing have identical horizontal close-packed layers. However, the hexagonal closest packing is obtained by stacking the layers in such a way that identity is repeated on every second layer while in cubic closest packing this identity is repeated on every third layer. In the transformation, the axis in the direction perpendicular to the plane of the paper (Fig. 1) is retained. The transformation from the orthorhombic to the rhombohedral cell is given by the following matrix:

$$\begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & -\frac{1}{2} \\ \frac{1}{3} & \frac{1}{3} & 0 \end{pmatrix}$$

This transition from hexagonal closest packing to cubic closest packing of boron polyhedra is comparable to that known to take place in metals. The similarity between B₁₂ groups and large metal atoms has already been pointed out (Matkovich, 1961) and in fact a classification of all B₁₂ borides has recently been proposed on the basis of packing of B₁₂ units (Matkovich, Giese & Economy, 1965). Use of packing models provides a means by which a complex reaction can readily be visualized in terms of regroupings of B₁₂ units. In addition, the observation that the single crystal form is retained during the transformation suggests that B₁₂ groups may rearrange as discrete units. This suggestion is strengthened by the fact that the number of B₁₂ icosahedra in a given specimen is the same before and after the transformation and all the boron atoms are tied up in B₁₂ groups in both structures. The transition requires a certain degree of shifting of boron icosahedra and indicates a high degree of internal stability for this boron grouping.

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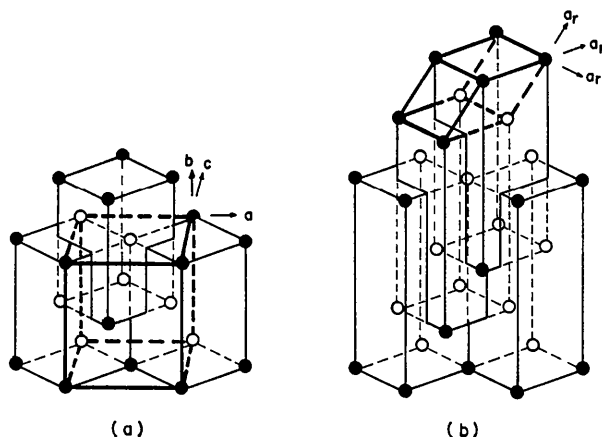


Fig. 1. A comparison of (a) orthorhombic and (b) rhombohedral structures of C₄AlB₂₄. Circles represent the centers of boron icosahedra. The icosahedra are arranged in an approximate hexagonal closest packing in the orthorhombic form and in an approximate cubic closest packing in the rhombohedral form. Aluminum and carbon atoms are not shown.

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Crystal data for some naphthylaminesulphonic acids and salts. By D. E. C. CORBRIDGE*, C. J. BROWN and S. C. WALLWORK†, *Research Laboratories, Imperial Chemical Industries Limited (Dyestuffs Division), Hexagon House, Blackley, Manchester 9, England*

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During the course of a preliminary investigation of the properties of certain dyestuffs intermediates, the unit-cell

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dimensions and space groups of a number of naphthylamine compounds were determined and are here placed on record. Most of the acids were exceedingly sparingly soluble in any solvents, and the preparation of suitable crystals was accomplished by simultaneous slow cooling and slow evaporation of aqueous solutions over a period of several months.