

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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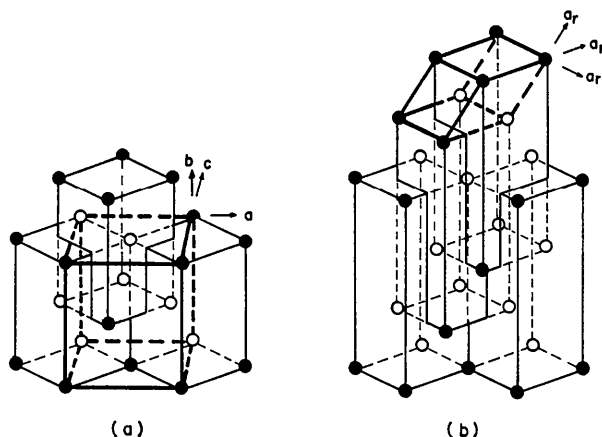


Fig. 1. A comparison of (a) orthorhombic and (b) rhombohedral structures of C₄AlB₂₄. Circles represent the centers of boron icosahedra. The icosahedra are arranged in an approximate hexagonal closest packing in the orthorhombic form and in an approximate cubic closest packing in the rhombohedral form. 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.

Table 1. *Naphthylaminesulphonic acids*

| | <i>a</i> | <i>b</i> | <i>c</i> | β | $\rho(\text{obs})$ | $\rho(\text{calc})$ | <i>Z</i> | Space group |
|---|----------|----------|----------|---------|--------------------|---------------------|----------|-------------|
| 1-Naphthylamine-2-sulphonic acid | 17.22 Å | 10.91 Å | 10.07 Å | — | 1.552 | 1.567 | 8 | $P2_1ca$ |
| 1-Naphthylamine-3-sulphonic acid | 12.78 | 11.70 | 6.82 | — | 1.474 | 1.451 | 4 | $Pbn2_1$ |
| 1-Naphthylamine-4-sulphonic acid (naphthionic acid) | 16.54 | 15.20 | 7.84 | — | 1.498 | 1.506 | 8 | $P2na$ |
| 1-Naphthylamine-5-sulphonic acid monohydrate | 16.77 | 7.84 | 8.05 | 96° | 1.518 | 1.521 | 4 | $P2_1/a$ |
| 1-Naphthylamine-6-sulphonic acid | 16.25 | 11.12 | 10.57 | — | 1.560 | 1.552 | 8 | $Pbca$ |
| 1-Naphthylamine-7-sulphonic acid monohydrate | 16.44 | 8.91 | 7.14 | — | 1.514 | 1.533 | 4 | $Pc2_1n$ |
| 1-Naphthylamine-8-sulphonic acid | 14.04 | 10.76 | 6.93 | — | 1.444 | 1.474 | 4 | $P2an$ |

Table 2. *Salts of 1-naphthylamine-4-sulphonic acid*

| | <i>a</i> | <i>b</i> | <i>c</i> | β | $\rho(\text{obs})$ | $\rho(\text{calc})$ | <i>Z</i> | Space group |
|------------------------------------|----------|----------|----------|---------|--------------------|---------------------|----------|-------------|
| Ammonium naphthionate monohydrate | 20.00 Å | 10.79 Å | 10.83 Å | 95.0° | 1.467 | 1.467 | 8 | $P2_1/n$ |
| Lithium naphthionate trihydrate | 12.80 | 9.81 | 12.14 | 122.14 | 1.48 | 1.46 | 4 | $P2_1/n$ |
| Sodium naphthionate tetrahydrate | 11.61 | 12.05 | 10.04 | 98.8 | 1.513 | 1.516 | 4 | $P2_1/c$ |
| Potassium naphthionate | 34.40 | 8.60 | 7.06 | — | 1.68 | 1.668 | 8 | $P2_1cn$ |
| Thallium naphthionate | 17.89 | 12.51 | 9.52 | — | 2.70 | 2.66 | 8 | $Pbca$ |
| Calcium naphthionate octahydrate | 23.52 | 11.93 | 9.73 | 95.0 | 1.530 | 1.534 | 4 | $P2_1/n$ |
| Magnesium naphthionate decahydrate | 14.08 | 8.30 | 12.86 | 103.0 | 1.47 | 1.470 | 2 | $P2_1/a$ |
| Zinc naphthionate enneahydrate | 45.22 | 14.33 | 8.58 | — | 1.60 | 1.604 | 8 | $P2_1ab$ |
| Cobalt naphthionate enneahydrate | 45.60 | 14.35 | 8.62 | — | 1.58 | 1.565 | 8 | $P2_1ab$ |
| Nickel naphthionate enneahydrate | 45.60 | 14.35 | 8.62 | — | 1.58 | 1.565 | 8 | $P2_1ab$ |

Table 3. *Miscellaneous salts of naphthylaminesulphonic acids*

| | <i>a</i> | <i>b</i> | <i>c</i> | β | $\rho(\text{obs})$ | $\rho(\text{calc})$ | <i>Z</i> | Space group |
|--|----------|----------|----------|---------|--------------------|---------------------|----------|--------------|
| Sodium 2-naphthylamine-6-sulphonate dihydrate | 26.71 Å | 11.20 Å | 7.91 Å | — | 1.588 | 1.579 | 8 | $Pn2b$ |
| Sodium 1-naphthylamine-5-sulphonate | 18.01 | 8.56 | 6.99 | — | — | 1.51 | 4 | $P2_12_12_1$ |
| Potassium 1-naphthylamine-5-sulphonate | 18.09 | 8.63 | 7.51 | — | — | 1.48 | 4 | $P2_12_12_1$ |
| Sodium naphthionate/bisulphite addition compound | 14.63 | 9.20 | 10.25 | 95.5° | 1.72 | 1.715 | 4 | $P2_1/n$ |
| Sodium naphthionate/bisulphite dimeric addition compound | 21.23 | — | 6.00 | — | 1.75 | 1.747 | 4 | $I\bar{4}$ |
| Zinc 1-naphthol-4-sulphonate octahydrate | 23.00 | 11.24 | 10.64 | — | 1.584 | 1.583 | 4 | $P2_12_1n$ |

No further crystallographic work has been done or is planned to be done on any of the acids listed in Table 1.

A number of salts of 1-naphthylamine-4-sulphonic acid were also investigated. These were readily soluble in water, and well-formed crystals of quite large size could easily be grown. The unit cells and space groups of these are listed in Table 2. It is remarkable that so few of these salts are isomorphous. The zinc, cobalt and nickel salts are obviously isomorphous and isostructural, and the calcium salt appears to be related to the sodium salt by doubling *a*, but otherwise there seem to be no resemblances between members of the series.

The structure of the sodium salt has been fully determined by three-dimensional X-ray analysis (Brown & Corbridge, 1966); some preliminary unpublished work has been done on the [*b*] projection of the calcium salt, and we have taken

some photographs of the potassium salt for intensity measurements, but otherwise no further work on these compounds is contemplated. The potassium salt is interesting in that the crystals can easily be bent reversibly without fracture, and cleavage readily occurs parallel to (100).

The cell dimensions and space groups of a few related compounds were also determined and these are listed in Table 3. The preparation and exact formulae of the sodium naphthionate/sodium bisulphite addition compounds are described in a paper on the mechanism of the Bucherer reaction (Cowdrey, 1946).

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Crystal data for ytterbium orthoferrite YbFeO_3 . By F. W. HARRISON, *Mullard Research Laboratories, Redhill, Surrey, England*

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The recent publication by Eibschütz (1965) on the lattice constants of polycrystalline samples of the orthoferrites of the heavier rare earths prompts a confirmatory report on powder data from a sample of YbFeO_3 prepared originally in single-crystal form. The data were obtained in these laboratories in 1960 from a crystal approximately a milli-

metre cube which was a by-product in the preparation by J. L. Page of crystals of ytterbium iron garnet from a lead-oxide solution.

The powder photograph was taken with a Philips No. 33524 Straumanis camera of diameter 114.6 mm and filtered iron radiation. The lower-angle lines were indexed on the