

STUDY OF COPPER-COBALTITE SPINEL FORMATION DURING SIMULTANEOUS DECOMPOSITION OF COPPER AND COBALTOUS NITRATES

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ABSTRACT

The formation of a copper-cobaltite spinel, $\text{Cu}_{0.9}\text{Co}_{2.1}\text{O}_4$, during simultaneous decomposition of copper and cobaltous nitrates has been investigated by magnetic, EPR and DTA methods and diffusive reflectance spectroscopy. It has been shown that the spinel appears as a result of a solid-state reaction between basic copper nitrate and anhydrous cobaltous nitrate which are intermediate products of the decomposition of the initial nitrate salts. During the solid-state reaction, an intermediate pre-spinel structure containing copper ions in the tetrahedral sites only is formed. This structure transforms into a spinel with partially inverse distribution of the copper cations in the tetrahedral and octahedral sites.

INTRODUCTION

The decomposition of transition-metal salt mixtures belongs to one of the most-used methods of preparation of catalytically active complex binary oxides. For example, cobalt-containing spinel oxides which are good catalysts of redox reactions [1] are usually prepared by this method. The formation of such a spinel oxide can be described by the equation



where AX and CoY are the salts of the metals A and Co, their anionic parts being X and Y, respectively.

However, the process is one-stage in only a few cases, which makes its study difficult. For this reason, a combination of physical and chemical methods should be applied, e.g. simultaneous measuring, in situ, of magnetic susceptibility and weight loss proved to be very appropriate, because it gave information on the changes in valence state and metal cation coordination at the different characteristic stages of spinel formation [2,3].

The possibility and conditions of synthesizing a mixed copper-cobaltic oxide with a spinel structure were not completely elucidated until recently

(e.g. see ref. 4 and the papers cited therein). The synthesis of stoichiometric copper cobaltite, CuCo_2O_4 , by a solid-state reaction at a high oxygen pressure was reported for the first time in 1975 [5]. The spinel obtained possessed a normal distribution of cations over the tetrahedral and octahedral sites ($\text{Cu}^{2+}[\text{Co}_2^{3+}]\text{O}_4$) and had a tetragonally distorted spinel cubic lattice. In previous papers [6,7] we have shown that almost stoichiometric copper-cobaltite spinel can also be obtained at atmospheric pressure by simultaneous decomposition of copper and cobaltous nitrates. At a decomposition temperature of 350°C , the maximum copper content in the spinel lattice corresponds to the composition $\text{Cu}_{0.9}\text{Co}_{2.1}\text{O}_4$. Under these conditions, the lattice is not tetragonally distorted and the cation distribution is partially inverse.

The purpose of the present paper was to study the mechanism of formation of a mixed copper-cobalt oxide, with a spinel structure and a composition of $\text{Cu}_{0.9}\text{Co}_{2.1}\text{O}_4$, during simultaneous decomposition of cobaltous and copper nitrates. The data from the study, in situ, of the weight loss and the magnetic susceptibility are complemented by data from optical and EPR studies of the most characteristic intermediate products of the decomposition process.

EXPERIMENTAL

The formation of $\text{Cu}_{0.9}\text{Co}_{2.1}\text{O}_4$ during decomposition of a mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (A.R., Merck) and $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ (A.R., Merck) was investigated. Appropriate amounts of the salts were mixed in a dry box. The copper and cobalt contents in the mixture and in the final product were controlled by atomic-absorption analysis.

The magnetic properties were studied within the temperature range $20\text{--}400^\circ\text{C}$ using a Faraday-type magnetic balance [8]. Simultaneously, the changes in magnetic susceptibility and sample weight were traced during the decomposition. At definite decomposition stages the process was quenched by a sudden drop of temperature, after which the temperature dependence of the magnetic susceptibility of the intermediate products was determined.

Standard DTA studies were made by a type 1500 Paulik–Paulik–Erdey apparatus (MOM, Hungary) within the range $20\text{--}1000^\circ\text{C}$ at a heating rate of 5°min^{-1} . The reference sample used was Al_2O_3 calcinated at 1500°C .

The diffusive reflectance spectra of powdery samples of the initial mixture and the intermediate products were recorded by a VSU-2P Carl Zeiss (Jena) spectrophotometer in the range $1000\text{--}250 \text{ nm}$. MgO was used as a reference medium with a 100% reflection. The Kubelka–Munk function, $F = (1 - R)^2 / 2R$ (R = relative reflectivity), characterizing the absorption coefficient, was calculated over the whole range.

The X-band EPR spectra were recorded at different temperatures ranging

from -196 to 20°C with an ERS 220/Q apparatus (Zentrum für wissenschaftlichen Gerätebau, AdW, Berlin).

EXPERIMENTAL RESULTS

Figure 1 shows the change in the gram-atomic magnetic susceptibility (χ_a) of $0.9 \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O} + 2.1 \text{ Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ (curve 1) and the relative weight loss of the sample (curve 2) during slow heating in the magnetic balance. Up to 190°C the sample weight changes monotonically. At 190 – 220°C this change is very sharp and is accompanied by a similar sharp change in the magnetic susceptibility. At 250°C the decomposition of the mixture is practically complete. Curve 3 presents the temperature dependence of the magnetic susceptibility of the final product, $\text{Cu}_{0.9}\text{Co}_{2.1}\text{O}_4$.

Figure 2 shows the temperature dependences of the reciprocal gram-atomic susceptibilities for several intermediate decomposition products. The mag-

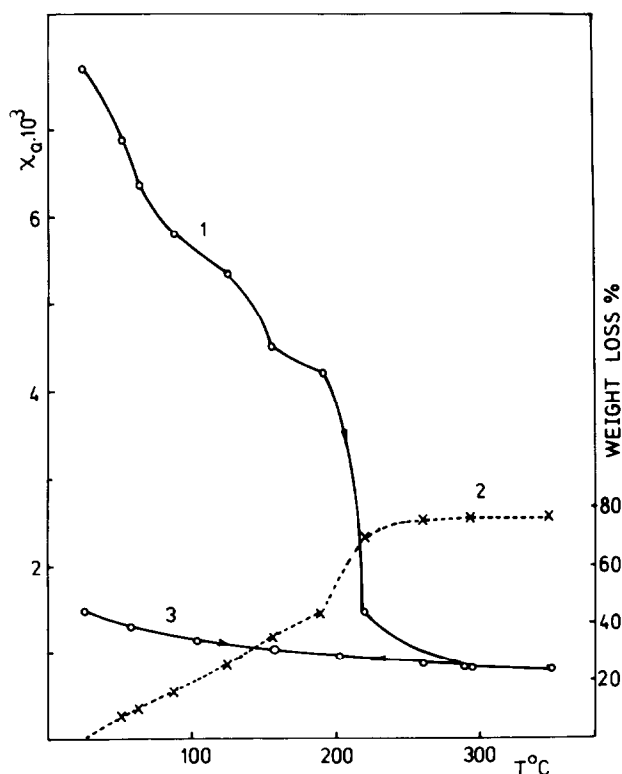


Fig. 1. Change in: 1, the gram-atomic magnetic susceptibility; 2, weight loss of a mixture of $2.1 \text{ Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O} + 0.9 \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O}$ during the decomposition. 3, Magnetic susceptibility of $\text{Cu}_{0.9}\text{Co}_{2.1}\text{O}_4$.

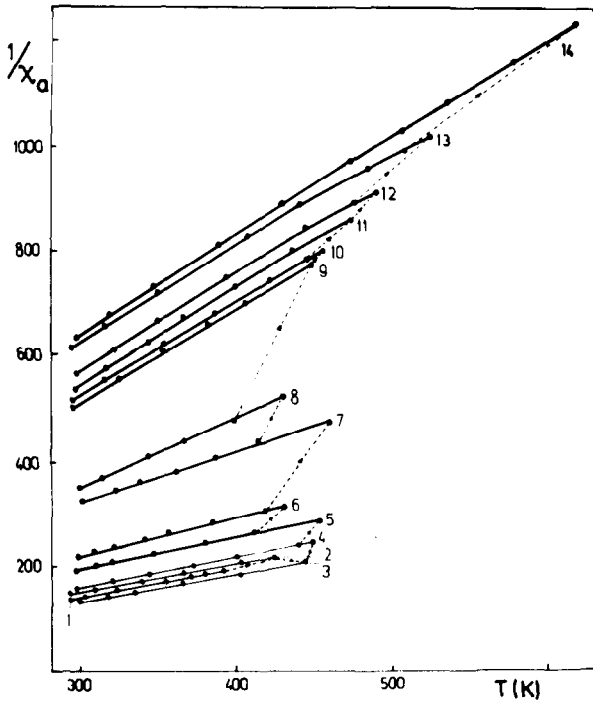


Fig. 2. Temperature dependence of the magnetic susceptibility for the intermediate decomposition products of a mixture of $2.1 \text{ Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O} + 0.9 \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O}$.

netic moment values per formula unit, $\text{Cu}_{0.9}\text{Co}_{2.1}\text{O}_4$, were calculated for each intermediate product. The dependence of this value on temperature is given in Fig. 3.

Figure 1–3 show that up to 190°C the magnetic moment is practically constant. Its value changes sharply at $190\text{--}220^\circ\text{C}$, after which it becomes constant again.

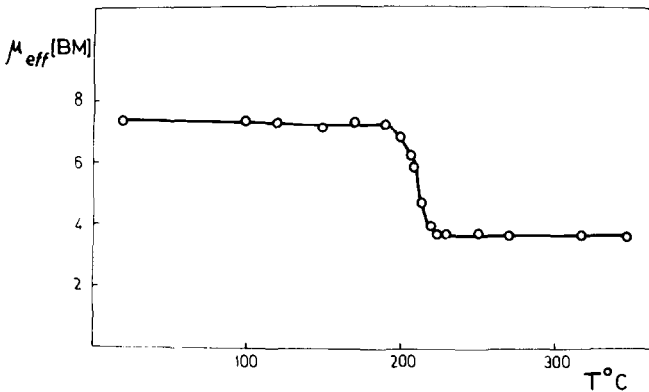


Fig. 3. Plot of the effective magnetic moment of a mixture of $2.1 \text{ Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O} + 0.9 \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O}$ vs. heating temperature.

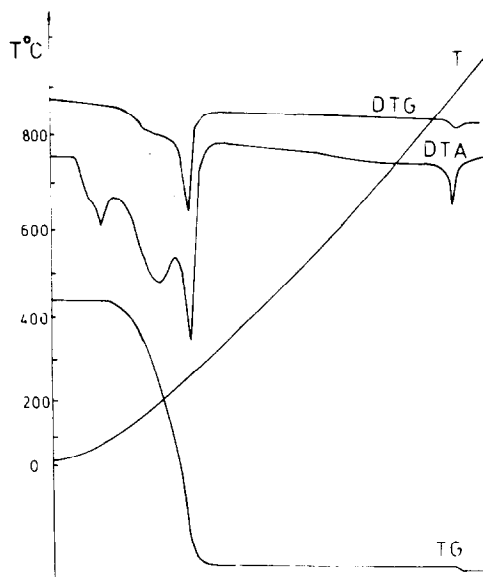


Fig. 4. DTA, DTG and TG decomposition curves of a mixture of 2.1 $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O} + 0.9 \text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$.

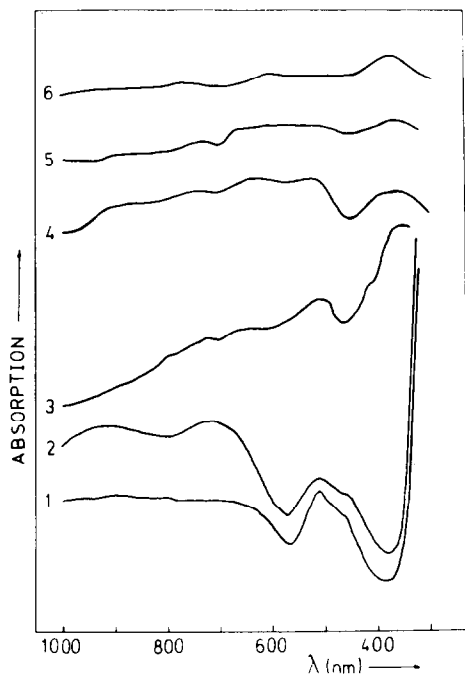


Fig. 5. Optical absorption spectra of some intermediate products of the decomposition of 2.1 $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O} + 0.9 \text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$. 1, Initial mixture. 2.1 $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O} + 0.9 \text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$; spectra of samples heated for 5 h at: 2, 150°C; 3, 180°C; 4, 200°C; 5, 220°C; 6, 350°C.

The DTA, DTG and TG curves of the decomposition of $0.9 \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O} + 2.1 \text{ Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ are presented in Fig. 4. The DTA curve has three endothermic peaks at 70, 190 and 260°C. Evidently, these peaks reflect the thermal effects of the main steps characterizing the process and indicate the intermediate products to be investigated thoroughly. At higher temperatures the weight decreases slightly and at 870°C there is one more endothermic peak.

Figure 5 shows the optical absorption spectra calculated by the Kubelka–Munk function from the reflectivities within the range 1000–250 nm for intermediate products corresponding to the characteristic stages of simultaneous decomposition of the two nitrates. Thus, curve 1 characterizes the initial mixture, whereas, curves 2–6 correspond to samples obtained after

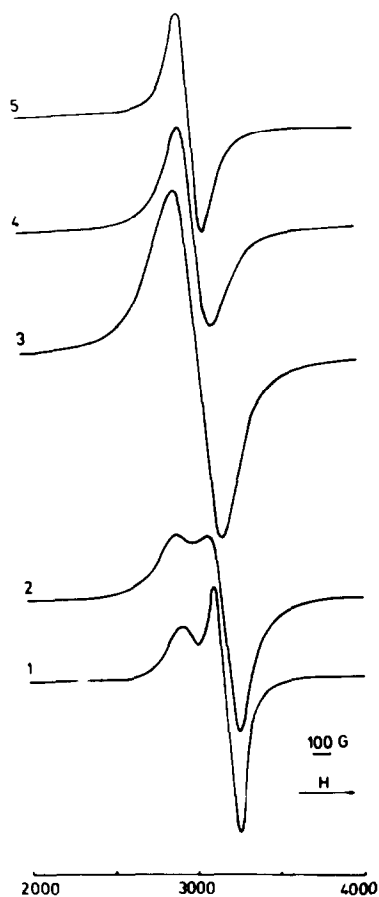


Fig. 6. EPR spectra at room temperature for some intermediate products of the decomposition of $2.1 \text{ Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O} + 0.9 \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O}$. 1, Initial mixture, $2.1 \text{ Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O} + 0.9 \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O}$; spectra of samples heated for 5 h at: 2, 150°C; 3, 180°C; 4, 200°C; 5, 220°C.

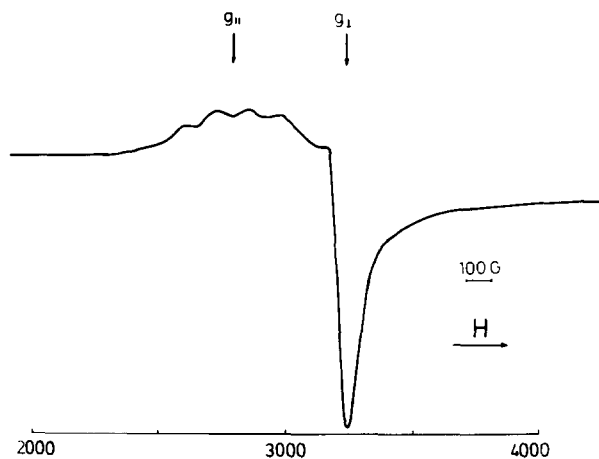


Fig. 7. EPR spectrum at -196°C for a mixture of $2.1 \text{ Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O} + 0.9 \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O}$ heated at 180°C for 5 h.

5 h heating of identical initial mixtures at 150 , 180 , 200 , 220 and 350°C , respectively. One can see that substantial changes in the optical spectrum occur at temperatures close to and above 180°C , which is in agreement with the results from the magnetic and thermogravimetric measurements. At this temperature, the edge of the strong absorption band at 370 nm disappears, and a new absorption peak appears at about 350 nm . At wavelengths above 500 nm the spectrum is also considerably altered.

The EPR spectra of the same intermediate samples recorded at room temperature are shown in Fig. 6. Spectrum 1 belongs to the initial mixture, whereas, spectra 2–5 correspond to the samples obtained at 150 , 180 , 200 and 220°C , respectively. The final compound produces no EPR signal at

TABLE 1

g factors and hyperfine structure constants, A , of powdery samples of different intermediate products of the decomposition of $2.1 \text{ Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O} + 0.9 \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O}$

Sample	g_{iso}	g_{\parallel}	g_{\perp}	ΔH_{p-p}^a	A (cm^{-1})
$\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O}$		2.338 ^a	2.071 ^a		
150°		2.331 ^a	2.070 ^a		
180°	2.188 ^a	2.407 ^b	2.077 ^b	208	0.0146
200°	2.189 ^a	2.410 ^b	2.077 ^b	164	0.0147
220°	2.192 ^a	2.414 ^b	2.081 ^b	145	0.0148
$\text{Cu}_2(\text{OH})_3\text{NO}_3$	2.196 ^a	2.416 ^b	2.083 ^b	84	0.0136

^a 20°C

^b -196°C

room temperature. It can be seen that spectra 1 and 2 are asymmetric, which is typical of paramagnetic centres having axial anisotropy, while the remaining spectra are almost symmetric singlets. In addition, the spectra of the initial mixture and the intermediate product obtained after heating for 5 h at 150°C are temperature-independent in the range -196-20°C, whereas the cooling of all the other samples leads to substantial changes and at -196°C their spectrum has the form shown in Fig. 7. Table 1 contains the values of g_{\parallel} , g_{\perp} and g_{iso} (for the symmetric singlets) and the constant of the hyperfine structure, A . The intensity of the symmetric singlet (curves 3,4 and 5 in Fig. 6) decreases with increasing temperature of preparation of the corresponding intermediate sample.

DISCUSSION

The magnetic and spectroscopic methods used in the present study gave information on the valence state and coordination of the metal cations in both initial and final compounds and in samples representing the different intermediate decomposition stages of the nitrate mixture. The two cations in the initial nitrates are bivalent and octahedrally coordinated, which is denoted by $\text{Cu}^{2+}(\text{O}_h)$ and $\text{Co}^{2+}(\text{O}_h)$. In our previous studies [6,9,10], it was shown that the copper-cobaltic oxides, $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$, obtained by calcination of the nitrate mixtures at 350°C have a partially inverse spinel structure



where $0 \leq x \leq 0.9$, and γ depends on x . If one assumes that the copper ions can only be bivalent, two combinations of valence states of the cobalt ions



and



will be compatible with the inverse distribution of the cations in the tetrahedral (T_d) and octahedral (O_h) sites of the cationic sublattice.

The spinel formation could be described as a series of changes in the copper and cobalt ion valencies and coordination polyhedra. These changes transform the initial state containing $\text{Cu}^{2+}(\text{O}_h)$ and $\text{Co}^{2+}(\text{O}_h)$ alone into the final II or III state. As can be seen in Fig. 3, at temperatures up to 180-190°C there is no evidence of any change in coordination and valence states of the cations irrespective of the weight loss. This means that the dehydration and eventual partial evolution of nitrogen oxides do not affect the symmetry of the crystal field created by the first coordination sphere and the valence state in this temperature range. This is also indicated by the optical spectra.

The broad band of optical absorption for the initial mixture (Fig. 5, curve 1) at 1000–630 nm can be ascribed to $d-d$ transitions in $\text{Cu}^{2+}(\text{O}_h)$. The peak at 510 nm is due to the ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$ transition in $\text{Co}^{2+}(\text{O}_h)$ while the shoulder at 460 nm could be attributed either to a ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition [11] or to splitting of the triplet ${}^4T_{1g}(\text{P})$ caused by the spin-orbital interaction [12]. The intense absorption below 370 nm is due to charge transfer. The heating of a sample at 150°C has no effect on the absorption of $\text{Co}^{2+}(\text{O}_h)$ ions (Fig. 5, curve 2). In the $\text{Cu}^{2+}(\text{O}_h)$ absorption spectrum, which is typical of a crystal field with axial symmetry, a better peak resolution is observed at 910 and 720 nm. The EPR spectrum is in agreement with these results. It is determined by the $\text{Cu}^{2+}(\text{O}_h)$ ions alone and also indicates axial anisotropy of the crystal field which changes its quantitative but not its qualitative characteristics in the case of the sample heated at 150°C (see Table 1).

After calcination of the initial mixture at 180°C for 5 h, the optical spectrum (Fig. 5, curve 3) shows the appearance of $\text{Co}^{3+}(\text{O}_h)$ ions which, according to ref. 13, could be identified by the absorption peaks at 560 and 350 nm corresponding to transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$. The absorption maximum of the $\text{Cu}^{2+}(\text{O}_h)$ ions is in this case at 720 nm, whereas the absorption peak at the lower energies has disappeared. After heating the sample at 200°C (Fig. 5, curve 4) and 220°C (Fig. 5, curve 5), the absorption at 510 nm gradually disappears, i.e. the $\text{Co}^{2+}(\text{O}_h)$ ions disappear. The sharp decrease of the magnetic moment between 190 and 220°C can be explained as due to the conversion of $\text{Co}^{2+}(\text{O}_h)$ into $\text{Co}^{3+}(\text{O}_h)$, because the latter has no magnetic moment in spinel cobaltites [14].

Thus, the results obtained for the range 180–220°C show that a spinel is formed since $\text{Co}^{3+}(\text{O}_h)$ ions appear while $\text{Co}^{2+}(\text{O}_h)$ ions disappear. It is tempting to associate the beginning of the spinel formation within this temperature range with the appearance of some definite intermediate products of copper and cobalt nitrate decomposition. The EPR spectra proved to be very helpful in the identification of these products.

The EPR spectra of the system under investigation show the changes in state of the Cu^{2+} ions alone. Since the pure final product of the reaction gave no EPR signal, the almost symmetrical singlet characterizing the samples obtained above 180°C could be associated with this intermediate product of copper nitrate decomposition at 180–190°C.

According to ref. 15, the thermal decomposition of $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ passes through basic copper nitrate, $\text{Cu}_2(\text{OH})_3\text{NO}_3$, as an intermediate product. The basic copper nitrate synthesized by the authors as described in ref. 16, showed optical absorption with a maximum at 720 nm and an EPR spectrum at -196°C which was quite similar to that given in Fig. 7 with $g_{\parallel} = 2.416$, $g_{\perp} = 2.083$ and $A = 0.0136 \text{ cm}^{-1}$. Irrespective of the differences which are more clearly expressed in the EPR spectra at room temperature (see Table 1), the close similarity to the parameters characterizing the optical absorption and EPR spectra of samples obtained above 180°C cannot be

overlooked. For this reason it should be concluded that basic copper nitrate is the intermediate decomposition product of copper nitrate which further reacts to form spinel copper cobaltite. The difference between the "intermediate" copper nitrate and the reference one as viewed by EPR and other methods will be discussed elsewhere.

The foregoing conclusions enable one to make a more-detailed description of the process as a function of the decomposition degree, α . A plot illustrating the dependence of the square of the effective magnetic moment on α (Fig. 8) may be used for that purpose. Up to $\alpha \approx 0.6$, the magnetic moment does not change. This conversion degree corresponds to temperatures of about 180–190°C, so that $0 \leq \alpha \leq 0.6$ is a range of dehydration and independent rearrangements within the initial salts without any reactions between them, i.e. this is the interval within which the actual "initial" reagents of the spinel formation appear.

If one assumes that at $\alpha = 0.6$ the whole amount of the initial copper nitrate has transformed into basic copper nitrate, the weight of the intermediate cobalt-containing product participating in the reaction could be estimated. With an accuracy of about 5% this product may be identified as anhydrous cobaltous nitrate, $\text{Co}(\text{NO}_3)_2$. This is in good agreement with previous studies [17,18] according to which the decomposition of $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ passes through such an intermediate species.

The interval $0.6 \leq \alpha \leq 0.9$ is characterized by a linear decrease of μ_{exp}^2 . Since the magnetic susceptibility ($\chi \sim \mu^2$) is an additive quantity which is at any moment equal to the sum of the magnetic susceptibilities of the initial substances and the final product, the above linear change shows directly that at $\alpha \geq 0.6$ the spinel formation has actually begun.

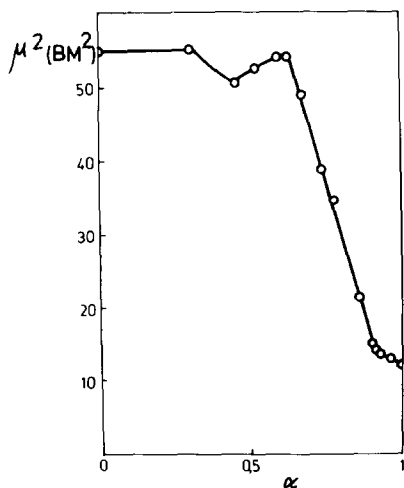
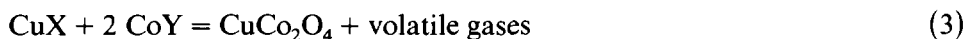


Fig. 8. Plot of the effective magnetic moment of a mixture of 2.1 $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ + 0.9 $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ vs. decomposition degree, α .

If, for the sake of brevity, the effective magnetic moment of Cu^{2+} in the basic copper nitrate is denoted by μ_{Cu} , and the effective magnetic moment for Co^{2+} in the corresponding intermediate cobalt-containing product, by μ_{Co} , then, on introducing a new variable of the reaction, denoted by z ($0 \leq z \leq 1$ when $0.6 \leq \alpha < 1$), we can write

$$\mu_{\text{exp}}^2 = z\mu_f^2 + 0.9(1-z)\mu_{\text{Cu}}^2 + 2.1(1-z)\mu_{\text{Co}}^2 \quad (2)$$

Here, μ_f is the magnetic moment per formula unit, $\text{Cu}_{0.9}\text{Co}_{2.1}$, in the reaction product. The extrapolation of the linear part of the curve in the range 0.6–0.9 to $z \rightarrow 1$ or $\alpha \rightarrow 1$, respectively, gives a μ_f value which is almost equal to that estimated for a normal spinel CuCo_2O_4 . The result is a seeming paradox: in spite of the additive “accumulation” of a normal spinel according to the reaction



where X and Y denote the anionic parts of the reacting intermediate products, the final product is an inverse spinel. This contradiction could be overcome using the scheme proposed by us for describing the formation of the spinel Co_3O_4 [2,3,7]. This process was studied recently by measuring, in situ, the magnetic susceptibility and the weight loss in the magnetic balance. At a decomposition degree $\alpha \approx 0.5$ of the initial $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ [which corresponds to the composition $\text{Co}(\text{NO}_3)_2$], the magnetic moment begins to decrease linearly and remains, up to a value of almost 1, smaller than the magnetic moment which was to be expected on the basis of the additive model according to which for each α within this range the sample should contain $(1-\alpha)$ moles of the decomposing salt and α moles of the normal spinel Co_3O_4 . This was assumed to be indicative of the existence of an intermediate pre-spinel structure with a $\text{Co}^{3+}(\text{O}_h)$ -to- $\text{Co}^{2+}(\text{T}_d)$ ratio higher than 2

$$\text{Co}_z^{2+}\square_{1-z}[\text{Co}_{3-z}^{3+}], \text{ where } 0 < z < 1 \quad (\text{IV})$$

This formula illustrates the gradual transition of 1/3 of the $\text{Co}^{3+}(\text{O}_h)$ ions to the tetrahedral sites, the transition



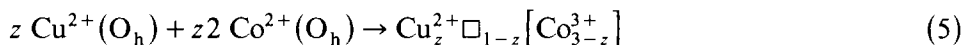
being regarded as a rate-limiting step.

When $z \approx 0$ and the anionic lattice consists mainly of oxygen anions, the intermediate structure should be considered as a species very close to the sesquioxide, Co_2O_3 . It is known that this oxide has been synthesized only at a high oxygen pressure [19].

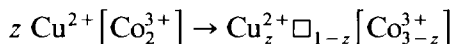
Let us assume that a pre-spinel structure with a cationic distribution over the tetrahedral and octahedral sites, given by

$$\text{Cu}_z^{2+}\square_{1-z}[\text{Co}_{3-z}^{3+}] \quad (\text{V})$$

is formed in the mixed system at $z \approx 0$. In this case, the Cu^{2+} ions are the first to enter the tetrahedral sites. Then the reaction (3) for the cationic partners could be written as



Since $\mu[\text{Co}^{3+}(\text{O}_h)] = 0$, the substitution



does not affect the magnetic moment value.

However, it is interesting that under these conditions the structure (V) does not develop to a normal copper cobaltite. Obviously, at a certain z_{max} the accumulation of more $\text{Cu}^{2+}(\text{T}_d)$ becomes unfavourable and Co^{2+} ions begin to occupy the tetrahedral sites. Simultaneously, the rest of the available Cu^{2+} ions enter the B-sites. It seems that this change in the mechanism occurs at conversion degrees of about 0.9, at which the slope of the curve μ_{exp}^2 vs. α changes (Fig. 8). Some unpublished results from investigations on the lattice parameter and the magnetic moment as functions of the copper content in $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ spinels gave values ranging from 0.2 to 0.3 for z_{max} [20].

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