

Thermogravimetric analysis was performed on a washed sample of  $\text{CaCrO}_3$  which was reduced in a stream of  $\text{H}_2/\text{Ar}$  (15%) at  $1000^\circ\text{C}$  to  $\text{CaO}$  and  $\text{Cr}_2\text{O}_3$ . Experimental weight loss was 5.98% and is to be compared to the theoretical loss of 5.71%.

The x-ray powder diffraction pattern of  $\text{CaCrO}_3$  could be completely indexed on the basis of an orthorhombic unit cell containing four formula units: ( $a = 5.287\text{\AA}$ ,  $b = 5.316\text{\AA}$ ,  $c = 7.486\text{\AA}$ ). The intensities are also in good agreement with those calculated for this orthorhombic cell. The type and degree of distortion from cubic symmetry are assumed to be those described by Geller [5] for  $\text{GdFeO}_3$  (space group  $\text{Pbnm}$ ). A comparison of observed and calculated intensities and interplanar spacings is given in Table 1. This type of distortion, which reduces the nearest-neighbor anion coordination of the A cation from 12 to 9+3, is found in every other known perovskite  $\text{CaBO}_3$  ( $B = \text{Ti, V, Mn, Mo, Ru}$ ) and appears to be due to the relatively small size of the  $\text{Ca}^{2+}$  ion (ionic radius  $\approx 0.98\text{\AA}$ ) and the existence of covalent character in the Ca-O bond.

A resistivity of  $1.4 \times 10^4$  ohm-cm at  $300^\circ\text{K}$  and  $1.1 \times 10^6$  ohm-cm at  $77^\circ\text{K}$  was obtained by the four-probe Van de Pauw method in a dense cylinder (2 mm dia. x 1 mm) taken from a pressure run. This indicates that the sample is semiconducting rather than metallic.

Magnetic susceptibility  $\chi_m$  was obtained with a vibrating-sample magnetometer and samples weighing about 200 mg. The material was studied in the temperature range  $4.2 < T < 300^\circ\text{K}$  and in magnetic fields up to 17.2 kOe. A nickel standard was used to calibrate the instrument. Figure 1(a) shows  $1/\chi_m$  vs  $T$  for  $\text{CaCrO}_3$  in a field of 10 kOe. Parasitic ferromagnetism appears below the antiferromagnetic Néel temperature  $T_N = 90^\circ\text{K}$ . Such parasitic ferromagnetism is a characteristic of the orthorhombic perovskites. Figure 1(b) displays the magnetization  $\sigma$  vs applied magnetic field  $H_a$  for three different temperatures. Below  $T_N$ , the magnetization obeys the usual formula for parasitic ferromagnetism:

$$\sigma = \sigma_0 + \chi_m H_a \quad (1)$$

giving  $\sigma_0 = 0.22, 0.295$  emu/gm at  $77$  and  $4.2^\circ\text{K}$ , respectively.

TABLE 1  
X-Ray Data for  $\text{CaCrO}_3$

HKL	$d_{\text{obs}}$	$I_{\text{obs}}$	$I_{\text{calc}}$	HKL	$d_{\text{obs}}$	$I_{\text{obs}}$	$I_{\text{calc}}$
110, 002	3.738	M	13	233, 125, 323,	1.265	VW	2
111	3.338	VW	6	215, 411			
020, 112, 200	2.646	VVS	100	042, 134, 330	1.250	VW	4
021, 201	2.489	VW	2	006, 314, 402	1.247	VW	1
120, 210	2.370	VW	1	240, 332, 116,	1.184	M	9
121	2.264	VW	1	420			
211, 103	2.255	W	5	135, 333	1.173	VW	3
022, 202	2.160	W	3	315	1.170	VW	1
113	2.076	VW	3	044	1.083	W	1
122, 212	2.003	VW	2	404	1.080	W	3
220, 004	1.872	VS	43	152	1.004	W	1
023, 221	1.816	W	4	244, 136	1.002	W	3
130, 222, 114,	1.674	W	9	424, 316, 512	1.000	M	9
310				440	0.937	VW	1
131, 311	1.638	W	7	008	0.935	VW	1
132, 024, 204,	1.327	S	37	352	0.884	W	1
312				336, 028, 532,	0.883	M	12
133, 115, 313	1.391	VW	2	208, 600			
040	1.328	W	2	260	0.840	VW	< 1
224, 400	1.323	M	14	444	0.838	W	2
141	1.270	VW	< 1	228, 620	0.837	W	4

$$\underline{a} = 5.287 \pm 0.004 \text{ \AA} \quad \underline{b} = 5.316 \pm 0.004 \text{ \AA} \quad \underline{c} = 7.486 \pm 0.005 \text{ \AA}$$

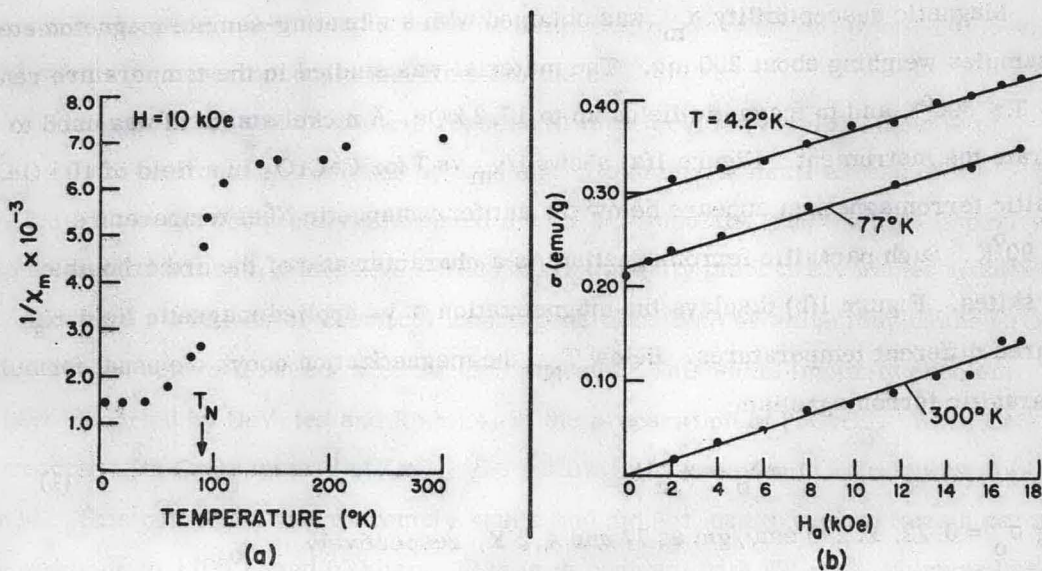


FIG. 1

Magnetic Properties of  $\text{CaCrO}_3$