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An Investigation of the $Cr_{1-x}Mn_xO_2$ Series and the Characterization of Orthorhombic $CrMnO_4$

B. L. CHAMBERLAND,* W. H. CLOUD,† AND C. G. FREDERICK

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

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Several members of the $Cr_{1-x}Mn_xO_2$ series were prepared in the tetrahedral anvil press by the reaction of CrO_2 with MnO_2. The tetragonal, rutile-type products were single-phase and have been characterized by crystallographic and magnetic measurements. The results are consistent with the formulations $Cr^{4+}_{1-2x}Cr^{3+}$ $Mn^{5+}O_2$ for $0 \leqslant x \leqslant 0.5$. At low manganese concentration, $x < 0.20$, the magnetic moments are consistent with ferromagnetic contribution from Mn^{5+}. A two-phase product was noted at the composition $x = 0.90$. The $CrMnO_4$ composition was found to have a powder pattern similar to that of orthorhombic PtO_2.

Introduction

Studies on the $Cr_{1-x}Mn_xO_2$ system have previously been reported by several groups (*1–6*). Siratori and Iida (*1–2*) prepared their phases by the solid state reaction of CrO_3 and MnO_2 under oxygen pressure, while Druilhe et al. (*4–6*) obtained products by the thermal decomposition of $Mn(NO_3)_2$ and CrO_3 with a final heat treatment under oxygen pressure. The crystallographic, magnetic, and electrical properties of the products have been reported (*1–6*).

The objectives of this research were to reinvestigate this system in order to isolate pure, single-phase products and to re-study the magnetic properties of various members to determine the magnetic interactions.

Experimental Methods

Pure MnO_2 was prepared (*7*) by the thermal decomposition of $Mn(NO_3)_2 \cdot 6H_2O$ in air at 500°C for 15 hr. The tetragonal lattice parameters were: $a = 4.3977 \pm 3$ and $c = 2.8778 \pm 3$ Å, in good agreement with previously reported cell constants (*8*).

Anal. Calcd. for MnO_2: O, 36.81; weight loss on reduction to MnO, 18.40%. Found: O, 35.97; weight loss, 18.23%.

Chromium dioxide, CrO_2, was prepared (*9*) by the hydrothermal reaction of CrO_3 with Cr_2O_3 at 400°C and 3000 atm in a sealed platinum capsule. The lattice dimensions of the CrO_2 reactant, dried in O_2 at 300°C for 1 hr, were: $a = 4.4199 \pm 6$ and $c = 2.9164 \pm 4$ Å. This material had a Curie temperature of 125°C.

Anal. Calcd. for CrO_2: O, 38.10; weight loss on reduction to Cr_2O_3: 9.54%. Found: O, 39.13; weight loss, 10.05%.

Various ratios of CrO_2 and MnO_2 mixtures were ground in an agate mortar and pestle, sealed in a platinum cylinder, and heated to 1000°C for 2 hr at 65 kbar pressure in a tetrahedral anvil press, then rapidly quenched under pressure to room temperature. All products for $0 \leqslant x \leqslant 0.75$ were single phase. At the composition $x = 0.90$ a two-phase product was obtained. An immiscibility gap in the CrO_2–MnO_2 system was previously noted by Siratori and Iida (*1*) in their study using different experimental conditions. The crystallographic data were obtained with a Hägg–Guinier camera utilizing Cu$K\alpha_1$ radiation and an internal KCl standard. The powder diffraction patterns were read on a Mann film reader, and lattice parameters were refined from the powder data by a least-squares technique.

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

† Deceased.

‡ Contribution No. 1929.

Attempts to prepare several members of this series by the hydrothermal reaction of MnO_2 with CrO_2 at 400°C and 3000 atm for 19 hr yielded only mixed rutile phases. One of these products was CrO_2 ($T_c = 120$ to 123°C), present in moderate to slight amounts. This ferromagnetic impurity masked the true magnetic behavior of the $Cr_{1-x}Mn_xO_2$ phases. This phase is believed responsible for the high and invarying Curie temperatures reported by previous authors (*1*, *5*) for several members of this series prepared at lower pressure.

The magnetic properties on the high-pressure phases were obtained using a Foner type vibrating sample magnetometer. The reported Curie temperatures were obtained from magnetization measurements in 300 Oe fields. Magnetic moments were calculated as $T \to 0$ and $1/H \to 0$ from the saturation magnetization data at 4.2 K in fields up to 10 kOe.

Results

The lattice parameters for the tetragonal, rutile-type products are given in Table I and are plotted in Fig. 1. The crystallographic data show that homogeneous products are formed for the compositions $0.005 \leqslant x \leqslant 0.33$ since the standard deviations in lattice parameters are less than 1.5 part/thousand. This agreement can only come from narrow powder diffraction lines and is indicative of homogeneity in the samples. The products with compositions $0.05 \leqslant x \leqslant 0.25$ are saturated in fields of 10 kOe at 4.2 K (Fig. 2). The magnetic transitions at low Mn concentration are sharp ($\Delta T_c \sim 15$ K) but broader at higher concentrations of $x = 0.25$ ($\Delta T_c \sim 40$ K). Products where x was greater than 33% show broader powder diffraction lines suggesting inhomogeneous compositions. Such broad powder patterns have been observed in other rutile phases, such as CrO_2–TiO_2, CrO_2–VO_2, CrO_2–GeO_2, and CrO_2–SnO_2. The magnetic data for compositions $0.33 \leqslant x \leqslant 0.75$ ($Cr_{1-x}Mn_xO_2$) are also quite similar to the other rutile systems, i.e., broad saturation magnetization vs temperature plots, no sharp Curie points and incomplete saturation at 10 kOe.

It should be noted that the composition $Cr_{0.5}Mn_{0.5}O_2$, or $CrMnO_4$, is orthorhombic with a distorted rutile-type structure as found for $CaCl_2$ and PtO_2 (*10*).

This orthorhombic product undergoes an irreversible endothermic transition at 650°C when heated under argon in a DTA cell. A weight loss was noted in this experiment and the residue was found to have a spinel-type structure with $a = 8.4551 \pm 4$ Å. The formulation of this residue is believed to be $Mn^{2+}[Cr^{3+}_{1.5}Mn^{3+}_{0.5}]O_4$. The orthorhombic $CrMnO_4$ appears to be a high-pressure modification.

The products obtained in the high-pressure experiments were microcrystalline to a doping concentration of 10% Mn.

TABLE I

CRYSTALLOGRAPHIC DATA FOR THE $Cr_{1-x}Mn_xO_2$ SYSTEM

x in $Cr_{1-x}Mn_xO_2$	a(Å)	c(Å)	c/a	Vol. (Å³)
0.005	4.4193 ± 4	2.9160 ± 4	0.6598	56.95 ± 1
0.010	4.4198 ± 5	2.9156 ± 4	0.6597	56.98 ± 1
0.025	4.4207 ± 3	2.9146 ± 3	0.6593	56.96 ± 1
0.050	4.4216 ± 4	2.9137 ± 3	0.6590	56.97 ± 1
0.100	4.4207 ± 5	2.9095 ± 4	0.6582	56.86 ± 1
0.250	4.4207 ± 7	2.8992 ± 4	0.6558	56.66 ± 2
0.333	4.4195 ± 5	2.8944 ± 4	0.6549	56.53 ± 1
0.500	(4.420 ± 3)[a]	2.8883 ± 7	0.6535	56.42 ± 3
0.667	4.4061 ± 9	2.8815 ± 7	0.6540	55.94 ± 2
0.750	4.4001 ± 6	2.8775 ± 5	0.6540	55.71 ± 2

[a] Average a (orthorhombic lattice parameter: $a = 4.399 \pm 3$; $b = 4.441 \pm 3$ Å).

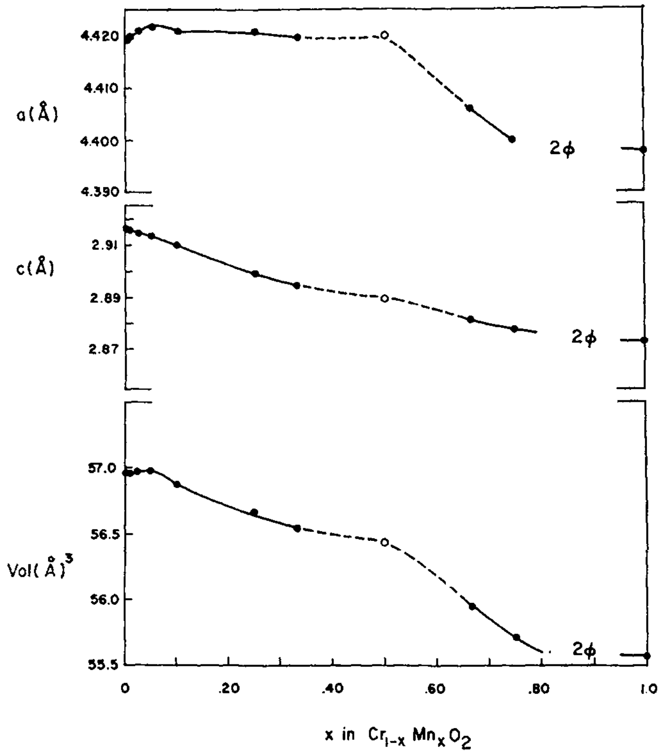

FIG. 1. Crystallographic data on the $Cr_{1-x}Mn_xO_2$ system as a function of x. (o) The orthorhombic phase at $x = 0.5$. 2ϕ indicates a two phase region.

Discussion

The crystallographic and magnetic results indicate that the phases prepared in this work are not contaminated with CrO_2, but neither are they homogeneous for the whole solid solution range; they are best prepared at high pressure. The 3 kbar experiments carried out in this study and the lower pressure experiments performed by previous workers (*1*–*6*) yield only heterogeneous phases contaminated with the ferromagnetic CrO_2 impurity which exhibits the overall high Curie temperature reported (*1*, *5*). This magnetic impurity masks the true changes in Curie temperature with increasing manganese concentration (Table II).

TABLE II

MAGNETIC DATA FOR THE $Cr_{1-x}Mn_xO_2$ SYSTEM

x in $Cr_{1-x}Mn_xO_2$	μ_B Ref. (*1*)	μ_B Ref. (*5*)	μ_B This work	T_c(K)
0.005	—	—	1.84	400
0.010	—	—	1.92	396
0.025	—	—	1.82	392
0.050	1.88	—	1.75	376
0.100	1.69	1.54	1.42	366
0.250	—	—	1.09	284
0.333	—	—	0.86	244
0.500	0.44	0.37	0.32	187
0.667	—	—	0.12	117

Under the high-pressure conditions utilized in this study, the rutile-type products show a consistent decrease in volume, *c*/*a* ratio, Curie temperature and magnetic moment.

There are several magnetic models based on possible formal valence states of the ions. The Cr^{3+} and Mn^{5+} valence states are intuitively reasonable since one would expect the redox reaction $Cr^{4+} + Mn^{4+} \rightarrow Cr^{3+} + Mn^{5+}$ to occur in a mixed system. The model in which $Cr^{4+}\uparrow$ $Cr^{3+}\uparrow$ $Mn^{5+}\downarrow$ has a slope similar to the experimental data (Fig. 3). The other models are not consistent with the observed data.

In addition to the models based on formal valence states of the ions, one might also consider the mixing of chromium bands with those of manganese. This approach would allow the

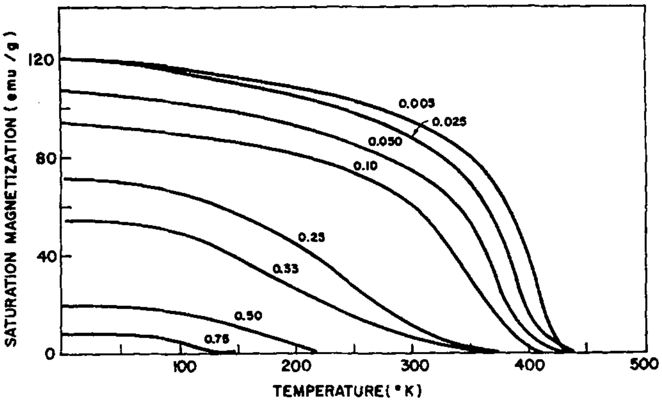

FIG. 2. The saturation magnetization (emu/g) for several $Cr_{1-x}Mn_xO_2$ compositions as a function of temperature (K). Data obtained at 10 kOe.

electrons to mix more easily within the permitted bands, but a smooth change in magnetic moment would be predicted. The observed magnetic behavior and the anomaly at $x = 0.5$ which gives rise to a distinct structure for $CrMnO_4$ would argue against such a simple model.

The small radius of Mn^{5+} is probably responsible for the reduction in unit cell volume. At $x = 0.50$ the phase formed is $Cr^{3+}Mn^{5+}O_4$, which can be indexed on an orthorhombic basis (distorted rutile-type structure). This symmetry and structure are also found for PtO_2.

Previous studies (*11*) have shown similar changes in the c/a ratio, volume, Curie temperature, and magnetic moment of CrO_2 as other transition metals are partially substituted for chromium. The isostructural and isoelectronic system $CrO_{2-x}F_x$ also shows (*12*) decreasing volume, decreasing c/a ratio, and decreasing Curie temperature with increasing values of c.

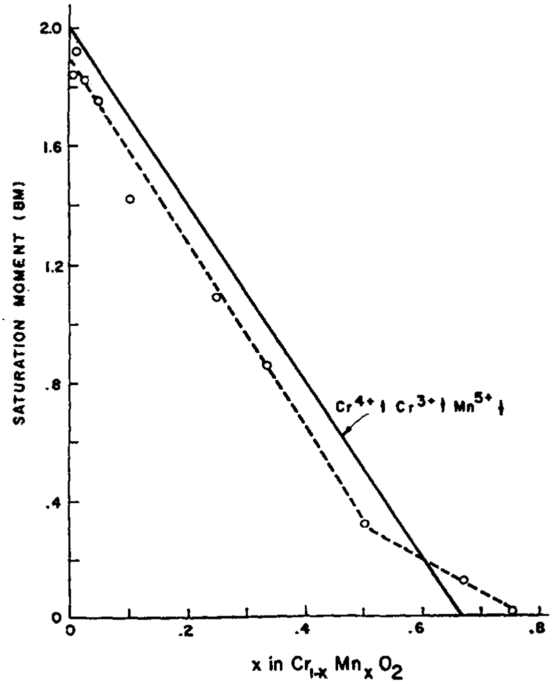

FIG. 3. Calculated (—) and observed (o--) saturation moment (BM) as a function of manganese content.

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