

## XV. The crystal structure of brookite.

By

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(With 6 figures.)

### I. Introduction.

In the study of the structure of a crystal with X-rays the effort has been made by many workers, especially Wyckoff and Dickinson in America, to eliminate rigorously all but one of the possible atomic arrangements consistent with the smallest unit of structure permitted by the experimental data, without reference to whether or not the arrangements were chemically reasonable or were in accord with assumed interatomic distances. The importance of this procedure arises from the certainty with which its results can be accepted. For although structure determinations by less rigorous methods have been found to be false, no important error has yet been detected in any investigation which interpreted photographic data solely with space-group theory aided by merely qualitative assumptions regarding the factors affecting the intensity of X-ray reflection. It would accordingly be desirable to conduct all structure determinations by this method; but unfortunately the labor involved in its application to complex crystals, involving more than a very few parameters, makes this impossible. Furthermore, if several different atoms are present in the structure, it is often necessary to make quantitative assumptions regarding their relative reflecting powers, so that for this reason too the rigorous method cannot be used.

But complex crystals are of great interest, and it is desirable that structure determinations be carried out for them even at the sacrifice of rigor. The method which has been applied in these cases is this: one atomic arrangement among all of the possible ones is chosen, and its agreement with the experimental data is then examined. If the agreement is complete or extensive, it is assumed that the structure is the correct one. Striking regularities in the intensities of reflection from simple planes may suggest an approximate structure. This occurred in

Dickinson's study of tin tetraiodide<sup>1)</sup>; he then considered values of the five parameters involved which differed only slightly from those suggested by the intensities of simple reflections, and found a set giving complete agreement with the Laue photographic data. On account of the large amount of experimental information accounted for by it, this structure can be confidently accepted as correct. In other cases it is necessary to make use quantitatively of relative reflecting powers or  $F$ -curves, and often agreement is found between the assumed structure and data from rotation photographs or ionization chamber measurements only; then the structure can usually be accepted as approximately correct, the uncertainty depending upon the paucity of the experimental data or the lack of agreement with them.

As a result of the recent increase in knowledge of the effective radii of various ions in crystals, Professor W. L. Bragg has suggested and applied<sup>2)</sup> a simple and useful theory leading to the selection of possible structures. His fundamental hypothesis is this: if a crystal is composed of large ions and small ions, its structure will approximate a close-packed arrangement of the large ions alone, with the small ions tucked away in the interstices. In case all of the close-packed positions are not occupied by large ions an open structure results. To apply this theory one determines the unit of structure in the usual way, and finds by trial some close-packed arrangement of the large ions of known radius (usually oxygen ions with a crystal radius of about 4.35 Å) compatible with this unit. The other ions are then introduced into the possible positions in such a way as to give agreement with the observed intensities, and if necessary the large ions are shifted somewhat from the close-packed positions. With the aid of this close-packing method Bragg and his co-workers have made a promising attack on the important problem of the structure of the silicate minerals.

During the investigation of the structure of brookite, the orthorhombic form of titanium dioxide, another method of predicting a possible structure for ionic compounds was developed. This method, which is described in detail in Section III of this paper, depends on the assumption of a coordination structure. It leads to a number of possible simple structures, for each of which the size of the unit of structure, the space-group symmetry, and the positions of all ions are fixed. In some cases, but not all, these structures correspond to close-packing of the large ions; when they do, the method further indicates

1) R. G. Dickinson, J. Am. Chem. Soc. **45**, 958. 1923.

2) W. L. Bragg and G. B. Brown, Pr. Roy. Soc., A, **110**, 34. 1926; W. L. Bragg and J. West, *ibid.*, A, **114**, 450. 1927.

the amount and nature of the distortion from the close-packed arrangement.

The general method of investigation which we used is the following. Spectral photographs from the three pinacoids provided accurate dimensions of the possible units of structure. Data from Laue photographs then led to the determination of the smallest allowable unit, and the presence and absence of reflections on Laue photographs served as criteria in finding the space-group symmetry. (Laue photographs rather than rotation photographs were used because the chance of error in assigning indices to Laue spots is very small<sup>1</sup>.) On applying the coordination theory we found that one of the predicted structures had the same space-group symmetry and unit of structure as the crystal itself. The predicted parameter values agreed reasonably well with the intensities of reflections on rotation photographs, and better agreement was obtained by changing one of the nine parameters slightly. On account of lack of knowledge of  $F$ -curves the intensities of Laue spots were not accounted for.

## II. The unit of structure and space-group.

Three forms of titanium dioxide,  $TiO_2$ , are known. Of these the crystal structures of the two tetragonal forms, rutile and anatase, have been thoroughly investigated<sup>2</sup>); in each case only one parameter is involved, and the atomic arrangement has been accurately determined. The third form, brookite, is orthorhombic, with axial ratios

$$0,8446 : 1 : 0,9444.$$

Data obtained from photographs of the  $K$ -radiation of molybdenum reflected from the ground pinacoids of a brookite crystal (variety arkansite from Magnet Cove, Ark.)<sup>3</sup>) are given in Table I. These lead to a unit with  $d_{100}/n_1 = 2,294 \text{ \AA}$ ,  $d_{010}/n_2 = 2,748 \text{ \AA}$ , and  $d_{001}/n_3 = 1,284 \text{ \AA}$ , in which  $n_1$ ,  $n_2$ , and  $n_3$  are the orders of reflection of the first lines on the photographs. Laue photographs were taken with the incident beam of X-rays at various small angles with the normal to (100) of a thin plate of brookite tabular on {100} (from Riedertobel, Uri Canton,

1) As an example of an incorrect space-group determination resulting from error in assigning indices to reflections on rotation photographs mention may be made of the assignment of olivine to  $V_h^5$  by Rinne, Leonhardt, and Hentschel (Z. Krist. **59**, 548. 1924). Bragg and Brown (Z. Krist. **63**, 538. 1926) determined the space-group of olivine to be  $V_h^{16}$  and pointed out the source of the previous error.

2) L. Vegard, Phil. Mag. **1**, 1151. 1926; G. Greenwood, *ibid.* **48**, 654. 1924; M. L. Huggins, Phys. Rev. **27**, 638. 1926.

3) We are indebted to Mr. René Engel for the crystals used in this research.

Table I.  
Spectral data.

$(hkl)$	Order of Reflection	Line (MoK)	Angle of Reflection	$d/n$
(400)	$2n_1$	$\beta$	$7^\circ 54,5'$	$4,586 \text{ \AA}$
	$2n_1$	$\alpha$	$8 \ 53,5$	$4,592$
	$3n_1$	$\alpha_1$	$13 \ 24$	$4,580$
	$3n_1$	$\alpha_2$	$13 \ 29$	$4,584$
	$4n_1$	$\gamma$	$15 \ 41$	$4,585$
	$4n_1$	$\beta$	$15 \ 59$	$4,583$
	$4n_1$	$\alpha_1$	$17 \ 59$	$4,584$
	$4n_1$	$\alpha_2$	$18 \ 6$	$4,582$
(010)	$n_2$	$\beta$	$6 \ 40$	$2,718$
	$n_2$	$\alpha$	$7 \ 30,5$	$2,716$
	$2n_2$	$\gamma$	$13 \ 14$	$2,718$
	$2n_2$	$\beta$	$13 \ 25$	$2,720$
	$2n_2$	$\alpha_1$	$15 \ 5$	$2,721$
	$2n_2$	$\alpha_2$	$15 \ 14$	$2,718$
(004)	$n_3$	$\gamma$	$13 \ 58$	$1,2835$
	$n_3$	$\beta$	$14 \ 14$	$1,2833$
	$n_3$	$\alpha_1$	$16 \ 0$	$1,2844$
	$n_3$	$\alpha_2$	$16 \ 6$	$1,2840$

Switzerland). The short wave-length limit of X-radiation present in the incident beam was  $0,24 \text{ \AA}$ ; values of  $n\lambda$  calculated for Laue spots on the basis of the unit obtained by putting  $n_1 = n_2 = n_3 = 1$  were found often to be much smaller than  $0,24 \text{ \AA}$ , so that this unit cannot be the correct one. The smallest unit which will account for the Laue data is that with  $n_1 = 4$ ,  $n_2 = 2$ ,  $n_3 = 4$ ; i. e., with<sup>1)</sup>

$$d_{100} = 9,166 \text{ \AA}, \quad d_{010} = 5,436 \text{ \AA}, \quad d_{001} = 5,135 \text{ \AA}.$$

The presence of all observed Laue spots, produced by planes belonging to over two hundred different forms, is accounted for by this unit. (Representative Laue data are recorded in Table II.) No evidence was found for the existence of a larger unit; hence this unit may be accepted as the true one. All indices used in this paper (including Table II) are referred to the axes of this unit of structure. The unit contains  $8TiO_2$ ; the density calculated from the X-ray data is  $4,12$ , within the range  $4,03$ — $4,22$  of the experimental determinations reported in Groth,

<sup>1)</sup> During the preparation of this manuscript, a note has appeared (A. Schröder, Z. Krist. **66**, 493, 1928) giving the dimensions of the unit of structure for brookite as  $a = 9,136 \pm 0,02$ ,  $b = 5,439 \pm 0,01$ ,  $c = 5,153 \pm 0,03 \text{ \AA}$ . No space-group determination or discussion of the atomic arrangement was reported.

Table II.

Laue data for  $n\lambda$  between 0,35 and 0,45 Å.

$(hkl)$	$d_{hkl}$	$n\lambda$	Estimated intensity
2 $\bar{4}$ 1	1,25 Å	0,42 Å	0,02
2 4 $\bar{4}$	1,20	,36	,5
1 4 $\bar{2}$	1,18	,44	,8
1 $\bar{2}$ 4	1,15	,44	,1
3 $\bar{4}$ $\bar{2}$	1,11	,37	,5
2 $\bar{4}$ 3	1,03	,40	a
2 3 $\bar{4}$	1,02	,37	1
3 $\bar{5}$ 1	1,00	,41	0,3
1 $\bar{1}$ 5	1,00	,44	,01
1 5 $\bar{2}$	0,99	,36	,1
4 $\bar{4}$ $\bar{3}$	,96	,42	,2
3 1 $\bar{5}$	,95	,36	,2
1 $\bar{2}$ 5	,95	,35	,1
2 5 $\bar{3}$	,89	,42	,4
4 $\bar{2}$ $\bar{5}$	,88	,35	,8
3 $\bar{5}$ 3	,87	,40	,5
2 $\bar{3}$ 5	,87	,41	,05
3 3 $\bar{5}$	,85	,38	,05
1 $\bar{1}$ 6	,84	,35	,15
1 1 6	,84	,43	,2
4 $\bar{6}$ 1	,83	,39	,15
5 $\bar{5}$ $\bar{3}$	,82	,41	,2
5 $\bar{6}$ $\bar{1}$	,80	,43	,1
3 $\bar{5}$ 4	,80	,37	,02
3 5 $\bar{4}$	,80	,43	,03
1 6 3	,79	,45	,2
5 $\bar{6}$ $\bar{2}$	,77	,36	,15
1 3 6	,77	,42	,2
2 7 $\bar{1}$	,75	,43	,05
1 5 5	,74	,42	,02
1 7 2	,74	,39	,2
1 4 6	,72	,40	,2
5 3 $\bar{6}$	,71	,45	,05
1 2 7	,70	,36	,1
2 $\bar{2}$ 7	,70	,35	,01
2 2 7	,70	,45	,05
3 $\bar{2}$ 7	,69	,44	,15
3 7 $\bar{3}$	,68	,40	,05
5 $\bar{7}$ 2	,68	,37	,05
7 $\bar{3}$ $\bar{6}$	,66	,43	,1
7 $\bar{7}$ $\bar{1}$	,66	,45	a
2 7 4	,65	,44	0,2
3 8 $\bar{1}$	,65	,44	,05

Table II (cont.).

$(hkl)$	$d_{hkl}$	$n\lambda$	Estimated intensity
4 6 $\bar{5}$	0,65 Å	0,38 Å	0,4
7 $\bar{7}$ $\bar{2}$	,64	,44	,15
7 $\bar{1}$ $\bar{7}$	,63	,44	,4
7 $\bar{2}$ $\bar{7}$	,62	,37	,03
6 $\bar{7}$ 4	,64	,44	,4
5 $\bar{4}$ 7	,61	,45	,05
4 8 $\bar{3}$	,60	,44	,03
2 3 8	,60	,37	,4
5 6 $\bar{6}$	,59	,36	,02
7 $\bar{8}$ 3	,57	,39	,04
3 7 6	,56	,43	,05
7 5 $\bar{7}$	,55	,44	,05
9 $\bar{4}$ $\bar{7}$	,54	,38	,02
4 2 9	,54	,43	,03
4 4 9	,54	,44	,03
5 · 10 · 2	,54	,45	,02
5 · 10 · $\bar{2}$	,54	,39	,02
40 · $\bar{1}$ · $\bar{9}$	,47	,36	,02
40 · 1 · $\bar{9}$	,47	,38	,03

and in good agreement with the experimental value 4,425 obtained by Schröder.

The presence of first-order reflections from all types of pyramidal planes (Table II) eliminates from consideration all space-groups based on any but the simple orthorhombic lattice  $I_0$ . Of these the following are further definitely eliminated<sup>1)</sup> by the occurrence of first-order reflections from the prism planes given in Table III:

$$C_{2v}^3, C_{2v}^6, C_{2v}^7, C_{2v}^8, C_{2v}^9, C_{2v}^{10}, \\ V_h^2, V_h^4, V_h^6, V_h^7, V_h^8, V_h^9, V_h^{10}, V_h^{12}, V_h^{13}, V_h^{14}, V_h^{16}.$$

If the structure is based on one of the space-groups

$$C_{2v}^1, C_{2v}^2, C_{2v}^4, C_{2v}^5, V_1, V_2, V_3, V_4, V_h^1, V_h^3, V_h^5, \text{ or } V_h^{11},$$

it is very difficult to account for the fact that no first-order reflections were observed from planes with  $h = 0$  and  $k$  odd,  $k = 0$  and  $l$  odd, or  $l = 0$  and  $h$  odd; these space-groups may accordingly be removed from consideration. But just these absences are required for any arrangement derived from  $V_h^{15}$ , which may hence be accepted as the correct space-group.

<sup>1)</sup> Space-group criteria are given by Bozorth and Pauling, J. Am. Chem. Soc. 47, 4568. 1925. Cf. also references in footnote 13, *ibid*.

Table III.

## Prism reflections.

a) Incident beam normal to (100).

$(hkl)$	$d_{hkl}$	$n\lambda$	Estimated intensity
1 4 0	1,33 Å	0,43 Å	a
1 0 4	1,26	,33	0,15
1 0 $\bar{4}$	1,26	,37	,20
2 0 5	1,00	,43	a
2 0 $\bar{5}$	1,00	,45	a
2 7 0	0,76	,28	0,03
4 7 0	,73	,49	a
4 $\bar{7}$ 0	,73	,44	a
4 0 $\bar{7}$	,70	,42	a
5 0 $\bar{8}$	,60	,44	0,02
b) Crystal tipped 14°			
0 3 4	1,70	0,47	a
0 3 2	1,47	,44	a
0 2 3	1,44	,42	3,5
0 4 1	1,31	,35	1,2
1 5 0	1,07	,48	a
0 4 3	1,06	,32	1,8
0 3 4	1,04	,31	a
1 0 5	1,01	,43	a
1 0 6	,85	,33	0,3
0 5 4	,82	,24	a
0 4 5	,81	,24	a
2 7 0	,76	,41	0,6
6 $\bar{7}$ 0	,69	,48	,2
3 0 8	,63	,38	,1
c) Crystal tipped 20°.			
0 2 $\bar{1}$	2,39	0,29	2
0 4 1	1,31	,47	1,9
0 4 $\bar{1}$	1,31	,27	0,5
0 1 4	1,24	,44	a
0 4 3	1,06	,44	0,3
0 5 1	1,06	,36	a
0 5 $\bar{1}$	1,06	,24	a
0 3 4	1,04	,43	a
3 $\bar{5}$ 0	1,02	,39	a
0 1 5	1,00	,34	a
3 0 $\bar{5}$	,97	,34	a
0 2 5	,96	,36	0,2
4 0 $\bar{5}$	,93	,49	a
1 0 6	,85	,40	0,5
0 5 4	,82	,34	a
0 4 5	,82	,33	0,1

Table III (cont.).  
c) Crystal tipped  $20^\circ$  (cont.).

$(hkl)$	$d_{hkl}$	$n\lambda$	Estimated intensity
5 $\bar{6}$ 0	0,84 Å	0,47 Å	a
5 0 $\bar{6}$	,77	,42	0,2
2 7 0	,76	,47	,6
4 0 7	,73	,32	a
2 0 7	,72	,43	a
6 $\bar{7}$ 0	,69	,42	0,17
3 0 8	,63	,43	,1
7 $\bar{8}$ 0	,60	,39	a
2 9 0	,59	,32	0,02
3 8 0	,50	,35	a

The coordinate positions for equivalent atoms provided by  $V_h^{15}$  are<sup>1)</sup>

$$4a: 0\ 0\ 0; \frac{1}{2}\ \frac{1}{2}\ 0; 0\ \frac{1}{2}\ \frac{1}{2}; \frac{1}{2}\ 0\ \frac{1}{2};$$

$$4b: \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}; 0\ 0\ \frac{1}{2}; \frac{1}{2}\ 0\ 0; 0\ \frac{1}{2}\ 0;$$

$$8c: x, y, z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \frac{1}{2} - x, \frac{1}{2} + y, z;$$

$$\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; x, \frac{1}{2} - y, \frac{1}{2} + z; \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z;$$

$$\frac{1}{2} + x, y, \frac{1}{2} - z.$$

Six parameters must be evaluated to determine the positions of  $8Ti$  and  $16O$  in the unit in case that both the no-parameter positions 4a and 4b are occupied, and nine parameters in case that all atoms are in positions 8c. A structure dependent on such a large number of parameters can not be determined by rigorous methods.

### III. The prediction of a structure with the coordination theory.

The structures of rutile and anatase, represented in Figs. 1 and 2, seem at first sight to have very little in common beyond the fact that each is a coordination structure, with six oxygen atoms about each titanium atom and three titanium atoms about each oxygen. On closer examination, however, it is found that from a certain point of view the structures are closely similar. Let us consider as the basis of the structures an octahedron with a titanium atom at its center and an oxygen atom at each corner. The rutile and anatase structures are both made of such octahedra sharing edges and corners with each other; in rutile two edges of each octahedron are shared and in anatase four. In both crystals the titanium-oxygen distance is a constant, with

1) R. W. G. Wyckoff, "The Analytical Presentation of the Results of the Theory of Space-Groups", Publ. Carnegie Institution No. 348, 1922.

the value  $1,95-1,96 \text{ \AA}$ . The basic octahedra are only approximately regular; they are in both rutile and anatase deformed in such a way as to cause each shared edge to be shortened from  $2,76 \text{ \AA}$  (the value for regular octahedra) to  $2,50 \text{ \AA}$ , other edges being correspondingly lengthened. (The distorted octahedra occurring in rutile and in anatase are indicated in Figs. 1 and 2.) Just such a distortion is to be expected, for the Coulomb repulsion of the two quadrivalent metal ions brought near each other when an edge is shared will cause the titanium-titanium distance to increase until the repulsion of the two oxygen ions defining

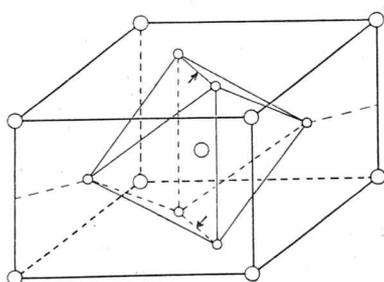


Fig. 1.

Fig. 1. The structure of rutile. Large circles represent the centers of titanium atoms, small circles those of oxygen atoms. One octahedron with oxygen atoms at its corners and a titanium atom at its center is shown; two of its edges, those indicated by arrows, are shared with adjoining octahedra.

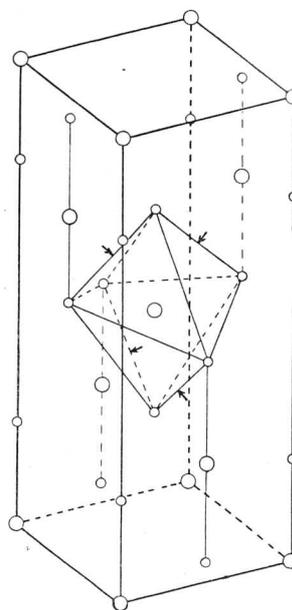


Fig. 2.

Fig. 2. The structure of anatase. Four edges of the octahedron shown, indicated by arrows, are shared with adjoining octahedra.

the shared edge becomes large enough to counteract the effect. The theoretical discussion<sup>1)</sup> of the rutile and anatase structures with the help of the known properties of ions has led to results which are in each case in quantitative agreement with the observed contraction of shared edges.

As a result of these considerations the following assumptions were made:

4. Brookite is composed of octahedra, each with a titanium atom at its center and oxygen atoms at its corners.

<sup>1)</sup> Linus Pauling, *Z. Krist.* **68**, 377. 1928.

2. The octahedra share edges and corners with each other to such an extent as to give the crystal the correct chemical composition.

3. The titanium-oxygen distance throughout is about  $1,95 \text{ \AA}$ . The octahedra are not regular, but are distorted in such a way as to maintain the titanium-oxygen distances constant and to shorten each shared edge to the length  $2,50 \text{ \AA}$ .

An infinite number of structures satisfy these conditions. The number of simple structures, that is, structures referable to a small unit, which do so is small. We made no attempt to consider exhaustively the possible simple structures, but instead investigated the two which presented themselves first. The second of these we have found to be the structure of brookite.

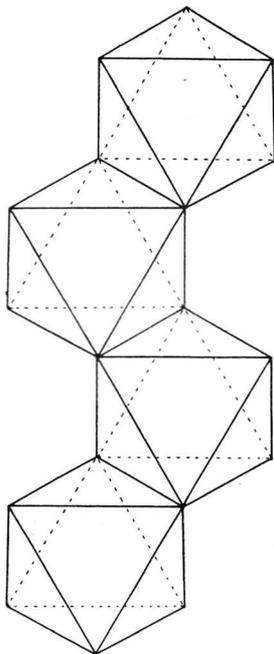


Fig. 3. A staggered string of  $(4 TiO_2)$  octahedra with shared edges.

In rutile there occur strings of octahedra in parallel orientation connected by shared edges; these strings, which extend in the direction of the  $c$ -axis, then are connected by sharing corners to form the complete crystal. This suggested that staggered strings such as are represented in Fig. 3, with two edges of each octahedron shared, might combine to form a reasonable structure. If the combination is effected by the sharing of corners alone the simple structure represented in Fig. 4 results. This structure, Structure *A*, has orthorhombic symmetry, and in fact the space-group symmetry  $V_h^{14}$ . Its unit of structure contains four octahedra  $(4 TiO_2)$ , and, if distortion is neglected, has the dimensions  $4,79 \text{ \AA}$ ,  $4,51 \text{ \AA}$ , and  $5,52 \text{ \AA}$ . It is not the structure of brookite.

The next simplest structure built from these staggered strings results if each octahedron shares one edge with an octahedron of an adjoining string. This structure is shown in Fig. 5. It is orthorhombic, and has the space-group symmetry  $V_h^{15}$ . The unit of structure contains eight octahedra  $(8 TiO_2)$ . Its dimensions, if the octahedra are assumed regular with edges  $2,76 \text{ \AA}$  long, are  $d_{100} = 9,02 \text{ \AA}$ ,  $d_{010} = 5,52 \text{ \AA}$ , and  $d_{001} = 4,79 \text{ \AA}$ . The space-group permits cyclical but not non-cyclical permutations of these dimensions.

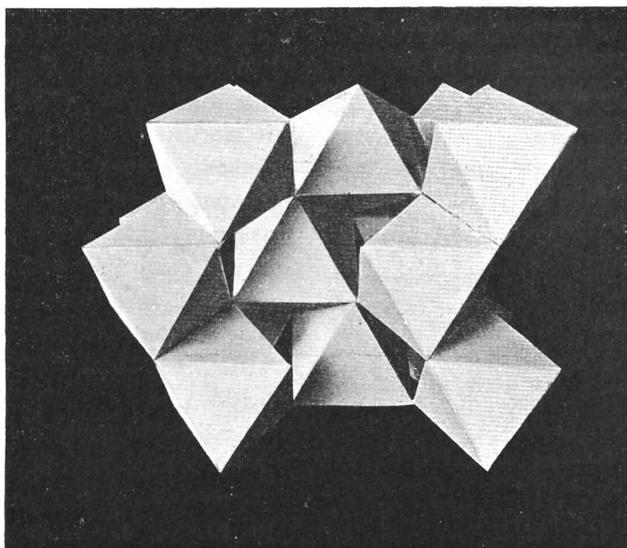


Fig. 4. A model representing a possible structure for  $TiO_2$  (Structure A), composed of staggered strings of octahedra (Fig. 3) combined by sharing octahedron corners only.

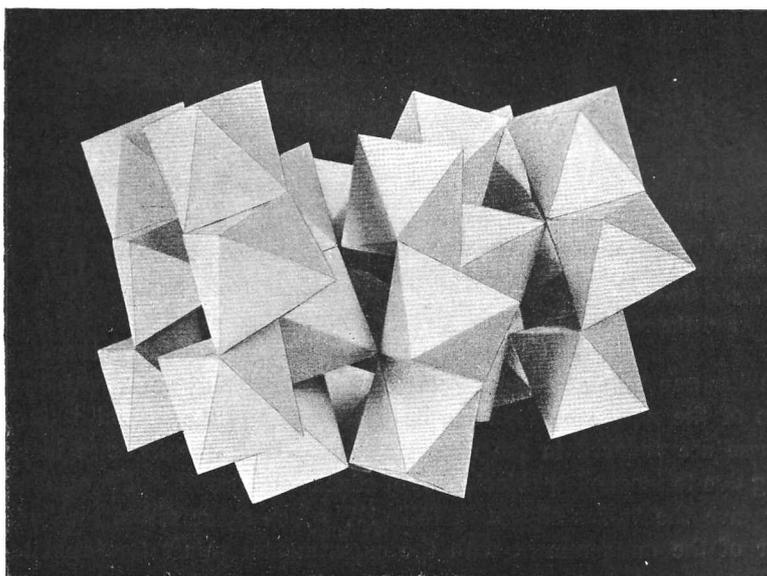


Fig. 5. A photograph of the model representing the structure of brookite.

The fact that brookite also was found experimentally to have the symmetry of  $V_h^{15}$  and to have  $8TiO_2$  in the unit suggests strongly that our second structure is to be attributed to this crystal. There is also approximate agreement (within 7%) in the dimensions of the unit. It

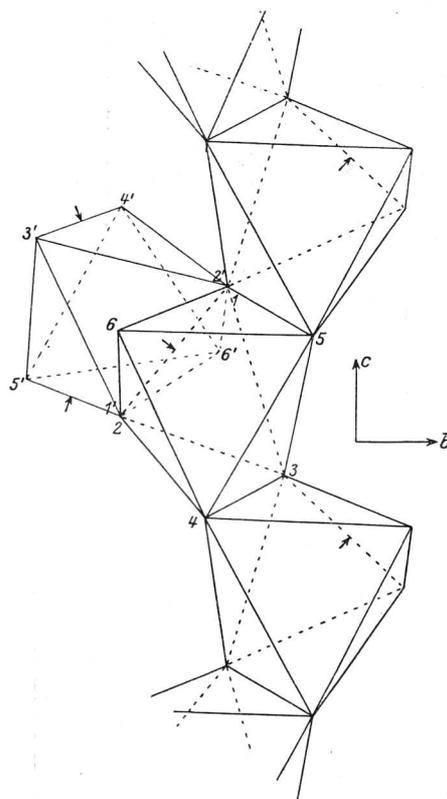


Fig. 6. A portion of the brookite structure, showing the three edges of each octahedron which are shared with adjoining octahedra, and the resulting deformation.

is worthy of mention that the choice of axes for comparison is not completely arbitrary: assuming that  $9.02 \text{ \AA}$  (model) is to be compared with  $9.166 \text{ \AA}$  (crystal), then the space-group requires that  $5.52 \text{ \AA}$  be compared with  $5.436 \text{ \AA}$  and  $4.79 \text{ \AA}$  with  $5.135 \text{ \AA}$ .

Since the analytical consideration of the effect of deformation appeared to be too complicated to permit its execution, the following method based upon the construction and measurement of a model was used. The basic distorted octahedron employed is shown in Fig. 6; in it all titanium-oxygen distances are equal to  $1.95 \text{ \AA}$ ; the three shared edges are  $2.50 \text{ \AA}$  long; and the other edges are chosen so as to be distorted as little as possible from their original lengths. Such octahedra were constructed to scale ( $2.54 \text{ cm.} = 1 \text{ \AA}$ ) from heavy paper, and were then glued together to represent a section of the crystal

including one unit of structure (Fig. 5). The carefully measured dimensions of the unit were found to be  $23.65 \text{ cm.}$ ,  $14.0 \text{ cm.}$ , and  $13.2 \text{ cm.}$ ; if these are reduced in the ratio  $2.57 \text{ cm.} = 1 \text{ \AA}$  (the increase in scale being due to incomplete coincidence of edges and corners of the octahedra) they give the values shown in Table IV, which agree within the limit of error of the measurement with the experimental values for brookite.

The suggested structure places eight titanium atoms and two groups of eight oxygen atoms each in the positions  $8c$ , with three sets of

Table IV.  
Dimensions of the unit of structure.

	$d_{100}$	$d_{010}$	$d_{001}$
From model, with undistorted octahedra	9,02 Å	5,52 Å	4,79 Å
From model, with distorted octahedra	9,20	5,45	5,43
Experimental, for brookite	9,166	5,436	5,435

parameter values. In order to predict values of these parameters the coordinates of the oxygen atoms were measured on the model, and positions were assigned the titanium atoms in the octahedra such as to make the titanium-oxygen distances nearly constant. Representing by  $x, y, z$ ;  $\xi, \eta, \zeta$ ; and  $X, Y, Z$  the parameters for oxygen of the first kind, oxygen of the second kind, and titanium, respectively, the values that were predicted are

$$\begin{array}{ccc}
 O_1 & O_2 & Ti \\
 x = 0,040 & \xi = 0,230 & X = 0,434 \\
 y = 0,455 & \eta = 0,405 & Y = 0,443 \\
 z = 0,480 & \zeta = -0,465 & Z = -0,427.
 \end{array}$$

These may be compared with those corresponding to undistorted octahedra, namely,

$$\begin{array}{ccc}
 O_1 & O_2 & Ti \\
 x = 0,000 & \xi = 0,250 & Y = 0,425 \\
 y = 0,424 & \eta = 0,425 & Y = 0,425 \\
 z = 0,250 & \zeta = -0,447 & Z = -0,083.
 \end{array}$$

It is seen that the parameter changes due to distortion are considerable, being equivalent to translations of atoms as large as 0,35 Å.

#### IV. Testing the structure with the intensities of X-ray reflections.

A number of rotation photographs were made with molybdenum  $K\alpha$  radiation filtered through a zirconium oxide filter to isolate the  $K\alpha$  line. The positions of useful reflections, the indices of the planes producing them, and their visually estimated intensities are given in Table V. The factor placed beside the estimated intensity is a correction for the varying time of reflection, namely  $V1 - (u\lambda/d \sin 2\theta)^2$ , where  $\lambda$  is the wave-length, and  $u$  and  $d$  represent respectively the index of the axis of rotation and the unit translation along it<sup>1</sup>). (A number of reflections

<sup>1</sup>) Ott, Z. Phys. **22**, 204. 1924.

not included in the tables occurred on each photograph; namely, those produced by planes whose traces in the developed or ground face of the crystal [the faces (100), (010), and (001) for Table V] were not perpendicular to the axis of rotation of the crystal. These reflections were not considered because of the probability that their intensities would be largely affected by absorption in the crystal.)

Table V.

Spectral reflections<sup>1)</sup>.

a) Planes of form (0kl).

1. Beam incident on (0 1 0).				2. Beam incident on (0 0 1).			
k =	2	4	6	l =	2	4	6
l = 0	w 4	s 4.7	w 4	k = 0	a 0.8	mw 9	vw 5

b) Planes of form (h0l).

1. Beam incident on (1 0 0)										
h =	2	4	5	6	7	8	9	10	12	14
l = 0	vw 0.2	ms 3.5		w 4.7		vs 4.7		a 0.5	mw 8	w 5.5
l = 2			s 0.8 1.2	w 0.8 3.5	mw 0.9 4	vw 0.9 3	mw 0.9 1.2	a 3.5		

2. Beam incident on (0 0 1)

l =	2	4	6
h = 1	m 6.5	vw 3.5	w 1.2
h = 2	mw 0.9 6	a 0.6	a 2.5
h = 3	mw 0.8 7	a 3	
h = 4		mw 0.9 1.2	

1) The estimated intensities of the various reflections are indicated by the abbreviations vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak; a, absent. The number placed below the estimated intensity for each plane gives the computed structure-factor.

c) Planes of form  $(h k 0)$ .

1. Beam incident on  $(1 0 0)$

$h =$	2	4	6	8	10
$k = 1$	s 0,7	vw 0,9	m	a	m
	8	2	4	3	10
$k = 2$		w 0,8	a	vw 0,9	a
		2	4,5	0,7	2,5

2. Beam incident on  $(0 1 0)$

$k =$	1	2	3	4	5	6	7
$h = 2$	s 0,7	vw 0,9	s 0,9	a	a	a	a
	8	2,5	10	0,8	5	6,5	11
$h = 4$		w 0,6	a	vw 0,9	a	mw 0,9	
		2,5	0,2	4	0,4	6	

Structure factors were calculated with the use of the predicted parameter values and with the assumption that the relative reflecting powers of titanium and oxygen atoms are proportional to their atomic numbers. These structure factors reproduced the salient features of the observed intensities for fifty forms; this general agreement is strong evidence that the predicted structure closely approximates the actual one. There was, however, disagreement in a few cases, when one reflection was observed to be stronger than another from a plane with larger interplanar distance despite the fact that its calculated structure factor was the smaller of the two. Accordingly, the parameter values were varied slightly, and a change of  $-0,004$  in  $X$  was found sufficient to remove most of the points of discrepancy. Structure factors calculated for the new parameter values with the assumption of relative reflecting powers proportional to atomic numbers are included in Table V. It will be seen that when qualitative consideration is taken of the effect of other factors causing a decrease in intensity with decrease in interplanar distance, the agreement for all fifty forms is good. The changed parameter values given in Table VI may accordingly be accepted as correct.

Table VI.

Final parameter values for brookite.

$O_1$	$O_2$	$T_i$
$x = 0,010$	$\xi = 0,230$	$X = 0,127$
$y = 0,155$	$\eta = 0,105$	$Y = 0,113$
$z = 0,180$	$\zeta = -0,465$	$Z = -0,127$

The few remaining discrepancies are probably due to error in the assumed relative reflecting powers. To test this, we made use of an  $F$ -curve for  $O^-$  obtained by linear extrapolation from  $Na^+$  and  $Cl^-$ , and one for  $Ti^{4+}$  from  $Cl^-$  and  $K^+$ . These  $F$ -curves (which are not reproduced here because of uncertainty in their derivation) lead to structure factors which are, for the same final parameter values, also in good but not complete agreement with the observed intensities. Possibly somewhat different  $F$ -curves (corresponding to non-linear extrapolation) would give better agreement, but because of the arbitrariness of this procedure no attempt was made to utilize it.

It is worthy of mention that the rotation photographs yield information substantiating the choice of  $V_h^{15}$  as the correct space-group. Thus no reflections occurred from  $\{100\}$ ,  $\{300\}$ ,  $\{500\}$ ,  $\{700\}$ ,  $\{900\}$ ,  $\{11\cdot0\cdot0\}$ ,  $\{13\cdot0\cdot0\}$ ,  $\{301\}$ ,  $\{501\}$ ,  $\{701\}$ ,  $\{901\}$ ,  $\{11\cdot0\cdot1\}$ ,  $\{401\}$ ,  $\{601\}$ ,  $\{801\}$ ,  $\{10\cdot0\cdot1\}$ ,  $\{12\cdot0\cdot1\}$ , etc. on one photograph recorded in Table V, although planes of all these forms were in positions favorable to reflection. Similar failures to reflect were observed on the other photographs.

On account of the lack of definite knowledge of the  $F$ -curves no attempt was made to account for the intensities of Laue spots.

### V. Discussion of the structure and the coordination method.

The structure found for brookite is that shown in Fig. 5. Each titanium atom is surrounded by six oxygen atoms and each oxygen by three titanium atoms. The various interatomic distances, given in Table VII, are similar to those in rutile and anatase; for example, the average titanium-oxygen distance is 1.95 Å. The oxygen-oxygen distances and the distortion of the basic octahedra have been discussed in the previous sections in the course of derivation of the structure.

Table VII.  
Interatomic distances in brookite.

$Ti-O_1$	1,919 Å	$O_1-O_3$	2,767 Å
$Ti-O_2$	1,942	$O_2-O_3$	2,818
$Ti-O_3$	1,929	$O_2-O_4$	2,997
$Ti-O_4$	1,976	$O_2-O_6$	2,817
$Ti-O_5$	1,983	$O_3-O_5$	2,731
$Ti-O_6$	1,953	$O_3-O_4$	2,514
		$O_4-O_5$	3,042
$O_1-O_2$	2,508	$O_4-O_6$	2,833
$O_1-O_6$	2,869	$O_5-O_6$	2,743
$O_1-O_3$	2,514		

We believe that our conclusions can be accepted with considerable certainty, for the agreement between the predicted structure and the experimental results in regard to space-group symmetry, size of the unit of structure, and intensities of reflections on rotation photographs is so striking as to remove nearly completely from consideration the possibility of its being accidental.

The arrangement of the oxygen atoms approximates double hexagonal close-packing<sup>1</sup>). It is evident, then, that Bragg's close-packing method of deriving a possible structure might have been used. But both hexagonal and double hexagonal close-packing of oxygen ions are roughly compatible with the observed unit (compare Rows 1 and 3 of Table IV). To decide between these possibilities intensity comparisons would be required, and in the absence of information regarding the nature of the deformation from regular close-packing this procedure might be very laborious. In anatase the oxygen ions approximate cubic close-packing; the axial ratio is, however, increased from 2,0 to 2,5 by deformation, and a knowledge of the size of the unit of structure would not suggest the close-packed arrangement with much certainty. Rutile provides an example of a structure which is easily derivable by means of the coordination theory, but in which the oxygen ions do not approach any type of close-packing whatever.

The close-packing method is more generally applicable in the case of crystals containing cations smaller than the titanium ion and showing correspondingly less deformation. The method is very powerful and simple, and already in the hands of Professor Bragg has led to a number of interesting structure determinations. The coordination method, though also simple in principle, is somewhat less easy to apply. The two methods are not distinct and mutually exclusive, but instead supplement each other and should be used together.

## VI. Summary.

Brookite,  $TiO_2$ , is found with the use of Laue and spectral photographs to have an orthorhombic unit of structure with  $d_{100} = 9,166 \text{ \AA}$ ,  $d_{010} = 5,436 \text{ \AA}$ , and  $d_{001} = 5,135 \text{ \AA}$ , containing  $8 TiO_2$ , and to have the symmetry of space-group  $V_h^{15}$ . A structure predicted by means of the

<sup>1</sup>) There are three close-packed layers from which all of the infinite number of close-packed structures can be built; namely, *A*, with an atom at  $X=0, Y=0$  ( $X, Y, Z$  being hexagonal coordinates); *B*, with an atom at  $X=\frac{1}{3}, Y=\frac{2}{3}$ ; and *C*, with an atom at  $X=\frac{2}{3}, Y=\frac{1}{3}$ . For hexagonal close-packing these layers are superposed in the order *ABABAB*..., for cubic close-packing in the order *ABCABC*..., and for double hexagonal close-packing in the order *ABACABAC*...

coordination theory had the same unit and space-group symmetry, and gave an atomic arrangement accounting for the intensities observed on rotation photographs. In this structure the eight titanium atoms and the sixteen oxygen atoms (in two groups of eight each) are in positions  $8c$  with the parameter values given in Table VI. The basic unit of the arrangement is an octahedron of oxygen ions about a titanium ion; the octahedra are combined as shown in Fig. 5 so that each shares three edges with adjoining ones. Interatomic distances are given in Table VII.

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