

The Crystal Structure of ScOF

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Scandium oxide fluoride, ScOF, crystallizes in the monoclinic space group $P2_1/c$. There are four formula units in the unit cell with the dimensions $a = 5.1673 \pm 0.0005$, $b = 5.1466 \pm 0.0005$, $c = 5.2475 \pm 0.0008$ Å, $\beta = 99^\circ 42' \pm 5'$. The structure has been refined by the method of least squares from three dimensional Weissenberg data. Evidence is presented for the distraction between oxygen atoms and fluorine atoms. Each scandium atom is surrounded by four oxygen and three fluorine atoms, the average distances being 2.10 and 2.20 Å, respectively. The coordination polyhedron and the linking of the polyhedra are the same as in the monoclinic modification of ZrO_2 .

EXPERIMENTAL

An intermediate phase in the system Sc_2O_3 - ScF_3 has been identified by X-ray powder analysis of samples prepared by heating mixtures of the two components at 1000°C for three days in sealed platinum tubes. ScF_3 was made from Sc_2O_3 (L. Light & Co., Ltd. 99.9 % pure) by dissolving in *p.a.* hydrofluoric acid and evaporating to dryness. As the 1:1 preparation gave a mono-phasic Guinier powder pattern, it was concluded that the composition of the phase is ScOF. The powder pattern, Table 2, could be indexed with the monoclinic unit cell reported in Table 1.

Table 1. Crystallographic data for ScOF.

	ScOF		ZrO ₂ (1,2)
Symmetry	monoclinic		
Unit cell	<i>a</i>	5.1673 ± 0.0005 Å	5.1454 ± 0.0005 Å (3)
	<i>b</i>	5.1466 ± 0.0005	5.2075 ± 0.0005
	<i>c</i>	5.2475 ± 0.0008	5.3107 ± 0.0005
	β	$99^\circ 42' \pm 5'$	$99^\circ 14' \pm 5'$
Systematically absent reflections		$0k0$ with $k = 2n + 1$ $h0l$ with $l = 2n + 1$	
Space group	$P2_1/c$	(No. 14)	
Unit cell content	4 ScOF		4 ZrO ₂
Density, observed	3.84 g/cm ³		
calculated	3.86 g/cm ³		

The X-ray density of 3.86 g/cm³, calculated with 4 ScOF in the unit cell, is in good agreement with the observed density 3.84 g/cm³, determined from the weight-loss in benzene.

The sample consisted of plate-like colourless crystals. The single crystal X-ray examinations revealed that they were all twinned on (100) and had their longest extension along the *c* axis.

Weissenberg patterns were taken about the *c* axis with nickel filtered copper radiation. Intensities were recorded by the multiple film technique. The plate used had the dimensions 0.031 × 0.023 × 0.010 mm. The intensities of the reflections from one of the twins were visually estimated by comparison with a set of timed exposures of a selected reflection. The data were not corrected for absorption. An estimation of its influence on the data was undertaken by calculation of the absorption in an untwinned crystal of the same size.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The single crystal examination confirmed the chosen unit cell and gave the following systematic absences: *h*0*l* with *l* = 2*n* + 1 and 0*k*0 with *k* = 2*n* + 1 determining the space group to *P*₂₁/*c*.

A comparison of the derived crystallographic data for ScOF with those reported for monoclinic ZrO₂,¹⁻³ Table 1, suggested that the two structures are isotypic. Some simple calculations showed that this was true and furthermore that both compounds had approximately the same positional parameters.

The atoms in ZrO₂ are in four-fold positions and McCullough and Trueblood² found that the oxygen atoms in the two sets have different functions in the structure. The oxygen atoms O_I are coordinated to three and the atoms O_{II} to four zirconium atoms. In ScOF the possibility existed that these two

Table 2. ScOF Guinier powder pattern, CuKα₁ radiation.

Intensity	sin ² θ _{obs}	<i>hkl</i>	sin ² θ _{calc}
m	0.02292	100	0.02287
m	0.04461	011	0.04457
w	0.04531	110	0.04527
st	0.05989	11 $\bar{1}$	0.05986
st	0.07507	111	0.07503
m	0.08876	002	0.08870
vw	0.08958	020	0.08959
vw	0.11098	012	0.11110
vw	0.11232	120	0.11246
w	0.11391	210	0.11387
vw	0.11885	$\bar{1}$ 12	0.11883
st	0.12100	$\bar{2}$ 11	0.12087
m broad	0.12699	{102	0.12672
		$\bar{1}$ 21	0.12707
vw	0.14241	121	0.14223
m	0.14912	112	0.14914
m	0.15113	211	0.15122
w	0.17219	$\bar{2}$ 12	0.17223
st	0.17823	022	0.17829
m	0.18111	220	0.18107
m	0.18601	$\bar{1}$ 22	0.18599
w	0.18806	$\bar{2}$ 21	0.18807
w	0.20578	300	0.20581

Table 3. Final atomic parameters in ScOF for different fluorine and oxygen arrangement and atomic parameters in ZrO_2 (8).

	ZrO_2		ScOF		
	Zr	Sc	Alt. 1	Alt. 2	Alt. 3
x	0.2758 ± 2	0.3073 ± 6	0.3080 ± 7	0.3077 ± 6	
y	0.0411 ± 2	0.0267 ± 5	0.0266 ± 6	0.0266 ± 6	
z	0.2082 ± 2	0.2129 ± 10	0.2122 ± 13	0.2124 ± 11	
$B \text{ \AA}^2$	0.303	0.33 ± 5	0.35 ± 6	0.36 ± 5	
	O_I	F	O	(F,O)	
x	0.0703 ± 15	0.0570 ± 18	0.0586 ± 24	0.0578 ± 20	
y	0.3359 ± 14	0.3254 ± 15	0.3237 ± 19	0.3243 ± 17	
z	0.3406 ± 13	0.3426 ± 31	0.3423 ± 48	0.3441 ± 36	
$B \text{ \AA}^2$	0.317	0.8 ± 2	-0.1 ± 3	0.3 ± 2	
	O_{II}	O	F	(F,O)	
x	0.4423 ± 15	0.4574 ± 18	0.4564 ± 25	0.4575 ± 21	
y	0.7549 ± 14	0.7525 ± 26	0.7519 ± 34	0.7519 ± 29	
z	0.4789 ± 13	0.4900 ± 26	0.4949 ± 34	0.4906 ± 28	
$B \text{ \AA}^2$	0.229	0.4 ± 2	1.6 ± 3	1.0 ± 2	
R	8.6 %	7.6 %	9.4 %	8.2 %	

sets consisted of one fluorine and one oxygen set. In order to determine if the structure was ordered in such a way, it was refined by the method of least squares from the $hk0$, $hk1$, and $hk2$ Weissenberg data using the FACIT EDB computer program.⁴ Of the 162 possible reflections, 120 were observed, but 10 of these, too intense with the exposure times employed to allow a correct estimation of their intensities, were consequently excluded from the refinement.

Three different refinements were performed starting from the ZrO_2 structure, *viz.* one with fluorine atoms in the O_I position, one with oxygen atoms in the O_I position and one with the oxygen and fluorine atoms randomly distributed over the O_I and O_{II} positions. In all the cases the refinement of the nine positional parameters, the three isotropic temperature factors and the three scale factors were based on the scattering factors for Sc^{3+} , F^- ,⁵ and O^{2-} ,⁶ corrected with the real part of the dispersion. The weighting scheme given by Hughes⁷ was used.

In Table 3 the resulting atomic parameters and corresponding R values (for 110 reflections) are given for the three alternatives of anion arrangement together with the coordinates of the monoclinic ZrO_2 . Although the positional parameters of the three alternatives are the same within the standard deviations, the first alternative gives a better fit to the observed data as shown by the lower R value and the lower standard deviations. In Table 4, a comparison is given between the observed structure factors and those calculated with the atomic parameters for this choice. The most pronounced divergence of the three alternatives is demonstrated in the values of the temperature factors of the anions which strongly indicate that the fluorine atoms are in the O_I position.

Table 4. Observed and calculated structure factors for ScOF, (* excluded from the refinements).

$h k$	$ F_c $	$ F_o $	$h k$	$ F_c $	$ F_o $	$h k$	$ F_c $	$ F_o $
$l = 0$			$l = 1$			$l = 2$		
1 0	23	17 *	-2 2	26	26	-6 1	4	< 9
2 0	4	< 4	-1 2	30	33	-5 1	9	< 12
3 0	42	36	0 2	1	< 6	-4 1	1	< 10
4 0	13	13	1 2	14	14	-3 1	7	< 8
5 0	37	36	2 2	19	19	-2 1	23	22
6 0	12	13	3 2	12	12	-1 1	7	8
1 1	13	12	4 2	8	< 11	0 1	14	15
2 1	20	20	5 2	5	< 9	1 1	37	32
3 1	0	< 5	-5 3	5	< 11	2 1	5	< 8
4 1	28	26	-4 3	37	34	3 1	13	15
5 1	1	< 7	-3 3	3	< 12	4 1	1	< 13
6 1	8	10	-2 3	29	29	5 1	10	< 11
0 2	17	20	-1 3	30	30	-6 2	21	18
1 2	13	14	0 3	0	< 8	-5 2	30	31
2 2	61	52 *	1 3	55	50	-4 2	12	< 13
3 2	41	37	2 3	4	< 9	-3 2	22	21
4 2	1	< 6	3 3	10	14	-2 2	13	14
5 2	26	29	4 3	35	36	-1 2	60	49 *
6 2	17	17	5 3	5	< 9	0 2	56	46 *
1 3	25	27	-5 4	13	11	1 2	10	11
2 3	22	20	-4 4	3	< 11	2 2	27	26
3 3	3	< 6	-3 4	29	29	3 2	19	18
4 3	7	10	-2 4	3	< 13	4 2	25	28
5 3	3	< 6	-1 4	2	< 10	5 2	23	25
0 4	39	38	0 4	35	38	-5 3	16	17
1 4	25	25	1 4	4	< 10	-4 3	21	22
2 4	16	16	2 4	17	18	-3 3	6	< 10
3 4	16	17	3 4	14	15	-2 3	13	14
4 4	6	9	4 4	4	< 10	-1 3	14	17
5 4	22	20	-4 5	14	13	0 3	10	10
1 5	19	21	-3 5	7	< 11	1 3	14	14
2 5	16	16	-2 5	19	20	2 3	0	< 10
3 5	20	21	-1 5	20	21	3 3	22	22
4 5	21	18	0 5	8	< 13	4 3	18	21
0 6	16	16	1 5	16	17	5 3	3	< 7
1 6	8	8	2 5	15	16	-5 4	16	12
2 6	12	12	3 5	18	20	-4 4	14	13
			-2 6	15	14	-3 4	29	29
			-1 6	16	17	-2 4	22	22
			0 6	22	21	-1 4	14	17
-6 1	23	22	1 6	4	< 9	0 4	15	15
-5 1	19	21	2 6	21	19	1 4	12	14
-4 1	34	32				2 4	31	32
-3 1	16	15				3 4	20	22
-2 1	48	36 *				4 4	12	14
-1 1	56	37 *	$l = 2$			-4 5	13	11
0 1	23	21	-6 0	29	29	-3 5	4	< 10
1 1	50	39 *	-5 0	15	19	-2 5	21	21
2 1	35	31	-4 0	7	< 10	-1 5	22	22
3 1	37	34	-3 0	75	49 *	0 5	17	17
4 1	30	30	-2 0	17	15	1 5	20	20
5 1	3	< 10	-1 0	2	< 5	2 5	15	17
-6 2	7	< 8	0 0	42	22 *	3 5	15	13
-5 2	12	14	1 0	26	23	-1 6	13	13
-4 2	7	< 13	2 0	66	49 *	0 6	22	19
-3 2	2	< 9	3 0	22	22	1 6	4	< 7
			4 0	7	< 13			

Table 5. Interatomic distances in the ScO_4F_3 polyhedron in ScOF.

Distance	Å	$\pm \sigma$ Å		Mean distance Å
Sc_1-F_3	2.13	0.02		
$-\text{F}_1$	2.19	0.02		
F_4	2.28	0.02		2.20
Sc_1-O_1	2.08	0.02		
$-\text{O}_4$	2.08	0.02		
$-\text{O}_3$	2.10	0.02		
$-\text{O}_2$	2.14	0.02		2.10
F_3-F_4	2.58	0.03	(shared edge)	
F_1-F_4	2.74	0.01		
F_1-F_2	2.78	0.02		—
O_1-O_2	2.58	0.03	(shared edge)	
O_2-O_3	2.62	0.01	»	
O_1-O_4	2.62	0.01	»	
O_3-O_4	2.64	0.03	»	2.62
F_1-O_2	2.55	0.02	(shared edge)	
F_4-O_3	2.55	0.02	»	
F_3-O_1	2.95	0.03		
F_3-O_4	2.96	0.02		
F_4-O_4	3.03	0.02		—

To estimate the influence of absorption on these results the refinements were repeated with the data corrected for the absorption in an untwinned crystal of the same size. However, as this correction yielded no significant changes, it was thought that the differences in the results of the three alternatives from uncorrected data were not dependent upon absorption. Likewise, no significant changes of the original results were obtained by use of the scattering factors for the neutral atoms.⁴

Although the evidence presented which favours the first alternative for the scandium oxide fluoride structure is not strictly conclusive, it appears significant enough in comparison, at least to exclude the two other alternatives.

DISCUSSION OF THE STRUCTURE

The structure of ScOF thus deduced is shown in Fig. 1. Each scandium atom is surrounded by four oxygen and three fluorine atoms. The coordination polyhedron around the cation and the linking of these polyhedra are the same as in monoclinic ZrO_2 . The ordered arrangement of oxygen and fluorine atoms is such that the oxygen atoms are part of the fluorite-like layers, described by McCullough and Trueblood for ZrO_2 .

The interatomic distances within the coordination polyhedron are given in Table 5. The Sc—O distances range from 2.08 to 2.14 Å with the average of 2.10 Å and the Sc—F distances from 2.13 to 2.28 Å with the average of 2.20 Å. The corresponding averages in ZrO_2 are 2.21 ($\text{Zr}-\text{O}_{\text{II}}$) and 2.07 Å

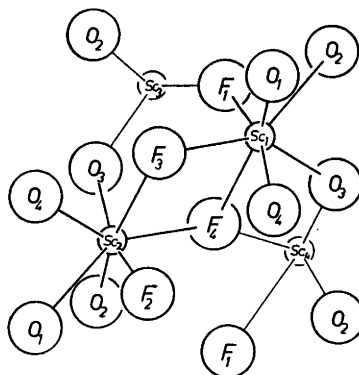


Fig. 1. Clinographic projection of the ScOF structure.

(Zr—O_I), these values taken from a recent structure refinement of ZrO₂.⁸ Thus, the Zr—O_I distance is shorter than the Zr—O_{II} distance while in ScOF the Sc—F distance is longer than the Sc—O distance.

All O—O, F—F, and O—F distances in the coordination polyhedron are of reasonable length. In particular they are shortened in the expected way for shared edges.

McCullough and Trueblood suggest that the shortening of the Zr—O_I distance relative to the Zr—O_{II} distance may be a result of the electrostatic imbalance at each corner of the Zr coordination polyhedron. Thus, at the corner occupied by O_I, triangularly surrounded by three zirconium atoms, the value of $\sum s = \sum \frac{z}{v} = 3 \cdot \frac{4}{7} = \frac{12}{7}$ and at the corner occupied by O_{II},

tetrahedrally surrounded by four zirconium atoms, $\sum s = 4 \cdot \frac{4}{7} = \frac{16}{7}$.²

Both these values are to be compared with -2 , the charge of the oxygen ion. Thus, there are deviations from the electrostatic valence rule⁹ amounting to $\pm \frac{2}{7}$ at each corner.

The value of $\sum s$ for ScOF at the two types of corners are $3 \cdot \frac{3}{7} = \frac{9}{7}$ (A_I) and $4 \cdot \frac{3}{7} = \frac{12}{7}$ (A_{II}). These values are to be compared with -1 and -2 , the charges of fluorine and oxygen ions. With this anion arrangement the electrostatic imbalance will favour a shortening of the Sc—A_{II} distance relative to the Sc—A_I distance. For the other two anion arrangements discussed, where the corresponding charges would be -2 and -1 (alternative 2) and -1.5 and -1.5 (alternative 3), the electrostatic imbalance would favour in the same way as in ZrO₂ a shortening of the Sc—A_I distance relative to the Sc—A_{II} distance.

In Sc₂O₃, where the oxygen atoms are surrounded tetrahedrally by four scandium atoms but where the scandium atoms are only coordinated by six oxygens, the average Sc—O distance was found to be 2.122 Å.¹⁰ The Sc—F distance has been reported to be 2.02 Å in ScF₃, which has a distorted ReO₃

structure with scandium octahedrally coordinated by fluorine.¹¹ A comparison between these figures and 2.10 (Sc—A_{II}) and 2.20 Å (Sc—A_I), the observed distances in ScOF, reveals that these distances are in accordance with the effect of the electrostatic imbalance resulting from oxygen atoms in the A_{II} position and fluorine atoms in the A_I position, the same anion arrangement as deduced from the refinement procedures.

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