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Synthesis and Properties of Several Members of the Series $CrO_{2-x}F_x$*

B. L. CHAMBERLAND†, C. G. FREDERICK, AND J. L. GILLSON

Central Research Department, E. I. du Pont de Nemours and Co.,
Experimental Station, Wilmington, Delaware 19898

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Several members of the $CrO_{2-x}F_x$ series were prepared by the reaction of CrO_2 with CrF_2 at high pressure in a tetrahedral anvil press. Homogeneous, single-phase products were obtained for $0 \leqslant x \leqslant 0.28$, which possess the rutile-type structure and are ferromagnetic. The products with values of $x < 0.10$ were obtained in single crystal form and four-probe transport properties indicate metallic conductivity. Crystallographic, magnetic, and some representative electrical properties are presented.

Introduction

The substitution of fluorine in the VO_2 matrix has recently been reported (*1*, *2*). The dramatic effect of this substitution was demonstrated by changes in the characteristic VO_2 crystallographic transition temperature, which decreased with increasing fluorine content. This decrease in transition temperature could be followed by crystallographic studies, by differential thermal analyses, or by the electrical transport properties.

In this paper, we report the effects of fluorine substitution in the rutile-type ferromagnet CrO_2 The solid solution between the two components CrO_2 and CrF_2 was examined crystallographically, and the changes in magnetic properties were studied by measuring Curie temperature and saturation moment. Finally, the transport properties were determined on single crystals via four-probe resistivity measurements in those instances where single crystals were obtained.

Experimental

Chromium dioxide, CrO_2, was prepared (*3*) by the hydrothermal reaction of CrO_3 and Cr_2O_3 at 400°C and 3000 atm in a sealed platinum capsule. The product was dried in a flowing O_2 atmosphere at 300°C for 1 hr. The tetragonal lattice parameters of the dried product were: $a = 4.4202 \pm 2$ and $c = 2.9168 \pm 2$ Å. The Curie temperature of this material was 400°K and the magnetic moment was 1.96 μ_B.

Chromous fluoride, CrF_2, was obtained from RIC/ROC and was used directly as received.

Various mixtures of CrO_2 and CrF_2 were weighed in a nitrogen-filled dry box, ground using an agate mortar and pestle, then placed into a platinum capsule for reaction in the tetrahedral anvil press. The reactions were carried out at 60–65 kbar pressure and 1200°C for 2 hr, then quenched to room temperature prior to the release of applied pressure.

The X-ray powder data were obtained with a Hägg–Guinier camera, and the films were read on a Mann optical densitometer. A least-squares refinement of the powder data generated the lattice dimensions.

Fluorine analyses were obtained on several of the products by the classical Willard and Winter method (*1*). The results were in good agreement with the nominal value for the fluoride ion in the original reactant charge (see Table I).

The magnetic data were obtained with a vibrating sample magnetometer from 4 to 420 K and magnetic fields of 300 Oe and 10 kOe. Reproducible measurements of the Curie temperature were also obtained on a force magnetometer in weak fields.

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* Contribution No. 1928 from the Central Research Department, E.I. du Pont de Nemours and Co., Experimental Station, Wilmington, DE 19898.

† Present address: University of Connecticut, Department of Chemistry, Storrs, CT 06268.

TABLE I

CRYSTALLOGRAPHIC DATA FOR MEMBERS OF THE SERIES $CrO_{2-x}F_x$

Value of x in $CrO_{2-x}F_x$		Lattice dimensions		Volume $(Å)^3$
Nominal	Anal. in product[a]	a (Å)	c (Å)	
0.02	0.028	4.4225 ± 5	2.9179 ± 4	57.069 ± 14
0.04	0.046	4.4240 ± 6	2.9185 ± 6	57.121 ± 17
0.06	0.059	4.4289 ± 6	2.9194 ± 5	57.265 ± 16
0.08	0.080	4.4320 ± 7	2.9203 ± 6	57.362 ± 18
0.10	0.100	4.4360 ± 8	2.9210 ± 7	57.481 ± 22
0.12	0.122	4.4381 ± 7	2.9221 ± 6	57.557 ± 19
0.14	—	4.4431 ± 8	2.9237 ± 6	57.716 ± 20
0.16	0.170	4.4486 ± 4	2.9258 ± 2	57.902 ± 11
0.17	0.176	4.4494 ± 5	2.9231 ± 3	57.868 ± 12
0.18	—	4.4479 ± 2	2.9256 ± 1	57.878 ± 5
0.20	0.200	4.4482 ± 2	2.9267 ± 1	57.909 ± 14
0.22	0.216	4.4523 ± 3	2.9268 ± 2	58.016 ± 7
0.24	0.230	4.4552 ± 6	2.9287 ± 4	58.131 ± 16
0.25	0.243	4.4584 ± 14	2.9266 ± 12	58.171 ± 38
0.26	0.257	4.4540 ± 8	2.9278 ± 7	58.081 ± 23
0.29	0.281	4.4578 ± 12	2.9274 ± 7	58.176 ± 31
0.30 → 0.40	—	Two phases		

[a] x based on fluorine analysis.

Four-probe resistivity data were obtained on single crystals of several members of the series over the temperature region 10 to 300 K (and 400 K in some instances).

Solid-state reactions of CrO_2 and CrF_3 at 1000°C and 3 kbar pressure and hydrothermal reactions between CrO_3 and $CrF_3 \cdot 3H_2O$ always gave $CrO_{2-x}F_x$ products contaminated with Cr_2O_3 as an impurity phase.

Results

Pure, homogeneous $CrO_{2-x}F_x$ compositions were prepared for $0 \leqslant x \leqslant 0.30$ by the solid state reaction of O_2-treated CrO_2 with CrF_2 at high pressure in a tetrahedral anvil press. The products possessed the rutile-type structure with lattice dimensions increasing with x (Table I and Fig. 1). An anomaly in the V vs x plot of Fig. 1 occurs at $x \approx 0.16$. Two phases were observed at higher

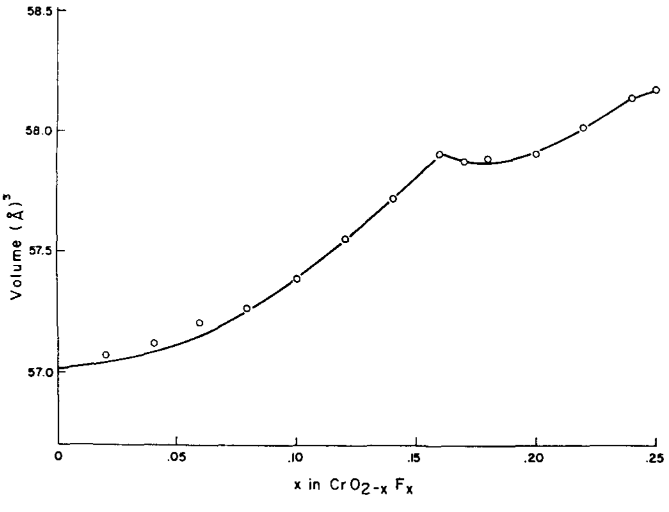

FIG. 1. Unit cell volume vs fluorine concentration (x) in the $CrO_{2-x}F_x$ system.

TABLE II

MAGNETIC DATA FOR MEMBERS OF THE SERIES $\mathrm{CrO}_{2-x}\mathrm{F}_x$

x in $\mathrm{CrO}_{2-x}\mathrm{F}_x$	T_c (K)	$\mu_{s_{\mathrm{obsd}}}$ (μ_B)
0	398	1.96
0.02	381	1.92
0.04	364	1.98
0.08	316	1.99
0.10	293	2.03
0.12	270	1.98
0.14	232	[a]
0.16	213	[a]
0.18	192	[a]
0.20	198	[a]

[a] A peak in the magnetization vs temperature plot is observed (see Fig. 3).

TABLE III

ELECTRICAL RESISTIVITY DATA FOR MEMBERS OF THE SERIES $\mathrm{CrO}_{2-x}\mathrm{F}_x$

x in $\mathrm{CrO}_{2-x}\mathrm{F}_x$	Resistivity in (298K)	Ω cm (4.2K)	Remarks
0.02	4.1×10^{-4}	1×10^{-4}	
0.04	5.3×10^{-4}	1.6×10^{-4}	
0.06	6.4×10^{-4}	1.5×10^{-4}	[a]
0.10	9×10^{-4}	5×10^{-4}	[b]
0.20	1×10^{-3}	8×10^{-4}	[c]

[a] Break observed at approximately 345K indicating T_c.

[b] Minimum at 50K observed in data.

[c] Broad minimum observed at approximately 75K.

fluorine concentrations. The limit of fluorine substitution in CrO_2 is approximately 28%.

The results of the magnetic measurements are tabulated in Table II. The Curie temperature continuously decreases with increasing fluorine concentration up to $x = 0.18$ where a minimum T_c is reached (Fig. 2). Magnetic moments were calculated as $T \to 0$ and $1/H \to 0$ from magnetization data. For concentrations from $0.12 \leqslant x \leqslant 0.20$ peaks appear in the magnetization vs temperature curve (Fig. 3) at approximately 100 K at 10 kOe and 140 K at 300 Oe independent of x.

Some representative electrical transport properties for several compositions in the $\mathrm{CrO}_{2-x}\mathrm{F}_x$ series are given in Table III. As the fluorine concentration increases, the resistivity increases; and the overall electrical conductivity of the system begins to show a positive temperature coefficient, indicative of semiconductivity.

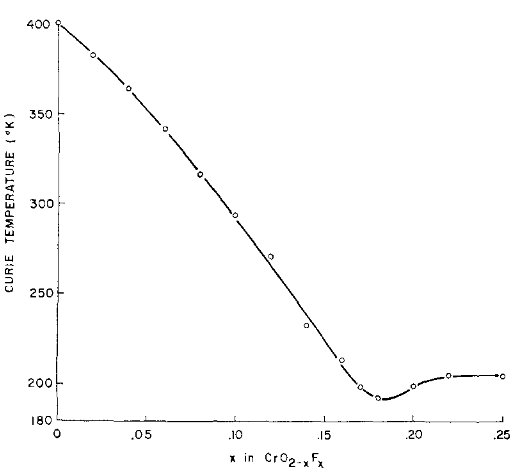

FIG. 2. Curie temperature (K) dependence on the fluorine concentration (x) in the $\mathrm{CrO}_{2-x}\mathrm{F}_x$ system.

Discussion

The increase in cell volume with increasing x in $\mathrm{CrO}_{2-x}\mathrm{F}_x$ is presumably caused by the larger Cr^{3+} ion, which charge compensates for the fluorine substitution in the CrO_2 matrix. The axial c/a ratio decreased in a linear manner up to an x value of 0.16. This system can be viewed as containing two magnetic cationic species, i.e., Cr^{4+} (d^2), and Cr^{3+} (d^3), in $\mathrm{Cr}^{4+}_{1-x}\mathrm{Cr}^{3+}_x\mathrm{O}^{2-}_{2-x}\mathrm{F}^-_x$.

The small deviation of μ_s from the 1.96 μ_B value of CrO_2 (Table II) and ferromagnetic behavior at 4.2 K indicates the presence of basically ferromagnetic interactions between Cr^{4+} and Cr^{3+} for compositions of $x < 0.12$. At higher fluorine concentrations, the Curie temperature reaches a minimum value and a peak appears in the magnetization vs temperature curve. The field dependence of the peak and the linearity of the magnetization with field to 10 kOe below the peak suggests that compositions of $x \geqslant 0.12$ are metamagnetic. The transport properties of the products in the region $(0.10 \leqslant x \leqslant 0.20)$ show a definite breakdown of metallic behavior. In the electrical properties of two such members ($x = 0.10$ and 0.20), minima were observed in the metamagnetic regions.

Substitution of Cr^{3+} ions in the CrO_2 matrix yields $\mathrm{Cr}^{4+}_{1-x}\mathrm{Cr}^{3+}_x\mathrm{O}_{2-(x/2)}$ derivatives (*4*). This

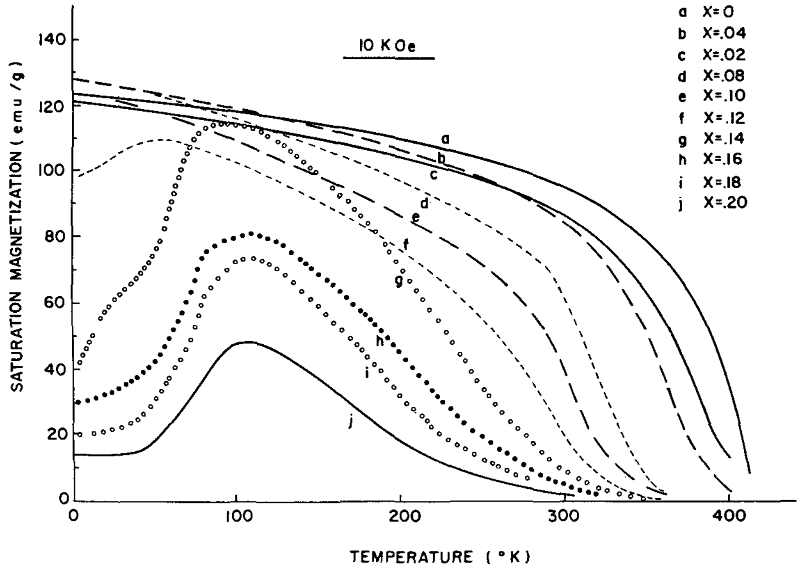

FIG. 3. Saturation magnetization (emu/g) vs temperature (K) for several members of the $CrO_{2-x}F_x$ series. Data obtained at magnetic fields of 10 kOe.

particular series shows an increase in the c/a ratio and Curie temperature but a decreasing magnetic moment with increasing x. This indicates more complex magnetic structures for the metamagnetic region ($x \geqslant 0.12$) of the $CrO_{2-x}F_x$ system.

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