

# The Preparation and Properties of Rutile-Type Transition Metal Oxyfluorides\*

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Rutile-type transition metal oxyfluorides have been prepared by various solid state reactions at 900–1300°C and 100 to 65,000 atm in sealed platinum capsules. The products include: TiOF, VOF, FeOF, the solid solutions  $Ti_2O_{4-x}F_x$  and  $V_2O_{4-x}F_x$ , and several mixed transition metal oxyfluorides of the type  $MM'O_3F$ . Single crystals suitable for physical measurements were obtained for TiOF, VOF, and FeOF. The oxyfluoride products, characterized by X-ray crystallographic techniques, were all found to have the rutile-type structure. The electrical and magnetic properties of these materials were determined.

## Introduction

The properties of the first row transition metal oxides and fluorides have been widely studied, but little is known as to the formation and properties of rutile-type oxyfluorides of these metals. Recently, the preparation and characterization of FeOF have been reported (1–4). Several mixed transition metal oxyfluorides have been disclosed by Hund (5), but these products have not been characterized. This study was initiated to prepare rutile-type transition metal oxyfluorides and to characterize the products by magnetic and electrical measurements.

## Experimental

### Reactants

Reagent-grade oxides,  $Fe_2O_3$ ,  $Cr_2O_3$ ,  $TiO_2$ ,  $V_2O_5$ , and  $V_2O_3$ , were used without further purification. The solid state reaction of  $V_2O_3$  and  $V_2O_5$  at 800°C in a sealed silica tube yielded pure  $V_2O_4$ .  $Ti_2O_3$  was prepared by arc melting Ti and  $TiO_2$  under argon. The fluorides  $FeF_3$  and  $TiF_3$  were obtained from Electronic Space Products, Inc.; anhydrous  $VF_3$  and  $CrF_3$  were prepared by passing anhydrous HF over  $VCl_3$  and  $CrCl_3$ , respectively, at 600°C in a nickel tube.

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Anal. calcd for  $VF_3$ : V, 47.2; F, 52.8

Found: V, 46.9; F, 53.5

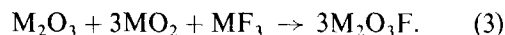
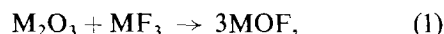
Calcd for  $CrF_3$ : Cr, 47.7; F, 52.3

Found: Cr, 46.8; F, 51.2

All manipulations of the anhydrous fluorides were carried out in a nitrogen-filled dry box, and reactant contact with air or water vapor was rigorously avoided.

### Synthesis

The general methods used to prepare transition metal oxyfluorides are represented by the following equations:



The intimately mixed reactants were sealed in evacuated platinum tubes (6-in. long  $\times$   $\frac{1}{2}$ -in. diam and having a 0.005-in. wall thickness). These tubes were placed in an internally heated pressure vessel which was used to a maximum of 1300°C and an argon pressure of 3000 atm. MOF compounds were also prepared in a tetrahedral anvil press (6) at 900–1300°C and 65 kbars pressure. These latter high pressure-high temperature experiments yielded crystalline products suitable for magnetic, electrical, and X-ray crystallographic investigations.

### Physical Property Determination

The electrical measurements on single crystals were made by a four-probe method and products obtained in the form of powders were measured with two probes on powder compacts at a pressure of 75,000 psi. Magnetic susceptibility between 4.2 and 400°K was measured with a Faraday balance, a vibrating sample magnetometer, or a mutual inductance bridge. Single crystal X-ray investigations were made with a precession camera, and X-ray powder data were obtained with either a Hägg-Guinier or a Debye-Scherrer camera. Lattice parameters were refined by least-squares using the powder data.

### Results

#### Titanium System

*TiOF*. The composition TiOF was prepared in the tetrahedral anvil press at 1200°C and 65 kbars by the reaction of TiF<sub>3</sub> and Ti<sub>2</sub>O<sub>3</sub> [Eq. (1)]. The product, obtained as small black crystals, was found to have tetragonal symmetry with  $a = 4.651 \text{ \AA}$  and  $c = 3.013 \text{ \AA}$ . The crystals had semiconducting electrical properties with a room-temperature resistivity of  $4.5 \Omega \text{ cm}$  and an activation energy of 0.17 eV (Fig. 1). The negative thermoelectric power ( $-290 \mu\text{V}/\text{deg}$  at 46°C) indicates that the charge carriers are electrons.

*Ti<sub>2</sub>O<sub>2.3</sub>F<sub>1.7</sub>*. At lower pressures (1000 atm) and at 950°C, the reaction between TiF<sub>3</sub> and Ti<sub>2</sub>O<sub>3</sub> yields a product having the composition Ti<sub>2</sub>O<sub>2.3</sub>F<sub>1.7</sub>.

Anal. calcd for Ti<sub>2</sub>O<sub>2.3</sub>F<sub>1.7</sub>: F, 19.6

Found: F, 19.4

The resistivity on a powder compact of this product at room temperature is  $17 \Omega \text{ cm}$  and the activation energy is 0.14 eV. The magnetic susceptibility in the region 200 and 300°K follows Curie-Weiss behavior with  $p_{\text{eff}}^2 = 2.4 \mu\text{B}^2$  and an intercept,  $\theta$ , of  $-77^\circ\text{K}$ . The negative value of  $\theta$  indicates antiferromagnetic order at low temperature; however, no maximum was observed in the susceptibility versus temperature curve. The lattice parameters of this rutile-type product were  $a = 4.626 \text{ \AA}$  and  $c = 2.979 \text{ \AA}$ . The smaller lattice parameters than those given above for stoichiometric TiOF indicate the presence of some tetravalent titanium.

*Ti<sub>2</sub>O<sub>3</sub>F*. Ti<sub>2</sub>O<sub>3</sub>F was prepared according to the reaction represented by Eq. (3). An intimate mixture of TiO<sub>2</sub>, Ti<sub>2</sub>O<sub>3</sub>, and TiF<sub>3</sub> was sealed in a platinum tube under high vacuum and heated at 1000°C and 100 atm for 12 hr. The reaction vessel contained

small black crystals which by analysis were found to be fluorine rich.

Anal. calcd for Ti<sub>2</sub>O<sub>2.9</sub>F<sub>1.1</sub>: Ti, 58.7; F, 12.8

Found: Ti, 57.0; F, 13.2, 13.4

The cell dimensions were found to be  $a = 4.63 \text{ \AA}$  and  $c = 2.96 \text{ \AA}$ . The resistivity data obtained on powder compacts indicated that the product was a semiconductor with a resistivity of  $3 \Omega \text{ cm}$  at room temperature.

*Ti<sub>2</sub>O<sub>3.33</sub>F<sub>0.66</sub>*. In another preparation of Ti<sub>2</sub>O<sub>3</sub>F, the reaction [Eq. (3)] was carried out at 900°C and 100 atm for 7 hr. The homogeneous, blue-black, crystalline product was characterized by elemental analyses as Ti<sub>2</sub>O<sub>3.33</sub>F<sub>0.66</sub>.

Anal. calcd for Ti<sub>2</sub>O<sub>3.33</sub>F<sub>0.66</sub>: Ti, 59.3; O, 33.0;

F, 7.76

Found: Ti, 57.1, 56.9;

O, 34.0; F, 7.55, 7.65

Its resistivity at room temperature was  $9 \Omega \text{ cm}$ , and the activation energy was 0.16 eV as measured on a powder compact.

#### Vanadium System

*VOF*. Low-pressure or autogeneous-pressure reactions of V<sub>2</sub>O<sub>3</sub> and VF<sub>3</sub> [Eq. (1)] always yielded heterogeneous products. In the tetrahedral anvil press at 65 kb pressure, however, the reaction proceeded at 1000°C to yield small black crystals of a vanadium oxyfluoride phase. Precession photographs obtained on a single crystal were consistent with the space group *P4/mmm* and the rutile-type structure. The lattice constants were found to be  $a = 4.623 \text{ \AA}$  and  $c = 3.025 \text{ \AA}$ . The resistivity data obtained on a single crystal of this product indicated semiconducting behavior with a room-temperature resistivity of  $60 \Omega \text{ cm}$  and an activation energy of 0.3 eV (Fig. 1).

In another tetrahedral anvil experiment, the preparation of VOF was closely duplicated, and the crystalline product was characterized. Its lattice parameters were  $a = 4.618 \text{ \AA}$  and  $c = 3.011 \text{ \AA}$ . The room-temperature resistivity on a single crystal was  $68 \Omega \text{ cm}$  with an activation energy of 0.21 eV. The susceptibility showed Curie-Weiss behavior down to 4.2°K. A small negative intercept ( $\theta = -10^\circ\text{K}$ ) indicated possible weak antiferromagnetic interactions. The Curie constant gave  $p_{\text{eff}}^2 \approx 7 \mu\text{B}^2$  which is in good agreement with the calculated free spin value of  $8 \mu\text{B}^2$  for trivalent vanadium. The magnetic properties of VOF are in striking contrast to those of isostructural and isoelectronic CrO<sub>2</sub> which is ferromagnetic with a Curie temperature of 394°K.

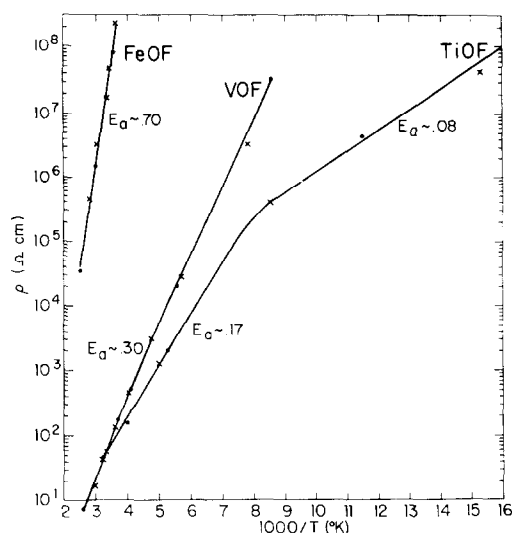


FIG. 1. Four-probe resistivity versus reciprocal temperature plots for single crystal, transition metal oxyfluorides. (• represents data obtained as temperature decreased, and × as temperature increased).

Rutile-type products with compositions approaching VOF could also be prepared at lower pressures, and large amounts were obtained by this mean for chemical and physical characterization. The reaction of  $V_2O_3$  and  $VF_3$  at  $1300^\circ C$  and 1000 atm was carried out in a sealed, evacuated platinum tube. A black crystalline product was obtained.

Anal. calcd for VOF: V, 59.3; F, 22.1

Found: V, 58.45; F, 21.6

X-ray studies on the pure product indicated the rutile-type structure having the lattice constants  $a = 4.596 \text{ \AA}$  and  $c = 3.002 \text{ \AA}$ . The theoretical X-ray density is  $4.50 \text{ g/cm}^3$ , whereas the observed density was  $4.46 \text{ g/cm}^3$ . A differential thermal analysis showed decomposition at  $515^\circ C$  and oxidation at higher temperatures to yield complex unidentified products.

$V_2O_{2.5}F_{1.5}$ . The reaction of  $VF_3$  and  $V_2O_3$  according to Eq. (1) in a sealed, evacuated platinum tube at  $700^\circ C$  and 3000 atm for 24 hr and then at  $500^\circ C$  for 2 hr yielded a black crystalline product and trace amounts of green crystals of  $VF_3$  which could be manually separated from the major phase. The product composition was  $V_2O_{2.5}F_{1.5}$  and the lattice parameters  $a = 4.58$  and  $c = 2.96 \text{ \AA}$ .

Anal. calcd for  $V_2O_{2.5}F_{1.5}$ : V, 59.8; F, 16.7

Found: V, 58.25; F, 16.8

$V_2O_3F$ .  $V_2O_3F$  was synthesized by two different chemical routes. The first method involved the

reaction of  $V_2O_3$ ,  $V_2O_5$ , and  $VF_3$  [Eq. (2)] at  $600\text{--}615^\circ C$  and 1000 atm for 13 hr in a sealed, evacuated platinum tube. The product, a homogeneous, blue-black crystalline oxyfluoride, was characterized by elemental analyses.

Anal. calcd for  $V_2O_3F$ : V, 60.3; O, 28.4; F, 11.25

Found: V, 59.7; O, 28.1; F, 11.95

This product has tetragonal symmetry with the lattice parameters:  $a = 4.57 \text{ \AA}$  and  $c = 2.94 \text{ \AA}$ . The susceptibility over the 200 to  $300^\circ K$  region followed Curie-Weiss behavior with a negative intercept ( $\theta = -70^\circ K$ ) and  $p_{eff}^2 \approx 11 \mu B^2$  as would be expected for  $V^{4+}V^{3+}O_3F$  (free spin value is  $11 \mu B^2$ ). No maximum in the susceptibility versus temperature curve (indicative of a Néel point) was observed.

In a different approach to  $V_2O_3F$ , a mixture of  $V_2O_4$ ,  $V_2O_3$ , and  $VF_3$  (Eq. 3) was heated in a sealed, evacuated platinum tube to  $800^\circ C$  at 1000 atm. The product was very similar to that described above.

Anal. found: V, 60.5; O, 28.25; F, 12.4

The lattice parameters of the tetragonal cell were  $a = 4.56 \text{ \AA}$  and  $c = 2.95 \text{ \AA}$ . The resistivity on a powder compact was  $0.9 \Omega \text{ cm}$  at room temperature with an activation energy of  $0.04 \text{ eV}$ .

$V_2O_{3.2}F_{0.8}$ . The reaction of  $V_2O_3$ ,  $V_2O_5$ , and  $VF_3$  [Eq. (2)] at  $1000^\circ C$  and autogeneous pressure for 5 hr in a sealed system gave a black crystalline solid. The lattice parameters were  $a = 4.574 \text{ \AA}$  and  $c = 2.949 \text{ \AA}$ , and elemental analyses indicated some deviation from the desired  $V_2O_3F$  composition.

Anal. calcd for  $V_2O_{3.2}F_{0.8}$ : V, 60.5; F, 9.03

Found: V, 60.0; F, 9.32

$V_2O_{3.3}F_{0.7}$ . In a high temperature-high pressure  $V_2O_3F$  experiment [Eq. (2)] at  $600^\circ C$  and 1000 atm for 13 hr, a product having tetragonal symmetry was isolated,  $a = 4.569 \text{ \AA}$  and  $c = 2.938 \text{ \AA}$ . The electrical resistivity value at room temperature on a powder compact was  $0.2 \Omega \text{ cm}$ .

Anal. calcd for  $V_2O_{3.3}F_{0.7}$ : V, 60.7; F, 7.92

Found: V, 62.2, 62.2;

F, 7.66; 7.64

#### Iron System

*FeOF*. The preparation of *FeOF* was studied at various pressures, and the highest yields of pure product were obtained in the tetrahedral anvil press at  $1000^\circ C$  under 65 kbars pressure. The product was found to have a rutile-type, tetragonal crystal structure with the parameters  $a = 4.662 \text{ \AA}$  and  $c =$

TABLE I  
MIXED TRANSITION METAL OXYFLUORIDES

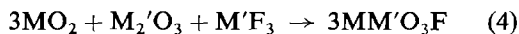
MM'O <sub>3</sub> F Composition	Lattice Parameters		Elemental Analyses						Electrical Properties	
			M		M'		F		$\rho_{25^\circ\text{C}}$ $\Omega \text{ cm}$	$E_a$ eV
	a (Å)	c (Å)	Calcd	Found	Calcd	Found	Calcd	Found		
FeVO <sub>3</sub> F	4.57	2.97	32.1	31.2	29.3	29.7	10.9	10.9	$1.6 \times 10^2$	0.22
VTiO <sub>3</sub> F	4.62	2.99	30.7	30.6	28.9	28.6	11.5	11.6	$9 \times 10^3$	0.25
FeTiO <sub>3</sub> F	~ 4.63	~ 3.01	32.7	35.6	28.0	27.5	11.1	10.1	$5 \times 10^5$	—

3.043 Å. Small, black crystals (reddish brown when finely divided) were formed, and these were found suitable for electrical and magnetic characterization. The room-temperature resistivity of FeOF was found to be  $2 \times 10^7 \Omega \text{ cm}$  with an activation energy of 0.70 eV (Fig. 1). The product was paramagnetic, the Mössbauer spectrum was observed to be identical to that previously reported (2), and the susceptibility at 298°K was field independent as expected for an antiferromagnet.

A differential thermal analysis obtained on a sample of FeOF indicated decomposition at 635°C and atmospheric pressure to form  $\alpha\text{-Fe}_2\text{O}_3$  and FeF<sub>3</sub>.

#### Mixed Transition Metal Oxyfluorides Having the Rutile-Type Structure

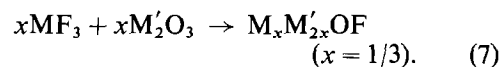
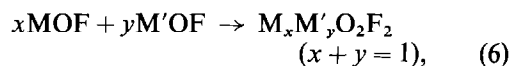
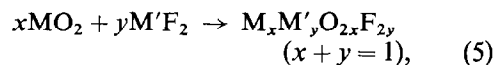
Several new mixed transition metal oxyfluorides of the type MM'O<sub>3</sub>F were also prepared. The general method of synthesis is expressed by the following equation. The reactions were carried out at 900°C under 100 atm in sealed, evacuated



platinum tubes in an internally heated pressure vessel. The homogeneous products obtained are described in Table I with elemental analyses and electrical resistivity data obtained on powder compacts. None of the products possessed spontaneous moments between 77 and 300°K; however, VTiO<sub>3</sub>F is antiferromagnetic with a Néel temperature of 19°K ( $p_{\text{eff}}^2 = 7.2 \mu\text{B}^2$ , while the calculated free-spin value is  $8 \mu\text{B}^2$ ).

Other mixed transition metal oxyfluorides (Table II) were prepared in the tetrahedral anvil press at 1000°C and 65 kbars pressure. The reactions are

expressed by the following equations.



#### Discussion

Since oxygen and fluorine have very similar ionic radii (7), the substitution of one for the other should not cause large structural defects. This type of substitution has been demonstrated by the formation of spinel-type (8, 9), magnetoplumbite (9), garnet-type (9, 10), and perovskite-type (11) oxyfluorides. Iron oxyfluoride, FeOF, was the only rutile-type transition metal oxyfluoride reported (1). We have now demonstrated the variety of substitutions possible in rutile-type transition metal and mixed transition metal compounds.

Most preparations required the use of external pressure on the system to retain the volatile transition metal fluoride and also to increase the yield of the oxyfluorides. At atmospheric pressure and 900–1000°C the yield of FeOF and VOF was quite small, and much of the fluoride was lost through sublimation. At autogeneous pressures the fluorine content was maintained, but segregation of the oxide and the fluoride was evident. The oxyfluoride yield under these conditions was also quite small. Normally, reaction at the highest pressures produced the most stoichiometric product and the highest yield. Our studies were confined primarily to the formation of  $\text{M}^{3+}\text{M}^{4+}\text{O}_3\text{F}$  and  $\text{M}^{3+}\text{OF}$  compositions; however, this research might also be extended to the formation of  $\text{M}^{2+}\text{M}^{4+}$  and  $\text{M}^+\text{M}^{5+}$  rutile oxyfluoride systems.

TABLE II  
MIXED TRANSITION METAL OXYFLUORIDES PREPARED AT HIGH PRESSURE

Composition	Reaction	Lattice Parameters		Magnetic Properties
		$a$ (Å)	$c$ (Å)	
Ti <sub>0.25</sub> Fe <sub>0.75</sub> O <sub>0.5</sub> F <sub>1.5</sub>	5	4.713	3.236	—
Ti <sub>0.5</sub> Fe <sub>0.5</sub> OF	5	4.644	3.010	—
Ti <sub>0.25</sub> Fe <sub>0.75</sub> OF	6	4.662	3.045	$p_{\text{eff}}^2 = 23.4 \mu\text{B}^2$ , $T_N \sim 100^\circ\text{K}$
Ti <sub>0.33</sub> Fe <sub>0.67</sub> OF	7	4.656	3.026	$p_{\text{eff}}^2 = 16 \mu\text{B}^2$ , $T_N \sim 80^\circ\text{K}$
Cr <sub>0.33</sub> Ti <sub>0.67</sub> OF	7	4.644	3.037	—
V <sub>0.33</sub> Ti <sub>0.67</sub> OF	7	4.643	3.013	—

Various lattice parameters of transition metal oxides, oxyfluorides, and fluorides are given in Table III. The general increase in  $a$  and  $c$  lattice parameters (and therefore, the volume) with increasing fluorine content is primarily due to the change in valence states of the cation, the tetravalent ion being smaller than the tri- or divalent ion.

TABLE III  
CRYSTALLOGRAPHIC DATA ON RUTILE-TYPE OXIDES,  
OXYFLUORIDES, AND FLUORIDES

Composition	Lattice Parameters		Volume	Reference
	$a$ (Å)	$c$ (Å)		
TiO <sub>2</sub>	4.594	2.958	62.43	(14)
Ti <sub>2</sub> O <sub>3</sub> F	4.63	2.96	63.45	<i>This work</i>
TiOF	4.651	3.013	65.18	<i>This work</i>
VO <sub>2</sub>	4.54	2.88	59.36	
V <sub>2</sub> O <sub>3</sub> F	4.57	2.94	61.40	<i>This work</i>
VOF	4.618	3.011	64.21	<i>This work</i>
VF <sub>2</sub>	4.804	3.237	74.70	(15)
CrO <sub>2</sub>	4.420	2.915	56.95	(14)
CrF <sub>2</sub> <sup>a</sup>			77.75	(14)
$\beta$ MnO <sub>2</sub>	4.396	2.871	55.48	(14)
MnF <sub>2</sub>	4.873	3.310	78.60	(14)
FeOF	4.662	3.043	66.14	<i>This work</i>
FeOF	4.647	3.048	65.82	(1)
FeF <sub>2</sub>	4.697	3.309	73.00	(14)
CoF <sub>2</sub>	4.695	3.180	70.10	(14)
NiF <sub>2</sub>	4.657	3.084	66.71	(14)

<sup>a</sup> Monoclinic cell (distorted rutile)  $a = 4.732$ ,  $b = 4.718$ ,  $c = 3.125$ ,  $\beta = 96^\circ 30'$ .

The smallest metal-metal distance in the rutile structure is  $c$ , the tetragonal axis of the unit cell. Goodenough (12) has derived an empirical expression for the critical metal-metal distance,  $R_c$ , in oxides. If  $R < R_c$  the compound should show metallic conductivity and a very low magnetic susceptibility. If  $R > R_c$  the compound should be a semiconductor. All the compounds in Table III should be semiconductors ( $R > R_c$ ) except Ti<sub>2</sub>O<sub>3</sub>F, VO<sub>2</sub>, and V<sub>2</sub>O<sub>3</sub>F. Although  $R < R_c$  for TiO<sub>2</sub>, there are no  $3d$  electrons available for conductivity. Metallic conductivity is observed in VO<sub>2</sub> (13) (above 65°C) but not in Ti<sub>2</sub>O<sub>3</sub>F and V<sub>2</sub>O<sub>3</sub>F. The oxyfluorides Ti<sub>2</sub>O<sub>3</sub>F and V<sub>2</sub>O<sub>3</sub>F have quite low-activation energies and are probably close to the border line between metallic and semiconducting behavior. Since the resistivities of Ti<sub>2</sub>O<sub>3</sub>F and V<sub>2</sub>O<sub>3</sub>F were measured on powders, these materials might really be metallic; however, in the case of V<sub>2</sub>O<sub>3</sub>F magnetic measurements showed Curie-Weiss dependence as expected for  $R > R_c$ .

The magnetic properties of the first-row transition metal oxides, oxyfluorides, and fluorides having the rutile structure are summarized in Table IV. The ordering is predominantly antiferromagnetic, except for CrO<sub>2</sub> which is ferromagnetic to 125°C. The preparation of VOF was of special interest since it is iso-electronic and isostructural with CrO<sub>2</sub>. The metal-metal distance in both VOF and CrO<sub>2</sub> is greater than the critical distance. However, CrO<sub>2</sub> shows metallic behavior and VOF is a semiconductor. The mechanism for metallic conductivity in CrO<sub>2</sub> is believed to be the covalent mixing of Cr orbitals of  $t_{2g}$  symmetry with oxygen  $p$  orbitals of  $\pi$  symmetry to form a narrow band (13). In VOF the higher ionic

TABLE IV  
MAGNETIC PROPERTIES OF RUTILE-TYPE OXIDES, OXYFLUORIDES, AND FLUORIDES

Composition	$d^n$	Magnetic Order	$T_N$ or $T_C$ (°K)	$\theta_K$	Reference
TiO <sub>2</sub>	$d^0$	Van Vleck paramagnetic	—	—	(17)
TiOF	$d^1$	Antiferromagnetic	—	-77	<i>This work</i>
VO <sub>2</sub>	$d^1$	Paramagnetic	—	—	(17)
VOF	$d^2$	Antiferromagnetic	—	-10	<i>This work</i>
V <sub>2</sub> O <sub>3</sub> F	$d^1-d^2$	Antiferromagnetic	—	-70	<i>This work</i>
VF <sub>2</sub>	$d^3$	Antiferromagnetic	40	—	(18)
CrO <sub>2</sub>	$d^2$	Ferromagnetic	394	—	(16)
CrF <sub>2</sub> <sup>a</sup>	$d^4$	Antiferromagnetic	53	—	(16)
MnO <sub>2</sub>	$d^3$	Antiferromagnetic	84	—	(16)
MnF <sub>2</sub>	$d^5$	Antiferromagnetic	72	-115	(16)
FeOF	$d^5$	Antiferromagnetic	315	—	(2, 3)
FeF <sub>2</sub>	$d^6$	Antiferromagnetic	79	-118	(16)
CoF <sub>2</sub>	$d^7$	Antiferromagnetic	37	-52	(16)
NiF <sub>2</sub>	$d^8$	Antiferromagnetic	78.5-83	-160	(16)
CuF <sub>2</sub> <sup>a</sup>	$d^{10}$	Antiferromagnetic	78	—	(16)

<sup>a</sup> Distorted rutile.

character of fluorine decreases this mixing giving an essentially ionic semiconductor. The much lower overlap in VOF reduces the ferromagnetic corner to body-center interaction so that the antiferromagnetic interaction between V ions along  $c$  dominates. This results in antiferromagnetism with a very low ordering temperature for this oxyfluoride composition.

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