THE CRYSTAL STRUCTURE OF TOPAZ

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An investigation of the orthorhombic crystal topaz, $Al_2SiO_4F_2$, with x-rays has been reported by Leonhardt.[1] With the aid of data from Laue and rotation photographs he found for the edges of the unit of structure, containing $4Al_2SiO_4F_2$, the values $d_{100} = 4.64$ Å, $d_{010} = 8.78$ Å, and $d_{001} = 8.37$ Å, and determined the space-group of the crystal to be V_h^{16}. A deduction of the atomic arrangement, dependent on about fifteen parameters, was not attempted; for such complicated structures cannot be treated by the usual methods.

By making use of the coördination theory of ionic crystals, I have predicted a structure for topaz which agrees satisfactorily with the experimental data. This structure is described in the following paragraphs.

The coördination theory, which has been applied successfully[2] to brookite, the orthorhombic form of titanium dioxide, is based on the assumption that the anions in a crystal are constrained to assume positions about the cations such that they indicate the corners of polyhedra of which the cations mark the centers. These polyhedra are the fundamentally important constituents of the crystal; retaining their form essentially, they are combined by sharing corners, edges, and faces in such a way as to build up a crystal with the correct stoichiometrical composition. Thus in rutile, anatase, and brookite there occur octahedra of oxygen ions about titanium ions; in rutile each octahedron shares two edges with adjoining octahedra, in anatase four, and in brookite three.

The fundamental polyhedra for topaz were assumed to be an octahedron of anions (oxygen and fluorine) about each aluminum ion and a tetrahedron of oxygen ions about each silicon ion. The anion-anion distance determining the length of a polyhedron edge was taken to be 2.72 Å throughout.[3] By piling these polyhedra together one structure was found, the unit of which approximated that observed for topaz. This structure is shown in figure 1, in which four layers of polyhedra to be superimposed are represented. On considering the distribution of microscopic symmetry elements for this predicted atomic arrangement its space-group was found to be V_h^{16}. The directions of the three axes are fixed for this space-group; using Niggli's convention (used by Leonhardt also), the c-axis is normal to reflection planes, the a-axis normal to glide planes with translational component $b/2$, and the b-axis normal to glide planes with translational component $a/2 + c/2$. The edges of the unit of structure are accordingly determined: their values, assuming the octahedra and
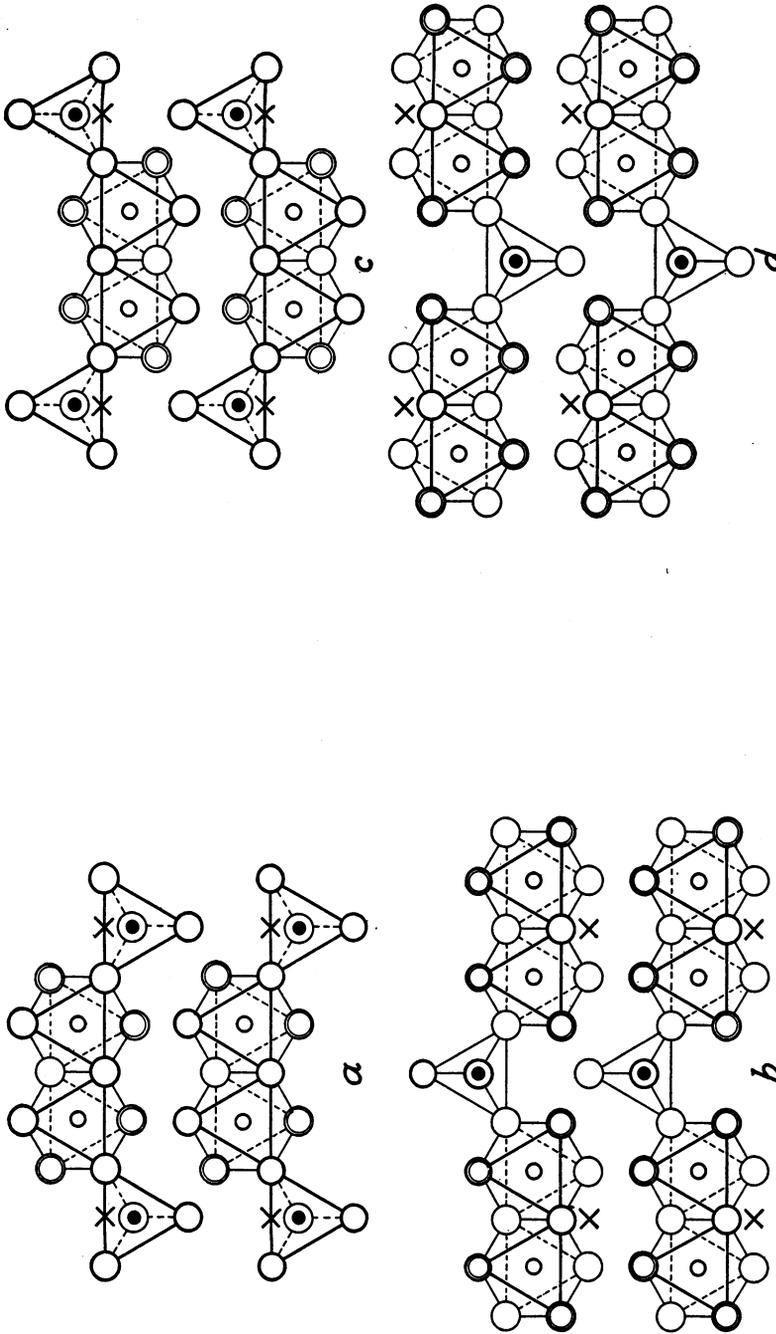
FIGURE 1

The arrangement of atoms in the crystal topaz. Large circles represent oxygen atoms, doubled large circles fluorine atoms, small open circles aluminum atoms, and small solid circles silicon atoms. The aluminum atoms are at the centers of the indicated octahedra, and the silicon atoms at the centers of tetrahedra. The four layers shown are to be superposed in the order *a, b, c, d*, with *d* uppermost. Crosses mark the projections of the corners of the unit of structure on the plane of the paper.

tetrahedra to be regular, are $d_{100} = 4.72$ Å, $d_{010} = 8.88$ Å and $d_{001} = 8.16$ Å. The unit contains $4Al_2SiO_4F_2$. The predicted structure leads to strong sixth order reflections from $\{100\}$ and $\{001\}$, and strong fourth and eighth order reflections from $\{010\}$, in agreement with Leonhardt's observations.

The concordance of the predicted structure and the experimental data in regard to space-group symmetry, size of unit, and intensity of reflections from the pinacoids makes it highly probable that the correct structure of topaz has been found. The effect of deformation (using the methods applied to brookite) will next be considered, leading to the more accurate determination of the atomic arrangement. It is anticipated that this consideration will result in predicted values for the edges of the unit of structure in still better agreement with the observed ones (as with brookite), and that the predicted atomic arrangement will account completely for the observed intensities of reflection of x-rays from various crystallographic planes.

The atomic positions and the parameter values for the approximate structure with undistorted polyhedra are:

$8a$: $xyz; x\,y\,\frac{1}{2} - z; \frac{1}{2} - x\,\frac{1}{2} + y\,z; \frac{1}{2} + x\,\frac{1}{2} - y\,\frac{1}{2} + z; \bar{x}\bar{y}\bar{z}; \bar{x}\,\bar{y}\,\frac{1}{2} + z;$
$$\frac{1}{2} + x\,\frac{1}{2} - y\,\bar{z}; \frac{1}{2} - x\,\frac{1}{2} + y\,\frac{1}{2} - z.$$
$4c$: $u\,v\,\frac{1}{4}; \bar{u}\,\bar{v}\,\frac{3}{4}; \frac{1}{2} - u\,\frac{1}{2} + v\,\frac{1}{4}; \frac{1}{2} + u\,\frac{1}{2} - v\,\frac{3}{4}.$
$4Si$ in $4c$ with $u = \frac{11}{12}$, $v = \frac{1}{16}$;
$8Al$ in $8a$ with $x = \frac{1}{12}$, $y = \frac{3}{8}$, $z = \frac{1}{12}$;
$8F$ in $8a$ with $x = \frac{1}{12}$, $y = \frac{3}{4}$, $z = \frac{1}{12}$;
$8O$ in $8a$ with $x = \frac{3}{4}$, $y = 0$, $z = \frac{1}{12}$;
$4O$ in $4c$ with $u = \frac{1}{4}$, $v = 0$;
$4O$ in $4c$ with $u = \frac{11}{12}$, $v = \frac{1}{4}$.

Each aluminum octahedron shares two edges with adjoining octahedra, and the four corners (oxygen ions) defining these edges are shared with tetrahedra. The other two corners, occupied by fluorine ions, are shared with octahedra. There are present in the structure SiO_4 groups; that is, tetrahedra having no elements in common with other tetrahedra; these tetrahedra share corners alone with octahedra. The oxygen ions, although crystallographically of three kinds, are from the standpoint of the coördination theory alike, for each is attached to two aluminum octahedra and one silicon tetrahedron. Each fluorine ion is shared between two octahedra.

The arrangement of the oxygen and fluorine ions is that of double hexagonal close-packing, so that Professor W. L. Bragg's methods of close-packing the large anions[4] could be applied to this crystal. But there are very many ways of distributing the cations with this anion arrangement, and the decision among them would have to be made by the laborious comparison of observed and predicted intensities of reflection, possibly involving the consideration of distortion of the anions from the close-

packed positions.   Furthermore (as for brookite also), both hexagonal and double hexagonal close-packing are roughly compatible with the observed unit, increasing the number of possibilities to be considered.   Bragg and West have, indeed, suggested with some reserve[4] that the anions in topaz are close-packed; their proposed type of close-packing is, however, incorrect, for it involves the identification of the hexagonal axis of the close-packed structure with the a-axis rather than the b-axis of topaz, and is, moreover, simple rather than double hexagonal close-packing.[5]

The further discussion of the structure of topaz will be published in the *Zeitschrift für Kristallographie.*

[1] J. Leonhardt, *Zeit. f. Krist.*, **59**, 216 (1924).

[2] Linus Pauling and J. H. Sturdivant, *Ibid.*, in press.

[3] Linus Pauling, *Jour. Amer. Chem. Soc.*, **49**, 763 (1927).

[4] W. L. Bragg and J. West, *Proc. Roy. Soc.*, **A114**, 450 (1927).

[5] Bragg and West report the dimensions of the unit of structure of topaz from their measurements to be $d_{100} = 4.64$ Å, $d_{010} = 8.79$ Å, and $d_{001} = 8.38$ Å, in good agreement with Leonhardt's values.

THE INTENSIVE DRYING OF LIQUIDS

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H. B. Baker has shown that liquids, gases and solids undergo a remarkable change in properties on prolonged and intensive drying with phosphorus pentoxide.[1]   Experiments are described here which have been made with the purpose of repeating and verifying these results.

Tubes containing phosphorus pentoxide and organic liquids were sealed up and allowed to stand for a period of years.   It was proposed to open the tubes after a drying time of 9 years (the time taken in Baker's experiments) and determine the physical properties of the liquid, such as boiling point, molecular weight, the capillary rise method, refractive index, etc.   At the end of four and a half years it was felt that several tubes should be opened in order that the speed of drying by the Baker method might be tested. The results are reported below.

Drying was carried out in hard glass tubes having a wall 2 mm. thick, and an external diameter of 18 mm.   The tubing chosen was free from visible imperfections, streaks, whorls, or cloudy areas which would indicate the existence of capillaries or fissures in the glass which might contain water. To make certain that the glass was free from capillaries it was heated to