

*X-Ray Analysis of the Crystal-Structure of Rutile and
Cassiterite.**

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The present paper deals with the results obtained in the investigation of the atomic structure of rutile and cassiterite by the X-ray spectrometer.

A detailed account of the method has been given by Prof. Bragg and his son, W. L. Bragg, in a series of papers communicated to the Royal Society. It consists essentially in allowing a narrow beam of monochromatic X-rays—in this case the rhodium rays—to fall on the face of the crystals, mounted on a spectrometer table, the axis of rotation of which passes through the face of the crystal. The beam is “reflected” by the atom planes parallel to this face, and thence passes into an ionisation chamber, containing methyl bromide in order to increase the ionisation current. The setting of crystal and chamber with regard to the incident beam corresponds to that for which ordinary light is reflected.

If θ = glancing angle of incidence; d = distance between the reflecting planes; λ = wave-length of the reflected wave; then Bragg has shown that the following formula holds—

$$2d \sin \theta = n\lambda, \quad \text{where } n = \text{order of the spectrum.}$$

Hence, since the beam is mainly monochromatic, we shall get a maximum or “special” reflection at that angle for which the characteristic rhodium ray is reflected according to the above equation.

Thus, knowing λ for rhodium, we can obtain the spacings of the atom planes parallel to the various faces from a determination of the angles of special reflection from those faces.

Before proceeding to give results, it may be advantageous to describe the crystals so as to render the nomenclature clear.

Rutile (TiO_2) and cassiterite (SnO_2), with which is usually classed zircon (ZrSiO_4), crystallise in the holohedral class of the tetragonal system. Fig. 1 represents a typical crystal of this group, and the crystallographic nomenclature may be conveniently explained with reference to it. Thus the plane OAD is called the 111 plane, and the intercepts of this face on a set of three mutually perpendicular axes give the ratios of the axes to which the crystal is referred.

* An account of research work carried out in the Memorial Physical Research Laboratory of the University College of South Wales and Monmouthshire, Cardiff.

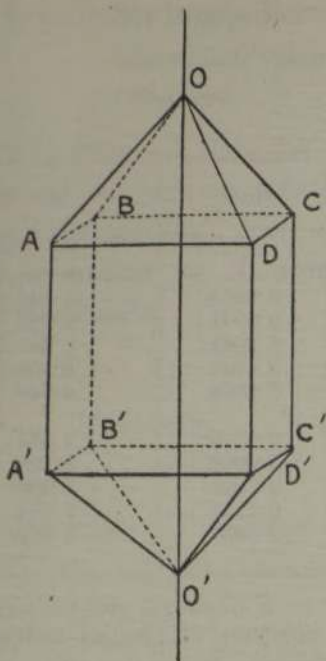


FIG. 1.

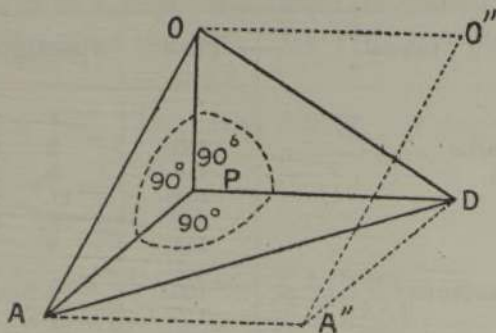


FIG. 2.

The symmetry of the crystal is such that it possesses:

- (a) A vertical axis of fourfold symmetry.
- (b) Four vertical planes of symmetry.
- (c) One equatorial plane of symmetry.

Hence the vertical axis is naturally taken to coincide with the axis of fourfold symmetry OO' , and the two equal horizontal axes as parallel and perpendicular to AC .

Thus (fig. 2)—

The ratios of the axes are as $PD : PA : PO$.

For rutile " " 1 : 1 : 0.644.

For cassiterite " " 1 : 1 : 0.67.

The other planes are referred to as follows:—

Plane.	Name.
$ACC'A'$ (fig. 1)	100
$ADD'A'$ (fig. 1)	110
$OAA''O''$ (fig. 2)	101
$ABCD$ (fig. 1) or PDA (fig. 2)	001

Both crystals have cleavage planes parallel to the 100, and also to the 110 faces, and are striated vertically on those faces.

For cassiterite	$\theta_{110} = 5^{\circ} 10'$
Calculated value for rutile	$\theta_{110} = 5^{\circ} 19'$
Observed " "	$\theta_{110} = 5^{\circ} 24'$

We may also calculate the number of molecules contained in the rectangular prism cut out between two basal planes by the 110 , $1\bar{1}0$, $\bar{1}10$, $\bar{1}\bar{1}0$ planes taken consecutively.

If m = mass of H atom; M = mol. wt.; ρ = density of crystal; N = no. of mols.,

$$N = \frac{d_{110}^2 \cdot d_{001} \cdot \rho}{M \cdot m}$$

For rutile $M = 80$; $\rho = 4.18$. Hence $N = 0.486$.

„ cassiterite $M = 151$; $\rho = 6.9$. „ $N = 0.506$.

since $d_{100} = \sqrt{2} d_{110}$, then the number contained in the elementary volume is 0.972 and 1.01 for rutile and cassiterite respectively, each of which is very approximately equal to 1.

Bearing of the Results on the Structure of Rutile and Cassiterite.

In applying the results to construct a model of the space-lattice representing the configuration of the atoms, complications arise owing to there being two kinds of atoms in the molecule. We have to bear in mind that the presence of the oxygen atoms may influence powerfully the spectra due to the metal atoms alone. Indeed, the Messrs. Bragg have adduced strong evidence in support of the view that an atom contributes to the amplitude of the reflected beam in proportion to its weight. With regard to the case under consideration, we have two isomorphous crystals in which the atomic weights of the metals composing them differ widely. Thus titanium has atomic weight 48, while that of tin is 119. Hence, while we might expect the oxygen in rutile to modify the spectra due to the metal atoms alone, even to the extent of cutting out some of the orders, we can fairly safely regard at least the position of the spectra given by cassiterite as being that characteristic of the lattice on which the metal atoms are built. As a matter of fact, the spectra in the two cases are remarkably similar.

Let us now attempt to construct a model which will explain the results obtained. From a consideration of the Bravais space lattices we are naturally led to try one of the two lattices characterising the tetragonal system of the form and dimensions shown in the diagram (for rutile), figs. 3 and 4.

It might at first sight be supposed that the ratio of d_{100} to d_{110} would decide between them; for in fig. 3 $d_{100} = \sqrt{2}d_{110}$, while in fig. 4 $d_{100} = d_{110}/\sqrt{2}$.

Owing, however, to the ambiguity in choosing the horizontal axes, this criterion does not avail.

But an examination of these two lattices shows that neither will explain

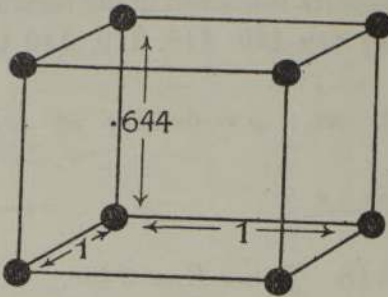


FIG. 3.

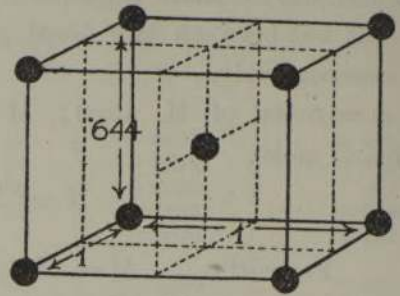


FIG. 4.

all the results. For taking fig. 3, we note that we have to associate 2 molecules with each point of the lattice as shown by the above calculation. Assuming 2 molecules associated with this elementary volume and knowing θ_{100} we can calculate the angles of reflection from the other faces.

The disagreement between this theory and experiment is shown below for rutile:—

Table II.

Face.	Calculated.		Observed.	
	°	'	°	'
110	5	20	5	24
001	5	55	11	56
101	7	0	6	58
111	7	58	4	0

Striking differences occur in the case of the 001 and the 111 planes, where we notice that the calculated values are half and double the observed values respectively. Similar objections may be urged against fig. 4.

Any lattice selected must not only give the right spacing, but also the right amount of mass per elementary volume; while, in addition, it must conform to the symmetry of the crystal as a whole, namely, the holohedral class of the tetragonal system.

Two lattices, or possibly three, appear to satisfy the requirements of the problem. They are shown in figs. 5, 6, and 7.

The arrangement of the planes and relative spacings of the reflecting planes for fig. 6 are shown in fig. 8.

In order to test these lattices further we may examine the intensities of the different orders.

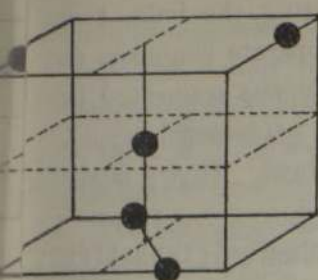


FIG. 5.

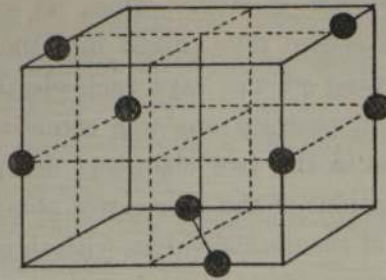


FIG. 6.

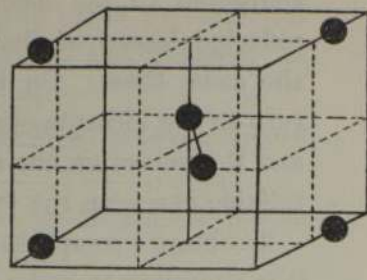


FIG. 7.

Plane.

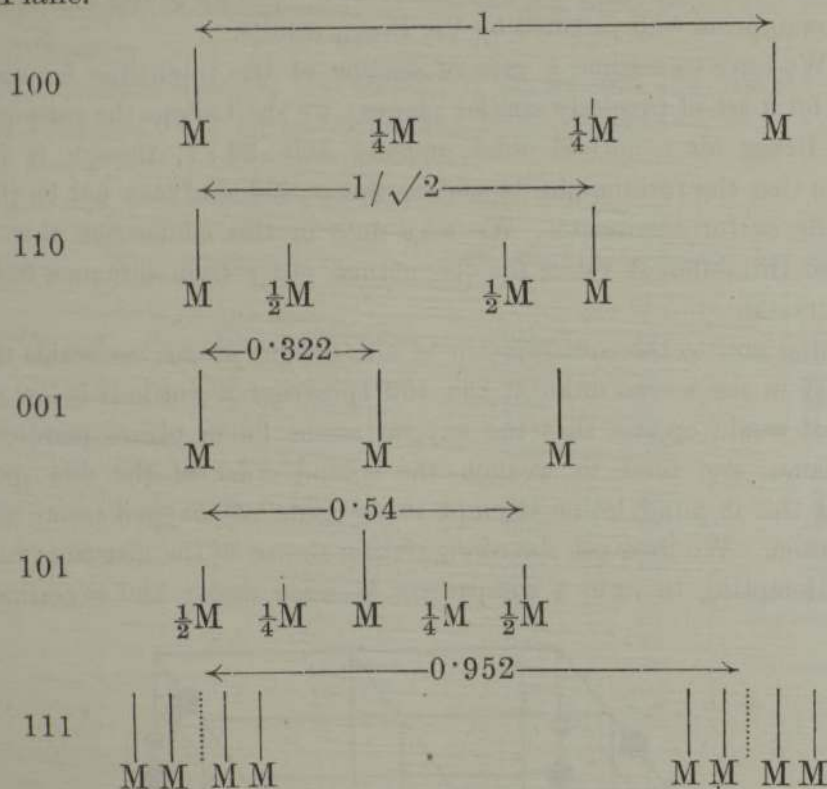


FIG. 8.

The method of determining the ratios was to set the crystal and chamber for a reflection, using a narrow incident beam, the slit of the chamber being sufficiently wide to take in the whole of the reflected radiation. The ionisation current was determined for all positions in the neighbourhood of the maximum by turning the crystal through successive small steps. The chief difficulty is due to the variation in intensity of the source. In order to obviate this as much as possible, a second slit was cut in the lead box containing the X-ray bulb. The beam issuing through this was reflected by a crystal into another ionisation chamber, the electrode of which could be

connected to the electroscope at will. Thus, on exciting the bulb, two reflected beams of characteristic rays passed into the separate chambers at the same time. On turning off the rays each electrode was connected in turn to the electroscope (in practice one was connected permanently to it), and the ionisation currents in the two chambers determined. Thus a fairly reliable check on the variations of the source was obtained.

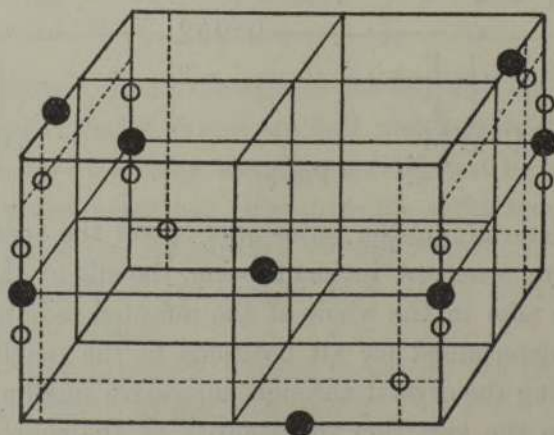
To obtain a comparison of theoretical values with those observed (Table III), it is necessary to make assumptions in two directions:—

(1) The scattering power of an atom: we shall assume that an atom contributes to the amplitude of the reflected beam in proportion to its mass—an assumption well justified by the Bragg results.

(2) We have to assume a rate of decline of the intensities for successive orders for a set of precisely similar planes: we shall adopt the ratio given by W. L. Bragg for a normal order, namely 100 : 20 : 7, though it is quite possible that the ratio might depend on the crystal, and may not be the same for rutile as for cassiterite. We may note in this connection that Vegard obtained two different ratios for the normal order from different faces of a silver crystal.

Turning now to the configuration of the oxygen atoms, we notice that the intensity in the second order of the 100 spectrum of rutile is below normal. Hence it would appear that the oxygen atoms lie in planes parallel to the 001 planes, and tend to weaken the second order of the 001 spectrum. Bearing this in mind, let us attempt to associate two oxygen atoms with one metal atom. We then get the configuration shown in the diagram (fig. 9).

In attempting to form a comparison between theory and experiment, we



● = metal atom
○ = oxygen „

FIG. 9.

have to remember that the comparison must necessarily be of an empirical character, owing both to the assumptions made and to the difficulty of comparing the ratios experimentally.

In view of the above considerations, a very close agreement between theory and experiment cannot be expected.

The following results show the agreement obtained by taking the lattice represented by fig. 9, assuming—

(1) That the metal atom between two consecutive 100 planes is displaced $0.403d$ and $0.375d$ for rutile and cassiterite respectively.

(2) The horizontal displacement of the oxygen atom is $0.111d$ from the nearest 100 plane.

(3) The distance between the metal 001 planes and the nearest oxygen plane is $0.25d$ and $0.32d$ for cassiterite and rutile respectively.

Table III.—Comparison of Intensities.

Crystal.	Plane.		1st order.	2nd order.	3rd order.
Cassiterite	100	Calculated ...	100	26	12
		Observed.....	100	25	18
	110	Calculated ...	100	58	40
		Observed.....	100	50	25
	001	Calculated ...	100	16	Not observed
		Observed.....	100	19	
Rutile	100	Calculated ...	100	27	8
		Observed.....	100	33	16
	110	Calculated ...	100	49	10
		Observed.....	100	50	20
	101	Calculated ...	100	30	Not observed
		Observed.....	100	30	
	001	Calculated ...	100	12	Not observed
		Observed.....	100	10	
	111	Calculated ...	40	100	Not observed
		Observed.....	50	100	

On the whole, there is a general agreement between the calculated and observed values of the intensities, and the calculated values are sufficient to account for the variation in the observed intensities of the spectra. As regards the other two lattices (figs. 5 and 7), it may be stated that they do not give an approximate agreement between the calculated and observed intensities.

The model presents many interesting features :—

(1) It possesses the full symmetry of the holohedral class of the tetragonal system.

(2) It has a tetragonal screw axis.

(3) Both the 100 and the 110 planes are indicated as cleavage planes.

(4) We note also that, in a sense, the crystal is enantiomorphous, two parts being obtained by a reflection across a 100 plane. This is interesting, on account of the fact that Bravais considered that crystals which showed twinning, such as that peculiar to rutile and cassiterite, to be of this character.

(5) The peculiar vertical arrangement of the metal atoms in the direction parallel to the axis may possibly be connected with the striations observed on the vertical faces.

NOTE.—After the above observations had been made and embodied in a paper, results obtained by a similar method were published by Dr. Vegard* on the structure of this group of crystals. His observations were in agreement with most of those given above, but differed in one or two vital respects, namely, the position of the reflections from the 100 and 111 faces, his values being twice as great as those given above. It was therefore thought highly advisable to repeat the observations on this point. For this a new X-ray tube had to be procured. Owing, however, to the war, considerable delay was caused, which prevented the confirmation being undertaken earlier. When, indeed, this became possible, all doubts about there being a reflection from the 100 face, as given above, were at once dispelled. As regards the reflection from the 111 faces, reflection at the angle stated above is quite definite in the case of rutile, though for cassiterite it is very small; still, calculation shows that this should be so.

It will be seen that these half-angle reflections can find no place in the model suggested by Vegard. It may be further noticed† that this model satisfies the crystal symmetry only on the assumption that certain elements of optical symmetry are of the nature of statistical effects, while the smaller wave-length of X-rays reveals an actual absence of these elements.

The good agreement obtained by Vegard between calculated and observed intensities depends partly on his assumptions of a different normal order (100:30:12) for cassiterite and zircon from the more ordinary ones (100:20:7) adopted for rutile. It may be pointed out, with respect to the unusual values (100:50) found by Vegard for the presumably normal order in the case of the 111 planes of silver, that narrowing the slit changed the ratio to 100:35. Without knowing the exact details of the experimental arrangements, it is difficult to say what the precise meaning of this change may be; it may be noted that the glancing angles for the 111 planes are smaller than those for the 100 planes, and it is not difficult to see that, with

* 'Phil. Mag.,' July, 1916.

† *Loc. cit.*, p. 81.

small glancing angles, under certain arrangements of the apparatus, an excessive slit width would lead to a fictitiously high ratio of the second to the first order spectrum.

The crystals used in the above investigation were excellent specimens, lent me by Dr. Hutchinson, of Cambridge, to whom my best thanks are due. I am also indebted to Prof. Bragg for the very kind interest he has shown in the work, and to Principal Griffiths, for his sympathy and kindness in considering my requirements. Further, I desire to express my heartiest thanks to Captain J. H. Shaxby for the valuable guidance and assistance he has rendered me throughout the work.

The Composition of the X-Rays from Various Metals.

By G. W. C. KAYE, M.A., D.Sc., Captain R.E. (T.).

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(From the National Physical Laboratory.)

In a paper published in the 'Philosophical Transactions'* in 1908, the writer described some experiments on the X-rays emitted by a variety of metals when used as anticathodes in an X-ray bulb. Among the results established was the homogeneity of a large proportion of the X-rays when the bulb was very "soft." The absorption curves of the several homogeneous radiations revealed their identities with the characteristic "secondary" radiations which Barkla and Sadler had then recently discovered.

The experiments described in the present paper are an extension of the above, and were carried out partly at the Cavendish Laboratory in 1908 and partly at the National Physical Laboratory just prior to the war. The writer's military duties have prevented the continuation of the work, and the results are now put on record in the hope that they may help to further the progress of the subject, to which the more precise method of the crystal-spectrometer has given a great impetus from a different point of view.

Apparatus.

The apparatus employed is sufficiently explained by fig. 1, which is approximately to scale. As in the earlier experiments, the various anti-

* Series A, vol. 209, p. 123.