

## 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 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.

