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

Andrzej Stokłosa

Received: 11 August 2010 / Revised: 9 February 2011 / Accepted: 13 February 2011 / Published online: 31 March 2011
© The Author(s) 2011. This article is published with open access at Springerlink.com

Abstract The point defect diagrams in nickel oxide $\text{Ni}_{1-\delta}\text{O}$, 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 the formation of nickel 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 nickel oxide · $\text{Ni}_{1-\delta}\text{O} \cdot \text{M}^+ \cdot \text{M}^{3+}$ ion dopes

Introduction

Nickel oxide $\text{Ni}_{1-\delta}\text{O}$ is considered as a model non-stoichiometric semiconductor oxide of p-type. The studies of optical and magnetical properties of pure and doped oxide [1–13] allowed for the determination of its electronic structure. Due to the low concentration of point defects, it is assumed that they form an ideal solution. In order to determine the point defect structure at high temperatures, the studies on the deviation from the stoichiometry were performed by the following methods: electrochemical [14–16], thermogravimetric [13, 17–21],

and via the studies of the electrical conductivity [10–13, 16, 17, 22–38]. The character of the dependence of the deviation from the stoichiometry on the oxygen pressure (the exponent close to $\approx 1/6$) formed the basis for the thesis that in $\text{Ni}_{1-\delta}\text{O}$, the dominating defects are double ionized nickel vacancies and electron holes. In the case of the electrical conductivity studies, however, the consistency is not complete. Many authors obtained the value of the exponent $1/n_\sigma$ close to $\sim 1/6$ [12, 16, 17, 38]. In most works, higher values were obtained (1/5), also close to 1/4 [10, 11, 22, 23, 25]. Using the above fact as a basis, it is assumed that in $\text{Ni}_{1-\delta}\text{O}$, single ionized vacancies are also present. It has been also shown that the differences in the $1/n_\sigma$ exponent, values are related to the influence of impurities on the concentration of electron holes [10–13, 28, 35]. Due to the narrow range in the studies on the deviation from the stoichiometry, a full point defect diagram has not yet been determined. On the other hand, using a simplified electroneutrality condition as our basis, the concentrations of electron holes and double ionized nickel vacancies were calculated. There are discrepancies in the concentration of single ionized vacancies. The studies on the chemical diffusion [19–21, 29–41] and of the self diffusion of nickel [19, 41–46], performed mainly at higher oxygen pressures, indicate that the matter transport in $\text{Ni}_{1-\delta}\text{O}$ occurs generally via double ionized nickel vacancies. A similar conclusion could be obtained from the relation between the concentration of defects, the diffusion coefficients, and the parabolic rate constants of nickel oxidation [21, 47–51].

A relatively simple defect structure in the $\text{Ni}_{1-\delta}\text{O}$, which was considered a model structure, was used to determine the influence of dopes on the electronic defects' concentration, electrical properties, and the matter transport in this oxide. Studies on the influence of ions: M^{3+}

A. Stokłosa (✉)
Faculty of Chemical Engineering and Technology,
Cracow University of Technology,
31-155 Cracow, Poland
e-mail: astoklos@indy.chemia.pk.edu.pl

(Cr₂O₃) [12, 27, 30, 36, 37, 52–60] and M⁺ (Li₂O) [6, 7, 40, 52, 53] have been performed. The obtained dependencies of the electrical conductivity on the oxygen pressure for doped oxides agree with the theoretical expectations. However, no information on the influence of dopes on the ionic defects' concentration is available.

The previous work [61] presented the results of the calculations of the point defect diagrams for pure and doped cobalt oxide, using the results of studies on the deviation from the stoichiometry by many authors, and it has been shown that when the interstitial cobalt ions are taken into account, there are drastic changes in the relations between defect concentrations and the oxygen pressure in “pure” oxide as well as in the oxide doped with M⁺ and M³⁺ ions.

The present work, still concerned with the issue of the concentrations of defects in oxides with defects in the cation sublattice, deals with the problem of the determination of the point defect diagram for nickel oxide Ni_{1-δ}O, pure and doped with M³⁺ and M⁺ metal ions, taking into

consideration all types of defects in the cation sublattice, also interstitial nickel ions. The following were used in the calculations of the diagrams: a method presented in the work [61] and the experimental values of the deviation from the stoichiometry obtained by many authors [13–15, 17, 18, 21] in the temperature range of 1,173–1,673 K.

Method of determining the point defect diagrams

The theoretical foundations of the above method are more widely presented in the work [61]. They are 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). The equation describing the process of the formation and the decay of the determined quantities of the point defects (mole fractions) as a result of the incorporation of 1 mole of oxygen has the form of:

$$\begin{aligned} & \frac{1}{2} \text{O}_2 + \frac{\Delta y_{\text{Ni}^{\bullet\bullet}} - \Delta y_{\text{Ni}^{\bullet}}}{\Delta y_{\text{V}''_{\text{Ni}}} + \Delta y_{\text{Ni}^{\bullet\bullet}}} \text{Ni}_i^{\bullet\bullet} + \frac{\Delta y_{\text{Ni}^{\bullet}} - \Delta y_{\text{Ni}^{\text{x}}}}{\Delta y_{\text{V}''_{\text{Ni}}} + \Delta y_{\text{Ni}^{\bullet\bullet}}} \text{Ni}_i^{\bullet} + \frac{\Delta y_{\text{Ni}^{\text{x}}}}{\Delta y_{\text{V}''_{\text{Ni}}} + \Delta y_{\text{Ni}^{\bullet\bullet}}} \text{Ni}_i^{\text{x}} = \\ & = \text{O}_\text{O} + \text{Ni}_i^{\text{x(surf)}} + \frac{\Delta y_{\text{V}''_{\text{Ni}}} - \Delta y_{\text{V}'_{\text{Ni}}}}{\Delta y_{\text{V}''_{\text{Ni}}} + \Delta y_{\text{Ni}^{\bullet\bullet}}} \text{V}''_{\text{Ni}} + \frac{\Delta y_{\text{V}'_{\text{Ni}}} - \Delta y_{\text{V}^{\text{x}}_{\text{Ni}}}}{\Delta y_{\text{V}''_{\text{Ni}}} + \Delta y_{\text{Ni}^{\bullet\bullet}}} \text{V}'_{\text{Ni}} + \frac{\Delta y_{\text{V}^{\text{x}}_{\text{Ni}}}}{\Delta y_{\text{V}''_{\text{Ni}}} + \Delta y_{\text{Ni}^{\bullet\bullet}}} \text{V}^{\text{x}}_{\text{Ni}} \\ & + \left(2 - \frac{\Delta y_{\text{V}'_{\text{Ni}}} + \Delta y_{\text{V}^{\text{x}}_{\text{Ni}}}}{\Delta y_{\text{V}''_{\text{Ni}}} + \Delta y_{\text{Ni}^{\bullet\bullet}}} \right) \text{h}^{\bullet} + \frac{\Delta y_{\text{Ni}^{\bullet}} + \Delta y_{\text{Ni}^{\text{x}}}}{\Delta y_{\text{V}''_{\text{Ni}}} + \Delta y_{\text{Ni}^{\bullet\bullet}}} \text{e}' \quad \Delta G_{\text{def}}^{\text{o}(\delta)} \end{aligned} \quad (1)$$

where Δy_i is the change of concentrations of individual defects relative to the concentration y_i^0 at the stoichiometric composition, $\Delta G_{\text{def}}^{\text{o}(\delta)}$ is the standard Gibbs energy of the process 1.

The dependence of the defect concentration on the oxygen pressure in the equilibrium state, resulting from the condition of equality of chemical potentials of the components from the Eq. 1, has the following form:

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

where the concentrations of point defects, resulting from the changes in the concentrations of individual defects (Δy_i), relative to the concentration (y_i^0) at the stoichiometric composition (per 1 mole of oxygen) are:

$$[\text{V}''_{\text{Ni}}] = y_{\text{V}''_{\text{Ni}}}^0 + \Delta y_{\text{V}''_{\text{Ni}}} - \Delta y_{\text{V}'_{\text{Ni}}} = y_{\text{V}''_{\text{Ni}}}^0 + \Delta y'_{\text{V}''_{\text{Ni}}} \quad (3a)$$

$$[\text{V}'_{\text{Ni}}] = y_{\text{V}'_{\text{Ni}}}^0 + \Delta y_{\text{V}'_{\text{Ni}}} - \Delta y_{\text{V}^{\text{x}}_{\text{Ni}}} = y_{\text{V}'_{\text{Ni}}}^0 + \Delta y'_{\text{V}'_{\text{Ni}}} \quad (3b)$$

$$[\text{V}^{\text{x}}_{\text{Ni}}] = y_{\text{V}^{\text{x}}_{\text{Ni}}}^0 + \Delta y_{\text{V}^{\text{x}}_{\text{Ni}}} \quad (3c)$$

$$[\text{Ni}_i^{\bullet\bullet}] = y_{\text{Ni}_i^{\bullet\bullet}}^0 - \Delta y_{\text{Ni}_i^{\bullet\bullet}} + \Delta y_{\text{Ni}_i^{\bullet}} = y_{\text{Ni}_i^{\bullet\bullet}}^0 - \Delta y'_{\text{Ni}_i^{\bullet\bullet}} \quad (3d)$$

$$[\text{Ni}_i^{\bullet}] = y_{\text{Ni}_i^{\bullet}}^0 - \Delta y_{\text{Ni}_i^{\bullet}} + \Delta y_{\text{Ni}_i^{\text{x}}} = y_{\text{Ni}_i^{\bullet}}^0 - \Delta y'_{\text{Ni}_i^{\bullet}} \quad (3e)$$

$$[\text{Ni}_i^{\text{x}}] = y_{\text{Ni}_i^{\text{x}}}^0 - \Delta y_{\text{Ni}_i^{\text{x}}} \quad (3f)$$

The work [61] demonstrated that the Eq. 2 for strictly determined concentrations of defects, which are present at the stoichiometric composition, $\delta \approx 0$, has the following form:

$$\begin{aligned} & \frac{1}{M} \ln(y_{V_{Ni}}^o) + \frac{\alpha_1}{M} \ln(y_{V_{Ni}}^o) + \frac{\alpha_2}{M} \ln(y_{V_{Ni}}^o) + \\ & + (2 - \frac{\alpha_1 + 2\alpha_2}{M}) \ln[h^\bullet] + \frac{\beta_1 + 2\beta_2}{M} \ln[e'] - \frac{1}{2} \ln(p_{O_2}^{(s)}) - \\ & - \frac{\beta}{M} \ln(y_{Ni_i^{\bullet\bullet}}^o) - \frac{\beta_1}{M} \ln(y_{Ni_i^{\bullet}}^o) - \frac{\beta_2}{M} \ln(y_{Ni_i^x}^o) = \frac{-\Delta G_{def}^{o(\delta \approx 0)}}{RT} \end{aligned} \quad (4)$$

where: α_1 , α_2 , β , β_1 , and β_2 , define the ratio of the concentrations of the individual defects to the concentration V_{Ni}'' :

$$\frac{y_{V_{Ni}}^o}{y_{V_{Ni}}^{o'}} = \alpha_1, \frac{y_{V_{Ni}}^o}{y_{V_{Ni}}^{o''}} = \alpha_2, \frac{y_{Ni_i^{\bullet\bullet}}^o}{y_{Ni_i^{\bullet}}^o} = 1, \frac{y_{Ni_i^{\bullet}}^o}{y_{Ni_i^x}^o} = \beta_1, \frac{y_{Ni_i^x}^o}{y_{V_{Ni}}^{o''}} = \beta_2$$

y_i^o is the concentration of a given defect i at the stoichiometric composition, $M = 2 + \alpha_1 + \alpha_2 + \beta_1 + \beta_2$, $\Delta G_{def}^{o(\delta \approx 0)}$ is the standard Gibbs energy of the process (1) at $\delta \approx 0$, $p_{O_2}^{(s)}$ is the oxygen pressure at which the oxide reaches the stoichiometric composition.

The standard Gibbs energy of the formation of nickel vacancies V_{Ni}'' and interstitial nickel ions $Ni_i^{\bullet\bullet}$ can be expressed by the equation:

$$\Delta G_{V_{Ni}}^o = (\Delta G_{def}^{o(\delta \approx 0)} - F - I) + 1/2 \Delta G_F^o \quad (5)$$

$$\Delta G_{Ni_i^{\bullet\bullet}}^o = -(\Delta G_{def}^{o(\delta \approx 0)} - F - I) + 1/2 \Delta G_F^o \quad (6)$$

where

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

when $\beta=1$ and $\alpha_1=\beta_1$, $\alpha_2=\beta_2$ then the value of the F term is 0:

On the other hand the I term is:

$$\begin{aligned} I &= \frac{\alpha_1 + \alpha_2}{M} \Delta G_{V_{Ni}}^o - \frac{\beta_1 + \beta_2}{M} \Delta G_{Ni_i^{\bullet}}^o + \frac{\alpha_2}{M} \Delta G_{V_{Ni}}^o \\ & - \frac{\beta_2}{M} \Delta G_{Ni_i^x}^o \\ &= 0 \end{aligned}$$

when standard Gibbs energy of the formation of defects with lower ionization degrees $\Delta G_{V_{Ni}}^o = \Delta G_{Ni_i^{\bullet}}^o$ and $\Delta G_{V_{Ni}}^o = \Delta G_{Ni_i^x}^o$ then $I=0$.

The obtained Eqs. 4 and 5 relate ΔG^o of the formation of the defects and their concentration at the stoichiometric composition. They can be used in their determination, and knowing their values is useful when calculating the concentrations of the defects at any oxygen pressure. Thus, if we have the value ΔG_i^o of the electronic defect formation, determined

from the electrical measurements, it is possible to adjust the values of ΔG_F^o and $\Delta G_{V_{Ni}}^o$, and, during the next steps, $\Delta G_{V_{Ni}}^o$ and $\Delta G_{V_{Ni}}^o$ in such a way that the obtained dependence of the deviation from the stoichiometry on p_{O_2} (resulting from the calculated concentrations of the defects) is consistent with the experimental values of δ .

At the first step, we assume that the concentration of defects with lower ionization degrees is insignificantly low. Knowing the value of ΔG_i^o and assuming the ΔG_F^o , we calculate the concentrations of electronic defects and ionic defects. The assumed values of ΔG_i^o and ΔG_F^o must fulfill the Eqs. 5 and also 4, at the appropriately adjusted values of $\Delta G_{V_{Ni}}^o$ and $p_{O_2}^{(s)}$. We assume that the concentration of nickel vacancies $[V_{Ni}]$ is the variable parameter, and we calculate the concentration $[Ni_i^{\bullet\bullet}]$ and the deviation from the stoichiometry δ . Taking into account, the electroneutrality condition, we calculate the concentration of electronic defects vs. $[V_{Ni}]$. The equilibrium oxygen pressure is calculated using the equilibrium constant for the reaction of the formation of vacancies V_{Ni}'' , their concentration, and the concentration of electron holes. 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. $\log(p_{O_2})$ curve and the experimental values of δ is corrected, by adjusting the values of ΔG_F^o and $\Delta G_{V_{Ni}}^o$ [when the condition (4) and (5) is fulfilled] in a way to obtain the consistency in the range of the small deviations from the stoichiometry.

Then, we consider the presence of defects with lower ionization degrees. We choose the values of $\Delta G_{V_{Ni}}^o$ and then $\Delta G_{V_{Ni}}^o$ to obtain, at higher values of the deviation, a full consistency with the experimental results of δ .

Results of calculations and discussion

Point defect concentrations in “pure” $Ni_{1-\delta}O$

When calculating the concentrations of the defects, the values of ΔG_i^o of the electronic defects’ formation, determined by Osburn and Vest [13], were used. The obtained dependence of ΔG_i^o on the temperature, which differed from the linear function, was described by the following polynomial:

$$\Delta G_i^o = 352.15 + 0.038 T - 9 \cdot 10^{-6} T^2$$

Analyzing the results of the studies of the deviation from the stoichiometry by different authors [13, 14, 18, 21] (see Fig. 1), it can be found that there are differences between them, but the dependence of δ on p_{O_2} has a similar character. The discrepancies between the δ values obtained

Fig. 1 Point defect diagrams in $\text{Ni}_{1-\delta}\text{O}$ obtained using the results of the studies of the deviation from the stoichiometry obtained by many authors: **a** for the temperature of 1,273 K, **b** 1,473 K, **c** 1,673 K. Points mark the results of studies: (empty circle, filled circle)—Osburn and Vest [13], (filled diamond)—Söckel and Schmalzried [14], (filled triangle)—Tretyakov and Rapp [15], (hollow square)—Tripp and Tallan [18], (filled square)—Haugrud and Norby [20], (empty triangle)—Mrowec and Grzesik [21]

by different authors can be thus caused mainly by a systematic error that relates to the method of the determination of the δ value. The value of ΔG_F^0 obtained on the basis of the results of Sockel, Schmalzried [14], Osburn, Vest [13], Mrowec, and Grzesik [21], and the temperature dependence of ΔG_F^0 was then determined. As a result of the calculations performed, it has been found that in the temperature range of 1,473–1,673 K, a good match of the dependence of the deviation from the stoichiometry on p_{O_2} to the experimental results of δ is obtained, taking into account only $[V_{Ni}']$ (also at higher oxygen pressures). Because in $Ni_{1-\delta}O$ vacancies with lower ionization degrees are also postulated, such values (maximal) of $\Delta G_{V_{Ni}'}^0$ and $\Delta G_{V_{Ni}^x}^0$ were chosen that the match is not worsened by them. Considering the defects with lower ionization degrees, the values of $\Delta G_{V_{Ni}'}^0$ were adjusted first, and then the values of $\Delta G_{V_{Ni}^x}^0$, although, in such a way that $\Delta G_{V_{Ni}'}^0 \geq \Delta G_{V_{Ni}^x}^0$.

Figure 1a–c illustrate the results of the calculations of the concentrations of ionic and electronic defects in $Ni_{1-\delta}O$, obtained for a series of temperatures (1,273, 1,473, and 1,673 K). As can be seen in Fig. 1a, there are significant differences between the results obtained by Osburn and Vest [13] and Tretyakov and Rapp [15]. When the same values of ΔG_F^0 were assumed, significantly different values of $\Delta G_{V_{Ni}'}^0$ were fitted (see Fig. 2). As a result, there are significant differences in the concentration of $[h^\bullet]$, $[V_{Ni}']$, and also in the concentration of vacancies with lower ionization degrees. In the case of the calculations for the results of Tretyakov and Rapp [15] (dotted line), the concentration $[V_{Ni}']$ is precisely equal to the deviation δ . In the case of the results of Osburn and Vest [13] (solid line) at low oxygen pressures, there are differences between the concentration $[V_{Ni}']$ and δ . On the other hand, the dependence of δ on p_{O_2} obtained by Tripp and Tallan [18] (dashed line) (Fig. 1a), has a bigger slope in relation to the results of Osburn and Vest [13]. However, despite relatively small differences in the values of δ , obtained in the above studies, there are significant differences between the concentrations $[V_{Ni}']$ and $[V_{Ni}^x]$. A bigger slope during the fitting to the results of Tripp and Tallan [18] was corrected by an adequate choice of values $\Delta G_{V_{Ni}'}^0$, $\Delta G_{V_{Ni}^x}^0$, and $\Delta G_{V_{Ni}^x}^0$. However, this slope could be caused, as will be shown below, by the influence of M^{3+} ions (as impurities) on the concentration of the defects (the deviation from the stoichiometry). Figure 1a shows the experimental values obtained by Osburn and Vest [13] [(blank circle) points] and the values calculated from the equation given by the above authors (describing the results obtained at higher temperatures) [solid circle) points]. As can be seen in Fig. 1a, the experimental values of δ are higher than the calculated values. This could be caused by the influence of M^{3+} ions on the concentration of the defects.

Figure 1b presents the results of the calculations using the results of the studies by Sockel and Schmalzried [14], and Osburn and Vest [13]; also the results of Mrowec and Grzesik [21] are marked, and, as can be seen, are slightly higher. As illustrated in Fig. 1b, there is a significant difference between the values of δ obtained by Sockel and Schmalzried [14] and those obtained by Osburn and Vest [13]. For the same values of ΔG_F^0 different values of $\Delta G_{V_{Ni}'}^0$ were adjusted. As can be seen, there is a significant difference between the concentrations $[V_{Ni}']$ and $[h^\bullet]$. (The concentration of electron holes for the results of Osburn and Vest [13] (solid line) accidentally overlaps with the dependence of δ on p_{O_2} for the results by Sockel and Schmalzried [14] (dashed line). Moreover, the curves for the results of Sockel and Schmalzried [14] are also fitted in Fig. 1b, whereby higher absolute values of $\Delta G_{V_{Ni}'}^0 = -72$ kJ/mol and $\Delta G_{V_{Ni}^x}^0 = -92$ kJ/mol are chosen in order to be close to the results of Haugsrud and Norby [20]. As can be seen in Fig. 1b, this caused a significant increase of the concentrations $[V_{Ni}']$ and $[V_{Ni}^x]$.

Figure 1c shows the results of the calculations for 1,673 K using the results of Osburn and Vest [13] (solid line) and those of Mrowec and Grzesik [21] (dashed line). Small differences in the values of δ also cause small differences in the obtained dependences of concentrations of the defects on p_{O_2} .

Analyzing the defect diagrams shown in Fig. 1, it can be found that in the range of higher oxygen pressures, the deviation from the stoichiometry is practically equal to the concentration $[V_{Ni}']$. However, in the range of low oxygen pressures, a higher concentration $[V_{Ni}']$ occurs than δ and there is also a comparable, lower concentration of interstitial ions $[Ni_i^{\bullet\bullet}]$. When the temperature increases, the concentration of the defects increases; also the range in which the concentration $[Ni_i^{\bullet\bullet}]$ is lower by about 1/2 order of magnitude ($\log([V_{Ni}']/[Ni_i^{\bullet\bullet}]) = 0.5$) increases. In the lower temperatures of 1,273–1,473 K, there is also a small concentration of vacancies $[V_{Ni}']$ and $[V_{Ni}^x]$. As can be seen in Fig. 1, in the range of the low pressures p_{O_2} , considering the interstitial $[Ni_i^{\bullet\bullet}]$ ions influences the concentrations $[Ni_i^{\bullet\bullet}]$, despite the fact that the dependence of δ on p_{O_2} practically does not change.

Figure 2 shows the dependences of ΔG_F^0 and $\Delta G_{V_{Ni}'}^0$ 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. As already mentioned, the values of ΔG_F^0 for the individual temperatures were calculated using the dependences of ΔG_F^0 on T , obtained on the basis of the results by Sockel and Schmalzried [14], Osburn and Vest, [13] and Mrowec and Grzesik [21] in the range of 1,473–1,673 K (Table 1). On the other hand, the values of $\Delta G_{V_{Ni}'}^0$ were fitted in such a way as to obtain the consistency with the experimental values of δ . As can be seen in Fig. 2, different values of

Fig. 2 The values: ΔG_F° of the formation of intrinsic ionic defects of Frenkel type, obtained at 1,471–1,673 K using the results of the deviation from the stoichiometry studies by: Sockel and Schmalzried [14]—points (plus sign), Osburn and Vest [13]—(empty square), Mrowec and Grzesik [21]—(filled circle), and $\Delta G_{V_{Ni}}^\circ$ of the formation

of vacancies (V_{Ni}'') using the results by: Osburn and Vest [13]—(filled square) (OV), Sockel and Schmalzried [14]—(multiplication sign) (SS), Tertyakov and Rapp [15]—(empty diamond) (TR), Tripp and Tallan [18]—(empty triangle) (TT), Mrowec and Grzesik [21]—(empty circle) (MG)

$\Delta G_{V_{Ni}}^\circ$ were obtained, although their temperature dependences have similar slopes. A small difference is observed where the results of Osburn and Vest [13] and Mrowec and Grzesik [21] are concerned. On the other hand, significantly bigger differences are present in the case of the results by Tertyakov and Rapp [15], Tripp and Tallan [18], and Sockel and Schmalzried [14] [(multiplication) points].

Figure 3 presents the values $\Delta G_{Ni^{2+}}^\circ$ of the formation of interstitial nickel ions (Ni_i^{2+}), calculated according to the Eq. 6. As can be seen, the dependencies of $\Delta G_{Ni^{2+}}^\circ$ on the temperature have similar slopes. The differences between the $\Delta G_{Ni^{2+}}^\circ$ values are related mainly to the different values of $\Delta G_{V_{Ni}}^\circ$ which were obtained using the results by the individual authors. It should be noted that the values of $\Delta G_{Ni^{2+}}^\circ$ and ΔG_F° have not been determined so far.

Figure 3 also shows the values of $\Delta G_{V_{Ni}}^\circ$ and $\Delta G_{V_{Ni}^{x}}^\circ$ of the formation of the vacancies with lower ionization degrees, which were obtained by fitting the curve of $\log \delta$ vs. $\log(p_{O_2})$ to the results of the studies by different authors. As was previously noted, such values (maximal) of $\Delta G_{V_{Ni}}^\circ$ were chosen so that the fit of the $\log \delta$ vs. $\log(p_{O_2})$ curve is not worsened by them. As observed in Fig. 3, where the results of authors [13, 18, 21] are concerned, the same values $\Delta G_{V_{Ni}}^\circ = \Delta G_{V_{Ni}^{x}}^\circ$ were fitted. It was assumed that the energy of interactions of a vacancy with the next electron hole in the ($V_{Ni}''2h^\bullet$) complex should not exceed ($V_{Ni}''h^\bullet$). As can also be seen in Fig. 3, where the results of Tripp and Tallan [18] are concerned, the fitted absolute values of $\Delta G_{V_{Ni}}^\circ$ are significantly larger. The absolute values of $\Delta G_{V_{Ni}^{x}}^\circ$ are slightly lower; they increase with the temperature

increase. This means that the fraction of concentration of neutral vacancies to single ionized vacancies would increase ($[V_{Ni}^x]/[V_{Ni}']$). Thus, the bonding energy in complexes ($V_{Ni}''2h^\bullet$) would have increased with the temperature increase, which seems improbable. As was already noted, the bigger slope of the $\log \delta$ vs. $\log(p_{O_2})$ dependence, obtained by Tripp and Tallan [18] in relation to the other results was corrected by fitting the appropriate values of $\Delta G_{V_{Ni}}^\circ$, $\Delta G_{V_{Ni}'}^\circ$, and $\Delta G_{V_{Ni}^{x}}^\circ$. Therefore, the obtained character, of the $\Delta G_{V_{Ni}^{x}}^\circ$ vs. T dependence, and also of the δ vs. p_{O_2} dependence, indicates that it could be related to the presence of impurities (M^+ ions). In Table 1, the determined enthalpies and entropies of individual defects, resulting from the relations presented in Figs. 2 and 3 are given. As can be observed, there is quite a good consistency between the values of the $\Delta H_{V_{Ni}}^\circ$ determined in the present work and those determined by different authors, assuming that $\delta = [V_{Ni}']$. The present differences between the values of $\Delta H_{V_{Ni}}^\circ$ are close to the differences occurring between the values of $\Delta G_{V_{Ni}}^\circ$.

Figure 4 shows the fitted values of the hypothetical pressure $p_{O_2}^{(s)}$, (fulfilling the Eqs. 4 and 5), at which NiO could reach the stoichiometric composition. As can be seen, these pressures are by a few orders of magnitude lower than the decay pressure of nickel oxide [62] (dashed line). The obtained monotonic character of the dependence of $p_{O_2}^{(s)}$ on the temperature is in accordance with the expectations. The occurring differences in $p_{O_2}^{(s)}$ values, yet similar character of the $p_{O_2}^{(s)}$ vs. T dependence, indicate that the results of the studies by different authors could be charged with a systematic error.

Table 1 The values of the enthalpy ΔH and the entropy ΔS of the formation of: intrinsic Frenkel defects, nickel vacancies (V_{Ni}''), interstitial nickel ions ($Ni_i^{\bullet\bullet}$), vacancies with lower ionization degrees (V_{Ni}') and (V_{Ni}^x) in $Ni_{1-\delta}O$, determined using the relations presented in Figs. 2 and 3 and these calculated by other authors assuming a simplified model of defects ($\delta = [V_{Ni}'']$)

Equilibrium	ΔH / (kJ/mol)	ΔS / (J/mol)	Reference
$[h^{\bullet}][e']$	334.9	41–42 ^b	[10, 11]
Frenkel	360±2	43±2	(SS ^a , OV ^a , MG ^a)
V_{Ni}''	236±2	–43±1	(OV ^a)
Eq. 1	240±1	–35±1	(MG ^a)
Eq. 1	265±2	–31±2	(TT ^a)
Eq. 1	227±23	–15±14	(TR ^a)
Eq. 1	238.6	–43.5	[6, 7]
Eq. 1	223.6	–5.3	[5]
Eq. 1	240.0	–35.3	[17]
Eq. 1	233.6	–44.2	[10, 11]
Eq. 1	248.9	–33.0	[8, 9]
Eq. 1	266.3		[15]
$Ni_i^{\bullet\bullet}$	122±2	84±2	(OV ^a)
$Ni_i^{\bullet\bullet}$	126±3	82±2	(MG ^a)
$Ni_i^{\bullet\bullet}$	93±2	72±2	(TT ^a)
$Ni_i^{\bullet\bullet}$	130±23	56±15	(TR ^a)
V_{Ni}'	–120±4	–47±3	(OV ^a)
V_{Ni}'	–109±8	–41±5	(MG ^a)
V_{Ni}'	–132±2	–28±2	(TT ^a)
V_{Ni}'	–147±16	–80±12	(TR ^a)
V_{Ni}'	–139.9		[15]
V_{Ni}^x	–120±4	–47±3	(OV ^a)
V_{Ni}^x	–109±8	–41±5	(MG ^a)
V_{Ni}^x	15±3	77±3	(TT ^a)
V_{Ni}^x	–147±16	–80±12	(TR ^a)

SS Sockel and Schmalzried, OV Osburn and Vest, MG Mrowec and Grzesik, TT Tripp and Tallan, TR Tretyakov and Rapp

^a Results of the deviation from the stoichiometry (used in the calculations noted in the present work) obtained by Sockel and Schmalzried [14], Osburn and Vest [13], Mrowec and Grzesik [21], Tripp and Tallan [18], and Tretyakov and Rapp [15]

^b A value dependent on the temperature

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 $1/n_\sigma \cong 1/6 - 1/5$ in the dependence of the deviation from the stoichiometry and the electrical conductivity on p_{O_2} formed the basis for the hypothesis that in the whole range of the $Ni_{1-\delta}O$ existence double ionized vacancies dominate. As can be seen in Fig. 5, the values of n_δ [(dashed) line] and n_h (solid line), using the results of Osburn and Vest [13] change, depending on p_{O_2} , from 6 to 5. A slightly different situation was obtained for the

results by Tripp and Tallan [18] (TT) and Sockel and Schmalzried [14] for the values $\Delta G_{V_{Ni}}^o = 72$ kJ/mol and $\Delta G_{V_{Ni}}^o = -92$ kJ/mol (SS, HN). The obtained character is a result of the influence of the concentration of vacancies $[V_{Ni}']$ and $[V_{Ni}^x]$ at higher oxygen pressures on the dependencies of δ and $[h^{\bullet}]$ on p_{O_2} . The influence is significantly bigger in the case of n_δ , and small in the case of n_h . 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, in most of the works the values of n_σ in the 5.8–5.3 range were obtained. Considering that these are average values in a given range p_{O_2} and charged with an error, the consistency is good. Many values of n_σ are lower than n_h . These differences can be connected with the influence of impurities on the concentration of electron holes.

It should be noted that the obtained dependence of ΔG_F^o on the temperature, despite the fact that it has a high correlation coefficient, has been determined from a small number of experimental values of the deviation from the stoichiometry [13, 21]. In the range of lower oxygen pressures, the determination was practically based on the results in one temperature [14]. Moreover, in the literature, there is no data verifying the value of ΔG_i^o of the formation of electronic defects and its temperature dependence. If more precise data is obtained, in a wider range of oxygen pressure, it can be expected that there will be some, rather small, changes in the character of the dependence of the concentrations of defects on p_{O_2} .

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

In the calculations of the point defects diagram for the doped oxide, the values of ΔG^o of the defects formation obtained for pure $Ni_{1-\delta}O$ have been used, based on the results of Osburn Vest [13] (Figs. 2 and 3). Due to a small concentration of interstitial nickel ions in $Ni_{1-\delta}O$, it was assumed that doped M^+ ions in the form of M_2O oxide and M^{3+} ions in the form of M_2O_3 oxide incorporate themselves into cation nodes and preserve their oxidation degree. Thus, in relation to the lattice they are charged negatively- and positively ($M_{Ni}^{\bullet}$), respectively. It has been assumed that the concentration of dope ions is sufficiently small to neglect their influence on the values of ΔG^o of the defects' formation. It was also assumed that the point defects still form an ideal solution.

M^+ ions dope (M_2O)

Figure 6 shows the results of calculations of the concentrations of the defects in the $(Ni_{1-y}M_y)_{1-\delta}O$ doped with

Fig. 3 The values of: $\Delta G_{Ni_i^{••}}^\circ$, $\Delta G_{V_{Ni}^x}^\circ$, and $\Delta G_{V_{Ni}^x}^\circ$ of the formation of respectively, interstitial nickel ions ($Ni_i^{••}$) (solid points), V_{Ni}^x (empty points), and V_{Ni}^x (solid points), obtained in individual temperatures using the results of the deviation from the stoichiometry studies by: Osburn and Vest [13] points—(filled square, empty square) (OV),

Socket and Schmalzried [14], and Haugsrud and Norby [20]—(*, plus sign, multiplication sign) (SS), Tretyakov and Rapp [15]—(filled diamond, empty diamond) (TR), Tripp and Tallan [18]—(filled triangle, empty triangle) (TT), and Mrowec and Grzesik [21]—(filled circle, empty circle) (MG)

M^+ ions in the quantity of: $y_M = 8 \cdot 10^{-6}$ mol/mol—(dashed) line, $1 \cdot 10^{-4}$ —(dashed) line, $1 \cdot 10^{-3}$ —(dotted) line, compared with the concentration in “pure” $Ni_{1-\delta}O$ (solid line) for two example temperatures, 1,373 and 1,573 K. As mentioned above, the character of the dependence of δ on p_{O_2} obtained by Tripp and Tallan [18] indicated that it could be related to the presence of the M^+ dope (Fig. 1a). Thus, a particular quantity of dope was chosen in order to obtain be consistent with the results of the studies of the deviation

from the stoichiometry [18] (Fig. 6a). (At 1,273 K, a similar quantity was fitted, $6 \cdot 10^{-6}$ mol/mol). The obtained quantity of dope at the level of $y_M = 10^{-5}$ mol/mol is close to the content of sodium ions with which the sample, as it transpires from the content analysis, has been contaminated due to the long studies [18]. The introduction of a content of M^+ ions higher by an order of magnitude (10^{-4} mole) causes more significant changes in the concentrations of the defects. Figure 6b presents the results of the calculations for

Fig. 4 The values of a hypothetical oxygen pressure $p_{O_2}^{(s)}$ whereby the NiO would reach the stoichiometric composition, obtained in individual temperatures using the results of the deviation from the stoichiometry studies by: Osburn and Vest [13] points—(filled square) (OV), Socket

and Schmalzried [14]—(empty diamond) (SS), Tretyakov and Rapp [15]—(filled diamond) (TR), Tripp and Tallan [18]—(empty triangle) (TT), and Mrowec and Grzesik [21]—(empty circle) (MG). The (dotted dashed) line—the equilibrium pressure Ni/NiO [62]

Fig. 5 The dependence of the derivative: $n_\delta = \log(p_{O_2})/d \log \delta$ and $n_h = \log(p_{O_2})/d \log [h^\bullet]$ on $\log p_{O_2}$ obtained for the dependence of the deviation δ and the concentration of electron holes $[h^\bullet]$ on p_{O_2} for the relations shown in Fig. 1a–c and obtained using the results by: Osburn and Vest [13]—(OV), Sockel and Schmalzried [14], Haugsrud and Norby [20]—(SS, HN), and Tripp and Tallan [18]—(TT)

1,573 K. As can be seen, due to the higher concentration of defects in “pure” $Ni_{1-\delta}O$, the influence of $1 \cdot 10^{-4}$ mol/mol of M^+ ions on the character of the dependence of the concentrations of the defects is significantly smaller. On the other hand, a higher dope content, ($y_{M'} = 10^{-3}$ mol/mol), causes a drastic change in the concentrations of the defects. As can be seen in Fig. 6, the introduction of M^+ into the nickel oxide causes a shift by a dozen orders of magnitude in the value of the oxygen pressure ($p_{O_2}^{(s)}$), where the oxide reaches the stoichiometric composition (relative to the pure oxide (see Fig. 4)). In the case of the content of $y_{M'} = 1 \cdot 10^{-3}$ mole $p_{O_2}^{(s)}$ 1 atm and it equals about 10^3 atm.

As can be seen in Fig. 6 in the range of low oxygen pressures, there is a significant concentration of $[Ni_i^{\bullet\bullet}]$ ions, which is higher than the concentration $[V_{Ni}']$. It depends both on the concentration of M^+ ions and on the temperature and it can be higher than the concentration $[V_{Ni}']$ even by a few orders of the magnitude. A result of the change in the concentrations of the defects, in the range of low p_{O_2} , is a high deviation from the stoichiometry, itself comparable with the dope concentration. However, a question can then be raised concerning whether such a high concentration of interstitial nickel ions is possible, especially when in the “pure” $Ni_{1-\delta}O$ it is relatively low. At such, a high increase of the concentration of the interstitial ions, the decay pressure of NiO should increase. Moreover, the possibility of small ions, e.g., lithium, being incorporated in interstitial positions should be considered, as well as the possibility of a change of the oxidation degree of M^+ ions during the process of the dope incorporation or the formation of $(M'_{Ni}h^\bullet)$ complexes.

As can be seen in Fig. 6, despite very drastic changes of the concentration of ionic defects, there occurs small increase of the concentration of electron holes, depending on the dope concentration and on the temperature. A

character of this relation is complex. As can be seen in Fig. 6a, at 1,373 K, at M^+ ion concentration, $y_{M'} = 1 \cdot 10^{-4}$ mol/mol, a range of oxygen pressure can be identified in which the concentration of electron holes is practically constant, close to the dope concentration. The width of this range decreases with the temperature increase and at 1,573 K, it practically disappears. However, as can be seen in Fig. 6b, a higher content of dope ($y_{M'} = 1 \cdot 10^{-3}$ mol/mol) causes, at higher oxygen pressures, the occurrence of a high concentration of electron holes, practically independent on p_{O_2} . Although, at low oxygen pressures their concentration decreases with the decrease of p_{O_2} . As can be observed in Fig. 6, the assumption that the concentration of electron holes is equal to the dope concentration is an excessive approximation and it is possible in the case of high dope content and in a determined range of p_{O_2} .

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 dependences presented in Fig. 6 and obtained for 1,273 K. As can be seen in Fig. 7 at 1,273 and 1,373 K, a small quantity of dope at the impurity level, and comparable with the concentration of defects at these temperatures, causes a small increase of the value $n_h > 6$ and in the range of $10^{-5} p_{O_2}$ 1 atm n_h , it is practically constant. The value of the exponent $e_\sigma > 6$ in the dependence of σ on p_{O_2} indicates that among the impurities, the sum of the concentrations of M^+ ions is higher than that of M^{3+} ions. Meier and Rapp [12], for a spectrally pure sample, obtained $n_\sigma = 6.1 - 6.5$. This could indicate that the sample contained impurities in the form of alkali metal ions, which is confirmed by the analysis of the composition [12]. A similar value of the exponent $n_\sigma = 6.24$ was obtained by Room et al. [38]. As indicated in Fig. 7 at 1,373 K, at the content of $y_{M'} = 1 \cdot 10^{-4}$ mol/mol, n_h increases rapidly, reaching high

Table 2 The values of the exponent $1/n_\sigma$ obtained for the dependence of the electrical conductivity (σ) of $\text{Ni}_{1-\delta}\text{O}$ on p_{O_2} , in a series of temperatures in individual ranges of the oxygen pressure, as

determined by different authors, and the average values of the exponent $1/n_h$ in the dependence of the concentration of electron holes on p_{O_2} , calculated in the same ranges p_{O_2} (Figs. 5, 9)

Reference	T/(K)	$p_{\text{O}_2}/(\text{atm})$	n_σ	n_h	y_M
[38]	1,273	$1\text{--}10^{-5}$	6.24	5.9–6	
[12]	1,273	$1\text{--}10^{-5}$	6.1	5.9–6	
[16]	1,273	$1\text{--}10^{-3}$	6	5.9–6	
[13]	1,273	$1\text{--}10^{-4}$	5.85	5.9–6	
[12]	1,273	$1\text{--}10^{-5}$	5.7	5.9–6	
[35]	1,273	$1\text{--}10^{-5}$	5.2	5.9–6	
[31]	1,273	$1\text{--}10^{-2}$	5	5.9–6	
[32, 33]	1,273	$1\text{--}10^{-3}$	5	5.9–6	
[34]	1,273	$1\text{--}10^{-4}$	4.3	5.9–6	
[10, 11]	1,273	$1\text{--}10^{-3}$	4.1	5.9–6	
[25]	1,273	$1\text{--}10^{-4}$	4.08	5.9–6	
[12]	1,273	$1\text{--}10^{-5}$	4	5.9–6	
[23]	1,273	$1\text{--}10^{-5}$	4	5.9–6	
[12]	1,373	$1\text{--}10^{-5}$	6.3–5.8	5.8	
[35]	1,373	$1\text{--}10^{-5}$	5.72	5.8	
[13]	1,373	$1\text{--}10^{-4}$	5.57	5.8	
[28]	1,373	$1\text{--}10^{-4}$	5.33	5.8	
[31]	1,373	$1\text{--}10^{-2}$	4.8	5.8	
[34]	1,373	$1\text{--}10^{-5}$	4.34–4.65	5.8	
[12]	1,373	$1\text{--}10^{-4}$	4.3	5.8	
[25]	1,373	$1\text{--}10^{-4}$	4.26	5.8	
[10, 11]	1,373	$1\text{--}10^{-3}$	4.1	5.8	
[12]	1,473	$1\text{--}10^{-5}$	6.2	5.9–5.8	
[13]	1,473	$1\text{--}10^{-4}$	5.74	5.9–5.8	
[35]	1,473	$1\text{--}10^{-5}$	5.68	5.9–5.8	
[10, 11]	1,473	$1\text{--}10^{-5}$	5.33	5.9–5.8	
[31]	1,473	$1\text{--}10^{-2}$	4.9	5.9–5.8	
[26]	1,478	$1\text{--}10^{-4}$	4.8	5.9–5.8	
[12]	1,473	$1\text{--}10^{-4}$	4.5	5.9–5.8	
[25]	1,473	$1\text{--}10^{-4}$	4.44	5.9–5.8	
[10, 11]	1,473	$1\text{--}10^{-3}$	4.2	5.9–5.8	
[34]	1,473	$1\text{--}10^{-4}$	4.27–5.18	5.9–5.8	
[23]	1,473	$1\text{--}10^{-6}$	4	5.9–5.8	
[17]	1,573	$1\text{--}10^{-4}$	6	5.9–5.1	
[13]	1,573	$1\text{--}10^{-4}$	5.76	5.9–5.1	
[26]	1,650	$1\text{--}10^{-4}$	5.3	5.8–5	
[34]	1,573	$1\text{--}10^{-4}$	4.35–5.49	5.9–5.1	
[10, 11]	1,573	$1\text{--}10^{-3}$	4.3	5.9–5.1	
[13]	1,673	$1\text{--}10^{-4}$	5.65	5.8–5	
[34]	1,673	$1\text{--}10^{-4}$	4.4–5.88	5.8–5	
[10, 11]	1,673	$1\text{--}10^{-4}$	4.3	5.8–5	
Cr					
[12]	1,273	$1\text{--}10^{-4}$	3.9	4	0.0019
[12]	1,273	$1\text{--}10^{-4}$	4.3		0.00595
[12]	1,273	$1\text{--}10^{-5}$	3.9		0.0395
[30]	1,273	$1\text{--}10^{-2}$	4		0.0115
[36, 37]	1,273	$1\text{--}10^{-4}$	4.29	4	0.001

Table 2 (continued)

Reference	T/(K)	$p_{O_2}/(\text{atm})$	n_σ	n_h	y_M
[36, 37]	1,273	$1\text{--}10^{-4}$	4.22		0.0062
[12]	1,373	$1\text{--}10^{-4}$	4		0.0019
[12]	1,373	$1\text{--}10^{-4}$	4.3		0.00595
[12]	1,373	$1\text{--}10^{-5}$	4		0.0395
[30]	1,373	$1\text{--}10^{-2}$	4		0.0115
[36, 37]	1,373	$1\text{--}10^{-4}$	4.45	4.1–4	0.001
[36, 37]	1,373	$1\text{--}10^{-4}$	4.3		0.0062
[30]	1,473	$1\text{--}10^{-2}$	4		0.0115
[36, 37]	1,473	$1\text{--}10^{-4}$	4.34	4.2–4	0.001
[36, 37]	1,473	$1\text{--}10^{-4}$	4.36		0.0062

Fig. 6 Point defect diagrams for pure $\text{Ni}_{1-\delta}\text{O}$ (solid line) obtained using the results of the deviation from the stoichiometry studies obtained by Osburn and Vest [13], and the oxide doped with M^+ ions for the dope content of $y_M = 8 \cdot 10^{-6} \text{ mol/mol}$ (---) line, $1 \cdot 10^{-4}$ (dashed dotted line), $1 \cdot 10^{-3}$ (dotted line), **a** for 1,373 K, **b** 1,573 K. The points mark the results of the studies for pure $\text{Ni}_{1-\delta}\text{O}$: Osburn and Vest [13]—(filled circle) (calculated), Tripp and Tallan [18]—(empty square)

Fig. 7 The dependence of the derivative $n_h = \log(p_{O_2})/d \log[h^\bullet]$ on $\log(p_{O_2})$, obtained for the dependence of the concentration of electron holes $[h^\bullet]$ on p_{O_2} at 1,273, 1,373, and 1,573 K for pure $Ni_{1-\delta}O$ (solid line) and the oxide doped with M^{3+} ions: for $y_{M^{3+}} = 8 \cdot 10^{-6}$ mol/mol—(---), $6 \cdot 10^{-6}$ —(dotted) line, $1 \cdot 10^{-4}$ —(dashed dotted) line, $1 \cdot 10^{-3}$ —(dotted) line

values, although at low oxygen pressures it decreases to the value of 5. On the other hand, at 1,573 K, the value of n_h increases only to 8. Thus, a change of n_h is not only dependent on the dope concentration, but also on the temperature (the total concentration of defects). As such, where the presence of M^{3+} dope is concerned, the character of the dependence of n_σ and n_δ on p_{O_2} will differ significantly.

M^{3+} ion dope (M_2O_3)

Figure 8 shows the results of the calculations of the defects concentrations after the introduction into $(Ni_{1-y}M_y)_{1-\delta}O$ a dope of M^{3+} ions in the quantity of: $y_{M^{3+}} = 6 \cdot 10^{-6}$ mol/mol—(---) line, $5 \cdot 10^{-5}$ —(dashed dotted) line, $1 \cdot 10^{-4}$ —(dashed) line and $1 \cdot 10^{-3}$ —(dotted) line, compared to the concentration in pure $Ni_{1-\delta}O$ (solid line) for two example temperatures 1,273 and 1,473 K. As was previously mentioned, the higher values of δ obtained by Osburn and Vest [13] at 1,273 K in relation to those calculated from the dependence obtained for higher temperatures can indicate that they are caused by the presence of M^{3+} dope as an impurity. As can be seen in Fig. 8a, for the dope content of $y_{M^{3+}} = 6 \cdot 10^{-6}$ as an impurity, a very good consistency with the experimental results of δ was obtained [13]. On the other hand, at 1,473 K, the above quantity of dope, due to a higher concentration of defects in pure $Ni_{1-\delta}O$, practically no longer influences their concentration. It should be noted that the concentration of M^{3+} ions as an impurity should be treated as an effective concentration, being the difference of the concentrations of M^{3+} and M^{+} ions. As can be seen in Fig. 8a at the dope content $y_{M^{3+}} = 1 \cdot 10^{-4}$ mol/mol, the concentration $[V''_{Ni}]$ is higher than in pure $Ni_{1-\delta}O$ at $p_{O_2} = 1$ atm. At 1,473 K, the above quantity of dope has a significantly smaller influence on the concentrations of the defects.

As can be observed in Fig. 8, with the increase of the M^{3+} dope ions' concentration, the deviation from the stoichiometry increases significantly and is close to the dope concentration. The concentration of vacancies $[V''_{Ni}]$ increases (this concentration is only slightly smaller than the deviation δ), and the concentration of $[V'_{Ni}]$ also increases. From the studies by many authors [12, 27, 30, 36, 37, 55–60], it transpires that the maximum chrome solubility in $Ni_{1-\delta}O$ is at about 1%. At such a content of M^{3+} ions, the concentration of vacancies is significantly higher than the concentration of defects in “pure” $Ni_{1-\delta}O$ and it should be the same as it is present in the oxide at high oxygen pressures. As can be seen in Fig. 8, when the concentration of the dope increases, the concentration of $[Ni_i^{\bullet\bullet}]$ and electron holes decreases, and also the concentration of electrons increases (it is still low, 10^{-9} mol/mol). Despite a significant increase in the concentration V''_{Ni} , the character of the dependence of the concentration of electron holes on p_{O_2} , changes only slightly in comparison to the dependence for pure $Ni_{1-\delta}O$.

The dependence of the derivatives $n_h = d \log(p_{O_2})/d \log[h^\bullet]$ on $\log(p_{O_2})$ is shown in Fig. 9. As illustrated in Fig. 9, even at low dope content, at 1,273 K, there occurs a quick decrease in the value of n_h from 6 to 4. At high dope contents, 10^{-3} mol/mol, n_h is practically equal to 4. With the temperature increase, due to a higher concentration of defects in “pure” $Ni_{1-\delta}O$, the influence of the dope concentration is smaller. Due to this, where the quantity of the dope M^{3+} as an impurity is low (10^{-5} – 10^{-4} mol/mol), n_h will clearly increase with the temperature increase. Such an effect was found by Farhi and Petot-Ervas [34] who obtained, e.g., for $p_{O_2} = 4.33 \cdot 10^{-3}$ atm, in the temperature range of 1,273–1,673 K, the increase of n_σ from 4.3 to 5.24 and a slightly lower increase at higher oxygen pressures. In Table 2, the values of the exponent $1/n_\sigma$ in the dependence

Fig. 8 Point defects diagrams for pure $\text{Ni}_{1-\delta}\text{O}$ (solid line) obtained using the results of the deviation from the stoichiometry studies determined by Osburn and Vest [13] and for the oxide doped with M^{3+} ions, for the dope content: $y_{\text{M}^{3+}} = 6 \cdot 10^{-6} \text{ mol/mol}$ (---), $5 \cdot 10^{-5}$ (dashed dotted line), $1 \cdot 10^{-4}$ (dashed dotted line), and $1 \cdot 10^{-3}$ (dotted line); **a** for the temperature of 1,273 K, **b** 1,473 K. The points mark the results of the studies for pure $\text{Ni}_{1-\delta}\text{O}$: Osburn and Vest [13]—(filled circle) calculated, (empty circle) experimental

of σ on $p\text{O}_2$ 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 $p\text{O}_2$). As can be seen, the obtained values of n_σ are in the range of 4–4.3, which, in the error limit, could be considered a good consistency. The values of n_σ obtained by many authors in the range of 4.2–4.5 in the case of “pure” $\text{Ni}_{1-\delta}\text{O}$ indicate that in these samples, the effective concentration of M^{3+} ions is significant (about 10^{-4} mole).

From the diagrams of the defects presented, it can be observed (Figs. 1, 6, and 8) that, due to a small concentration of defects in $\text{Ni}_{1-\delta}\text{O}$, the impurities in the form of M^+ and M^{3+} ions can essentially influence the dependence of the defects’ concentration on $p\text{O}_2$. This is why it is necessary to simultaneously perform the measurements of the deviation from the stoichiometry

and the electrical conductivity in the widest possible range of $p\text{O}_2$; the comparison of these measurements then indicates the type and quantity of the dominating impurities. Conclusions about the structure of the defects that are based only on the electrical conductivity could be erroneous.

Conclusions

The obtained point defect diagrams in $\text{Ni}_{1-\delta}\text{O}$ indicate that the proposed method of calculation enables the full interpretation of the deviation from the stoichiometry studies (in the entire range of the oxide’s existence). This method considers not only the dominating defects (vacancies) but also the interstitial ions.

Fig. 9 The dependence of the derivative $n_h = \log(p_{O_2})/d \log[h^\bullet]$ on $\log(p_{O_2})$, obtained for the dependence of the concentration of electron holes $[h^\bullet]$ on p_{O_2} , for 1,273, 1,473, 1,673 K, for pure $Ni_{1-\delta}O$ (solid line) and doped with M^{3+} ions for the content: $y_{M^{3+}} = 6 \cdot 10^{-6} \text{ mol/mol}$ (---) line, $5 \cdot 10^{-5}$ (dashed dotted) line, $1 \cdot 10^{-4}$ (dashed dotted) line, $1 \cdot 10^{-3}$ (dotted) line

Using the results of the studies on the deviation from the stoichiometry obtained at 1,173–1,673 K by many authors, the point defect diagrams for pure $Ni_{1-\delta}O$ in the range of oxygen pressure from 1 atm to the oxide decay pressure have been determined. Using the results of the studies of Sockel and Schmalzried [14], Osburn and Vest [13], and Mrowec and Grzesik [21] as a basis, the values of ΔG_F° of the formation of Frenkel defects have been determined, as well as their temperature dependence (in the range of 1,473–1,673 K), which was used in the interpretation of the results by other authors. The obtained temperature dependencies of ΔG° on the formation of nickel vacancies with different ionization degrees have similar slopes (similar values of the entropy of the formation) but different values of the enthalpy. The differences present are caused mainly by a systematic error related to the method of the determination of the absolute values of the deviation from the stoichiometry, which can be particularly seen in the case of results obtained by the authors [14, 15, 20]. In the range of higher oxygen pressures, the concentration of nickel vacancies ($[V_{Ni}']$) is practically equal to the deviation from the stoichiometry. In the range of low oxygen pressures, the concentration of interstitial nickel ions is significant; it is lower than the concentration of nickel vacancies. When the temperature increases, the concentration of defects increases; the range of oxygen pressure, in which the concentration $[Ni_i^{\bullet\bullet}]$ is lower by about 1/2 order of magnitude ($\log([V_{Ni}']/[Ni_i^{\bullet\bullet}]) = 0.5$) also increases.

The characteristic of the dependence of the concentration of electron holes on p_{O_2} is close to the characteristic of the dependence of the deviations from the stoichiometry, and, additionally, there is practically no dependence on the temperature.

Using the determined values of ΔG° of the defects' formation for the "pure" nickel oxide, the dependences of defects concentrations for $(Ni_{1-y}M_y)_{1-\delta}O$ doped with M^+ and M^{3+} ions were determined. Due to a small concentration of ionic defects in $Ni_{1-\delta}O$, the characteristic of the dependence of the deviation from the stoichiometry and the concentration of electron holes on p_{O_2} is even influenced by small quantities of impurities in the form of metal ions with other valence than 2+.

It has been shown that even a low quantity of the M^+ dope causes that the oxide should reach its stoichiometric composition in the range of its existence. In the range of negative deviations from the stoichiometry, the concentration of interstitial nickel ions is significant and higher at low oxygen pressures than the concentration of nickel vacancies. Also, the concentration of electron holes increases in relation to that in the non-doped oxide.

As a result of the increase of the M^{3+} ions' concentration, the concentration of cation vacancies increases and the concentration of electron holes decreases.

The influence of dopes on the concentration of ionic defects and on the deviation from the stoichiometry is much larger than the influence on the concentration of electron holes, which causes significant differences in the characteristic of the dependencies of δ and σ on p_{O_2} . The discrepancies in the values of the exponent in the dependencies of the electrical conductivity on p_{O_2} , obtained by different authors, could be related to the presence of impurities, among which the effective concentration of M^{3+} or M^+ ions is the most important. A relatively small concentration of M^{3+} ions, especially at lower temperatures where the dope amount is comparable to the concentration of defects, can erroneously indicate the presence of single ionized vacancies $[V_{Ni}']$.

Open Access This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

References

- Kröger FA (1964) The chemistry of imperfect crystal. North-Holland, Amsterdam
- Kröger FA (1974) The chemistry of imperfect crystal. North-Holland, Amsterdam
- Kofstad P (1972) Nonstoichiometry, diffusion and electrical conductivity in binary metal oxides. Wiley, New York
- Smyth DM (2000) The defect chemistry of metal oxides. Oxford University Press, New York
- Autin IG, Springthorpe AJ, Smith BA, Turner CE (1967) Proc Phys Soc 90:157
- Bosman AJ, Crevecoeur C (1966) Phys Rev 144:763
- Bosman AJ, Crevecoeur C (1967) Phys Rev 158:736
- Adler D, Feinleib J (1970) Phys Rev B 2:3112
- Adler D, Feinleib J (1968) Phys Rev Lett 21:1010
- Bransky I, Tallan NM (1968) J Chem Phys 49:1243
- Bransky I, Tallan NM (1973) J Chem Phys 58:1263
- Meier GH, Rapp RA (1971) Z Phys Chem NF 74:168
- Osburn CM, Vest RW (1971) J Phys Chem Solids 32:1331, 1343
- Sockel HG, Schmalzried H (1968) Ber Bunsenges Phys Chem 72:745
- Tretyakov YD, Rapp RA (1969) Trans Metall Soc AIME 245:1235
- Pizzini S, Morlotti R (1967) J Electrochem Soc 114:1179
- Mitoff SP (1961) J Chem Phys 35:882
- Tripp WC, Tallan NM (1970) J Am Ceram Soc 53:531
- Koel GJ, Gellings PJ (1972) Oxid Met 5:185
- Haugsrud R, Norby T (1998) Solid State Ionics 111:323
- Mrowec S, Grzesik Z (2004) J Phys Chem Solids 65:1651
- Baumbach HH, Wagner C (1934) Z Phys Chem B24:59
- Uno R (1967) J Phys Jpn 22:1502
- Cox JT, Quinn CM (1969) J Mater Sci 4:33
- Error NG, Wagner JB Jr (1969) Phys Status Solidi 35:641
- Volpe ML, Reddy J (1970) J Chem Phys 53:1117
- Sockel HG, Ilschner B (1971) Z Phys Chem NF 74:284
- Stroud JE, Bransky I, Tallan NM (1973) J Chem Phys 58:1263
- Dereń J, Jarzębski ZM, Mrowec S, Walec T (1971) Bull Acad Pol Sci Ser Sci Chim 19:147, 153
- Mrowec S, Nowotny J, Walec T, Wójcikiewicz T (1973) Bull Acad Pol Sci Ser Sci Chim 21:829
- Dereń J, Mrowec S (1973) J Mater Sci 8:545
- Ikeda Y, Nii K, Béranger G, Lacombe P (1974) Trans Jpn Inst Met 15:441
- Ikeda Y, Nii K, Béranger G, Lacombe P (1976) Trans Jpn Inst Met 17:419
- Farhi R, Petot-Ervas G (1978) J Phys Chem Solids 39:1169–1175
- Nowotny J, Sadowski A (1979) J Am Ceram Soc 62:24
- Nowotny J, Obłakowski J, Sadowski A, Wagner JB Jr (1980) Oxid Met 14:437
- Nowotny J, Obłakowski J, Sadowski A, Wagner JB Jr (1981) Oxid Met 15:191
- Rom I, Jantscher W, Sitte W (2000) Solid State Ionics 135:731
- Price JB, Wagner JB Jr (1966) Z Phys Chem NF 49:257
- Nowotny J, Wagner JB Jr (1973) J Am Ceram Soc 56:397
- Stokłosa A (1981) Bull Acad Pol Sci Ser Sci Chim 29:141
- Lindner R, Åkerström A (1957) Discuss Faraday Soc 23:133
- Shim MT, Choi JS, Moore WJ (1957) J Phys Chem 26:802
- Shim MT, Choi JS, Moore WJ (1962) J Phys Chem 66:1308
- Klotsman SM, Tomofeyev AN, Trakhtenberg ISH (1962) Fiz Met Metalloved 14:428
- Atkinson A, Taylor RI (1978) J Mater Sci 13:427
- Kubaszewski O, Goldbeck O (1948) Z Metallkunde 39:158
- Baur JP, Bartlett RW, Ong JN, Fassel WM (1963) J Electrochem Soc 110:185
- Fueki K, Wagner JB Jr (1965) J Electrochem Soc 112:384
- Przybylski K, Stokłosa A (1975) Oxid Met 9:441
- Godlewski K, Stokłosa A, Walec T (1978) Bull Acad Pol Sci Ser Sci Chim 26:951
- Hauffe K, Block J (1951) Z Phys Chem 198:438
- Schwab GM, Schmid H (1962) J Appl Phys 33:426
- Perkins RA, Rapp RA (1973) Metall Trans 4:193
- Nowotny J, Rekas M (1984) Solid State Ionics 12:253
- Wood GC, Hodgkiess T (1966) Nature [London] 211:1358
- Greskovich C (1970) J Am Ceram Soc 53:498
- Słoczyński J, Kowalski Z, Wójcikiewicz T (1972) J Mater Sci 7:1369
- Bender B, Williams DW, Notis MR (1980) J Am Ceram Soc 63:542
- Degraix H, Gravelle PC, Teichner SJ, Turlier P (1976) J Solid State Chem 18:69
- Stokłosa A (2011) Ionics (in press)
- Pankratz LB (1982) Thermodynamic properties of elements and oxides, bulletin 672. US Bureau of Mines, Washington