VI. Results of crystal analysis

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From (9), (10) we have

$$en_2q_2 = \frac{\alpha i}{\alpha - \gamma} - \left(eN_1q_1' + \frac{\gamma i}{\alpha - \gamma} \right) e^{(\alpha - \gamma)\delta}.$$

We have also

$$iV_0 = Xe(N_1q_1'\lambda' + n_2q_2\lambda) - E ;$$

so that a third relation is required in order that we should know N_1, n_2, and i.

According to J. J. Thomson's theory, when there is only one kind of ion in the tube,

$$\sqrt{i} = aV + b.$$

It is our intention to discuss the experimental results in their bearing on this and other theories in a future paper.

Our thanks are due to the authorities of the Presidency College, Calcutta, for affording us facilities for carrying ɟon the above investigations.

VI. *Results of Crystal Analysis.*
By L. VEGARD, *Dr. phil., University of Christiania* *.

[Plate III.]

§ 1. IN a previous paper † I gave an account of the crystalline structure of silver, as determined by the Bragg reflexion method. The X-ray spectrometer was in principle the same as that constructed by Bragg, only differing with regard to details which were mentioned in the paper.

Since then the work has been continued, and some of the results obtained will be given in this paper.

Besides some results concerning the structure of gold and lead, which were announced in a paper read before "Kristiania Videnskapselskap" on November 19, 1915, the present paper will chiefly deal with the more elaborate and complicated case, the determination of the structure of the Zircon group, represented by the minerals zircon ($ZrSiO_4$), rutile (TiO_2)$_2$, and tinstone (kassiterite) (SnO_2)$_2$, which are, as far as I know, the first cases of tetragonal crystals which have yet been analysed ‡.

Not being aware of the fact that the Spinel group recently has been analysed by W. H. Bragg §, I have also made an

* Communicated by the Author.
† L. Vegard, Phil. Mag. Jan. 1916.
‡ An account of the analysis of the Zircon group was given in a lecture in *Kristiania Vid. Selsk.* March 10, 1916.
§ W. H. Bragg, Phil. Mag. Aug. 1915, p. 305.

analysis of the structure of this group. The following spectra have been measured :—Magnetite (111), (110), and (100); spinel (111), (110), and (100) ; gahnite (111). The experimental results, as well as the lattice constructed from them, were in close agreement with the results of Bragg ; so a more detailed account will be superfluous.

§ 2. *The Structure of Gold and Lead.*

The elements copper, silver, gold, and lead all have crystals which belong to the holohedral class of the cubic system, and from a crystallographic point of view we should expect gold and lead to have a similar space-lattice to that found for copper * and silver † ; but still I think an actual determination will be of interest, as several lattices might give the right symmetry.

The gold crystals used for the experiments were kindly lent me by Professor W. C. Brögger. The one specimen had the form of an octahedron, but as it had linear dimensions of the order of only one millimetre, we did not with our instrument detect any reflexion from it. The specimen used had the common form of a thin plate, twinned about its principal face (111).

The crystal plate being quite thin, we only got reflexion from the face (111).

The lead crystal was produced artificially. Several methods were tried—*e. g.*, a gradual cooling of the molten substance, and sublimation of the metal in an electric furnace ; but although crystals were formed, they mostly consisted of branches made up of small individual crystals, but we got no crystal face fit for our purpose.

The method which proved most successful was to let lead precipitate on a piece of zinc from a solution of lead-acetate.

In this way we got crystal leaves formed in a similar way to the gold plates with the principal face (111), which gave quite a strong reflexion.

In fig. 1 are given the relative strength and the position of the reflexion maxima for the face (111) of gold and lead as observed with narrow slits (0·4 mm.). The normal variation of intensity with increasing order shows that the "point-planes" parallel to the face (111) are equal and equidistant, and in the simple case of a cubic crystal *with one sort of atoms there can only be one lattice, which satisfies this condition and gives the right glancing angle.*

* W. H. Bragg, Phil. Mag. xxviii. (1915) p. 355.
† L. Vegard, *loc. cit.*

For a given lattice we can, as shown by W. H. and W. L. Bragg, calculate the glancing angle (θ) when we know the density (ρ) of the crystal, the atomic weight (A), and the wave-length (λ) of the X-rays.

Fig. 1.

Gold (III)

Lead (III)

Settingangle of chamber
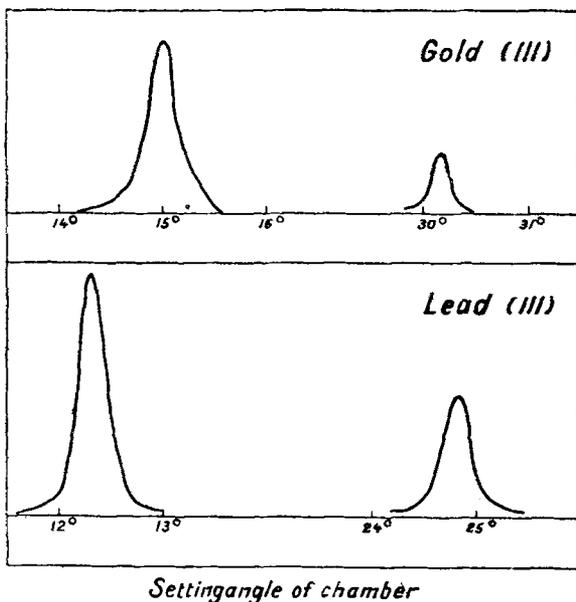
Let the side of the elementary cube be a, and the number of atoms associated with a cube of side a be n, then

$$a^3 = \frac{n\mathrm{A}}{\rho\mathrm{N}}, \qquad \cdots \cdots (1)$$

where N is the number of atoms in a gram-atom (N = $61\cdot5 \times 10^{22}$).

Let the spacing of the (111) planes be

$$d_{111} = \epsilon a,$$

then

$$\epsilon a = \frac{\lambda}{2 \cdot \sin \cdot \theta_1}, \qquad \cdots \cdots (2)$$

where θ_1 is the glancing angle of the first order.

From (1) and (2) we get

$$\sin \theta_1 = \frac{1}{\epsilon \sqrt[3]{n}} \cdot \frac{\lambda}{2} \sqrt[3]{\frac{\rho\mathrm{N}}{\mathrm{A}}}.$$

F 2

For the simple cube lattice (a) : $n = 1$, $\epsilon = \dfrac{1}{\sqrt{3}}.$

For the cube-centred lattice (b) : $n = 2$, $\epsilon = \dfrac{1}{2\sqrt{3}}.$

For the face-centred lattice (c) : $n = 4$, $\epsilon = \dfrac{1}{\sqrt{3}}.$

A lattice like that of diamond $\left(n = 8,\ \epsilon = \dfrac{1}{\sqrt{3}} \right)$ is excluded on account of the normal distribution of intensities.

Calling the glancing angles in the three cases θ_a, θ_b, θ_c, we get

$$\sin \theta_a = \sin \theta_b \sin \theta_c.]$$

In Table I. are given the glancing angles for gold and lead calculated for the three lattices, and also the observed values, which are in perfect agreement with the values calculated on the assumption of *a face-centred lattice*.

<div align="center">TABLE I.</div>

	Calculated.			Observed.
	θ_a.	θ_b.	θ_c.	θ_1.
Gold	11° 55′	19° 08′	7° 28′	7° 26′
Lead	9° 47′	15° 38′	6° 09′	6° 09′·5

Thus it is proved that gold and lead crystals have the same lattice as copper and silver.

§ 3. *The Structure of the Zircon Group.*

The mineral zircon is a compound with the chemical formula $ZrSiO_4$. It may be considered as an addition product of equivalent portions of the two dioxides (ZrO_2, SiO_2), or as the Zr-salt of an acid of Si corresponding to a formula $Zr(SiO_4)$.

The zircon crystals belong to the tetragonal system of the bipyramidal class. Isomorphous with zircon are found a number of substances, of which the following are the best known:

Rutile $(TiO_2)_2$, kassiterite $(SnO_2)_2$, and thorite $(ThSiO_4)$, the latter being analogous to zircon.

The determination of the structure of these substances will be of special interest also for the reason that there are a

number of analogous dioxides which show quite a different crystal form; and in some cases the very same dioxide occurs in several forms. Thus the titanium dioxide (TiO_2) is found in three modifications, viz., the two tetragonal forms rutile and anastase, and the rhombic bipyramidal modification brookite.

Generally we should expect that the determination of the crystalline structure of isomeric substances would lead to important results, and especially in cases where we know the energy of transformation from one modification to another ; for this energy should equal the difference of potential energy of the system of atoms in the two modifications ; and from this equality we may expect to be able to draw valuable information with regard to the law of the forces acting between the atoms, or the forces which constitute the chemical binding.

The present paper will deal only with the determination of the structure of the zircon group ; but I hope to be able to extend the investigation also to the other modifications, and to treat the more general atomic problem mentioned above.

The specimens of *zircon* crystals at my disposal had only the faces (110) and (111) well developed. The *rutile* and *kassiterite* crystals, of which we had very fine specimens, had the faces (100), (110), (111), (101), but no face parallel to the base (001)*.

In cases where the crystal has no face parallel to the planes from which the reflexion is to be found, we have generally † been able to find an edge parallel to the plane in question, and the crystal has been mounted with this edge horizontal and the reflexion-plane vertical.

In this way the reflexions from the zircon planes (100), (101), (001), and the plane (001) of rutile have been determined †. In this case, however, we cannot claim quite the same accuracy for the glancing angle and the intensity as when the reflexion is found from a plane crystal surface ; but still the accuracy will be sufficient for our present purpose.

§ 4.

The results of observations are given in Table II. and graphically represented in fig. 2. For each of the three minerals the glancing angles and intensity for several orders have been found for the five reflexion-planes (110), (100), (111), (001), (101) †.

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* All crystals were kindly lent me by Professor W. C. Brögger, of the Mineralogical Laboratory.

† With the exception of the (001) plane of Sn_2O_4.

TABLE II.

Substance.	Face.	Order.						
		1.	2.	3.	4.	5.	6.	8.
Zircon (ZrSiO₄)	(110)	5° 21' / 1·00	10° 45' / 0·42	16° 13' / 0·26	21° 50' / 0·04			
	(100)	7° 43' / 1·00	15° 35' / 0·68					
	(111)	4° 1' / 0·80	8° 3' / 0·40	12° 3' / 0·40		20° 30' / 0·05	24° 50' / 0	34° 15' / 0·03
	(001)	11° 54' / 1·00	24° 21' / 0·30					
	(101)	7° 4' / 1·00	14° 15' / 0·56	21° 40' / 0·08 (?)				
Rutile (TiO₂)₂	(110)	5° 26' / 1·00	10° 55' / 0·62	16° 30' / 0·20	22° 18' / 0·03			
	(100)	7° 44' / 1·00	15° 36' / 0·84	23° 47' / 0·35	32° 28' / 0·03			
	(111)	— / 0	8° 5' / 1·00	— / 0	16° 20' / 1·00	0	25° 0' / 0	
	(001)	11° 57' / 1·00	24° 28' / 0·28					
	(101)	7° 4' / 1·00	14° 14' / 0·06	21° 40' / 0·11	29° 22' / 0·01			
Kassiterite (SnO₂)₂	(110)	5° 14' / 1·00	10° 30' / 0·62	15° 51' / 0·30	21° 22' / 0·11			
	(100)	7° 28' / 1·00	15° 4' / 0·60	23° 0' / 0·23	31° 20' / 0·04 (?)			
	(111)	—	7° 39' / 0·17	— / 0	15° 26' / 1·00	— / 0	23° 32' / 0	32° 12' / 0·13
	(001)	— / 0						
	(101)	6° 42' / 1·00	13° 30' / 0·64	20° 29' / 0·40	27° 49' / 0·23			

Fig. 2.
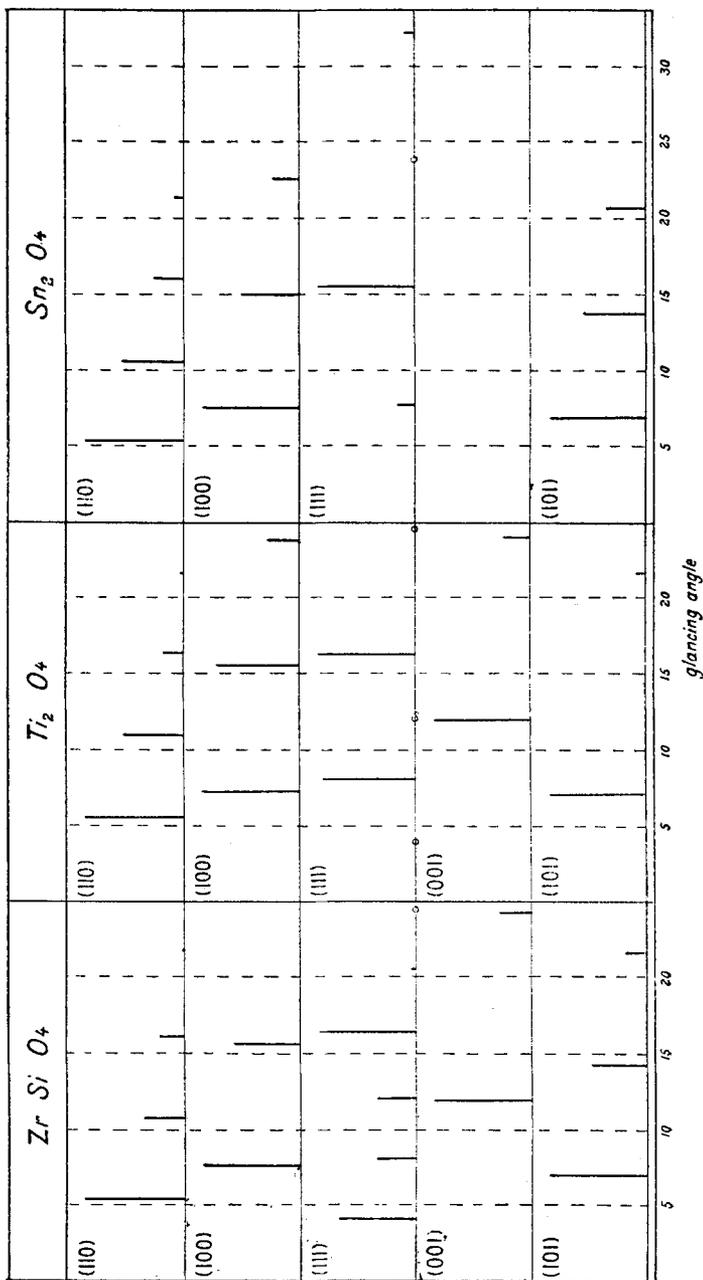
We observe the position of the chamber. If the position angle of the chamber for spectra of the order n and i be α_n and α_i, then

$$\cot \theta_i = \frac{n}{i} \operatorname{cosec} \frac{\alpha_n - \alpha_i}{2} - \cot \frac{\alpha_n - \alpha_i}{2}. \quad . \quad . \quad . \quad (3)$$

For each face the intensity of the strongest maximum is put equal to 1. Thus it is only the intensities of different orders corresponding to one and the same face which should be comparable.

The intensities of the reflexion are measured in the following way:—

The slit, which the primary beam has to pass before striking the crystal, is made quite narrow, while the slit in front of the chamber is kept open, and the ionization is measured for angles which are near to the glancing angle of the spectrum in question.

The maximum ionization current (when the ionization of the " white radiation " has been subtracted) is taken as a measure of the intensity of reflexion.

In order to make certain that the intensities thus measured correspond to the same strength of the primary beam, the intensity measurements for each face were carried out rapidly and in symmetrical order.

§ 5. *Interpretation.*

The interpretation is based on the fundamental equation of Bragg, combining the spacing d, the glancing angle θ, and the wave-length λ :

$$n\lambda = 2d \sin \theta_n. \quad . \quad . \quad . \quad . \quad (4)$$

From the values of θ given in Table II. we can calculate the spacing for any reflexion-face.

In Table III. are given the absolute values of $d_{100} = d_{010}$ and d_{001}, as calculated from (4) ($\lambda = 0{\cdot}607 \times 10^{-8}$). Column 3 gives the ratios $\dfrac{d_{001}}{d_{100}}$ and column 4 the ratios c'/a' of the crystallographic axes, as taken from P. Groth, *Chemische Krystallographie.*

We see that in the case of zircon and rutile,

$$\frac{d_{001}}{d_{100}} = \frac{c'}{a'}.$$

In the case of kassiterite the reflexion from (001) has not been found ; but from the similarity between the spectra of

the three substances, there can be no doubt that also for kassiterite the ratio $\dfrac{d_{001}}{d_{100}}$ is equal to c'/a'.

The elementary cell has a volume

$$d_{100}^2 \, d_{001} = d_{100}^3 \, \frac{c'}{a'},$$

and the number of molecules n associated with this volume is

$$n = \frac{N\rho}{M} \frac{c'}{a'} \, d_{100}^3 \; ; \qquad \ldots \ldots \quad (5)$$

ρ is the density, N the number of molecules in a gram-molecule, M is the molecular weight; and in order to preserve the analogy between the three substances, we write the molecular formula for rutile Ti_2O_4 and for kassiterite Sn_2O_4.

The number n is given in the last column of Table III.; and we see that within the limit of experimental error the number n is equal to $1/8$ for all three substances, or in a rectangular prism with sides $2d_{100}$, $2d_{100}$, and $2d_{001}$ there should be *just one molecule*.

TABLE III.

Substance.	d_{100}.	d_{001}.	$\dfrac{d_{001}}{d_{100}}$.	$\dfrac{c'}{a'}$.	n.
$ZrSiO_4$	cm. $2\cdot30\times10^{-8}$	cm. $1\cdot47\times10^{-8}$	0·640	0·639	0·124
Ti_2O_4	2·26 ,,	1·46 ,,	0·646	0·644	0·123
Sn_2O_4	2·335 ,,	......	......	......	0·123

Before proceeding further in our attempt to arrange the atoms, we shall make a few remarks regarding our elementary lattice, and the formation of compound lattices and some of their properties.

Our elementary lattice will be a prism with one atom in each corner. Let the side of its square base be a, and height c; then the spacing of a simple elementary lattice would be

$$d_{100} = a, \qquad d_{001} = c, \qquad d_{110} = \frac{a}{\sqrt{2}},$$

$$d_{101} = \frac{a}{\sqrt{1 + \left(\dfrac{a}{c}\right)^2}}, \qquad d_{111} = \frac{a}{\sqrt{2 + \left(\dfrac{a}{c}\right)^2}}. \quad (6a)$$

In describing the compound lattices it may be convenient
to refer the lattices to a rectilinear coordinate system. We
let the origin coincide with one of the atomic centres, and
the z-axis be parallel to the tetragonal axis and the x- and
y-axes parallel to the other sides of the lattice.

Any other elementary lattice which may be made to
cover the primary one by a simple translatory movement is
completely determined with regard to position by giving the
coordinates of one of its points. Very often it is most
convenient to give the coordinates of the point nearest to
the origin, which we shall call the *point of construction*.

Thus a face-centred lattice is made up of four simple lattices
with the following construction-points :

$$(000), \quad (a/2,\, a/2,\, 0), \quad (0,\, a/2,\, c/2), \quad (a/2,\, 0,\, c/2),$$

and the spacings :

$$d_{100} = a/2, \qquad d_{001} = c/2, \qquad d_{110} = \frac{a}{2\sqrt{2}},$$

$$d_{101} = \frac{a}{2\sqrt{1+\left(\frac{a}{c}\right)^2}}, \qquad d_{111} = \frac{a}{\sqrt{2+\left(\frac{a}{c}\right)^2}}. \qquad . \quad (6\,b)$$

The lattice corresponding to the cube-centred lattice has
construction-points

$$(000) \quad \text{and} \quad (a/2,\, a/2,\, c/2),$$

and spacings

$$d_{100} = a/2, \qquad d_{101} = c/2, \qquad d_{110} = \frac{a}{\sqrt{2}},$$

$$d_{101} = \frac{a}{\sqrt{1+\left(\frac{a}{c}\right)^2}}, \qquad d_{111} = \frac{a}{2\sqrt{2+\left(\frac{a}{c}\right)^2}}. \quad . \quad (6\,c)$$

A lattice analogous to that of diamond is composed of two
parallel face-centred lattices with the construction-points

$$(000) \quad \text{and} \quad (a/4,\, a/4,\, c/4),$$

and has the following spacings :

$$d_{100} = a/4, \qquad d_{001} = c/4, \qquad d_{110} = \frac{a}{2\sqrt{2}},$$

$$d_{101} = \frac{a}{2\sqrt{1+\left(\frac{a}{c}\right)^2}}, \qquad d_{111} = \frac{a}{\sqrt{2+\left(\frac{a}{c}\right)^2}}. \quad . \quad (6\,d)$$

Returning to our crystals, we shall first consider the most general type, zircon. In the cell $(2d_{100}) . (2d_{100}) . (2d_{110})$ there should be placed

one atom of Zr, *one* atom of Si, and *four* oxygen atoms.

The simplest way in which we might arrange the atoms of Zr and Si in the cell would be to suppose the Zr atoms arranged in a simple elementary lattice, for which we put $a = 2d_{100}$ and $c = 2d_{001}$, and the Si atoms in a similar lattice with construction-point $(a/2, a/2, c/2)$; but such an arrangement would make the spacing of the (100) and (001) planes. twice as large as they are actually observed.

The spacings being inversely proportional to $\sin \theta$, we can easily make a comparison with the observed angles and those to be expected for the four types of lattices previously constructed, and we notice at once that the observed spacings. have a relation to each other similar to those of equation (6 *d*) corresponding to the diamond type of lattice, and a calculation will show that within the limit of experimental error the ratios expressed in (6 *d*) are satisfied by observations, or

$$\left. \begin{array}{l} \sin \theta_{100} : \sin \theta_{001} : \sin \theta_{110} : \sin \theta_{1\hat{0}1} : \sin \theta_{111} \\[2mm] = 4 : 4\frac{a}{c} : 2\sqrt{2} : 2\sqrt{1 + \left(\frac{a}{c}\right)^2} : \sqrt{2 + \left(\frac{a}{c}\right)^2} \\[2mm] = 4 : 6{\cdot}26 : 2{\cdot}83 : 3{\cdot}71 : 2{\cdot}11. \end{array} \right\} \quad (7)$$

From equations (6 *d*) we find for the sides of the elementary lattice :

$$a = 4d_{100},$$

$$c = 4d_{001}.$$

Now in a lattice of the diamond type there are 8 points associated with a volume equal to that of the elementary lattice (a^2c), and consequently in a cell $(a/4, a/4, c/4)$ there should be 1/8, or exactly the number which is found for Zr or Si atoms in the elementary cell $d_{100}^2 d_{001}$.

This leads us to the assumption *that in zircon the Zr and Si atoms are arranged in a lattice of the diamond type.*

Regarding the relative position of the Zr and Si lattices, it is not necessarily determined from symmetry. The only condition to be fulfilled is that corresponding points of the two lattices must be situated on the tetragonal axis, or the position of one must be derived from the position of the other by a translation parallel to the c-axis. If the construction-point for the Zr atoms has the coordinates (000), the

coordinates for the construction-point of the Si lattice will be $(00l)$, where $0 < l < c$.

To get further, we must take into account the distribution of intensities for different spectra. An important fact in this connexion is that the face (001) gives a normal distribution of intensities. This fact limits the possible values of l to $c/4$ or $c/2$.

The assumption $l = c/4$, however, leads to consequences in conflict with observations. Thus it cannot explain that the face (101) gives a nearly normal distribution of intensities, and we have as the only possibility :

$$l = c/2.$$

The arrangement of the Zr and Si atoms is shown in fig. 3. We might also come to this lattice in another way. It might be considered as composed of two lattices of the rock-salt type with points of construction (000) and $(a/4, a/4, c/4)$, corresponding to the diamond type.

Fig. 3.

● *Zr atoms*

○ *Si* —,,—
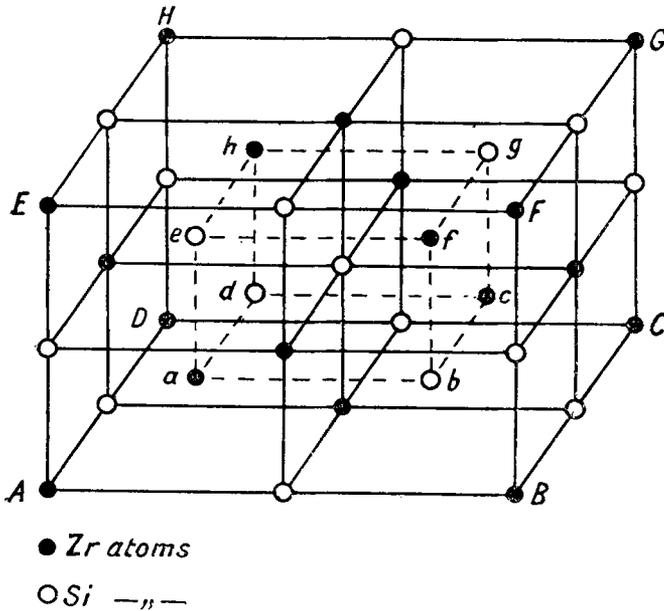
From the isomorphism of the three minerals we should expect the lattices of the metal atoms to be found by substitution of the atoms in the zircon lattice with corresponding

atoms of the other substances. In both cases—for Ti_2O_4 as well as for Sn_2O_4—the Zr and Si atoms are to be substituted with the same sort of atoms. This will considerably alter the type of the lattice and make it much simpler. In fact, the metal atoms will be arranged in a prism-centred lattice with sides $2d_{100}$, $2d_{100}$, $2d_{001}$: but in order to preserve the analogy with zircon, we shall suppose the lattice formed in the same way from an elementary lattice, $a = 4d_{100}$, $c = 4d_{001}$.

From the equations (6 c) and (6 d) we see that the ratios for the spacings (100) (001) (110) (101) should be unaltered; but for the face (111) the spacing would in comparison be four times smaller than in the case of zircon, or the *sine* of the first-order glancing angle four times as large.

As a matter of fact this does not occur.

It is only the spectra corresponding to the orders 1, 3, 5, &c. of zircon which have vanished for the (111) face in the case of TiO_4 and Sn_2O_4, and the spacings have the following ratios :

$$d_{100} : d_{001} : d_{110} : d_{101} : d_{111}$$

$$= 1/4 : \frac{c}{4a} : \frac{1}{2\sqrt{2}} : \frac{1}{2\sqrt{1 + \left(\frac{a}{c}\right)^2}} : \frac{1}{2\sqrt{2 + \left(\frac{a}{c}\right)^2}}. \quad . \quad (8)$$

This apparent discrepancy, however, is not fatal to the correctness of the assumed arrangement of the metal atoms; for as a matter of fact the first-order spectrum for the face (111) in the case of Ti_2O_4 and Sn_2O_4 *is produced entirely by the oxygen atoms.*

§ 6. *The Arrangement of the Oxygen Atoms.*

In the case of zircon the observed spacings for all the reflexion planes considered are just the same as we should get from the lattice of Zr and Si without the oxygen atoms : hence it follows that the arrangement of the oxygen atoms must be determined from the intensity measurements. Only in the case of rutile and kassiterite the maxima of order 1, 3, 5, &c. for the face (111) should be due entirely to the oxygen atoms.

The problem before us is to arrange the oxygen atoms in the Zr-Si lattice—with four atoms to each pair of (Zr-Si) atoms—in such a way that the distribution of intensities of the reflexion maxima is explained and the crystallographic symmetry accounted for.

There are two different types of arrangements according to the view we take with regard to the chemical nature of the substances. The one view is expressed in the formulæ : $Zr(SiO_4)$, $Ti(TiO_4)$, $Sn(SnO_4)$; and if these were the right expressions, the structure—even in the case of rutile and kassiterite—should distinguish between two sorts of metallic atoms.

According to the other view, zircon is considered as a kind of addition product of two dioxides ZrO_2, SiO_2; and if we substitute Zr and Si with either Ti or Sn, we should expect to get a lattice where all Ti or Sn atoms are equal.

In accordance with the first view, we should arrange four atoms of oxygen round each of the Si atoms in accordance with the symmetry of the crystal.

We have to consider the following three arrangements :—

(1) The four O-atoms are placed along the tetragonal axis through the Si atom, and with the O-atoms symmetrically arranged on both sides of the Si atom.

(2) The four O-atoms are arranged in a plane through the Si atom perpendicular to the C-axis with tetragonal symmetry with regard to this axis. There are two different arrangements. If we take the Si atom as origin the O-atoms will be situated in the (xy) plane and will either have the coordinates :

$$(l,l),\ (-l,l),\ (l,-l),\ (-l,-l),\ \text{or}\ (l,0),\ (0,l),\ (0,-l),\ (-l,0),$$

where l is a parameter.

(3) The oxygen atoms are arranged on the diagonals AG, BH, &c., fig. 3. Let the construction-points of the two face-centred Si lattices be (000) and $(a/4,\ a/4,\ c/4)$, then the construction-points of the oxygen lattices would be :

$$(\epsilon_1 a,\ \epsilon_1 a,\ \epsilon_1 a),\quad (-\epsilon_1 a,\ -\epsilon_1 a,\ \epsilon_1 c),\quad (-\epsilon_1 a,\ \epsilon_1 a,\ -\epsilon_1 c)$$

$$(\epsilon_1 a,\ -\epsilon_1 a,\ -\epsilon_1 c),\ \text{and}$$

$$\left(\frac{a}{4}+\epsilon_2 a,\ \frac{a}{4}+\epsilon_2 a,\ \frac{c}{4}+\epsilon_2 c\right),\ \left(\frac{a}{4}-\epsilon_2 a,\ \frac{a}{4}-\epsilon_2 a,\ \frac{c}{4}+\epsilon_2 a\right),$$

$$\left(\frac{a}{4}-\epsilon_2 a,\ \frac{a}{4}+\epsilon_2 a,\ \frac{c}{4}-\epsilon_2 c\right),\ \left(\frac{a}{4}+\epsilon_2 a,\ \frac{a}{4}-\epsilon_2 a,\ \frac{c}{4}-\epsilon_2 c\right).$$

To get the right spacing for the face (100), ϵ_1 and ϵ_2 must have the same numerical value; but still we have to distinguish between the two cases :

$$(3\,a)\ \ \epsilon_1 = \epsilon_2,$$

$$(3\,b)\ \ \epsilon_1 = -\epsilon_2.$$

This arrangement will be clear by noticing that if $a = c$ the oxygen atoms would be arranged in the corners of tetrahedra with the Si atoms at the centres.

None of these arrangements, however, is able to explain the experiments. Thus the types (1), (2), and (3 a) would make the second order spectrum of the face (111) vanish, contrary to observations.

The question whether the oxygen atoms might be arranged according to (3 b) is of fundamental importance with regard to the properties of the atoms. If the atoms were arranged in this way, *the tetragonal lattice could be considered as a cubic lattice compressed in the direction of one of the principal axes, and there would be nothing in the geometry of the lattice to explain its tetragonal form.*

The compression of the lattice would be due *to symmetry properties of the centres (atoms)*, and under the conditions present the atoms would exert a different force in the direction of the tetragonal axis from that in a direction perpendicular to it.

The arrangement (3 b), however, cannot be accepted although it gives a finite value for the second order spectrum of the face (111) ; but no value of ϵ will satisfactorily explain the actual intensity-distribution observed. Thus in order to account for the disappearance of the first order spectrum of (111) for rutile and kassiterite, we must put $\epsilon = -1/8$. With this value of ϵ the amplitude in the case of rutile would be given by the formula :

$$A_{111} = 1 + 1 \cdot 38 \cos n \frac{\pi}{2},$$

which would give a ratio of the intensity of the first to that of the second order equal to about 16 : 1, while the spectra actually observed are in the ratio 1 : 1.

In a similar way we can show that we cannot arrange the oxygen atoms round each of the Zr atoms, when the Zr atoms are to take up a central position in groups of four O-atoms.

Let us then try to associate two oxygen atoms with each Si and Zr atom. The O-atoms must be situated on a straight line through the Si or Zr atom considered and at equal distances on both sides of it ; but the distance from a Si atom to the two neighbouring O-atoms may not be equal to the corresponding distance for the Zr atom.

Then the determination of the lattice under these conditions would involve the determination of the two distances (parameters) and the orientation of the lines through the

Zr and Si atoms relative to the axis of the crystal and
relative to each other.

With regard to the direction of the lines, let us first
determine their position with regard to the tetragonal axis,
and consider the following three cases :—

(1) All lines are parallel to the tetragonal axis. This
orientation is excluded because for zircon it would make the
second order spectrum of face (111) vanish.

(2) The lines belonging to one sort of atoms (Zr say)
might be parallel to the tetragonal axis, the lines of the
other sort perpendicular to this axis. The latter lines are
divided into two groups in such a way that an individual
of one group is perpendicular to one of the other. Such an
arrangement would not explain the distribution of the
intensities of the face (111) for zircon and the disappearance
of the first order spectrum of the (111) face of rutile and
kassiterite.

(3) All lines are perpendicular to the tetragonal axis.
Let us consider the lines through the Zr atoms. The lines
through the atoms belonging to one of the face-centred Zr
lattices must be perpendicular to the lines through the atoms
of the other face-centred lattice. In order to preserve the
right spacing for the faces (100) and (111), the lines must
be drawn so as to halve the angle between the sides (a) of
the square base of the lattice.

The lines through the Si atoms must be arranged in the
same way.

Fig. 4.

● Zr atoms

O Si —ₙ—
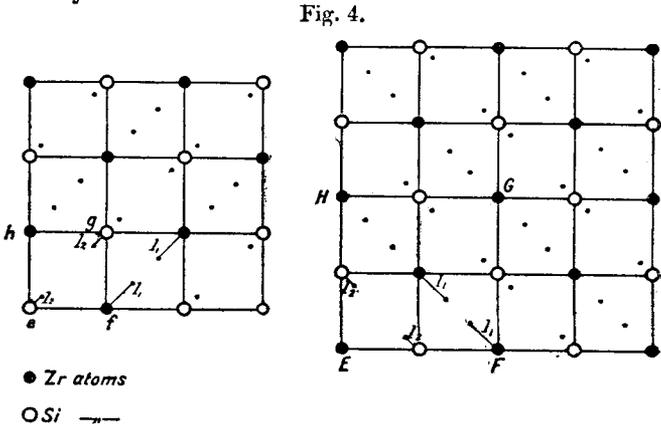
With regard to the relative position of the lines through
the Zr atoms and those through the Si atoms, there are two
different possibilities, which will be apparent from fig. 4,

which gives the distribution of points in two consecutive planes (001).

In a plane (001) either all lines may be parallel as shown in the figure, or the lines through Si can be drawn perpendicular to those through the Zr atoms. The latter arrangement is excluded as it would not explain the distribution of intensities of the (111) face.

We shall then consider the arrangement represented in fig. 4, which, as will be seen, with a proper choice of the parameters ϵ_1 and ϵ_2, will give the right lattice for the *zircon group.* This lattice is composed of 12 face-centred lattices with the construction-points which are given in Table IV.

TABLE IV.

Atom.	x.	y.	z.
Zr $\left\{\vphantom{\begin{matrix}0\\0\end{matrix}}\right.$	0 $-a/4$	0 $a/4$	0 $c/4$
Si $\left\{\vphantom{\begin{matrix}0\\0\end{matrix}}\right.$	$a/2$ $a/4$	0 $a/4$	0 $c/4$
O associated with Zr.. $\left\{\vphantom{\begin{matrix}0\\0\\0\\0\end{matrix}}\right.$	$\epsilon_1 a$ $-\epsilon_1 a$ $-a/4+\epsilon_1 a$ $-a/4-\epsilon_1 a$	$\epsilon_1 a$ $-\epsilon_1 a$ $a/4-\epsilon_1 a$ $a/4+\epsilon_1 a$	0 0 $c/4$ $c/4$
O associated with Si... $\left\{\vphantom{\begin{matrix}0\\0\\0\\0\end{matrix}}\right.$	$a/2+\epsilon_2 a$ $a/2-\epsilon_2 a$ $a/4+\epsilon_2 a$ $a/4-\epsilon_2 a$	$\epsilon_2 a$ $-\epsilon_2 a$ $a/4-\epsilon_2 a$ $a/4+\epsilon_2 a$	0 0 $c/4$ $c/4$

Curiously enough, this lattice does not apparently possess the same symmetry elements as the crystal; thus the planes (100) and (010) are not symmetry planes with respect to the points of the lattice, and the lattice possesses no tetragonal screw axis.

But still the lattice has the properties necessary to explain the symmetry of the crystals.

Let a (100) plane containing Zr and Si atoms divide the lattice in two parts I and II. The points of the mirror image of I do not coincide with equivalent points of II; but they can be brought to coincide by a translatory motion along the three axes ($x=a/4$, $y=a/4$, $z=c/4$).

The distance moved being of atomic dimensions, the
difference of position of the points II and those of the image
of I is not to be detected as long as we regard the properties
shown by a large number of atoms.

Thus this asymmetry should not even be felt by ordinary
light waves because one wave-length would cover some
thousand atoms ; first when we come to a wave-length of
the order of that of Röntgen rays, the want of symmetry
with regard to the face (100) can be detected.

From these considerations we arrive at the following
general rule.

Fig. 5.

Arrangement of atoms in
(110) plane

⊕ *Zr atoms*
○ *Si   "*
• *0   "*
---- *Lines of intersection with (111) planes*
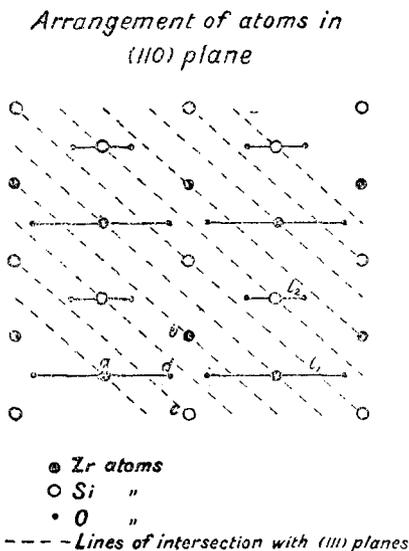
In order that a certain space lattice shall explain an
element of symmetry ascribed to the finite crystal, it will be
sufficient that the lattice possesses a symmetry of the follow-
ing kind :

*The lattice must be brought to coincidence with itself by
performing on it the operation characteristic of the symmetry
element in question and a translatory movement* $x = \epsilon_1 a$,
$y = \epsilon_2 b$, *and* $z = \epsilon_3 c$, *where* a, b, c *are the sides of the elementary
lattice, and* ϵ_1, ϵ_2, ϵ_3 *quantities not greater than unity.*

§ 7. *Calculation of Intensities and Determination of the Parameters.*

When the rays are reflected from a face with equivalent and equidistant planes the intensity distribution is said to be normal, and according to Bragg it is characterized by a gradual diminution of intensities with increasing order.

The exact law for this variation is not known. Bragg * finds that the intensities corrected for the temperature effect as derived from the formula of Debye † are approximately inversely proportional to the square of the order number (n). The cause of this variation is yet unknown.

In spite of the fact that the rate of variation will vary from one case to another, it will generally not be difficult to see from the observed intensities whether the spectrum is normal or not. The criterion is not so much the rapidity with which the intensity falls with increasing order, but much more a typical regular form of the intensity curve.

The problem of finding the distribution of intensities in the case that not all the reflexion planes of the face are identical, has been treated by W. H. and W. L. Bragg. The calculation is based on the assumption that the amplitude reflected from a certain point-plane is proportional to the mass associated with unit area of the plane.

In view of the theory of secondary radiation given by Sir J. J. Thomson ‡, it would be more natural to suppose the amplitude proportional to the *number of electrons* per unit area, and introducing the atom-model of Rutherford and Bohr we should put the reflecting power of an atom proportional to the atomic number.

As the atomic number for most elements is approximately proportional to the atomic weight, it will make very little difference whether we use atomic weights or atomic numbers; but as it must be the number of electrons and not the gravitational mass which is concerned, we shall introduce the atomic numbers in our calculations.

Let unit area of the reflecting plane be composed of ν_1 atoms of atomic number N_1, ν_2 atoms of atomic number N_2, &c., then the number of electrons per unit area (μ) will be

$$\mu = \nu_1 N_1 + \nu_2 N_2 + \ldots \ldots \ldots \quad (9)$$

* W. H. Bragg & W. L. Bragg, 'X-Rays and Crystal Structure,' p. 193.

† P. Debye, *Verh. d. D. Phys. Ges.* xv. 1913 ; *Ann. d. Phys.* 1914, p. 49.

‡ Sir J. J. Thomson, 'Conduction of Electricity through Gases,' p. 321.

Let the face considered have a spacing d_0. A length equal to d_0 on the normal to the face will be cut by a number of point-planes (r) with numbers of atoms per unit area $\mu_1, \mu_2 \ldots \mu_r$.

We select an arbitrary point (0) on the normal, and call the distances from this point to the (r) planes

$$d_1 \ d_2 \ldots d_i \ldots d_r.$$

The intensity of the reflected wave from such a face has been calculated by Bragg in the case of $r = 2$ and a general geometrical method is given *.

The general analytical expression for the intensity will be

$$\mathrm{I}_n = k_n \, \mathrm{A}_n{}^2 \quad \ldots \ldots \quad (10)$$

k_n is a factor which W. H. and W. L. Bragg put proportional to the intensities of the normal spectrum, and they give the following values

$n=$	1	2	3	4	5
$\mathrm{K}_n=$	100	20	7	3	1

A_n is the calculated amplitude which is given by the formulæ :

$$\left.\begin{array}{l} \mathrm{A}_n{}^2 = f_1(n)^2 + f_2(n)^2 \\[2mm] f_1(n) = \sum\limits_{i=1}^{i=r} \mu_i \cos n \, 2\pi \dfrac{d_i}{d_0} \\[4mm] f_2(n) = \sum\limits_{i=1}^{i=r} \mu_i \sin n \, 2\pi \dfrac{d_i}{d_0} \end{array}\right\} \quad \ldots \ldots \quad (11)$$

In a great number of cases we can give the point 0 such a position that the r planes are symmetrically arranged with regard to this point, and as $\sin(-\alpha) = -\sin\alpha$, the quantity $f_2(n) = 0$.

The lattice of the zircon group as given in Table IV. will give the spacing shown in fig. 6 for the five faces experimented upon. Of these the face (001) has identical and equidistant planes and should give a normal spectrum which is also in agreement with experiments. The intensities of the spectra of the four other faces should be given by the following expressions for $f_1(n)$ and $f_2(n)$:—

* W. L. Bragg, Proc. Roy. Soc. lxxxix. p. 483 (1914).

Fig. 6.

$Zr\ Si\ O_4$
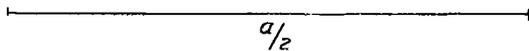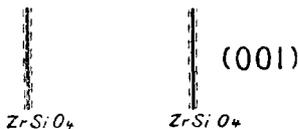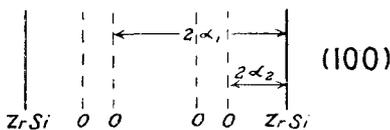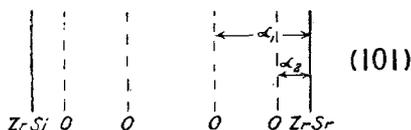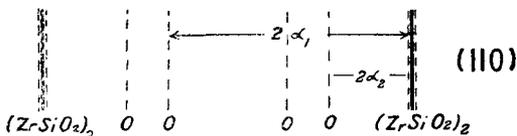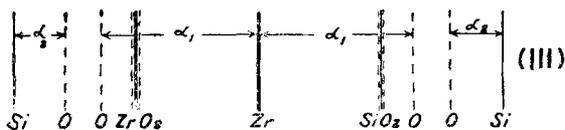
$$Face\ (111) \begin{cases} f_1(n) = N_1 + (-1)^n N_2 + (N_1 + N_2 + 4N_3)\cos n\dfrac{\pi}{2} \\ \qquad\quad + 2N_3\,(\cos n\alpha_1 + (-1)^n\cos n\,\alpha_2). \\ f_2(n) = (N_1 - N_2)\sin n\dfrac{\pi}{2}. \end{cases}$$

$$(110) \begin{cases} f_1(n) = (N_1 + N_2 + 2N_3) + N_3\,(\cos n2\alpha_1 + \cos n2\alpha_2). \\ f_2(n) = 0. \end{cases}$$

$$(101) \begin{cases} f_1(n) = (N_1 + N_2) + 2N_3\,(\cos n\alpha_1 + \cos n\alpha_2). \\ f_2(n) = 0. \end{cases}$$

$$(100) \begin{cases} f_1(n) = (N_1 + N_2) + 2N_3\,(\cos 2n\alpha_1 + \cos 2n\alpha_2). \\ f_2(n) = 0. \end{cases}$$

(12)

N_1, N_2, N_3 are the atomic numbers of Zr, Si, and O respectively, or atoms which may substitute them in the lattice.

The angles α_1 and α_2 are connected to the two parameters ϵ_1 and ϵ_2 (Table IV.) in the following way :

$$\alpha_1 = 4\pi\epsilon_1, \quad \alpha_2 = 4\pi\epsilon_2.$$

§ 8. *Zircon.*

To get the intensities of zircon we have in equations (9) to put

$$N_1 = 40, \; N_2 = 14, \; N_3 = 8 \; ;$$

and putting

$$\alpha_1 = \pi - \beta,$$

we get

$$(111) \quad \begin{cases} f_1(n) = 40 + (-1)^n 14 + 86 \cos n\dfrac{\pi}{2} + (-1)^n 16 \; (\cos n\beta \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad + \cos n\alpha_2). \\ f_2(n) = 26 \sin n\dfrac{\pi}{2} \end{cases}$$

$$(110) \quad \begin{cases} f_1(n) = 70 + 8 \; (\cos 2n\beta + \cos 2n\alpha_2). \\ f_2(n) = 0. \end{cases}$$

$$(101) \quad \begin{cases} f_1(n) = 54 + 16 \, ((-1)^n \cos n\beta + \cos n\alpha_2). \\ f_2(n) = 0. \end{cases}$$

$$(100) \quad \begin{cases} f_1(n) = 54 + 16 \; (\cos 2n\beta + \cos 2n\alpha_2). \\ f_2(n) = 0. \end{cases}$$

$$(13)$$

In determining the intensities we shall have to remember that the spectra from the faces (101) and (100) were determined by reflexion from an edge of the crystal. Especially in the case of the (100) face the reflexion to be observed was very weak ; and under these conditions we must expect too low a value for the first order spectrum, because a smaller portion of the primary beam will be reflected into the chamber when the glancing angle is small.

The reflexion from the (101) face was better ; but in this case also the first order spectrum is found too weak in comparison with those of higher order.

The spectra for the faces (111) and (110), however, are very accurately determined ; but we see from the expression for $f_1(n)$ that the spectrum of the face (110) will be very nearly normal, and the position of the oxygen atoms will affect the intensities very little. Still, we notice from fig. 2 that the intensity of the third order spectrum is too large as compared with that of the second order.

The spectrum (111), on the other hand, is very much influenced by the position of the oxygen atoms, and will form our main basis for the determination of α_1 and α_2.

The values of $f_1(n)$ and $f_2(n)$ for the (111) face are given in Table V. for $n = 1, 2, \ldots 6$.

TABLE V.

n.	$f_2(n)$.	$f_1(n)$.	I obs.	k.
1	1·63	$1\cdot63 - (\cos\ \beta + \cos\ \alpha_2)$	0·80	1·00
2	0	$-2\cdot00 + (\cos 2\beta + \cos 2\alpha_2)$	0·40	0·30
3	$-1\cdot63$	$1\cdot63 - (\cos 3\beta + \cos 3\alpha_2)$	0·40	0·12
4	0	$8\cdot75 + (\cos 4\beta + \cos 4\alpha_2)$	1·00	0·05
5	$-1\cdot63$	$1\cdot63 - (\cos 5\beta + \cos 5\alpha_2)$	0·05	0·015
6	0	$-2\cdot00 + (\cos 6\beta + \cos 6\alpha_2)$	0	0·005

In column 4 are given the relative intensities observed and in the last column the relative intensities of a normal spectrum. These values are somewhat different from those given by Bragg, because the spectra of the crystals considered usually gives a normal spectrum with relatively stronger maxima of higher order.

Comparing the values of the last two columns, we see that β and α_2 must be given such values that the intensity of the first order spectrum is diminished and that of the third increased.

Consequently

$$\cos\beta + \cos\alpha_2 = 2\cos\frac{\beta + \alpha_2}{2}\cos\frac{\beta - \alpha_2}{2} \text{ must be positive (I.)}$$

$$\cos 3\beta + \cos 3\alpha_2 = 2\cos 3/2(\beta + \alpha_2)\cos 3/2(\beta - \alpha_2)$$
$$\text{must be negative (II.)}$$

As both β and α_2 must be less than π, condition I. gives that

$$\beta + \alpha_2 < \pi.$$

As the atoms must have a distance which is of the order of the length d_{100}, neither α_2 nor β can have a very small value. Then we can suppose $\cos 3/2(\beta - \alpha_2)$ positive, and from condition (II.) we get

$$\frac{\pi}{3} < \beta + \alpha_2 < \pi.$$

Now in order that the oxygen atoms may considerably reduce the intensity of the first order spectrum $\beta + \alpha_2$ must be considerably smaller than π, and we should expect both α_2 and β to be in the first quadrant, somewhere between $25°$ and $90°$.

To determine β and α_2 more accurately we could calculate the intensities for varying values of β and α_2. We can arrive at fairly good values more quickly by means of a graphical method. We can very quickly draw curves representing $\cos n\beta + \cos n\alpha_2$ for various values of β, α_2 and n. In fig. 7 the curves are given for $\beta = 60°$ and for values of α_2 varying from $0°$ to $180°$, and for $n = 1, 2, 3, 4, 5, 6$.

Fig. 7.
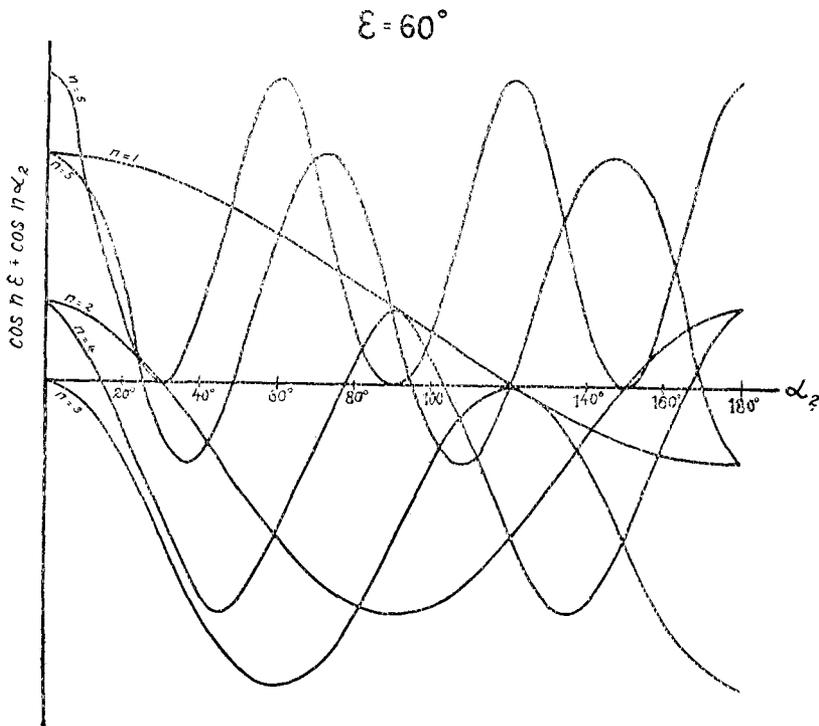
In this way I have found that the following values will give the best agreement with observations:

$$\beta = 30°, \quad \alpha_2 = 60°.$$

In the formula for $f_1(n)$ of the face (111) and also for the

(110) and (100) faces, the values of β and α_2 may be interchanged without altering the value of $f_1(n)$; and consequently we might equally well satisfy these faces with $\alpha_2 = 30°$ and $\beta = 60°$. The face (101), however, does not permit such an interchange, and the fact that this face gives a comparatively strong second order reflexion will make the combination $\beta = 60°$, $\alpha_2 = 30°$ impossible.

With our present knowledge with regard to the laws governing the intensity variations we cannot claim a very great accuracy for the angles α_2 and β. In the present case our experimental material is also somewhat limited—thus, if accurate intensity measurements for the (101) and (100) faces were available, we should probably reduce the possible errors in the values of β and α_2 still more.

In Table VI. are given the values of A^2 and the calculated and observed intensities corresponding to $\beta = 30°$ and $\alpha_2 = 60°$ for the faces (111) and (101).

TABLE VI.

	(111)			(101)		
n.	A^2.	I_{cal}.	I_{obs}.	A^2.	I_{cal}.	I_{obs}.
1......	2·73	91	80	9·5	100	100
2......	4·0	40	40	11·4	36	56
3......	9·6	38	40	5·6	7	8
4......	60·0	100	100			
5......	6·3	3	5			
6......	4	0·7	0			

The agreement between calculated and observed values is a very good one, and in view of the fact that the intensities of the other faces are also explained, we see that there can be no doubt that the lattice given in Table IV. is the right one, and that we have found very nearly the true values of α_2 and β.

The values found for these angles give the following values for the two parameters of the lattice :

$$\epsilon_1 = \frac{\alpha_1}{4\pi} = \frac{\pi - \beta}{4\pi} = \frac{5}{24},$$

$$\epsilon_2 = \frac{\alpha_2}{4\pi} = \frac{1}{12}.$$

The distances l_1 and l_2 (figs. 4, 5) from the Zr and Si atoms to the oxygen atoms will be

$$l_1 = \epsilon_1 a \sqrt{2} = 2 \cdot 71 \times 10^{-8} \text{ cm.}$$

$$l_2 = \epsilon_2 a \sqrt{2} = 1 \cdot 08 \times 10^{-8} \text{ cm.}$$

The distance from the Zr atom to one of the oxygen atoms associated with it is more than twice the corresponding distance for Si, a fact which may be due to the greater affinity between the Si and O atoms.

§ 9. *Rutile and Kassiterite.*

If the lattices of $(TiO_2)_2$ and $(SnO_2)_2$ belong to the type given in Table IV., the spectra should be derived from the formulæ (12) by inserting the corresponding values of the atomic numbers.

In both cases $N_1 = N_2 = N$, and for the (111) face we get

$$(111) \begin{cases} f_1(n) = N(1 + (-1)^n) + 2(N + 2N_3) \cos n \dfrac{\pi}{2} \\ \qquad\qquad + 2N_3 (\cos n\alpha_1 + (-1)^n \cos n\alpha_2). \\ f_2(n) = 0. \end{cases}$$

Now the Röntgen ray analysis shows that spectra of uneven order with regard to n disappear ; consequently we have for all values of q :

$$f_1(2q-1) = 0 = 2N_3 (\cos (2q-1)\alpha_1 - \cos (2q-1)\alpha_2),$$

which gives

$$\alpha_1 = \alpha_2 = \alpha.$$

This is an important result as it shows that in each of the two minerals all the metal atoms are identical as regards their relation to the oxygen atoms, and it is impossible to consider rutile say—as a titanum—titanate.

The amplitudes for the four cases considered will be

$$\left. \begin{aligned} A_{111} &= N + (-1)^n(N + 2N_3) + 2N_3 \cos 2n\alpha, \\ A_{110} &= N + N_3 + N_3 \cos 2n\alpha, \\ A_{101} &= N + 2N_3 \cos n\alpha, \\ A_{100} &= N + 2N_3 \cos 2n\alpha. \end{aligned} \right\} \quad \cdot \cdot \ (14)$$

The expression for A_{111}, A_{110}, and A_{100} will not be altered if we substitute $\pi - \alpha$ for α. Which of these two is the right value can be decided by means of the (101) spectrum.

For $(TiO_2)_2$ we find as the best value $\alpha = 111°\cdot5$, and for $(SnO_2)_2$ $\alpha = 112°\cdot5$.

In the case of SnO_2 it is only the (111) and (100) spectra which can be used for the determination of α; for the (110) spectrum is very nearly normal regardless of the value we give α, and the (101) spectrum is determined from a very small face, which will cause the observed first-order spectrum to be too weak.

In Table VII. are given the values of A^2 and K and the calculated and observed intensities.

The agreement is a very good one; thus the lattice given in Table IV. can explain the typical distribution of intensities observed.

TABLE VII.

$(TiO_2)_2$, $\alpha = 111°\cdot5$.

	(111)				(101)		
k.	A^2.	I_{cal}.	I_{obs}.	k.	A^2.	I_{cal}.	I_{obs}.
100	2·99	100	100	100	1·02	100	100
20	14·6	98	100	20	0·41	8	6
7	0·14	0·3	0	7	5·15	35	11
3	7·55	7·7	5	3	2·13	6	1
	(100)				(110)		
100	0·42	100	100	100	9·32	100	100
20	2·08	98	85	20	14·6	31	50
7	4·00	66	35	7	19·3	14	16
3	0·14	0	0	3	7·55	2·4	3

$(SnO_2)_2$, $\alpha = 112° 5$.

	(111)				(100)		
100	2·92	18·5	17	100	5·85	100	100
30	52·5	100	100	30	9·82	51	60
12	0·1	0	0	12	14·75	30	28
5	39·1	12·5	13	5	4·55	4	4

The results of the calculation are collected in Table VIII., giving the parameters ϵ and the distances l (figs. 4, 5) for the three crystals.

TABLE VIII.

Crystal.	a.	ϵ.	l.
ZrSiO$_2$ { Zr ...	150°	5/24	$2\cdot71° \times 10^{-8}$
{ Si ...	60°	1/12	1·08 ,,
(TiO$_2$)$_2$	111°·5	0·155	1·99 ,,
(SnO$_2$)$_2$	112°·5	0·157	2·08 ,,

Photographs of a model of the zircon lattice are shown in Plate III.

§ 10. *The Molecular Structure of the Lattice.*

The Röntgen-ray analysis has shown that crystals are built up of atomic lattices; and in a number of cases previously treated by W. H. and W. L. Bragg the arrangement of the atomic lattices has left no room for such a thing as a molecule. Suppose, for instance, that in a crystal of rock-salt we fix our attention to a certain Na atom, we cannot from the geometrical arrangement tell which Cl atom is associated with it. This fact, however, does not without further proof necessarily involve any fundamental change in our conception of the chemical binding as taking place between pairs of atoms (Na–Cl).

The atoms might possibly be connected up in pairs in such a way that all requirements of symmetry were fulfilled.

In the case of rock-salt and similar substances there should be *four* pairs of simple cubic lattices, and the lines connecting each pair should be arranged with cubic symmetry; but as we have three equal directions in the crystal and four pairs, such an arrangement *does not seem possible.*

If, however, we regard our lattice for the Zircon group, we notice that each of the Zr or Si atoms is associated with two oxygen atoms; thus the groups SiO$_2$ and ZrO$_2$ form a kind of "molecular elements" of the lattice. This is not merely a way of regarding the geometrical arrangement of the atoms; but we have reason to believe that the groups SiO$_2$ and ZrO$_2$ form chemically saturated compounds. First of all, the fact that the oxygen atoms are closer to the Si than to the Zr atoms goes to support this view, and, further,

a peculiarity with the geometry of the lattice will make the assumption of molecules almost a necessity.

Let us consider the arrangement of atoms in the (110) plan of zircon, fig. 5. The triangle (a b c) has a Zr atom in two of its corners and a Si atom in the third. Now an oxygen atom d belonging to the Zr atom a will—on account of the geometry found for the lattice—have equal distances to the Zr atom b and the Si atom c (fig. 5). Now the chemical-affinity forces must necessarily be different for (Zr–O) and (Si–O), and if such forces were acting between the oxygen atom d and any of the atoms c and b, we cannot explain an equilibrium position of the oxygen atom d which makes the distances (d–b) and (d–c) equal.

§ 11. *The Structure of Thorite.*

As mentioned in the introduction, the mineral thorite ($ThSiO_4$) also belongs to the Zircon group. This mineral, however, occurs in the so-called "metamict" form, which indicates a state in which the outer appearance of a crystal is preserved, but the substance itself has in the course of time become isotropic.

Thus the crystals, when examined with polarized light, give no indication of an optical axis, and it seems as if the atomic arrangement in a lattice has become unstable.

Now it would be a matter of interest to see how these crystals behave towards Röntgen rays. Do they give any reflexion? Or does a "metamict" crystal possess any trace of its original lattice?

I have made a series of experiments with a number of different minerals to investigate this point. A full account of these experiments will be given later. In this connexion I shall only mention that the mineral thorite gave no X-ray reflexion at all, although several very fine crystals were tested. Thus the Röntgen-ray analyses have shown that the lattice of thorite was completely broken down, and only the outer form has been preserved to indicate the atomic framework which once existed in the crystal. All symmetry properties, however, go to support the view, that the atoms must have been arranged in a lattice of the zircon type.

§ 12. *Remarks regarding the Intensities of the Normal Spectrum.*

W. H. Bragg and W. L. Bragg have found that the intensities of a normal spectrum gradually diminish with increasing order. As an average they put the relative

intensities equal to 100, 20, 7, 3 for the orders 1, 2, 3, 4.
These numbers, however, contain the influence of tem-
perature, which will tend to diminish the intensities of
higher order as compared with those of low order. Cor-
rected for temperature effect the intensities should be
approximately inversely proportional to the square of the
order number. As also apparent from the way in which
Bragg has stated the law, it can only be considered as
tentative and as a first approximation ; and I want here to
give some facts which indicate that the intensity law cannot
be quite so simple.

In the case of silver we have to deal with well-defined
crystals of only one element, and the two faces considered
(100) and (111) give both a normal spectrum * ; but the
intensity falls off much more rapidly for the first than for
the second face.

The face (111) gives an abnormally slow rate of fall with
increasing order. I have made a careful examination of
this point, comparing the first and second order of the two
faces, but could only confirm the result first obtained. Also
the (111) faces of gold and lead show the same abnormally
slow rate of fall. The results of the intensity measurements
are given in Table IX.

TABLE IX.

	Face.	Opening of slit.	Order.		
			1.	2.	3.
Silver ....{	(100)	1 mm.	100	20	7
	,,	,,	100	25	
	,,	0·5 mm.	100	19·5	
	(111)	1 mm.	100	51	11
	,,	,,	100	50	
	,,	0·5 mm.	100	35	
Gold ....{	(111)	—	100	35	
	,,	0·5 mm.	100	48	
Lead	(111)	—	100	49	

Also the face (110) of the Zircon group gives an
abnormally slow rate of fall of the intensities, even when
we take into account the effect of the oxygen atoms. Thus
in the case of tinstone, where the oxygen atoms can have
very little influence, the distribution corrected for the

* Vegard, Phil. Mag. Jan. 1916.

disturbing influence of oxygen should be 100, 62, 30, 8 of a normal spectrum of the orders 1, 2, 3, 4.

As, in the case of silver, the value of θ occurring in the Debye temperature factor should be the same for both faces, the rate of fall of the intensity will be different for face (100) and (111) of silver, even if we correct for temperature in the way given by Debye.

So long as we know so little about the cause of the intensity variation, it will be difficult to say anything definite with regard to the explanation of the observed differences.

It might be possible that the temperature factor is different for different faces even in the case of a cubic crystal. On account of the different elastic properties along different point-planes, such an explanation might not be unlikely. But if it should be impossible to account for the difference of intensity variation by differences of the temperature factor, we should probably have to suppose that the atoms had different reflexion properties in different directions.

Summary.

1. The lattice of *gold* and *lead* has been determined, and found identical with that of copper and silver.

2. The structure of the Zircon group has been completely determined. The Si as well as the Zr atoms are arranged in tetragonal lattices of the *diamond type*. In the case when Si and Zr are replaced by identical atoms Ti or Sn, we get a simple *prism-centred* lattice for the metallic atoms.

3. The tetragonal structure is not *produced by symmetry properties of the atomic centres, but by the tetragonal arrangement of the oxygen atoms.*

4. The lattice has a sort of *molecular structure* with molecules of the type MO_2, where M is an atom of Si, Zr, Ti, or Sn. The three atoms forming one molecule are situated on a straight line and with M in a central position. This line might be called the molecular axis.

The positions of the oxygen atoms are determined, when we know the directions of the molecular axes and the distance to the central atom M (molecular distance). The fact that the molecular distance is different for different central atoms M, as also certain geometrical relations of the zircon lattice, goes to support the view that the groups MO_2 form chemically bound molecules.

5. For all the minerals considered, the molecular axes are equally arranged and are always perpendicular to the tetragonal axis, which accounts for the fact that the ratio c/a is smaller than unity and almost equal for all minerals.

6. The " metamict" crystal of thorite gave no X-ray reflexion. The lattice is completely destroyed.

7. Experiments on the intensities of the normal spectrum have shown that different faces of the same crystal give a different law of the variation of intensities with increasing order.

I have much pleasure in thanking Professor W. C. Brögger for lending me, from the excellent collection of his laboratory, the crystals necessary for this research, as also for the kind interest he has taken in the work.

I am also very much pleased to thank Mr. H. Schjelderup for his most valuable assistance in making the observations on which the present work is based.

Physical Institute, Christiania.
        March 31, 1916.

VII. *On Aerial Waves generated by Impact. By* SUDHAN
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    Scholar in the University of Calcutta**.

1. *Introduction.*

HERTZ, in his well-known paper† on the collision of elastic solids, shows that when two bodies impinge on each other with moderate velocities, the elastic distortions are more or less entirely localized over the region of contact, and that the duration of impact, though in itself a very small quantity, is a large multiple of the gravest period of free vibrations of either body. It follows, therefore, that no appreciable vibrations of the solids are set up by the impact, and that all parts of the impinging bodies, except those infinitely close to the point of impact, move as parts of rigid bodies.

In a recent paper ‡ Lord Rayleigh has investigated the circumstances of the first appearance of sensible vibrations in the case of two impinging spheres, and his results seem to show that if vibrations are excited at all, the leading term in the radial displacement at the point of contact during the

* Communicated by Prof. C. V. Raman, M.A.
    † Hertz's ' Miscellaneous Papers,' English Edition, p. 146. [See also Love's ' Treatise on Elasticity,' Second Edition, p. 195.]
    ‡ Lord Rayleigh, "On the Production of Vibrations by Forces of Relatively Long Duration with Application to the Theory of Collisions," Phil. Mag. vol. xi. pp. 283–291 (1906). ['Scientific Papers,' vol. v. pp. 292–299.]
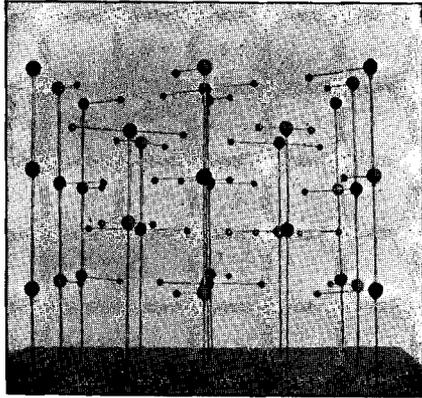
a.
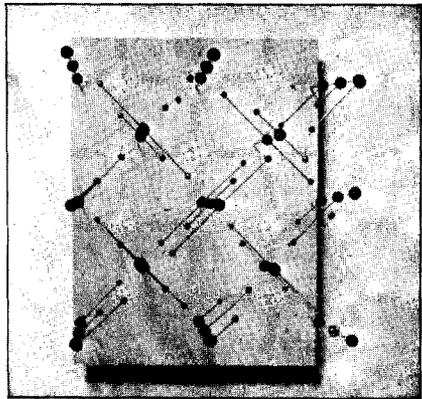
b.

Zircon lattice.

a in the direction of the *a*-axis.

b　　,,　　,,　　,,　*c*-axis.