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On the Defect Structure and Transport Properties of Co_3O_4 Spinel Oxide

Abstract: Defect structure and transport properties of Co_3O_4 cobalt oxide have been studied as a function of temperature and oxygen pressure, using marker and thermogravimetric techniques. It has been found that the oxidation of CoO to form Co_3O_4 follows parabolic kinetic, being thus diffusion controlled. Marker experiments have demonstrated that cation sublattice of Co_3O_4 oxide is predominantly disordered, but the defect structure is rather complex. At very low oxygen pressures, close to the dissociation pressure of the oxide, interstitial cations are the predominant point defects, while at high pressures cation vacancies predominate. This behavior is reflected in complex dependence of the parabolic rate constant of CoO oxidation on oxygen pressure. At low pressures, namely, parabolic rate constant of the reaction increases with oxygen pressure, reaching then virtually constant value in intermediate pressure range and increases again in highest pressure range. Theoretical analysis of kinetic results in terms of point defect thermodynamics confirmed the above conclusion, concerning complex defect structure of $Co_{3\pm y}O_4$ oxide. Finally, self-diffusion coefficient of cations in the discussed oxide has been calculated as a function of temperature and oxygen pressure from kinetic rate measurements, using Wagner's theory of metals oxidation.

Keywords: Co_3O_4, defects, oxidation kinetics, mechanism, diffusion

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1 Introduction

Transition metal oxides are being increasingly utilized in a number of branches of modern technology due to their various physico-chemical properties [1–3]. Among these materials, oxides with spinel structure are particularly important. Cobalt oxide, Co_3O_4, with normal spinel structure is one of the most important representative of this group of materials, because of its various technological applications, exhibiting among others gas sensor behavior [4], solar energy reflecting properties [5], catalytic activities [6–8], as well as being a precursor for anode materials in Li-ion rechargeable batteries [9], a.s.o. Thus, extensive investigations are being carried out in order to optimize the production technology of this material. This optimization needs first of all detailed knowledge of the type and concentration as well as the mobility of ionic and electronic point defects in the crystalline lattice of the Co_3O_4 oxide and its semiconductive properties [10–14].

In order to create the rational possibilities to affect these properties, the thermodynamics and kinetics of predominant point defects must be known, deciding on fundamental physico-chemical properties of semiconducting oxide materials [10–12, 15]. For instance, a detailed knowledge of the defect structure and transport properties of metal deficient nickel oxide, $Ni_{1-y}O$ [11, 13], made it possible to apply successively this material in a number of branches of heterogeneous catalysis. Unfortunately, it is impossible to say the same as far as the Co_3O_4 oxide is concerned, because its preparation technology remains far from optimal state. This situation results on one hand from considerable experimental difficulties resulting from extremely low rate of the formation of this oxide during oxidation of the CoO and on the other hand, from complicated defect structure. The complex defect situation in this material results from crystallographic structure, in which bivalent cations occupy the tetrahedral sites and trivalent cations octahedral positions [1, 16]. The existance of cations in two different oxidation states results, in fact, in the presence of two cation sublattices, which create considerable difficulties in describing the thermodynamics and kinetics of such defect structure [14]. On the

other hand, detailed knowledge of this structure and in particular, ionic and electronic defect concentrations and their mobilities are absolutely necessary for designing optimal production of micro- and nano-technology of the discussed oxide [10–12].

Due to experimental difficulties mentioned above, this problem remains unsolved so far, in spite of enormous number of data reported in the literature [17–22]. The results of electrical conductivity measurements for instance, have not even explained so far, if the discussed oxide is a p- or n-type semiconductor, or else shows intrinsic electronic behavior [14]. Marker experiments, in turn, are also controversial. Przybylski and Smeltzer [21] for instance, have found gold marker located in the interior of Co_3O_4 product of CoO oxidation, suggesting that the cation subllatice of Co_3O_4 is predominantly disordered ($Co_{3\pm y}O_4$). However, these experiments have not explained if the predominant disorder results from cation vacancies and electron holes, or else from interstitial cations and quasi-free electrons. In addition, these results have been obtained in air atmosphere using not very pure starting material (99.92 %Co) and at one temperature only (1173 K), which does not exclude the possibility of inversion of predominant defect type with temperature and oxygen pressure changes. Alcock and Hocking [23] on the other hand, using spectrally pure material, found gold marker on the surface of Co_3O_4 layer, indicating clearly that in contrast to Przybylski and Smeltzer [21] results, the anion sublattice is predominantly disordered. Such position of marker indicates, namely, that Co_3O_4 layer grows by the inward diffusion of oxygen. It should also be added, that the scratch formed on the flat, ideally polished mirror-like surface of CoO, was reflected after oxidation on the surface of Co_3O_4 layer, confirming the conclusion, followed from marker results. Exactly the same situation has been observed by Rapp and Lee during molybdenum sulphidation [24]. It has been found, namely, that the scratch made on the surface of molybdenum sample remained visible after sulphidation on the surface of MoS_2 scale. This phenomenon – like in the case of CoO oxidation – was in agreement with marker results, which showed that gold markers, placed before sulphidation on the surface of Mo specimen, remained on the surface of MoS_2 scale.

It follows from these remarks that as far as the type of predominant defects in Co_3O_4 is concerned, the situation is highly controversial.

Even worse situation is observed in the case of transport properties of this oxide. So far, namely, self-diffusion coefficient of oxygen in $Co_{3\pm y}O_4$ oxide has only been studied using heavy oxygen isotope ^{18}O [25]. Extremely high activation energy has been found, equal 736 kJ/mol, which suggests interstitial or interstitialcy diffusion mechanism, however, the lack of information concerning the influence of oxygen pressure excludes the possibility of any conclusions to be formulated concerning the type of minority defects. The fundamental problem, however, consists in the explanation of the type of **predominant** ionic and electronic defects and subsequently their concentration and mobility, because these defects determine the main physico-chemical properties of semiconducting oxide materials. The explanation of these problems needs extensive experimental studies and theoretical considerations.

The present paper is an attempt to explain definitely, if cation or anion sublattice in Co_3O_4 oxide is predominantly disordered and subsequently to get preliminary information on transport properties of this oxide in studying the kinetics of CoO oxidation as a function of temperature and oxygen activity.

2 Materials and experimental procedure

Marker experiments as well as oxidation rate measurements of CoO to Co_3O_4 have been carried out as a function of temperature (973–1173 K) and oxygen pressure (10–10^5 Pa) using microthermogravimetric apparatus of new generation described elsewhere [26].

In order to eliminate – as much as possible – the impurities in starting material, high purity cobalt (99.9999 at.%) in the form of rectangular plates (1.5 × 2.5 cm^2) with the thickness of 0.02 cm and mirror-like surfaces have been completely oxidized at 1273 K in Ar-He-O_2 gas mixture with the partial pressure of oxygen lower than the dissociation pressure of Co_3O_4 at this temperature, i.e. at $p_{O_2} = 10^3$ Pa (Fig. 1). $Co_{1-y}O$ samples obtained in this way were dense and coarse-grained (Fig. 2) and showed virtually theoretical density, as well as the total concentration of impurities in this material was lower than 10^{-5}%. These samples were subsequently thermally homogenized 24 hours at 1273 K and $p_{O_2} = 10^5$ Pa.

To solve the problem, which sublattice in Co_3O_4 oxide is predominantly disordered indeed, marker experiments have been carried out. Thin gold film of about 1 μm thickness was vacuum evaporated on the surface of CoO sample through copper mesh, what resulted in the formation of small islands of gold spread over the specimen surface. A number of CoO samples marked in this way was then oxidized at several temperatures (973 K, 1073 K, 1173 K) and oxygen pressures (10^2, 10^3 and 10^5 Pa). After terminating

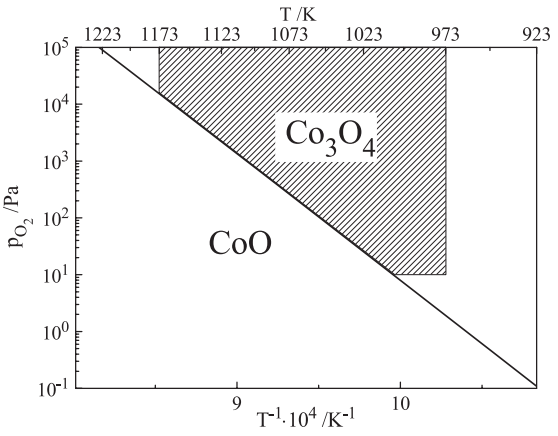

Fig. 1: The part of phase diagram of Co-O system, illustrating the temperature and pressure ranges, in which the CoO oxidation rate measurements have been carried out (dashed area).

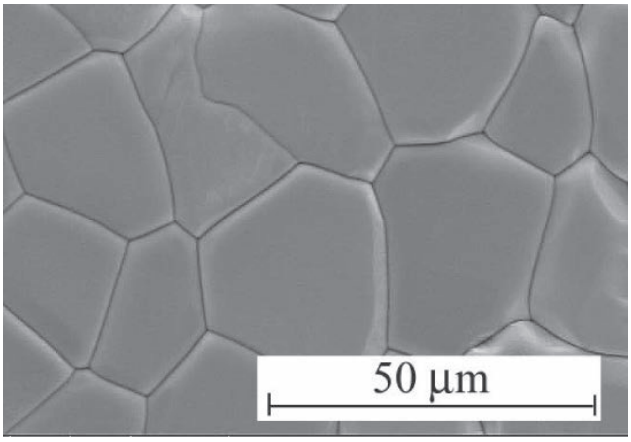

Fig. 2: The microphotograph of the surface of the CoO starting material, obtained at 1273 K under oxygen pressure equal 10^3 Pa.

the oxidation process, cross-sections of these samples were made in order to determine the position of markers in the reaction product (Co_3O_4) using scanning electron microscope.

Oxidation rate measurements have been carried out using continuous gravimetric method by following the weight gains of the oxidized CoO samples as a function of time at constant temperature and oxygen pressure with the accuracy of the order of 10^{-6} g. The partial pressure of oxygen in ternary Ar-He-O_2 gas mixture, flowing with the constant rate (30 ml/min) through the reaction chamber, was obtained by suitable composition of this atmosphere of the total pressure of 10^5 Pa.

The application of two carrier gases (helium and argon) needs an explanation. If, namely, only one carrier gas is used (as usual in the past) to obtain oxidizing gas mixture, the Archimedes effect is to be expected when the oxygen partial pressure in such a mixture is changed [27]. If, namely, oxygen pressure in Ar-O_2 gas mixture is decreased, the weight of the sample seemingly decreases, because of higher density of argon as compared to oxygen. As a consequence, the registered weight gains of the oxidized sample are lower than those resulting from the oxidation process. On the other hand, in He-O_2 atmosphere opposite effect is observed [27]. In order to eliminate this systematic error in oxidation rate measurements, two carrier gases have been used with Ar/He ratio chosen in such a way that the density of this carrier gas mixture was exactly the same as that of oxygen. It should be stressed that this problem is particularly important in those cases when the oxidation process proceeds very slowly and consequently weight gains of the oxidized sample are very low, like during CoO oxidation.

3 Results and discussion

Marker experiments have demonstrated that at every temperature and oxygen pressure, gold marker islands were always found in the interior of the Co_3O_4 layer, formed on the surface of CoO. This is illustrated in Fig. 3, showing the position of gold markers in Co_3O_4 layer, formed at 1173 K and $p_{O_2} = 10^5$ Pa. The same marker positions have been observed in experiments carried out at different temperatures and oxygen pressures. From Fig. 3 it follows clearly that markers are located in the interior of Co_3O_4 layer,

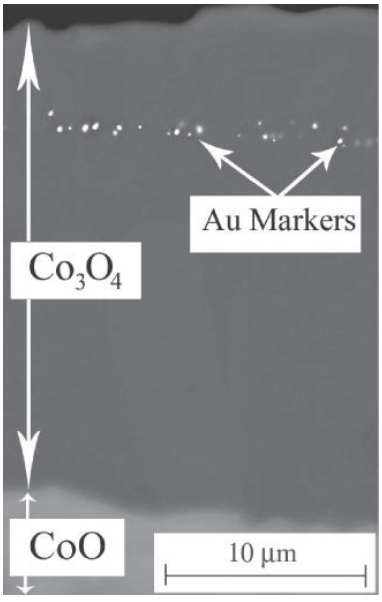

Fig. 3: Cross-section of CoO sample marked with Au islands after oxidation at 1173 K and oxygen pressure equal to 10^5 Pa.

dividing it into two parts, the outer one being three times thinner than the inner layer. Such location of the markers in the interior of reaction product of CoO oxidation indicates explicitly that the outer layer of Co_3O_4 formed **above** the markers was growing on the outer Co_3O_4-O_2 interface owing to the outward diffusion of cations and electrons in agreement with the following reaction:

$$3Co^{+n} + 3ne^- + 2O_2 \rightarrow Co_3O_4 \quad (1)$$

On the other hand, the inner layer formed **beneath** the markers has been developed at the inner CoO-Co_3O_4 interface due to the following displacement reaction:

$$12CoO \rightarrow 3Co_3O_4 + 3Co^{+n} + 3ne^- \quad (2)$$

In these reactions n = 8/3, being the effective charge of the simultaneously diffusing Co^{+2} and Co^{+3} cations through the spinel phase of Co_3O_4, growing on CoO during its oxidation. The growth mechanism of Co_3O_4 layer on the surface of CoO substrate is schematically presented in Fig. 4. It may be then concluded that cation sublattice of the Co_3O_4 oxide is predominantly disordered, because if anion defects would prevail, the marker should be found at the outer surface of Co_3O_4 layer, as shown schematically in Fig. 5.

The results of marker experiments described above are in agreement with those reported by Przybylski and Smeltzer [21], being however, in contrast with the results obtained by Alcock and Hocking [23] during oxidation of CoO in air at 1073 K. These authors have found, namely, gold markers located on the surface of Co_3O_4 layer, as depicted schematically in Fig. 5, suggesting consequently that the anion sublattice of Co_3O_4 oxide is predominantly disordered. They stated in addition that scratches originally present on the CoO specimen surface were reflected

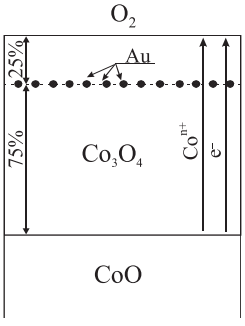

Fig. 4: Schematic representation of the growth mechanism of the Co_3O_4 oxide layer in the case when cation sublattice of this oxide is predominantly disordered.

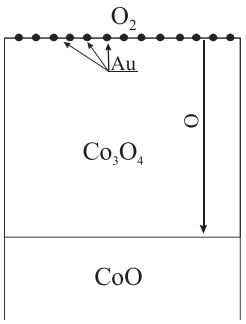

Fig. 5: Schematic representation of the growth mechanism of the Co_3O_4 oxide layer in the case when anion sublattice of this oxide is predominantly disordered.

on the surface of Co_3O_4 oxidation product, like in the case of molybdenum sulphidation [24]. Thus, our marker results and those reported by Przybylski and Smeltzer [21] remain in dramatic contrast with those obtained by Alcock and Hocking [23]. It is difficult at present to explain explicitly the source of this disagreement. However, it is possible to suppose that the presence of markers at the surface of reaction product, found by Alcock and Hocking, may originate from inadequate adherence of markers to the substrate surface before reaction, as well as from other reasons, as suggested by Gil and Bruckman [28]. On the other hand, the location of the markers in the interior of reaction product shows unmistakably and explicitly that the outer layer of this product formed **above** the markers was growing due to the outward diffusion of cations. Thus, the final conclusion is, that undoubtedly cation sublattice of Co_3O_4 oxide is predominantly disordered. Consequently, the chemical formula of the discussed oxide should be written in the following way: $Co_{3\pm y}O_4$.

However, marker experiments had not explained if cation vacancies and electron holes, or else interstitial cations and quasi-free electrons predominate. This problem can be solved in studying the dependence of the oxidation rate of CoO on oxygen pressure under the assumption that the oxidation process follows parabolic rate law, being thus diffusion controlled. In fact, such a course of CoO oxidation was observed by Przybylski and Smeltzer [21], however, at one temperature (1073 K) only and under one oxygen pressure ($1.2 \cdot 10^3$ Pa). Thus, in order to obtain the reasonable explanation of this fundamental problem, oxidation rate measurements of CoO to form Co_3O_4 have been carried out as a function of oxygen pressure (10–10^5 Pa) at different temperatures (973–1173 K).

Careful oxidation rate measurements have demonstrated that the oxidation of $Co_{1-y}O$ to $Co_{3\pm y}O_4$ follows strictly parabolic rate law at all the temperatures and pres-

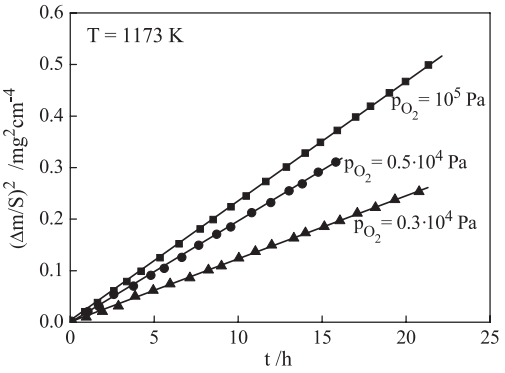

Fig. 6: The results of oxidation rate measurements of CoO, presented in parabolic system of coordinates for several oxygen pressures, obtained at 1173 K.

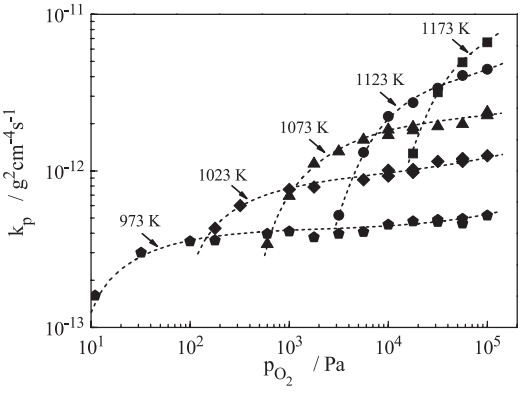

Fig. 7: The pressure dependence of parabolic rate constant of CoO oxidation presented in double logarithmic plot for several temperatures.

sures studied, being thus diffusion controlled. Fig. 6 shows for illustration several oxidation runs, presented in parabolic system of coordinates for different oxygen pressures, obtained at 1173 K. It follows from these data that the parabolic rate constant, expressed in $g^2cm^{-4}s^{-1}$, changes with oxygen pressure. This dependence is illustrated in Fig. 7 in double logarithmic plot for several temperatures. As can be seen, the pressure dependence of the parabolic rate constant of CoO oxidation is rather complex. At lowest oxygen pressures, close to the dissociation pressure of Co_3O_4 oxide, the parabolic rate constant starts to grow with increasing pressure, reaching virtually a constant value and subsequently it is growing again with oxygen pressure in highest pressure range. These differences are rather small but in order to stress this complex behavior of pressure dependence of k_p is schematically shown in Fig. 8.

This complex behavior can be interpreted in terms of Wagner's theory of metals oxidation [29, 30]. From this

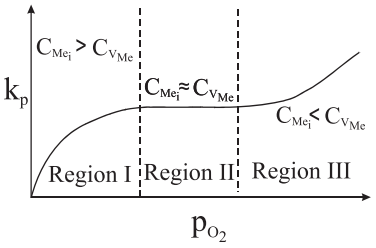

Fig. 8: Schematic illustration of the pressure dependence of the parabolic rate constant of the CoO oxidation.

theory it follows, namely, that if the mobility of predominant ionic defects in the oxidation product does not virtually depend on their concentration, the parabolic rate constant of the reaction, k_p, is directly proportional to the difference of the concentration of these defects, C_d, between the outer and inner surface of the growing oxide layer:

$$k_p = const(C''_d - C'_d)\exp\left(-\frac{E}{RT}\right) \tag{3}$$

where E is activation energy; C'_d and C''_d denote defect concentrations, expressed in mole fractions, at the inner and outer surface of the reaction product, respectively.

From point defect thermodynamics it follows that if interstitial cations in a simple divalent metal oxide (MeO) constitute predominant defects and thereby the oxide is a metal excess n-type semiconductor ($Me_{1+y}O$), defect concentration decreases with increasing oxygen pressure:

$$[Me_i^{n\bullet}] = const\ p_{O_2}^{-1/(2n+1)} \tag{4}$$

On the other hand, if cation vacancies predominate and consequently oxide is a metal-deficit p-type semiconductor ($Me_{1-y}O$), defect concentration increases with increasing oxygen pressure:

$$[V_{Me}^{n'}] = const\ p_{O_2}^{1/(2n+1)} \tag{5}$$

where n denotes the degree of defects ionization (Kröger-Vink notation is used throughout of this paper [31]). Thus, considering equation 3, the pressure dependence of the parabolic rate constant of $Me_{1\pm y}O$ oxide formation can be described by the following two relationships, respectively:

$$k_p = const((p''_{O_2})^{-1/(2n+1)} - (p'_{O_2})^{-1/(2n+1)}) \tag{6}$$

$$k_p = const((p''_{O_2})^{1/(2n+1)} - (p'_{O_2})^{1/(2n+1)}) \tag{7}$$

Passing now to the cobalt oxide under investigation, again two limiting cases should be considered. If one

assumes, namely, that in this oxide interstitial cations and quasi-free electrons are the predominant defects, i.e. discussed oxide is metal excess n-type semiconductor ($Co_{3+y}O_4$), the formation of this disorder can be described by the following defect equilibrium:

$$Co_3O_4 \Leftrightarrow 3Co_i^{8/3\bullet} + 8e' + 2O_2 \tag{8}$$

If, on the other hand cation vacancies and electron holes would predominate, i.e. discussed oxide is a metal deficit p-type semiconductor ($Co_{3-y}O_4$), this defect situation is described the following quasi-chemical reversible reaction:

$$2O_2 \Leftrightarrow 3V_{Co}^{8/3'} + 8h^\bullet + 4O_O^x \tag{9}$$

However, Koch and Wagner have shown [32] that Co_3O_4 oxide is intrinsic semiconductor, what implies that the concentration of electronic defects is orders of magnitude higher from that resulting from nonstoichiometry (eq. 8 and 9) and consequently is pressure independent. Considering this fact ($[e'] \cong [h^\bullet] \cong const$) and applying mass action law and appropriate electroneutrality conditions to defect equilibria described by equations 8 and 9, one obtains the following pressure dependence of the concentration of interstitial cations and cation vacancies in $Co_{3+y}O_4$ and $Co_{3-y}O_4$ oxides, respectively:

$$[Co_i^{8/3\bullet}] \Leftrightarrow const\ p_{O_2}^{-2/3} \tag{10}$$

$$[V_{Co}^{8/3'}] \Leftrightarrow const\ p_{O_2}^{2/3} \tag{11}$$

Introducing these relationships into equation 3 one obtains finally theoretical equations, describing the pressure and temperature dependence of the parabolic rate constant of CoO oxidation under assumption that interstitial cations (eq. 12) or cation vacancies (eq. 13) predominate:

$$k_p = A((p'_{O_2})^{-2/3} - (p''_{O_2})^{-2/3}) \exp\left(-\frac{E_i}{RT}\right) \tag{12}$$

$$k_p = B((p''_{O_2})^{2/3} - (p'_{O_2})^{2/3}) \exp\left(-\frac{E_V}{RT}\right) \tag{13}$$

where A and B are constants and E_i and E_V denote activation energies of cation diffusion in $Co_{3+y}O_4$ (E_i) and in $Co_{3-y}O_4$ (E_V). Thus, considering kinetic results presented in Fig. 7, it may be concluded that eq. 12 describes the situation observed at lowest oxygen pressures (Region I in Fig. 8), when interstitial cations predominate, while eq. 13 – describes the behavior at highest pressures (Region III), where cation vacancies are the predominant point defects. Summing up these two last relationships, one obtains finally theoretical pressure and temperature dependence of the parabolic rate constant of CoO oxidation, under the assumption of the discussed complex defect structure of $Co_{3\pm y}O_4$ oxide:

$$k_p = A((p'_{O_2})^{-2/3} - (p''_{O_2})^{-2/3}) \exp\left(-\frac{E_i}{RT}\right) + B((p''_{O_2})^{2/3} - (p'_{O_2})^{2/3}) \exp\left(-\frac{E_V}{RT}\right) \tag{14}$$

In order to proof the above theoretical considerations, concerning the defect structure of Co_3O_4 oxide, experimental results presented in Fig. 7 have been utilized for numerical determination of activation energies of oxidation reaction as well as the pre-exponential factors A and B in eq. 14. The results of these calculations led to the following relationship (p_{O_2} is normalized to 10^5 Pa):

$$k_p = 1.2 \cdot 10^5((p'_{O_2})^{-2/3} - (p''_{O_2})^{-2/3}) \exp\left(-\frac{377\ kJ/mol}{RT}\right) + 10^{-7}((p''_{O_2})^{2/3} - (p'_{O_2})^{2/3}) \exp\left(-\frac{110\ kJ/mol}{RT}\right) \tag{15}$$

Using this expression the calculated pressure dependence of the parabolic rate constant of CoO oxidation has been shown for several temperatures in Fig. 9 on the background of experimental results presented previously in Fig. 7. Very good agreement between experimental results and theoretical calculations confirms the assumption that the defect structure of the studied oxide is really complex and changes with oxygen pressure from interstitial cations

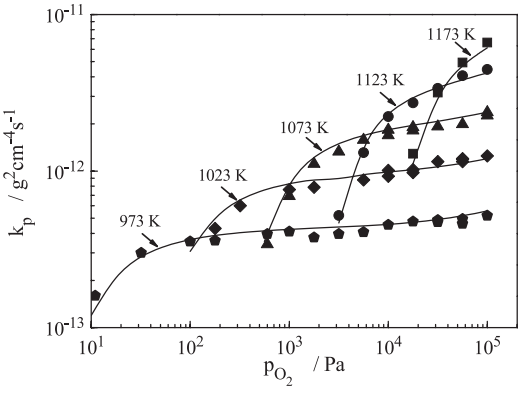

Fig. 9: The pressure dependence of the parabolic rate constant of CoO oxidation determined experimentally (points) and calculated from eq. 14 (solid lines).

to cation vacancies predominant. In particular, at very low oxygen pressures, close to dissociation pressure of Co_3O_4 oxide interstitial cations predominate, while at pressures several order of magnitude higher than the dissociation pressure of the Co_3O_4 oxide, cation vacancies are the predominant point defects. This inversion of predominant defect disorder with oxygen pressure is reflected in complex pressure dependence of the parabolic rate constant of CoO oxidation, illustrated in Figs. 7 and 8.

In region I, when interstitial cations predominate, their concentration at the inner CoO/Co_3O_4 interface, where they are created, reaches the highest value determined by the local thermodynamic equilibrium at this interface, being thus independent on oxygen pressure in the surrounding atmosphere. Thus, at lowest oxygen pressures (region I), close to dissociation pressure of Co_3O_4 oxide, the growth rate of this oxide will increase with oxygen pressure, because the difference of defect concentration in the growing oxide layer will increase, as schematically shown in Fig. 10. However, further increase of oxygen pressure will have lower and lower influence on the difference of defect concentration in the growing oxide layer, because of approaching of defect concentration at the Co_3O_4-O_2 phase boundary to the zero value (see Fig. 10). Consequently, the oxidation rate will approach a constant value, as shown schematically in Fig. 8 (region II). At highest pressures finally (region III), the oxidation rate starts to increase again with oxygen pressure (Figs. 7 and 8), because the second type of ionic defects becomes important. These defects – cation vacancies – are created, namely, at the outer Co_3O_4-O_2 interface and consequently their concentration increases with oxygen pressure (eq. 11). The lowest concentration of this type of defects, is located at the inner CoO-Co_3O_4 phase boundary, where they are annihilated, being thus independent on the ambient oxygen pressure. Thus, the difference of the concentration of these defects in the growing oxide layer will increase with increasing oxygen pressure, which will be reflected in increasing oxidation rate, as shown schematically in Fig. 8, in agreement with experimental results presented in Fig. 7.

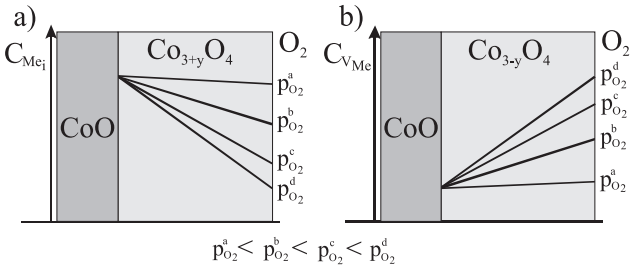

Fig. 10: Schematic representation of defect concentration gradients in the growing $Co_{3+y}O_4$ (Fig. 10a) and in $Co_{3-y}O_4$ (Fig. 10b) oxide layers, forming on CoO during its oxidation.

As the slowest step of the oxidation rate of CoO is the outward diffusion of cations in $Co_{3\pm y}O_4$ oxide, the self-diffusion coefficient of these species in this oxide can be estimated from the parabolic rate constant of the CoO oxidation using Wagner's theory of metal oxidation [29, 30]. To apply this theory, one should assume that the mobility of point defects determining the oxidation rate does not depend on their concentration and the diffusing cations are completely ionized. Very low oxidation rate of CoO strongly suggests that the concentration of predominant defects (interstitial cations and/or cation vacancies in $Co_{3\pm y}O_4$) is very low. It may be then concluded that the mobilities of both types of ionic defects are concentration independent and the diffusing species are completely ionized. In this situation from Wagner's theory it follows that the parabolic rate constant of Co_3O_4 formation can be related to the self-diffusion coefficient of cations, D_{Co}, in this oxide by the following simple equation:

$$k'_p = (1 + |n|) D_{Co} \tag{16}$$

where n is degree of defect ionization.

In this relationship the parabolic rate constant k'_p is expressed in cm^2s^{-1} in agreement with Tamman's parabolic rate law [33, 34]:

$$x^2 = 2k'_p t \tag{17}$$

where x is a thickness of the oxidation product at time t. Thus, the parabolic rate constant, k_p, calculated from gravimetric rate measurements and expressed in $g^2cm^{-4}s^{-1}$ must be recalculated into k'_p using the following relationship:

$$k_p = 2\left(\frac{M_O}{\bar{V} \cdot Z_O}\right)^2 k'_p \tag{18}$$

where $\bar{V}$ denotes the equivalent volume of Co_3O_4; M_O – the atomic weight of oxygen, and Z_O – the valency of anions. Further, n value must be taken as equal 8/3 being the average value of two types of Co^{+2} and Co^{+3} cation charges and in addition, it should be noted that k_p value reflects only the formation of one fourth of Co_3O_4 oxide layer. Consequently, the appropriate equation describing the relation between parabolic rate constant of CoO oxidation and the self-diffusion coefficient of cations in Co_3O_4 oxide assumes the following form:

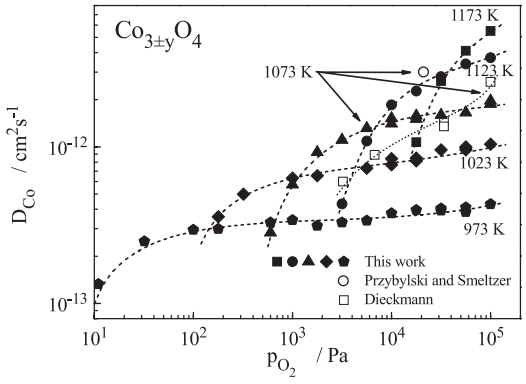

Fig. 11: Pressure dependence of self-diffusion coefficient of cobalt in $Co_{3\pm y}O_4$ oxide calculated from oxidation rate measurements of CoO, presented in double logarithmic plot for several temperatures. The results of these calculations are compared with D_{Co} value calculated by Przybylski and Smeltzer [21] as well as with data calculated for several oxygen pressures from oxidation rate measurements carried out by Dieckmann [35].

$$k_p = \frac{1}{8}\left(\frac{M_O}{\overline{V}\cdot Z_O}\right)^2 (1+|n|)D_{Co} \qquad (19)$$

The results of these calculations are shown in Fig. 11 illustrating the dependence of D_{Co} on oxygen pressure in double logarithmic plot. It follows from this diagram that the self-diffusion coefficient of cations in Co_3O_4 oxide is very low indeed and in addition, this coefficient is not a simple power function of oxygen pressure, as in the case of semiconducting oxides ($Ni_{1-y}O$, $Co_{1-y}O$) with simple defect structure. From this diagram it follows also, that the self-diffusion coefficient of cobalt in Co_3O_4 calculated from the results described in the present paper is in excellent agreement with the value reported by Smeltzer and Przybylski [21] for 1073 K, as well as with data calculated from oxidation rate measurements reported by Dieckmann [35] for the same temperature.

4 Conclusions

Experimental results and theoretical considerations described in the present paper allow the following conclusions to be formulated.

Using marker method and the precise oxidation rate measurements, controversial problem in the literature, concerning the type of predominant disorder in Co_3O_4 oxide, has definitely been solved. It has been demonstrated that independently on temperature and oxygen pressure, cation sublattice of this oxide, having normal spinel structure, is predominantly disordered. However, defect structure is rather complex, as at very low oxygen pressures interstitial Co^{+2} and Co^{+3} cations are the predominant point defects, while at higher oxygen pressures, cation vacancies predominate ($Co_{3\pm y}O_4$). Consequently, parabolic rate constant of CoO oxidation to form $Co_{3\pm y}O_4$ oxide is not a simple power function of oxygen pressure, like in the case of bivalent metal oxides, $Me_{1\pm y}O$, showing simple defect structure. Complex pressure dependence of the parabolic rate constant of CoO oxidation has been explained in terms of point defect thermodynamics. Self-diffusion of cations in $Co_{3\pm y}O_4$ oxide has been calculated as a function of temperature and oxygen pressure, using Wagner's theory of metal oxidation. It has been shown that the activation energy of diffusion of interstitial cations of the discussed oxide is considerably higher than that proceeding via cation vacancies, which is in agreement with the theory of solid state diffusion.

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