same translation, applied to plane 1b, carries it directly over $\bar{1}b$. If these translations are combined with an interchange of the levels of the planes 1a, 1b then a twinned configuration is achieved, i.e. 1a, 1b become the mirror images of $\bar{1}a$, $\bar{1}b$ respectively, with respect to the mirror plane D. The homogeneous component of the twinning displacements is $\mathbf{T}'$, and the reshuffle vector is identified with the interplanar spacing vector between 1a, 1b. For the rhombohedral (110) mode, and the α-uranium (130) mode, referred to hereafter as Y_1-modes, the shear $S = T'/d$ accords, in both magnitude and direction, with the experimentally determined macroscopic shear. This consideration, and the fact that the stacking configuration of 1a, 1b is favourable for interchange, suggest that the interchange mechanism describes the actual net displacements of 1a, 1b when mechanical twinning takes place in Y_1-modes.

When the horizontal reshuffle mechanism is applied to Y_1-modes, it is found that $T > T'$. Conversely, when the vertical interchange mechanism is applied to X_1-modes, it is found that $T' > T$. Consequently, the nature of the mode defined by any given rational composition plane, i.e. whether an X_1-mode or a Y_1-mode, may be established at once by working out $\mathbf{T}$ and $\mathbf{T}'$ and comparing their magnitudes. In all cases, the vector of smaller magnitude predicts the magnitude and direction of the observed macroscopic shear. Bearing in mind that the smaller of the two vectors $\mathbf{T}$, $\mathbf{T}'$ defines the smallest possible semihomogeneous parallel to K_1 that twins the crystal, we are led to the conclusion given in the introduction.

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The Crystal Structure of NbO_2F and TaO_2F

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(*Received* 26 *March* 1956)

Niobium dioxyfluoride and tantalum dioxyfluoride have the ReO_3 structure in which fluorine atoms and oxygen atoms are randomly distributed in octahedral positions about the metal atom. The simple cubic unit cell for NbO_2F has a = 3·902±0·001 Å; and for TaO_2F, a = 3·896±0·003 Å.

Preparation

A weighed quantity of 99·9% Ta metal was dissolved in 48% aq. HF (reagent grade) in a platinum crucible at ~80° C. The clear colorless solution was evaporated to dryness on a steam bath and then heated at 250° C. for 1 hr. Subsequent heating for 1 hr. at 250° C. resulted in 0·19% weight loss. The white powder was analyzed chemically: 76·1±0·5% Ta, 9·04±0·10% F, 0·15±0·01% H (oxygen was not determined directly). Tantalum dioxyfluoride was found to be stable in air at 300° C. but decomposed above 500° C. into Ta_2O_5. When heated in dry oxygen TaO_2F lost some tantalum, presumably by volatilization of TaF_5.

Niobium dioxyfluoride was prepared by digesting pseudohexagonal Nb_2O_5 (Frevel & Rinn, 1955) in 48% aq. HF, evaporating the solution to dryness, and heating the resultant white powder at 250° C. for 1 hr. A larger quantity of NbO_2F was prepared by dissolving niobium metal in 48% aq. HF and heating the solid from evaporation to 275° C. for 5 hr. A chemical analysis yielded 62·6±0·5% Nb, 15·61±0·10% F, 0·21±0·01% H.

X-ray data and structure identification

Powder diffraction patterns were obtained with filtered Cu $K\alpha$ radiation in a cylindrical G.E. camera (71.8 mm. radius) and with a Norelco diffractometer. Relative intensities measured photographically compared favorably with the integrated intensities from the diffractograms. No indication of preferred orientation of crystallites was observed between pressed powder samples and carefully loaded samples. The patterns obtained could be indexed on the basis of a primitive cubic cell. Prolonged exposures or slow scanning failed to reveal any additional lines requiring a larger unit cell. The powder of tantalum dioxyfluoride was found to be isotropic under a polarizing microscope. A comparison of the powder pattern of $TiOF_2$ (Voores & Donohue, 1955) with that of TaO_2F immediately suggested the correct structure; namely,

Table 1. *Powder diffraction data of* TaO_2F

Space group, *Pm*3*m*.

$a = 3·896 \pm 0·003$ Å, based on Cu $K\alpha_1 = 1·54050$ Å and Cu $K\alpha_2 = 1·54434$ Å.

$(I/I_1)_o$ = observed integrated intensity relative to the {100} reflection.

$(I/I_1)_c$ = calculated relative intensity.

The atomic scattering factors for Ta^+, O, F^- were obtained from *International Tables for the Determination of Crystal Structures* (1935). The temperature factor was taken as $B = 2·0$ Å². The average discrepancy $R = 0·113$.

{*hkl*}	*a* (Å)	$(I/I_1)_o$	$(I/I_1)_c$
100	3·898	1·00	1·000
110	2·757	0·58	0·530
111	2·250	0·11	0·122
200	1·947	0·16	0·180
210	1·742	0·44	0·364
211	1·591	0·15	0·192
220	1·377	0·11	0·098
300 }	1·299	0·17	0·031
221 }			0·123
310	1·232	0·06	0·078
311	1·175	0·04	0·049
222	1·125	0·03	0·031
320	1·081	0·05	0·066
321	1·041	0·07	0·093
400	0·9740	0·01	0·016
410	0·9449	0·07	0·052
411 }	0·9185	0·04	0·041
330 }			0·021
331	0·8939	0·03	0·033
420	0·8714	0·05	0·067
421	0·8503	0·11	0·118

Table 2. *Powder diffraction data of* NbO_2F

$a = 3·902 \pm 0·001$ Å; $R = 0·095$.

{*hkl*}	*d* (Å)	$(I/I_1)_o$	$(I/I_1)_c$
100	3·903	1·00	1·000
110	2·761	0·38	0·358
111	2·254	0·03	0·042
200	1·951	0·24	0·199
210	1·745	0·38	0·318
211	1·593	0·14	0·121
220	1·380	0·11	0·098
300 }	1·301	0·15	0·025
221 }			0·100
310	1·2339	0·05	0·047
311	1·1767	0·03	0·019
222	1·1267	0·03	0·030
320	1·0824	0·05	0·052
321	1·0430	0·05	0·059
400	0·9757	0·01	0·015
410	0·9466	0·05	0·041
411 }	0·9198	0·03	0·026
330 }			0·013
331	0·896	0·009	0·015
420	0·8725	0·05	0·062
421	0·8516	0·08	0·093

placing one tantalum atom at (0, 0, 0) and 2 oxygen atoms and one fluorine atom at $(0, 0, \frac{1}{2})$ $\circlearrowright$. The data of Tables 1 and 2 confirm the structure. On the basis of one 'molecule' of TaO_2F per unit cell, the calculated density is 6·51 g.cm.$^{-3}$; whereas the density determination of the powder in He gave a value of $5·99 \pm 0·13$ g.cm.$^{-3}$ at 26·7° C. From the chemical analysis it is evident that the composition of the powder does not correspond to pure TaO_2F. Infra-red analysis of a nujol mull of the oxyfluoride (dried at 250° C. for 2 hr.) revealed the presence of some water of hydration but no H–F linkage. The insertion of any water molecules into the structure (one H_2O per 5·5 unit cells) would raise the density above 6·51 g.cm.$^{-3}$. The density would likewise be raised if one assumed a solid solution of TaO_2F and TaF_3 (Gutmann & Jack, 1951). Moreover, a measurement of the hydrogen evolved during the digestion of the metal revealed the tantalum in solution to be quinquevalent within 2%. The water content of the solid, as originally obtained on the steam bath, analyzed severalfold higher than that of the material dried at 250° C.; yet the lattice constant did not change upon loss of water. In the case of NbO_2F the same situation obtained. Back-reflection measurement of the completely resolved $K\alpha$ doublets of {421} and {422} showed that the cube edge remained constant within 0·0002 Å in going from a water content of 5·7% H_2O to 1·9% H_2O. In view of the above findings it was concluded that the impure tantalum dioxyfluoride consists of crystalline TaO_2F and an amorphous phase with a probable composition $TaOF_3.yH_2O$, where $y = 2·7$ (dependent on temperature and duration of drying) and the mole fraction of the amorphous phase is equal to 0·066.

Discussion

The structure of TaO_2F consists of $Ta(O, F)_6$ octahedra sharing all six corners with adjacent octahedra. In Table 3 a comparison is made of substances isomorphous or isostructural with TaO_2F. It is noteworthy that the M–X separation is nearly independent of the atomic number of the metal atom and is significantly shorter than the sum of the ionic radii.

Table 3. *Comparison of* $MO_{3-n}F_n$ *compounds*

Substance	*a* (Å)	$M-X$ (Å)	Sum of ionic radii (Å)
MoF_3	3·8985±0·0005*	1·95	2·1
TaF_3	3·9012±0·0002	1·95	2·1
NbO_2F	3·902±0·001	1·95	2·09
TaO_2F	3·896±0·003	1·95	(2·09)
$TiOF_2$	3·798±0·005	1·90	2·05
ReO_3	3·742±0·006†	1·87	2·1

* Gutmann & Jack, 1951. † Meisel, 1932.

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