Acta Cryst. (1970). B**26**, 2129

The Crystal Structure of Stoichiometric Yttrium Oxyfluoride, YOF

By A. W. Mann* and D. J. M. Bevan*

School of Chemistry, University of Western Australia, Nedlands, Western Australia

(*Received* 20 *November* 1969)

Powder intensity data for stoichiometric rhombohedral YOF have been obtained with a Hägg–Guinier focusing camera using Cu $K\alpha_1$ radiation. The space group is $R\bar{3}m$ and the hexagonal unit-cell dimensions are $a=3\cdot797$, $c=18\cdot89$ Å. A full-matrix least-squares refinement of the data to a final R index of 0·073 has been carried out. From this refinement it appears that the structure has Y–F distances of 2·41 and 2·47 Å which are somewhat longer than the corresponding Y–O distances (2·24 and 2·34 Å). The structural details, in particular that of a large oxygen–oxygen interlayer distance along the unique threefold axis, fit well with the assumption that YOF is a predominantly ionic structure.

Zachariasen (1951) has reported studies of the crystal chemistry of the 5*f*-series of elements in which he described the rhombohedral form of stoichiometric LaOF and YOF. The space group was quoted as $R\bar{3}m$, the structure containing two formula units per unit cell. Intensity calculations led him to suggest a model for the structures in which the atoms were ordered into the special 2(*c*) set of the rhombohedral representation [set 6(*c*) in the hexagonal representation]. The values quoted for the single variable parameter for each atom, $u=\pm 0\cdot242$ for La, Y: $v=\pm 0\cdot122$ (or 0·370) for F: $w=0\cdot370$ (or 0·122) for O, are also those for the single variable parameters in the hexagonal representation. The alternative figures in parenthesis were finally rejected by him on the grounds that observed metal–fluorine distances are invariably shorter than corresponding metal–oxygen distances.

In the course of a detailed study of phases and structures occurring in the pseudo-binary system Y_2O_3–YF_3 (Bevan, Mann, Cameron, Brauer & Roether, 1968), we have refined room-temperature powder data on the unique, stoichiometric, rhombohedral YOF phase, from which it appears that the alternative parameters for oxygen and fluorine given by Zachariasen are more appropriate.

Structure determination

Several samples in the composition range $YX_{2.02}$ to $YX_{1.96}$ (X = O + F) were prepared from physical mixtures of YF_3 (3*N* purity) and Y_2O_3 (4*N* purity). The pelleted samples were annealed under an atmosphere of nitrogen or in sealed platinum capsules at temperatures up to 1100° C, and then cooled slowly to room temperature over a period of several days. Analyses were made for fluorine and yttrium by a pyrohydrolysis method (Warf, Cline & Tevebaugh, 1954). Diffraction patterns of the sample finally chosen for structural study contained only the extremely sharp reflexions of rhombohedral YOF. These were obtained with a Hägg-Guinier camera and strictly monochromatic Cu $K\alpha_1$ radiation. All possible reflexions up to $\sin^2\theta=0\cdot5020$ were observed. The data are shown in Table 1: the hexagonal and rhombohedral cell parameters, obtained from a least-squares refinement, are: $a_H=3\cdot797\pm0\cdot001$, $c_H=18\cdot89\pm0\cdot01$ Å and $a_R=6\cdot666\pm0\cdot002$ Å, $\alpha_R=33\cdot09\pm0\cdot01°$ respectively. The unit-cell content is 6YOF for the hexagonal unit (2YOF for the rhombohedral unit) and the observed (pycnometric) and calculated densities, 5·1 and 5·23 g.cm^{-3}. Integrated diffraction intensities were obtained from microdensitometer traces of a series of films ranging in exposure times from 30 to 1920 minutes. Corrections were made for sample absorption, oblique incidence of the diffracted beam on the film, Lorentz and polarization factors (Sas & de Wolff, 1966).

Refinement was carried out in space group $R\bar{3}m$ on a PDP6 computer to which the full-matrix, least-squares (*ORFLS*) program (Busing, Martin & Levy, 1962) had been adapted. The close relationships between this structure and the fluorite structure, already pointed out by Zachariasen (1951), determined the initial placing of the atoms in ideal fluorite positions on the threefold axis of the hexagonal cell, *viz.* positions 6(*c*) with $z=0\cdot250$ for Y, $z=0\cdot125$ for O, and $z=0\cdot375$ for F. The difference in the atomic scattering curves for oxygen and fluorine (Cromer & Waber, 1965) provided sufficient asymmetry for the refinement to proceed sensibly to a value of $R=\sum||F_o|-|F_c||/\sum|F_o|$ of 0·170, with $z=0\cdot2409\pm0\cdot0003$ for Y, $z=0\cdot115\pm0\cdot001$ for O, and $z=0\cdot374\pm0\cdot001$ for F. 36 independent measurements, each with unit weight, were used to refine 4 parameters.

The data contain two pairs of overlapping reflexions: on the basis of the calculated structure factors for these it was possible to eliminate one reflexion from each pair, and the refinement then proceeded to a value of $R=0\cdot104$ without further significant change in the atom positions. Inspection of observed and calculated structure factors then suggested that the four strongest re-

---

* Present address: School of Physical Sciences, The Flinders University of South Australia, Bedford Park, South Australia.

Table 1. *Observed and calculated values of* $\sin^2\theta$ *and structure factors for* YOF

$\sin^2\theta$		$h\ k\ l$		
Observed	Calculated	(hexagonal)	$\lvert F_o\rvert$	F_c
0·01489	0·01497	0 0 3	30·8	−30·0
0·05653	0·05652	1 0 1	14·8	9·8
0·05990	0·05987	0 0 6	192·7	*
0·06148	0·06152	0 1 2	172·9	*
0·08153	0·08147	1 0 4	108·4	127·2
0·09654	0·09644	0 1 5	56·4	56·0
0·13484	0·13471	0 0 9	117·9	107·6
0·13646	0·13635	1 0 7	91·1	−96·6
0·16136	0·16130	0 1 8	213·0	*
0·16469	0·16459	1 1 0	228·5	*
0·17965	0·17956	1 1 3	26·3	−22·4
0·22128	0·22111	0 2 1	117·7	*
0·22128	0·22117	1 0 10		−150·4
0·22456	0·22446	1 1 6	161·9	−178·5
0·22618	0·22610	2 0 2	178·9	−181·5
0·23954	0·23949	0 0 12	103·7	85·9
0·24608	0·24606	0 2 4	118·2	115·1
0·25611	0·25610	0 1 11	85·6	−81·4
0·26104	0·26103	2 0 5	43·3	46·9
0·29936	0·29930	1 1 9	93·1	87·2
0·30096	0·30094	0 2 7	84·0	−78·3
0·32595	0·32589	2 0 8	197·4	201·4
0·33595	0·33593	1 0 13	100·4	101·4
0·37416	0·37420	0 0 15	155·3	−140·5
0·38088	0·38083	0 1 14	126·7	−119·9
0·38587	0·38570	2 1 1	89·5	*
0·38587	0·38576	0 2 10		−129·8
0·39080	0·39069	1 2 2	157·5	−155·9
0·40420	0·40408	1 1 12	93·5	80·5
0·41077	0·41065	2 1 4	114·6	106·3
0·42081	0·42069	2 0 11	84·5	−72·6
0·42575	0·42563	1 2 5	41·6	41·0
0·46550	0·46553	2 1 7	70·3	−66·9
0·48048	0·48062	1 0 16	148·3	127·9
0·49023	0·49048	1 2 8	168·4	171·2
0·49348	0·49376	3 0 0	191·7	186·4
0·50029	0·50052	0 2 13	89·4	90·0

* Not included in final refinement.

flexions were affected by extinction, and when these were removed from the refinement a final value of $R=0·076$ was obtained. Final atom positions and standard deviations are shown in Table 2.

Table 2. *Final atomic parameters*

	x	y	z	$\sigma(z)$
Y	0·000	0·000	0·2412	0·0001
O	0·000	0·000	0·117	0·001
F	0·000	0·000	0·372	0·001

Due to the absence of high-angle data no attempt was made to refine isotropic temperature factors for the atoms which were fixed at $B=0·30$ for Y and $B=0·40$ for oxygen and fluorine (Holmberg, 1966). However, variation of these to extremes had little effect on the final result. Likewise, replacement of atomic by ionic scattering factors caused no change. Final agreement between the observed and calculated structure factors is shown in Table 1. Refinement from the ideal fluorite positions in $R\bar{3}m$ confirmed the presence of a centre of symmetry.

In an attempt to ascertain whether or not initial shifts by the least-squares program had been in the correct direction, form factors for the two anions placed in their final positions were interchanged, and further refinement carried out. Without significant change in these positions, the value of $R=0·083$ was higher and the standard deviations slightly so.

These values of R are almost identical with those found by Holmberg (1966) in his study of ScOF for two of three (the third value is still higher) alternative distributions of O and F atoms, and he concluded that the

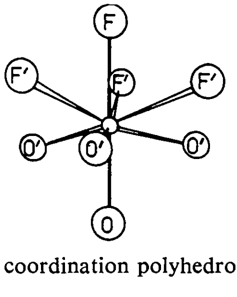

Fig. 1. Metal coordination polyhedron in YOF.

difference was sufficiently significant to exclude all but one. We also conclude that, for YOF, the positions obtained from the direct refinement (Table 2) are probably correct for this structure. Electrostatic energy calculations for stoichiometric YOF (Templeton, 1957) based on Zachariasen's two alternative structures tend to confirm this conclusion. Interatomic distances with standard deviations are given in Table 3.

Table 3. *Interatomic distances*

Primes refer to symmetry-related atoms in adjacent asymmetric units.

		Distance	σ
Y	O	2·24 Å	0·02 Å
Y	O′	2·34	0·02
Y	F	2·41	0·02
Y	F′	2·47	0·02
O	O′	2·87	0·02
F	F′	2·63	0·02

Discussion

The atomic parameters (Table 2) differ from those quoted by Zachariasen mainly in the interchange of the oxygen and fluorine atoms. His intensity data do not distinguish the two, and his choice is based wholly on the assumption of shorter metal–fluorine distances compared with metal–oxygen distances. The converse of this, as observed in the present study (Table 3), parallels Holmberg's (1966) observations on monoclinic ScOF, the mean Sc–O distance being about 0·10 Å shorter than the mean Sc–F distance.

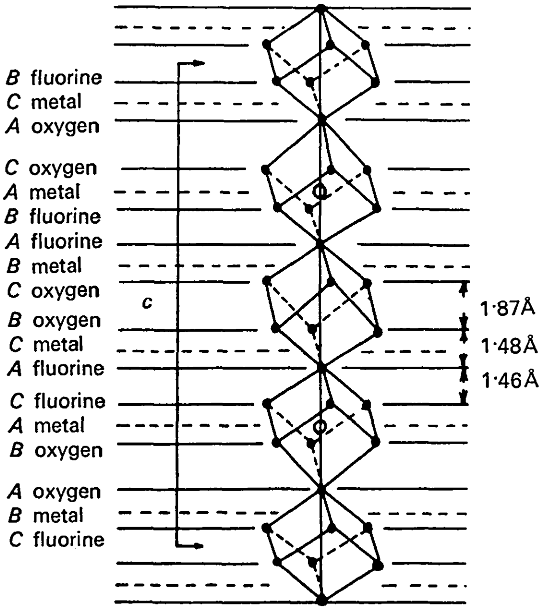

Fig. 2. Unique axis layering sequence and anion interlayer distances.

Fig. 1 shows the yttrium coordination polyhedron in YOF, the direction of the c axis of the hexagonal unit (vertical) being the now unique [111] direction of the parent fluorite structure. The extent to which this is distorted in YOF is illustrated in Table 4 where various bond angles are listed for the two structures: O–Y–O angles have increased and F–Y–F angles decreased relative to the corresponding angles in the fluorite structure. Fig. 2 shows the sequence of close-packed layers perpendicular to the hexagonal c axis in YOF. The layers of Y all lie between a layer of O and a layer of F and somewhat closer to the O layer. Any two adjacent O layers, with no metal layer between, are separated by 1·87 Å compared with a 1·46 Å separation for corresponding F layers. The whole picture is consistent with what would be expected if the structure were mainly ionic and electrostatic forces were predominant.

Table 4. *Comparison of bond angles in* YOF *and in ideal fluorite*

Angle	YOF	σ	Ideal fluorite
F′-Y-F′	103·7°	0·3°	109·47°
O′-Y-O′	116·2	0·4	
F—Y-F′	65·3	0·4	70·52
O -Y-O′	77·8	0·5	

References

Bevan, D. J. M., Cameron, R. S., Mann, A. W., Brauer, G. & Roether, U. (1968). *J. Inorg. Nuclear Chem. Letters*, **4**, 241.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). Oak Ridge National Laboratory Report No. ORNL-TM-305.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.

Holmberg, B. (1966). *Acta Chem. Scand.* **20**, 1082.

Sas, W. H. & de Wolff, P. M. (1966). *Acta Cryst.* **21**, 826.

Templeton, D. H. (1957). *Acta Cryst.* **10**, 788.

Warf, J. C., Cline, W. D. & Tevebaugh, R. D. (1954). *Analyt. Chem.* **26**, 342.

Zachariasen, W. H. (1951). *Acta Cryst.* **4**, 231.