

## Preparation and Magnetic Properties of CrOCl

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Chromium oxide chloride, CrOCl, was prepared by the vapour phase transport method from a mixture of chromium sesquioxide and anhydrous chromium chloride and was as well prepared in a solid state reaction from a mixture of anhydrous chromium chloride and titanium oxide. The magnetic properties were investigated between 4.2 and 300 K. The compound is paramagnetic and the susceptibility follows the Curie-Weiss law from 150 to 300 K. In the paramagnetic range  $\mu$  for the chromium atom is  $3.66 \mu_B$ .

The compound is antiferromagnetic at 4.2 K. Neutron diffraction powder patterns were measured at 300 K and at 4.2 K. The magnetic reflections were indexed on the basis of a magnetic unit cell with  $a_M = a$ ,  $b_M = 4b$ , and  $c_M = c$ , where  $a$ ,  $b$ ,  $c$  are the dimensions of the chemical unit cell. The magnetic structure is collinear with the spins in the direction of the  $z$ -axis.

The oxide chlorides, MeOCl, of the transition elements titanium, vanadium, chromium, and iron are isomorphous with crystal structures belonging to the orthorhombic space group  $Pmmn$ . The structure is a layer structure with a packing of atoms similar to that found in the crystal structure of lepidocrocite,  $\gamma$ -FeOOH. Little is known about the magnetic properties of the transition metal oxide chlorides. The magnetic properties of iron oxide chloride, FeOCl, was investigated by Grant<sup>1</sup> using the gamma resonance technique down to 6 K, and a paramagnetic to an antiferromagnetic transition was observed with a Néel temperature of 92 K. Schäfer and Wartenpfehl<sup>2</sup> investigated the magnetic properties of chromium oxide chloride, CrOCl, in the temperature range 90 to 295 K and reported the compound to be paramagnetic in that temperature range and to

follow the Curie-Weiss law. A more detailed investigation of the magnetic properties of chromium oxide chloride is reported below.

### EXPERIMENTAL

*Chemistry and X-ray technique.* Chromium oxide chloride was prepared from a mixture of chromium sesquioxide,  $\text{Cr}_2\text{O}_3$ , and anhydrous chromium chloride,  $\text{CrCl}_3$ , by the vapour phase transport method. A stoichiometric mixture of the two compounds was thoroughly mixed in an agate mortar and was pressed into pellets at a force of 35 ton. The pellets (10 g) were placed with an excess of 5 g  $\text{CrCl}_3$  in a quartz ampoule (diameter 3 cm, length 30 cm), and the ampoule was placed in a tube furnace with 2/3 of the ampoule inside the furnace and 1/3 of the ampoule sticking out of the furnace (see Fig. 1). The bottom of the ampoule was thus positioned in the middle of the furnace where the temperature was measured using a Pt-PtRh-thermocouple. As a result of this mounting a temperature gradient was established along the ampoule. The furnace was heated to 921 °C and

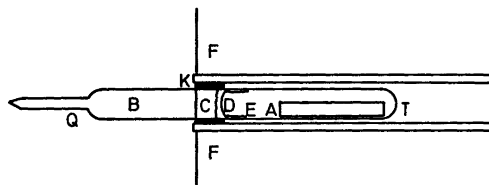


Fig. 1. Sketch of the experimental arrangement used in the vapour phase growth of CrOCl. F: Electric furnace. K: Thermal insulating material. Q: Quartz ampoule. T: Pt-PtRh-thermocouple. A: Pellets of  $\text{CrCl}_3 - \text{Cr}_2\text{O}_3$  mixture and excess of  $\text{CrCl}_3$ . B: Thin layer of  $\text{CrCl}_3$ . C: Thick plug of  $\text{CrCl}_3$ . D: Layer of CrOCl. E: Crystals of  $\text{Cr}_2\text{O}_3$ .

Table 1. X-Ray powder pattern of CrOCl  
 $a = 3.863(4)$  Å,  $b = 3.182(2)$  Å,  $c = 7.694(7)$  Å.

h k l	$d_{\text{obs}}$	$d_{\text{calc}}$	I
0 0 1	7.694	7.693	s
1 0 1	5.451	5.452	s
1 1 0	2.455	2.456	s
0 1 2		2.452	
1 1 1	2.341	2.340	m
1 0 3	2.134	2.137	vw
1 1 2	2.074	2.070	vw
0 1 3	2.000	1.997	w
2 0 0	1.934	1.932	m
2 0 1	1.873	1.873	w
1 1 3	1.776	1.774	w
1 0 4	1.720	1.722	vw
0 2 0	1.591	1.591	m
0 2 1	1.556	1.558	w
2 1 2	1.518	1.517	m
1 2 1	1.445	1.445	m
2 1 3	1.388	1.388	m
3 0 1	1.271	1.270	vw
2 2 0	1.227	1.228	w
0 2 4		1.226	
3 0 2	1.221	1.221	vw

s: strong, m: medium, w: weak  
vw: very weak.

kept at that temperature for 6 d. The compounds formed and transported in the ampoule were: A thin layer of CrCl<sub>3</sub> in the part of the ampoule that was outside the furnace, a thick layer of CrCl<sub>3</sub> where the ampoule entered the furnace, and where the temperature gradient must be rather steep. This layer covered the whole cross section of the ampoule and was approximately 1 cm thick so that it had divided the ampoule in a cold section outside and a hot section inside the furnace. On the hot side of

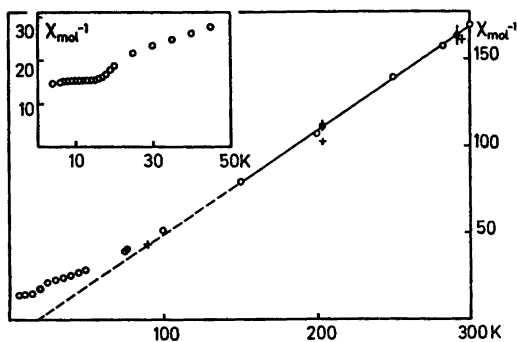


Fig. 2. Inverse molar susceptibility of CrOCl vs. temperature. Open circles indicate values obtained by the vibrating sample magnetometer, filled circles values obtained by the Gouy method, and the crosses values obtained from Ref. 2. The sample used in the Gouy measurements were prepared by the vapour transport method and may contain small impurities (of CrCl<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub>). This was, however, not detectable in the powder pattern of the sample.

the CrCl<sub>3</sub> layer was a layer of CrOCl followed by a thin layer of green crystals that were identified as Cr<sub>2</sub>O<sub>3</sub>. A sample of CrOCl was isolated mechanically from the two other compounds and was used in an investigation of the magnetic properties using the Gouy method.

Chromium oxide chloride was also prepared from a stoichiometric mixture of anhydrous CrCl<sub>3</sub> and titanium oxide, TiO<sub>2</sub>, using a modified version of the procedure described by Schäfer and Wartenpfehl.<sup>2</sup> The mixture of the two compounds was placed in rubber molds which were sealed, evacuated and pressed at an isostatic pressure of 5000 atm. The rods of the mixture were discharged from the molds and placed in boats of aluminium oxide in a quartz tube connected over a cold trap to a mercury diffusion pump. The quartz tube was placed in an electric tube furnace and was evacuated to a vacuum of less than 1 mmHg. This vacuum was maintained during the experiment. The tube was slowly heated from room temperature to 800 °C over a period of 5 h, and was then heated further to 900 °C over a period of 5 h, followed by cooling to room temperature. The titanium tetrachloride formed by the reaction condensed in the cooler parts of the reaction tube and in the cold trap. The mixture was completely transformed to chromium oxide chloride by this procedure. CrOCl prepared in this way was used in the further investigations.

All compounds obtained in the preparations were identified by the X-ray powder patterns. X-Ray powder patterns were taken with a Guinier camera using CuK<sub>α</sub> radiation,  $\lambda = 1.54051$  Å, and sodium chloride ( $a_{\text{NaCl}} = 5.6389$  Å) as an internal standard. The X-ray powder pattern of CrOCl is listed in Table 1. The intensities of the powder lines were determined visually.

**Magnetic measurements.** The magnetization of chromium oxide chloride was measured at the temperatures 77, 205, and 295 K using the Gouy method. The sample was placed in a bath cryostat with liquid nitrogen, and with a mixture of solid CO<sub>2</sub> and methanol to obtain the temperatures below room temperature. The magnetization was measured at magnetic fields up to 6.000 Ørsted. The susceptibility of the compound found at 77 K was weakly field dependent. The magnetization was further investigated at temperatures from 4.2 K to room temperature using a vibrating sample magnetometer. A magnetic field of 2520 to 10 070 Ørsted was applied. Fig. 2 shows  $\chi_{\text{mol}}^{-1}$  vs the temperature. From room temperature to 150 K the compound is paramagnetic and the susceptibility follows the Curie-Weiss law with a paramagnetic temperature  $\theta_p = 18$  K. The molar Curie constant is  $C_M = 1.673$ , corresponding to  $\mu = 3.66 \mu_B$ . At temperatures below 150 K, the susceptibility deviates from the Curie-Weiss law. At 100 K the deviation is significant and in the low temperature range from 4.2 to 30 K the inverse susceptibility falls off rapidly from 30

Table 2. Observed and calculated nuclear intensities on absolute scale.  $\lambda = 1.154 \text{ \AA}$ .  $R = 6.6 \%$ .

h k l	$\theta$	$I_{\text{obs}}$	$I_{\text{calc}}$	$\Sigma I_{\text{calc}}$
0 0 1	4.31	0.86	1.08	
1 0 1	9.65	9.66	11.15	
0 1 1	11.35	3.14	2.78	
1 0 2	12.25	8.17	9.77	
0 0 3	13.04	7.44	8.46	
1 1 0	13.62		19.28	50.55
0 1 2	13.65	47.69	31.27	
0 1 3	16.84	9.78	10.39	24.23
2 0 0	17.43	23.51	22.10	
0 0 4	17.50		2.13	
2 0 1	17.99	2.16	1.41	69.32
1 1 3	19.03	46.10	45.70	
1 0 4	19.63	6.20	3.25	48.55
0 2 0	21.32	21.76	19.57	
0 2 1	21.80		1.15	69.32
2 0 3	22.02	71.19	13.41	
0 0 5	22.08		6.21	48.55
2 1 2	22.41		48.55	

Table 3. Observed and calculated magnetic intensities on absolute scale.

h k l	Model I			Model II		
	$I_{\text{obs}}$	$I_{\text{calc}}$	$\Sigma I_{\text{calc}}$	$I_{\text{calc}}$	$\Sigma I_{\text{calc}}$	
0 1 0	0.26	0.27	0.27	0.36	0.36	
0 1 -1	0.37	0.79	0.79	0.39	0.42	
0 1 1		0		0.03		
0 3 0	1.29	1.02	1.02	1.34	1.34	
0 3 -1	3.92	0	2.94	1.02	3.87	
0 3 1		0.58		0.30		
1 1 0	3.92	2.06	2.94	2.37	3.87	
0 1 -2		0.18		0.12		
0 1 2	2.66	0.12	3.48	0.06	2.51	
-1 1 -1		1.62		0.58		
1 1 1	2.66	1.86	1.93	1.93	2.51	
		$R = 29 \%$		$R = 4.7 \%$		
		$\mu = 4.06 \mu_B$		$\mu = 3.36 \mu_B$		

to 15 K, then passes through a plateau between 15 and 10 K and decreases slowly from 10 to 4.2 K. This indicates that the compound has a magnetically ordered state at 4.2 K.

**Neutron technique.** Neutron diffraction powder patterns of CrOCl were measured at room temperature, at 100 K and at 4.2 K using a neutron diffractometer at Centre d'Études Nucléaires, Grenoble. The neutron wave length was 1.157 Å. The sample was placed in a 10 mm diameter cylindrical vanadium container. The powder patterns obtained at 100 K and at room temperature were identical, but the diagram taken at 4.2 K showed five additional magnetic reflections. The room temperature powder pattern is listed in Table 2 and the magnetic reflections from the pattern measured at 4.2 K are listed in Table 3. The magnetic reflections were

indexed using an orthorhombic cell with  $a_M = a$ ,  $b_M = 4b$ , and  $c_M = c$ , where  $a$ ,  $b$ , and  $c$  are the unit cell parameters of the chemical cell. Lorentz corrections,  $LP(\theta) = (\sin \theta \cdot \sin 2\theta)^{-1}$  has been applied to the intensities listed in Tables 2 and 3.

## CRYSTAL DATA AND STRUCTURE REFINEMENT

Chromium oxide chloride is orthorhombic with space group  $Pm\bar{m}n$ , No. 59. The unit cell parameters are  $a = 3.863(4) \text{ \AA}$ ,  $b = 3.182(2) \text{ \AA}$ ,

Table 4. Atomic coordinates and temperature factors with standard deviations.

Atom	$x$	$y$	$z$	$B (\text{Å}^2)$
Cr	1/4	1/4	0.105(5)	2(1)
O	1/4	3/4	0.944(3)	2(1)
Cl	1/4	3/4	0.328(3)	1.6(7)

Table 5. Atomic coordinates and spins of the eight chromium atoms in the magnetic cell.  $z = 0.105$ .

Atom No.	$x$	$y$	$z$	Spin	Model I	Model II
1	1/4	1/16	$z$	$S_1$	$S_x$	$S_x$
2	1/4	5/16	$z$	$S_2$	$S_y$	$-S_x$
3	1/4	9/16	$z$	$S_3$	$-S_y$	$-S_x$
4	1/4	13/16	$z$	$S_4$	$-S_y$	$S_x$
5	-1/4	-1/16	$-z$	$S_5$	$-S_x$	$-S_x$
6	-1/4	-5/16	$-z$	$S_6$	$-S_y$	$S_x$
7	-1/4	-9/16	$-z$	$S_7$	$-S_y$	$S_x$
8	-1/4	-13/16	$-z$	$S_8$	$S_y$	$-S_x$

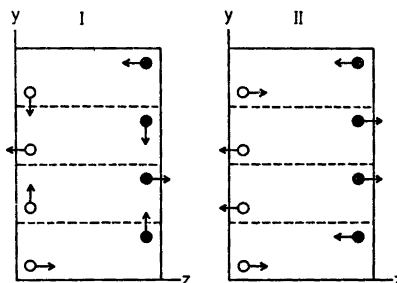


Fig. 3. Projection of Model I and Model II of the magnetic structure in the [100] direction. Chromium atoms at  $x = 1/4$  and  $x = 3/4$  are shown as open circles and filled circles, respectively.

$c = 7.694(7)$  Å, and the unit cell contains two formula units. The chromium atom is in site *a* and the chlorine and oxygen atoms are in site *b*. Using the atomic positions reported by Forsberg<sup>3</sup> for the structure as values for the atomic parameters, and the intensities of the reflections listed in Table 2, atomic positions and isotropic temperature factors were refined. Two different programs were used. The program F418 by Rietveld,<sup>4,5</sup> using a refinement on the profile intensities of the reflections, and the program LINUS<sup>6</sup> using the integrated neutron powder intensities in the refinement. Atomic coordinates and temperature factors obtained by the two methods did not deviate significantly from each other. Table 4 shows the final values of the parameters with their standard deviations obtained with the program LINUS at an *R*-value of 6.6 %, and Table 2 contains the corresponding calculated intensities. The atomic scattering length of Cr, O, and Cl used were 0.353, 0.580, and 0.958 ( $\times 10^{-12}$  cm), respectively.<sup>7</sup>

### MAGNETIC STRUCTURE

From the magnetic measurements the compound is assumed to be antiferromagnetic. The magnetic cell is *a*, 4*b*, *c* and the chromium atoms are placed in the positions listed in Table 5. The antiferromagnetic configuration  $\vec{S}_1 = -\vec{S}_5$ ,  $\vec{S}_2 = -\vec{S}_6$ ,  $\vec{S}_3 = -\vec{S}_7$ , and  $\vec{S}_4 = -\vec{S}_8$  is assumed. Magnetic reflections are not observed for  $k = 2n$ . This indicates a magnetic structure with  $\vec{S}_1 = -\vec{S}_3$  and  $\vec{S}_2 = -\vec{S}_4$ . Two models for the magnetic structure is considered. *Model I* is a non collinear structure with the spins in the *yz*-plane.  $\vec{S}_2$  is perpendicular to  $\vec{S}_1$ . Going from atom position 1 up to 4, the spins are turning  $\pi/2$  for each step, which gives a periodicity of four chemical unit cells to the magnetic cell. The model is similar to the model for the magnetic structure of FeOCl suggested by Grant<sup>1</sup> from gamma resonance spectroscopy. *Model II* is a collinear model with  $\vec{S}_1 = \vec{S}_4$  and  $\vec{S}_2 = \vec{S}_3$ . This too gives a periodicity of four chemical unit cells to the magnetic cell, see Fig. 3.

Using the program F-418 by Rietveld<sup>4,5</sup> and the form factor for chromium reported by Delapalme and Sivardiere<sup>8</sup> the two models of the magnetic structures were refined. For *Model I* the best agreement between observed and

calculated magnetic intensities was obtained with  $\vec{S}_1$  parallel to the *z*-axis and  $\vec{S}_2$  parallel to the *y*-axis. This gave a magnetic moment  $\mu = 4.06 \mu_B$  for the chromium atom and an *R*-value of 29 %. Especially the reflection having contributions from (01-1) and (011) had a too large calculated value. As this result was the best obtained of several combinations of the non collinear model, *Model I* was rejected. For *Model II* the best agreement between observed and calculated magnetic intensities was obtained with  $\vec{S}_1$  parallel to the *z*-axis and  $\vec{S}_2 = -\vec{S}_1$ . This model gave a magnetic moment  $\mu = 3.36 \mu_B$  for the chromium atom and an *R*-value of 4.7 %.

### CONCLUSION

The investigation of the magnetic properties of CrOCl shows the compound to be antiferromagnetic at 4.2 K with a collinear magnetic structure. The inverse susceptibility *vs.* the temperature follows the Curie-Weiss law from 150 K to room temperature.  $\theta_p$  is 18 K.

Atomic parameters obtained in the neutron diffraction experiment are in agreement with the parameters determined with X-ray diffraction.<sup>3</sup>

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### REFERENCES

- Grant, R. W. *J. Appl. Phys.* 42 (1971) 1619.
- Schäfer, H. and Wartenpfehl, F. *Z. Anorg. Allg. Chem.* 308 (1961) 282.
- Forsberg, H. E. *Acta Chem. Scand.* 16 (1962) 777.
- Rietveld, H. M. *Program F418-Fortran IV Version*. Reactor Centrum Nederland, Petten (N. H.), The Netherlands.
- Rietveld, H. M. *J. Appl. Cryst.* 2 (1969) 65.
- Busing, W. R., Martin, K. O. and Levy, H. A. (1962). *ORFLS, A Fortran Crystallographic Least Squares Program*, Oak Ridge National Laboratory Report, ORNL-TM-305. LINUS is a 1971 version of ORFLS.
- Coherent Neutron Scattering Amplitudes*, Massachusetts Institute of Technology, 1972.
- Delapalme, A. and Sivardiere, J. *Longueurs de Fermi, Facteurs de Forme Magnetiques, Rayons Ioniques*, Laboratoire de Diffraction Neutronique, C.E.N.G., Grenoble, France.

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