

XV. The crystal structure of brookite.

By

Linus Pauling and J. H. Sturdivant in Pasadena.

(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 tetraiodide¹⁾; 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 applied²⁾ 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 small¹.) 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 investigated²); 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.)³) 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)	$2n_1$	β	$7^\circ 54,5'$	$4,586 \text{ \AA}$
	$2n_1$	α	$8 \ 53,5$	$4,592$
	$3n_1$	α_1	$13 \ 24$	$4,580$
	$3n_1$	α_2	$13 \ 29$	$4,584$
	$4n_1$	γ	$15 \ 41$	$4,585$
	$4n_1$	β	$15 \ 59$	$4,583$
	$4n_1$	α_1	$17 \ 59$	$4,584$
	$4n_1$	α_2	$18 \ 6$	$4,582$
(010)	n_2	β	$6 \ 40$	$2,718$
	n_2	α	$7 \ 30,5$	$2,716$
	$2n_2$	γ	$13 \ 14$	$2,718$
	$2n_2$	β	$13 \ 25$	$2,720$
	$2n_2$	α_1	$15 \ 5$	$2,721$
	$2n_2$	α_2	$15 \ 14$	$2,718$
(004)	n_3	γ	$13 \ 58$	$1,2835$
	n_3	β	$14 \ 14$	$1,2833$
	n_3	α_1	$16 \ 0$	$1,2844$
	n_3	α_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., with¹⁾

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

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,

¹⁾ 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.

