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A MAGNETIC STUDY OF THE FORMATION OF $NiCo_2O_4$

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ABSTRACT

The mechanism of $NiCo_2O_4$ formation was investigated by magnetic methods and thermogravimetry. This compound was obtained by simultaneous decomposition of cobalt(II) and nickel(II) salts in air at temperatures up to 350°C. It was shown that $NiCo_2O_4$ has the spinel structure of $Co^{2+}[Ni^{3+}Co^{3+}]O_4$. The decomposition process passes through the formation of paramagnetic Co^{3+}, Co^{2+} and Ni^{3+} ions, which were stabilized in the ferrimagnetic spinel lattice of $NiCo_2O_4$.

INTRODUCTION

The interest in spinels has increased considerably in recent years with a view to their application as catalysts for redox reactions. For example, it has been established that $NiCo_2O_4$ is catalytically active in respect of both the oxidation of CO and hydrocarbons [1] and the reduction of nitrogen oxides [2]. It can also be used as an electrocatalyst [3]. The mechanism of catalytic action is closely associated with the structure, stoichiometry and cation distribution in the spinel lattice. However, with most spinel catalysts these problems are still disputable. According to Andrushkevich et al. [4], a spinel phase with the composition of $NiCo_2O_4$ is obtained at temperatures up to 350°C. X-Ray and neutron diffraction studies gave no unambiguous data on the valence state of Co and Ni ions in the A and B sites of the spinel lattice [5]. The compound is ferrimagnetic and has a Neel temperature of 350 K [6] or 500 K [5]. The net magnetic moment as derived from the magnetic measurement does not correspond to any of the structures proposed [5]. At temperatures above 400°C $NiCo_2O_4$ is thermally unstable [3]. Hence, the investigation based on measurement data concerning the temperature dependence of the magnetic susceptibility above the Neel temperature is also unreliable.

On the other hand, only the DTA and TG studies of the preparation of $NiCo_2O_4$ [7] gave no sufficient information on the formation mechanism of a spinel structure from the initial cobalt and nickel salts. For this reason, the purpose of the present paper was to apply magnetic and thermogravimetric methods to the study of the mechanism of $NiCo_2O_4$ preparation. The magnetic methods were chosen because they are highly sensitive towards small amounts of ferromagnetic admixtures, such

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as ferrimagnetic $NiCo_2O_4$, and give information on the valence state of the transition metal and its coordination.

EXPERIMENTAL

The decomposition of a mixture of $2\,CoCO_3 \cdot 3\,Co(OH)_2 \cdot n\ H_2O$ (A.R., Carlo Erba) and $Ni(NO_3)_2 \cdot 6\,H_2O$ (A.R., Merck) containing 50.50% Co and 20.19% Ni, respectively, was investigated. The mixture was prepared with a view to obtaining a Co:Ni atomic ratio of 2:1. The magnetic studies were carried out in the temperature range 20–400°C using a magnetic apparatus constructed on the basis of the Faraday method [8]. The changes in magnetic properties and weight of the samples were studied in the course of the decomposition process. The magnetic susceptibility was measured at definite stages of the decomposition process after quenching the latter by a sharp decrease of temperature.

The DTA, DTG and TG studies were made with a Paulik–Paulik–Erdey apparatus, type 1500 (MOM, Hungary) at temperatures ranging from 20 to 1000°C and a heating rate of 5°C min^{-1}. Al_2O_3 calcined at 1500°C was used as reference.

RESULTS

Figure 1 shows the results from measurements of the gram-atomic magnetic susceptibility of a mixture of $2\,CoCO_3 \cdot 3\,Co(OH)_2 \cdot n\ H_2O + Ni(NO_3)_2 \cdot 6\,H_2O$ with a Co:Ni atomic ratio of 2:1 (curve 1) and the percent weight decrease (curve 2) during the decomposition. Traces of ferrimagnetism appear on heating above 220°C. At 300°C the decomposition is practically complete. Curve 3 corresponds to the magnetic properties of $NiCo_2O_4$.

Figure 2 shows, in coordinates $1/\chi_a - T$, the results on the temperature dependence of the magnetic susceptibility for some intermediate stages obtained during the $NiCo_2O_4$ formation by quenching the decomposition process. The magnetic moment calculated as a function of the heating temperature is given in Fig. 3. A comparison of Figs. 1–3 shows that the change in weight of the sample below 140°C is due to the partial removal of the water of crystallization, no changes in the coordination and the valency state of the initial Co^{2+} and Ni^{2+} ions being observed. When the sample is heated up to 210°C, the temperature dependence of the magnetic susceptibility obeys the Curie–Weiss law and the magnetic moment decreases due to the decomposition of cobalt(II) carbonate and nickel(II) nitrate, which is associated with a change in the valency state of the paramagnetic ions. At higher temperatures, deviations from the Curie–Weiss law are observed and the magnetic susceptibility sharply increases due to the appearance of a ferromagnetic component as a result of formation of $NiCo_2O_4$.

Figure 4 presents the DTA, TG and DTG data on the decomposition of a mixture of $2\,CoCO_3 \cdot 3\ Co(OH)_2 \cdot n\ H_2O + Ni(NO_3)_2 \cdot 6\ H_2O$. The DTA curve has four

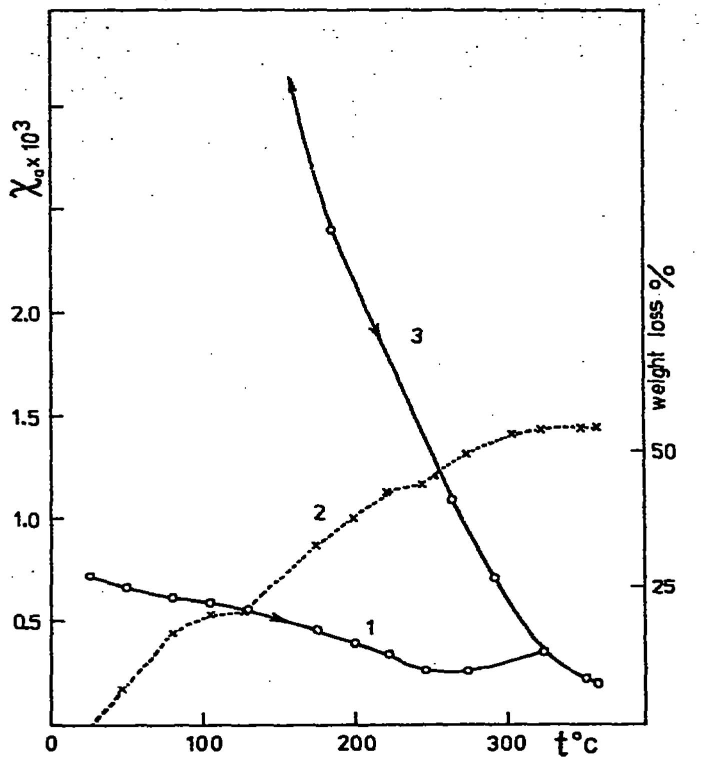

Fig. 1. Change in the gram-atom magnetic susceptibility (curve 1) and the weight (curve 2) of a sample of 2 $CoCO_3 \cdot 3\ Co(OH)_2 \cdot n\ H_2O + Ni(NO_3)_2 \cdot 6\ H_2O$ (Co : Ni = 2 : 1) depending on the heating temperature. Curve 3, magnetic properties of $NiCo_2O_4$.

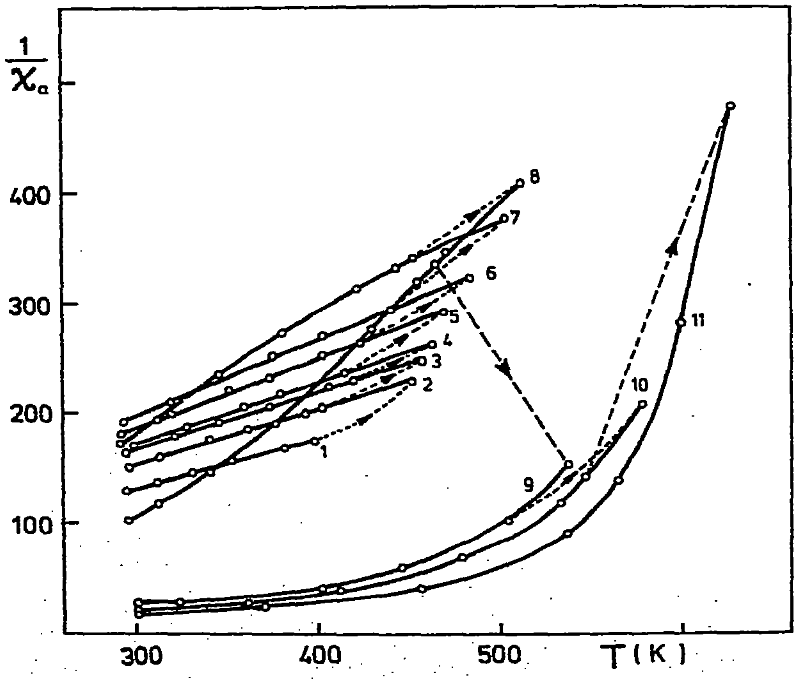

Fig. 2. Temperature dependence of the magnetic susceptibility for different decomposition stages of 2 $CoCO_3 \cdot 3\ Co(OH)_2 \cdot n\ H_2O + Ni(NO_3)_2 \cdot 6\ H_2O$ (curves 1–10). Curve 11, reciprocal magnetic susceptibility of the end product $NiCo_2O_4$.

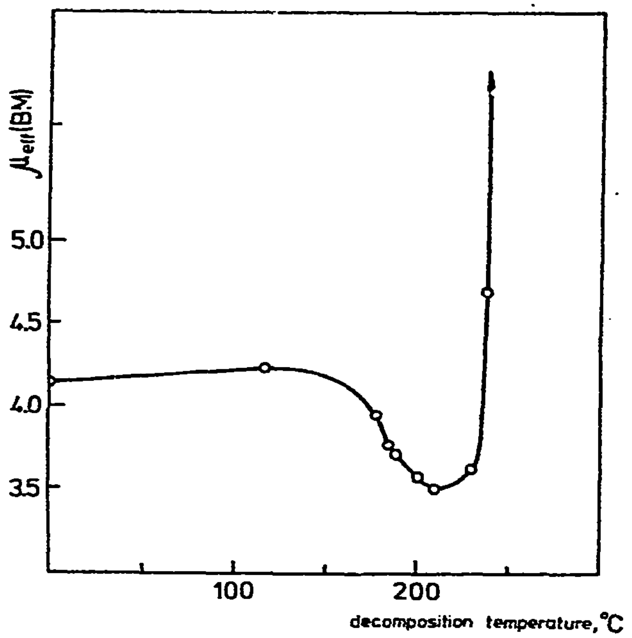

Fig. 3. Change in the effective magnetic moment of a 2 $CoCO_3 \cdot 3\ Co(OH)_2 \cdot n\ H_2O + Ni(NO_3)_2 \cdot 6\ H_2O$ mixture depending on the heating temperature.

endothermal peaks which, on the basis of the results from the magnetic measurements, can be interpreted as follows.

The peak at 60°C corresponds to melting of $Ni(NO_3)_2 \cdot 6\ H_2O$ in the water of

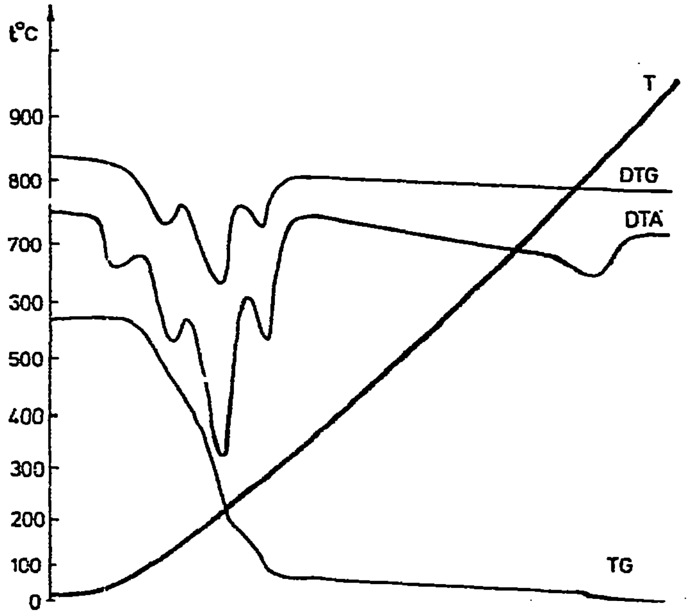

Fig. 4. TG, DTA and DTG data for the decomposition of 2 $CoCO_3 \cdot 3\ Co(OH)_2 \cdot n\ H_2O + Ni(NO_3)_2 \cdot 6\ H_2O$.

crystallization. The TG curve shows no weight changes.

At 140°C 2 molecules of the water of crystallization are removed from $Ni(NO_3)_2 \cdot 6 H_2O$.

At 220°C decomposition of nickel(II) nitrate and cobalt(II) carbonate occurs and leads to the formation of Co and Ni ions with magnetic properties differing from those of the initial products, no spinel structure being obtained.

At 290°C the decomposition process is accompanied by the formation of the final spinel structure of $NiCo_2O_4$.

At higher temperatures the TG curve indicates continuous weight loss, no sharp DTA peak being observed. According to Bliznakov et al. [9], the nickel is gradually removed from the spinel lattice at these temperatures. At 820°C the spinel is decomposed. The fact that the decomposition of the initial salts and the formation of the spinel structure do not proceed simultaneously, is confirmed by the change in magnetic properties and weight of the initial mixture of $2 CoCO_3 \cdot 3 Co(OH)_2 \cdot n H_2O + Ni(NO_3)_2 \cdot 6 H_2O$, established by a study under isothermal conditions (Fig. 5) at 200°C (curves 1, 1′), 220°C (curves 2, 2′) and 260°C (curves 3, 3′). During decomposition at 200°C both the sample weight and the magnetic susceptibility decrease monotonically. At 220°C the magnetic susceptibility and the sample weight

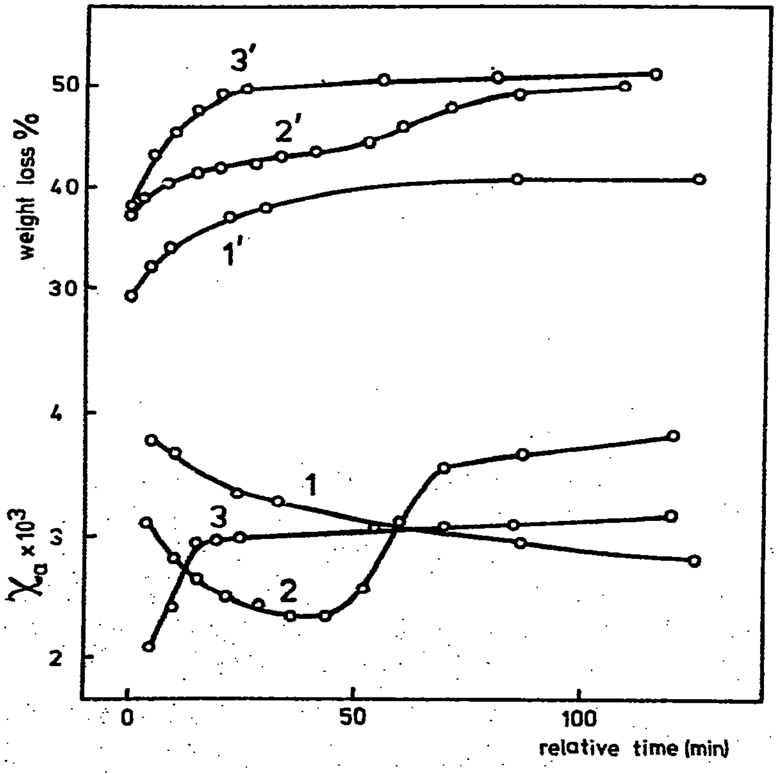

Fig. 5. Change in magnetic properties and weight loss of a sample of $2 CoCO_3 \cdot 3 Co(OH)_2 \cdot n H_2O + Ni(NO_3)_2 \cdot 6 H_2O$ during decomposition at temperatures of 200°C (curves 1, 1′), 220°C (curves 2, 2′) and 260°C (curves 3, 3′).

decrease until a certain decomposition degree is attained (weight loss 43%), after which the magnetic susceptibility begins to increase due to the formation of a spinel structure with ferrimagnetic properties. The kinetics of decomposition also change. At 260°C the magnetic susceptibility increases at once due to the predominance of the process of spinel formation.

DISCUSSION

The results from the magnetic studies show that the decomposition of $2\,CoCO_3 \cdot 3\,Co(OH)_2 \cdot n\,H_2O + Ni(NO_3)_2 \cdot 6\,H_2O$, accompanied by the formation of $NiCo_2O_4$, occurs in three stages:

(1) decomposition without a change of the magnetic moment. The Co^{2+} and Ni^{2+} ions show no change in the valency state and remain in octahedral coordination as in the initial salts;

(2) decrease in the magnetic moment;

(3) formation of a spinel with ferrimagnetic properties.

As was already pointed out, the distribution of the cobalt and nickel ions in the octahedral and tetrahedral sublattices of the spinel structure of $NiCo_2O_4$ is not exactly established. In principle, two normal (I and II) and two inverse (III and IV) $NiCo_2O_4$ structures are possible:

I $Ni^{2+}[Co_2^{3+}]O_4$
II $Co^{2+}[Ni^{3+}Co^{3+}]O_4$
III $Co^{3+}[Ni^{2+}Co^{3+}]O_4$
IV $Ni^{3+}[Co^{2+}Co^{3+}]O_4$

There may also be combinations of these four structures, which can be written as

$$Ni^{2+}_{1-x-y-z}Co^{2+}_{x}Co^{3+}_{y}Ni^{3+}_{z}[Co^{3+}_{2-x-y-z}Ni^{3+}_{x}Co^{2+}_{z}Ni^{2+}_{y}]O_4$$

where, $0 \leqslant x, y, z \leqslant 1$. Structure I should be eliminated on the basis of the ferrimagnetic properties of this spinel.

The formation of $NiCo_2O_4$ from the initial cobalt and nickel salts can be considered as a result of three processes: (a) a redox reaction at fixed coordination; (b) changes in the coordination polyhedron without a change in the valency state, and (c) structural transformations. The formation of a spinel structure with ferrimagnetic properties corresponds to the latter process. The change in the effective magnetic moment during the decomposition of the initial salts indicates changes in the valency state and coordination of the cobalt and nickel ions prior to the formation of the ferrimagnetic spinel structure.

The experimentally observed decrease in the magnetic moment during the decomposition of the initial salts may be due to the following changes in the electronic structure and in the strength and symmetry of the crystal field of cobalt and nickel ions

$Ni^{2+}(O_h)_m \rightarrow Ni^{3+}(O_h)_s$

$Co^{2+}(O_h)_m \rightarrow Co^{3+}(O_h)_s$

$Co^{2+}(O_h)_m \rightarrow Co^{2+}(O_h)_s$

$Co^{2+}(O_h)_m \rightarrow Co^{2+}(T_d)$

Here m and s denote a middle or strong crystal field. The magnetic moment will change with the degree of decomposition, α, depending on the distribution of the cations in the structure of $NiCo_2O_4$. Figure 6 shows the experimentally determined change in the magnetic moment as a function of the degree of decomposition, α. The value of the magnetic moment in $NiCo_2O_4$ as determined by extrapolation is 2.7 BM. Figure 7 shows the theoretical magnetic moments of the four principal $NiCo_2O_4$ structures, the magnetic moment of their combinations at various degrees of inversion, x, and the experimentally determined value of the magnetic moment in $NiCo_2O_4$. Evidently, four of the structures have a magnetic moment which is equal to that determined experimentally:

$Co^{2+}[Ni^{3+}Co^{3+}]O_4$

$Ni_{1-x}^{2+}Co_x^{2+}[Co_{2-x}^{3+}Ni_x^{3+}]O_4 \quad (x=0.9)$

$Ni_{1-x}^{2+}Co_x^{3+}[Co_{2-x}^{3+}Ni_x^{2+}]O_4 \quad (x=0.28)$

$Ni_{1-x}^{2+}Ni_x^{3+}[Co_{2-x}^{3+}Co_x^{2+}]O_4 \quad (x=0.2)$

On the basis of the stabilization energy, the appearance of the Ni^{2+} and Ni^{3+} ions in tetrahedral position is not very probable [10]. Thus, the only possible distribution

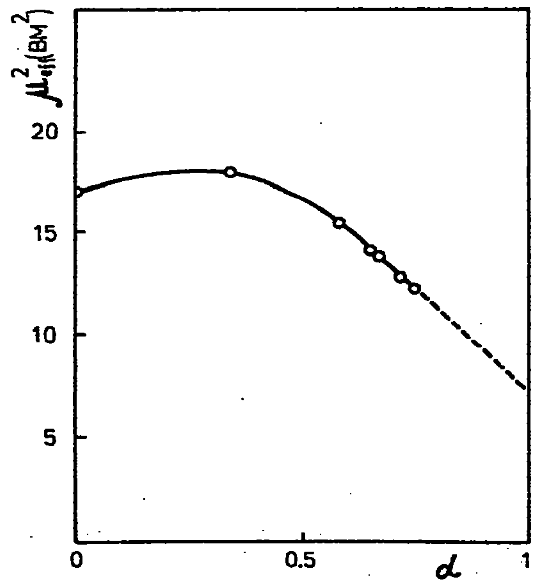

Fig. 6. Change in the magnetic moment of a $2\,CoCO_3 \cdot 3\,Co(OH)_2 \cdot n\,H_2O + Ni(NO_3) \cdot 6\,H_2O$ mixture depending on the degree of decomposition.

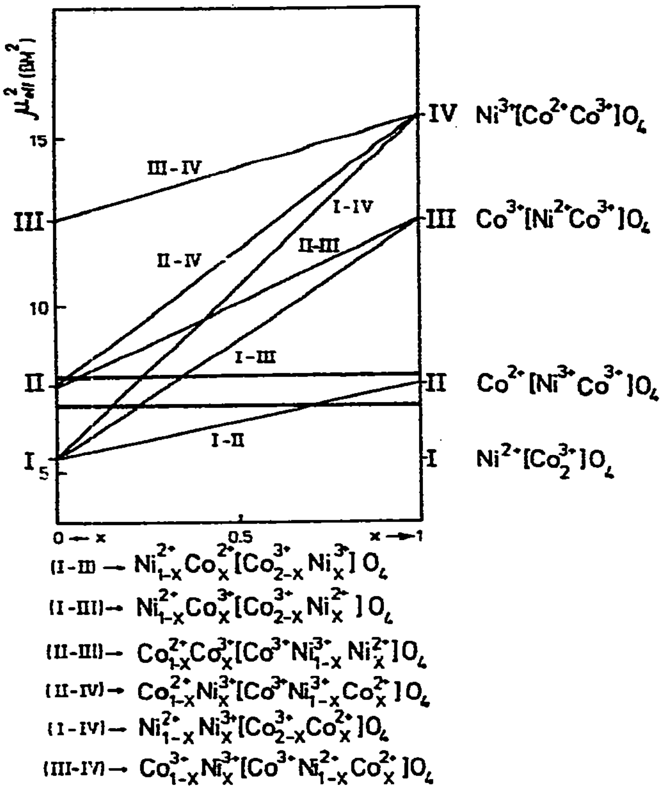

Fig. 7. Theoretical magnetic moments of the possible structures of $NiCo_2O_4$.

of the cations in the structure of $NiCo_2O_4$ is $Co^{2+}[Ni^{3+}Co^{3+}]O_4$, where the Co^{2+} ions are in a high-spin state in the A sites whereas the Co^{3+} and Ni^{3+} ions are in a low-spin state in the B sites. Such a structure for the nickel cobaltite was first proposed by Blasse [11] on the basis of rather general considerations. It can be recalled here that at low temperatures Ni^{3+} ions in octahedral positions seem to be thermodynamically stable species [12].

Thus, the simultaneous decomposition of $2\,CoCo_3 \cdot 3\,Co(OH)_2 \cdot n\,H_2O + Ni(NO_3)_2 \cdot 6\,H_2O$ takes place with the formation of paramagnetic $Ni^{3+}(O_h)_s$, $Co^{2+}(T_d)$ and $Co^{3+}(O_h)_s$ ions, which were stabilized in the ferrimagnetic spinel lattice of $NiCo_2O_4$.

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