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The Refinement of the Crystal Structure of Iron Oxyfluoride, FeOF

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A precise structural refinement of ferric oxyfluoride (FeOF) has been carried out by means of single-crystal diffraction methods. The symmetry is tetragonal, space group $P4_2/mnm$ with a cell having dimensions: $a = 4.654 \pm 0.003$, $c = 3.058 \pm 0.003$ Å and containing two formula units. The structure was refined by full-matrix least squares to a conventional reliability factor of 0.032 and a weighted factor of 0.024. The structure of this compound, which is of the rutile type, is discussed.

Introduction

There has been a number of MOF (M = 3*d* transition element) compounds found to possess the rutile type structure. A complete single-crystal structural determination of one of these compounds fitted in well with the systematic investigation of the metallic oxyfluorides that we have undertaken at the laboratory.

The ferric oxyfluoride has been prepared for the first time by Hagenmuller et al. (*1*). The powder pattern indicated a rutile type structure, much different from the layer type structure of ferric oxyfluoride (*2*, *3*) whose structure was recently refined by Lind (*4*).

The two ferric oxyhalides, FeOF and FeOCl are antiferromagnetic. The magnetic structure of FeOF has been determined by Chappert and Portier (*5*, *6*). The Néel temperature is 315 ± 10 K. The electric field gradient which is directed along the octahedral axis, is perpendicular to the spin direction, and the spins are parallel to the *c*-axis. Two magnetic sublattices can be distinguished: one formed by the iron atoms at the corners of the crystallographic unit cell and the other by the iron atoms at the center of this cell. In each sublattice the coupling is ferromagnetic and between the two sublattices the coupling is antiferromagnetic. In the course of this magnetic study Chappert and Portier raised the question whether the oxygen and fluorine atoms are ordered or statistically distributed.

The ferric oxyfluoride was the first MOF oxyfluoride found to have the rutile structure. Later the work of Chamberland, Sleight and Cloud (*7*) confirmed the results on FeOF and showed that TiOF and VOF have the same structure.

In this work the structure of FeOF was refined and so brings further detailed knowledge to that already obtained by the systematic structural investigation of MOF-type oxyfluorides (*8*–*10*).

Experimental Methods

Ferric oxyfluoride was prepared by reaction of stoichiometric, amounts of α-Fe_2O_3 and FeF_3 in a platinum crucible at 950°C and 1 bar of oxygen pressure (*1*). The single crystals were obtained by heat treating the FeOF powder under pressure of 60 kbar in a platinum crucible at 900°C for 5 min and then slow cooling for 1 hr.

An examination of the patterns obtained by the Weissenberg and precession methods led to the systematic extinctions $0kl: k + l = 2n + 1$ and a Laüe symmetry of $4/mmm$. This information is consistent with space group $P4_2/mnm$ and is in agreement with that established previously by the powder method.

The unit-cell parameters were obtained from precession photographs and later refined by the method of least squares using 2θ angles measured on the diffractometer. The following cell constants were found:

$$a = 4.654 \pm 0.003; \qquad c = 3.058 \pm 0.003 \text{ Å}.$$

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR FeOF[a]

Atom	Position	x	y	z	β_{11}	β_{33}	β_{12}[b]
Fe	2(a)	0	0	0	218 (6)	129 (6)	−70 (9)
(O,F)	4(f)	0.3018 (9)	0.3018 (9)	0	140 (18)	187 (19)	−47 (12)

[a] The standard deviations shown in parentheses here and in the text refer to the last decimal position of the respective value.

[b] The temperature factor expression used was $\exp[-10^{-4}\ (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Constraints placed on the β_{ij} are: position 2(a) and 4(f), $\beta_{11} = \beta_{22}$, $\beta_{13} = \beta_{23} = 0$.

The measured density was 4.53 ± 0.01 g cm^{-3} and the calculated density 4.58 g cm^{-3} for a cell containing two motifs. The reported error for the parameters represents the average deviation in the observed values.

A single crystal in the form of an irregular sphere and of average width 0.05 mm was used for data collection. The intensities were measured with a four-circle automatic Picker diffractometer using monochromated Mo$K\alpha$ ($\lambda = 0.7105$ Å) radiation up to $\theta = 45°$ and θ–2θ scanning. The background was measured at both sides of the reflexion for a period of 40 sec. A reflexion was considered as observed if the net count was greater than twice the standard deviation. A total of 87 reflexions were measured that were significantly above zero. These data were corrected for Lorentz-polarization effect, but not for absorption ($\mu t \approx 0.3$). The error due to absorption was considered to be very small due to this small μt.

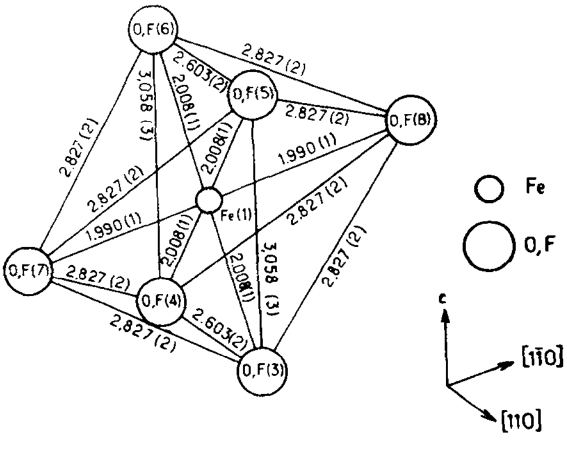

FIG. 1. Coordination octahedron of the metal in FeOF.

Structure Refinement

As in the case of rutile, the two iron and the four oxygen and fluorine atoms can be placed at positions 2(a), (0, 0, 0), and 4(f), (x, x, 0) respectively, of the space group $P4_2/mnm$. A three-dimensional Patterson synthesis was calculated, which confirmed the position of the iron atom and indicated the value of x as 0.305. No evidence of any ordering was observed. It was therefore assumed that the oxygen and fluorine atoms were randomly distributed on this fourfold position.

A number of cycles of isotropic refinement was performed with the atoms at the above positions, giving an R value:

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} = 0.13.$$

Due to this relatively high R value a Fourier synthesis was carried out, but it revealed no additional concentration of electron density except for the atoms placed above. At this time an anisotropic refinement was attempted, and after several cycles the R value was lowered to 0.032, as there was considerable thermal anisotropy involving both the cations and the anions.

The refinement was carried out by means of a full-matrix least-squares algorithm (*11*). The atomic scattering factors for iron, oxygen and fluorine were those of Cromer and Waber (*12*).

The function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes and w the weight, was minimized. In the first stages of the refinement unit weights were used for all reflexions and at the end the weighting scheme, $w = 1/[1 + ((|F_o| - a)/b^2)]$, was employed, where a and b are two curve fitting constants which determine the shape of the

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR FeOF

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
0 0 2	1961	1966	1 2 1	1455	1482	2 4 0	603	603
0 0 4	871	879	1 2 2	309	317	2 4 1	290	259
0 0 6	493	482	1 2 3	814	811	2 4 2	478	485
0 1 1	1296	1281	1 2 5	416	447	2 4 4	284	315
0 1 3	744	731	1 3 0	915	912	2 5 1	645	632
0 1 5	386	397	1 3 1	344	320	2 5 3	455	460
0 2 0	737	710	1 3 2	708	692	2 6 0	258	247
0 2 2	645	627	1 3 3	202	167	2 6 2	190	217
0 2 4	373	368	1 3 4	387	407	3 3 0	992	988
0 3 1	1508	1504	1 4 0	344	339	3 3 2	756	766
0 3 3	882	857	1 4 1	672	661	3 3 4	476	472
0 3 5	469	486	1 4 2	244	243	3 4 0	210	258
0 4 0	926	903	1 4 3	451	443	3 4 1	590	592
0 4 2	707	696	1 4 5	266	278	3 4 2	232	205
0 4 4	417	426	1 5 0	627	607	3 4 3	397	421
0 5 1	222	228	1 5 2	492	499	3 4 5	245	272
0 5 3	222	179	1 5 4	332	334	3 6 1	272	303
0 6 0	440	436	1 6 0	264	207	3 6 3	257	239
0 6 2	381	374	1 6 1	301	318	3 7 0	262	279
0 6 4	285	264	1 6 2	236	174	4 4 0	375	403
0 7 1	360	340	1 6 3	227	246	4 4 2	324	342
0 7 3	267	269	2 2 0	1569	1623	4 4 4	231	241
1 1 0	1799	1827	2 2 1	139	148	4 5 1	204	257
1 1 1	863	857	2 2 2	1159	1132	4 6 0	246	272
1 1 2	1211	1214	2 2 4	624	613	4 6 1	185	201
1 1 3	306	313	2 3 0	124	115	4 6 2	254	242
1 1 4	620	609	2 3 1	554	539	4 6 3	155	158
1 1 6	342	348	2 3 3	356	369	5 5 0	372	396
1 2 0	582	564	2 3 5	218	233	5 5 2	328	349

weighting curve (*13*). This procedure led to a final weighted R value:

$$wR = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2} = 0.024.$$

Throughout the refinement one overall scale factor was used.

The final positional and thermal parameters are given in Table I, and the final structure factors for observed reflexions are shown in Table II.

Results and Discussion

The structure in terms of coordination polyhedra as well as in projection is shown in Figs. 2 and 3. The particular octahedron with its relevant distances is given in Fig. 1.

The rutile structure can be described as consisting of hexagonal compact layers of anions which, if they were perfect would have a parameter $u = 0.25$. In fact, these layers are tetragonally distorted with an actual u parameter

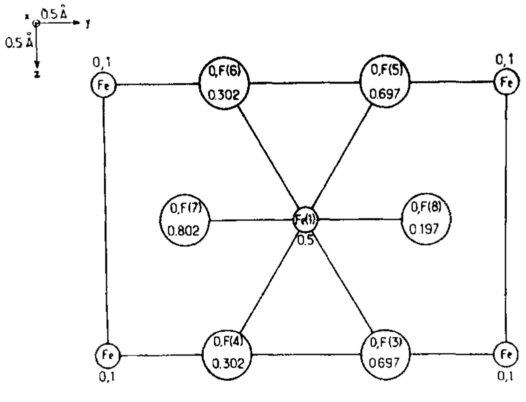

FIG. 2. Projection of the structure on the *ac* plane.

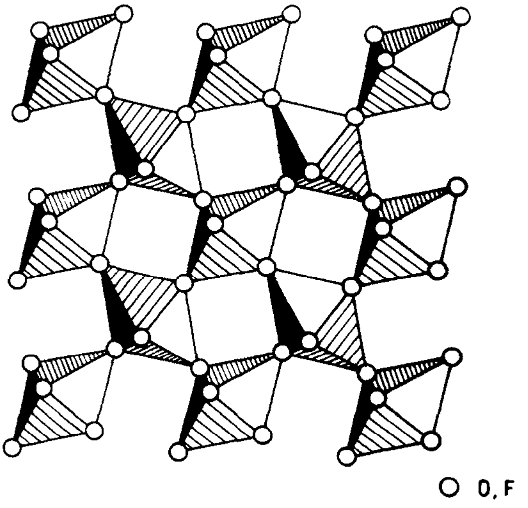

FIG. 3. The structure of FeOF viewed along the *c* axis.

TABLE III

INTERATOMIC DISTANCES AND ANGLES

Bond distances	Fe–O,F (4)	2.008 (1) Å
	Fe–O,F (7)	1.990 (1) Å
Edges of octahedra	O,F (6)–O,F (8)	2.827 (2) Å
	O,F (6)–O,F (5)	2.603 (2) Å
	O,F (5)–O,F (3)	3.058 (3) Å
Bond angles	O,F (6)–Fe–O,F (5)	80.80 (0.05)°
	O,F (5)–Fe–O,F (3)	99.20 (0.05)°
	O,F (5)–Fe–O,F (8)	90°

of approximately 0.30 for all the compounds having the rutile structure.

The oxygen and fluorine atoms are statistically distributed at the corners of a distorted octahedron (Fig. 1). These octahedra share edges, forming chains along the *c*-axis. The parallel chains are connected together by sharing corners, thus forming a three-dimensional network structure (Fig. 3). In the iron octahedron there are two types of Fe–(O,F) distances (Fig. 1): in the (110) plane there are distances of 2.008 (1) Å, whereas in the $(1\bar{1}0)$ plane the Fe–(O,F) distance is 1.990 (1) Å (Table III). These distances agree well with the sum of the effective ionic radii [$r_{Fe^{3+}} = 0.675$, $r_{O^{2-}} = 1.40$, and $r_{F^-} = 1.33$ Å (*14*)] of approximately 2.010 Å, with those found in FeF_3 [Fe–F = 1.92 Å (*12*)], FeOCl [Fe–O = 1.964 and 2.100 Å (*4*)], γ-FeO(OH) [Fe–O = 2.00 Å (*13*)] and in α-Fe_2O_3 [Fe–O = 1.945 and 2.116 Å (*17*)].

The degree of distortion from an ideal octahedron can be seen from the angles of 80.80 (0.05)° and 99.20 (0.05)° instead of 90° (Table III), they are about the same as those found in FeOCl and α-Fe_2O_3.

Anion–anion distances of 2.603 (2), 2.827 (2) and 3.058 (3) Å have been found, as well as Fe–Fe distances of 3.629 (3) and 3.058 (3) Å (along the *c* axis). The fact that in the *c* direction the octahedra share edges, could allow a direct coupling of the t_{2g} orbitals. Actually, no overlap takes place which is evident from the fact that FeOF is an insulator [$\rho_{25°C} = 2 \times 10^7$ Ω cm (*7*)] which is in agreement with the fact that the Fe–Fe distance of 3.058 Å is much longer than the critical distance $R_c = 2.90$ Å (*18*) above which there is no possibility of metallic conduction. In order to explain the ferromagnetic spin coupling along the *c* axis, the mechanism of double correlation at 90° can be considered using the orbitals e_g–p_σ–$p_{\sigma'}$–e_g. On the other hand, since the chains of octahedra share only corners with each other, the magnetic interactions between these chains can only be of an indirect nature (coupling by superexchange at 130° of the type e_g–p_σ–e_g and t_{2g}–p_π–t_{2g}).

The thermal vibrational anisotropy observed for the iron atoms, $U_{11}/U_{33} \approx 4$, which means that the vibrational ellipsoid is very much flattened perpendicularly to the *c* axis, could be explained in the following manner. The magnetic interactions in the *c* direction could be of sufficient intensity to prevent excessive vibration, although it is doubtful whether the magnetic energy is stronger than the elastic energy of the lattice. A more likely explanation is that this anisotropy can be attributed to the repulsion between the t_{2g} orbitals directed in this direction which prevents a greater amplitude of vibration. A further contribution could come from the partial covalent character of the Fe–(O,F) bonds in the (110) plane which contains the common edge of the octahedra (Fe–(O,F) distances in this plane are longer), this covalency limiting the vibration possibilities along the *c* axis.

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