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ON THE MECHANISM OF PREPARATION OF Co_3O_4 FROM VARIOUS SALTS

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ABSTRACT

The mechanism of preparation of Co_3O_4 by thermal decomposition of cobaltous salts (oxalate, nitrate, carbonate) was studied using magnetic methods and thermogravimetry. The effective magnetic moment of the Co ion passes through a minimum (2,2–2,3 BM) before the formation of Co_3O_4 (2.55 BM). It is shown that the first decomposition stage of cobaltous salts in air is the formation of Co^{3+} ions in octahedral coordination without passing through the intermediate stage of metallic Co and CoO. The results from the magnetic studies are in agreement with thermodynamic calculations.

INTRODUCTION

The preparation of cobaltous oxide by thermal decomposition of cobaltous salts has been studied by a number of authors[1–5]. The decomposition of cobaltous oxide in vacuo or in an inert medium is one of the processes studied in detail. Here, the following reactions can take place:

$$\begin{aligned} &CoC_2O_4 \rightarrow CoO + CO + CO_2 \\ &CoO + CO \rightarrow Co + CO_2 \end{aligned} \qquad (1)$$

or

$$CoC_2O_4 \rightarrow Co + 2CO_2 \qquad (2)$$

The final product of the decomposition of cobaltous salts in air at temperatures below 800°C is Co_3O_4. In the literature, there are contradictory opinions on the mechanism of preparation of Co_3O_4. According to some authors[3, 4], decomposition in the presence of oxygen proceeds at first according to (1) or (2), after which rapid oxidation to Co_3O_4 takes place. However, other authors[1, 5] are of the opinion that decomposition of cobaltous oxalate in air leads immediately to Co_3O_4 without an intermediate stage of CoO and Co. These mechanisms are proposed on the basis of DTA and TG investigations on the decomposition process. Moreover, there is no direct evidence of the existence of definite intermediate phases. The results of DTA and TG studies of other cobaltous salts (nitrate)[2] do not suffice either to elucidate the mechanism of Co_3O_4 preparation by thermal decomposition of these salts.

The purpose of the present paper was to study the change in magnetic properties of some cobaltous salts (oxalate, nitrate, carbonate) during the process of their thermal decomposition in air with a view to elucidating the mechanism of preparation of Co_3O_4. We chose this method owing to the high sensitivity of the magnetic methods with respect to the presence of very small amounts of ferromagnetic phases such as ferromagnetic cobalt as well as because these methods give information on the valency state of the transition metal and its environment.

EXPERIMENTAL

Commercially available $CoC_2O_4 \cdot 4H_2O$, $Co(NO_3) \cdot 6H_2O$ (A.R., Merck) and $2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$ (A.R., Carlo Erba) containing 26.92, 20.26 and 50.50% cobalt, respectively, were used for the investigations.

The magnetic susceptibility of the samples during their thermal decomposition was measured with a special apparatus constructed on the basis of the Faraday method. The pole pieces were of Sucksmith type and the field intensity was 8000 G. The apparatus is described in detail in ref. 6. In the present study, an improved variation of the apparatus was used; all parts were made of glass and connected by means of teflon links and stopcocks. This eliminated the possibility of grease vapour coming into the reaction space. The apparatus enabled us to work at a vacuum up to 10^{-6} Torr or in an atmosphere of various gases, to vary the temperature between 88 and 670 K, and to trace the changes in weight of the sample, i.e., to make TG investigations.

Method

Samples of about 5 mg situated in glass ampoules were placed into the reaction space of the magnetic apparatus. The magnetic susceptibility was measured with a stepwise increase in temperature. Simultaneously, the changes in weight of the sample during decomposition were determined. On reaching a definite decomposition stage of the cobaltous salt, the temperature was sharply decreased and the magnetic susceptibility was measured. Thus, the temperature dependence of the magnetic susceptibility was measured for each stage during the process of decomposition. This enabled us to check the validity of the Curie-Weiss law at each stage of the process:

$$x_{gi} = \frac{\mu_{eff}^2}{A^2(T - \theta)} \qquad (3)$$

Here, x_{gi} is the gram-ion magnetic susceptibility, μ_{eff}, the effective magnetic moment in BM, T, the absolute temperature, θ, the Weiss constant, and A, a constant equal to 2.828. The calculation of the magnetic moment enabled us to determine the valency state of the metal at each stage of decomposition; by the Weiss constant, the changes in interactions of the cobalt ion were judged.

RESULTS AND DISCUSSION

Figure 1 shows results from measurements of the specific magnetic susceptibility of $CoC_2O_4 \cdot 4H_2O$ (curve 1) and the per cent weight loss of the sample (curve 3) depending on temperature. Up to 240°C, the weight changes stepwise, which corresponds to the different dehydration degrees of cobaltous oxalate. The results are in agreement with the studies of the dehydration of this salt by other authors[1, 5]. With the changes in weight, the temperature dependence of the specific magnetic susceptibility also varies (curves 1a and 1b). Above 240°C the sample weight and the specific magnetic susceptibility sharply decrease. When the sample weight becomes constant (at 280–360°C, the temperature of preparation of Co_3O_4), the temperature dependence of the magnetic susceptibility is completely reversible (curve 2).

Figure 2 contains the data. in coordinates $1/x_{gi}$–T, during some stages of the process obtained by quenching the decomposition stage according to the method described in the Experimental section. It is evident that the Curie-Weiss law is observed. The effective magnetic moments and the Weiss constants for the different decomposition stages were calculated. The values obtained are given in Table 1. The effective magnetic moment decreases. beginning with the value of 5,32 BM and passing through a minimum at 2.27 BM, and then increases again up to 2.54 BM. The Weiss constant passes from a negative value to a positive one, after which it becomes negative again. Values of 2.54 BM for the effective magnetic moment and Weiss constants of 50–120 K correspond to Co_3O_4[7, 8]. The results obtained show that,

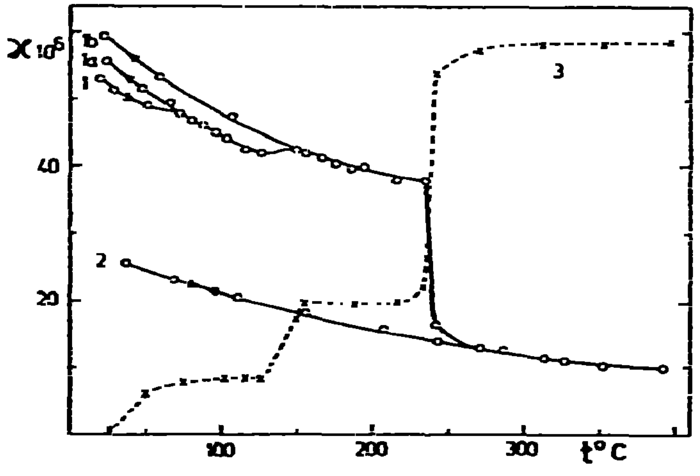

Fig. 1. Dependence on temperature (°C) of the specific magnetic susceptibility, *x*, and the weight loss of a $Co_2O_4 \cdot 4H_2O$ sample. (1) — Magnetic susceptibility of the initial sample; (2) — magnetic susceptibility of the final product; (3) = per cent weight loss of the sample; (1a) and (1b) — magnetic susceptibility for different dehydration degrees of the sample.

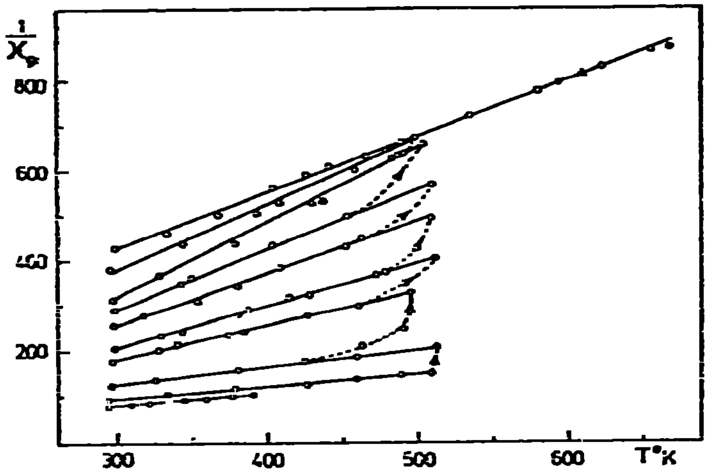

Fig. 2. Dependence of $1/\chi_g$ on temperature (K) for different decomposition degrees of $CoC_2O_4 \cdot 4H_2O$.

TABLE 1

CHANGES IN THE EFFECTIVE MAGNETIC MOMENT OF THE Co-ION (μ_{eff}) AND THE WEISS CONSTANT (θ) FOR DIFFERENT STAGES OF DECOMPOSITION OF A $CoC_2O_4 \cdot 4H_2O$ SAMPLE

μ_{eff}(BM)	θ(K)	
5.32	−13	
5.34	−45	
4.84	−89	
3.78	+8	
3.47	+37	
3.34	+38	
2.94	+72	
2.63	+75	
2.46	+73	
2.28	+81	
2.27	+92	
2.35	+44	
2.54	−50	Co_3O_4

during decomposition of cobaltous oxalate in air, no metallic cobalt is formed which would have been oxidised immediately. If such a phase existed, we should have found a ferromagnetic component in the samples as was the case with cobaltous oxalate decomposition in vacuo (10^{-4} Torr). It is known[9] that Co^{2+} has a ground term ^4F, and in an octahedral field the effective magnetic moment considerably differs from its "spin-only" value due to the spin-orbit coupling. The data for Co^{2+} octa obtained experimentally are 5.2–5.6 BM. In a tetrahedral field, the effective magnetic moment of Co^{2+} is 4.0–4.4 BM due to the weaker orbital contribution. The effective magnetic moment for Co^{3+} in a strong octahedral field is zero, whereas the effective magnetic moment in a weak octahedral or tetrahedral field are 5.0 and 4.8, respectively. Therefore, during decomposition of cobaltous oxalate in air no intermediate CoO appears, since its magnetic moment obtained experimentally is 5.4 BM (Co^{2+} being in octahedral coordination). Our experimental data on the effective magnetic moment at a definite decomposition stage of cobaltous oxalate (lower than that of Co_3O_4) show the appearance of a larger amount of Co^{3+} in octahedral coordination than in

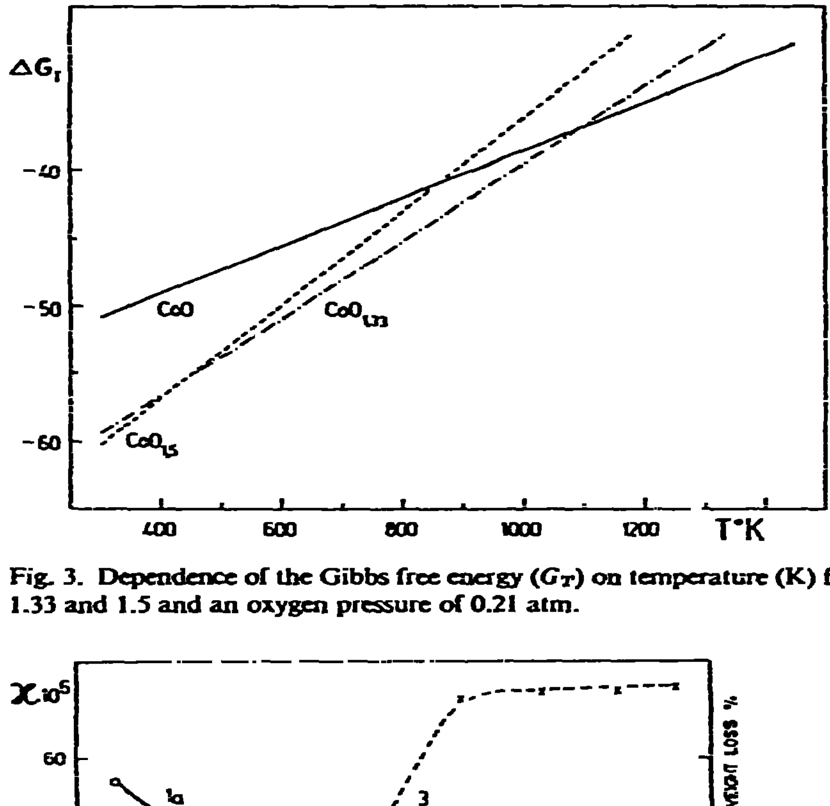

Fig. 3. Dependence of the Gibbs free energy (G_T) on temperature (K) for a CoO_x sample at x = 1, 1.33 and 1.5 and an oxygen pressure of 0.21 atm.

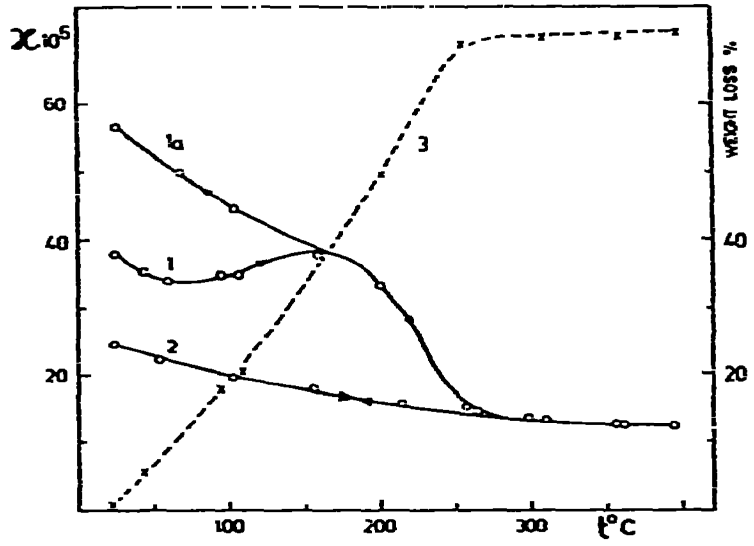

Fig. 4. Dependence on temperature (°C) of the specific magnetic susceptibility, x, and of the weight loss of a $Co(NO_3) \cdot 6H_2O$ sample. (1) = Magnetic susceptibility of the initial sample; (2) = magnetic susceptibility of the final product; (3) = per cent weight loss of the sample; (1a) = magnetic susceptibility of a partially dehydrated sample.

the case of Co_3O_4. Therefore, it can be assumed that the first stage of cobaltous oxalate decomposition in air is the formation of Co^{3+} ions in octahedral coordination. The positive values of the Weiss constant are also indicative of interactions differing from those in Co_3O_4, CoO and CoC_2O_4.

The existence of such a possibility is supported by the results obtained in a thermodynamic study of the reaction

$$Co + \frac{x}{2} O_2 \rightarrow CoO_x$$

The changes in the Gibbs free energy depending on temperature at $x = 1$, 1.33 and 1.5 and an oxygen pressure of 0.21 atm are given in Fig. 3. The values of ΔG_T are obtained according to ref. 10. As is evident from Fig. 3, one can expect $CoO_{1.5}$ to appear at temperatures lower than 500 K and an oxygen pressure of 0.21 atm. A stable phase above this temperature (up to 1100 K) is Co_3O_4. Hence, during thermal

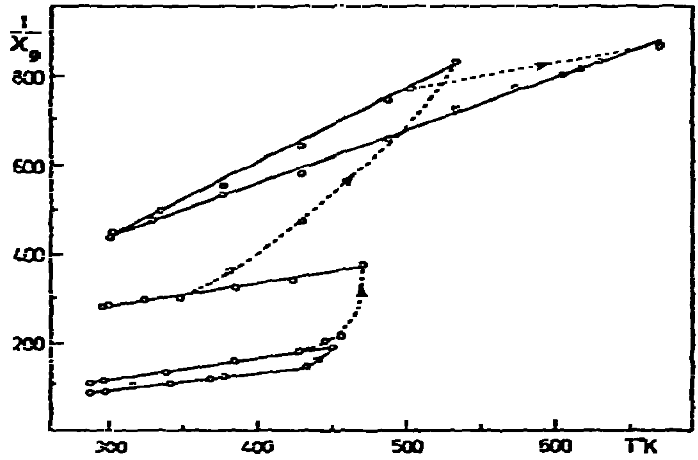

Fig. 5. Dependence of $1/x_{g}$ on temperature (K) for different degrees of decomposition of $Co(NO_3)_2 \cdot 6H_2O$.

TABLE 2

CHANGES IN THE EFFECTIVE MAGNETIC MOMENT OF THE Co-ION (μ_{eff}) AND THE WEISS CONSTANT (θ) FOR DIFFERENT STAGES OF DECOMPOSITION OF A $Co(NO_3) \cdot 6H_2O$ SAMPLE

μ_{eff} (BM)	θ (K)	
4.70	+ 12	
4.01	+ 97	
3.54	+ 127	
2.2	+ 45	
2.58	− 71	Co_3O_4

decomposition of cobaltous oxalate, Co^{3+} ions in octahedral coordination appear first due to their higher stability within this temperature range.

Figure 4 shows the results from analogous studies of $Co(NO_3)_2 \cdot 6H_2O$ decomposition. Obviously, continuous dehydration takes place. Above 160°C, partial decomposition of the salt proceeds (curve 3). The changes in the specific magnetic susceptibility corresponds to the changes in the sample composition (curves 1 and 1a). Co_3O_4 is the stable phase above 280°C (curve 2). Figure 5 shows the results from measurements of the temperature dependence of the magnetic susceptibility for different stages of decomposition of cobaltous oxide. The values obtained for μ_{eff} and θ are given in Table 2. Here again, the magnetic moment passes through a

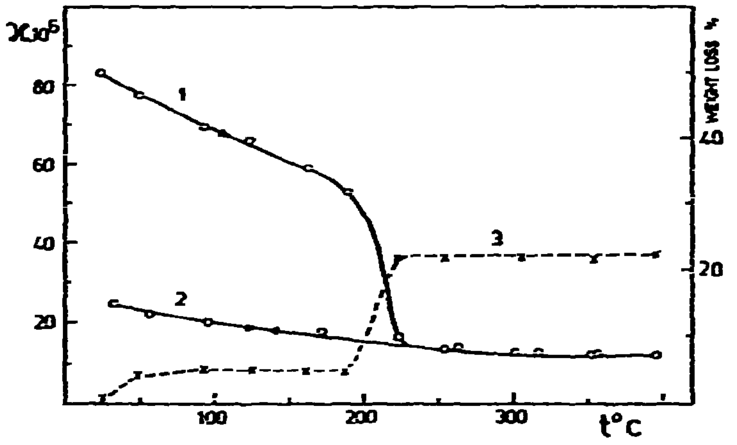

Fig. 6. Dependence on temperature (°C) of the specific magnetic susceptibility, x, and the weight loss of a $2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$ sample. (1) = Magnetic susceptibility of the initial sample; (2) = magnetic susceptibility of the final product; (3) = per cent weight loss of the sample.

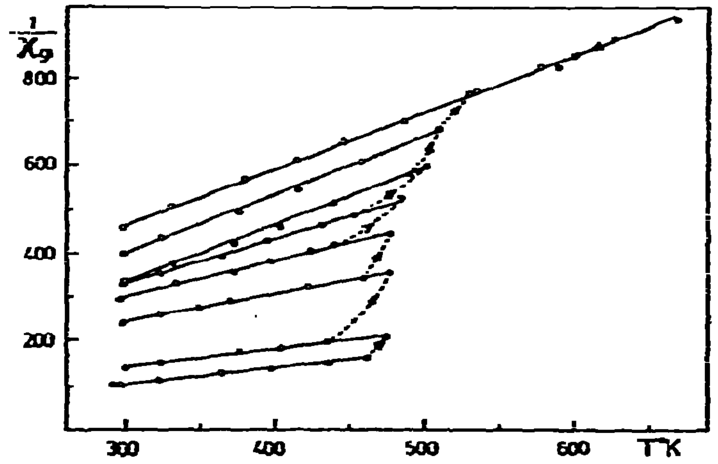

Fig. 7. Dependence of $1/x_g$ on temperature (K) for different decomposition degrees of $2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$.

TABLE 3

CHANGES IN THE EFFECTIVE MAGNETIC MOMENT OF THE Co-ION (μ_{eff}) AND THE WEISS CONSTANT (θ) FOR DIFFERENT STAGES OF DECOMPOSITION OF A $2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$ SAMPLE

μ_{eff}(BM)	θ(K)	
4.93	−15	
4.58	−80	
3.49	−70	
3.09	−58	
2.77	−15	
2.46	+48	
2.45	+2	
2.55	−71	Co_3O_4

minimum (2.2 BM) before the formation of Co_3O_4 (2.54 BM). Positive values for the Weiss constant are obtained at certain stages of decomposition.

In the decomposition of $2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$ at 200°C, the sample weight sharply decreases (Fig. 6, curve 3), which is followed by a decrease in the specific magnetic susceptibility (curve 1). The stable phase above 230°C is Co_3O_4 (curve 2). Figure 7 shows the changes in the temperature dependence of the magnetic susceptibility for some decomposition stages of the basic cobaltous carbonate. Table 3 presents the values of μ_{eff} and θ for the different stages of decomposition.

The results obtained enable one to assume that the decomposition of cobaltous salts (the oxalate, nitrate and carbonate) takes place with the formation of Co^{3+} ions in octahedral position, without passing through the stages of metallic cobalt and CoO.

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