

## Magnetic and Electrical Transport Properties of $\text{CaCrO}_3$

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Received March 17, 1971

The preparation of crystalline  $\text{CaCrO}_3$  and some of its magnetic and electrical properties are reported. The electrical resistivity is metal like. The high-temperature susceptibility is Curie-Weiss paramagnetic with  $\theta = -920^\circ\text{K}$ , indicative of antiferromagnetic interactions; a break in the susceptibility at about  $325^\circ\text{K}$  suggests antiferromagnetic ordering at that temperature. A first-order transition occurs at  $90^\circ\text{K}$  accompanied by the appearance of a very small ferromagnetic moment and a discontinuity in the resistivity. X-ray data indicate that this is an 0-orthorhombic  $\rightarrow$  0'-orthorhombic crystallographic transformation. The low temperature state is probably a canted antiferromagnet.

### Introduction

Chromium(IV) oxide is ferromagnetic and metallically conducting (1). Ternary oxides,  $\text{ACrO}_3$ , where A is Ca (2), Sr (3), Ba (4), Pb (5), have recently been prepared at high pressure and their electrical and magnetic properties have been determined. Electrical measurements on powder compact of  $\text{CaCrO}_3$  showed semiconductor behavior (2). This paper reports the preparation of crystalline  $\text{CaCrO}_3$  and its magnetic and electrical characterization.

### Experimental

#### Reagents

Chromium(IV) oxide was prepared by hydrothermal reaction of  $\text{Cr}_2\text{O}_3$  and  $\text{CrO}_3$  at  $400^\circ\text{C}$  and 3000 atm; the product was then dried in an  $\text{O}_2$  atmosphere for two hours at  $300^\circ\text{C}$ . Calcium oxide was prepared by the thermal decomposition of  $\text{CaCO}_3$  (obtained from Spex Industries—5N purity) at  $1000^\circ$  in a high vacuum system. All manipulations of the reactants were carried out in a drybox under a dry nitrogen atmosphere to prevent hydration and the formation of  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$ .

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### Preparation

Intimately mixed stoichiometric amounts of  $\text{CaO}$  and  $\text{CrO}_2$ , sealed in small platinum capsules, were heated in a tetrahedral anvil press at 65 kbars and  $1000^\circ\text{C}$  for one hour, then quenched while still under pressure. The product contained some acid-soluble phase  $\beta\text{-CaCr}_2\text{O}_4$  and crystalline  $\text{CaCrO}_3$ . The black crystals of  $\text{CaCrO}_3$  were isolated by manual separation under a microscope.

### Crystallographic Properties

Powder diffraction data were obtained at room temperature on a Hägg-Guinier camera using monochromatic  $\text{CuK}\alpha_1$  radiation and an internal KCl standard. The diffraction films were read on a Mann film reader and indexed on the basis of a distorted perovskite cell; cell constants were refined by a least squares computer program. The cell was orthorhombic with  $a = 5.289 \pm .001 \text{ \AA}$ ,  $b = 5.316 \pm .001 \text{ \AA}$ , and  $c = 7.487 \pm .001 \text{ \AA}$  in agreement with Ref. (2).

Low-temperature data were obtained with a General Electric XRD-5 diffractometer using Ni filtered copper radiation and an internal diamond standard. Liquid nitrogen data were indexed on the basis of an orthorhombic cell; cell constants refined by least squares were  $a = 5.269 \pm .002$ ,  $b = 5.306 \pm .002$ ,  $c = 7.405 \pm .003$ . Diffractometer scans in the 004, 132, and 312 reflection regions showed an abrupt change in cell somewhere between  $78^\circ\text{K}$

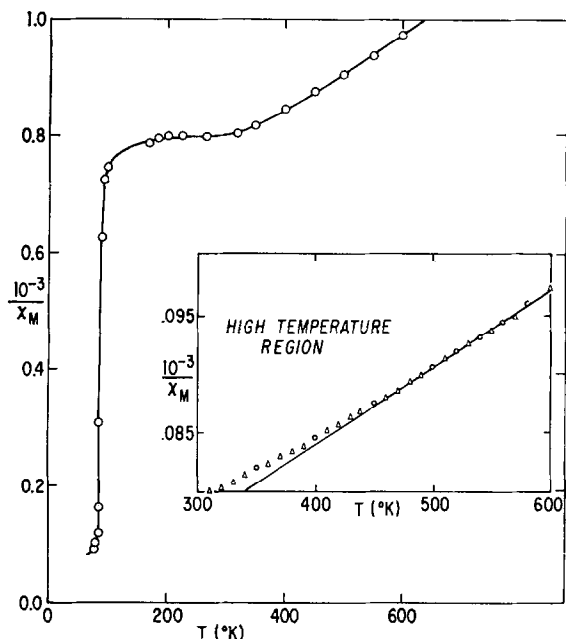


FIG. 1. Temperature dependence of magnetic susceptibility at 8000 Oe. Note that the ordinate scale on the insert should be multiplied by 10.

and 115°K with virtually no further change from 115°K to 300°K.

#### Magnetic Properties

Magnetic data in the temperature range 78–600°K were obtained with a Faraday balance (Figs. 1 and

2). Parasitic ferromagnetism was observed below the sharp transition at 90°K. At 300°K and above, the magnetic susceptibility was field independent. The high-temperature magnetic susceptibility fits the Curie-Weiss law with paramagnetic moment of 3.6 BM and  $\theta = -920^\circ\text{K}$ .

#### Electrical Properties

Results of single-crystal four-probe resistivity versus temperature measurements are shown in Fig. 3. The crystal was selected from the same sample used in the magnetic characterization. The room-temperature resistivity is  $770 \mu\Omega\text{-cm}$ ; the temperature dependence is approximately linear; and the resistivity ratio ( $\rho_{300}/\rho_{4.2}$ ) is about 25. The Seebeck coefficient is less than  $10 \mu\text{V}/^\circ\text{K}$  at about 285°K.

#### Discussion

The chemistry of the reaction of CaO with  $\text{Cr}_2\text{O}_3$  at high pressure and temperature is complex. It is known (6) that slight traces of moisture in the reactants can lead to  $\text{CrOOH}$ . Goodenough, *et al.* (2) report that the stoichiometric reaction includes varying amounts of  $\text{Cr}_2\text{O}_3$  in the  $\text{CaCrO}_3$  powder product. In this work, the product contained crystalline  $\text{CaCrO}_3$  and some  $\beta\text{-CaCr}_2\text{O}_4$  but no  $\text{Cr}_2\text{O}_3$ .

The presence of some  $\beta\text{-CaCr}_2\text{O}_4$  in the product from stoichiometric amounts of reactants suggests that nonstoichiometry in the  $\text{CaCrO}_3$  product is

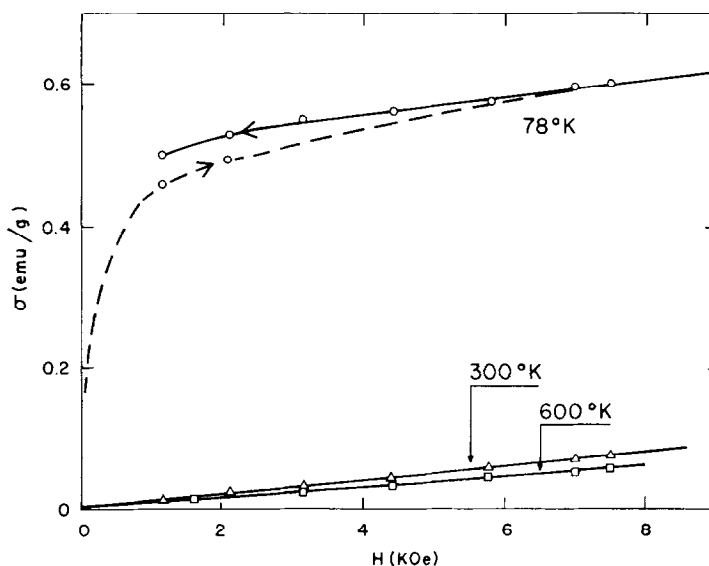


FIG. 2. Field dependence of magnetization.

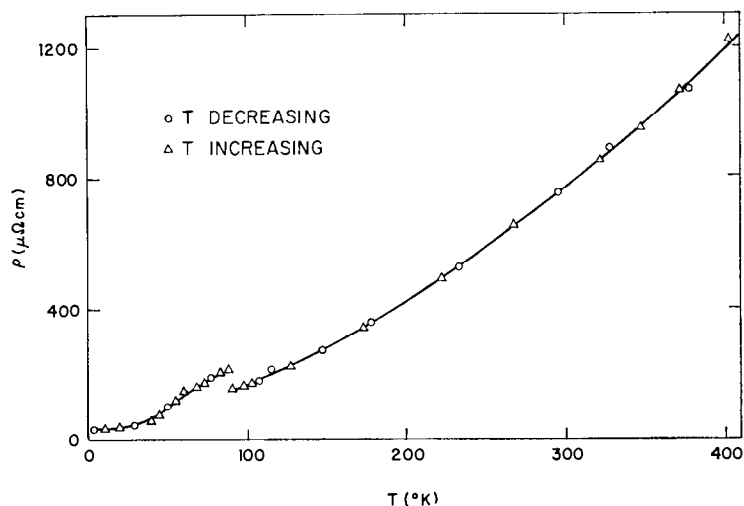


FIG. 3. Electrical resistivity.

possible. The sample volume was not sufficient for a chemical analysis but the X-ray data are in agreement with that previously reported (2) for  $\text{CaCrO}_3$ . The sharp transition observed in the magnetic susceptibility of a 4 mg sample composed of many individual crystals shows that the sample was quite homogeneous. We, therefore, assume that the material characterized is a pure perovskite phase,  $\text{Ca}_{1-y}\text{CrO}_{3-x}$ , where  $y$  and  $x$  are unknown but probably small and uniform within the sample.

The report (2) that  $\text{CaCrO}_3$  is semiconducting was not confirmed in our work. Its metallic nature is clear from the near-linear positive temperature dependence of the resistivity, the high-resistivity ratio, and the low Seebeck coefficient. The difference may be a result of differing stoichiometry between the two samples. Gross differences in composition seem unlikely, however, since the cell constants are in good agreement. A more reasonable explanation is the difference that might be expected between measurements made on powder versus single crystals. Electrical measurements on powder samples can lead to erroneous conclusions, especially when the material is susceptible to oxidation or reduction forming a new phase at the grain boundaries. Since  $\text{CaCrO}_3$  is easily reduced to insulating  $\text{Cr}^{+3}$  derivatives, measurements on powder samples should be viewed with caution. Our single crystal measurements are, therefore, believed to be more representative of the intrinsic electrical behavior of  $\text{CaCrO}_3$ .

The high-temperature Curie-Weiss magnetic susceptibility indicates local moment-like behavior with antiferromagnetic interactions. The deviation from

Curie-Weiss behavior below  $470^{\circ}\text{K}$  suggests the formation of an antiferromagnetically ordered state with Néel point probably around  $325^{\circ}\text{K}$ . The field-independent magnetic susceptibility in this region shows the absence of a spontaneous moment in this temperature range.

A sharp transition to a canted antiferromagnetic state with magnetization about twice that reported by Goodenough, *et al.* (2) occurs at  $90^{\circ}\text{K}$  (cf., the spontaneous moment at  $78^{\circ}\text{K}$  shown in Fig. 2). The discontinuity in the electrical resistivity also at  $90^{\circ}\text{K}$ , as well as the sharpness of the transition in the magnetic data, points toward a first-order transition. The magnitude and abruptness of the change in cell constants indicate that this is a crystallographic transition of the  $0$ -orthorhombic  $\rightarrow$   $0'$ -orthorhombic type discussed by Goodenough, *et al.* (2).

Although ferromagnetic order in metallic systems is becoming more common, the occurrence of antiferromagnetic order in this metallic  $d^2$  system is somewhat of an oddity and deserves special attention. Presumably both the good electrical conductivity and the Curie-Weiss behavior of the magnetic susceptibility arise from the  $d$  electrons of  $\text{Cr}^{+4}$  in a band narrow enough to give the appearance of a localized paramagnetic moment, but wide enough to allow good metallic conductivity. The high paramagnetic moment is, in fact, slightly larger than that expected for a spin only  $d^2$  state. A similar high moment was observed (7) for the isoelectronic system  $\text{V}^{+3}$  in  $\text{LaVO}_3$  which also shows a discontinuity in the electrical properties at low temperature.

*Note Added in Proof:* Since the moment for a localized  $d^2$  system in a cubic field is expected to be temperature dependent, parameters from a simple Curie-Weiss fit can be misleading. The observed susceptibility data agree with that expected for  $\text{Cr}^{+4}$  in the strong field limit for a spin-orbit coupling constant of  $130.0 \text{ cm}^{-1}$  and a Weiss constant of  $-375^\circ\text{K}$ ; the observed moments are 2.76, 2.84, 2.90 B.M. at 400, 500,  $600^\circ\text{K}$ ; corresponding theoretical values for  $\text{Cr}^{+4}$  are 2.75, 2.83, 2.89 B.M.

### Acknowledgment

We are grateful to W. R. Dolinger and W. J. Evans for technical assistance, J. F. Whitney and staff for X-ray analysis, and W. Bindloss and D. B. Rogers for helpful discussions.

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