Acta Chemica Scandinavica A 30 (1976) 133—136

Hydrothermal Preparation and Magnetic Properties of α-CrOOH, β-CrOOH, and γ-CrOOH

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The chromium oxide hydroxides, α-CrOOH, β-CrOOH, and γ-CrOOH were prepared using hydrothermal techniques. The unit cell parameters at 293 K were determined for α- and β-CrOOH. All samples of γ-CrOOH were X-ray amorphous and chemical analysis showed a smaller chromium content (55.0 %) than corresponding to the formula γ-CrOOH (61.3 %). The infra red spectra of γ-CrOOH indicate that the compound contains water of hydration.

The magnetic properties of the three compounds have been investigated between 75 and 293 K using the Faraday method. α-CrOOH is paramagnetic and the magnetic moment of Cr^{3+} is 3.74 ± 0.05 μ_B. β-CrOOH shows a deviation from the Curie-Weiss law at temperatures below 225 K. The magnetization has a broad maximum in the temperature range 90 to 140 K corresponding to a Néel temperature of approximately 120 K. In the paramagnetic temperature range the magnetic moment of Cr^{3+} is 3.91 ± 0.10 μ_B. γ-CrOOH is paramagnetic in the investigated temperature range and the magnetic moment of Cr^{3+} is 3.71 ± 0.05 μ_B.

The oxide hydroxide of chromium, CrOOH, can be prepared in three polymorphic forms, using hydrothermal techniques.[1–9] α-CrOOH has a layer structure with short hydrogen bonds.[10–11] β-CrOOH has an indium oxide hydroxide structure,[12] and is a dense phase with short hydrogen bonds.[8,13] γ-CrOOH is assumed to have the same structure as lepidocrocite, γ-FeOOH.[9] Unit cell parameters and space group for two modifications of CrOOH are listed in Table 1. The magnetic properties of β-CrOOH and γ-CrOOH have not been investigated before. The magnetic properties of α-CrOOH have been investigated in the temperature range 66 to 530 K using the Gouy method.[14] In this work samples were prepared for investigations of hydrogen bonding and magnetic properties of the three compounds.

Table 1. Unit cell parameters and magnetic data for chromium oxide hydroxides.

Compound	Unit cell parameters in Å			Space group	θ_N (K)	θ_P (K)	Molar Curie Constant C_M Exp.	Magnetic moment in μ_B	Ref.
	a	*b*	*c*						
α-CrOOH	2.979(5)	2.979(5)	13.37(2)			−170.9	1.74	3.74(5)	This work
	2.976(1)	2.976(1)	13.36(1)	$R\bar{3}m$					11
						−276	1.9342	3.93	14
β-CrOOH	4.862(2)	4.298(2)	2.955(1)		120	−102.1	1.91	3.91(10)	This work
	4.861	4.292	2.960	$P2_1nm$					5,13
γ-CrOOH						−106.9	1.72	3.71(5)	This work

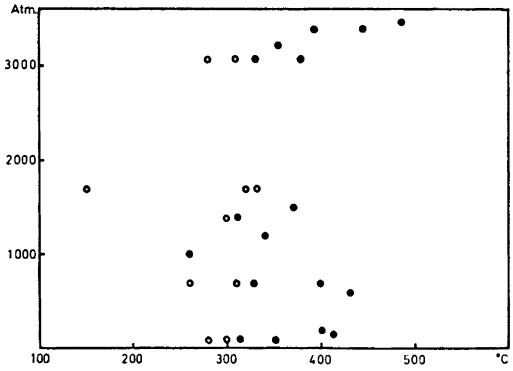

Fig. 1. Pressure temperature region used in the preparation of γ-CrOOH, open circles, and α-CrOOH, filled circles.

EXPERIMENTAL

Chemistry and X-ray technique. α-CrOOH and γ-CrOOH were obtained by reduction of chromate with formate under hydrothermal conditions. The solution used was 1 M with respect to Na_2CrO_4 and 1.5 M with respect to HCOONa. A conventional hydrothermal technique was used.[15] Fig. 1 shows the pressure-temperature region used. At temperatures below 250 °C pure γ-CrOOH is formed and at temperatures above approximately 320 °C pure α-CrOOH is formed. In a temperature range from 250 to 320 °C γ-CrOOH contaminated with α-CrOOH is obtained, and the α-CrOOH content is increasing with increasing temperature used in the hydrothermal preparation. X-Ray powder patterns were taken of all products from the hydrothermal preparation using a Guinier camera with Cu$K\alpha_1$ radiation, $\lambda = 1.54051$ Å, or Co$K\alpha_1$ radiation, $\lambda = 1.78892$ Å, and sodium chloride ($a_{NaCl} = 5.6389$ Å) or germanium ($a_{Ge} = 5.6576$ Å) as internal standards. The unit cell parameters for α-CrOOH obtained from such a measurement are listed in Table 1. All samples of pure γ-CrOOH were amorphous. Chemical analyses were made of α-CrOOH and γ-CrOOH using a standard thiosulfate-iodine titration of chromate. (Found for α-CrOOH: Cr 60.3. Calc.: Cr 61.3. Found for γ-CrOOH: Cr 55.0. Calc.: Cr 61.3). A thermogravimetric analysis of γ-CrOOH shows a weight loss in the temperature range 80 to 240 °C corresponding to a 7 % water content of the sample. The weight loss in the temperature range 240 to 430 °C corresponds to the formation of Cr_2O_3 from the chromium oxide hydroxide, (see Table 2). A Guinier powder pattern of a sample of γ-CrOOH heated to 715 °C for 24 h had only lines of Cr_2O_3.

β-CrOOH was prepared from CrO_3 by reduction under hydrothermal conditions. CrO_2 was obtained from CrO_3 by dry decomposition. CrO_3 was sealed in gold ampoules and heated from 375 to 415 °C at an external hydrostatic pressure up to 300 MPa for 75 h. Approximately 650 mg of CrO_3 was then sealed in gold ampoules with 2 g of oxalic acid, $(COOH)_2 . 2H_2O$, and 1 ml of water, and was treated hydrothermally at temperatures from 350 to 405 °C and pressure from 170 to 230 MPa for 73 h. Guinier powder patterns of the products were obtained as described above, and the unit cell parameters obtained are listed in Table 1. Chemical analyses of β-CrOOH were made using the same procedure as for α-CrOOH. (Found: Cr 59.5. Calc.: Cr 61.3).

Infra red spectra. The IR spectra of the three chromium compounds were recorded over the frequency range 4000 to 300 cm^{-1} with a Perkin-Elmer 180 spectrophotometer using pellets of mixtures of 1 mg of sample and 200 mg of KBr. The spectra are shown in Fig. 2.

Magnetic measurements. The magnetization of α-CrOOH, β-CrOOH, and γ-CrOOH was measured at temperatures from 75 to 293 K using the Faraday method. The sample was placed in a flow cryostat cooled with liquid nitrogen, and the magnetization was recorded with an electrobalance. The magnetic field was calibrated using Mohrs salt, $(NH_4)_2 Fe(SO_4)_2 . 6H_2O$, $\chi_g = 32.2 \times 10^{-6}$, and erbium

Table 2. Experimental conditions for hydrothermal preparation of samples of γ-CrOOH and chromium content. (Theoretical value for γ-CrOOH: 61.3 %).

Exp. No.	Temp. °C	Pressure MPa	Time in	Guinier powder pattern	Chromium content in %
1	260	70	24	amorphous	56.35
2	300	8	26	amorphous	54.70
3	310	170	72	traces of α-CrOOH	54.56
γ-CrOOH containing 7 % of water					56.8
γ-CrOOH corrected for the water content					61.0

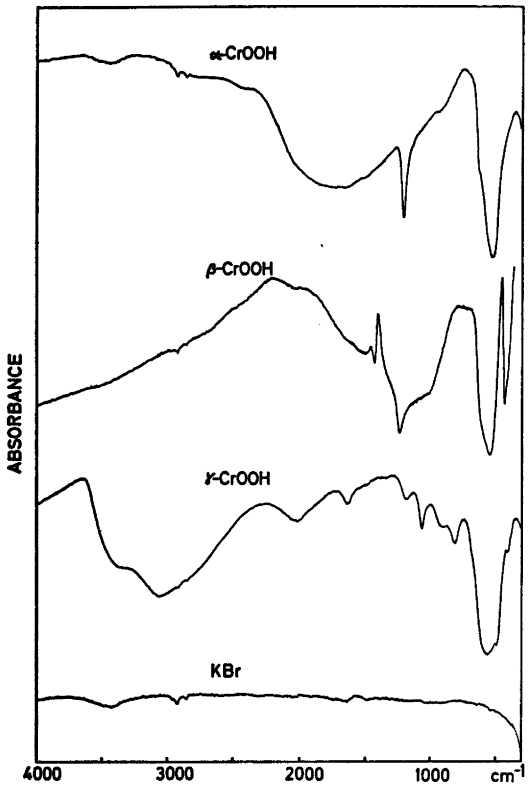

Fig. 2. Infra red spectra of α-CrOOH, β-CrOOH, γ-CrOOH, and KBr.

oxide hydroxide, ErOOH, $\chi_g = 181.8 \times 10^{-6}$, as standards. Fig. 3 shows χ_{mol}^{-1} *vs.* temperature for α-CrOOH and for γ-CrOOH. The two compounds are paramagnetic in the temperature range investigated and the susceptibilities follow the Curie-Weiss law, $\chi_{mol} = C_M/(T-\theta_p)$.

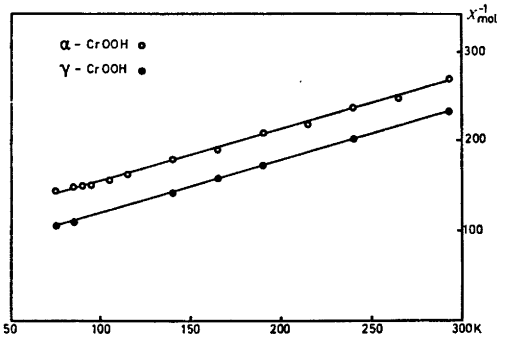

Fig. 3. χ_{mol}^{-1} *vs.* temperature for α-CrOOH and γ-CrOOH.

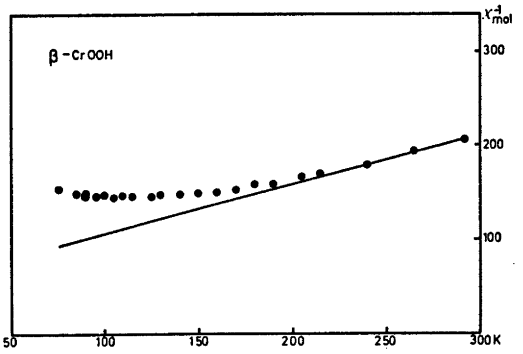

Fig. 4. χ_{mol}^{-1} *vs.* temperature for β-CrOOH.

The magnetic data for the two compounds are listed in Table 1. Fig. 4 shows χ_{mol}^{-1} *vs.* temperature for β-CrOOH. The susceptibility follows the Curie-Weiss law from room temperature to approximately 225 K and below this temperature the deviation from the Curie-Weiss law is significant. The magnetization has a broad maximum in the temperature range 90 to 140 K corresponding to a Néel temperature of approximately 120 K. The magnetic data for β-CrOOH are listed in Table 1.

CONCLUSIONS

The hydrothermal investigation yielded the three chromium compounds α-CrOOH, β-CrOOH, and γ-CrOOH. The two compounds α-CrOOH, and β-CrOOH could be identified *via* chemical analysis and their X-ray diffraction powder patterns, that were indexed with unit cell parameter very similar to previously reported values (see Table 1). γ-CrOOH could only be made as X-ray amorphous samples. The chemical analysis is not in satisfactory agreement with the formula γ-CrOOH suggested by Hund,[9] who reported the X-ray powder pattern for γ-CrOOH and showed it to be similar to that of γ-FeOOH. No chemical analysis are given in Ref. 9 for γ-CrOOH. The results of some chemical analyses on samples of γ-CrOOH are listed in Table 2. A content of water in the samples may explain the low values of the chromium analysis.

The infra red spectra of the three compounds are different from each other (see Fig. 2). α-CrOOH has a broad absorption band in the frequency range 2000 – 1400 cm^{-1} with a minimum at 1700 cm^{-1}. A short hydrogen

bond of 2.49 ± 0.02 Å has been reported for α-CrOOH.[11] β-CrOOH shows a broad and rather weak absorption band in the frequency range $1850 - 1450$ cm^{-1}, and the structure of the compound will have a short hydrogen bond of 2.4 ± 0.2 Å.[13] γ-CrOOH shows a broad absorption band at 3500 cm^{-1}, characteristic for free water. The lack of characteristic OH^--absorption bands in α-CrOOH and β-CrOOH are possibly due to the short hydrogen bonds.

The magnetic data for α-CrOOH found in this investigation are different from the previously reported values; the greatest differences are found for θ_p (see Table 1). The crystal structure of β-CrOOH is very similar to that of CrO_2 and can be described as a deformed rutile structure. The magnetic data for the two compounds are, however, very different from each other, and the magnetic superexchange must have different character in the two compounds. CrO_2 becomes ferromagnetic with a Curie temperature of 118 °C [16] and β-CrOOH shows an antiferromagnetic nature below 120 K. γ-CrOOH is paramagnetic in the temperature range investigated.

Acknowledgements. I am indebted to Carlsbergfondet for the use of some of the high pressure equipments and to Statens Naturvidenskabelige Forskningsråd for the use of the Faraday magnetometer. Mr. N. J. Hansen and Miss G. Petersen are acknowledged for valuable assistance in measuring magnetic data and in recording IR spectra. Mrs. B. Saustrup Kristensen is acknowledged for the thermogravimetric analysis.

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Received July 29, 1975.