ture and crystallography of the tetraphenylarsonium triiodide (in which the bent triiodide ion is reported to have bonds of equal length) is sufficiently different from that of ammonium triiodide for environmental or packing effects to be responsible for differences in anion geometry. In the case of CsI_3 the structures are closely similar; a similar explanation can scarcely be envisaged. However, the most recent structural study (Tasman & Boswijk, 1954) was a refinement carried out by Fourier methods using 98 $0kl$ reflexions and we may question the reliability of the I–I–I interbond angle. In commencing our refinement with Mooney's positional parameters, the residual of 0·32 indicated clearly that her structure does not completely fit our observational data.

In the light of the studies made by Brown & Nunn on the effect of the crystalline environment on the configuration of the triiodide ion, the lattice field over the anion in ammonium triiodide is expected to be unsymmetrical, thus stabilizing the configuration with unequal interiodine bonds. This hypothesis is supported by the similarity of the thermal parameters of each of the three iodine atoms which together make up the anion. The short I–N distance of 3·624 Å may be evidence for a form of hydrogen bonding between the ammonium group and the triiodide ion. This would raise the possibility of rotation or torsion of the cation about the N–H···I axis as is the case in NH_4I (Plumb & Hornig, 1953).

Copies of the observed and calculated structure factors listing are available from the authors upon request.

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The Crystal Structure of Trigonal Diboron Trioxide*

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Diboron trioxide, B_2O_3, crystallizes in space group $P3_1$ with cell dimensions $a=4\cdot336$, $c=8\cdot340$ Å. The cell contains three B_2O_3 units. The structures previously proposed by Berger and by Strong & Kaplow are incorrect. The structure was determined by the superposition frequency method, and refined by least-squares to $R=0\cdot059$ from diffractometer data. The structural unit is an infinite chain or ribbon of BO_3 triangles, very similar to the metaborate ribbon, $(BO_2)_{\infty}^{-\infty}$. These ribbons are interconnected, so that each oxygen atom has four oxygen neighbours at 2·30–2·43 Å distance. Both boron atoms are trigonally coordinated to oxygen with bond lengths 1·34–1·40 Å.

Introduction

Although diboron trioxide† (B_2O_3) plays a central role in modern glass technology and research, neither the structure of B_2O_3 I‡ nor the vitreous solid form have been satisfactorily determined. B_2O_3 will not crystallize from the melt under ambient pressure conditions. Solid diboron trioxide was known only in the vitreous state until Kracek, Morey & Merwin (1938) found B_2O_3 I to form as a fine powder during dehydration of metaboric acid under carefully controlled conditions. After failing to grow a useful single crystal by this process, Berger (1952, 1953) was forced to use data from powder photographs in an attempt to determine the structure. The basic units of Berger's structure were two different irregular tetrahedra of oxygen atoms each surrounding a boron atom. This structure has been considered unsatisfactory in several respects (*e.g.* Wells, 1962), particularly as it results in two

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* Presented in part at the A.C.A. Meeting of August, 1967 (paper V2).

† Terminology suggested by the Advisory Subcommittee on the Nomenclature of Boron Compounds, American Chemical Society [*Inorg. Chem.* (1968). 7, 1945].

‡ Terminology introduced by Prewitt & Shannon (1968) for the phase previously designated α-B_2O_3.

different BO_4 tetrahedra with six different B–O bond lengths ranging from 1·31 to 2·14 Å. In this laboratory a least-squares refinement (Hamilton, 1961) on Berger's powder data was attempted from his positional parameters. The attempt was abandoned when the refinement diverged. The tetrahedrally coordinated structure proposed by Berger was also puzzling because in various borate systems there is a regular variation of the fraction of boron atoms in fourfold coordination as a function of increasing alkali content (both in glasses and crystals); yet in each instance there was an obvious trend towards only threefold coordinated boron as the composition approached B_2O_3 (see Krogh-Moe, 1960*a*,*b*, 1962*a*,*b*; Greenblatt & Bray, 1967).

A further incentive for a redetermination of the structure of B_2O_3 I came from nuclear magnetic resonance (n.m.r.) experiments in this laboratory and elsewhere. Because n.m.r. spectra provide independent evidence for certain structural features of both vitreous and crystalline diboron trioxide, a brief summary of these results will be given.

The utility of n.m.r. spectroscopy follows from its sensitivity to the asymmetry of electric fields at atom sites in solids. In particular, the n.m.r. spectrum of ^{11}B exhibits a characteristic splitting proportional to the electric field gradient at the ^{11}B nucleus. This splitting is observed to be marked for B atoms in planar BO_3 groupings but vanishes for B atoms in BO_4 tetrahedral configurations (Bray, Edwards, O'Keefe, Ross & Tatsuzaki, 1961). Silver & Bray (1958) observed a marked splitting in the ^{11}B n.m.r. spectra of B_2O_3 glass, and thus demonstrated that only threefold coordination of O existed around the B atoms (see also Silver, 1960; Milberg, Belitz & Silver, 1960). Triangular coordination of the boron atoms in glassy B_2O_3 has also been suggested from X-ray radial distribution (Warren, Krutter & Morningstar, 1936; Despujols, 1958) and infrared absorption (Parsons & Milberg, 1960; Simon, 1960; Borrelli, McSwain & Su, 1963). Later it was observed in this laboratory and elsewhere (Svanson, Forslind & Krogh-Moe, 1962) that B_2O_3 I gave n.m.r. spectra essentially identical to that of vitreous B_2O_3.

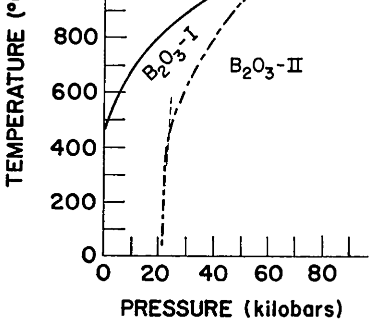

Fig. 1. The phase diagram of B_2O_3 as established by MacKenzie & Claussen (1961).

The n.m.r. absorption for BO_4 groups is sharper and stronger than that for BO_3 groups (Bray *et al.*, 1961; Silver & Bray, 1958) and thus the absence of sharp components in the spectrum of B_2O_3 I precludes the presence of tetrahedral BO_4 groups in this material. The magnitude of the observed splitting in B_2O_3 I, which closely approximates the value observed in materials known to have approximately planar BO_3 groups, is further evidence for the presence of such groups in B_2O_3 I. The absence of more than one distinguishable splitting suggests that all of the BO_3 groups in B_2O_3 I are bonded in similar configurations.

Kline, Bray & Kriz (1968) have also recently discussed the B_2O_3 I structure; they concluded from n.m.r. observations that it contains only three-coordinated boron.*

A new study of the B_2O_3 I structure (Strong & Kaplow, 1968) was published while this paper was in preparation. Strong & Kaplow showed that a minor distortion of the structure proposed by Berger results in an arrangement having only three-coordinated boron, and which gives acceptable agreement with a 'radial distribution function' derived from X-ray powder data. It will be shown that the structure proposed by Strong & Kaplow is incorrect, but does contain the correct structural unit of B_2O_3 I.

Synthesis of B_2O_3 crystals

The phase diagram of B_2O_3 as established by MacKenzie & Claussen (1961) is shown in Fig. 1. Because the object of the present work was to produce a single crystal of the low pressure phase B_2O_3 I, the working region was restricted to pressures below 20 kbar to avoid formation of B_2O_3 II. On the other hand it was desirable to work with as high a melt temperature as possible, following the assumption that the melt viscosity would be more strongly influenced by temperature than by pressure. This assumption is based on the experience of Harrison & Tiller (1965) and Harrison (1964), who have used the phenomenon to grow large single crystals of selenium (also a glass former) under pressure. Most of this work was thus conducted in the region between 10 and 15 kbar.

The apparatus used was a simple steel piston cylinder using internal heating (Fig. 2). Samples were contained either in graphite or platinum. Most of the later work was performed in platinum, which was more successful at containing the molten B_2O_3 under pressure and presented fewer difficulties in sample recovery (graphite tended to adhere to the sample, rendering difficult microscopic examination of crystallized regions).

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* Svanson & Johansson (1969) discuss their n.m.r. studies in a recent paper, also concluding that boron is three-coordinated in B_2O_3 I.

The actual positions of the phase boundaries shown in Fig. 1 are not well established because crystallization is dominated by kinetic considerations. Also, in this work there were uncertainties of approximately 10% in both the pressure and temperature parameters (pressure was calculated from the applied load on the piston, and temperature was determined from the power input to the heater, which had been calibrated against a thermocouple in a separate experiment).

Our approach was to pressurize the sample at room temperature, heat at constant pressure to a temperature somewhat above the estimated melt temperature, and then to cool slowly through the solidification region. Samples were examined for single crystals by petrographic methods. Two single crystals, produced in two separate experiments, were found:

JS–XII–40. Grown in graphite at 10 kbar with the temperature decreased from 800 to 300 °C at 0·6 °.min^{-1}. Most of the sample was non-crystalline with the exception of small spherical nodules on the surface. A flat single-crystal approximately 0·1 mm in largest dimension was recovered.

JS–XIII–53. Grown in platinum at 15 kbar. Held for $3\frac{1}{2}$ hours at 700 °C and cooled to 500 °C at 0·5 °.min^{-1} followed by a rapid quench to room temperature. Most of the sample was poorly crystallized, giving a very broad B_2O_3 I X-ray diffraction pattern, with the exception of some well crystallized nodules near the edge. A crystal somewhat larger than JS–XII–40 was recovered.

Some difficulty was encountered in reproducing the results. It is suspected that some of these difficulties may be related to the water content of the glass. Vitreous B_2O_3 was prepared by dehydration of Mallinckrodt analytical reagent grade H_3BO_3, as described by MacKenzie (1959). Most of the diboron trioxide came from the same batch. As samples were needed this material was repeatedly melted and poured into molds. It was observed that upon subsequent meltings higher temperatures (by several hundred degrees) were required to produce a liquid of low enough viscosity for pouring. It is assumed that the glass lost some water on each melting (see Uhlmann, Hays & Turnbull, 1967).

Crystal data

The first crystal that was found (JS–XII–40) had an irregular blade shape. Cell dimensions and diffraction symmetry were found to agree with Berger's published data for B_2O_3 I. The crystal became spoiled, however, by hydration. The second crystal (JS–XII–53), was a euhedral hexagonal bipyramid. This crystal was coated with silicone grease, by which means it has been preserved for more than a year.

The Laue symmetry was observed to be $\bar{3}$ (from Weissenberg photographs recorded with Cu $K\alpha$ radiation). The only observed absences were $00l$; $l=3n$. The space group is thus unequivocally shown to be one of the enantiomorphs $P3_1$, or $P3_2$; $P3_1$ was arbitrarily chosen.

A conventional Weissenberg camera (Supper) was modified (Herbstein, 1963) to allow reflections to be recorded in the back reflection region ($2\theta \leq 173°$) with Straumanis film mounting. A least-squares procedure (Burnham, 1962) was used to refine the cell dimensions, using 20 high-angle reflections. One-parameter correction terms for camera eccentricity and film shrinkage were refined with the cell dimensions. This gave $a=$

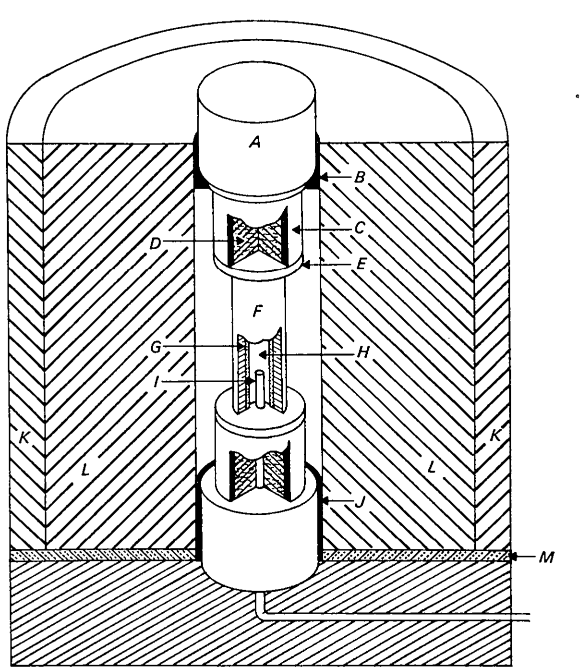

Fig. 2. High pressure cell used for the growth of B_2O_3 I crystals: *A*, hardened steel piston; *B*, beryllium-copper extrusion rings; *C*, hardened steel current ring; *D*, pyrophyllite insulation inside current ring; *E*, molybdenum current disc; *F*, carbon heater; *G*, protective sleeve inside heater (pyrophyllite or boron nitride); *H*, sample cavity; *I*, thermocouple in sample cavity; *J*, pyrophyllite insulation around bottom plug for electrical isolation; *K*, soft steel safety ring around die; *L*, steel die; *M*, mica insulation.

Table 1. *Final atomic parameters*

Corresponding standard deviations are given in parentheses.

	x	*y*	*z*	*B*
O(1)	0·5468 (30)	0·3972 (32)	0·0000 (00)	0·82 (0·16)
O(2)	0·1485 (21)	0·6004 (33)	0·0775 (09)	0·75 (0·16)
O(3)	0·0045 (24)	0·1608 (36)	−0·1291 (23)	0·58 (0·12)
B(1)	0·2229 (48)	0·3926 (47)	−0·0198 (26)	1·28 (0·39)
B(2)	0·8281 (43)	0·6031 (45)	0·0921 (24)	0·81 (0·36)

4·3358 (5), $c=8{\cdot}3397$ (18) Å which agree well with Berger's data ($a=4{\cdot}334$, $c=8{\cdot}334$ Å, no error estimates given). Wavelengths used in the present study were $\lambda(\text{Cu } K\alpha_1)=1{\cdot}54051$ Å, $\lambda(\text{Cu } K\alpha_2)=1{\cdot}54433$ Å (*International Tables for X-ray Crystallography*, 1962).

The first set of intensity data were visually estimated from Weissenberg photographs of layers 0*kl*, 1*kl*, 2*kl*, (Cu $K\alpha$) and 3*kl* (Mo $K\alpha$). Layers were scaled by means of equivalent reflections in different layers. The structure was solved and partially refined ($R=0{\cdot}13$) with this set of data. To improve the accuracy of bond length determination a second set of data was measured.

Data used in the final refinement were collected by AUSSIE,* the 3M-2018 computer-controlled X-ray diffractometer. 2θ scans were made using Zr-filtered Mo $K\alpha$ radiation. All accessible reflections in a hemisphere out to $2\theta=65°$ were measured; when averaged over equivalent reflections, 130 unique reflections were significantly ($>2\sigma$) above the background.

Solution of the structure

Initial attempts at solving the structure by examination of the three-dimensional Patterson function were unsuccessful. A three-dimensional Patterson function was computed, the coefficients of which had been treated with a divergent sharpening function (Abrahamsson & Maslen, 1963). The sharpening resulted from multiplying the coefficients corresponding to point atoms at rest by the diverging function $\exp[3{\cdot}0(\sin^2\theta/\lambda^2)]$. This sharpened Patterson function was contoured on transparent Lucite sheets which were used to build a three-dimensional model of the Patterson function. Four vectors corresponding to reasonable oxygen–oxygen distances were chosen, but no real progress could be made toward solution of the structure.

Table 2. *Observed structure amplitudes and the corresponding calculated amplitudes and phases for* B_2O_3 I

h	k	l	F_o	F_c	α	h	k	l	F_o	F_c	α	h	k	l	F_o	F_c	α
0	0	3	17.0	16.9	42	2	0	7	5.4	6.0	32	4	-3	1	6.3	5.5	62
0	0	6	5.9	6.7	87	2	1	-6	8.5	8.7	83	4	-3	2	6.9	6.6	262
0	0	9	18.4	18.0	-59	2	1	-5	9.0	9.1	256	4	-3	3	8.2	8.4	35
0	1	-5	13.3	13.3	110	2	1	-4	11.7	12.1	246	4	-2	-3	9.1	9.6	37
0	1	-4	11.0	10.7	-54	2	1	-2	4.2	4.1	141	4	-2	0	3.9	3.8	172
0	1	-3	26.0	26.0	138	2	1	-1	4.5	3.6	-41	4	-2	2	6.8	5.9	165
0	1	-2	35.9	36.4	153	2	1	2	5.8	6.1	64	4	-2	3	9.3	9.5	119
0	1	4	6.5	6.6	50	2	2	-6	5.8	5.9	57	4	-1	-3	8.1	8.0	-52
0	2	-6	9.1	9.8	-80	2	2	2	6.7	6.3	13	4	-1	-2	7.0	6.8	201
0	2	-4	17.4	17.5	-55	2	2	6	5.7	6.0	216	4	-1	-1	6.5	6.4	32
0	2	-3	11.0	10.5	-39	3	-4	-5	4.8	5.1	-11	4	-1	0	8.1	7.8	-50
0	3	-6	10.4	11.6	97	3	-3	1	8.4	8.1	255	4	-1	1	12.8	12.4	251
1	-2	-8	9.6	9.5	128	3	-3	2	13.0	13.1	146	4	-1	3	7.8	8.1	79
1	-2	-7	4.7	4.6	161	3	-3	3	7.7	7.4	40	4	0	-4	5.0	3.8	5
1	-1	-10	8.6	8.3	15	3	-2	-5	10.7	11.3	-50	4	0	-3	6.0	5.5	142
1	-1	-9	5.9	5.7	-56	3	-2	-4	10.6	11.1	6	4	0	0	7.2	6.2	176
1	-1	1	5.2	5.9	70	3	-2	-3	8.1	7.5	-24	4	0	1	4.6	4.2	-40
1	0	-7	15.3	14.9	145	3	-2	-1	13.7	13.9	-19	4	0	2	5.8	4.9	260
1	0	-6	10.9	11.8	-81	3	-2	0	8.4	8.5	266	4	0	4	4.0	2.9	-8
1	0	-5	10.3	10.7	229	3	-1	-6	8.2	8.4	115	4	1	-3	5.6	5.1	225
1	0	-3	13.9	13.4	141	3	-1	-5	9.0	9.8	210	4	1	-1	4.6	4.2	34
1	0	1	19.2	19.8	-44	3	-1	-4	11.5	12.3	127	4	1	1	5.2	5.0	104
1	0	11	6.4	5.6	24	3	-1	0	9.3	8.1	269	4	1	4	5.8	5.2	226
1	1	-5	9.9	9.2	-65	3	-1	1	14.4	14.2	6	4	1	5	6.3	5.6	112
1	1	-3	7.2	6.6	226	3	-1	2	5.5	4.9	110	4	2	-1	6.0	4.9	236
1	1	1	23.8	22.9	-32	3	-1	3	8.0	7.9	55	4	2	1	5.9	6.2	45
1	1	8	8.9	9.4	88	3	0	-9	8.0	9.0	232	5	-3	-6	6.4	5.3	218
1	2	-5	10.7	10.9	152	3	0	-7	5.6	6.0	-30	5	-3	0	7.3	7.4	214
1	2	-4	10.8	11.4	5	3	0	-6	9.3	9.5	-79	5	-3	2	4.3	5.6	51
1	3	8	6.2	6.2	184	3	0	-4	7.2	8.6	196	5	-2	-2	8.0	9.3	-5
2	-2	-5	7.4	8.0	190	3	0	0	12.5	12.3	175	5	-2	0	7.3	7.2	218
2	-2	1	8.2	8.9	72	3	0	1	4.5	2.9	-48	5	-2	6	6.5	5.5	18
2	-2	2	20.3	20.4	148	3	0	2	14.7	14.8	267	5	-1	-3	5.3	4.5	65
2	-1	-5	9.6	9.4	175	3	0	3	14.4	14.0	222	5	-1	-1	4.8	4.9	58
2	-1	-3	7.0	6.3	53	3	0	7	7.2	7.9	37	5	-1	1	5.6	5.0	153
2	-1	-2	11.8	9.8	177	3	1	-8	6.4	6.6	94	5	-1	4	6.1	5.2	129
2	-1	0	4.4	6.8	24	3	1	-4	5.5	4.3	186	5	-1	5	6.1	5.8	141
2	-1	1	25.3	24.1	-59	3	1	3	8.1	8.5	0	5	0	0	7.5	8.2	2
2	-1	2	12.1	9.7	235	3	1	5	5.4	4.7	151	5	0	2	8.7	8.4	269
2	0	-7	9.8	9.9	-34	3	2	-3	5.4	4.9	175	6	-3	-1	5.9	4.8	74
2	0	-5	9.2	9.0	235	3	3	0	4.7	3.4	-29	6	-3	1	5.9	4.5	104
2	0	-4	14.2	15.2	4	4	-4	1	13.8	13.7	72	6	-2	1	6.5	6.4	229
2	0	-3	7.1	7.5	144	4	-3	-1	12.5	12.3	222						
2	0	0	2.0	2.9	6	4	-3	0	8.2	8.1	-52						

Application of the superposition frequency method (Gorres & Gaertner, 1965; Gorres & Jacobson, 1964) to the sharpened Patterson function immediately revealed the structure. Each of the four possible oxygen–oxygen vectors was separately studied. The origin of each vector was tentatively placed at every point of a grid ($\simeq 0{\cdot}1$ Å mesh) in the basal plane (this simplification from the three-dimensional search that is usually necessary is a consequence of the polar space group, allowing the z coordinate of one atom to be arbitrarily chosen). In each tentative vector position a check was made for agreement of all vectors generated by the space-group symmetry with the observed peaks of the Patterson function. Two vectors were rejected outright; the other two vectors satisfied all checks with their origins at only one location, approximately the same ($\simeq 0{\cdot}3$ Å apart) for both vectors. Each vector thus gave two tentative atomic positions. The merit of each of the two pairs of tentative atomic positions was studied separately.

Each point on a three-dimensional grid ($\simeq 0{\cdot}1$ Å mesh) in the cell was regarded as a possible atomic site. As such, all vectors were generated between it and its symmetry equivalents and the two tentatively located atoms and their symmetry equivalents. A check was made to determine whether all the generated vectors appeared in the Patterson function. One pair of tentative positions gave only two small peaks. The other (correct) pair of positions showed one large peak at a position which was later confirmed to be an oxygen site. At this stage we were confident of having correctly located the three independent oxygen atoms.

The threshold level, below which value the Patterson map was regarded as 'noise', was then lowered. Using the three tentatively located atoms, the superposition frequency method showed only two prominent peaks, corresponding to the two independent boron atoms. After the Patterson map had been prepared, the total computing time (CDC-3600) for all the false and correct trials outlined above was 15 minutes.

A structure calculation for all five atoms of the trial model gave an agreement $R=0{\cdot}26$.

Refinement of atomic parameters

Least-squares refinement of the atomic positional and isotropic thermal parameters, and the film scaling factors reduced R to 0·13 with the photographic data (172 observed reflections, 47 unobserved).* Continuing the refinement with the diffractometer data (130 observed reflections) reduced R to 0·059 (20 parameters†). Although the calculated estimated standard deviations are little different from those obtained with the film

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* Automated Unattended Supervisory System for Intensity Evaluation (Gurr, 1965).

* Using the *ORFLS* program (Busing, Martin & Levy, 1962).

† Using the *UMLSTQ* program (Finger, 1966).

data, the new bond lengths and angles are much more uniform between chemically equivalent bonds. Three-dimensional difference Fourier syntheses gave no evidence of anisotropic thermal motion, nor any other meaningful residual electron density. However complete anisotropic refinement was made. The *R* index improved from 0·0586 with 20 parameters to 0·0494 with 45 parameters, a ratio of 1·19. This improvement is not significant at the 25% probability level, using the Tables given by Hamilton (1964). Results of the anisotropic refinement are therefore not presented, since anisotropic refinement is not warranted by the present data.

Atomic form factors used were those for neutral B and O (*International Tables for X-ray Crystallography*, 1962). The largest off-diagonal element of the atomic position correlation matrix was only 0·73, so that the least-squares refinement proceeded without the difficulties sometimes encountered for polar space-groups (Geller, 1961; Megaw, 1962).

Final atomic parameters and their estimated standard deviations calculated from the full matrix are shown in Table 1. Table 2 shows the observed structure amplitudes and the calculated amplitudes and phase angles for the atomic parameters given in Table 1.

Discussion of the structure of B_2O_3 I

In agreement with previous conclusions based on n.m.r. data, the coordination of both boron atoms in the asymmetric unit is planar trigonal. The dimensions of the two distinct types of BO_3 triangles are given in Fig. 3, which also illustrates the similarity of the two types of triangles. The hypothesis that the triangles are completely regular, with all O–O lengths equal, may be rejected at the 99·5% confidence level (Hamilton,

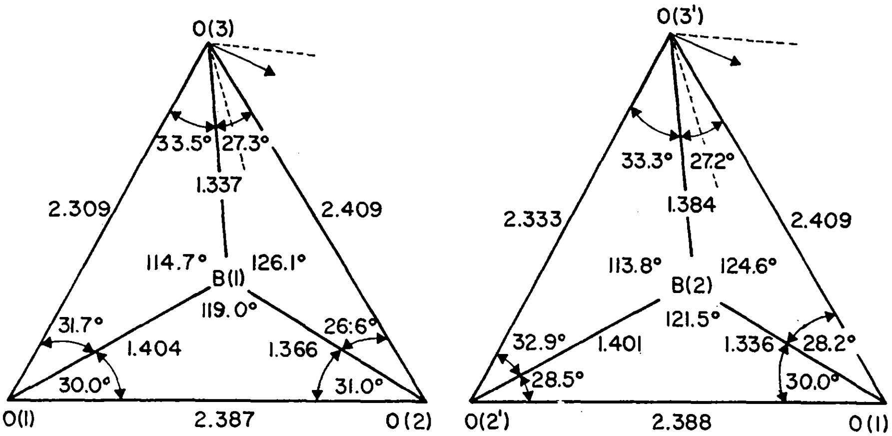

Fig. 3. Dimensions of the two crystallographically distinct BO_3 triangles in the B_2O_3 I structure.

Table 3. *Comparison of* O–O *and* B–O *distances in various* BO_3 *triangles*

Crystal	O–O	B–O	Reference
$Ca_2B_6O_{11}.1H_2O$	2·36 Å	1·38 Å	Clark, Appleman & Christ (1964)
Colemanite	$2{\cdot}37_6$	$1{\cdot}37_6$	Clark, Appleman & Christ (1964)
Meyerhofferite	$2{\cdot}36_2$	$1{\cdot}36_4$	Clark, Appleman & Christ (1964)
$Ca_2B_6O_{11}.9H_2O$	2·35	1·37	Clark, Appleman & Christ (1964)
Inyoite	$2{\cdot}38_1$	$1{\cdot}37_2$	Clark, Appleman & Christ (1964)
Tunellite	2·36	1·36	Clark (1964)
Ulexite		1·37	Clark & Appleman (1964)
Hambergite	2·367	1·367	Zachariasen, Plettinger & Marezio (quoted by Clark, Appleman & Christ).
Probertite	2·26–2·39	1·30–1·39	Kurbanov, Rumanova & Belov (1964)
Hydroboracite	2·39	1·38	Rumanova & Ashirov (1964)
Cs triborate		1·38	Krogh-Moe (1960*a*)
K pentaborate		1·34	Krogh-Moe (1959)
K pentaborate.$4H_2O$		1·359	Zachariasen & Plettinger (1963)
Mg pyroborate (triclinic)	2·395	1·384	Block, Burley, Perloff & Mason (1959)
Mg pyroborate (monoclinic)	2·37	1·36	Takeuchi (1952)
Orthoboric acid	2·356	1·361	Zachariasen (1954)
Borax		1·36	Morimoto (1956)
β-Metaboric acid	2·367	1·367	Zachariasen (1963)
Na metaborate	2·392	1·382	Marezio, Plettinger & Zachariasen (1963*a*), Zachariasen (1937)
Ca metaborate	2·372	1·372	Marezio, Plettinger & Zachariasen (1963*b*)
Li metaborate	2·376	1·373	Zachariasen (1964)
B_2O_3 I	2·372	1·372	This study

1964). It would seem that the triangles are distorted by forces between non-bonded atoms. An almost perfectly regular triangle can be achieved by displacing O(3) in the directions marked by the arrows in Fig. 3. However, such a displacement would bring the neighbouring O(1) and O(2) atoms even closer than the present distances of 2·86 and 2·84 Å. Atoms O(1) and O(2) each have only this one approach with O(3) that is less than 3·0 Å. Thus, it seems plausible that the observed distortions of the triangles are the result of packing forces in the crystal that have displaced O(3) from the position that it would otherwise occupy. The hypothesis that the two triangles are identical (in the orientation shown in Fig. 3) cannot be rejected even at the 50% confidence level.

The averages of the six independent O–O and B–O distances in the two triangles are 2·372 and 1·372 Å respectively. These values are very similar to those observed in other crystals containing BO_3 triangles as may be seen from Table 3. A comparison such as that made in Table 3 does not consider truly equivalent bonds, since the bond order of B–O bonds in BO_3 triangles will also depend on the external bonds to the triangles. Coulson & Dingle (1968) made Hückel molecular-orbital calculations for various B–O bond types. They calculated a bond order of approximately 0·4 for BO–B bonds and approximately 0·6 for $B–O^-$ bonds in isolated $(BO_2)_\infty^{-\infty}$ ribbons. The average B–O distance of 1·372 Å for B_2O_3 I corresponds to a bond order of approximately 0·5 on the bond order – bond length curve of Coulson & Dingle. The average B–O distance of 1·372 Å for B_2O_3 I also agrees well, as it should, with the length assumed by Zachariasen (1963) for a bond of 'strength' 1·0 (1·365 Å). A value of 1·37 ± 0·02 Å is quoted as the mean B–O distance for three-coordinated boron by Waugh (1968).

Some of the more important bond lengths and angles in the B_2O_3 I structure are listed in Table 4. Errors estimated from the full least-squares matrix, and including the contribution of unit-cell errors, are also shown.*

There are several viewpoints from which one may describe the manner in which BO_3 triangles are linked to form the three-dimensional structural network, but we choose to emphasize the infinitely long planar ribbon shown in bold outline in Fig. 4. This ribbon is very similar to the $(BO_2)_\infty^{-\infty}$ ribbon that is a characteristic of the structure of lithium metaborate (Zachariasen, 1964) and calcium metaborate (Marezio, Plettinger & Zachariasen, 1963*b*). In those two structures the $(BO_2)_\infty^{-\infty}$ ribbons are isolated, and are bonded to the cations by ionic forces. In B_2O_3 I all oxygen atoms are

Table 4. *Bond distances and angles* (*and estimated errors thereof*) *for* B_2O_3 I

The Table also shows, for each atom, all other atoms within a coordination sphere of radius 2·9 Å.

Distances

Central atom O(1)–		Central atom O(2′)–		Central atom O(3′)–	
O(2)	2·387 (14) Å	O(1′)	2·387 (14) Å	O(1′)	2·309 (11) Å
O(2′)	2·388 (14)	O(1)	2·388 (14)	O(1^{iv})	2·408 (12)
O(3)	2·309 (15)	O(3′)	2·409 (18)	O(2′)	2·409 (13)
O(3″)	2·408 (18)	O(3″)	2·333 (15)	O(2^{v})	2·333 (11)
O(3′)	2·860 (15)	O(3‴)	2·835 (16)	O(1)	2·860 (18)
B(1)	1·404 (19)	B(1′)	1·366 (23)	O(2^{iv})	2·835 (18)
B(2)	1·336 (22)	B(2)	1·400 (19)	B(1′)	1·337 (18)
B(2″)	2·636 (20)	B(1‴)	2·616 (21)	B(2″)	1·384 (17)
				B(1^{iv})	2·822 (18)
				B(2^{iv})	2·826 (18)

Central atom B(1′)–		Central atom B(2)–	
O(1′)	1·404 (19) Å	O(1)	1·336 (22) Å
O(2′)	1·366 (23)	O(2′)	1·400 (21)
O(3′)	1·337 (18)	O(3″)	1·384 (17)
O(2^{iv})	2·616 (20)	O(1^{v})	2·636 (19)
O(3^{iv})	2·822 (21)	O(3^{v})	2·826 (20)
B(2)	2·489 (29)	B(1)	2·489 (29)
B(2′)	2·489 (29)	B(1′)	2·489 (29)
B(2″)	2·498 (10)	B(1″)	2·498 (10)

Angles

Central atom O(1)			Central atom O(2′)			Central atom O(3′)		
O(2)	O(3)	61·7 (5)°	O(1)	O(3″)	61·3 (6)°	O(1′)	O(2′)	60·8 (4)°
O(2′)	O(3″)	58·2 (5)	O(1′)	O(3′)	57·5 (6)	O(1^{iv})	O(2^{v})	60·5 (5)
B(1)	B(2)	130·5 (14)	B(1′)	B(2)	128·3 (14)	B(1′)	B(2″)	133·4 (11)
O(2)	O(3″)	72·5 (4)	O(1′)	O(3″)	167·2 (23)	O(1^{iv})	O(2′)	96·9 (4)
O(2′)	O(3)	166·5 (23)	O(1)	O(3′)	73·2 (4)	O(1′)	O(2^{v})	172·7 (23)

Central atom B(1)			Central atom B(2)		
O(1)	O(2)	119·0 (14)°	O(1)	O(2′)	121·5 (12)°
O(1)	O(3)	114·7 (19)	O(1)	O(3″)	124·6 (16)
O(2)	O(3)	126·1 (16)	O(2′)	O(3″)	113·8 (16)

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* Using the *UMBADTEA* program (Finger, 1966).

bridging, so that the ribbons in B_2O_3 I are interconnected. The least-squares plane of the ribbon in B_2O_3 I is given in Table 5, from which it will be seen that the maximum deviation from planarity is 0·08 Å. If one regards this infinitely long ribbon as the fundamental structural unit, the complete structure may be considered as consisting of an assemblage of screw-related ribbons, each ribbon being linked to its neighbours by the sharing of atom O(3). While the coordination of O(1) and O(2) is planar, this is not true of O(3), as is shown in Table 5 and Fig. 5.

It is interesting to note that the incorrect structure of B_2O_3 I derived by Strong & Kaplow (1968) from a one-dimensional radial distribution function contains essentially this same ribbon. Since Strong & Kaplow have shown that their structure involved only a minor distortion from that given by Berger (1952, 1953), it becomes clear how these two false solutions (Berger; Strong & Kaplow) arose. The true structure has essentially the same radial distribution of interatomic distances as the model proposed by Strong & Kaplow, and since those authors did not have the advantage of single-crystal data they had no grounds for rejecting their model. An attempt was made to refine Strong and Kaplow's model with our intensity data, but the least-squares process did not converge (best $R > 0·5$, with several negative temperature factors).

The B–O–B angles in the ribbons in B_2O_3 I are 130·5 and 128·3° for B(1)–O(1)–B(2) and B(1′)–O(2′)–B(2) respectively, while the angle B(1″)–O(3″)–B(2) involved in the linkage between adjacent symmetry-related ribbons is 133·4°.

The closest approaches to each boron atom, apart from the oxygen atoms at the corners of their respec-

Table 5. *Various least-squares planes through the* B_2O_3 I *structure*

Plane equations are given in the form $AX+BY+CZ=D$ where the (X,Y,Z) coordinates refer to the crystal axial system, the units being Å. Δ is the distance (Å) to the plane. The coordinates (x,y,z) are the fractional atomic coordinates, referred to the crystal axes.

1. Plane of the $(BO_2)_\infty^{-\infty}$ ribbon shown bold in Fig. 4.
$0·00194X+0·63201Y-0·68247Z=1·16816$

Distance from plane of atoms forming the plane

	X	Y	Z	Δ
O(1)	0·5468	0·3972	0·0000	−0·075
O(2)	0·1485	0·6004	0·0775	0·037
O(3)	0·0045	0·1608	−0·1291	0·007
B(1)	0·2229	0·3926	−0·0198	0·022
B(2)	0·8281	0·6031	0·0921	−0·032
O(2′)	1·1485	0·6004	0·0775	0·046
O(3″)	0·8392	0·8437	0·2042	−0·011
B(1′)	1·2229	0·3926	−0·0198	0·030
O(1′)	1·5468	0·3972	0·0000	−0·067
O(3′)	1·0045	0·1608	−0·1291	0·016
B(2′)	1·8281	0·6031	0·0921	−0·024
O(2″)	2·1485	0·6004	0·0775	0·054
O(3‴)	1·8392	0·8437	0·2042	−0·003

2. Plane of B(1) and the triangle around it (see Fig. 3).
$0·05159X+0·60300Y-0·68567Z=1·16745$

Distance from plane for atoms forming the plane

	X	Y	Z	Δ
O(1)	0·5468	0·3972	0·0000	−0·007
O(2)	0·1485	0·6004	0·0775	−0·008
O(3)	0·0045	0·1608	−0·1291	−0·008
B(1)	0·2229	0·3926	−0·0198	0·022

Distance from plane of atoms not forming the plane

	X	Y	Z	Δ
B(2)	0·8281	0·6031	0·0921	0·068
O(2′)	1·1485	0·6004	0·0775	0·216
O(3″)	0·8392	0·8437	0·2042	0·058
B(1′)	1·2229	0·3926	−0·0198	0·246
O(1′)	1·5468	0·3972	0·0000	0·217
O(3′)	1·0045	0·1608	−0·1291	0·216
B(2′)	1·8281	0·6031	0·0921	0·292
O(2″)	2·1485	0·6004	0·0775	0·440
O(3‴)	1·8392	0·8437	0·2042	0·282

3. Plane of B(2) and the triangle around it (see Fig. 3).
$-0·04434X+0·64198Y-0·69700Z=0·99615$

Distance from plane of atoms forming the plane

	X	Y	Z	Δ
O(1)	0·5468	0·3972	0·0000	0·004
B(2)	0·8281	0·6031	0·0921	−0·012
O(2′)	1·1485	0·6004	0·0775	0·004
O(3″)	0·8392	0·8437	0·2042	0·004

Distance from plane of atoms not forming the plane

	X	Y	Z	Δ
O(2)	0·1485	0·6004	0·0775	0·196
O(3)	0·0045	0·1608	−0·1291	0·201
B(1)	0·2229	0·3926	−0·0198	0·169
B(1′)	1·2229	0·3926	−0·0198	−0·024
O(1′)	1·5468	0·3972	0·0000	−0·188
O(3′)	1·0045	0·1608	−0·1291	0·009
B(2′)	1·8281	0·6031	0·0921	−0·204
O(2″)	2·1485	0·6004	0·0775	−0·189
O(3‴)	1·8392	0·8437	0·2042	−0·188

4. Plane of both B(1) and B(2) and their surrounding triangles.
$0·00760X+0·62633Y-0·68594Z=1·16640$

Distance from plane of atoms forming the plane

	X	Y	Z	Δ
O(1)	0·5468	0·3972	0·0000	−0·070
O(2)	0·1485	0·6004	0·0775	0·026
O(3)	0·0045	0·1608	−0·1291	0·009
B(1)	0·2229	0·3926	−0·0198	0·020
B(2)	0·8281	0·6031	0·0921	−0·028
O(2′)	1·1485	0·6004	0·0775	0·059
O(3″)	0·8392	0·8437	0·2042	−0·016

Distance from plane to atoms not forming the plane

	X	Y	Z	Δ
B(1′)	1·2229	0·3926	−0·0198	0·053
O(1′)	1·5468	0·3972	0·0000	−0·037
O(3′)	1·0045	0·1608	−0·1291	0·042
B(2′)	1·8281	0·6031	0·0921	0·005
O(2″)	2·1485	0·6004	0·0775	0·092
O(3‴)	1·8392	0·8437	0·2042	0·017

tive triangles (1·336–1·404 Å), are by other non-related boron atoms. Thus, B(1) has three neighbouring B(2) atoms at 2·489, 2·489 and 2·498 Å. Likewise B(2) has three B(1) neighbours at these same distances. The next-nearest oxygen atom to B(1) is at 2·616 Å, while for B(2) the distance is 2·626 Å. Thus it is clear that the boron coordination is not distorted tetrahedral. Crystalline B_2O_3 I does not include the boroxol group ($B_3O_{4.5}$) as a structural element. It has been suggested from Raman spectra (Goubeau & Keller, 1953;

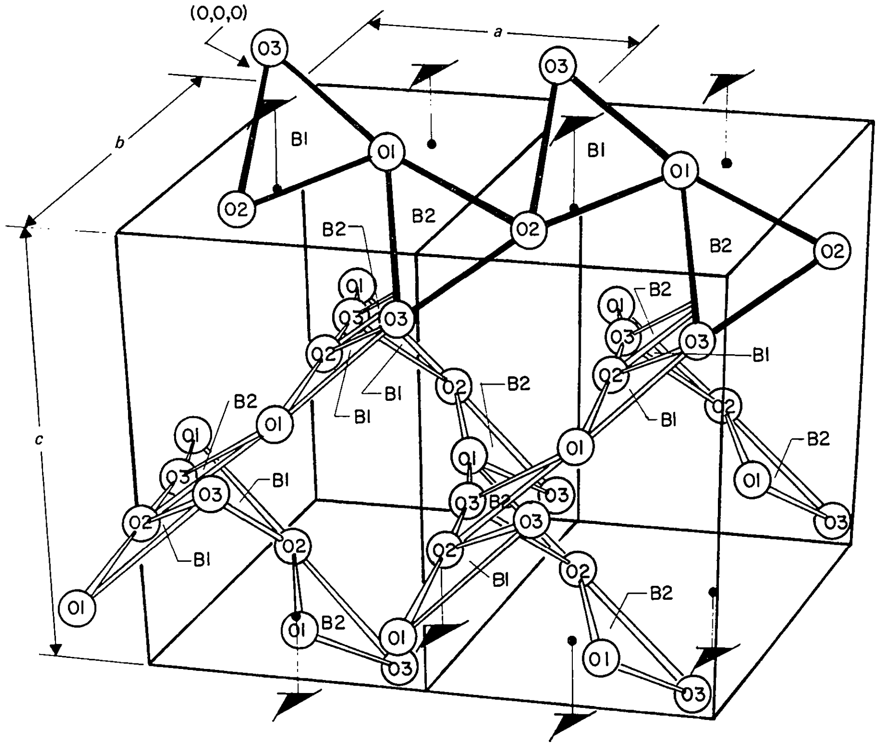

Fig. 4. Two unit-cells of the B_2O_3 I structure.

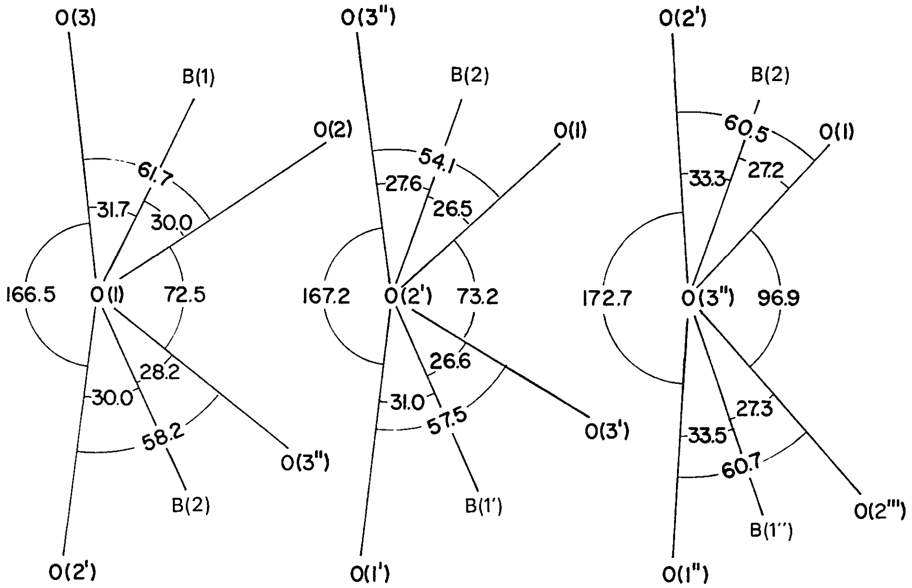

Fig. 5. Nearest-neighbour coordination of the three crystallographically distinct oxygen atoms in the B_2O_3 I structure. The sums of the bond angles for O(1), O(2) and O(3) are 358·9, 352·0 and 390·8° respectively.

Krogh-Moe, 1958) that the boroxol unit is a structural entity in B_2O_3 glass. However, Tarasov & Stroganov (1956) note that the low temperature heat capacity curve of B_2O_3 glass is consistent with a chain structure. It would be worthwhile to re-examine the glass by Raman spectroscopy, especially in the range where ring flexing modes would appear, in order to decide between boroxol rings or ribbons of the type occurring in B_2O_3 I.

The oxygen atoms in B_2O_3 I are by no means close-packed. Each oxygen atom has four near neighbours (2·30–2·43 Å) plus either one or two more remote neighbours (2·81–2·85 Å). It is atom O(3), the atom through which adjacent ribbons are linked, that has the higher coordination.

The high pressure phase, B_2O_3 II (Prewitt & Shannon, 1968), has a calculated density $D_c = 3{\cdot}11$ g.cm^{-3}, while D_c for B_2O_3 I is only 2·56 g.cm^{-3}. In the B_2O_3 II structure there are only two independent oxygen atoms. Atom O(1) has six near oxygen neighbours (2·36–2·44 Å), while O(2) has nine (2·36–2·44 Å). In view of this marked difference in coordination between B_2O_3 I and B_2O_3 II it is perhaps not so difficult to understand why no transformation between these two phases has ever been observed (*e.g.* MacKenzie & Claussen, 1961).

Possible reasons for the difficulty in crystallizing B_2O_3 I from the melt have been discussed in detail by Uhlmann, Hays & Turnbull (1967). One suggestion was that the boron–oxygen coordination polyhedron in the crystal might be different from that in the liquid. This is now seen not to be true. If it is indeed true that B_2O_3 glass contains boroxol rings perhaps the 'crystallization anomaly' stems from the necessity of opening these rings to form the ribbons of B_2O_3 I. It is hoped that knowledge of the B_2O_3 I structure will encourage further attempts to elucidate the reasons for the lack of crystallization from the melt at ambient pressure.

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The Crystal Structure of Anilite

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Anilite, Cu_7S_4, is a new mineral first described from the Ani Mine, Akita, Japan. It is orthorhombic with space group *Pnma*, with $a=7\cdot89$, $b=7\cdot84$, $c=11\cdot01$ Å, $Z=4$, $D_x=5\cdot68$ g.cm^{-3}. Three-dimensional data (Cu $K\alpha$ radiation) were collected from integrating Weissenberg photographs taken from a synthetic crystal. The structure was determined by the Patterson method and refined by full-matrix least squares. The residual was $R=0\cdot144$ for the 450 reflexions observed. The sulphur atoms approximate a cubic face-centred arrangement and the copper atoms are ordered in the interstices. The ordered distribution of the copper atoms results in slight displacements of the sulphur atoms from the positions of cubic closest packing. The structure contains five kinds of copper atom, occurring in tetrahedral and triangular coordinations. In one case the copper atom is displaced toward an edge of the tetrahedron. Two kinds of layer parallel to (011) alternate with each other: in one layer the chains of edge-sharing octahedra of sulphur atoms, three of whose faces are occupied by copper atoms, extend parallel to the *a* axis; in the other, pairs of edge-sharing tetrahedra around copper atoms are linked into chains, which extend parallel to the *a* axis. The layers are linked by isolated octahedra, two faces of which are occupied by copper atoms.

Introduction

There are a number of compounds with apparently nonstoichiometric composition among sulphide minerals. Examples of such minerals in the Cu–S system are djurleite, $Cu_{1\cdot97}S$ (Djurle, 1958; Morimoto, 1962; Roseboom, 1962, 1966; Takeda, Donnay, Roseboom & Appleman, 1967) and anilite, $Cu_{1\cdot75}S$ or Cu_7S_4 (Morimoto, Koto & Shimazaki, 1969). Digenite, $(Cu, Fe)_{1\cdot8-x}S$, is also considered to be an example of this type, the composition being very close to the Cu–S system.

The crystal structures of the high-temperature forms of digenite and chalcocite have been studied (Morimoto & Kullerud, 1963; Wuensch & Buerger, 1963; Sadanaga, Ohmasa & Morimoto, 1965). In these structures the sulphur atoms are in cubic or hexagonal closest packing and the copper atoms statistically occupy the interstices.

Many crystallographic studies on the minerals mentioned above indicate that their structures are super-structures of the high-temperature forms of digenite or chalcocite (Buerger & Buerger, 1944; Morimoto & Kullerud, 1963). On the basis of the change in cell dimensions and lowering of symmetry relative to the high-temperature forms, the super-structures of these minerals are considered to result from ordered arrangements of copper atoms and slight displacements of sulphur atoms from the positions of closest packing.

In order to elucidate the relationships between apparent nonstoichiometry and crystal structure, especially in super-structures of sulphides, it was necessary to obtain accurate crystal structures of these minerals. Among these minerals, the structure of low chalcocite was recently reported (Evans, 1968). In this investigation the crystal structure of anilite has been determined. The results help towards an understanding of the transition or decomposition mechanisms of copper sulphides in general.

Experimental

Material

Natural crystals from the Ani Mine, Akita, Japan and synthetic crystals of composition $Cu_{1\cdot75}S$, give the