The Structure of Beryl, $Be_3Al_2Si_6O_{18}$.

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1. The structure of beryl, described in this paper, has some interesting features. In the first place, the ratio of silicon to oxygen atoms in the molecule is that of a metasilicate. As far as we know, no other example of a metasilicate has as yet been completely analysed (Wyckoff* has made some measurements on diopside $MgCa(SiO_3)_2$, but has only succeeded in determining its space group). Although the ratio of silicon to oxygen is as one to three, we find no SiO_3 groups in beryl. We find instead an arrangement of oxygen atoms around a silicon atom of exactly the same conformation as the groups $(SiO_4)^{==}$ in typical orthosilicates such as olivine† and garnet.‡ In this metasilicate the ratio of one silicon to three oxygen atoms is effected by a sharing of two oxygen atoms of each tetrahedral SiO_4 group with neighbouring groups. Thus the structure forms an intermediate stage between the orthosilicates and the structures of quartz§ and christobalite|| where every oxygen atom is shared by silicon atoms. This interesting feature may throw some light on the structure of other metasilicates. In the second place, we have analysed the structure by making careful quantitative measurements of the absolute intensity of X-ray reflexion, and interpreting these measurements by the formulæ which have proved to hold for simpler cases. The structure is one of moderate complexity, depending on seven parameters. We hope to show that all these parameters can be directly and accurately fixed. The analysis is greatly simplified when quantitative data are available, and there appears to be no reason why structures with many more parameters should not be attacked in the same direct manner.

2. Beryl belongs to the holosymmetric class of the hexagonal system. Groth ('Chemische Krystallographie') quotes the axial ratio—

$$a : c = 1 : 0 \cdot 4989,$$

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* Wyckoff, 'Am. Journ. Sci.,' vol. 9, p. 379 (1925).

† W. L. Bragg and Brown, 'Zeitschr. für Kristallogr.' (1926).

‡ Menzer, 'Zeitschr. für Kristallogr.,' vol. 63, p. 157 (1926).

§ W. H. Bragg and Gibbs, 'Roy. Soc. Proc.,' A, vol. 109, p. 405 (1925).

|| Wyckoff, 'Am. Jour. Sci.,' vol. 9, p. 448 (1925).

and gives the density as being between $2 \cdot 6$ and $2 \cdot 7$. We have found the following values for the axes, measured by the X-ray spectrometer—

$$c = 9 \cdot 17 \pm 0 \cdot 01 \text{ Å.}$$

$$a = 9 \cdot 21 \pm 0 \cdot 01 \text{ Å.}$$

These lead to an axial ratio—

$$a : c = 1 : 0 \cdot 9956,$$

the c axis being twice as long as is ordinarily assumed. Since these are the true axes of the space group, they will be used below. The plane usually termed $(10\bar{1}1)$, for instance, will here be given its true indices $(10\bar{1}2)$.

Calculation shows that the unit cell of the hexagonal space lattice contains two molecules of $Be_3Al_2Si_6O_{18}$. The X-ray measurements lead to a value $2 \cdot 661$ for the density.

Four space-groups may correspond to a structure of the dihexagonal bipyramidal class. They are distinguished as follows :—

D^1_{6h} No abnormal spacings.

D^2_{6h} $(m \, o \, \bar{m} \, l)$ and $(m \, m \, \overline{2m} \, l)$ halved if l is odd.

D^3_{6h} $(m \, o \, \bar{m} \, l)$ halved if l is odd.

D^4_{6h} $(m \, m \, \overline{2m} \, l)$ halved if l is odd.

A survey of the observed reflexions shows that the beryl structure is based on the space group D^2_{6h}.* The following reflexions were investigated :—

Type $\{000l\}$ Present. Even orders up to 000.20.
Absent. Odd orders up to 000.19.

Type $\{m \, o \, \bar{m} \, o\}$ All orders up to eighth present.

Type $\{m \, m \, \overline{2m} \, o\}$ All orders up to eighth present, with exception of seventh order.

Type $\{m \, o \, \bar{m} \, l\}$ Present $(10\bar{1}2) \ldots (40\bar{4}8)$, $(10\bar{1}4) \ldots (30\bar{3}12)$, $(10\bar{1}6)$, $(20\bar{2}.12)$, $(10\bar{1}8)$, $(20\bar{2}2)$, $(40\bar{4}4)$, $(60\bar{6}6)$.
Absent. $(10\bar{1}1)$, $(30\bar{3}3)$, $(50\bar{5}5)$, $(70\bar{7}7)$, $(10\bar{1}3)$, $(10\bar{1}5)$.

* *Cp.* Niggli, ' Geometrische Krystallographie des Discontinuums,' p. 350 (1919). We have referred below to the adaption of space-group theory to X-ray analysis by Astbury and Yardley, rather than to the pioneer work of Niggli in this field, or to that of Wyckoff, because the later treatment gives the results in so convenient and compact a form.

Type $\{m\,m\,\overline{2m}\,l\}$ Present $(11\overline{2}2)\ldots(66\overline{1}26)$, $(22\overline{4}2)$, $(11\overline{2}4)$, $(22\overline{4}8)$
$(11\overline{2}6)$, $(22\overline{4}12)$, $(11\overline{2}8)$.

Absent. $(11\overline{2}1),(11\overline{2}3),(11\overline{2}5),(11\overline{2}7),(22\overline{4}1),(33\overline{6}1)$,
$(33\overline{6}3)$, $(55\overline{10}5)$, $(66\overline{12}3)$, $(77\overline{14}7)$, $(99\overline{18}3)$.

General type.   Present $(12\overline{3}1)\ldots(48\overline{12}4)$, $(31\overline{4}1)$, $(3\overline{1}\overline{2}1)\ldots(12\overline{4}84)$,
$(5\overline{2}\overline{3}3)$, $(4\overline{1}\overline{3}1)$, $(12\overline{3}93)$.

It is only in the planes of the general type that the true length of the "c"
axis is apparent. Since planes $(m\,o\,\overline{m}\,l)$ and $(m\,m\,\overline{2m}\,l)$ are halved if l is odd,
the space group must be D^2_{6h}.

3. The symmetry elements of D^2_{6h} are shown in fig. 1, which is a copy of the
corresponding figure due to Astbury and Yardley.[*] The conventions adopted
to indicate the symmetry are described in their paper. A group of formula
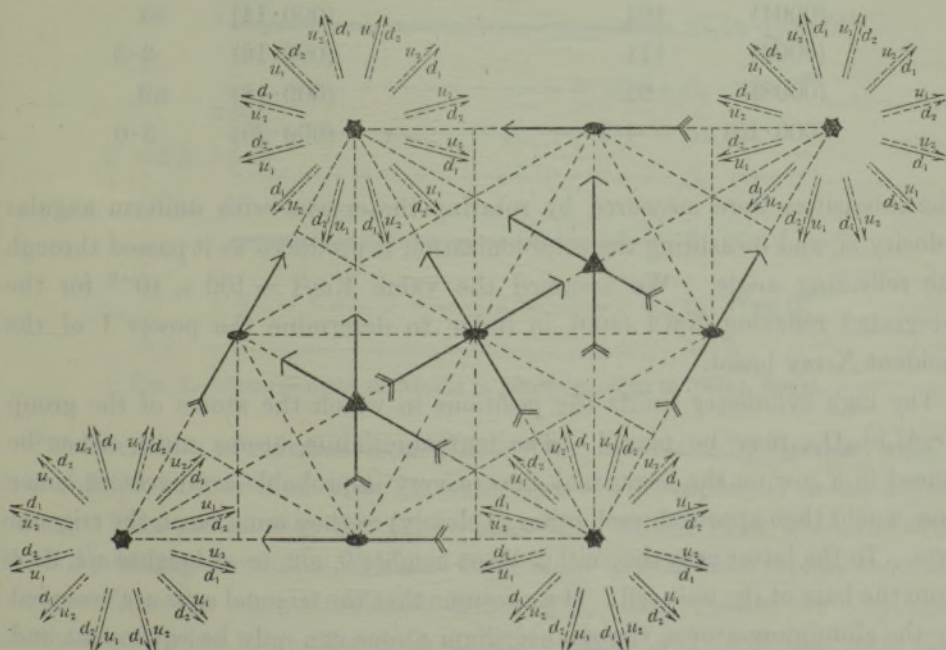$Be_6Al_4Si_{12}O_{36}$, lies in each unit cell.

Fig. 1.—Symmetry Elements of Beryl (c axis parallel to plane of paper).

It will be seen from the figure that there are sixfold, threefold and twofold
axes parallel to the c axis. Reflexion planes of symmetry perpendicular to
the c axis exist at heights $c/4$, $3c/4$ from the base of the unit cell. The planes

* Astbury and Yardley, 'Phil. Trans. Roy. Soc.,' A, vol. 224, p. 221 (1924).

at heights 0, $c/2$, c are occupied by a network of twofold axes, those at a height c being shown in the figure as thick arrows. There are a number of glide planes shown as dotted lines, parallel to the hexagonal axis.

An atom in the general position is multiplied by the operations of symmetry into 24 within the unit cell. Since the group within the cell is $Be_6Al_4Si_{12}O_{36}$, the only atoms in the general position can be a group of 24 oxygen atoms. As we shall see, all other atoms lie in positions at heights 0, $c/4$, $c/2$, $3c/4$ in the unit cell. This indicates a very simple structure for the planes (000l), and we will analyse these in the first place.

The intensities of reflexion were in all cases compared with the reflexion NaCl (400) as standard, RhK_α rays being used. The absolute values for the integrated reflexion ρ for the planes (000l) are given below :

Table I.—$\rho \times 10^6$, (000l) planes.

(0002)	160	(000·12)	19
(0004)	104	(000·14)	10
(0006)	111	(000·16)	3·5
(0008)	92	(000·18)	nil.
(000·10)	4·0	(000·20)	3·0

The intensities were measured by rotating the crystal with uniform angular velocity ω, and measuring the total ionization E produced as it passed through the reflecting angle. We assumed the value $E\omega/I = 100 \times 10^{-6}$ for the integrated reflexion NaCl (400), in order to determine the power I of the incident X-ray beam.

The high symmetry limits the positions in which the atoms of the group $Be_6Al_4Si_{12}O_{36}$ may be placed. The four aluminium atoms must either be placed in a row on the hexagonal axes (a very improbable arrangement, since they would then approach each other so closely) or they must be on the trigonal axes. In the latter case they either lie at heights 0, $c/2$, or at heights $c/4$, $3c/4$ from the base of the unit cell. If we assume that the trigonal axes are occupied by the aluminium atoms, the six beryllium atoms can only be equivalent and lie on the twofold axes parallel to c. Like the aluminium atoms, they lie either at heights 0, $c/2$, or at heights $c/4$, $3c/4$. In the case of the twelve silicon atoms we may again assume it highly improbable that they should be arranged in rows on the vertical axes. Alternatively, they may lie in two rings of six atoms around the hexagonal axes, being in this case all equivalent to each other. These rings lie at heights 0, $c/2$, or $c/4$, $3c/4$ in the unit cell. In the former

case each silicon lies on a twofold axis perpendicular to the c axis, in the latter case on a reflexion plane parallel to (0001). Twelve of the oxygen atoms are governed by exactly the same conditions as the twelve silicon atoms. The remaining twenty-four atoms lie in the general position, and hence have a parameter parallel to the c axis.

From the foregoing it will perhaps be clear that in explaining the strength of the (000l) spectra we have a limited number of alternatives to test, and that in each case there is only a single parameter (governing the c displacement of twenty-four oxygen atoms) which can be adjusted to give a correspondence between calculated and observed intensities. It is therefore a simple matter to choose between these alternatives. The only arrangement which corresponds with the spectra is shown in fig. 2.
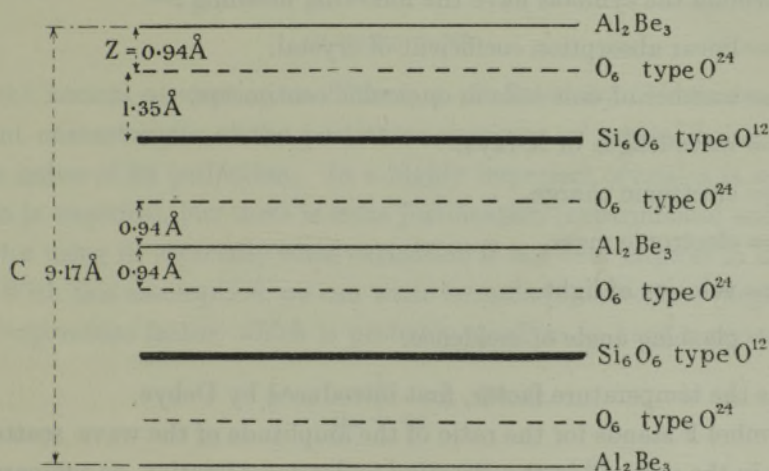

FIG. 2.—Arrangement of Atoms in planes parallel to (000l), Beryl.

The intensities of reflexion from planes (000l) are decidedly stronger when l is a multiple of four than when l is a multiple of two, especially in the higher orders. This proves that the planes containing silicon must alternate with those containing aluminium, since the effect of the oxygen atom rapidly becomes very small as the angle of reflexion is increased. The effect of the beryllium atoms is small, but it is sufficient to make it possible to say that they lie in the planes containing aluminium atoms when the final quantitative examination of intensities is carried out as described in the next paragraph. One-third of the oxygen atoms lie in the same planes as the silicon atoms. The remainder lie in the general position. Their displacement parallel to the c axis is fixed by the distance z indicated in fig. 2. The general features of the intensities show immediately that z has a value of about $0\cdot94$ Å. This position is required,

for instance, to explain the strength of (0006) and the weakness of (000.10). The type of analysis which leads to this result is so well known that it is perhaps unnecessary to go into it further here.

The question as to whether the groups Si_6O_6, or Al_2Be_3, lie on the reflexion planes perpendicular to the c axis may be left open for the present, since it does not affect the discussion of intensities in the next paragraph. Other considerations show that the groups Si_6O_6 lie on these planes.

4. The formula for the absolute intensity ρ of integrated reflexion by the face of an imperfect crystal is as follows :—* † ‡

$$\rho = \frac{E\omega}{I} = \frac{1}{2\mu} n^2 \lambda^3 F^2 \frac{e^4}{m^2 c^4} \frac{1}{\sin 2\theta} \frac{1 + \cos^2 2\theta}{2} e^{-B \sin^2 \theta}. \tag{1}$$

In this formula the symbols have the following meaning :—

μ = linear absorption coefficient of crystal.

n = number of unit cells in one cubic centimetre.

λ = wave-length of X-rays.

e = electronic charge.

m = electronic mass.

c = velocity of light.

θ = glancing angle of incidence.

$e^{-B \sin^2 \theta}$ is the temperature factor, first introduced by Debye.

The symbol F stands for the ratio of the amplitude of the wave scattered by all atoms in the unit cell in the direction under consideration, as compared with the wave scattered by a single electron in similar circumstances. The value of F varies with the direction of the incident and scattered X-ray beam. The contribution of each atom to the scattered wave will depend on the arrangement of the electrons in the atom, and the combination of these contributions into a single scattered wave will depend on the relative positions of the atoms in the unit cell.

In the present analysis we will use the observed intensities of X-ray reflexion to determine F for a number of crystal planes. From these values of F the atomic positions will be directly deduced.

F can be calculated from formula (1) by using the observed values of ρ and

* Darwin, ' Phil. Mag.,' vol. 27, pp. 315 and 675 (1914), vol. 43, p. 800 (1922).

† Compton, A. H., ' Phys. Rev.,' vol. 9, p. 29 (1917).

‡ Bragg, James and Bosanquet, ' Phil. Mag.,' vol. 41, p. 309 (1921), vol. 42, p. 1 (1921), vol. 44 (Sept., 1922). James and Randall, vol. 1, p. 1020 (1926).

substituting known values for the other factors which appear. The only quantity which needs especial consideration is the absorption coefficient μ. When a crystal has more than a certain degree of perfection, the effective absorption coefficient is increased by " primary " and " secondary " extinction, very fully discussed by Darwin in his 1922 paper cited above. In the case of certain (000l) reflexions from beryl, the structure is sufficiently well known to a first approximation for it to be possible to calculate values of F which cannot be far from the truth. Using these in formula (1), a comparison with the observed values of ρ show that extinction is appreciable, being of the same order as the normal absorption coefficient in the case of the strongest reflexions.

Our procedure has been as follows. We have assumed that we can represent the effective absorption coefficient μ by the formula

$$\mu = \mu_0 + \alpha\rho \qquad (2)$$

μ_0 is the normal absorption coefficient, ρ the intensity of reflexion, and α a constant characteristic of the particular specimen of crystal being examined and an index of its perfection. In a highly imperfect crystal α is zero. This formula is empirical, but there is some justification (experimental and theoretical*†) for using it, especially when extinction is not very large as in the present case. With this assumption, we can write formula (1) as follows (neglecting the final temperature factor, which is probably small in so hard a crystal) :—

$$\rho = \frac{1}{\mu_0 + \alpha\rho} A . F^2 . \Theta. \qquad (3)$$

Here

$$A = \tfrac{1}{4} \frac{n^2 \lambda^3 e^4}{m^2 c^4} = 1 \cdot 01 \times 10^{-8} \text{ for beryl}$$

$$\Theta = \frac{1 + \cos^2 2\theta}{\sin 2\theta}.$$

The value of μ_0 for beryl, based on Windgärdh's‡ tables, is 5·64.

We now consider the planes (000l) which have a very simple structure. The scattering curves for beryllium, aluminium, silicon and oxygen are taken from the tables prepared by Hartree, these being slightly modified by the results of quantitative measurements made on certain simple crystals. The values of the scattering power of the atoms, as compared with that of a single electron, are given for a series of angles at the end of the paragraph. In comparing

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* Darwin, *loc. cit.*
† Bragg, James and Bosanquet : James and Randall, *loc. cit.*
‡ Windgärdh, ' Zeitschr. f. Phys.,' vol. 8, p. 363 (1922).

calculated and observed values of ρ in order to get the best agreement, there are two variables which can be adjusted'; these are the distance z, determining the position of the 24 oxygen atoms (paragraph 3), and the coefficient α, which determines extinction. It has already been seen that z has a value of about $0 \cdot 94$ Å. This value will be assumed for a first approximation, and formula (3) checked, using a series of values of α in order to discover the one which gives the best agreement. It is perhaps simplest to show this agreement by calcu-lating A from the observed intensities, using formula (3) and comparing it with what is known to be the right value, $1 \cdot 01 \times 10^{-8}$.

Table II.

Indices.	$\rho \times 10^4$	$F^2\Theta \times 10^{-4}$.	$A = \left(\dfrac{\rho (5 \cdot 64 + \alpha\rho)}{F^2\Theta} \right) \times 10^8$			
			$\alpha = 0$	$\alpha = 6 \times 10^4$	$\alpha = 7 \times 10^4$	$\alpha = 8 \times 10^4$
(0002)	1·60	27·5	0·33	0·88	0·98	1·07
(0004)	1·04	13·4	0·43	0·92	1·00	1·09
(0006)	1·11	14·1	0·44	0·97	1·04	1·14
(0008)	0·92	11·6	0·45	0·88	0·98	1·03

It is clear that the assumption of no extinction leads to obviously incorrect values. The value 7×10^4 for the coefficient α gives both the best correspond-ence between values of A calculated from different spectra, and the best agree-ment with the true value $1 \cdot 01 \times 10^{-8}$. This value for α will therefore be chosen. A knowledge of α makes it possible to correct for extinction, and to substitute for the observed reflexion ρ the idea reflexion ρ' which would be observed with an ideally imperfect crystal. All our observations have been corrected in this way, and used to determine the values of F for each reflexion.

We can now make a final adjustment by seeing whether a better estimate of the distance z can be obtained when extinction is allowed for. The value of 7×10^4 for α is assumed, and A calculated for a series of values of z.

Table III.

Indices.	Values of A for distances z of oxygen atoms from Al_2Be_3 planes in Å.							
	1·02	1·00	0·98	0·96	0·94	0·92	0·90	0·88
(0002)	0·73	0·78	0·83	0·90	0·98	1·05	1·13	1·21
(0004)	1·22	1·19	1·13	1·08	1·00	0·93	0·88	0·82
(0006)	1·38	1·28	1·18	1·12	1·04	0·99	0·96	0·92
(0008)	0·76	0·81	0·85	0·90	0·98	1·02	1·09	1·17

The value $0 \cdot 94$ already assumed is seen to be the best, and z appears to lie definitely between $0 \cdot 92$ Å and $0 \cdot 96$ Å. The oxygen atom is therefore at a distance of $1 \cdot 35$ Å from the planes Si_6O_6, as shown in fig. 2.

The following table gives the values of F for the atoms Be, Al, Si, O, which have been used in the calculations :—

Table IV.—Values of F.

Sin θ.	0·0	0·1	0·2	0·3	0·4	0·5	0·6
Beryllium	2	1·95	1·65	1·60	1·35	1·05	0·75
Aluminium	10	9·55	8·30	6·65	4·90	3·45	2·25
Silicon	13	11·7	9·4	7·4	5·6	4·2	2·8
Oxygen	9	6·9	3·6	1·6	0·5	0·2	0·1

It is difficult to decide what initial values of F to adopt. We have chosen the values 13 and 9 for silicon and oxygen, in an attempt to allow for the distortion of the oxygen atoms grouped around the silicon atom. If the figures 10 and 10 had been chosen, a test shows that the position assigned to the atom would be almost exactly the same. The former figures, however, do undoubtedly give a more consistent agreement with observed intensities. The form of the F curves beyond sin $\theta = 0 \cdot 2$ is taken from Hartree's tables, and the curves continued on to the maxima 13 and 9 for silicon and oxygen respectively.

5. The symmetry elements of the unit cell are shown in fig. 1. The atoms have to be arranged in accordance with these symmetry elements and in a way which explains the observed intensities of spectra. Certain general considerations lead at once to an approximate solution of the structure.

The distance between neighbouring oxygen atoms may be expected to be about $2 \cdot 7$ Å. W. L. Bragg and G. Brown[*] have pointed out that this is the case in BeO, Al_2O_3, $BeAl_2O_4$, Mg_2AlO_4, and Mg_2SiO_4. In the structure of garnet, $Ca_3Al_2Si_3O_{12}$, recently analysed by Menzer,[†] the distance between neighbouring oxygen atoms varies from $2 \cdot 65$ to $2 \cdot 85$ Å. James has shown that this interatomic distance exists in $BaSO_4$,[‡] and Wasastjerna in $CaSO_4$.[§] Fig. 2 shows that the twenty-four oxygen atoms in the general positions are arranged on sheets parallel to (0001), which are at a distance of $0 \cdot 94$ Å on either side of the planes marked Al_2Be_3, and at a distance of $1 \cdot 35$ Å on either side of the planes marked Si_6O_6. If the distance between oxygen atoms is to be about $2 \cdot 7$ Å in

[*] W. L. Bragg and Brown, ' Roy. Soc. Proc.,' A, vol. 110, p. 34 (1926).
[†] *Loc. cit.*, paragraph 1.
[‡] James and Wood, ' Roy. Soc. Proc.,' A, vol. 109, p. 598 (1925).
[§] Wasastjerna, ' Soc. Scient. Fenn., Comm. Phys.-Math.,' vol. 2, p. 26 (1926).

beryl, it is at once clear that these latter planes are the reflexion planes of the structure, each oxygen atom being at a distance of $2 \cdot 7$ Å from its mirror image. If this were not the case and the planes marked Al_2Be_3 were the reflexion planes,
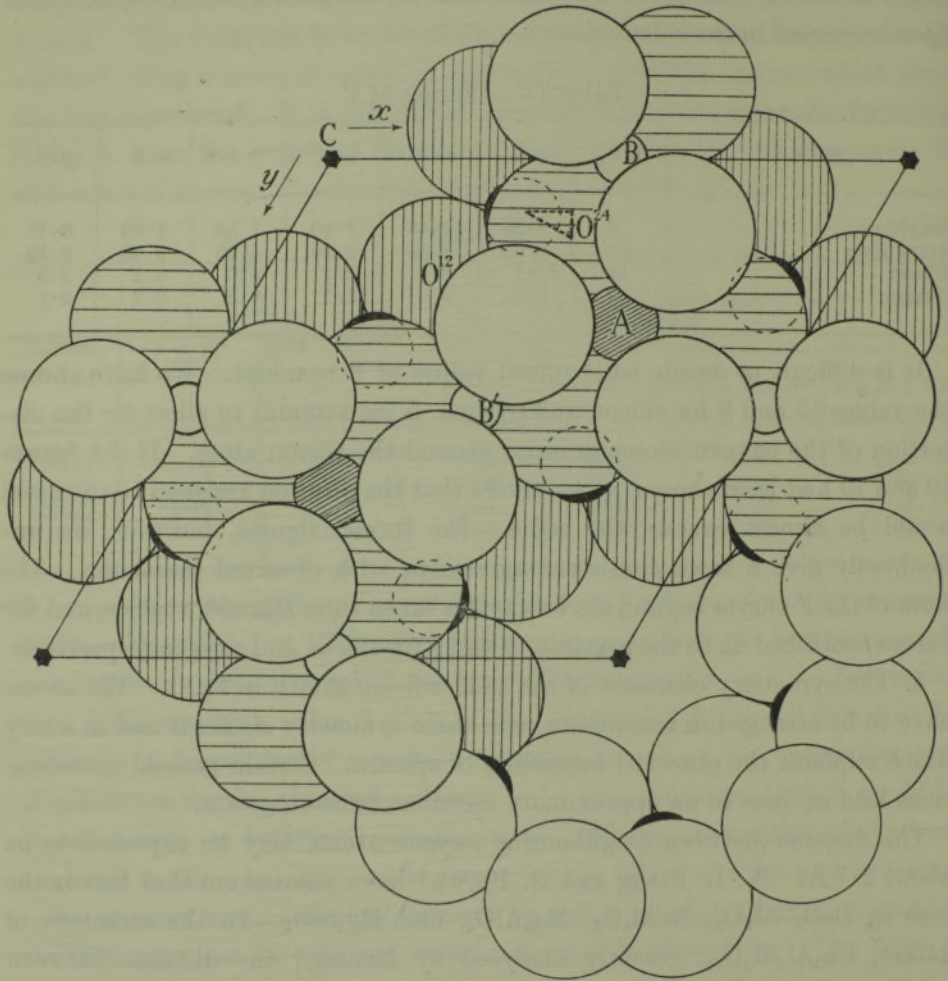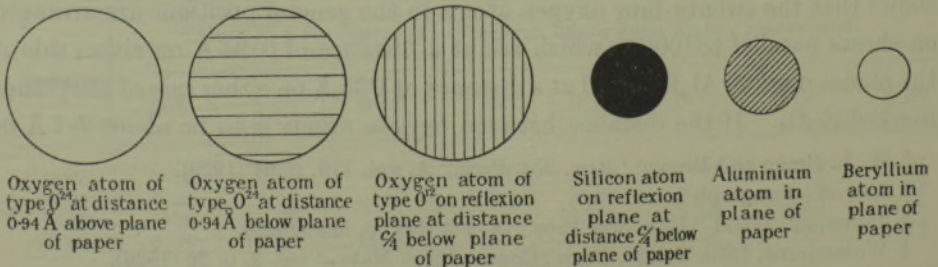
FIG. 3.—Diagram of Beryl Structure, viewed parallel to c axis, showing positions of half the atoms in the unit cell.

Oxygen atom of type O^{24} at distance $0 \cdot 94$ Å above plane of paper	Oxygen atom of type O^{24} at distance $0 \cdot 94$ Å below plane of paper	Oxygen atom of type O^{12} on reflexion plane at distance $\frac{c}{4}$ below plane of paper	Silicon atom on reflexion plane at distance $\frac{c}{4}$ below plane of paper	Aluminium atom in plane of paper	Beryllium atom in plane of paper

KEY TO FIG. 3.

the distance between oxygen atoms would be $1 \cdot 9$ Å, which is too small to be probable.

In fig. 3, the lines indicate the upper sides of the unit cell. The aluminium and beryllium atoms lie in this upper plane, and the reflexion plane is at a distance $c/4$ ($2 \cdot 29$ Å) below. One of the twenty-four oxygen atoms which are in the general position will lie within the confines of the triangle ABC, and at a distance $0 \cdot 94$ Å beneath the plane of the diagram (the alternative position in the triangle AB′C is not distinct, since it is only necessary to translate the origin of co-ordinates a distance $c/2$ to arrive at it). This atom is lightly shaded, and is marked O^{24} in the figure. Three twofold axes at right angles to each other intersect in the Be atom at B, and these axes convert the oxygen atom at O^{24} into a tetrahedral group around B.

Assuming that no oxygen atom approaches much closer than $2 \cdot 7$ Å to any other oxygen atom, the possible positions for the atom O^{24} are very limited. It must not be closer than about $1 \cdot 35$ Å to any twofold axis, or to the reflexion plane (we have already shown that it is actually at a distance of $1 \cdot 35$ Å from the reflexion plane). It must not lie closer than $\dfrac{2}{\sqrt{3}} \times 1 \cdot 35$ Å to a trigonal axis, or $2 \times 1 \cdot 35$ Å to a hexagonal axis, or it will be too close to the other atoms around these axes. If we assume as an extreme case that the atoms may approach within $2 \cdot 5$ Å of each other, trial shows that the atom is confined to the small triangular area around O^{24} outlined in the figure. If one atom is placed anywhere in this region, the others into which it is turned by the symmetry elements will have the positions indicated in the figure by the unshaded and lightly-shaded circles. The unshaded circles are at a height $0 \cdot 94$ Å above the plane, the lightly-shaded circles at a depth $0 \cdot 94$ Å below it. Each beryllium atom lies at the centre of four oxygen atoms arranged tetrahedrally, every aluminium atom at the centre of six oxygen atoms arranged at the corners of an octahedron.

The aluminium, beryllium, and twenty-four of the oxygen atoms are thus accounted for. It remains to place the twelve silicon atoms and twelve oxygen atoms of the second sort on the reflexion planes at a depth $c/4 = 2 \cdot 29$ Å below the plane of the diagram. The oxygen atoms will lie in groups of six around the hexagonal axes, and there is just room for such a group, indicated by the heavily-shaded circles. The typical atom of this group is marked O^{12} in the figure. Each pair of heavily-shaded atoms lying in the reflexion planes forms a tetrahedral group with a pair of lightly-shaded atoms which are images of each other in the plane. This suggests that the silicon atoms may be at the

centre of these tetrahedra, and this supposition will be tested. The silicon atoms would be invisible in the structure as represented here, but for the sake of clearness their positions are indicated by the portions of black circles, continued as dotted lines. The diagram in fig. 3 shows the positions of those atoms which are grouped on either side of the reflexion plane at a depth of $c/4$. A similar group, obtained from the first by rotation about an axis at a depth of $c/2$, is placed on either side of the reflexion plane at a depth $3c/4$, but is not shown in the figure.

The positions finally assigned to the atoms depend in no way on assumptions as to interatomic distance. This preliminary investigation merely indicates probable values for the parameters and so shortens the analysis.

6. *Determination of Parameters.*—The structure has seven parameters, of which one has been already determined. The parameters fix the positions of the silicon atoms (two parameters), the twenty-four oxygen atoms of the first type (three parameters), and the twelve oxygen atoms of the second type (two parameters).

Since the only parameter parallel to the c axis is known, the rest can be got by considering the projection of the structure on $(000l)$ and examining the planes around the c zone. The silicon and oxygen atoms lie in rings of six around the hexagonal axes. We have found it convenient to consider the ring as a diffracting unit when dealing with planes around the c zone. The resultant scattered wave of six atoms in a ring will have the same phase as that of a wave scattered from a point at the centre. The ratios of the contribution of the six atoms to that of a single atom at the centre depends on—

(a) The ratio nr/d where "r" is the distance from the centre to each atom "d" the spacing of the reflecting planes, "n" the order of the spectrum.

(b) The angle β made by the line, joining the centre of the ring to one of the atoms, with the reflecting planes. The angle β need only be considered to vary between $0°$ and $30°$ owing to the repeat of the atoms around the hexagonal ring.

We have plotted curves showing the value of the ratio for values of nr/d up to $7 \cdot 0$, and for several values of β. Some of the curves are shown in fig. 4. The ratio is given by the expression

$$S = 2 \left\{ \cos\left(\frac{2\pi nr}{d}\sin\beta\right) + 2\cos\left(\frac{\sqrt{3}\pi nr}{d}\cos\beta\right)\cos\left(\frac{\pi nr}{d}\sin\beta\right) \right\}. \qquad (4)$$

These curves can be used for any case where the projection of a structure on a plane has hexagonal symmetry, such as the planes around certain zones of the
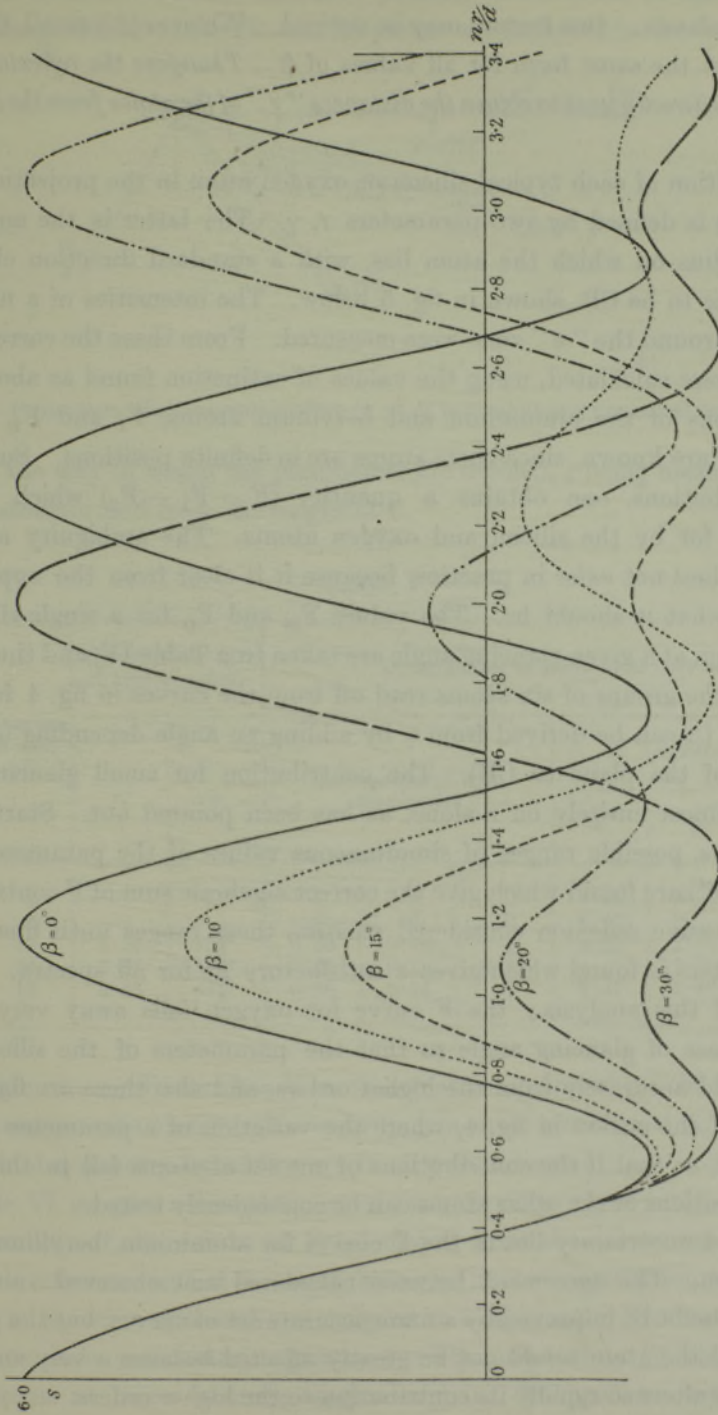
Fig. 4.

cubic or trigonal classes when these have a centre of symmetry, as well as for hexagonal classes. One feature may be noticed. When nr/d is small, the curves have almost the same form for all values of β. *Therefore the reflexions of low order can be directly used to obtain the distances " r " of the atoms from the hexagonal axes.*

The position of each typical silicon or oxygen atom in the projection on the " c " plane is defined by two parameters r, γ. The latter is the angle made by the radius on which the atom lies, with a standard direction chosen for convenience to be CB, shown in fig. 5 below. The intensities of a number of reflexions around the " c " zone were measured. From these the corresponding F values were calculated, using the values of extinction found as above. The contributions of the aluminium and beryllium atoms, F_1 and F_2, to these values of F are known, since these atoms are in definite positions. Subtracting the contributions, one obtains a quantity $(F - F_1 - F_2)$ which must be accounted for by the silicon and oxygen atoms. The ambiguity about the sign of F does not exist in practice, because it is clear from the approximate structure what it should be. The values F_{Si} and F_O for a single silicon and oxygen atom at a given glancing angle are taken fron Table IV, and the required factor for the groups of six atoms read off from the curves in fig. 4 for values of r and γ (β can be derived from γ by adding an angle depending on the inclination of the plane to CB). The contribution for small glancing angles depends almost entirely on r alone, as has been pointed out. Starting with these orders, possible ranges of simultaneous values of the parameters r (Si), r (O^{12}), r (O^{24}), are found which give the correct algebraic sum of F contributions. Each successive reflexion considered narrows these ranges until finally a set of parameters is found which gives a satisfactory fit for all spectra. Various factors aid this analysis; the F curve for oxygen falls away very quickly with increase of glancing angle so that the parameters of the silicon atom can be fixed accurately from the higher orders, and also there are flat regions on some of the curves in fig. 4, where the variation of a parameter produces little effect, so that if the contributions of one set of atoms fall in this region various positions of the other atoms can be conveniently tested.

The chief uncertainty lies in the F curves for aluminium, beryllium, silicon and oxygen. The agreement between calculated and observed values of F would no doubt be improved by a more accurate set of curves, but the positions assigned to the atom would not be greatly affected because a very small shift of an atom alters so rapidly its contribution to the higher orders.

The values of the parameters finally chosen are given below, both in the

(r, γ) form and as distances measured parallel to the sides of the unit cell. The definite positions of the Be and Al atoms are included in the list. Fig. 5
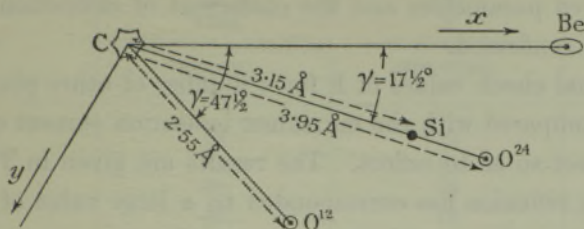
FIG. 5.—Projection, showing parameters (r, γ) of typical atoms projected on (0001).

illustrates the way in which the parameters are defined, z being measured away from the observer and from the origin at C.

Table V.

Atom.	Number in unit cell.	Co-ordinates rγ, of typical atom.		Co-ordinates of position in unit cell.					
				As fraction of unit translation.			In Ångström units.		
		r.	γ.				x.	y.	z.
Al	4	—	—	$\frac{2}{3}$	$\frac{1}{3}$	0	6·14	3·07	0
Be	6	—	—	$\frac{1}{2}$	0	0	4·605	0	0
Si	12	3·15	17¼°	0·39	0·12	$\frac{1}{4}$	3·55	1·09	2·29
O²⁴	24	3·95	17¼°	0·48	0·15	0·10	4·45	1·37	0·94
O¹²	12	2·55	47½°	0·30	0·24	$\frac{1}{4}$	2·81	2·17	2·29

The origin of co-ordinates has been chosen at the point where the horizontal twofold axes cut the *c* axis. The co-ordinates may be referred to an origin at a centre of symmetry by adding c/4 to all z co-ordinates.

In Table VI we give a complete list of the reflexions whose intensities have been measured, of the values of F calculated from these intensities by the formula for reflexion, and of the algebraic sums of the contribution to F made by atoms in the structure we have assigned to the crystal. The two columns of F values show satisfactory agreement. The uncertainty in values of F for the atoms at larger glancing angles explains discrepancies between the two columns for higher orders.

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Since numerical agreement between calculated and observed values of F for about thirty planes has been obtained by adjusting eight variables, consisting of seven parameters and the coefficient of extinction, the assigned structure is well confirmed.

As an additional check values of F for a number of other planes have been calculated and compared with the maximum ionisation current observed when the crystal was set so as to reflect. The results are given in Table VII. In all cases a strong reflexion has corresponded to a large value of F and a weak

Table VI.

I. Indices.	II. Sin θ.	III. ρ × 10⁶.	IV. Intensity $\rho' \times 10^6$ (Corrected for Extinction).	V. ± F (Calculated from IV).	VI. F (for atoms in position of Table V).
(10$\bar{1}$0)	0·0387	95	206	67	−68
(11$\bar{2}$0)	0·0663	22	28	34	−40
(0002)	0·0669	160	478	137	139
(20$\bar{2}$0)	0·0774	38	56	50	−55
(30$\bar{3}$0)	0·1159	8·1	8·9	24	24
(22$\bar{4}$0)	0·1326	1·0	1·0	12	12
(0004)	0·1340	104	238	134	134
(40$\bar{4}$0)	0·1546	25·6	33·7	55	−50
(50$\bar{5}$0)	0·1935	39·6	58·6	82	−87
(33$\bar{6}$0)	0·1999	14·5	17·5	45	−45
(0006)	0·2007	111	264	178	174
(60$\bar{6}$0)	0·2320	14·2	16·7	48	43
(44$\bar{8}$0)	0·2650	trace	—	—	−7
(0008)	0·2675	92	197	180	184
(70$\bar{7}$0)	0·2709	4·0	4·3	27	−20
(80$\bar{8}$0)	0·3094	16·9	20·4	63	60
(55.$\overline{10}$.0)	0·3313	trace	—	—	14
(000.10)	0·3343	4·0	4·3	30	35
(90$\bar{9}$0)	0·3483	nil	—	—	−4
(10.0.$\overline{10}$.0)	0·3870	nil	—	—	−6
(66.$\overline{12}$.0)	0·3995	17	20·6	76	78
(000.12)	0·4014	19	23·7	82	102
(77.$\overline{14}$.0)	0·4641	nil	—	—	−3
(000.14)	0·4679	10	11·0	60	36
(88.$\overline{16}$.0)	0·5300	nil.	—	—	−1
(00016)	0·5350	3·5	3·7	40	56
(00018)	0·6021	nil	—	—	16
(00020)	0·6686	3·0	3·2	40	34

reflexion to a small value of F. The figures in column II are very approximate estimates of intensity, and should be compared with the figures in column IV, to which they should be roughly proportional.

Table VII.

I. Indices.	II. Peak (maximum ionization current).	III. F (calculated from structure).	IV. $F^2\Theta \times 10^{-3}$.
$(31\bar{4}0)$	33	30	6·8
$(62\bar{8}0)$	nil	12	0·46
$(21\bar{3}0)$	90	65	38
$(42\bar{6}0)$	53	70	23
$(41\bar{5}0)$	190	84	40
$(82\bar{1}00)$	nil	13	0·42
$(51\bar{6}0)$	10	19	1·7
$(22\bar{4}2)$	17	12	0·92
$(44\bar{8}4)$	32	30	2·7
$(66\bar{1}\bar{2}6)$	27	23	1·0
$(44\bar{8}2)$	120	61	10
$(31\bar{2}1)$	430	75	50
$(62\bar{4}2)$	130	55	13

7. *Fourier Analysis of Electron Distribution.*—A very elegant method of analysis has recently been developed by Duane and used by Havighurst. It was first suggested by W. H. Bragg in 1915,* though it could not then be directly applied to the determination of electron distribution because measurements of absolute intensities of reflexion were not available. If a set of crystal planes be considered, the distribution of diffracting matter in sheets parallel to the planes is a periodic function of the distance z, measured perpendicularly to the planes, which is repeated at intervals " d " equal to the spacing of the planes. Such a distribution can be represented by a Fourier series in the ordinary way. W. H. Bragg showed that the amplitude of reflexion by the planes for the first order of reflexion owed its existence to the first coefficient of the Fourier series, that of the second order to the second coefficient, and so on. Conversely, if the amplitude of reflexion in a number of orders is measured experimentally, a curve representing the electron distribution in sheets parallel to the planes can be built up by adding together the terms of the Fourier series. The idea underlying the method is precisely that used in Abbé's treatment of the resolving power of a microscope. The microscope is supposed to be focussed on a grating which is transmitting homogeneous light. Spectra are formed in a plane between the objective and the eyepiece, and these spectra in their turn act as sources of light and build up an image of the grating which is viewed by the eyepiece. The information as to the structure of the grating

* W. H. Bragg, ' Phil. Trans. Roy. Soc.,' A, vol. 215, p. 253 (1915).

which the microscope gives depends on the number of spectra which the aperture of the objective allows to pass. If the first three orders are formed, for example, an image of the grating will be seen which corresponds to the sum of the first three terms in a Fourier series, which, when complete, would give the distribution of amplitude transmitted in passing from line to line of the grating. The analogy between the X-ray and optical problems is complete except in that it is possible to use the eyepiece to view the image formed in the microscope, whereas in the case of X-rays and a crystal it is only possible to measure the intensities of the spectra. The summation of the Fourier series is carried out automatically in the image plane of the microscope, but it has to be done by calculation in the second case.

Duane* has put the necessary formulæ in a very simple form. Havighurst† has used them in order to calculate the electron distribution in sodium chloride and other simple crystals, basing his results on figures given by W. L. Bragg, James and Bosanquet. To use the method, it is necessary to have measurements of the quantities we have termed " F." In order to get an accurate representation of the electron density, values of F should be known for all orders up to a point where they become very small as compared with the lower orders.

We are indebted to a private communication by Prof. A. H. Compton, of Chicago, for the precise form in which the formula is quoted here. Let the total number of electrons in the unit cell of volume V be Z. The distribution of these electrons in sheets parallel to a given set of crystal planes with spacing " d " will be examined. An area A on the planes will be chosen such that $Ad = V$, the volume of the unit cell containing Z electrons. The number of electrons in the volume $A\,dz$ is given by the expression

$$Z f(z)\, d z$$

where z is measured perpendicularly to the crystal planes and

$$\int_{-d/2}^{d/2} f(z)\, dz = 1.$$

It will in addition be supposed that the crystal has centres of symmetry. This case is much more simple to treat than that of a crystal without such centres, since it avoids the complication of difference of phase in the components of the Fourier series. It can then be shown that

$$Zf(z) = \frac{Z}{d} + \frac{2F_1}{d} \cos \frac{2\pi z}{d} + \frac{2F_2}{d} \cos \frac{4\pi z}{d} + \dots + \frac{2F_n}{d} \cos \frac{2\pi n z}{d} + \dots \quad (5)$$

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* Duane, ' Proc. Nat. Acad. Sci.,' vol. 11, 8, p. 489 (1925).

† Havighurst, ' Proc. Nat. Acad. Sci.,' vol. 11, 8, pp. 502 and 507 (1925).

where $F_1, F_2 \ldots F_n \ldots$ are the values of F calculated from the observed intensities of reflexion.

Substituting the experimental values of " F " in this formula, a curve can be obtained which shows the electron distribution parallel to any given set of crystal planes. In applying this to a crystal such as beryl, due regard must be paid to the sign of F. The experimental values of F are given in column V of Table VI and their signs may be got from the calculated values in column VI.

The curves of figs. 6 and 7 show the distribution of electron-density in sheets parallel to (0001), (10$\bar{1}$0), (11$\bar{2}$0) of beryl. The curves are values of $Zf(z)$ calculated from formula (5). Since the curves are symmetrical, it is only necessary to show one half of the complete " repeat " of the pattern in each case. The (0001) spacing is halved, and therefore the corresponding curve in fig. 6 must be repeated four times in order to get the distribution between planes a distance $9 \cdot 17$ Å apart, the length of the c axis (*cf.* fig. 2). In the other two cases one may suppose the curves reflected in the $Zf(z)$ axis so as to give the complete pattern. The area within the square gives the scale of the figure in each case.
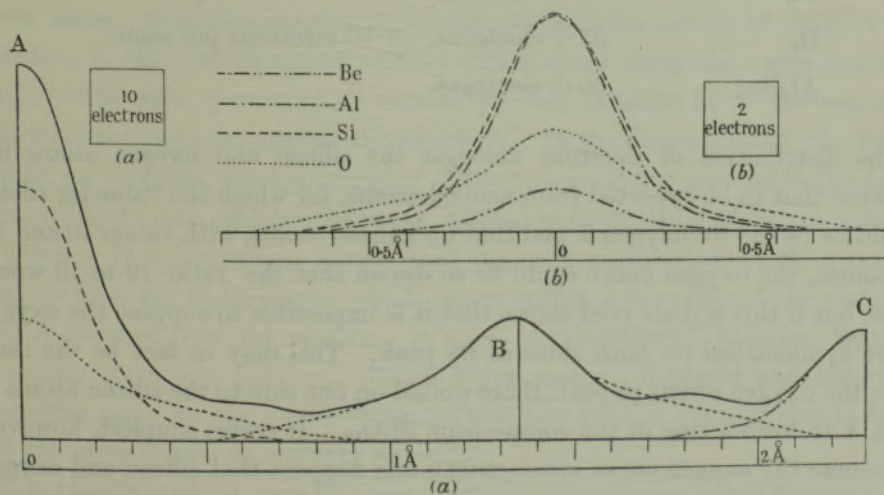

FIG. 6.

The structure of the (000l) planes is very simple, and it is possible to analyse the curve so as to obtain an idea of the distribution of electrons in the various atoms. The peak B in the middle of the curve is due to six oxygen atoms of the group $Be_6Al_4Si_{12}O_{36}$. The peak A on the left when completed by reflexion is due to six silicon atoms and six oxygen atoms. Therefore, by subtracting from it the peak B, one may obtain a curve representing the effect of the six silicon

atoms alone.   Some latitude is possible in choosing the exact form of the oxygen peak where the peaks A and B overlap, but it will be clear from the figure that there is not much choice, since the sum of the two oxygen curves cannot exceed the total height of the $Zf(z)$ ordinate at any point.   Similarly, by subtracting that part of the oxygen curve which extends towards the peak C one obtains a curve for the distribution of electrons in the group Al_2Be_3.   The complete distribution of electron density is made up of these four components, Si_6 and O_6 at A, O_6 at B, Al_2Be_3 at C.   The components are shown as dotted curves in the figure.

The total area under the curve measures the number of electrons in the unit cell.   This number is 532, and one quarter of these, 133, are represented by the area under the part of the curve in fig. 6A.   Similarly, the areas under the dotted curves measure the number of electrons associated with Si_6, O_6, and Al_2Be_3.   (It will be realised that the numbers of atoms will be in the right ratio for a molecule $Be_3Al_2Si_6O_{18}$ when the curve is repeated by reflexion.)   These areas, as drawn in the figure, give the following numbers of electrons.

Si_6 . .   . .   74·8 electrons.   12·47 electrons per atom.

O_6 . .   . .   53·7 electrons.   8·95 electrons per atom.

Al_2Be_3 . .   30·1 electrons.

The distribution of electrons amongst the silicon and oxygen atoms lies between that to be expected from neutral atoms, for which the value for silicon would be 14 and for oxygen 8, and that for ionized atoms, with values 10 and 10. Of course, the oxygen curve could be so drawn that the ratio 10 to 10 would exist, but if this is done trial shows that it is impossible to suppose the oxygen curve symmetrical on both sides of its peak.   This may in fact be the case, since the oxygen atoms in peak B are united on one side to the silicon atoms in peak A to form a ring of the composition Si_6O_{18}.   It seems simplest, however, to assume the oxygen curve symmetrical, and suppose that silicon and oxygen divide the electrons between them in the ratio of about 12·5 to 9.   The point involved here is an interesting example of the power of Duane's direct method of analysis.   We are not correct in speaking of the atoms as being in definite "positions" except when we may assume that the distribution of electrons around them is highly symmetrical.

The number of electrons in the aluminium and beryllium atoms separately cannot be deduced from the curve for Al_2Be_3 and we have arbitrarily split up this curve into two components of area corresponding to 11·4 and 2·4

electrons. In this way curves are obtained for the electron distribution in the atoms Be, Al, Si, O which are shown in fig. 6.

It is now possible to compare the experimental curves for the distribution of electrons in sheets parallel to the planes ($10\bar{1}0$) and ($11\bar{2}0$) given by the Fourier analysis, with the distribution got by adding together the contributions from the various atoms. The positions of the atoms are fixed by the parameters of Table V, and the structure of the planes is indicated in fig. 7. As will be seen the comparison is not unfavourable. The Fourier series is not complete and the addition of higher terms might eliminate some of the chief differences between the two curves. In addition, the distributions for the various atoms deduced from the (000l) planes may be incorrect. For instance, the fit would be improved if beryllium were given more electrons and aluminium fewer.

The method of Fourier analysis proposed by Duane may well prove to be a more simple and direct method of finding structures than the method usually followed, in which atomic arrangements are assumed and their effects compared with experiment. Duane's method has the supreme merit of presenting, in the form of a single curve, the information yielded by *all* orders of reflexion from a given plane. One can imagine it possible to take the curves of electron distribution in the various atoms, and by sliding them along the z axis in a way conformable with symmetry to obtain the best possible fit to the observed Fourier curve and so to analyse the structure. In the simple case of the (000l) planes, for example, the displacement of the oxygen atoms parallel to the c axis is immediately read off from the curve, instead of being deduced from a number of orders. It is interesting to note that the peak of the curve in fig. 6 is at a distance from the Si_6O_6 planes, which agrees within 1 per cent. of the distance 1·35 Å deduced from the spectra. It must be remembered, however, that an extinction coefficient has been chosen which makes calculated and observed intensities agree for the (000l) planes, so that the Fourier analysis should here give the same results as ordinary analysis.

Though this method may be more direct, it depends like other methods on accurate measurements of the quantity we have called " F." If " F " is known for a large number of planes, analysis will be possible by one method or another. In its turn, " F " depends on the estimation of the effect of extinction. All other factors can be allowed for, and the experimental measurements of intensity present no difficulties. *Accurate allowance for extinction appears to be the key o the analysis of complex structures.*

Whatever method of analysis is finally adopted it seems necessary to work out an approximate structure in the first place. The Duane method cannot be
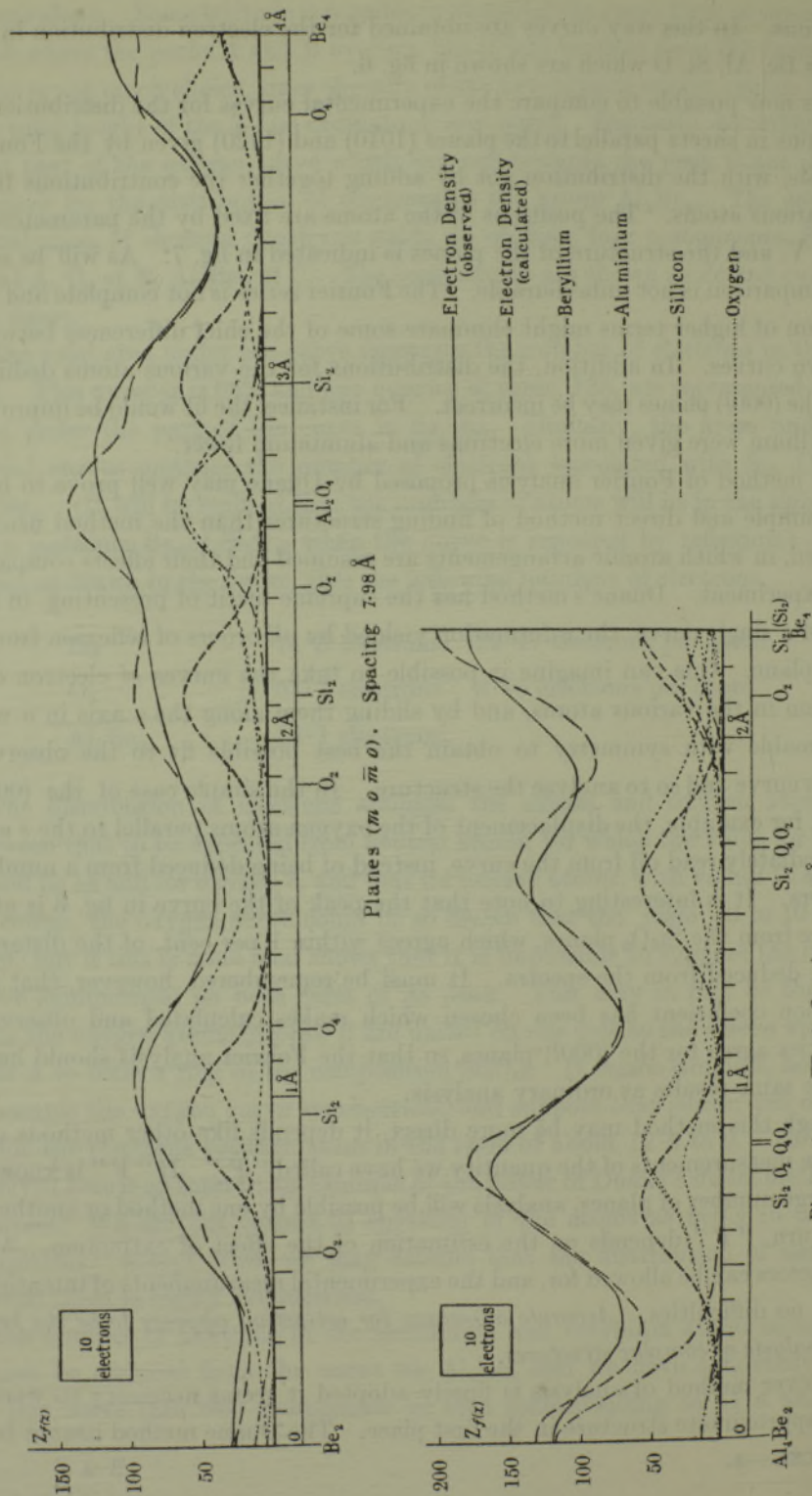
Fig. 7.—Fourier Analysis of Planes $(m\ o\ \overline{m}\ o)$ and $(m\ m\ \overline{2m}\ o)$ in Beryl. Correction: $Z_{f(z)}$ should read $Zf(z)$.

Planes $(m\ o\ \overline{m}\ o)$. Spacing 7·98 Å.

Planes $(m\ m\ \overline{2m}\ o)$. Spacing 4·605 Å.

Electron Density (observed)
Electron Density (calculated)
Beryllium
Aluminium
Silicon
Oxygen

applied until the signs of the coefficient " F " are fixed by preliminary analysis, for the observed intensities only give the squares of these quantities. Probably the most convenient procedure will be to combine the trial and error method of assuming structures, and calculating the spectra to be expected from them, with the Fourier analysis method, the latter being used to make the final adjustments of atomic position and to indicate the accuracy of the results.

8. *Discussion of the Structure.*—In the beryl structure every silicon atom is surrounded by four oxygen atoms arranged tetrahedrally, every aluminium atom by six oxygen atoms at the corners of an octahedron, and every beryllium atom by four oxygen atoms on a distorted tetrahedron. The silicon and oxygen atoms form rings of the composition Si_6O_{18}. These rings have a hexagonal axis and equatorial plane of symmetry, and are arranged around the hexagonal axes. They are composed of SiO_4 groups, each group joined to its neighbour on either side in the ring by an oxygen atom held in common. The rings are stacked on each other along the hexagonal axes, forming a series of open channels, for no atomic centre is nearer than $2\cdot55$ Å to a hexagonal axis. The rings are linked together by the aluminium and beryllium atoms as shown in fig. 3. The whole structure is like a honeycomb, with the hexagonal axes passing down the centres of the cells and with walls formed of closely packed oxygen atoms. The open channels in the structure parallel to the *c* axis are very striking, and suggest investigations into properties they might confer on the crystal.

Table VIII.—*Interatomic Distances.*

Si Group	$O^{12} - O^{24} = 2\cdot54$ Å
	$O^{24} - O^{24} = 2\cdot70$ Å
	$O^{12} - O^{12} = 2\cdot55$ Å
	$Si - O^{24} = 1\cdot57$ Å
	$Si - O^{12} = 1\cdot58$ Å
Al Group	$O^{24} - O^{24}$ (parallel to (0001)) $= 2\cdot93$ Å
	$O^{24} - O^{24}$ (common to Be group) $= 2\cdot52$ Å
	$O^{24} - O^{24}$ (parallel to (10$\bar{1}$0)) $= 2\cdot54$ Å
	$Al - O^{24}$ $= 1\cdot94$ Å
Be Group	$O^{24} - O^{24}$ (parallel to (0001)) $= 2\cdot91$ Å
	$O^{24} - O^{24}$ (parallel to (10$\bar{1}$0)) $= 2\cdot52$ Å
	$O^{24} - O^{24}$ (parallel to (11$\bar{2}$0)) $= 3\cdot03$ Å
	$Be - O^{24}$ $= 1\cdot73$ Å

The groups of oxygen atoms around Be, Al and Si are similar to the groups in garnet, $Ca_3Al_2Si_3O_{12}$, analysed by Menzer. In garnet each calcium atom

3 A 2

is surrounded by four oxygen atoms, each aluminium by six oxygen atoms, and each silicon by four oxygen atoms. In both crystals the distances between oxygen atoms are everywhere about $2 \cdot 7$ Å. The distances between neighbouring atoms in beryl are given in Table VIII.

In conclusion we wish to express our gratitude to Dr. A. Hutchinson, F.R.S., for providing us with crystal specimens. Part of the apparatus used in the investigation was presented to the laboratory by the General Electric Company of America.

Structure in the Secondary Hydrogen Spectrum—IV.

By O. W. RICHARDSON, F.R.S., Yarrow Research Professor of the Royal Society.

§ 1. *Fulcher's Bands.*

Fulcher's bands, as extended by himself[*] and Allen,[†] consisted of six sets of five lines in the red whose wave numbers obey a parabolic law very closely, both when the lines within each set are compared and when corresponding lines in each set are compared from set to set. There were also four sets of four lines in the green with similar properties. The numerical coherence of these lines has been ably discussed by Curtis,[‡] and I have nothing to add to that discussion except to say that on plates taken by Mr. Wilfred Hall with a 21-foot grating the line $\lambda = 6127 \cdot 40$ ($16315 \cdot 64\nu$) is shown resolved with one component which preliminary measures place at $\lambda = 6127 \cdot 21$, the value suggested by Fulcher. It thus appears that the anomaly in this line is due to blending and not to a perturbation.

In addition to the foregoing lines Fulcher included four other lines in the first four sets in the red, which he denoted by the letters S_4, S_5, S_6, S_7. These lines follow the parabolic law from set to set, but their interrelation within each set is far from obvious. An attempt to include them in a consistent scheme has been made by Dieke,[§] who arranges the vertical series of Allen (S_3, S_2, S_1, S_0, S_{-1})

[*] Fulcher, ' Phys. Rev.,' vol. 21, p. 375 (1923).

[†] Allen, ' Roy. Soc. Proc.,' A, vol. 106, p. 69 (1924).

[‡] Curtis, ' Roy. Soc. Proc.,' A, vol. 107, p. 570 (1925).

[§] Dieke, ' Proc. Kon. Akad. v. Wet. Amsterdam,' vol 27, p. 490 (1924).