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THÈSE

PRÉSENTÉE

A L'UNIVERSITÉ DE BORDEAUX I

POUR OBTENIR LE TITRE DE

DOCTEUR DE L'UNIVERSITÉ
(MENTION SCIENCES)

PAR

ANDRZEJ MAŁECKI

DECOMPOSITION THERMIQUE ET PROPRIETES ELECTRIQUES DE Co_3O_4

Soutenue le 9 juillet 1985, devant la Commission d'examen:

MM. P. HAGENMULLER	<i>Président</i>
M. POUCHARD.....	} <i>Examineurs</i>
J. ETOURNEAU.....	
J.P. DOUMERC.....	

Ce travail a été réalisé au Laboratoire de Chimie du Solide du Centre National de la Recherche Scientifique, dirigé par Monsieur le Professeur HAGENMULLER, lors de nos séjours à BORDEAUX. Nous lui exprimons notre profonde gratitude pour l'accueil exceptionnel qu'il nous a réservé, l'aide matérielle et morale ainsi que l'intérêt qu'il a porté à ce travail.

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"Kinetics of Thermal Decomposition of Co_3O_4 Powder and Single Crystals"

J. Solid. State Chem., 56, 49 (1985).

PUBLICATION n° 2

"Kinetics of Thermal Decomposition of Co_3O_4 Powder and Single Crystals, Kinetic Model"

J. Solid State Chem. (to be published).

PUBLICATION n° 3

"A simple but Very Close Approximation to the Serin-Ellickson Equation"

J. Thermal Anal. 29, 367 (1984).

PUBLICATION n° 4

"Growth and Electrical Properties of Pure and Ni-doped Co_3O_4 single Crystals"

Mat. Res. Bull. 19, 989 (1984).

SUMMARY

SUMMARY

Co_3O_4 has been extensively studied from the point of view of possible industrial applications such as catalysis and electrocatalysis for oxidation reactions. Fundamental studies are less numerous and they mainly concern magnetic and structural properties.

Low spin $3d^6$ configuration of Co^{3+} in Co_3O_4 and electrocatalytic behaviour permitted to expect interesting anodic photoelectrochemical properties. However crystals grown by standard C.V.T. techniques were highly stoichiometric, they are practically insulators at room temperature. For photoelectrochemical studies it was necessary actually to obtain semiconducting crystals. The methods which could be considered for that purpose were doping, slight reduction or decomposition. A slight reduction process could not be used as Co_3O_4 is easily reduced to cobalt metal even at the relatively low temperature of 570 K. Hence the decomposition method was chosen as a first step in the preparation of semiconducting crystals of Co_3O_4 for electrodes.

An examination of the existing literature on the thermal decomposition of Co_3O_4 reveals that many of the previous authors confined their studies to the temperature and heat of decomposition, only a few extended their investigations to the chemical kinetics of decomposition. Several discrepancies and contradictions in these studies could justify a reinvestigation of the kinetics of the generally accepted reaction : $\text{Co}_3\text{O}_4 \rightarrow 3 \text{CoO} + 1/2 \text{O}_2$ (publication n° 1).

In publication 1 these kinetics has been detailly described. Numerical analysis of experimental data led to a new kinetic equation :

$$1 - 2\alpha/3 - (1 - \alpha)^{2/3} = kt^n$$

where α is the degree of decomposition, t the time and k and n parameters. Atcivation energy was also found to vary with degree of decomposition.

On the base of results given in publication 1, new kinetic model has been developped (publication 2). This model has been derived from Ginstling-Brounshtein model in which it additionally has been assumed that activation energy varies with α . In Ginstling-Brounshtein model as well as in the one proposed here it is assumed the rate limiting step to be diffusion through a layer of product forming on the surface of grains of reactant. Formation of such a layer has been clearly observed on cross section of partially decomposed single crystals. The layer has been found to be very compact and well attached to the surface of crystals which justify possibility of applying a such diffusional kinetic model (publications n° 1 and 2).

During working out our results a simple but very close approximation to the Serin-Ellickson equation was found. This approximation appeared to be very helpful due to the relatively complicated from of the quoted equation (publication n° 3).

Finally it may be ascertained that due to the layer-type decomposition of the single crystals of Co_3O_4 semiconducting homogeneous crystals cannot be obtained by partial decomposition.

An alternative way for preparation of semiconducting crystals of Co_3O_4 was doping. Substitution of cobalt for nickel in the spinel structure of Co_3O_4 gives rise to significant increase of electrical conductivity at room temperature by three orders of magnitude. Ni atoms are located

in the octahedral sites with both oxidation states 2+ and 3+ (publication n° 4).

Due to lack of data concerning electrical properties of single crystals of pure Co_3O_4 , conductivity and thermopower have also been investigated between 25 and 900 K. Results have been interpreted on the base of an intrinsic behaviour which differs from previous investigations carried out on polycrystalline samples.

As expected Ni doping led to crystals exhibiting a semiconducting behaviour. However Ni doped Co_3O_4 electrodes have shown high instability in used electrolytes which prevented obtaining reproducible results.

Finally results given in papers 1 to 4 have led to :

- a complete description of kinetics of thermal decomposition of Co_3O_4 single crystals as well as powder,
- extension of Ginstling-Brounshtein's model assuming activation energy to vary with degree of decomposition which leads to new kinetic equation,
- a simple and practically helpful approximation to Serin-Ellickson equation,
- interpretation of electrical properties of highly stoichiometric Co_3O_4 single crystals,
- explanation of structural and electrical properties of Ni-doped Co_3O_4 single crystals.

PUBLICATION N° 1

Kinetics of Thermal Decomposition of Co_3O_4 Powder and Single Crystals

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Kinetics of thermal decomposition in vacuum of Co_3O_4 powder as well as single crystals has been investigated. Discrepancies with the results of previous authors have been discussed. Decomposition of Co_3O_4 proceeds through formation of a compact layer of CoO and hence diffusion is the rate-limiting factor. The experimental curves $\alpha(t)$ can be described for $0.05 < \alpha < 0.85$ using a modified Ginstling-Brounshtein equation: $1 - 2\alpha/3 - (1 - \alpha)^{2/3} = kt^n$ where the activation energy varies with the degree of decomposition. © 1985 Academic Press, Inc.

Introduction

Single crystals of Co_3O_4 have been prepared and characterized for the purpose of photoelectrochemical studies. However, crystals grown by standard C.V.T. techniques were highly stoichiometric, they are practically insulators at room temperature. For photoelectrochemical studies it was necessary actually to obtain semiconducting crystals. The methods which could be considered for that purpose were doping, slight reduction, or decomposition. A slight reduction process could not be used as Co_3O_4 is easily reduced to cobalt metal even at the relatively low temperature of

570 K. Hence the decomposition method was chosen as a first step in the preparation of semiconducting crystals of Co_3O_4 for electrodes.

An examination of the existing literature on the thermal decomposition of Co_3O_4 reveals that many of the previous authors (1-5) confined their studies to the temperature and heat of decomposition, only a few (6-9) extended their investigations to the chemical kinetics of decomposition. Several discrepancies and contradictions in these studies could justify a reinvestigation of the kinetics of the generally accepted reaction: $\text{Co}_3\text{O}_4 \rightleftharpoons 3\text{CoO} + \frac{1}{2}\text{O}_2$.

The previous investigators carried out their kinetic studies using different types of Co_3O_4 . Ichimura and Komatsu (6) used only powders, Deshmukh *et al.* (8) powders as well as sintered spherical pellets, Berthod (7) both powder and single crystals. Joly and Gerard (9) did not indicate

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which material they used, but it was probably a powder sample. It is worthwhile to note that only Berthod attempted to investigate single crystals, but he could not obtain reliable results by isothermal decomposition and instead used only the polythermal method applying the Satava model (10) to calculate the activation energy of the process. For describing the kinetic curves $\alpha(t)$, (where α is the degree of decomposition and t the time), Ichimura and Komatsu (6), Joly and Gerard (9), Deshmukh *et al.* (8), used the equation

$$1 - (1 - \alpha)^{1/3} = kt \quad (1)$$

However, in Ref. (8), this equation was considered as valid for the powder and for the so-called first decomposition stage of the pellets. The second decomposition stage of these pellets was described by these authors using Jander's equation

$$[1 - (1 - \alpha)^{1/3}]^{2/3} = kt \quad (2)$$

Berthod (7) for $\alpha < 0.4$ proposed a so-called Carter-Valensi equation

$$\frac{\Delta}{\Delta - 1} - (1 - \alpha)^{2/3} - \frac{1}{\Delta - 1} [1 + (\Delta - 1)\alpha]^{2/3} = kt \quad (3)$$

where Δ is the ratio of the molar volume of the product to the molar volume of substrate, and also the relation

$$\alpha^2 = kt \quad (4)$$

But Joly and Gerard extended the validity of (4) up to $\alpha = 0.7$ and 0.8.

It seems that, except for Ichimura and Komatsu, the previous authors could not fit the experimental data with an equation that describes correctly the results over the whole decomposition range.

Various values of activation energy were reported by the previous authors. For powders the values given by Ichimura and Komatsu (6) and Deshmukh (8) were 366.6 kJ/mole (87.7 kcal/mole) and 392.9 \pm 8.4

kJ/mole (94 \pm 2 kcal/mole), respectively. But for pellets Deshmukh gave two different values, 397.7 \pm 25.1 kJ/mole (95 \pm 6 kcal/mole) and 539.2 \pm 29.3 kJ/mole (129 \pm 7 kcal/mole) corresponding to his first and second stage of decomposition. Berthod (7) could not find an activation energy for a powder sample and ascertained that the apparent value determined from the reaction speed, changed with α , being between 627 and 1254 kJ/mole (150–300 kcal/mole). But for single crystals, using the Satava method of polythermal analysis, he obtained two different values: 309.3 kJ/mole (74 kcal/mole) and 384.6 kJ/mole (92 kcal/mole) for α either below or above 0.35, respectively.

Due to these discrepancies the present authors report new experimental results and a new description of the kinetics of thermal decomposition of Co_3O_4 , both in powder and single-crystal forms.

Experimental Techniques and Sample Preparation

The powder samples studied were commercial Co_3O_4 (Cerac Inc. 99.95%). Single crystals were obtained by a standard C.V.T. technique using quartz ampoules. The transport agents were Cl_2 , HCl , or TeCl_4 . Crystals grown after about a 1-week run, ranged in a size between 1 and 3 mm (Fig. 1). The identity of the crystals was confirmed by powder X-ray diffraction.

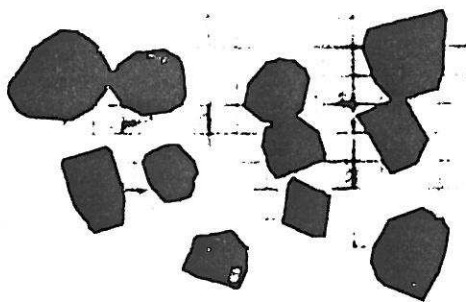


FIG. 1. Single crystals of Co_3O_4 .

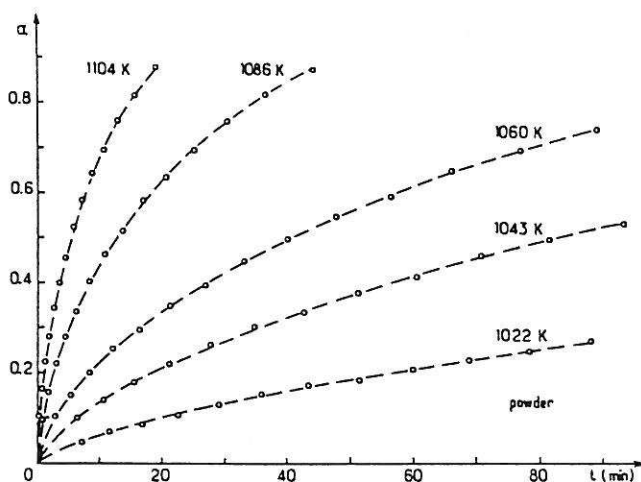


FIG. 2. The $\alpha(t)$ curves for thermal decomposition of Co_3O_4 powder.

Kinetics determination were made with a SETARAM thermal balance (± 0.05 mg). Thermal decomposition studies in isothermal conditions were carried out under an oxygen partial pressure of 0.67 Pa. For each experiment a 100-mg sample was used in a platinum holder. The single crystals chosen for these measurements had approximately the same dimensions, each edge being about 1 mm. A rapid heating rate for 40–50°C/mm was used so as to reach the desired temperature as quickly as possible. When a constant temperature was attained the loss of mass as a function of time was automatically recorded. The degree of decomposition was calculated as the ratio of the loss of mass to the total loss of mass at the end of the reaction.

Results and Discussions

Kinetic measurements for powder and single crystal samples were made at five selected temperatures; 1022, 1043, 1060, 1086, 1104 K for powder samples, 1158, 1175, 1183, 1211, and 1231 K for single crystals. The $\alpha(t)$ curves for powder and single crystals are given in Figs. 2 and 3.

In order to choose an appropriate kinetic equation it was necessary to know whether the decomposition product formed a layer or was dispersed in the crystal bulk. From Figs. 4a and b showing the cross section of crystals decomposed up to $\alpha = 0.1$ and 0.6, respectively, the formation of a layer is clearly visible. In order to describe the experimental curves, several so far used kinetic equations corresponding to layer-type decomposition were tried, but it was apparently impossible to find a single equation accounting satisfactorily for the entire range of α . However, a relatively good agreement with the experimental data for both powder and single crystals could be achieved, thanks either to Eq. (1) or to the Ginstling-Brounshtein equation

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = kt \quad (5)$$

A plot against t of $1 - (1 - \alpha)^{1/3}$ and $1 - 2\alpha/3 - (1 - \alpha)^{2/3}$ for Eqs. (1) and (5), respectively, gave linear dependencies for $0.15 < \alpha < 0.75$. The coefficient of correlation obtained from least-squares methods were in the range of 0.985 to 0.995, values which appear to be satisfactory. However, the intercept which should have been at the

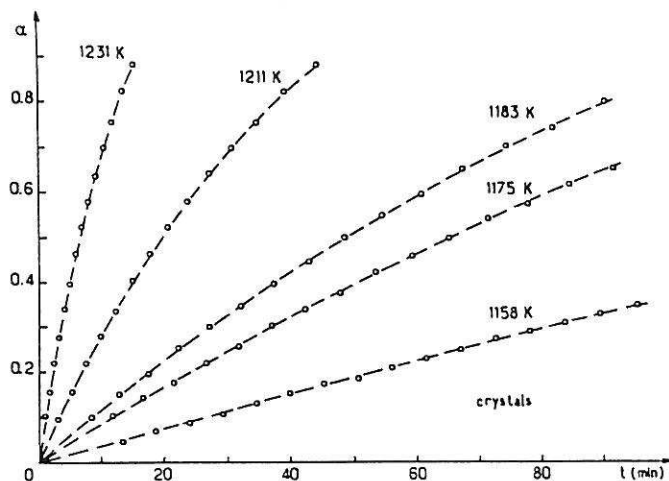


FIG. 3. The $\alpha(t)$ curves for thermal decomposition of Co_3O_4 single crystals.

origin showed a conspicuous shift. This shift could be attributed to an experimental error, but statistical tests showed that the

probability of a zero intercept did not exceed 5% and hence that the shift could not be ignored. It was therefore thought that none of these equations truly described the experimental data and that the agreement with the experimental value of α in the range of 0.15–0.75 was in fact only a numerical coincidence. It became thus impossible to use any of the known kinetic equations to describe our experimental data. A similar situation prevailed actually before in the studies carried out by Berthod and Deshmukh. While Berthod failed to find a suitable equation, Deshmukh *et al.* attempted to describe their data for the kinetics of decomposition of pellets using two different equations, (1) and (2). The second decomposition stage, for $\alpha > 0.6$, was described by Deshmukh using Jander's equation (2), a choice which is rather surprising as this equation is in principle only valid for small values of α (0.15 or 0.20). One may assume that this apparent fitting with Jander's equation for $\alpha > 0.20$ is merely a numerical agreement and has in fact no physical meaning.

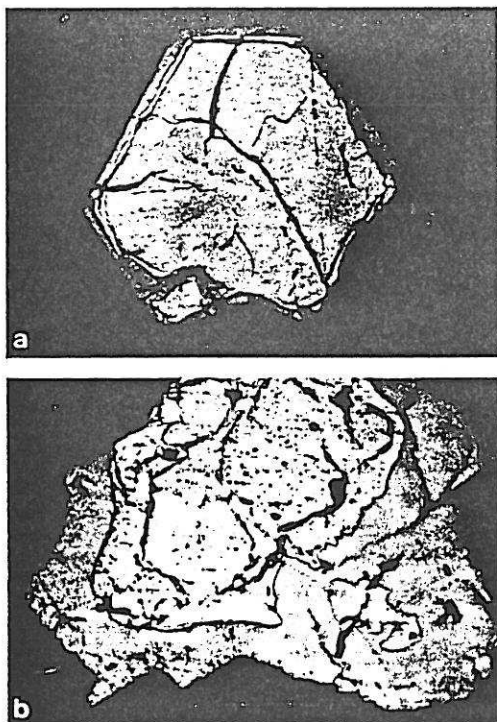


FIG. 4. Cross section of partially decomposed single crystals of Co_3O_4 : (a) $\alpha = 0.1$; (b) $\alpha = 0.6$.

Before considering the ability of Eq. (1) to describe the reaction, it is necessary to take into consideration two important fac-

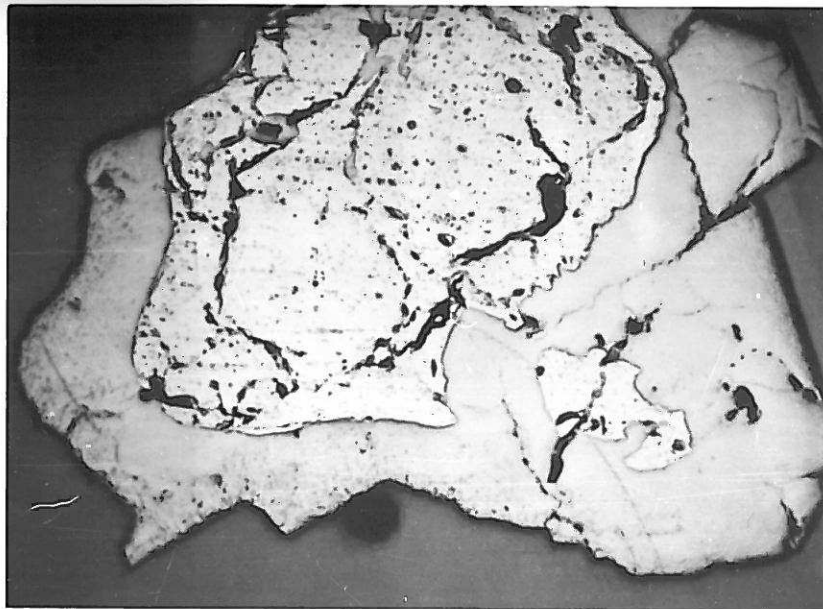
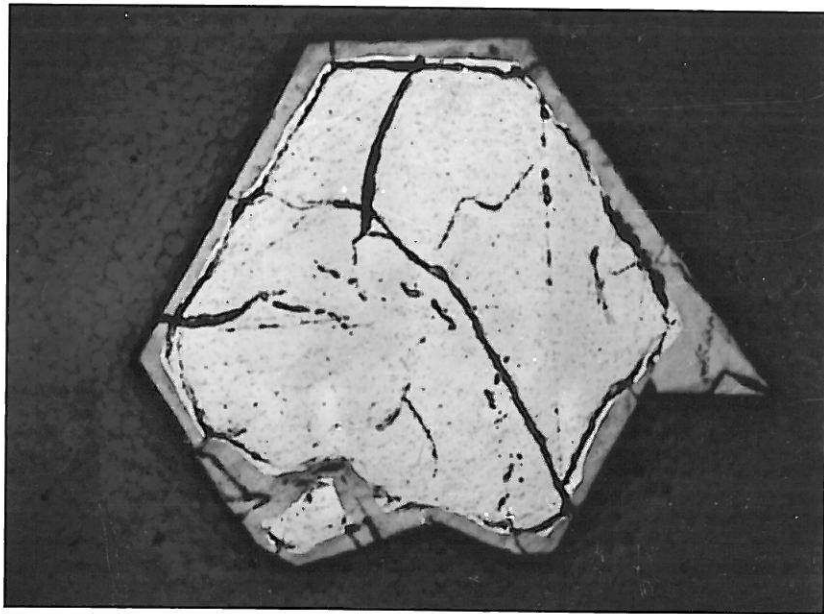


FIG. 4. Cross section of partially decomposed single crystals of Co_3O_4 : (a) $\alpha = 0.1$; (b) $\alpha = 0.6$.

tors, namely the compactness of the layer of the material and then the reversibility of the reaction. Indeed this equation does not take into account the influence of the layer on the surface reaction. In the thermal decomposition of Co_3O_4 a dense and compact layer of CoO is formed as observed by Deshmukh *et al.* (8) and also in the present work (Figs. 4a and b). Such a layer should hinder the transport of oxygen from the surface on which the reaction occurs and therefore should have an influence on the speed of the reversible reaction itself. This is quite in contradiction with the assumption under which Eq. (1) is derived.

From the above considerations, and also from the observations of the previous authors (7, 8), it may be assumed that the speed of the Co_3O_4 decomposition is diffusion controlled. As it has already been emphasized that none of the known diffusional models could be applied, it became necessary to look for a more satisfactory description of the present results.

During different trials made to fit experimental data with the kinetic equations, it was found that when $\ln[1 - 2\alpha/3 - (1 - \alpha)^{2/3}]$ was plotted against $\ln t$, extremely high values of straight-line coefficients of correlation (0.9992–0.9999) were obtained for a large α domain: 0.05–0.85. This corresponds to fitting of data to the Ginstling–Brounshtein equation using logarithmic coordinates instead of those mentioned earlier. Using such a system of coordinates the Ginstling–Brounshtein equation takes the form

$$F(\alpha) = \ln[1 - 2\alpha/3 - (1 - \alpha)^{2/3}] = \ln k + \ln t \quad (6)$$

If this equation is suitable for the experimental data, then the plot of $F(\alpha)$ against $\ln t$ should give a straight line with a slope equal to 1. In our case, although a good straight line was observed, the slope was found to be between 1.82 and 2.07 or 1.18 and 1.30 for single crystals or powders, re-

TABLE I
RESULTS OF FITTING OF EXPERIMENTAL DATA
FOR POWDER

T (K)	n	k	r
1022	1.385	1.871×10^{-5}	0.99997
1043	1.358	9.312×10^{-5}	0.99988
1060	1.295	3.078×10^{-4}	0.99997
1086	1.229	1.618×10^{-3}	0.99987
1104	1.184	5.203×10^{-3}	0.99973

spectively. Statistical tests confirmed that this difference between the obtained and the expected value of the slope was quite significant. The probability of the event that the true value of the slope was 1 rather than those observed, due to experimental errors, was not greater than 1%. Simultaneously statistical tests for the coefficient of correlation of the straight-line dependency given by Eq. (6) showed that the probability was smaller than 1%, i.e., it was really a straight-line dependency. As a result of these tests, the following equation was able to describe our experimental data:

$$\ln[1 - 2\alpha/3 - (1 - \alpha)^{2/3}] = \ln k + n \ln t \quad (7)$$

or

$$1 - 2\alpha/3 - (1 - \alpha)^{2/3} = kt^n \quad (8)$$

Assuming this to be a true kinetic equation, it was used to work out our results. Tables I and II give the parameters n and k

TABLE II
RESULTS OF FITTING OF EXPERIMENTAL DATA
FOR SINGLE CRYSTALS

T (K)	n	k	r
1158	2.072	1.290×10^{-6}	0.99971
1175	2.028	7.660×10^{-6}	0.99932
1183	1.981	1.671×10^{-5}	0.99947
1211	1.899	1.271×10^{-4}	0.99938
1231	1.823	1.178×10^{-3}	0.99917

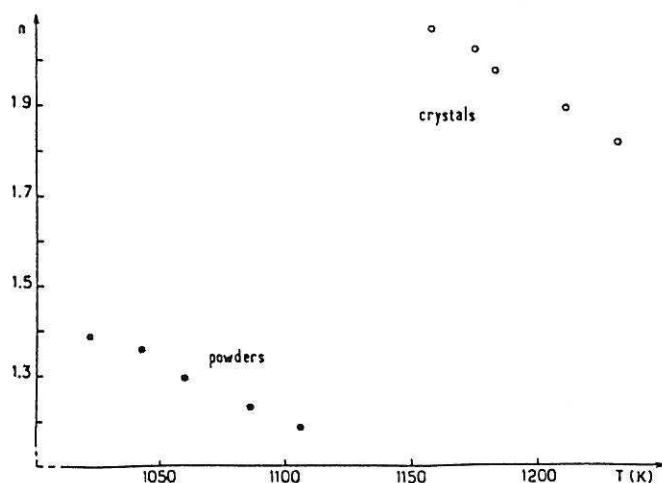


FIG. 5. Temperature dependency of n in Eq. (8) for powder and single crystal.

and the correlation coefficient r for the thermal decomposition of powder and single crystals, respectively.

In Figs. 2 and 3, it is possible to find out the quality of the fitting (the points correspond to experimental data and the curves to the calculated values using n and k from Tables I and II). It can be pointed out that the parameters n and k are temperature dependent, as illustrated for n in Fig. 5.

The next problem was to determine the activation energy, which required the knowledge of the ratio constant. Since both n and k parameters are temperature dependent, none of them could be used as ratio constant. Using Eq. (8), it was possible to find for the reaction speed:

$$\frac{d\alpha}{dt} = \frac{K(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}} [1 - 2\alpha/3 - (1-\alpha)^{2/3}] \quad (9)$$

where

$$K = \left(\frac{2}{3}\right)nk^{1/n} [1 - 2\alpha/3 - (1-\alpha)^{2/3}]^{-1/n} \quad (10)$$

The temperature dependency of the reaction speed concerns only K . But it is mathematically impossible to separate Eq. (9)

into two parts, one depending on α and the other one on the temperature. Therefore it was necessary to assume that the expression (10) corresponded to the reaction constant as supposed previously by one of the authors (11).

In such a case we can expect, for a given value of α , K to obey an Arrhenius law

$$K = K_0 e^{-E/RT} \quad (11)$$

where K_0 is a constant, E the energy of activation, R the perfect gas constant.

TABLE III
FITTING OF K VALUES TO THOSE GIVEN BY AN
ARRHENIUS EQUATION FOR DIFFERENT VALUES OF
 α (POWDER)

α	E (kJ/mole)	k_0	r	ΔE (kJ/mole)
0.1	457.3	1.89×10^{22}	0.9999	4.3
0.2	436.8	6.00×10^{20}	0.9998	4.9
0.3	424.3	7.51×10^{19}	0.9997	5.6
0.4	415.1	1.63×10^{19}	0.9997	6.1
0.5	407.6	4.74×10^{18}	0.9996	6.5
0.6	401.3	1.64×10^{18}	0.9996	6.9
0.7	395.4	6.28×10^{17}	0.9995	7.3
0.8	390.0	2.51×10^{17}	0.9994	7.7

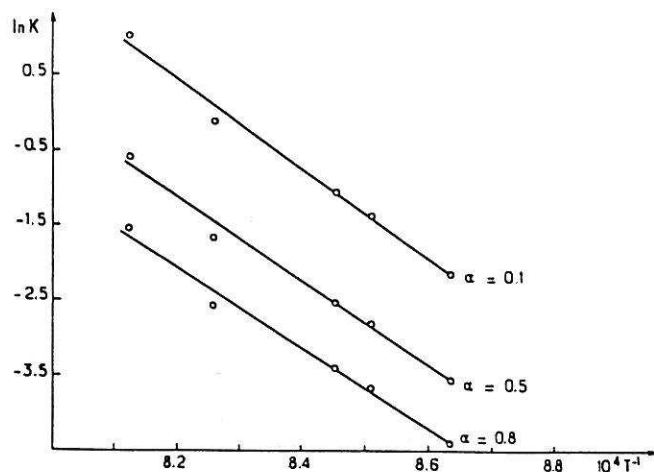


FIG. 6. Plot of $\ln K$ against $10^4 \times T^{-1}$ for Co_3O_4 single crystals for different values of α .

Because K is also a function of α , we must expect that either K_0 or E or both of them depend on α . Tables III and IV give results of the fitting of the K values with those of the Arrhenius equation for different values of α . The tables also give the correlation coefficients and the most probable error on the determination of the activation energy, ΔE .

Figures 6 and 7 show examples of fittings of $\ln K$ to the values given by an Arrhenius

equation for different values of α (0.1, 0.5, and 0.8). It can be seen from these plots that the activation energy is a function of α , as illustrated in Fig. 8. This observation is in good agreement with the difficulties encountered by Berthod (7) who also noticed such a dependency. Table IV shows clearly however that the uncertainty ΔE is large relative to the influence of α on the activation energy E .

The values of the activation energy are

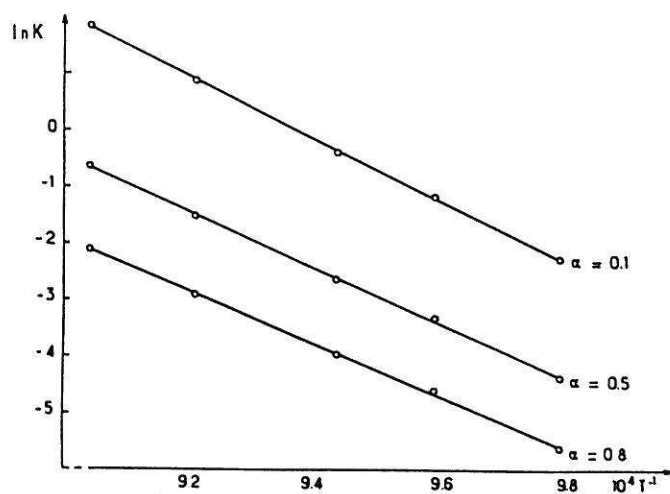


FIG. 7. Plot of $\ln K$ against $10^4 \times T^{-1}$ for Co_3O_4 powder for different values of α .

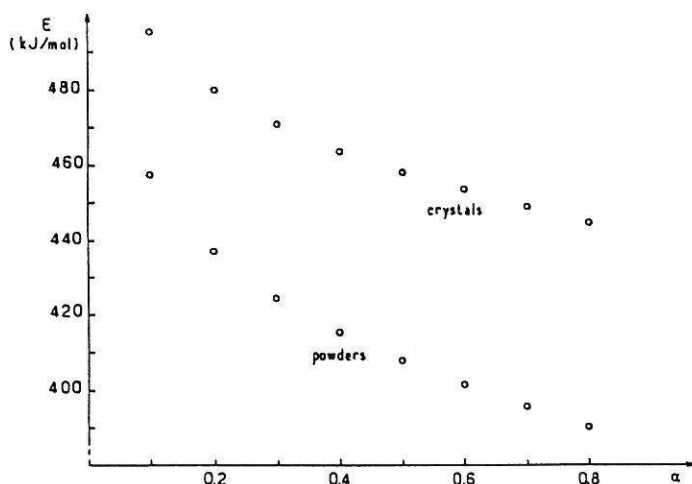


FIG. 8. Dependency of activation energy on α for single crystals and powders.

close to those given by Deshmukh *et al.* (6), however it must be emphasized that the values found here show a dependency on α .

Conclusions

In conclusion we may say that we obtained an equation which has the following features: (i) it describes experimental curves $\alpha(t)$ for a wide range of α -values with high accuracy; (ii) it leads to determination of activation energy as a function of

α ; (iii) it derives from Ginstling–Brounshstein equation.

Therefore, Eq. (8) can be considered as kinetic equation. The only difference between this equation and that of Ginstling–Brounshstein lies in the introduction of n parameter which actually takes into account the observed change of activation energy with α . Such an interpretation is analogous to that reported earlier for the modification of the Zhuravlev equation used to explain kinetics of the reduction of V_2O_5 by gaseous ammonia (11). However, the apparently linear temperature dependency of n as well as the large difference obtained for the n -values between single crystals and powder (Fig. 5) remains to be explained.

Equation (8) is able to describe the thermal decomposition of both powder and single crystals with comparable efficiency. The activation energy for powder seems to be lower than that obtained for single crystals. However, statistical tests do not confirm this hypothesis with high enough probability (not greater than 80%).

Finally, it may be ascertained that due to the layer-type decomposition of the single crystals of Co_3O_4 , semiconducting homoge-

TABLE IV
FITTING OF K VALUES WITH THOSE OF AN
ARRHENIUS EQUATION FOR DIFFERENT VALUES OF
 α (SINGLE CRYSTALS)

α	E (kJ/mole)	k_0	r	ΔE (kJ/mole)
0.1	495.3	1.94×10^{21}	0.9947	29.4
0.2	479.9	1.96×10^{20}	0.9946	29.0
0.3	470.7	4.93×10^{19}	0.9944	28.8
0.4	463.6	1.79×10^{19}	0.9944	28.6
0.5	458.1	7.87×10^{18}	0.9943	28.4
0.6	453.5	3.89×10^{18}	0.9942	28.3
0.7	448.9	2.06×10^{18}	0.9941	28.2
0.8	444.8	1.12×10^{18}	0.9941	28.1

neous crystals cannot be obtained by partial decomposition. It will be necessary to investigate the possibility of doping single crystals of Co_3O_4 by transition elements to get such a material.

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PUBLICATION N°2

KINETICS OF THERMAL DECOMPOSITION OF Co_3O_4 POWDER AND SINGLE CRYSTALS. KINETIC MODEL

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ABSTRACT

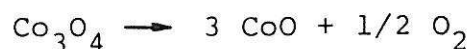
Thermal decomposition of Co_3O_4 leads to the formation of a layer of CoO . This layer has been found to be very compact and well attached to the surface of partially decomposed single crystal. On the base of these observations and previous work devoted to numerical analysis of experimental data α vs. t it is shown that kinetic of the reaction can be described using a model derived from Ginstling Brounshtein's model in which it is assumed that activation energy varies as a function of α .

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INTRODUCTION

In a previous paper we have shown that kinetic of thermal decomposition of Co_3O_4 :



under oxygen partial pressure of 0.67 Pa can be described with a very high accuracy by equation [1] :

$$1 - 2\alpha/3 - (1-\alpha)^{2/3} = kt^n \quad (1)$$

where α is the degree of decomposition, k and n are constants. The above equation which did not appeared previously in literature has been found directly from kinetic analysis of experimental curves α vs.t. It has also been shown that equation (1) could be considered as kinetic equation because it leads to determination of activation energy and it can be connected to Ginstling-Brounshtein equation :

$$1 - 2\alpha/3 - (1-\alpha)^{2/3} = kt \quad (2)$$

Activation energy has been found to vary with degree of decomposition (see tables 2 and 3).

Ginstling-Brounshtein model is based on assumptions that the product of reaction forms a layer on the surface of the grains and that diffusion of reactants through the layer is the rate limiting step. Existence of a layer was observed in our previous work [1] for decomposition of single crystals of Co_3O_4 .

In the present paper we will try to show that the texture of the layer support hypothesis that diffusion across the layer can be the rate limiting step. On the other hand the changes of compositions of the layer can simply explain the evolutions of activation energy during the reaction.

We will also show that it is possible to derive equation [1] by modification of Ginstling-Brounshtein model

using a phenomenological assumption concerning changes of activation energy.

TEXTURE OF THE LAYER

In reference [1] formation of a layer of product on the surface of thermally decomposed single crystals of Co_3O_4 was observed. However there was given no information concerning the nature of this layer which could support hypothesis that diffusion through the layer could be the rate limiting step.

During decomposition oxygen is formed on the boundary between layer of the product and non decomposed crystal. If diffusion through the layer is the rate limiting step the layer should be compact (without cracks or channels) and well attached to the crystal.

Optical microscope as well as scanning electron microscope observations of the cross section of partially decomposed single crystals have shown that the layer is extremely compact and very well attached to the surface to non decomposed crystal. As an example, figure 1 gives a photograph of a cross section of a single crystal partially decomposed ($\alpha = 0,5$), using optical microscope (X 1000).

Fig. 2 shows that even at higher magnification (x 4000) using scanning electron microscope we can see neither any cracks in the layer, nor any gap at the boundary between layer and single crystal. On Fig. 2 are also shown results of electron microprobe analysis giving the variation of the concentration of cobalt which allow to clearly distinguish the regions corresponding to the layer and single crystal respectively.

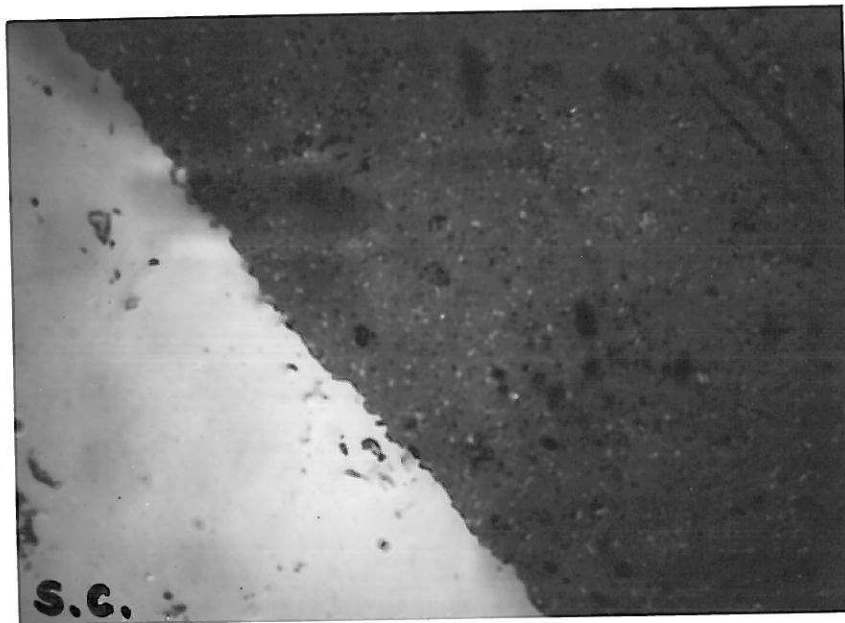


Fig.1 - Cross section of a partially decomposed single crystal of Co_3O_4 (optical microscope, X1000).

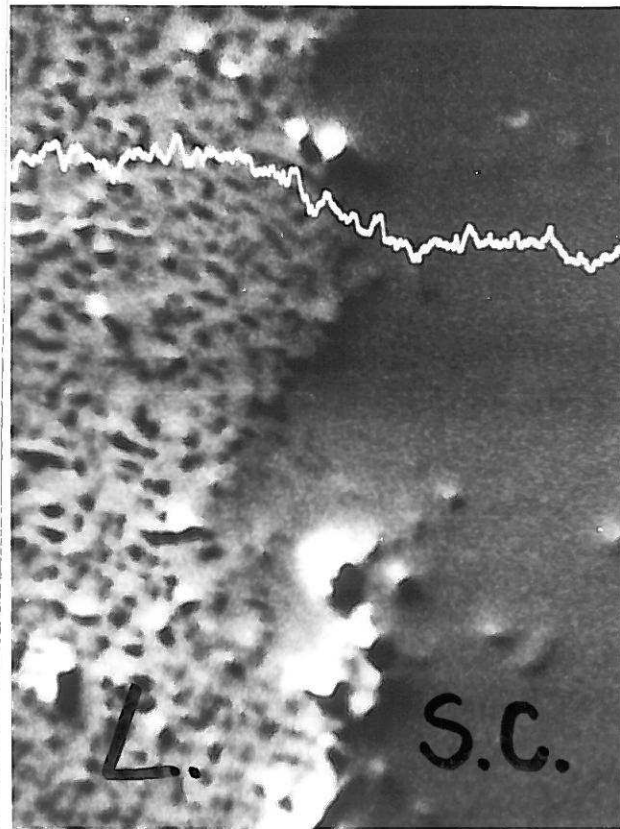


Fig.2 - Cross section of a partially decomposed single crystal of Co_3O_4 (SEM, $\times 4000$).

Finally the above observations are in agreement with the hypothesis that diffusion across the layer can be rate limiting step of the reaction. Therefore it is not surprising that an equation corresponding to a diffusional kinetic model could be used for working out results in ref. [1].

KINETIC MODEL

In ref. [1] we have pointed out that equation (1) could be related to Ginstling-Brounshtein model. On the other hand it has been suggested that difference between equations (1) and (2) could be due to variation of activation energy during the reaction. Using a method analog to that proposed in ref. [2] for a modification of Zhuravlev's model it is possible to show that equation (1) can be derived from Ginstling-Brounshtein model.

Equation (2) in differential form can be written as

$$\frac{d\alpha}{dt} = k \frac{(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}} \quad (3)$$

where the rate constant k depends only on temperature :

$$k = k_0 \exp (-E/RT) \quad (4)$$

where E is the activation energy which corresponds to the diffusional process which is the rate limiting step.

Let us assume as in ref. [2] that the form of variation of activation energy $E(t)$ during the reaction is given by :

$$\frac{dE(t)}{dt} = \frac{k_E}{t} \quad (5)$$

where k_E is a constant.

It can be seen that equation (5) contains assumption that $E(t)$ tends to a constant value as the reaction approaches completion which takes into account the fact that the medium where diffusion occurs no longer evolves.

By integration of (5) :

$$E(t) = k_E \ln t + \text{const.} \quad (6)$$

For determination of integration constant in the above equation we can take that for $t = t_{0.5}$ (i.e. for $\alpha = 0.5$) :
 $E(t_{0.5}) = E_{0.5}$, thus :

$$E(t) = E_{0.5} + k_E \ln \frac{t}{t_{0.5}} \quad (7)$$

We have now to assume that even in the case where $E(t)$ has the form given above equation (4) remains valid.

Substitution of (7) into (4) and the of (4) into (3) gives :

$$\frac{d\alpha}{dt} = k_0 t_{0.5}^{k_E/RT} \exp(-E_{0.5}/RT) \frac{(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}} t^{-k_E/RT} \quad (8)$$

After integration of (8) :

$$1 - 2\alpha/3 - (1-\alpha)^{2/3} = K' T^n \quad (9)$$

where :

$$n = 1 - K_E/RT \quad (10)$$

and

$$K' = \frac{1}{n} \left[\frac{2}{3} k_0 t_{0.5}^{1-n} \exp(-E_{0.5}/RT) \right] \quad (11)$$

From equation (9) for $t = t_{0.5}$ and $\alpha = 0.5$ we can obtain :

$$t_{0.5} = \frac{3n}{2k_c} \left[\frac{2}{3} - \left(\frac{1}{2} \right)^{2/3} \right] \exp(E_{0.5}/RT) \quad (12)$$

Eliminating $t_{0.5}$ from equation (11) using equation (12) leads to final form of equation (9) :

$$1 - 2\alpha/3 - (1-\alpha)^{2/3} = KT^n \quad (13)$$

where :

$$K = 0.03671 \left[18.16 \frac{k_0 \exp(-E_{0.5}/RT)}{n} \right]^n \quad (14)$$

Form of equation (13) is identical to equation (1).

In the above model determination of activation energy leads to determination of the function $E(\alpha)$. Fitting of experimental data (i.e. curves α vs. t) to equation (13) for different temperatures led to values of n and K parameters given in ref. [1]. From n values, using equation (10) we can determine the values of the coefficient of proportionality k_E in equation [5]. Results are given in table 1 for powder and single crystals.

Using equation (14) written in the form :

$$0.05506 n \left[\frac{K}{0.03671} \right]^{1/n} = k_0 \exp(-E_{0.5}/RT)$$

and plotting the logarithm of the left hand side of the above equation vs. $1/T$ gives values of $E_{0.5}$.

From equation (13) we have :

$$t = \left[\frac{1 - 2\alpha/3 - (1-\alpha)^{2/3}}{K} \right]^{1/n} \quad (15)$$

TABLE I

k_E values for powder and single crystals.

POWDER		SINGLE CRYSTALS	
T K	k_E kJ/mol	T K	k_E kJ/mol
1022	-3.27	1158	-10.32
1043	-3.10	1175	-10.04
1060	-2.60	1183	-9.05
1086	-2.07	1211	-9.05
1104	-1.69	1231	-8.42

and

$$t_{0.5} = \left[\frac{0.03671}{K} \right]^{1/n} \quad (16)$$

Knowing $E_{0.5}$ and substituting (15) and (16) into (7) leads to expression of $E(\alpha)$:

$$E(\alpha) = E_{0.5} + \frac{(1-n)RT}{n} \ln \frac{1-2\alpha/3 - (1-\alpha)^{2/3}}{0.03671} \quad (17)$$

Validity of equation (17) is, of course limited to the range of α -values for which time dependency of α can be described by equation (13). This validity domain for thermal decomposition of Co_3O_4 corresponds to $0.1 < \alpha < 0.8$ as shown in ref. [1]. Values of activation energy for this range of α are given in tables 2 and 3 for powder and single crystals respectively.

DISCUSSION

Previously [1] equation (1) has been proposed as kinetic equation on the base of numerical analysis of experimental data.

In the present paper are given two additional evidences which support the above proposition :

- both optical and scanning electron microscope observations showed that a compact and well attached layer of product is formed on the surface of partially decomposed single crystals. In such conditions transport of oxygen through the layer should be hindered and therefore the kinetics of thermal decomposition of Co_3O_4 should be controlled by diffusion

- equation (1) can be derived from Ginstling-Brounshtein diffusional model by introducing an assumption concerning change of activation energy during the reaction.

Such a change of activation energy is indeed expected since layer being formed during the reaction should be generally considered as a dynamic system in which the following phenomena can take place :

- evolution of the texture due to growth of grains, recrystallisation effects and so on,
- evolution of chemical composition. It should be observed especially when product of decomposition either further reacts giving another phase or it is non-stoichiometric compound. In the present case the product of thermal decomposition of Co_3O_4 is CoO which is non stoichiometric. In addition this compound is formed simultaneously with oxygen. Due to equilibrium between defected cobalt monoxide and oxygen some changes in concentration of defects should be observed.

As reaction proceeds volume of the layer of course increase while the area of the boundary between layer and single crystals on which oxygen is generated decrease. Both above phenomena should lead to changes of oxygen activity within the layer and consequently lead to change of concentration of defects.

Physical and chemical modifications of the layer just above mentioned has strong influence on transport phenomena in the layer and could be responsible for the evolution of activation energy for diffusion.

These remarks seem to be confirmed by the observations of a strong influence of external partial pressure of oxygen on the value of activation energy of thermal decomposition of Co_3O_4 [4].

Previously variations of activation energy have been found as a function of $\alpha|1|$. On the base of the model developed in this paper an analytical form of the function $E(\alpha)$ is given (equation (17)). Tables 2 and 3 show that the range of variation of activation energy found using equation (17) is narrower than that found previously.

This difference is not surprising due to following reasons. Equation (1) contains two parameters both of them depending on temperature, thus activation energy ought to be hidden either in one or both of these parameters. As in ref. [1], equation (1) was obtained by numerical analysis of experimental curves α vs. t , the relationship between activation energy and parameters n and K could not be known. Therefore for determination of activation energy it was assumed that in the derivative of equation (1) which can be written as :

$$\frac{d\alpha}{dt} = \frac{K(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}} \left[1-2\alpha/3 - (1-\alpha)^{2/3} \right]$$

where :

$$K = \left(\frac{3}{2}\right)nk^{1/n} \left[1-2/3 - (1-\alpha)^{2/3} \right]^{-1/n}$$

all the part depending on temperature can be considered as rate constant.

Although there are no strong theoretical basis for above assumption it was the unique way for a rough evaluation of activation energy. On the other hand model developed in this paper leads to a relationship between $E(\alpha)$ and n and K parameters. As far as the present model can be considered as describing accurately the kinetics of thermal decomposition of Co_3O_4 , equation (17) should quantitatively describe the variation of activation energy vs α .

It is worthwhile to emphasize that table 2 and 3 show that in fact $E(\infty)$ is temperature independent. Such temperature independency is required for determination of $E_{0.5}$ using equation (14).

It is also a criterion for applications of the model developed in this paper since it contains the assumption, that rate constant obeys Arrhenius's law.

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(to be published).

PUBLICATION N°3

Short Communication

A SIMPLE BUT VERY CLOSE APPROXIMATION TO THE SERIN-ELLICKSON EQUATION

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The Serin-Ellickson equation,

$$\alpha = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp\left(-\frac{n^2 \pi^2 D t}{a^2}\right),$$

where D is the diffusion coefficient and a the radius of a spherical body, can be approximated with high accuracy in a wide range of α values by

$$\alpha = \frac{3x^2}{\pi^2} + \frac{6x}{\pi\sqrt{\pi}},$$

where $x^2 = \frac{D\pi^2 t}{a^2}$.

One of the commonly used expressions in the study of chemical kinetics and diffusion in a spherical body is the Serin-Ellickson equation:

$$\alpha = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) e^{-\frac{n^2 D \pi^2 t}{a^2}} \quad (1)$$

where D is the diffusion coefficient, a the radius of the sphere and t the time. D or D/a^2 can be determined by fitting the experimental $\alpha(t)$ reaction rate curves to Eq. (1). Due to the complex form of this equation, the determination of the D values is time-consuming and involves the use either of standard precalculated tables or graphs or of computerised programmes [1-3].

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In this communication, the authors propose the simplest so far known, but very close approximation of the above equation, overcoming all the routine and laborious calculations normally involved in fitting the experimental data to the Serin-Ellickson equation.

Let us write:

$$x^2 = \frac{D\pi^2 t}{a^2} \quad (2)$$

Equation (1) can be written as:

$$\alpha = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) e^{-n^2 x^2} \quad (3)$$

The first differential of Eq. (3), considering x^2 as the variable, is:

$$\frac{d\alpha}{d(x^2)} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} e^{-n^2 x^2} \quad (4)$$

The series in Eq. (4) can be expressed in another way:

$$\sum_{n=1}^{\infty} e^{-n^2 x^2} = -\frac{1}{2} + \frac{\sqrt{\pi}}{x} \left[\frac{1}{2} + \sum_{n=1}^{\infty} e^{-\frac{n^2 \pi^2}{x^2}} \right] \quad (5)$$

When $x^2 < 1.4$, the sum of the series on the right-hand side of Eq. (5) becomes very small, and for practical purposes it can be neglected with respect to $1/2$.

On the other hand, if $x^2 \cong 1.4$, Eq. (3) gives $\alpha \cong 0.9$. This result implies that for $x^2 < 1.4$ the nearly full range of α usually investigated has been taken into account.

Equation (4) can now be written as:

$$\frac{d\alpha}{d(x^2)} \cong \frac{6}{\pi^2} \left[-\frac{1}{2} + \frac{\sqrt{\pi}}{2x} \right] \quad (6)$$

By integration of Eq. (6) we obtain the following approximation of the Serin-Ellickson equation:

$$\alpha \cong -\frac{3x^2}{\pi^2} + \frac{6x}{\pi\sqrt{\pi}} \quad (7)$$

The difference Δ in the values of α given by the Serin-Ellickson equation (3) and Eq. (7) is less than 10^{-3} for $\alpha \cong 0.9$. It rapidly decreases with decreasing α , as shown in Table 1.

Table 1 Values of Δ for different ranges of α

α	< 0.9	< 0.84	< 0.78	< 0.7
Δ	$< 10^{-3}$	$< 10^{-4}$	$< 10^{-5}$	$< 10^{-7}$

By solving Eq. (7), we obtain:

$$x = \sqrt{\pi} \left[1 - \left(1 - \frac{\pi}{3} \alpha \right)^{\frac{1}{2}} \right] \quad (8)$$

Equation (8) enables the calculation of x from the experimental values of α . From a plot of x^2 against t via Eq. (2) we can obtain $D\pi^2/a^2$ directly, and the value of the diffusion coefficient D if the radius a of the sphere is known.

At this point it may be emphasized that, even if the diffusion coefficient D is a function of t , Eq. (8) allows determination of the experimental curve $D(t)$, which is otherwise very difficult using the original Serin-Ellickson equation directly.

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PUBLICATION N°4

GROWTH AND ELECTRICAL PROPERTIES OF PURE AND
Ni-DOPED Co_3O_4 SINGLE CRYSTALS

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ABSTRACT :

Single crystals of pure and Ni-doped Co_3O_4 spinel-type phases have been grown by C.V.T. Electrical conductivity and thermopower measurements have been performed between 25 and 950 K. Ni-doping gives rise to a significant increase of electrical conductivity at room temperature by three orders of magnitude. The obtained results suggest that the Ni atoms are located in the octahedral sites of the spinel lattice with both oxidation states 2+ and 3+, as illustrated by the formula : $\text{Co}_{1-y}^{2+}\text{Co}_y^{3+}[\text{Co}_{2-x}^{3+}\text{Ni}_{2-x-y}^{2+}\text{Ni}_{x-y}^{3+}]_4\text{O}_4$.

Introduction

Co_3O_4 which has a normal cubic spinel structure $\text{Co}^{2+}[\text{Co}_2^{3+}]_4\text{O}_4$ has been studied by many investigators mostly by magnetic measurements (1-7).

Although it has been found to be a p-type semi-conductor (8, 9), a detailed report of its electrical properties over a wide temperature range is lacking except for a recent determination of the conductivity of polycrystalline samples at low temperature (12-300 K). Two other earlier investigations (10,11) have also been carried out on polycrystalline samples but at room temperature, where the conductivity was studied as a function of stoi-

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chiometry for the purpose of understanding the catalytic properties.

To the author's knowledge, there is no report on the electrical properties of either pure or doped single crystals of Co_3O_4 . In this paper the results of electrical measurements performed on single crystals of pure and Ni-doped Co_3O_4 are given along with a brief discussion on the oxidation state of nickel in the Co_3O_4 matrix.

Experimental

Single crystals of pure and Ni-doped Co_3O_4 have been grown by standard CVT method. Commercial "Pro-analyse" Co_3O_4 and NiO powders were mixed in appropriate concentrations. The transport agents have been either HCl or Cl_2 . The normal pressure of gas filling quartz ampoules (300 x 20 mm) has been 200 torr at room temperature. The optimum temperatures at the source and deposit zone for the growth of pure crystals have been 1250 and 1130 K respectively. For Ni-doped crystals, the temperature of the source has been increased up to 1330 K. Each experimental run lasted for 250-350 hours.

Nearly perfect octahedral crystals have been obtained ranging in size between 3 and 4 mm (Fig. 1). Their spinel-type structure has been confirmed by X-ray diffraction. The lattice constants of pure and doped cubic Co_3O_4 did not show any noticeable difference.

Each crystal of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ used for electrical measurements has been analysed thanks to an electronic microprobe analyser. The distribution of Ni has been found to be uniform in the crystals.

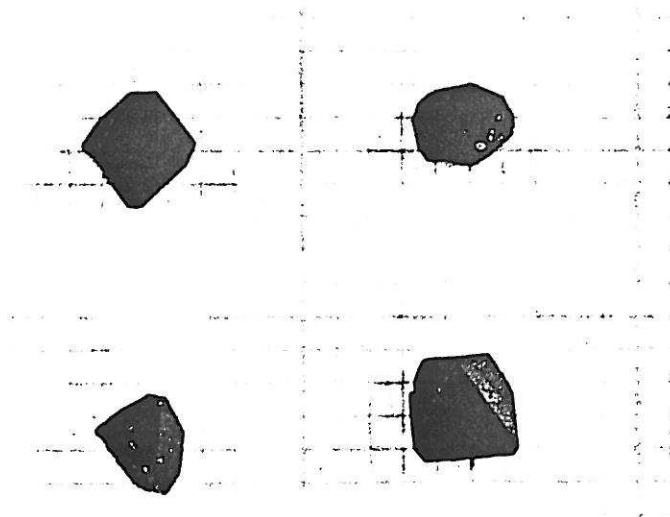


FIG. 1

Crystals of Co_3O_4
(1 division = 1 mm)

Electrical conductivity and thermoelectric power have been measured between 25 and 950 K. For conductivity determinations the four probe method has been used. Ohmic contacts have been achieved using platinum paint. The thermopower cells used at high and low temperature have already been described (12).

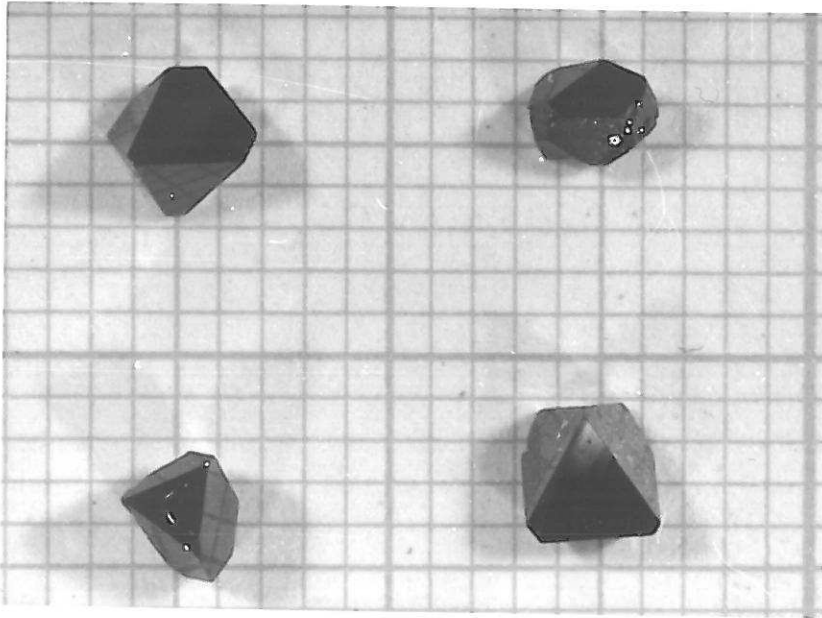


FIG. 1
Crystals of Co_3O_4
(1 division = 1^{mm})

Results and discussion

Electrical conductivity σ and thermopower α have been measured for Co_3O_4 and $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ crystals with $x = 0.053, 0.013$ and 0.132 . Fig. 2 and 3 give the $\log \sigma$ vs. $1/T$ plots for the pure and Ni-doped crystals above 100 K and below room temperature respectively. The variation of α with T is given in Fig. 4. From an examination of the figures some features seem obvious :

a) a large increase of the electrical conductivity between pure Co_3O_4 and the least doped sample, this difference becoming relatively smaller between the following samples with higher dopant concentrations.

b) The sign of thermopower changes from negative to positive at a temperature T_s which decreases with increasing dopant concentration (Table I).

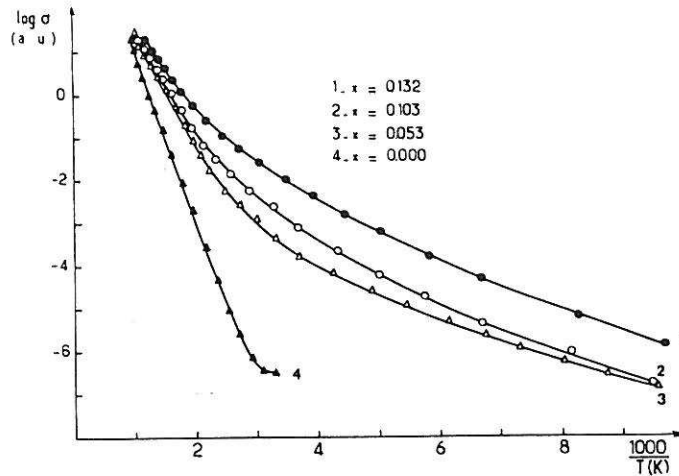


FIG. 2
Electrical conductivity of pure and Ni-doped Co_3O_4 single crystals between 100 and 950 K

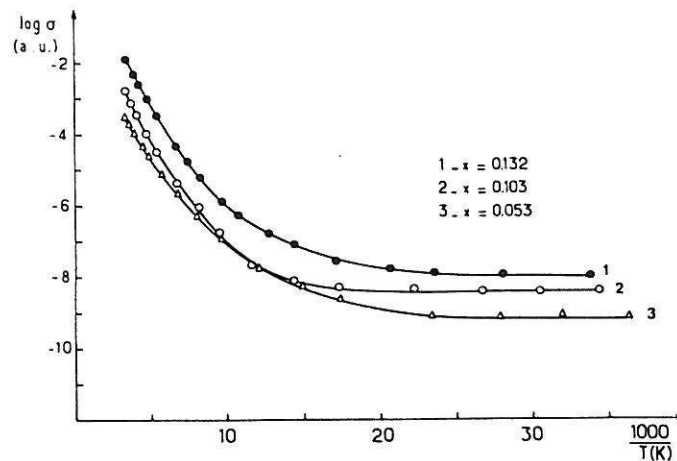


FIG. 3
Electrical conductivity of Ni-doped Co_3O_4 single crystals between 25 and 300 K

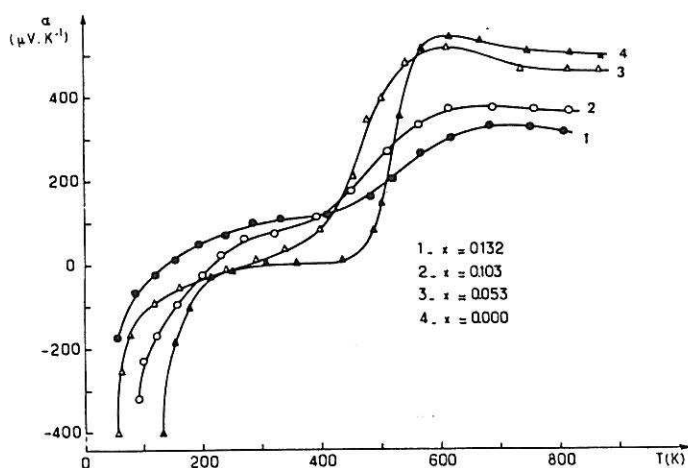


FIG. 4
Thermopower vs. temperature of pure
and doped Co_3O_4 crystals

TABLE I

Temperature of the change of thermopower sign with dopant concentration

x	0.000	0.053	0.103	0.132
T_s (K)	300	260	195	145

In order to interpret the above results it seemed necessary to discuss primarily two aspects of the problem :

- the conduction mechanism in pure Co_3O_4
- the possible oxidation state of nickel and its distribution between tetrahedral and octahedral sites of the spinel lattice.

1 - Pure Co_3O_4

Previous authors (9) have proposed to explain the electrical conductivity of pure polycrystalline Co_3O_4 by the existence of some acceptor levels located above the Co^{2+} 3d band in tetrahedral sites. These acceptor levels are Co^{3+} ions trapped at cationic vacancies in tetrahedral sites.

Since the single crystals of Co_3O_4 grown presently by C.V.T. have been found to show a very high resistivity ($\rho > 10^6 \Omega \cdot \text{cm}$ at room temperature), the chances of considering a high concentration of vacancies are minimised. Furthermore, this model is unable to account for the sign change of α which in our Co_3O_4 single crystals becomes negative below 300 K (Fig. 4).

Moreover, thermal variation of electrical conductivity and thermopower could actually be explained considering only intrinsic generation of carriers (Fig. 5) :

(a) Excitation of an electron from the $3d_{t_2}$ levels of Co^{2+} in tetrahedral sites ($\text{Co}_{\text{Td}}^{2+}$) to the empty e_g band of Co^{3+} in octahedral sites ($\text{Co}_{\text{Oh}}^{3+}$). Let E_1 be the energy difference between these two levels. Electrons in the Oh sites and holes in the Td sites have mobility μ_1 and μ_2 respectively.

(b) Generation of electron-hole pairs in the Oh sites giving rise to electrons in the e_g band and holes in the t_{2g} band of $\text{Co}_{\text{Oh}}^{3+}$. Since t_{2g} levels are more stable in Oh sites than t_2 levels in Td sites E_2 is expected to be much larger than E_1 (Fig. 5). Let μ_3 be the mobility of holes in the $3d_{t_{2g}}$ band of $\text{Co}_{\text{Oh}}^{3+}$.

From structural considerations we could expect that $\mu_3 \gg \mu_1 > \mu_2$. With the assumption that μ_2 is thermally activated and can overcome μ_1 at a temperature close to T_S , it is possible to obtain a variation of α vs. T which has a shape qualitatively similar to that observed*

2 - Ni-doped Co_3O_4

2-1- Nickel oxidation state

Regarding the location of nickel in the NiCo_2O_4 spinel, the previous investigators have eliminated its presence in Td sites on the basis of energy considerations (13) as well as from experimental determinations (14, 15). Using this statement, only two limiting possibilities remain to be considered for the oxidation state of nickel in Oh sites :

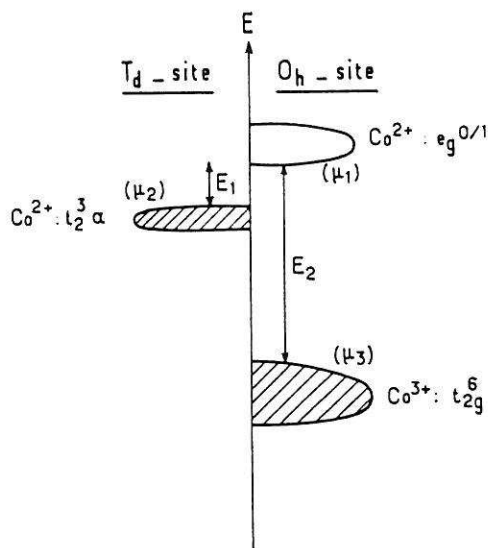
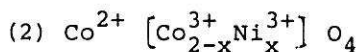
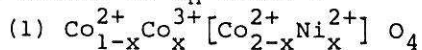


FIG. 5
Schematic energy diagram for
stoichiometric Co_3O_4

* The thermopower is given by $\alpha = \frac{\sum (\sigma_i / \sigma) \alpha_i}{\sigma}$, where σ_i and α_i are the conductivity and thermopower contributions of carriers of i-type.

The behaviour of α at high temperature and the strong differences of activation energies for the electrical conductivity between pure and doped crystals (Table II) suggest that in doped samples intrinsic behaviour is no longer dominant even at high temperature.

TABLE II
Activation energy for the electrical conductivity of pure and Ni-doped single crystals of Co_3O_4

x	0.000	0.053	0.103	0.132
Activation energy between 400 and 950 K (eV)	0.79	0.52	0.49	0.40

Under such conditions only occurrence of Ni^{2+} in octahedral sites can provide extrinsic generation of both kinds of carriers (electrons and holes), required to explain the change of sign of the Seebeck coefficient with temperature (Fig. 4).

Above 700 K, α becomes temperature independent, which suggests that the number of carriers is no longer activated. The decrease of the thermoelectric-power with increasing dopant concentration is in qualitative agreement with Heikes' law $\alpha = \frac{k}{e} \ln \frac{1-C}{C}$, where C is the ratio of the number of holes to the number of available sites. However the high values obtained for α (Fig. 4) suppose a hole concentration about one order of magnitude smaller than the total nickel concentration (Table III). This implies that only one part of nickel contributes to the creation of holes and consequently that nickel is present in both 2+ and 3+ oxidation states. Hence, when nickel is introduced into the Co_3O_4 matrix, the following formula is expected :

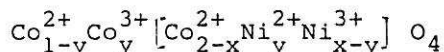
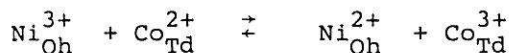


TABLE III
Hole concentration calculated in Ni-doped samples, above 700 K, using Heikes' law

x	0.053	0.103	0.132
$\alpha (\mu\text{V} \cdot \text{K}^{-1})$	470	375	332
C	0.004	0.013	0.02

with approximately 10 % of the total nickel amount in divalent state, generating an equivalent number of Co^{3+} acceptors in tetrahedral sites (Fig. 6). These holes are likely trapped as $\text{Co}_{\text{Td}}^{3+}$ ions located in tetrahedral sites adjacent to octahedra containing Ni^{2+} ions (Fig. 6b).

The existence of Ni^{3+} in Co_3O_4 seems at first sight rather surprising as one expects a priori that the equilibrium:



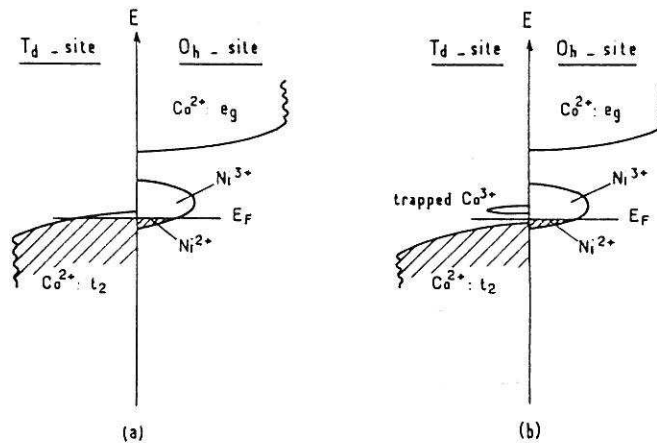


FIG. 6

Energy diagram (at 0 K) of Ni-doped Co_3O_4 near the Fermi level, assuming either (a) that holes are in the $\text{Co}_{\text{Td}}^{2+} : t_2$ band or (b) that they are trapped at acceptor levels ($\text{Co}_{\text{Td}}^{3+}$)

should be shifted towards the right hand side. However, Co_3O_4 being a normal spinel, the stabilization of Ni^{3+} in octahedral sites probably results from the fact that the Td sites can no longer accept Co^{3+} cations beyond a certain limit due to accommodation difficulties.

This interpretation is in agreement with the observations of Blasse et al. (14) and Mehandjiev et al. (15) who in their investigations on the NiCo_2O_4 spinel found all nickel atoms to occupy octahedral sites as Ni^{3+} . However, we think that the existence of a small amount of Ni^{2+} in NiCo_2O_4 cannot be excluded.

2-2- Conduction mechanisms in doped crystals

The large increase of the conductivity (Fig. 2 and 3) and the evolution of activation energy (Table II) show that the introduction of dopant plays an important role in the whole temperature range considered.

As already emphasized, only a minor fraction of nickel is divalent, so that electrons can jump from an occupied site (Ni^{2+}) to an empty one (Ni^{3+}), giving rise to an impurity band type conduction.

Such a mechanism is generally expected to be predominant at low temperature and can account for the negative sign of the thermopower. The activation energy for the conductivity below 50 K is unexpectedly small for an impurity conduction. Such a behaviour has, however, also been observed for impurity band conduction in

Li⁺-doped NiO and discussed by Austin and Mott (17).

As the temperature increases two situations can be considered whether :

- (i) holes in tetrahedral sites occupy energy levels at the top of the $\text{Co}_{\text{Td}}^{2+} : t_2$ band (Fig. 6a)
- (ii) they are trapped as $\text{Co}_{\text{Td}}^{3+}$ ions localized in tetrahedra adjacent to octahedra containing Ni^{2+} ions (Fig. 6b).

In case (i) the negative sign of α at low temperature requires a mobility of holes (μ_2) in the $\text{Co}_{\text{Td}}^{2+} : t_2$ band lower than the mobility (μ_4) of electrons in the O_h Ni-impurity band. The change of sign of the thermopower can be accounted for if we assume that the activation energy of μ_2 is larger than that of μ_4 so that μ_2 can become higher than μ_4 above T_S .

In case (ii) the thermopower is negative at very low temperature since electrons in the impurity band are more numerous than holes in the $\text{Co}_{\text{Td}}^{2+} : t_2$ band. At rising temperature holes are progressively excited into the $\text{Co}_{\text{Td}}^{2+} : t_2$ band and the positive component of the thermopower increases and becomes predominant above T_S .

The temperature at which the thermopower sign changes decreases as Ni-content increases (Table I). This feature may result from the increase of hole concentration in case (i) or from the increase of acceptor concentration going along with a decreasing ionization energy in case (ii).

Finally, at high temperature, as we have already emphasized, the positive thermopower seems to obey Heikes' law. This could logically imply that conduction is then mainly due to hopping of holes in the $\text{Co}_{\text{Td}}^{2+} : t_2$ band.

Acknowledgments

The authors are indebted to S. Angelov for helpful discussions.

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