

Point defect diagrams for pure and doped cobalt oxide $\text{Co}_{1-\delta}\text{O}$ in the temperature range of 1,173–1,673 K (*D*)

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Abstract The point defect diagram in non-stoichiometric cobalt oxide $\text{Co}_{1-\delta}\text{O}$, pure and doped with M^{3+} and M^+ metal ions, taking into consideration all of the types of defects in the cation sublattice are presented in this work. A new method was used for the calculations of the diagrams. This method is based on the derived relations between the standard Gibbs energies of formation of cobalt vacancies and the intrinsic ionic and electronic defects; it also uses the experimental values of the deviation from the stoichiometry. The calculations were performed using the results of studies obtained by many authors in the temperature range of 1,173–1,673 K.

Keywords Point defect diagrams · Non-stoichiometric cobalt oxide · $\text{Co}_{1-\delta}\text{O}$ · M^+ and M^{3+} ion dopes

Introduction

The studies on the structure of defects in the cobalt oxide $\text{Co}_{1-\delta}\text{O}$ were the subject of a relatively high number of works [1–4]. In order to determine this structure, the studies on the deviation from the stoichiometry were performed, using the electrochemical method [5, 6] and the thermogravimetric method [7–17], as well as the studies on electrical conductivity [3, 4, 7–11, 18–34] and on the Seebeck effect [4, 9, 11, 16, 22, 30, 33, 34]. Similar characters of the relation of the deviation from the stoichiometry and the electrical conductivity on the oxygen

pressure (the value of exponent near 1/4) were the basis for adopting the thesis that in the whole range of the oxide's existence the dominating defects are single-ionized cobalt vacancies and electron holes. Based on the method of Brouwer [35], and using the results of studies on the deviation from the stoichiometry, a simplified point defect diagram has been determined but without allowing for the concentration of interstitial cobalt ions [3, 4, 16, 33]. The calculations of defect concentrations have been performed for a model of defects in which double-ionized vacancies dominate, taking into account the activity coefficient of defects [3, 4, 16]. A good consistency with the experimental results has been also obtained when it was assumed that the dominating defects are defect complexes of type $[(V_{\text{Co}}'')_4\text{Co}_i^{\bullet\bullet}]$ [3, 4, 16], as proposed by Catlow and other authors [36–39]. During the interpretation of the results of the studies on electrical conductivity, other types of defect complexes have also been considered [29, 40–42]. At low p_{O_2} pressures, it is postulated that beside the cobalt vacancies there are also interstitial cobalt ions present [3, 14, 32, 43–46]. Due to the narrow range of the studies on the deviation from the stoichiometry and their accuracy, despite the relatively good consistency of the proposed models with the experimental results, the problem concerning the structure of the defects remains open. From the studies on the chemical diffusion [6, 12, 13, 17, 23, 27, 28, 32, 47–55] and cobalt self-diffusion [3, 16, 56–59], mostly performed at higher oxygen pressures, it transpires that the matter transport occurs mainly via single-ionized cobalt vacancies. A similar conclusion can be derived from the relation between the defect concentration, the diffusion coefficients, and the parabolic rate constants of cobalt oxidation [60–64]. However, it has been concluded that the total concentration of cobalt vacancies is higher than that resulting from the studies on the deviation from the

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stoichiometry [14, 64]. Furthermore, there are discrepancies in the results of the studies of the chemical diffusion coefficients and their dependence on oxygen pressure.

A relatively simple defect structure in the $\text{Co}_{1-\delta}\text{O}$, which was considered a model structure, was used to determine the influence of dopes on the defect concentration, the electrical properties, and the matter transport in this oxide. Studies on the influence of ions M^{3+} (Cr_2O_3 , Ti_2O_3 , In_2O_3) [17, 21, 31, 33, 34] and M^+ (Li_2O) [9, 11, 29, 30, 65] have been performed. Fisher and Wagner Jr. [9] have found that the lithium doped CoO , at the oxygen pressure of about 10^{-3} atm, reaches the stoichiometric composition. This fact has not yet been fully explained. The obtained relations of the electrical conductivity on oxygen pressure for doped oxides are consistent with the theoretical expectations.

The present work treats the problem of the determination of the point defect diagram in non-stoichiometric cobalt oxide $\text{Co}_{1-\delta}\text{O}$, pure and doped with M^{3+} and M^+ metal ions, taking into consideration all of the types of defects in the cation sublattice, also interstitial cobalt ions, which have been postulated in several works. The bases for the diagrams' calculations were: a method prepared by the author of this work and the experimental values of the deviation from the stoichiometry in the temperature range of 1,173–1,673 K, obtained by many authors [5–17].

Method for calculating the point defect diagrams

Determination of defect concentrations in a non-doped oxide

The Eqs. 33, 36, and 37 obtained in “Appendix” link concentrations of different defects near the stoichiometric composition; these concentrations depend on the values: following the standard Gibbs energy of the formation of intrinsic electronic defects, ΔG_i^0 ; ionic defects (Frenkel), ΔG_F^0 ; and cobalt vacancies with the highest ionization degree, $\Delta G_{V_{Co}''}^0$, and lower ionization degrees, $\Delta G_{V_{Co}'}^0$ and $\Delta G_{V_{Co}^x}^0$. The above relations can be used for the determination of these values. Then, the determined values allow the calculations of the defect concentrations for any oxygen pressure (deviation from the stoichiometry). Thus, if we have the value ΔG_i^0 of the electronic defects formation, determined from the electrical measurements, it is possible to adjust the values ΔG_F^0 and $\Delta G_{V_{Co}''}^0$, $\Delta G_{V_{Co}'}^0$, and $\Delta G_{V_{Co}^x}^0$, in such a way that the obtained dependence of the deviation from the stoichiometry on p_{O_2} , (resulting from the calculated defect concentrations) is consistent with the experimental values of δ . The individual values can be determined in several stages of calculations.

At the first step, we assume that the concentration of the defects with lower ionization degrees is insignificantly low. Knowing the value of ΔG_i^0 and assuming the ΔG_F^0 , we then calculate the concentrations of the electronic defects and

ionic defects. The above assumed values of ΔG_i^0 and ΔG_F^0 must fulfill the Eqs. 36 and 37, at the appropriately adjusted values of $\Delta G_{V_{Co}''}^0$ and $p_{\text{O}_2}^{(s)}$. This means that the following condition must be fulfilled (Eq. 37):

$$\Delta G_{V_{Co}''}^0 - \left[\left(\Delta G_{\text{def}}^{0(\delta \approx 0)} - F - I \right) + 1/2 \Delta G_F^0 \right] = 0 \tag{1}$$

The value of $\Delta G_{\text{def}}^{0(\delta \approx 0)}$ is calculated using Eq. 36.

Then, we assume the concentration of cobalt vacancies as a variable parameter (V_{Co}''). We calculate the concentration $[\text{Co}_i^{\bullet\bullet}]$ and the deviation from the stoichiometry δ vs. $[V_{Co}'']$.

The concentration of electronic defects vs. $[V_{Co}'']$ is calculated by solving the following quadratic equation:

$$\left([h^{\bullet}] - 2[V_{Co}''] - [V_{Co}'] + 2[\text{Co}_i^{\bullet\bullet}] + [\text{Co}_i^{\bullet}] \right) [h^{\bullet}] = \exp(-\Delta G_i^0/RT), \tag{2}$$

which takes into account the electroneutrality condition.

The equilibrium oxygen pressure is calculated using the concentration of the vacancies $[V_{Co}'']$, the concentration of electron holes, and the equilibrium constant for the reaction (6) $\left(\Delta G_{V_{Co}''}^0 \right)$.

The obtained relation between the deviation from the stoichiometry and p_{O_2} is then verified with the experimental values of δ . The difference between the $\log \delta$ vs. $\log(p_{\text{O}_2})$ curve and the experimental values of δ is corrected by adjusting the values of ΔG_F^0 and $\Delta G_{V_{Co}''}^0$ (when the condition (1) is fulfilled) in a way which obtains the consistency in the range of the small deviations from the stoichiometry.

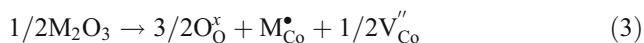
At the next step, we consider the presence of defects with lower ionization degrees. We choose the value of $\Delta G_{V_{Co}'}^0$ and then the value of $\Delta G_{V_{Co}^x}^0$ in such a way as to obtain the full consistency with the experimental results of δ (at higher values of the deviation). In the calculations of the concentrations of the defects with lower ionization degrees, we use the concentrations of the defects with a higher ionization degree, the concentration of electronic defects, and the appropriate equilibrium constants. A change in the individual values and in the defect concentrations causes a perturbation of the electroneutrality condition. Due to this, the calculations should be performed until this condition is fulfilled.

Determination of the defect concentrations in a doped oxide

Using the determined values of ΔG_n^0 of the defects formation for the pure oxide, it is relatively easy to determine the concentrations of the defects that form after introducing metal ions with another oxidation degree than 2+. We assume that the incorporated ions of the dope do

not influence the values of ΔG_n^0 of the defect formation. We also assume that the point defects still form an ideal solution.

The process of doping the cobalt oxide with M^{3+} metal ions in the form of M_2O_3 oxide is described by the reaction:

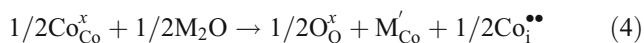


An introduction of y_{M^3} moles of M^{3+} ions into a cobalt oxide with the stoichiometric composition (these ions occupy the cation nodes) causes the increase of the concentration of cobalt vacancies by $1/2y_{M^3}$. The concentration of vacancies is then expressed by:

$$[V_{Co}''] = y_{V_{Co}''}^0 + 1/2y_{M^3} = y_{V_{Co}''}^{o(d)}$$

where $y_{V_{Co}''}^{o(d)}$ is the concentration of $[V_{Co}'']$ after introducing the dope. A change of the concentration $[V_{Co}'']$ will cause changes in concentrations of other defects.

On the other hand, the process of doping the cobalt oxide with M^+ metal ions in the form of M_2O oxide is described by the reaction:



Thus, the introduction of y_{M^+} moles of M^+ ions into an oxide with the stoichiometric composition will cause an increase of the concentration $[Co_i^{\bullet\bullet}]$ by $1/2y_{M^+}$. The concentration $[Co_i^{\bullet\bullet}]$ is then expressed by:

$$[Co_i^{\bullet\bullet}] = y_{Co_i^{\bullet\bullet}}^0 + 1/2y_{M^+} = y_{Co_i^{\bullet\bullet}}^{o(d)}$$

where $y_{Co_i^{\bullet\bullet}}^{o(d)}$ is the concentration of $[Co_i^{\bullet\bullet}]$ ions after introducing the dope. A change of $[Co_i^{\bullet\bullet}]$ concentration will cause changes in concentrations of the remaining defects.

Results of calculations and discussion

Point defect concentrations in non-doped $Co_{1-\delta}O$

The calculations used the values of ΔG_i^0 of the electronic defect formation obtained by Nowotny and Rekas [4] based on a wide analysis of the results of electrical conductivity measurements and the Seebeck effect. As a result of the performed calculations, it was found that the change of the ΔG_F^0 value influences the curve of δ vs. p_{O_2} practically in the range of oxygen pressures below $p_{O_2} < 10^{-5}$ atm. At low oxygen degrees, the studies have been performed only by Schmalzried et al. [5, 6]. The results of the above authors obtained in the temperature range 1,273–1,473 K and Fisher Tannhauser [8], Bransky and Wimmer [11] at higher temperatures were used to determine the values of ΔG_F^0 and their temperature dependence. When considering

the defects with lower ionization degrees, it was assumed that $\Delta G_{V_{Co}'}^0 = \Delta G_{Co_i^\bullet}^0$ and $\Delta G_{V_{Co}''}^0 = \Delta G_{Co_i^{\bullet\bullet}}^0$.

Figure 1a–d shows the results of the calculations of the concentrations of cobalt vacancies and interstitial cobalt ions in $Co_{1-\delta}O$, obtained for a series of temperatures (1,273–1,573 K). In lower temperatures, a similar curve as at 1,273 K (Fig. 1a) was obtained. Similarly, the defect diagrams for temperatures higher than 1,573 K are very close to that shown in Fig. 1d. As can be seen in Fig. 1, there is quite a good consistency between the results of the studies of the deviation from the stoichiometry obtained by different authors. As can be seen in Fig. 1, the dependence of δ in p_{O_2} in the whole range of p_{O_2} has a similar character (the exponent being about 1/6–1/4). However, in the individual temperatures and ranges of p_{O_2} , the dependences of the defect concentrations on p_{O_2} change significantly. At low oxygen pressures, there are significant concentrations of $[V_{Co}'']$ and $[Co_i^{\bullet\bullet}]$, which relatively strongly increase when the temperature rises. Simultaneously, the range in which the concentrations of these defects are comparable grows. At 1,273 K and at lower temperatures, the dominating defects, in a wide range of oxygen pressures, are $[V_{Co}'']$ vacancies. When the temperature increases, the range p_{O_2} in which these vacancies dominate decreases, and the concentrations of vacancies $[V_{Co}'']$ and $[V_{Co}^x]$ begin to influence the deviation from the stoichiometry. However, at these temperatures there are significant concentrations of $[V_{Co}'']$ and $[Co_i^{\bullet\bullet}]$, weakly dependent on p_{O_2} . Thus, the assumption that single-ionized vacancies dominate in the $Co_{1-\delta}O$ is too big a simplification.

Figure 2 shows the dependences of ΔG_F^0 and $\Delta G_{V_{Co}''}^0$ on the temperature, obtained by fitting the curve of $\log \delta$ vs. $\log(p_{O_2})$ to the results of the studies by different authors. The values of ΔG_F^0 for the individual temperatures, shown in Fig. 2, were calculated using the dependence of ΔG_F^0 on T , obtained from the results of authors of [5, 6, 8, 11] (Table 1), and the values of $\Delta G_{V_{Co}''}^0$ were fitted in a way to obtain the consistency with the experimental data (considering the defects with a lower ionization degree) [5–17]. As can be seen in Fig. 2, the values of $\Delta G_{V_{Co}''}^0$ obtained using the results by different authors are close. However, when it is above 1,500 K, the changes are larger and indicate a change in the nature of the dependence of $\Delta G_{V_{Co}''}^0$ on T . In Fig. 2, the values of $\Delta G_{V_{Co}''}^0$ calculated by Dieckmann [3] ((multiplication sign*) points) taking into account only the cobalt vacancies are marked. Figure 2 also presents the values $\Delta G_{Co_i^{\bullet\bullet}}^0$ of the formation of interstitial cobalt ions ($Co_i^{\bullet\bullet}$), calculated according to the Eq. 38. These values have not been determined so far.

Figure 3 shows the values of $\Delta G_{V_{Co}'}^0$ and $\Delta G_{V_{Co}^x}^0$ of the formation of the vacancies with lower ionization degrees, which were obtained by fitting the curve of $\log \delta$ vs.

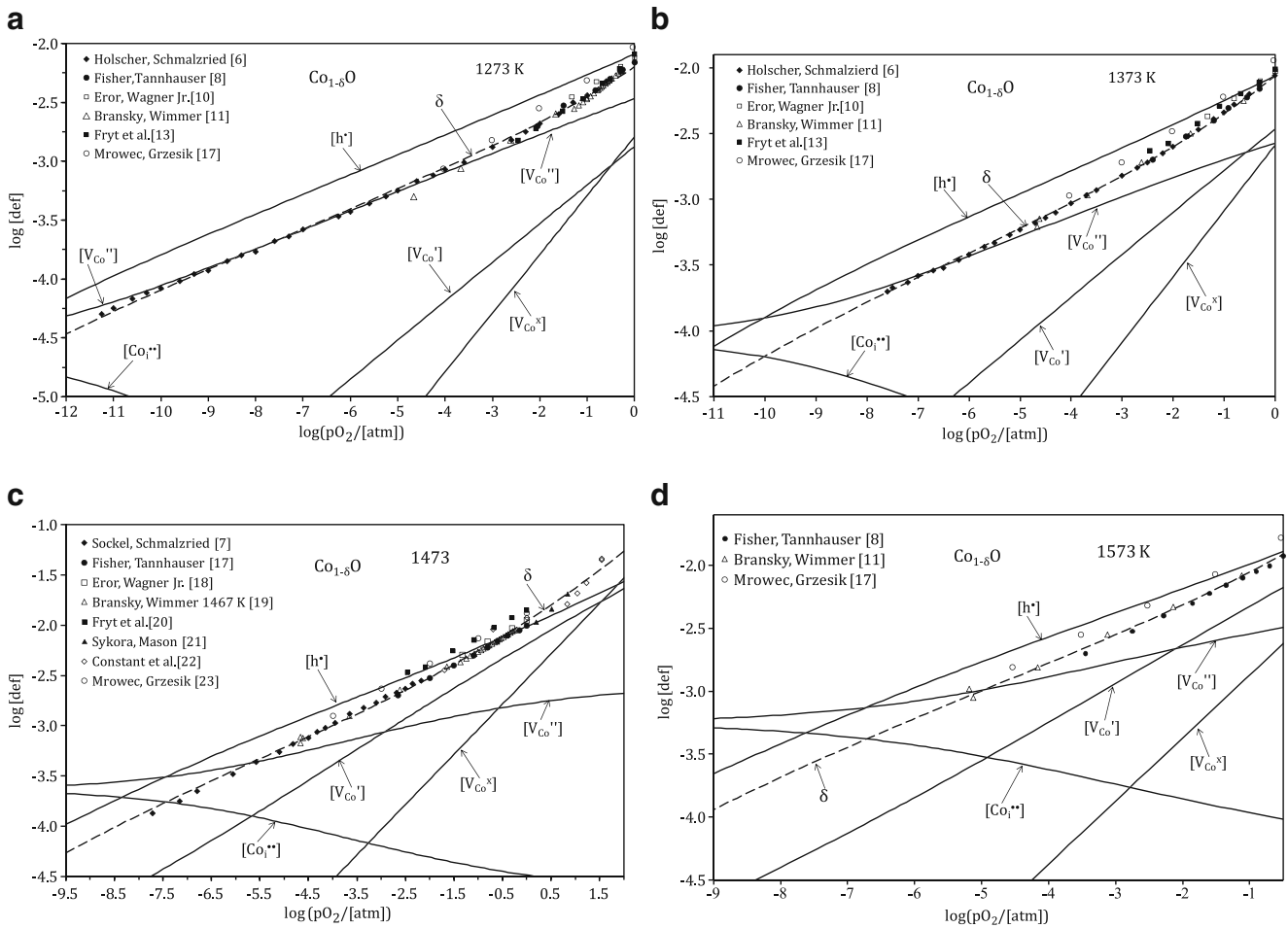
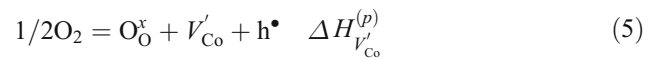


Fig. 1 Diagrams of point defects in $\text{Co}_{1-\delta}\text{O}$ obtained with the use of results of the deviation from the stoichiometry studies of Schmalzried et al. [5, 6]: **a–c** for temperatures 1,273–1,473 K and **d** Bransky and Wimmer [11] and Fisher and Tannhauser [8] for 1,573 K. The points mark the results of studies: (solid diamonds)—Schmalzried et al. [5,

6], (solid circle)—Fisher and Tannhauser [8], (empty square)—Eror and Wagner [10], (empty triangle)—Bransky and Wimmer [11], (solid square)—Fryt et al. [13], (solid triangle)—Sykora and Mason [15], (empty diamond)—Constant et al. [16], and (empty circle)—Mrowec and Grzesik [17]

$\log(p_{\text{O}_2})$ to the results of the studies of the different authors. In Fig. 3, the values of $\Delta G_{V'_{\text{Co}}}^0$ and $\Delta G_{V''_{\text{Co}}}^0$ calculated by Dieckmann [3] ((multiplication sign \times , $*$) points), taking into account only the cobalt vacancies, are marked. As can be seen in Fig. 3, the values of $\Delta G_{V'_{\text{Co}}}^0$ are negative and their absolute values increase with the temperature increase. This means that with the temperature increase the fraction of the concentration of single-ionized vacancies $[V'_{\text{Co}}]/[V''_{\text{Co}}]$ would increase. Thus, the bonding energy in complexes ($V''_{\text{Co}}, \text{h}^*$) would have increased, which seems improbable. As can be seen in Fig. 3a, change in the nature of the temperature dependence of $\Delta G_{V'_{\text{Co}}}^0$ occurs on the above 1,500 K. This fact indicates that the defects structure is more complex, and the existence of defect complexes, proposed by Catlow and other authors, should be considered [36–42]. In Table 1, the determined enthalpies and entropies of individual defects, resulting

from the relations presented in Figs. 2 and 3, are given. The values of $\Delta H_{V'_{\text{Co}}}^{(p)}$ of the formation of V'_{Co} vacancies are also given, according to the reaction:



according to the adopted model in which in $\text{Co}_{1-\delta}\text{O}$ single-ionized cobalt vacancies dominate. As can be seen, there are differences between the values of $\Delta H_{V'_{\text{Co}}}^{(p)}$ determined in the present work and those determined by the different authors. This difference results from the fact that the concentration of interstitial cobalt ions is not considered.

Figure 4 shows the adjusted values of the hypothetical pressure ($p_{\text{O}_2}^{(s)}$) (fulfilling the Eqs. 36 and 1), at which CoO could reach the stoichiometric composition. As can be seen in the temperature range 1,173 to 1,373 K, these pressures are by a few orders of magnitude lower than the

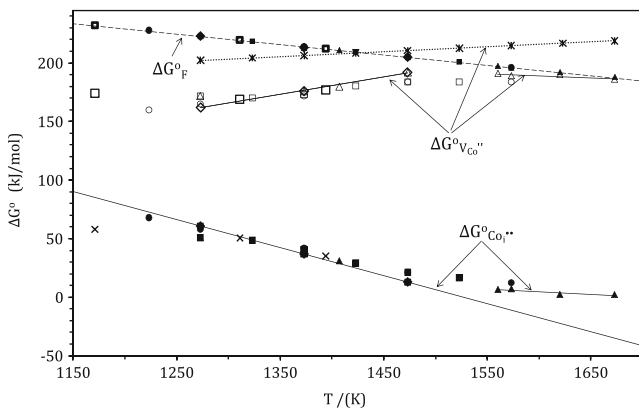


Fig. 2 The values of: ΔG_F° (solid points), $\Delta G_{V''Co}^\circ$ (empty points), and $\Delta G_{Co_i'''}^\circ$ (solid points) of the formation of intrinsic Frenkel-type defects, cobalt vacancies $V''Co$, and interstitial cobalt ions Co_i''' , obtained at 1,171–1,673 K using the results of studies on the deviation from the stoichiometry of Schmalzried et al. [5, 6]—points (solid diamond, empty diamond), Fisher and Wagner [9]—(inverse bullet, empty square, multiplication sign), Fisher and Tannhauser [8] and Bransky and Wimmer [11]—(solid triangle, empty triangle), Fryt et al. [13]—(solid square, empty square), and Mrowec and Grzesik [17]—(solid circle, empty circle). The (*) points denote the values of $\Delta G_{V''Co}^\circ$ obtained by Dieckmann [3]

decomposition pressure of cobalt oxide [66] (dashed line). However, this difference decreases with the temperature. The obtained monotonic character of the dependence of $(p_{O_2}^{(s)})$ on the temperature is in accordance with the expectations, and it could serve as a verification of the calculations.

From the studies on electrical conductivity and on the Seebeck effect, it transpires that the ratio of mobility of electrons vs. electron holes is about $\mu_h/\mu_e=0.1$ [4, 8, 11, 21, 22, 26]. The oxygen pressure $(p_{O_2}^{(sm)})$, at which the oxide should show a minimum in the electrical conductivity, should thus be shifted in the direction of higher oxygen pressures in relation to $(p_{O_2}^{(s)})$. In Fig. 4, the values of oxygen pressure at which the concentration ratio $[h^\bullet]/[e'] = 10$ are marked. This figure also indicates the values of $(p_{O_2}^{(sm)})$ at which the value of the Seebeck effect should be zero ((empty square) points) [8, 22, 26, 30]. As can be seen, at 1,373 and 1,473 K, a good consistency was obtained.

Figure 5 shows the dependence of the derivatives: $n_\delta = \log(p_{O_2})/d \log \delta$ and $n_h = \log(p_{O_2})/d \log [h^\bullet]$ on $\log(p_{O_2})$, obtained for the curves presented in Fig. 1. As has been already mentioned, the values of exponents $1/n_\delta$ and $1/n_h \cong 1/4$ in the dependence of the deviation from the stoichiometry and the electrical conductivity formed the basis for hypothesizing that single-ionized vacancies dominate in the complete range of the $Co_{1-\delta}O$ existence. As can be seen in Fig. 5, the values of n_δ and n_h change, depending on p_{O_2} in the range from 3 to 6. The experimental values of $1/n_\delta$, most often determined in narrow ranges of oxygen pressures, are close to the values

shown in Fig. 5. Table 2 gives the values of exponents $1/n_\sigma$ from the dependence of σ on p_{O_2} , obtained by many authors, and their comparison with the values of n_h in similar ranges of oxygen pressures, obtained in the present work (Fig. 5). As can be seen in Table 2, there are differences between the values of n_σ and n_h . They could be connected with the fact that at higher values of the deviation from the stoichiometry, there is a significant concentration of defect complexes. Their presence will cause the dependence of the concentration of electron holes on p_{O_2} to be a power function with the exponent higher than $1/4$.

It should be also emphasized that the calculations were performed with the assumption that the defects form an ideal solution, meaning that the standard enthalpies of the formation of the defects are independent from their concentration. It is possible, for example, to consider the activity coefficients based on the Debye–Hückel theory. As there are difficulties in determining the absolute values of the deviation from the stoichiometry, enhancement of the results by taking into account the activity coefficients does not seem justified at this level of accuracy. The eventual error related to a deviation from the ideal system is included in the values of $\Delta G_{V''Co}^\circ$ and $\Delta G_{Co_i'''}^\circ$. However, a larger error can be caused by the presence of impurities in the form of metal ions with other valences that are $2+$.

Point defect concentrations in doped $(Co_{1-y}M_y)_{1-\delta}O$

M^+ ion dope (M_2O)

In the calculations of the point defect diagram for the doped oxide, the values of ΔG° of the defects formation obtained for pure $Co_{1-\delta}O$ have been used (Figs. 2 and 3). Figure 6 shows the results of the calculations of the defects' concentrations in the $(Co_{1-y}M_y)_{1-\delta}O$ doped with M^+ ions. The quantity of dope was chosen in such a way as to obtain a consistency with the results of studies on the deviation from the stoichiometry for $(Co_{1-y}Li_y)_{1-\delta}O$, obtained by Fisher and Wagner [9]. Figure 6a, b shows the results of the calculations for an oxide with a low dope content. As can be seen in these figures, a good fit has been obtained for the dope content $y_M = (4 - 7) \cdot 10^{-4} \text{ mol/mol}$ —dashed line. This value is higher by one order of magnitude ($y_M = 4 \cdot 10^{-5}$) than that obtained by Fisher and Wagner [9]. The analysis of the lithium content was performed after multi-hour measurements, which, according to the authors of the work [9], is an underestimated value. They also found a lack of repetitiveness of results (they have observed a hysteresis effect). The content of lithium in the examined monocrystal was at the level of the defects' concentration, thus small changes in lithium content being due to evaporation could have caused the lack of repetitiveness

Table 1 The values of enthalpy ΔH and entropy ΔS of formation of Frenkel defects, cobalt vacancies, V'_{Co} and interstitial ions Co_i^{**} , vacancies V''_{Co} and V^x_{Co} (Eqs. 7 and 8), and of formation vacancies V'_{Co} (Eq. 5) determined via the relations shown in Figs. 2 and 3, and calculated by other authors with the assumption of simplified defects models

Equilibrium	ΔH (kJ/mol)	ΔS (J/mol)	ΔT (K)	Ref.
$[h^{\bullet}][e']$	289.45	20.7		[4]
Frenkel	336±7	89±2	1,273–1,473	(SHS)
Frenkel	333±2	87±5	1,273–1,673	(SHS and FT, BW)
V''_{Co}	–29±8	–150±6	1,273–1,473	(SHS)
Eq. 6	246±26	–35±16	1,500–1,673	(FT, BW)
	90±17	–63±12	1,273–1,523	(FMW)
	71±15	–74±11	1,223–1,573	(MG)
	149	–42		[3]
	169	34		[11]
	143	–47		[12]
Co_i^{**}	366±1	239±1	1,273–1,473	(SHS)
Eq. 9	80±26	47±16	1,500–1,673	(FT, BW)
	246±18	151±13	1,273–1,523	(FMW)
	267±16	164±11	1,223–1,573	(MG)
V'_{Co}	166±2	163±3	1,273–1,473	(SHS)
Eq. 7	172±10	166±7	1,373–1,473	(FT,BW)
	–128±5	–39±3	1,500–1,673	(FT, BW)
	121±15	131±10	1,273–1,523	(FMW)
	59±12	88±9	1,223–1,473	(MG)
	77	–27		[3]
	78	–15		[12]
	74	21		[11]
V^x_{Co}	–92±8	–30±6	1,273–1,473	(SHS)
Eq. 8	–100±3	–36±2	1,273–1,673	(FT, BW)
	–106±5	–41±4	1,273–1,523	(FMW)
	–94±3	–32±2	1,273–1,573	(MG)
	–51	–7		[3]
V'_{Co}	137	12	1,273–1,473	(SHS)
Eq. 5	211	69	1,273–1,523	(FMW)
	130	15	1,223–1,473	(MG)
	77	–27	1,273–1,673	[3]
	54	39	1,259–1,620	[8, 14]
	60	33	1,273–1,423	[10]
	95	13	1,273–1,673	[11]
	78	–15	1,223–1,523	[12]
	59	35	1,273–1,573	[14]
	64	28	1,223–1,673	[17]

(SHS), (FT, BW), (FMW), and (MG) stand for, used in calculations in the present work, the results of the deviation from the stoichiometry obtained by Schmalzried et al. [5, 6]; Fisher and Tannhauser [8] and Bransky and Wimmer [11]; Fryt et al. [12]; and Mrowec and Grzesik [17], respectively

as well as the lower analyzed content. Figure 6a–c shows the results of the calculations for “pure” $Co_{1-\delta}O$ assuming that the deviations of δ at low oxygen pressures are the result of the presence of impurities in the form of M^+ ions (dotted line). Considering the error of the measurement of very small mass changes at the above oxygen pressures, the obtained quantities of dope, at the level of $y_{M'} = 1 \cdot 10^{-4}$ mol/mol, as an impurity, are very probable. Figure 6c presents defect diagrams for an oxide containing $y_{M'} = 1.44 \cdot 10^{-3}$ mol/mol of M^+ ions. As can be seen, at 1,394 K a full consistency has been obtained

with the results of the deviation from the stoichiometry for a sample containing the same quantity of lithium [9]. A full consistency is found also for the oxygen pressure at which the doped oxide reaches the stoichiometric composition. Figure 6d, e shows examples of calculations for 1,273 and 1,473 K for the dope content $y_{M'} = 5.13 \cdot 10^{-3}$ and $1.18 \cdot 10^{-2}$ mol/mol. For an oxide with such a content of lithium, Petot-Ervas et al. [29] performed the studies on the electrical conductivity.

As can be seen in Fig. 6, the introduction of M^+ ions into the cobalt oxide causes a shift by a dozen orders of

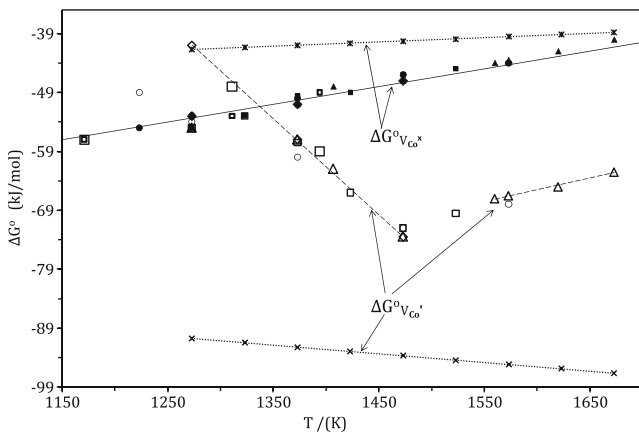


Fig. 3 The values of: $\Delta G_{V'Co}^{\circ}$ and ΔG_{VCo}° , of the formation of $V'Co$ (empty points) and VCo (solid points) obtained in individual temperatures using the results of deviation from the stoichiometry studies of: Schmalzried et al. [5, 6]—points (solid diamond, empty diamond), Fisher and Wagner [9]—(inverse bullet, empty square), Fisher and Tannhauser [8] and Bransky and Wimmer [11]—(solid triangle, empty triangle), Fryt et al. [13]—(solid square, empty square), and Mrowec and Grzesik [17]—(solid circle, empty circle). The (multiplication sign \times , \ast) points denote the values of $\Delta G_{V'Co}^{\circ}$ and ΔG_{VCo}° obtained by Dieckmann [3]

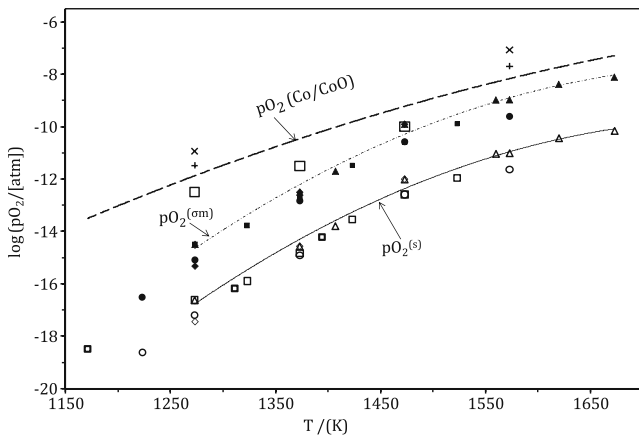


Fig. 4 The values of hypothetical oxygen pressure ($p_{O_2}^{(s)}$) (empty points) whereby the CoO would reach the stoichiometric composition and the ($p_{O_2}^{(\sigma m)}$) (solid points) where the ratio of the concentrations: $[h^{\bullet}]/[e'] = 10$, obtained in the individual temperatures using the results of studies on the deviation from the stoichiometry obtained by: Schmalzried et al. [5, 6]—points (solid diamond, empty diamond), Fisher and Wagner [9]—(inverse bullet, empty circle), Fisher and Tannhauser [8] and Bransky and Wimmer [11]—(solid triangle, empty triangle), Fryt et al. [13]—(solid square, empty square), and Mrowec and Grzesik [17]—(solid circle, empty circle). Points (plus sign) values of ($p_{O_2}^{(\sigma m)}$) for the content of M^{3+} ions $y_{M^{3+}} = 5 \cdot 10^{-3}$ mol/mol, (multiplication sign) $1 \cdot 10^{-2}$ mol/mol. The points (empty square) mark the values of ($p_{O_2}^{(\sigma m)}$) whereby the Seebeck effect could be zero [22, 26, 30]. The dashed line—the equilibrium pressure Co/CoO [66]

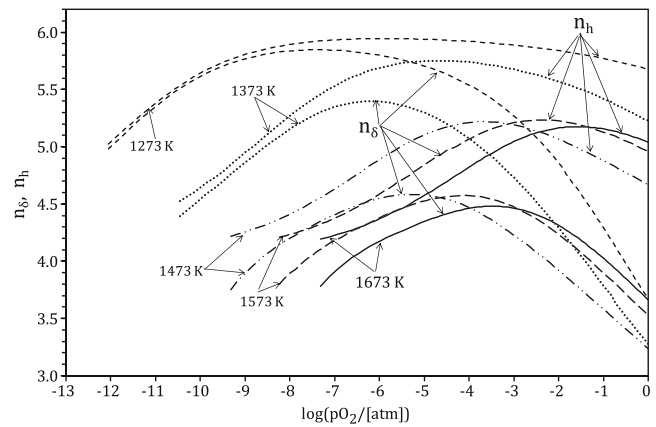


Fig. 5 The dependence of the derivative: $n_{\delta} = d \log(p_{O_2}) / d \log \delta$ and $n_h = d \log(p_{O_2}) / d \log [h^{\bullet}]$ on $\log(p_{O_2})$ on obtained for the dependence of the deviation δ and the concentration of electron holes $[h^{\bullet}]$ on p_{O_2} for the relations shown in Fig. 1a–d and obtained at 1,673 K

magnitude in the value of the oxygen pressure at which the oxide reaches the stoichiometric composition, relative to the pure oxide (see Fig. 4). Thus, negative values of δ are not connected with the measurement error—this possibility was considered by the authors of the work [9]—but they are a result of a change of the concentrations of the defects. As can be seen in Fig. 6, in the range below $p_{O_2} < 10^{-5}$ atm, there is a significant concentration of $[Co_i^{\bullet\bullet}]$ ions, which is higher than the concentration of $[V'Co]$ by as much as over than one order of magnitude. It depends on the dope concentration and on the temperature. A result of the change of the defects' concentrations, outside a narrow range (one to two orders of magnitude) near the stoichiometric composition, is a high deviation from the stoichiometry, comparable with the dope concentration.

As can be seen in Fig. 6, despite very drastic changes in the concentration of ionic defects, a relatively big increase of the concentration of electron holes occurs, depending on the dope concentration and on the temperature. The character of this relationship is complex. It is possible to identify a range of oxygen pressures in which the concentration of electron holes is practically constant and close to the dope concentration (see Fig. 6d). The width of this range decreases with the temperature increase, and at 1,473 K, it practically disappears. A similar characteristic of the dependence of the electrical conductivity was obtained by Petot-Ervas et al. [29]. However, they did not perform the studies at low oxygen pressure—at this range, the conductivity of a doped oxide should decrease. The decrease of the electrical conductivity with the decrease of oxygen pressure is indicated by the studies of Bransky and Wimmer [11], performed with samples featuring a low lithium content.

Figure 7 shows the dependence of the derivative changes: $n_h = d \log(p_{O_2}) / d \log [h^{\bullet}]$ on $\log(p_{O_2})$, obtained for the relationships given in Fig. 6. As can be seen, with the oxygen pressure decrease the n_h increases, reaching

Table 2 The values of the exponent $1/n_\sigma$ obtained for the dependence of electrical conductivity σ on p_{O_2} in a series of temperatures in individual ranges of oxygen pressure, obtained by different authors, and the average values of the exponent $1/n_h$ in the dependence of electron hole concentration on p_{O_2} , calculated in the same ranges p_{O_2} (Figs. 5, 7, and 9)

Ref.	T (K)	p_{O_2} (atm)	n_σ	n_h	y_M
[24]	1,173	$0.3\text{--}10^{-4}$	3.5–4.4	5.4–5.8	
[8]	1,191	$10^{-4}\text{--}10^{-11}$	5.7–6.1	5.8–5.5	
[29]	1,223	$1\text{--}10^{-7}$	3.48–5.74	5.3–5.9	
[8]	1,259	$1\text{--}10^{-3}$	3.8–4.3	5.7–5.9	
[34]	1,270	$1\text{--}10^{-2}$	3.43 ± 0.1	5.7–5.9	
[29]	1,273	$1\text{--}10^{-7}$	3.35–5.8	5.8–5.9	
[10]	1,273	$1\text{--}10^{-4}$	3.8 ± 0.1	5.7–5.9	
[24]	1,273	$1\text{--}10^{-4}$	3.5–4.4	5.7–5.9	
[25]	1,273	$1\text{--}10^{-3}$	3.5 ± 0.07	5.7–5.9	
[33]	1,300	$0.2\text{--}3\cdot 10^{-4}$	3.88 ± 0.12	5.5–5.8	
[33]	1,300	$0.2\text{--}3\cdot 10^{-4}$	4.20 ± 0.24	5.5–5.8	
[29]	1,373	$1\text{--}10^{-5}$	3.28–5.02	5.2–5.7	
[10]	1,373	$1\text{--}10^{-4}$	3.9 ± 0.3	5.2–5.7	
[25]	1,373	$1\text{--}10^{-3}$	3.28 ± 0.09	5.1–5.7	
[34]	1,470	$1\text{--}10^{-2}$	3.43 ± 0.1	5.1–5.2	
[29]	1,473	$1\text{--}10^{-5}$	3.58–5.17	5.1–4.6	
[10]	1,473	$1\text{--}10^{-4}$	3.8 ± 0.2	5.1–4.8	
[24]	1,473	$1\text{--}10^{-4}$	4–4.4	5.1–4.8	
[25]	1,473	$1\text{--}10^{-3}$	3.72 ± 0.16	5.1–5.0	
[11]	1,573	$10^{-5}\text{--}10^{-8}$	6	4.6–4.2	
[29]	1,573	$1\text{--}10^{-4}$	3.47–4.76	5.1–5.2	
[25]	1,573	$1\text{--}10^{-3}$	3.84 ± 0.13	5.1–5.2	
[8]	1,599	$1\text{--}10^{-3}$	3.8–4.3	5.1–5.0	
[8]	1,599	$10^{-3}\text{--}10^{-10}$	5.7–6.1	4.1–4	
[29]	1,673	$1\text{--}10^{-4}$	3.35–5.07	5.1–4.8	
[25]	1,673	$1\text{--}10^{-3}$	3.64 ± 0.15	5.1–5.0	
[29]	1,273	$1\text{--}10^{-2}$	6–10	7.4–15	Li $5.13\cdot 10^{-3}$
[29]	1,373	$1\text{--}10^{-2}$	6–10	7.0–12	$5.13\cdot 10^{-3}$
[29]	1,473	$1\text{--}10^{-2}$	4.5–7	5.9–10	$5.13\cdot 10^{-3}$
[29]	1,273	$1\text{--}10^{-1}$	6.5–10	14–25	$1.18\cdot 10^{-2}$
[29]	1,373	$1\text{--}10^{-1}$	6.5–10	12–20	$1.18\cdot 10^{-2}$
[29]	1,473	$1\text{--}10^{-2}$	5–10	9–17	$1.18\cdot 10^{-2}$
[33]	1,300	$0.2\text{--}3\cdot 10^{-4}$	4.6 ± 0.2	4.4–4.2	Cr $4.9\cdot 10^{-3}$
[33]	1,300	$0.2\text{--}3\cdot 10^{-4}$	3.83 ± 0.12	4.1–4.0	$9\cdot 10^{-3}$
[32]	1,270	$1\text{--}10^{-2}$	3.32 ± 0.1		In $2.85\cdot 10^{-3}$
[32]	1,270	$1\text{--}10^{-2}$	3.02 ± 0.1	4.9–4.6	$8.74\cdot 10^{-3}$

high values, although at low oxygen pressures, it decreases to 4. In Table 2, the values of the exponent $1/n_\sigma$ in the dependence of the electrical conductivity on p_{O_2} for doped oxides, obtained by Petot-Ervias et al. [29], are given and compared with the values of n_h obtained in the present work (Fig. 7) (in similar ranges of p_{O_2}). As can be seen in Figs. 6 and 7, the assumption that the concentration of electron holes is equal to the dope concentration is an excessive approximation.

M^{3+} ion dope (M_2O_3)

Figure 8 shows the results of the calculations of the changes in the defect concentrations after the introduction, into the $(Co_{1-y}My)_{1-\delta}O$ oxide, of a dope of M^{3+} ions: $y_{M^{\bullet}} = 5 \cdot 10^{-3}$ mol/mol—dashed-dotted line and $1 \cdot 10^{-2}$ mol/mol—dashed line. They are compared to the concentration in the pure $Co_{1-\delta}O$ (solid line) for two example temperatures, 1,273 and 1,573 K. The depend-

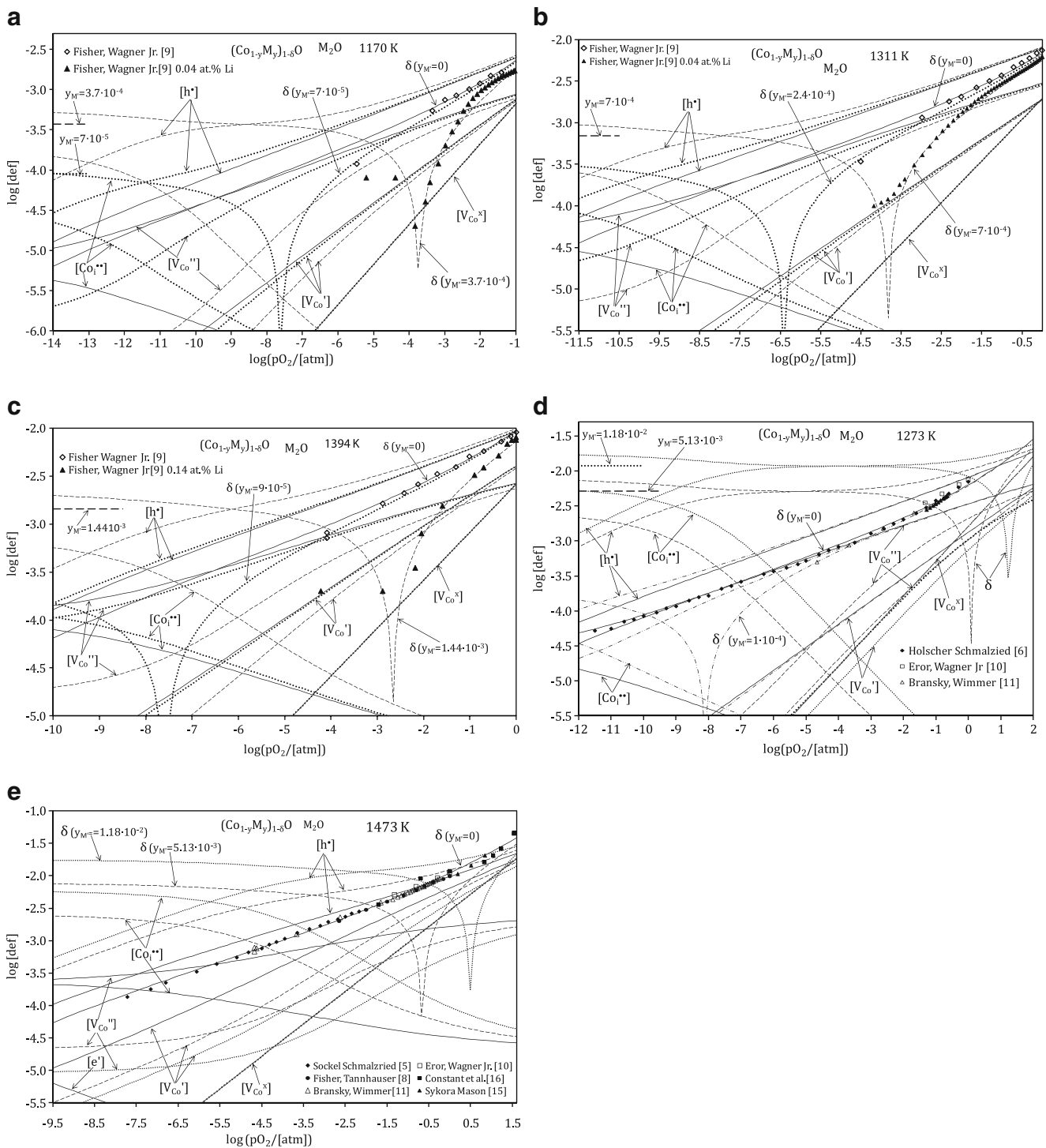


Fig. 6 Diagrams of point defects for “pure” $\text{Co}_{1-\delta}\text{O}$ (solid line) and for the $(\text{Co}_{1-y}\text{M}_y)_{1-\delta}\text{O}$ doped with M^{II} ions (dashed lines) obtained using the results of the studies on the deviation from the stoichiometry obtained by: Fisher and Wagner [9] (points (solid triangle) **a** for 1,170 K and the dope content $y_{\text{M}} = 7 \cdot 10^{-5}$ mol/mol—dotted line, $3.7 \cdot 10^{-4}$ mol/mol—dashed line, **b** 1,311 K $y_{\text{M}} = 2.4 \cdot 10^{-4}$ mol/mol—dotted line, $7 \cdot 10^{-4}$ —dashed line, **c** 1,394 K $y_{\text{M}} = 9 \cdot 10^{-5}$ mol/mol—dotted line, $1.44 \cdot 10^{-3}$ —dashed), **d** Holscher Schmalzried [6] for 1,273 K and $y_{\text{M}} = 1 \cdot 10^{-4}$ mol/mol—dashed-dotted line, $5.13 \cdot 10^{-3}$ —dashed line,

$1.18 \cdot 10^{-2}$ —dotted line, **e** Sockel and Schmalzried [5], Bransky and Wimmer [10], for 1,473 K and $y_{\text{M}} = 5.13 \cdot 10^{-5}$ mol/mol—dashed line, $1.18 \cdot 10^{-2}$ —dotted line. The points mark the results of studies for pure $\text{Co}_{1-\delta}\text{O}$: (solid diamond)—Schmalzried et al. [5, 6], (solid circle)—Fisher and Tannhauser [8], (empty diamond)—Fisher and Wagner [9], (empty square)—Error and Wagner [10], (empty triangle)—Bransky and Wimmer [11], (solid triangle)—Sykora and Mason [15], and (solid square)—Constant et al. [16]

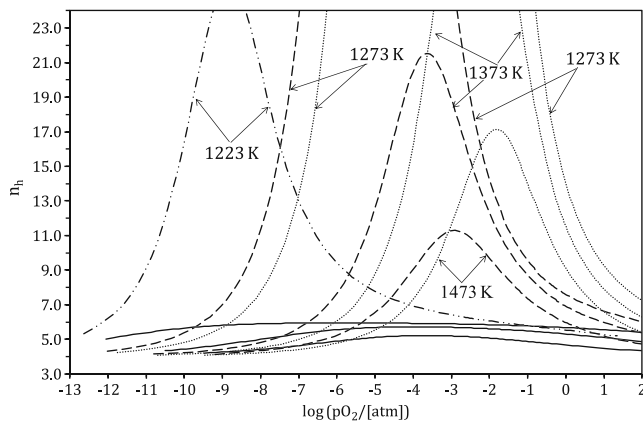


Fig. 7 Dependence of the derivative $n_h = d\log(p_{O_2})/d\log[h^\bullet]$ on $\log(p_{O_2})$, obtained for the dependence of the concentration of electron holes $[h^\bullet]$ on p_{O_2} shown in Fig. 6 at 1,223 K for $y_{M'} = 7.5 \cdot 10^{-4}$ mol/mol—dashed-dotted line, 1,273–1,473 K for $y_{M'} = 5.13 \cdot 10^{-3}$ mol/mol—dashed line and $1.18 \cdot 10^{-2}$ —dotted line and $y_{M'} = 0$ —solid line

ences of δ and of the concentration $[V_{Co}^{\prime\prime}]$ vs. p_{O_2} are also marked, for the dope content of $y_{M'} = 3 \cdot 10^{-2}$ mol/mol—dotted line. The quantity of dope was chosen in order to allow for the comparability with the results of the studies on the deviation from the stoichiometry in a doped oxide, Cr_2O_3 , performed by Mrowec and Grzesik [17] and with the studies on the electrical conductivity performed by many authors [21, 31, 33, 34]. The defect diagrams at other temperatures look similar. As can be seen in Fig. 8, with the increase of the concentration of M^{3+} , the deviation from the stoichiometry increases significantly and it is relatively close to the experimental values [17]. A good consistency obtained for the content $y_{M'} = 3 \cdot 10^{-2}$ mol of M^{3+} ions can be surprising (dotted line). As it transpires from the results

of the studies of Nowotny et al. [33, 44, 45], as well as from the studies of other authors [21, 31], the maximal solubility of Cr in CoO is at about 1%. Thus, it can be expected that on the crystal surface, the formation of a thin layer of spinel $CoCr_2O_4$ or nuclei of this phases occurs [44]. In the spinel structure, within the cation sublattice, there is a significant concentration of non-occupied octahedral voids, which are only partially compensated by metal ions in tetrahedral voids. As a result, generally, per $(Co, Cr)_{1-\delta}O$ phases, an apparent increase of the concentration of cobalt vacancies can be observed (an increase of the deviation from the stoichiometry). It should be noted that at such a high concentration of dope ions, an influence over the value of ΔG_n^0 of the defects formation can be expected. Other considerations are: the formation of defect complexes and the interactions between defects (activity coefficients). As can be seen in Fig. 8, the concentrations of the vacancies $[V_{Co}^{\prime\prime}]$ are slightly lower than the deviation from the stoichiometry, which in a wide range of p_{O_2} is practically equal to the dope concentration. At higher oxygen pressures, there is a small increase in the deviation from the stoichiometry. As can be seen in Fig. 8a, the concentration of $[V_{Co}^{\prime\prime}]$ increases with the increase of the dope content. As can be seen in Fig. 8, according to the expectations, both concentrations of electron holes and $[Co_i^{\bullet\bullet}]$ decrease and the concentration of electrons increases when there is a higher amount of dope. Near the decomposition pressure, the concentration of electron holes is comparable to the concentration of electrons. Assuming that the ratio of mobilities is $\mu_{h^\bullet}/\mu_{e^-} = 0.1$ [4], in Fig. 4 the values of oxygen pressure ($p_{O_2}^{(\sigma m)}$) at which the ratio $[h^\bullet]/[e^-] = 10$ have been marked. As can be seen in Fig. 4,

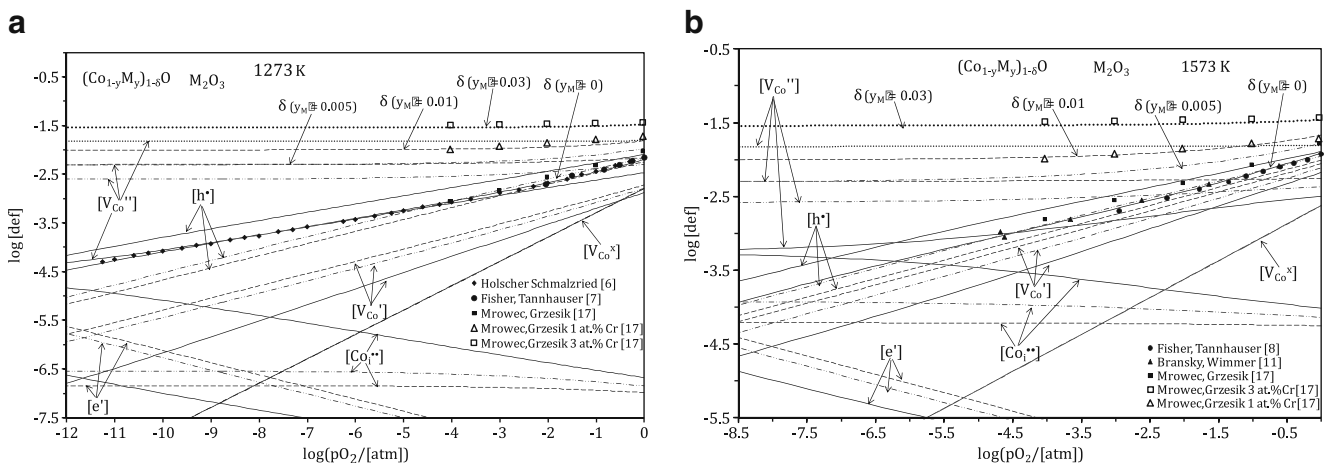


Fig. 8 Diagrams of point defects for pure $Co_{1-\delta}O$ (solid line) and for the $(Co_{1-y}M_y)_{1-\delta}O$ doped with M^{3+} ions (dashed line) obtained using the results of the studies on the deviation from the stoichiometry obtained by: **a** Schmalzried et al. [5, 6] for 1,273 K and **b** Bransky and Wimmer [11] for 1,573 K, for the dope content: $y_{M'} = 5 \cdot 10^{-3}$ mol/mol—dashed-dotted line, $1 \cdot 10^{-2}$ —dashed line,

$3 \cdot 10^{-2}$ —dotted line. The points mark the results of studies for pure $Co_{1-\delta}O$: (solid diamond)—Hölscher Schmalzried et al. [6], (solid circle)—Fisher and Tannhäuser [8], (solid triangle)—Bransky and Wimmer [11], (solid square)—Mrowec and Grzesik [17] and for Cr content $y_{Cr} = 1 \cdot 10^{-2}$ mol/mol points—(empty triangle), $3 \cdot 10^{-2}$ mol/mol—(empty square)

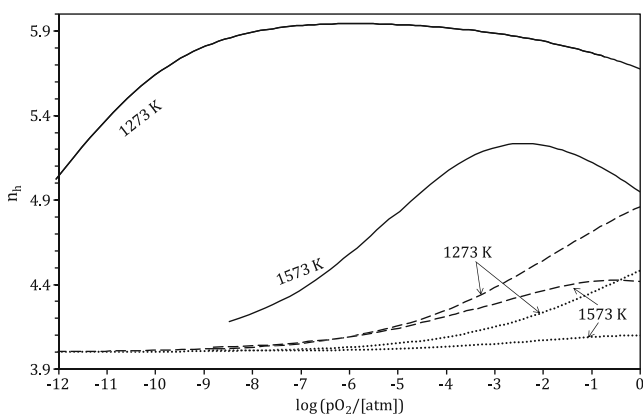


Fig. 9 Dependences of the derivative $n_h = d\log(p_{O_2})/d\log[h^\bullet]$ on $\log(p_{O_2})$ obtained for the dependence of the concentration of electron holes $[h^\bullet]$ on (p_{O_2}) (Fig. 8) and for the oxide doped with M^{3+} ions, for $y_M = 5 \cdot 10^{-3}$ mol/mol—dashed line, and $1 \cdot 10^{-2}$ —dotted line and $y_M = 0$ —solid line

these pressures are higher than the oxide decomposition pressure, which is in accordance with the presence of a minimum of the electrical conductivity in $(Co_{1-y}M_y)_{1-\delta}O$ oxide doped with Cr and Ti [21].

The dependence of the derivatives $n_h = \log(p_{O_2})/d\log[h^\bullet]$ on p_{O_2} is shown in Fig. 9. As can be seen in Fig. 9, the values of n_h in a wide range of p_{O_2} are near 4. They increase only at high oxygen pressures. The characteristic of the dependence is practically consistent with the studies of the electrical conductivity. In Table 2, the values of the exponent n_σ obtained for the dependence of σ on p_{O_2} for oxides doped with M^{3+} ions, obtained by many authors, are given and compared with the values of n_h obtained in the present work (Fig. 9) (in a similar range of p_{O_2}).

Conclusions

The obtained point defect diagrams in $Co_{1-\delta}O$ indicate that the proposed method of calculation enable the full interpretation of deviation from the stoichiometry studies (in the entire range of the oxide's existence). This method considers not only dominating defects (vacancies) but also interstitial ions, which have not been determined so far.

In the previous of a simplified method, only in the range where the determined types of defect dominated, the values of equilibrium constants (one to four values) for the considered reactions of the defects formation were adjusted in such a way that the calculated defects' concentrations fulfilled the electroneutrality condition. In the proposed method, knowing ΔG_F^0 of the electronic defects' formation, first the ΔG_F^0 , $\Delta G_{V_{Co}}^0$, are adjusted, and then $\Delta G_{V_{Co}}^0$ and $\Delta G_{V_{Co}^x}^0$ (connected by the relations 33, 36, and 1), and the obtained dependence of the deviation from the

stoichiometry is verified with the experimental results of δ . Thus, this approach is completely different.

The point defect diagrams in pure $Co_{1-\delta}O$, in the range from 1 atm to the oxide decomposition pressure, have been determined using the results of the deviation from the stoichiometry studies at 1,173–1,673 K obtained by many authors.

Using the results of Schmalzried et al. [5, 6], Fisher and Tannhauser [8], and Bransky and Wimmer [11], the values of ΔG_F^0 of the formation of Frenkel defects were determined, as well as their temperature dependence, which was then used in the interpretation of the results of different authors. The values of $\Delta G_{V_{Co}}^0$ of the cobalt vacancies' formation were determined, using the results of studies by many authors, which, with few exceptions, were consistent. The differences in the values of the deviation from the stoichiometry, observed between the results of the studies of different authors, in the range of high deviations from the stoichiometry (near p_{O_2} 1 atm), were corrected by adjusting the values of $\Delta G_{V_{Co}}^0$ of the formation of single-ionized and neutral vacancies $\Delta G_{V_{Co}^x}^0$. A change in the nature of the temperature dependence of $\Delta G_{V_{Co}}^0$ and $\Delta G_{V_{Co}^x}^0$ occurs on the above 1,500 K. The decrease in the value of $\Delta G_{V_{Co}}^0$ of the formation of single-ionized vacancies with the temperature increase indicates that in $Co_{1-\delta}O$ at high deviations from the stoichiometry a more complex defect structure could be present. Therefore, the presence of defect complexes and/or interactions between defects (activity coefficients) should also be considered. This problem will be presented in the next work.

The obtained point defect diagrams indicate that when the temperature increases, the dependences of the concentrations of individual defects on the pressure p_{O_2} vary significantly despite the fact that the character of the dependence of the deviation from the stoichiometry is rather close (exponent 1/4). This is related before all else to the fact that the interstitial cobalt ions are taken into account.

The character of the dependence of the electron holes' concentration on p_{O_2} is practically independent from the temperature and varies to a small degree with the temperature increase, but to use this basis for a conclusion whereby in the whole range of the oxide existence single-ionized vacancies dominate is an excessive approximation.

It has been shown that the oxygen pressures at which the minimum of the electrical conductivity should occur are lower than the oxide decomposition pressure. However, they are consistent with the extrapolated values resulting from the studies of the Seebeck effect.

Using the determined values of ΔG^0 of the defect formation for the pure cobalt oxide, the dependencies of

the defects' concentrations for $(Co_{1-y}M_y)_{1-\delta}O$ doped with M^+ and M^{3+} ions were determined. The determined diagrams for the oxide doped with M^+ ions are consistent with the results of the studies on the deviation from the stoichiometry. It has been shown that even a low quantity of the dope causes the oxide to reach its stoichiometric composition in the range of its existence. In the range of negative values of the deviation from stoichiometry, there is a significant concentration of interstitial cobalt ions which causes a shift of the value of the oxygen pressure at which the oxide reaches the stoichiometric composition. It showed full consistency with the results of Fisher and Wagner [9]. The concentration of electron holes also increases in relation to that in the non-doped oxide, which is consistent with the studies on the electrical conductivity.

The obtained defect diagrams for the oxide doped with M^{3+} ions are consistent with the studies on the deviation from the stoichiometry and the electrical conductivity. As a result of the increase of the M^{3+} ions' concentration, the concentration of the cobalt vacancies increases and the concentration of electron holes decreases. Due to these changes near the oxide decomposition pressure, the concentrations of the electronic defects are comparable. The determined oxygen pressures for which the ratio of the concentration of electron holes to the concentration of electrons is $[h^\bullet]/[e'] = 10$ are consistent with the pressures at which the minimum of the electrical conductivity of the oxide $(Co_{1-y}M_y)_{1-\delta}O$ doped with Cr and Ti occurs.

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Appendix

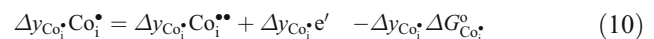
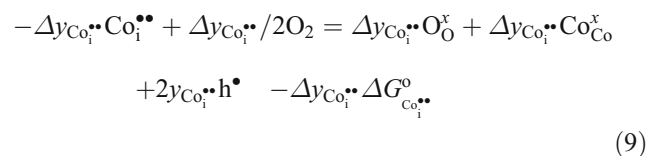
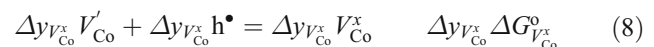
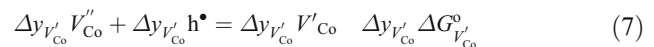
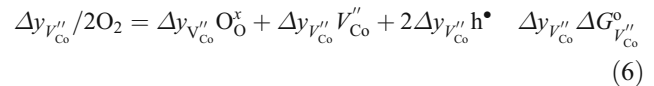
Theoretical background of the method for calculating the point defect diagrams

Determining the defect concentrations in non-doped $Co_{1-\delta}O$

The method of determining the point defect diagram in an oxide with defects in the cation sublattice is based on the equation describing the state that is formed as a result of oxygen incorporation and formation of a definite deviation from the stoichiometry (at a given oxygen pressure).

We assume that the point defects still form an ideal solution. The initial state for the calculations of defect concentrations is assumed to be the stoichiometric composition of the oxide, in which there is a determined

concentration of intrinsic ionic defects (Frenkel defects) and electronic defects. As a result of the increase in oxygen pressure and the formation of the deviation from the stoichiometry δ , the reactions of the formation of the cobalt vacancies and the decrease of the concentration of interstitial cobalt ions in the $Co_{1-\delta}O$ oxide, according to the Kröger–Vink symbolism can be described by the following reactions:



where Δy_n design the changes in the concentrations of the individual defects relative to the concentrations that occur at the stoichiometric composition and ΔG_n^0 are standard Gibbs energies of the individual reactions. By adding the reactions (6)–(11) and dividing them by the total quantity of the incorporated oxygen $(\Delta y_{V''_{Co}} + \Delta y_{Co_i^{\bullet\bullet}})$, we get the equation describing the formation and decay of the determined quantities of point defects (mole fractions) as a result of the incorporation on 1 mol of oxygen atoms (into a determined, sufficiently large volume of the oxide):

$$\begin{aligned} & \frac{1}{2} O_2 + \frac{\Delta y_{Co_i^{\bullet\bullet}} - \Delta y_{Co_i^{\bullet}} Co_i^{\bullet\bullet}}{\Delta y_{V''_{Co}} + \Delta y_{Co_i^{\bullet\bullet}}} \\ & + \frac{\Delta y_{Co_i^{\bullet}} - \Delta y_{Co_i^x} Co_i^{\bullet}}{\Delta y_{V''_{Co}} + \Delta y_{Co_i^{\bullet\bullet}}} + \frac{\Delta y_{Co_i^x}}{\Delta y_{V''_{Co}} + \Delta y_{Co_i^{\bullet\bullet}}} Co_i^x = O_O \\ & + Co_{Co}^{x(surf)} + \frac{\Delta y_{V''_{Co}} - \Delta y_{V'_{Co}} V_{Co}''}{\Delta y_{V''_{Co}} + \Delta y_{Co_i^{\bullet\bullet}}} + \frac{\Delta y_{V'_{Co}} - \Delta y_{V^x_{Co}} V'_{Co}}{\Delta y_{V''_{Co}} + \Delta y_{Co_i^{\bullet\bullet}}} \\ & + \frac{\Delta y_{V^x_{Co}} V_{Co}^x}{\Delta y_{V''_{Co}} + \Delta y_{Co_i^{\bullet\bullet}}} + \left(2 - \frac{\Delta y_{V'_{Co}} + \Delta y_{V^x_{Co}}}{\Delta y_{V''_{Co}} + \Delta y_{Co_i^{\bullet\bullet}}} \right) h^\bullet \\ & + \frac{\Delta y_{Co_i^{\bullet}} + \Delta y_{Co_i^x} e'}{\Delta y_{V''_{Co}} + \Delta y_{Co_i^{\bullet\bullet}}} \quad \Delta G_{def}^{o(\delta)} \quad (12) \end{aligned}$$

The standard Gibbs energy of the above process $\Delta G_{\text{def}}^{o(\delta)}$ (the resultant standard Gibbs energies of the defects' formation per 1 mol of oxygen atoms) is the sum ΔG_n^o of processes 6–11 and is expressed by the equation:

$$\begin{aligned} \Delta G_{\text{def}}^{o(\delta)} &= \frac{\Delta y_{V_{\text{Co}}''}}{\Delta y_{V_{\text{Co}}''} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{V_{\text{Co}}''}^o - \frac{\Delta y_{\text{Co}_i^{\bullet\bullet}}}{\Delta y_{V_{\text{Co}}''} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{\text{Co}_i^{\bullet\bullet}}^o + \\ &+ \frac{\Delta y_{V_{\text{Co}}'}}{\Delta y_{V_{\text{Co}}'} + \Delta y_{\text{Co}_i^{\bullet}}} \Delta G_{V_{\text{Co}}'}^o - \frac{\Delta y_{\text{Co}_i^{\bullet}}}{\Delta y_{V_{\text{Co}}'} + \Delta y_{\text{Co}_i^{\bullet}}} \Delta G_{\text{Co}_i^{\bullet}}^o + \\ &+ \frac{\Delta y_{V_{\text{Co}}^x}}{\Delta y_{V_{\text{Co}}^x} + \Delta y_{\text{Co}_i^x}} \Delta G_{V_{\text{Co}}^x}^o - \frac{\Delta y_{\text{Co}_i^x}}{\Delta y_{V_{\text{Co}}^x} + \Delta y_{\text{Co}_i^x}} \Delta G_{\text{Co}_i^x}^o \end{aligned} \tag{13}$$

From the condition of the equality of the chemical potentials of components from the Eq. 12 in the equilibrium state, the dependence of the defects' concentration on the oxygen pressure adopts the following form:

$$\begin{aligned} &\frac{\Delta y_{V_{\text{Co}}''}}{\Delta y_{V_{\text{Co}}''} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \ln[V_{\text{Co}}''] + \frac{\Delta y_{V_{\text{Co}}'}}{\Delta y_{V_{\text{Co}}'} + \Delta y_{\text{Co}_i^{\bullet}}} \ln[V_{\text{Co}}'] \\ &+ \frac{\Delta y_{V_{\text{Co}}^x}}{\Delta y_{V_{\text{Co}}^x} + \Delta y_{\text{Co}_i^x}} \ln[V_{\text{Co}}^x] + \left(2 - \frac{\Delta y_{V_{\text{Co}}''} + \Delta y_{V_{\text{Co}}^x}}{\Delta y_{V_{\text{Co}}''} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \right) \\ &\ln[h^{\bullet}] + \frac{\Delta y_{\text{Co}_i^{\bullet}} + \Delta y_{\text{Co}_i^x}}{\Delta y_{V_{\text{Co}}''} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \ln[e'] - 1/2 \ln p_{\text{O}_2} - \\ &\frac{\Delta y_{\text{Co}_i^{\bullet\bullet}}}{\Delta y_{V_{\text{Co}}''} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \ln[\text{Co}_i^{\bullet\bullet}] - \frac{\Delta y_{\text{Co}_i^{\bullet}}}{\Delta y_{V_{\text{Co}}''} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \ln[\text{Co}_i^{\bullet}] \\ &- \frac{\Delta y_{\text{Co}_i^x}}{\Delta y_{V_{\text{Co}}''} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \ln[\text{Co}_i^x] = \frac{-\Delta G_{\text{def}}^{o(\delta)}}{RT} \end{aligned} \tag{14}$$

where the concentrations of the individual point defects (per 1 mol of oxide) are:

$$[V_{\text{Co}}''] = y_{V_{\text{Co}}''}^o + \Delta y_{V_{\text{Co}}''} - \Delta y_{V_{\text{Co}}''} = y_{V_{\text{Co}}''}^o + \Delta y_{V_{\text{Co}}''} \tag{15}$$

$$[V_{\text{Co}}'] = y_{V_{\text{Co}}'}^o + \Delta y_{V_{\text{Co}}'} - \Delta y_{V_{\text{Co}}^x} = y_{V_{\text{Co}}'}^o + \Delta y_{V_{\text{Co}}'} \tag{16}$$

$$[V_{\text{Co}}^x] = y_{V_{\text{Co}}^x}^o + \Delta y_{V_{\text{Co}}^x} \tag{17}$$

$$[\text{Co}_i^{\bullet\bullet}] = y_{\text{Co}_i^{\bullet\bullet}}^o - \Delta y_{\text{Co}_i^{\bullet\bullet}} + \Delta y_{\text{Co}_i^{\bullet\bullet}} = y_{\text{Co}_i^{\bullet\bullet}}^o - \Delta y_{\text{Co}_i^{\bullet\bullet}} \tag{18}$$

$$[\text{Co}_i^{\bullet}] = y_{\text{Co}_i^{\bullet}}^o - \Delta y_{\text{Co}_i^{\bullet}} + \Delta y_{\text{Co}_i^x} = y_{\text{Co}_i^{\bullet}}^o - \Delta y_{\text{Co}_i^{\bullet}} \tag{19}$$

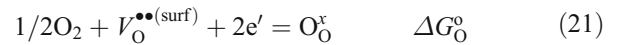
$$[\text{Co}_i^x] = y_{\text{Co}_i^x}^o - \Delta y_{\text{Co}_i^x} \tag{20}$$

where y_n^o are the concentrations of the individual defects at the stoichiometric composition. The Eqs. 13 and 14, where one type of defect dominates, have a simple and well-established form, and are used in the determination of the enthalpy and entropy of their formation.

Relations between the standard Gibbs energies of the defects formation

The process of the formation of cobalt vacancies is related to the process of oxygen incorporation and to the proper process of the formation of a cobalt vacancy. Thus, it can be analyzed in the following steps:

- A molecule of oxygen on the oxide surface undergoes dissociative adsorption and, taking an electron, becomes a nodal ion:

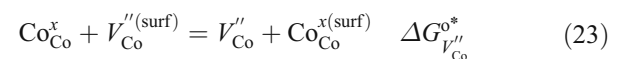


where $V_{\text{O}}^{\bullet\bullet(\text{surf})}$ is a two-positive surface oxygen vacancy and ΔG_{O}^o is the standard Gibbs energy of the oxygen incorporation. Simultaneously with this process, the process of the formation of electronic defects must occur, according to the reaction:



where ΔG_i^o is the standard Gibbs energy of the process of the formation of electronic defects.

Such a state causes the formation of a gradient of chemical potential of metal and oxygen, which results in the diffusion of metal ions to the surface and in the formation of cation vacancies. The proper process of the formation of cobalt vacancies is thus presented by the reaction:



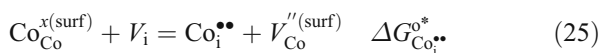
where $V_{\text{Co}}^{\prime\prime(\text{surf})}$ is a surface cobalt vacancy and $\Delta G_{V_{\text{Co}}^{\prime\prime}}^{o*}$ of the above process is the standard Gibbs energy of their formation.

The standard Gibbs energy of the formation of the cation vacancies (according to the Eq. 6) is a sum of ΔG_n^o of processes 21–23:

$$\Delta G_{V_{\text{Co}}^{\prime\prime}}^o = (\Delta G_{\text{O}}^o + 2\Delta G_i^o) + \Delta G_{V_{\text{Co}}^{\prime\prime}}^{o*} \tag{24}$$

Similarly, the process of the formation of interstitial cobalt ions is related to the release of an oxygen atom, according to the processes 21 and 22, going in an inverse direction, and to the passage of a cobalt ion

from the surface to an interstitial position, which is described by the reaction:



where $\Delta G_{\text{Co}_i^{\bullet\bullet}}^{\circ*}$ is the *standard Gibbs energy of the process of the formation of interstitial cobalt ions*. The standard Gibbs energy of the formation of the interstitial cobalt ions is the sum of ΔG° of the processes of the oxygen release (Eqs. 21 and 22) and the formation of $\text{Co}_i^{\bullet\bullet}$ (Eq. 25):

$$\Delta G_{\text{Co}_i^{\bullet\bullet}}^{\circ} = -(\Delta G_{\text{O}}^{\circ} + 2\Delta G_i^{\circ}) + \Delta G_{\text{Co}_i^{\bullet\bullet}}^{\circ*} \quad (26)$$

- The standard Gibbs energy of the reaction (12) is thus the sum of the ΔG° of the incorporation of 1 mol of oxygen and of the formation and the decay of the appropriate fractions of concentration of the defects which is expressed by the equation:

$$\begin{aligned} \Delta G_{\text{def}}^{\circ(\delta)} &= \Delta G_{\text{O}}^{\circ} + 2\Delta G_i^{\circ} + \frac{\Delta y_{V_{\text{Co}}^{\prime\prime}}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{V_{\text{Co}}^{\prime\prime}}^{\circ*} \\ &- \frac{\Delta y_{\text{Co}_i^{\bullet\bullet}}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{\text{Co}_i^{\bullet\bullet}}^{\circ*} + \frac{\Delta y_{V_{\text{Co}}^{\prime}}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{V_{\text{Co}}^{\prime}}^{\circ} \\ &- \frac{\Delta y_{\text{Co}_i^{\bullet}}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{\text{Co}_i^{\bullet}}^{\circ} + \frac{\Delta y_{V_{\text{Co}}^x}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{V_{\text{Co}}^x}^{\circ} \\ &- \frac{\Delta y_{\text{Co}_i^x}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{\text{Co}_i^x}^{\circ} \end{aligned} \quad (27)$$

- The sum of standard Gibbs energies of the formation of defects in the cation sublattice is equal to the standard Gibbs energy of the formation of intrinsic Frenkel-type defects ($\Delta G_{\text{F}}^{\circ}$):

$$\Delta G_{V_{\text{Co}}^{\prime\prime}}^{\circ} + \Delta G_{\text{Co}_i^{\bullet\bullet}}^{\circ} = \Delta G_{V_{\text{Co}}^{\prime\prime}}^{\circ*} + \Delta G_{\text{Co}_i^{\bullet\bullet}}^{\circ*} = \Delta G_{\text{F}}^{\circ} \quad (28)$$

The energetic changes in a crystal resulting from the formation of cation vacancies and interstitial ions can be different. Generally, the difference between the heat effects of their formation should be non-zero:

$$\Delta G_{V_{\text{Co}}^{\prime\prime}}^{\circ*} - \Delta G_{V_{\text{Co}}^{\prime\prime}}^{\circ} = D \neq 0 \quad (29)$$

The standard Gibbs energy of the formation of ionic defects can be thus related to the $\Delta G_{\text{F}}^{\circ}$ of the formation

of intrinsic Frenkel-type defects by the following equations:

$$\Delta G_{V_{\text{Co}}^{\prime\prime}}^{\circ*} = 1/2(\Delta G_{\text{F}}^{\circ} + D) \quad (30)$$

$$\Delta G_{\text{Co}_i^{\bullet\bullet}}^{\circ*} = 1/2(\Delta G_{\text{F}}^{\circ} - D) \quad (31)$$

The standard Gibbs energy of the process 12 (Eq. 27) then has the form of:

$$\begin{aligned} \Delta G_{\text{def}}^{\circ(\delta)} &= \Delta G_{\text{O}}^{\circ} + 2\Delta G_i^{\circ} + \frac{1}{2}D + \frac{\Delta y_{V_{\text{Co}}^{\prime\prime}} - \Delta y_{\text{Co}_i^{\bullet\bullet}}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{\text{F}}^{\circ} + \\ &+ \frac{\Delta y_{V_{\text{Co}}^{\prime}}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{V_{\text{Co}}^{\prime}}^{\circ} - \frac{\Delta y_{\text{Co}_i^{\bullet}}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{\text{Co}_i^{\bullet}}^{\circ} + \\ &+ \frac{\Delta y_{V_{\text{Co}}^x}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{V_{\text{Co}}^x}^{\circ} - \frac{\Delta y_{\text{Co}_i^x}}{\Delta y_{V_{\text{Co}}^{\prime\prime}} + \Delta y_{\text{Co}_i^{\bullet\bullet}}} \Delta G_{\text{Co}_i^x}^{\circ} \end{aligned} \quad (32)$$

Near the stoichiometric composition ($\delta \approx 0$) the value of $\Delta G_{\text{def}}^{\circ(\delta \approx 0)}$ according to the Eq. 32 is dependent on $\Delta G_{\text{O}}^{\circ}$ of oxygen incorporation, on the D parameter and on the values of the terms being the product of the determined fractions of forming and decaying defects and $\Delta G_{\text{F}}^{\circ}$ and $\Delta G_{\text{n}}^{\circ}$ of defects with lower ionization degrees.

The standard Gibbs energy of the defects' formation in an oxide near the stoichiometric composition

It can be easily shown that near the stoichiometric composition (when $\delta \approx 0$), the fractions of changes in the defect concentrations in the Eq. 32 tend to the values of fractions of concentrations that are present at the stoichiometric composition. The Eq. 32 then has the following form:

$$\begin{aligned} \Delta G_{\text{def}}^{\circ(\delta \approx 0)} &= \Delta G_{\text{O}}^{\circ} + 2\Delta G_i^{\circ} + \frac{1}{2}D + \frac{1 + \alpha_1 + \alpha_2 - \beta - \beta_1 - \beta_2}{1 + \alpha_1 + \alpha_2 + \beta + \beta_1 + \beta_2} \Delta G_{\text{F}}^{\circ} + \\ &+ \frac{\alpha_1 + \alpha_2}{M} \Delta G_{V_{\text{Co}}^{\prime}}^{\circ} - \frac{\beta_1 + \beta_2}{M} \Delta G_{\text{Co}_i^{\bullet}}^{\circ} + \frac{\alpha_2}{M} \Delta G_{V_{\text{Co}}^x}^{\circ} - \frac{\beta_2}{M} \Delta G_{\text{Co}_i^x}^{\circ} \end{aligned} \quad (33)$$

where α_1 , α_2 , β , β_1 , and β_2 determine the relative ratios of concentrations of the appropriate defects:

$$\begin{aligned} \frac{y_{V_{\text{Co}}^{\prime}}^{\circ}}{y_{V_{\text{Co}}^{\prime\prime}}^{\circ}} &= \alpha_1, & \frac{y_{V_{\text{Co}}^x}^{\circ}}{y_{V_{\text{Co}}^{\prime\prime}}^{\circ}} &= \alpha_2, & \frac{y_{\text{Co}_i^{\bullet\bullet}}^{\circ}}{y_{V_{\text{Co}}^{\prime\prime}}^{\circ}} &= \beta, & \frac{y_{\text{Co}_i^{\bullet}}^{\circ}}{y_{V_{\text{Co}}^{\prime\prime}}^{\circ}} &= \beta_1, \\ \frac{y_{\text{Co}_i^x}^{\circ}}{y_{V_{\text{Co}}^{\prime\prime}}^{\circ}} &= \beta_2 \end{aligned}$$

$$M = 1 + \alpha_1 + \alpha_2 + \beta + \beta_1 + \beta_2$$

When $\beta=1$ and $\alpha_1=\beta_1$ and $\alpha_2=\beta_2$, then the value of the (F) term:

$$F = \frac{1 + \alpha_1 + \alpha_2 - \beta - \beta_1 - \beta_2}{1 + \alpha_1 + \alpha_2 + \beta + \beta_1 + \beta_2} \Delta G_F^o = 0 \tag{34}$$

On the other hand, when $\Delta G_{V_{Co}''}^o = \Delta G_{Co_i^*}^o$ and $\Delta G_{V_{Co}^x}^o = \Delta G_{Co_i^*}^o$, the I term has a near-zero value:

$$I = \frac{\alpha_1 + \alpha_2}{M} \Delta G_{V_{Co}''}^o - \frac{\beta_1 + \beta_2}{M} \Delta G_{Co_i^*}^o + \frac{\alpha_2}{M} \Delta G_{V_{Co}^x}^o - \frac{\beta_2}{M} \Delta G_{Co_i^*}^o = 0 \tag{35}$$

Furthermore, the Eq. 14 has the following form:

$$\begin{aligned} & \frac{1}{M} \ln(y_{V_{Co}''}^o) + \frac{\alpha_1}{M} \ln(y_{V_{Co}'}^o) + \frac{\alpha_2}{M} \ln(y_{V_{Co}^x}^o) + \\ & + (2 - \frac{\alpha_1 + 2\alpha_2}{M}) \ln[h^*] + \frac{\beta_1 + 2\beta_2}{M} \ln[e'] - \frac{1}{2} \ln(p_{O_2}^{(s)}) - \\ & - \frac{\beta}{M} \ln(y_{Co_i^*}^o) - \frac{\beta_1}{M} \ln(y_{Co_i^*}^o) - \frac{\beta_2}{M} \ln(y_{Co_i^*}^o) = \frac{-\Delta G_{def}^{o(\delta \approx 0)}}{RT} \end{aligned} \tag{36}$$

where $p_{O_2}^{(s)}$ is the oxygen pressure at which the oxide reaches the stoichiometric composition.

Using the Eqs. 33 and 36 (as well as Eqs. 24, 26, 30, and 31), we get the expressions determining the standard Gibbs energy of the formation of cobalt vacancies:

$$\Delta G_{V_{Co}''}^o = (\Delta G_{def}^{o(\delta \approx 0)} - F - I) + 1/2 \Delta G_F^o \tag{37}$$

and that of interstitial cations:

$$\Delta G_{Co_i^*}^o = -(\Delta G_{def}^{o(\delta \approx 0)} - F - I) + 1/2 \Delta G_F^o \tag{38}$$

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