fiber repeat. A temperature function corresponding to $B = 30$ Å^2 was used in the computation. This temperature factor is probably too large by about 5 Å^2 but the general character of the Patterson function would not be changed materially by this correction. A comparison of the theoretical function with the two experimental Pattersons shows that only a few general conclusions can be drawn as to the possible applicability of an α-helix model to the structures which the Patterson diagrams represent. The dissimilarity between the calculated projection and the Patterson diagram for collagen indicates that it is improbable that single α-helices are major structural components of that compound. There are some points of similarity with the poly-γ-methyl-L-glutamate function, particularly in the region of the line $x \cong 3{\cdot}0$ Å. The main point of disagreement between these two functions is the absence of any well distinguished peaks along the line $x \cong 1{\cdot}0$ Å in the theoretical function. This probably reflects the fact that the peaks at $x \cong 1{\cdot}0$ Å in the observed functions are artifacts or the result of disorientations in the structure which were not duplicated in the theoretical function. The line $\varphi(0, x).x$ from the calculated projection is included in Fig. 2(*a*) for purposes of comparison with the experimental curves. In all comparisons between the observed and theoretical functions at large x values it must be kept in mind that no side-chain atoms, other than a β carbon atom, were included in the latter. The general rise of the observed functions for values of x greater than 5 Å is of course due to main-chain, side-chain and interchain interactions, which appear to be more and more important because of the weighting on x.

Conclusion

It has been found that cylindrical Patterson functions calculated from relatively meager X-ray data given by a fibrous protein and a synthetic poly-peptide yield only general, semi-quantitative information about the structures of these compounds. More detailed conclusions might be reached if the resolution of the projections were improved; this might be achieved by the inclusion of more intensity data at shorter spacings.

We would like to thank Dr S. Frankel and Mr W. Chaplin of the Digital Computing Laboratory for their assistance in planning those phases of the calculations which involved punched card methods.

This work was supported in part by Contract Nonr 220(05) between the California Institute of Technology and the Office of Naval Research.

References

MacGillavry, C. H. & Bruins, E. M. (1948). *Acta Cryst.* **1**, 156.

Pauling, L. & Corey, R. B. (1951*a*). *Proc. Nat. Acad. Sci., Wash.* **37**, 235.

Pauling, L. & Corey, R. B. (1951*b*). *Proc. Nat. Acad. Sci., Wash.* **37**, 272.

Pauling, L., Corey, R. B. & Branson, H. R. (1951). *Proc. Nat. Acad. Sci., Wash.* **37**, 205.

Radiography in Modern Industry (1947). Rochester: Eastman Kodak Company, X-ray Division.

Vineyard, G. H. (1951). *Acta Cryst.* **4**, 281.

Yakel, H. L., Jr. (1953). *Acta Cryst.* **6**, 724.

Acta Cryst. (1955). **8**, 25

The Structure of Titanium Oxydifluoride

By Karl Vorres and Jerry Donohue

Department of Chemistry, University of Southern California, Los Angeles, California, U.S.A.

(*Received* 19 *July* 1954)

The structure of titanium oxydifluoride, $TiOF_2$, has been determined from X-ray powder photographs. The structure consists of titanium atoms octahedrally coordinated by randomly distributed oxygen and fluorine atoms, these octahedra sharing all six corners with neighboring octahedra. It is shown that powder data previously attributed to TiF_4 are probably due to $TiOF_2$.

Experimental

In the course of a study of various halides of titanium, titanium oxydifluoride, $TiOF_2$, was obtained as the product of hydrolysis of titanium tetrafluoride; it was also prepared by the hydrolysis of titanium trifluorochloride, and from the reaction of aqueous or anhydrous hydrogen fluoride with titanium dioxide (Vorres & Dutton, 1954). The oxydifluoride, when purified, was a white powder. The various methods of preparation did not give any single crystals. Powder specimens were sealed in glass capillaries and photographed in a Straumanis-type camera with filtered Cu $K\alpha$ radiation, $\lambda = 1{\cdot}542$ Å. Relative intensities

were estimated by use of the multiple-film technique.

The pattern obtained could be indexed on the basis of a simple cubic unit cell, with

$$a_0 = 3{\cdot}798 \pm 0{\cdot}005 \text{ Å} .$$

There was no evidence of lines due to a larger unit or to a structure of lower symmetry. The measured density was 2·92 g.cm.$^{-3}$; there is thus one molecule of $TiOF_2$ per unit cell (calculated density, 3·09 g.cm.$^{-3}$). There are only two structures possible which are consistent with the observed cubic symmetry and unit-cell size; both require a random distribution of the one oxygen and two fluorine atoms in the positions 3(*d*) of the space group O_h^1–$Pm3m$:

(*A*) Ti in 1(*a*) at (0,0,0), O and 2 F atoms at $(0,0,\frac{1}{2})$⟳;

and

(*B*) Ti in 1(*b*) at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, O and 2 F atoms at $(0,0,\frac{1}{2})$⟳.

Intensities for structures *A* and *B* were calculated using the atom form factors of Viervoll & Ögrim (1949) and Qurashi (1954), and a temperature factor $B = 1{\cdot}43$ Å^2. The comparison between observed and calculated intensities is presented in Table 1, where it

Table 1. *Powder data for* $TiOF_2$

hkl	d_o (Å)	I_c; structure *A*	I_c; structure *B*	I_o
100	3·76	1540	254	1387
110	2·67	186	186	187
111	2·18	5	886	4
200	1·89	365	365	431
210	1·69	383	89	450
211	1·54	61	61	94
220	1·34	141	141	180
221, 300	1·26	126	35	150
310	1·20	23	23	19
311	—	1	181	< 1
222	1·09	40	159	41
320	1·050	45	14	45
321	1·012	26	26	37
400	0·949	18	18	4
410, 322	0·921	68	23	56
411, 330	0·895	18	18	11
331	—	1	66	< 1
420	0·850	73	73	49
421	0·829	77	27	56
332	—	16	16	< 1

is seen that structure *A* is obviously the correct one for $TiOF_2$. The average discrepancy

$$R = \Sigma|I_o - I_c| \div \Sigma I_o$$

is 0·142.

Discussion

The structure of $TiOF_2$ consists of titanium atoms octahedrally coordinated by randomly distributed oxygen and fluorine atoms. The TiX_6 octahedra share all six corners with adjacent octahedra. The Ti–*X* distances are 1·90 Å, as compared with the Ti–O distance of 1·96 Å in rutile. The sum of the ionic radii for Ti–F and Ti–O are 2·04 Å and 2·08 Å respectively. Additional examples of oxyfluorides in which there is a random distribution of oxygen and fluorine atoms are AcOF (Zachariasen, 1951), PuOF, $ThOF_2$ (Zachariasen, 1949), and $(NH_4)_3MoO_3F_3$ (Pauling, 1924). Structure *A* is also shown by ReO_3, while CrO_3 and WO_3 have slightly deformed versions of it (Wells, 1950). Structure *B*, for which the four atoms in the cell lie in the positions of cubic closest packing, is said to be found in the compounds $AuCu_3$, $PdCu_3$, $PtCu_3$ (Johnson & Linde, 1925, 1927), $NaPb_3$ (Zintl & Harder, 1931), $CaPb_3$, $CaSn_3$, $CaTl_3$ (Zintl & Neumayr, 1933).

The ASTM data for TiF_4 (*X-Ray Diffraction Patterns*, 1945) are interesting in that they contain every line of the pattern for $TiOF_2$, and, moreover, the three strongest lines listed for TiF_4 are the strongest lines for $TiOF_2$. Since TiF_4 will react extremely readily with any trace of moisture it is highly probable that the sample of TiF_4 used had hydrolyzed to a large extent and the pattern obtained is essentially that of $TiOF_2$.

The authors wish to acknowledge the guidance and encouragement of Dr Frederic B. Dutton in the work dealing with the preparation of the titanium oxyfluoride.

References

Johnson, C. H. & Linde, T. O. (1925). *Ann. Phys., Lpz.* **78**, 439.
Johnson, C. H. & Linde, T. O. (1927). *Ann. Phys., Lpz.* **82**, 449.
Pauling, L. (1924). *J. Amer. Chem. Soc.* **46**, 2738.
Qurashi, M. M. (1954). *Acta Cryst.* **7**, 310.
Viervoll, H. & Ögrim, O. (1949). *Acta Cryst.* **2**, 277.
Vorres, K. S. & Dutton, F. B. (1954). *J. Amer. Chem. Soc.* In the press.
Wells, A. F. (1950). *Structural Inorganic Chemistry*, 2nd ed., p. 306. Oxford: Clarendon Press.
X-Ray Diffraction Patterns (1945). Philadelphia: A.S.T.M.
Zachariasen, W. H. (1949). *Acta Cryst.* **2**, 388.
Zachariasen, W. H. (1951). *Acta Cryst.* **4**, 231.
Zintl, E. & Harder, A. (1931). *Z. Phys. Chem.* **154**, 47.
Zintl, E. & Neumayr, S. (1933). *Z. Elektrochem.* **39**, 86.