Semiconducting and transport properties of mono- and polycrystalline nickel oxide

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On the basis of high-temperature studies of electrical conductivity of poly- and monocrystalline nickel oxide and making use of the results of studies on chemical diffusion coefficients obtained by several authors and in the present work, the structure of point defects in nickel oxide has been considered. It has been shown that in the temperature range 900 to 1300°C and at the oxygen pressure from 10^{-4} to 1 atm there occur in nickel oxide singly- and doubly-ionized cationic vacancies in comparable quantities.

Assuming such to be the model of defect structure in $Ni_{1-y}O$, the equilibrium concentration of cationic vacancies as a function of temperature has been calculated for the oxygen pressure of 1 atm. It has been shown that the results obtained are in good agreement with the results of direct determinations of concentration of cationic vacancies in NiO.

1. Introduction

Systematic studies on physico-chemical properties of nickel oxide were initiated about forty years ago by the classical works of Wagner and his co-workers [1-4]. In subsequent years these studies showed continuous growth, the peak of which was noted in the last decade [5-31]. This was due to the fact that nickel oxide was considered a model semiconductor, although results of the most recent experiments seem to indicate that this choice was not the most fortunate. The main reason for choosing NiO as a model substance was the fact that this oxide is thermo-dynamically stable over a very wide range of temperatures and oxygen pressures and hence its physico-chemical properties can be relatively easily studied as a function of these two parameters. On the other hand considerable experimental difficulties have been encountered in studies of some basic properties of this oxide. For instance, the current carrier mobility in this oxide is exceptionally small (of the order of 10^{-3} cm²/V sec at room temperature) which practically excludes the possibility of applying the Hall method. Moreover, deviations from stoichiometry – even at very high temperatures – are so small (of the order of 10^{-2} at. % in 1000°C) that determination of their dependence on temperature and oxygen pressure is very

difficult. Finally a number of experimental data indicate that structure of point defects in the crystalline lattice of NiO is more complex than that observed in other transition metal oxides which are to be represented by nickel oxide [6, 7].

In spite of these facts, extensive experimental material collected in the recent years on physico-chemical properties of nickel oxide, in particular on its semiconducting and transport properties, makes it possible to formulate some general conclusions concerning oxide semiconductors of hole-type conductivity. The present work is an attempt at summing-up results of studies on electrical and transport properties of nickel oxide which has enabled the authors to propose a model of defect structure of this oxide.

2. General considerations

Nickel oxide is a p-type semiconductor with the real deficit of metal $(Ni_{1-y}O)$. This implies that in the wide range of temperatures and oxygen pressures, the anionic sublattice of this oxide is practically non-defected, whereas the cationic sublattice contains vacancies and the equivalent number of electron holes.

Although many experimental facts concerning both single- and polycrystalls of NiO have been collected, there exist considerable discrepancies as to the ionization degree of cationic vacancies

and activation energy of their formation in this material. The recent data of Osburn [31] show that these parameters are strongly influenced by purity of the material under study. The data on mobility of cationic vacancies – a basic parameter enabling determination of time of homogenization of a material in given thermodynamic conditions – are lacking at present.

The discrepancies mentioned above, result initially from the fact that the majority of studies performed on nickel oxide pertain to conditions distant from thermodynamic equilibrium. Moreover, the manner of treating the material prior to experiments, differed markedly in various works. In the majority of works the sufficiently-high temperatures of homogenization of samples were not applied. Finally self-diffusion of nickel and oxygen – though determined for both on poly- and monocrystalline material – have not been measured as a function of the oxygen pressure, which does not allow the formulation of any conclusions about the ionization degree of the defects.

A relatively large number of data may be found in the current literature on electrical conductivity of NiO measured under conditions of thermodynamic equilibrium as dependent on oxygen pressure and temperature [8, 11, 16, 19-23, 31]. The results of these studies differ markedly and only one of them [31] is concerned with both mono- and polycrystalline material.

3. Defect equilibria in nickel oxide

To discuss the results of experimental studies it is necessary to consider at the beginning defect equilibria in nickel oxide. As already mentioned nickel oxide is, in the wide range of temperatures and pressures, a p-type semiconductor with the real deficit of metal ($Ni_{1-y}O$). This implies that cationic vacancies and electron holes formed at the crystal surface as a result of the reaction with the surrounding oxygen, are the predominant defects of the structure. Incorporation of oxygen into the crystalline lattice of NiO and successive processes of ionization of cationic vacancies, can be described by the following quasi-chemical equations:

$$\tfrac{1}{2}O_2 \rightleftharpoons V_{Ni} + O_O \qquad (1)$$
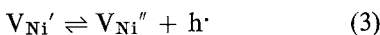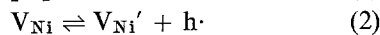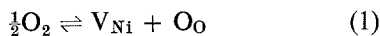
$$V_{Ni} \rightleftharpoons V_{Ni}' + h \cdot \qquad (2)$$

$$V_{Ni}' \rightleftharpoons V_{Ni}'' + h \cdot \qquad (3)$$

where according to Kröger and Vink nomenclature V_{Ni}, V_{Ni}' and V_{Ni}'' are respectively non-ionized, singly and doubly ionized cationic

vacancies, $h \cdot$ is the electron hole, O_O oxygen ion in a lattice-site position.

Applying the law of mass action and conditions of the lattice electroneutrality to these equations, we obtain three limiting cases for the dependence of the concentration of ionic and electronic defects on the equilibrium oxygen pressure and temperature:

$$y \cong [V_{Ni}]_{total} = [V_{Ni}] = const \cdot p_{O_2}^{\tfrac{1}{2}} \exp - \left(\frac{\varDelta H_f}{RT}\right) \qquad (4)$$

$$y \cong [V_{Ni}]_{total} = [V_{Ni}'] = h \cdot =$$
$$const\, p_{O_2}^{\tfrac{1}{4}} \exp . - \left(\frac{\tfrac{1}{2}\varDelta H_f}{RT}\right) \qquad (5)$$

$$y \cong [V_{Ni}]_{total} = [V_{Ni}''] = \tfrac{1}{2}h \cdot =$$
$$const\, p_{O_2}^{\tfrac{1}{6}} \exp - \left(\frac{\tfrac{1}{3}\varDelta H_f}{RT}\right) \qquad (6)$$

where y is the deviation from stoichiometry according to the stoichiometric formula $Ni_{1-y}O$, the brackets denote concentration of given defects in molar fractions, $\varDelta H_f$ is the enthalpy of formation of one mole of defects, $[V_{Ni}]$ is a concentration of given defects in molar fractions, $[V_{Ni}]_{total}$ is the total concentration of cationic vacancies.

Equation 4 is derived by applying the law of mass action to the equilibrium given by Equation 1, hence it describes the limiting case in which practically all cationic vacancies in a crystal are, in the given range of temperatures and oxygen pressures, non-ionized.

Equation 5 on the other hand, is related to equilibrium 2 in which case, practically all cationic vacancies are singly ionized. In this case the concentration of vacancies is equal to the concentration of electron holes and the simplified electroneutrality condition assumes the form:

$$[V_{Ni}'] = [h \cdot] . \qquad (7)$$

Finally Equation 3 describes the third limiting case in which doubly-ionized cationic vacancies are the predominant defects. In this case the concentration of electron holes is twice as high as the concentration of cationic vacancies:

$$[V_{Ni}''] = \tfrac{1}{2}[h \cdot] \qquad (8)$$

Obviously in a real crystal cationic vacancies of various ionization degrees may occur in comparable quantities.

It follows from the above considerations that enthalpy of defect formation and degree of their ionization in a given range of oxygen pressure

and temperature, can be determined by studying deviation from stoichiometry y, as a function of oxygen pressure and temperature. Very small deviation from stoichiometry in the case of nickel oxide, makes these studies exceptionally difficult. Five papers reporting results of such studies can be found in the available literature [16-18, 30, 31] the differences between them are, however, considerable.

On the other hand, it follows from Equations 5 and 6 that some information about enthalpy of defect formation and degree of their ionization can be obtained by studying the concentration of electronic defects as a function of oxygen pressure and temperature. Although direct determination of the electron-hole concentration is even more difficult than determination of the cationic-vacancies concentration, one can make use of the fact that the former concentration is proportional to electrical conductivity of the oxide, which can be determined with relatively-high accuracy in conditions of thermodynamic equilibrium. The electrical conductivity of an oxide is related to the concentration of holes by:

$$\sigma = [h \cdot] \, \mu_h \cdot q^+ \qquad (9)$$

where μ_h, is a hole mobility and q^+ is a positive elementary charge.

The temperature dependence of mobility of current carriers in transition metal oxides may assume various forms depending on mechanism of transport of these carriers [6]. Mechanism of carriers transport in NiO is disputable. According to some authors it takes place in a narrow band, according to others, the hopping mechanism operates.

It follows from a number of works carried out with various methods that transport of holes in nickel oxide is an activated process, i.e., that the hole mobility is an exponential function of temperature. This function, although of complex character, may be described, with good approximation, by the following simple empirical equation:

$$\mu_h \cdot = \text{const} \cdot \exp \left(- \frac{\Delta H_m^{h \cdot}}{RT} \right) \qquad (10)$$

where $\Delta H_m^{h \cdot}$ is the activation energy of motion of holes. Substituting Equation 10 into Equation 9, and making use of Equations 4 to 6 we obtain the general dependence interrelating electrical conductivity of the oxide with temperature and oxygen pressure:

$$\sigma = \text{const} \, p_{O_2}^{1/n} \exp \left(- \frac{2}{n} \frac{\Delta H_f + \Delta H_m^{h \cdot}}{RT} \right) \qquad \ldots \ldots (11)$$

where n depends on ionization degree of the defects and is contained between $\frac{1}{4}$ and $\frac{1}{6}$.

It follows from this dependence that studying electrical conductivity of nickel oxide as a function of oxygen pressure and temperature in the conditions of thermodynamic equilibrium, one may determine the exponent $1/n$ and hence degree of ionization of cationic vacancies and the total activation energy of conductivity. This latter is a sum of enthalpy of defect formation and activation energy of motion of holes. The empirical formula which interrelates the measured value of the electrical conductivity of the oxide, oxygen pressure and temperature has a form:

$$\sigma = \text{const} \cdot p_{O_2}^{1/n} \exp \left(- \frac{E_\sigma}{RT} \right) . \qquad (12)$$

Comparison of Equations 11 and 12 yields:

$$E_\sigma = \frac{2}{n} \Delta H_f + \Delta H_m^{h \cdot} . \qquad (13)$$

Table I summarizes the results of high-temperature studies on electrical conductivity of nickel oxide. As seen from this comparison, there exist few data concerning dependence of the electrical conductivity on equilibrium partial pressure of oxygen and moreover these data are not adequate to formulate unanimous conclusions about the degree of defect ionization. The exponent $1/n$ in Equation 12 varies from $\frac{1}{4}$ to $\frac{1}{6}$. Considerable differences exist also between the values of the activation energy of electrical conductivity.

4. Diffusion of cationic vacancies and nickel ions in the crystalline lattice of NiO

Full description of transport properties of a given material requires the knowledge of three different diffusion coefficients: D_{Ni}, D_V and D_{chem}. The first two are self-diffussion coefficients of nickel ions and cationic vacancies in the crystal lattice of $Ni_{1-y}O$, the third one is the diffusion coefficient of vacancies when the gradient of vacancy concentrations is present in the crystal. All three parameters essentially are never equal to each other and in particular the values of D_{Ni} and D_V differ by several orders of magnitude. Moreover, activation energy of chemical diffusion and of defect diffusion are not equal

TABLE I Data concerning the results of electrical conductivity measurements in NiO at high temperatures

Reference	Investigated material	Temperature range [°C]	Oxygen partial-pressure range [atm]	Atmosphere	Value of $1/n$ from Equation 12	$E\sigma$ from Equation 12 [kcal mol^{-1}]
[1]	Polycrystalline	800 – 1000	$2 \times 10^{-4} - 1$	$CO + CO_2$	$\frac{1}{4}$	—
[11]	Monocrystalline	1182 – 1762	$5 \times 10^{-7} - 1$	$O_2, O_2 + Ar$	$\frac{1}{4} - \frac{1}{6}$	24.7
[16]	Monocrystalline	600 – 1350	$10^{-4} - 1$	$O_2, O_2 + Ar$	$\frac{1}{6}$	23.30
[19]	Polycrystalline	800 – 1100	$10^{-2} - 1$	$N_2 + O_2$	$\frac{1}{6}$	14.7 – 36.8
[20]	Monocrystalline	1000 – 1250	$1.3 \times 10^{-6} - 0.21$	air	$\frac{1}{4}$	23.2
[21]	Monocrystalline	1000 – 1600	$10^{-6} - 1$	$O_2, O_2 + Ar$ $CO + CO_2$	$\frac{1}{4}$	21.2
[22]	Polycrystalline	950	$10^{-2} - 7.5 \times 10^2$	O_2	$\frac{1}{5}$	—
[23]	Monocrystalline	950 – 1200	$10^{-4} - 1$	$O_2, O_2 + Ar$	$\frac{1}{4}$	21.7 – 25.4
[31]	Monocrystalline Polycrystalline	900 – 1400	$10^{-4} - 1$	O_2	$\frac{1}{6}$	18.6

to the activation energy of the diffusion of nickel ions. The diffusion coefficient of vacancies is, as a rule, independent of their concentration, whereas the coefficient D_{Ni} is directly proportional to this concentration. As implied by the theory of diffusion [32, 33] when defect concentration is expressed in molar fractions, D_V is simply a proportionality coefficient:

$$D_{Ni} = D_V[V_{Ni}] . \qquad (14)$$

As the concentration of nickel vacancies in nickel oxide is of the order of 10^{-4}, from Equation 14 it follows that in the case of nickel oxide D_{Ni}, it is about four times smaller than D_V.

The knowledge of these two coefficients is necessary for description of the transport properties of a given material. These coefficients characterize mobility of two different elements of structure; ions and vacancies which constitute essential components of a crystal lattice. The self-diffusion coefficient of nickel ions characterizes the mobility of cations in the lattice, which determines the rate of sintering, grain growth, decomposition (reduction) of the oxide, kinetics of its formation, etc. Coefficients D_V and D_{chem} on the other hand are the measure of mobility of vacancies which determines the rate equalization of defect concentrations in a crystal and hence allows the evaluation of time of homogenization of a material, etc.

The temperature dependence of coefficient D_V results from the effect of temperature on frequency of "jumps" of cationic vacancies and is given by the following expression:

$$D_V = \text{const} \cdot \exp \left(- \frac{\Delta H_m^d}{RT} \right) . \qquad (15)$$

ΔH_m^d is the activation energy of movement of

cationic vacancies which is equal to the height of energy barrier surmounted by nickel cations when jumping to the adjacent vacancy. The constant comprises an entropy term of vacancy motion beside other parameters [32].

The temperature dependence of D_{Ni} can be obtained by substituting Equation 15 to Equation 14 and making use of Equations 4 to 6:

$$D_{Ni} = \text{const} \cdot p_{O_2}^{1/n} \exp \left(- \frac{\frac{2}{n} \Delta H_f + \Delta H_m^d}{RT} \right) \qquad (16)$$

where the constant comprises also an entropy term involved at the formation of defects. From comparison of Equations 11 and 16 it follows that the dependence of self-diffusion coefficient of nickel on oxygen pressure has the same character as the corresponding dependence of the electrical conductivity, whereas the temperature coefficient (activation energy) has a different physical meaning.

Finally the temperature dependence of the chemical diffusion coefficient has the following form:

$$D_{chem} = \text{const} \cdot \exp \left(- \frac{\Delta H_m^d}{RT} \right) . \qquad (17)$$

As seen, D_V and D_{chem} show the same characteristic of temperature dependence, which is understandable, as both these coefficients characterize mobility of the vacancies. However, the absolute values of these coefficients are equal to each other only in a special case, as they are interrelated by the following Equation 34:

$$D_{chem} = (1 + |z|) D_V \qquad (18)$$

where z is the degree of ionization of vacancies.

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It follows from this dependence that only when cationic vacancies are non-ionized [$z = 0$; Equilibrium 1], $D_{chem} = D_V$. When the vacancies are singly or doubly ionized then $D_{chem} > D_V$. These differences come from the fact that chemical diffusion coefficient characterize mobility of the vacancies in the conditions in which the gradient of vacancy concentration is present in the crystal, whereas the diffusion coefficient of vacancies characterizes the situation in which thermodynamic equilibrium is established between the crystal and its surroundings. When the vacancies have no effective charge ($z = 0$), then irrespective of the conditions under which the diffusion occurs – whether it is at equilibrium or at the gradient of concentration – no factors influencing the value of the defect diffusion coefficient occur in the crystal ($D_{chem} = D_V$).

When, however, cationic vacancies are partly or fully ionized, then the crystal contains an equivalent number of electron holes, the mobility of which is several orders of magnitude higher than the mobility of the vacancies. If in the crystal of such defect situation, a gradient of chemical potential appears producing a gradient of defect concentration, then an orientated motion of defects begins, more mobile electron holes overtaking the cationic vacncies. Between such an assembly (ionic defect–electronic defect) an electrostatic field appears which accelerates diffusion of electron holes. This phenomenon is called an ambipolar diffusion.

The diffusion coefficients discussed above, cannot be determined in direct measurements. The only possibility of their determination lies in application of tracer technique but the self-diffusion coefficients of atoms (or ions) determined with this method and termed the tracer diffusion coefficients D_T are burdened with a symmetric error resulting from the correlation effect [33]. In contrast to uncorrelated motion of defects and hence the parent atoms, the movement of tracer atoms shows a defined correlation degree. The self-diffusion coefficient of parent atoms and diffusion coefficient of tracer atoms are interrelated by:

$$D^T = f \cdot D \qquad (19)$$

where f is the correlation coefficient.

This latter coefficient is dependent on many parameters, however, for a number of crystal structures and various diffusion mechanisms, values of f have been calculated with high accuracy. For nickel oxide structure and the vacancy mechanism of nickel ion diffusion in cationic sublattice, $f = 0.78$. Thus the self-diffusion coefficient of nickel in NiO may be derived from the results of radioisotopic studies from the relation:

$$D_{Ni} = \frac{D_{Ni}^T}{0.78} \cdot \qquad (20)$$

D_{Ni} can be also determined with high accuracy indirectly from the measurements of kinetics of nickel oxidation [15, 36].

The activation energy of diffusion, E_D, may be determined from the temperature dependence of D_{Ni} according to the equation:

$$D_{NI} = const \cdot exp\left(-\frac{E_D}{RT}\right). \qquad (21)$$

Comparing Equation 21 with Equation 16 we get:

$$E_D = \frac{2}{n} \Delta H_f + \Delta H_m^d. \qquad (22)$$

It follows from Equations 13 and 22 that both parameters E_σ and E_D contain the enthalpy of defect formation which enables determination of this latter function on two independent ways provided the degree of defect ionization and values of $\Delta H_m^{h'}$ and ΔH_m^d are known. The values of $\Delta H_m^{h'}$ can be derived from the measurements of Hall or Seebeck effect, which are difficult to realize at high temperatures. The value of ΔH_m^d can be, on the other hand, determined relatively simply, by studying the temperature dependence of the chemical diffusion coefficient.

There exist several methods for determination of the chemical diffusion coefficient in metal oxides [34, 35]. Only one of them described by Price and Wagner [24] was applied for determination of the chemical diffusion coefficient in nickel oxide. This is the only work to date, giving quantitative data about the chemical diffusion coefficient in nickel oxide which does not agree with theoretical suppositions, in particular with respect to the values of ΔH_m^d. In view of this fact the studies of electrical conductivity and chemical diffusion on poly- and monocrystalline nickel oxide have been carried out.

5. Apparatus and materials

Electrical conductivity [7] and chemical diffusion [8] were measured on sintered polycrystalline samples and on single crystals of nickel oxide prepared from the same starting material. Poly-

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crystalline samples were obtained by thermal decomposition of hydrated ammonium-nickel sulphate. The decomposition was carried out in platinum crucibles at 1100° C for 4 h. One part of nickel oxide thus obtained was used for preparation of single crystals, another was pressed into rectangular bars 5 × 5 × 30 mm. The bars were then annealed in air at 1600° C for 12 h. After this treatment, the specimens were microscopically compact, showed metallic glaze and their grain size was 0.1 mm. The results of spectral analysis for content of impurities in the material are listed in Table II.

TABLE II Impurity content in poly- and mono-crystalline NiO (ppm)

Element	Polycrystalline	Monocrystalline
Na	1	1
Mg	5	5
Al	5	5
Si	30	50
S	5	5
Ca	1	5
Ti	1	1
V	—	—
Cr	—	—
Fe	5	1
Co	10	10
Cu	1	1

The monocrystalline samples were prepared with the Verneuill method in the hydrogen-oxygen burner [37]. The rate of crystal growth was about 6 mm/h. The single crystals obtained had the form of cylinders, 15 mm in diameter and 30 mm long. From the crystals, the bars analogous to those of polycrystalline NiO were prepared. After polishing on the grindstone covered with diamond powder the specimens had the size 2.5 × 4.2 × 11 mm. The electrical conductivity was also measured on polycrystalline NiO obtained by thermal decomposition of nickel hydroxide. The preparation of these samples was described in [38].

Electrical conductivity of poly- and monocrystalline samples was measured in an apparatus shown schematically in Fig. 1. The sample was placed in a quartz tube fixed in an oven 50 cm long. The temperaure in the measurement chamber was controlled with a Pt-PtRh thermocouple and regulated automatically. The required partial pressure of oxygen was obtained by passing a laminar stream of argon-oxygen mixture through the chamber under pressure

slightly exceeding atmospheric. The total linear velocity was 0.22 cm sec^{-1}. To obtain the constant flow and the constant composition of the gas, the system of mixers and capillary flow-meters was applied. The gas passed upwards through the chamber leaving it by the upper opening through which the current and measurement leads were also led. The sample was suspended on these leads. Such a system provided simplicity of the apparatus and ensured (as checked by separate measurements) the control and stability of the partial pressure of oxygen in the measurement chamber.

6. Results of electrical conductivity measurements

The electrical conductivity measurements were carried out with a conventional four-probe method consisting in the arrangement of two measuring probes and two independent current leads. The four leads were made of platinum wire 0.2 mm diameter. The wires were fixed on a NiO sample by wrapping the sample with them in the specially cut slots. A d.c. of 1 mA from a transistor supplier passed through the sample. The potential difference between the two measuring probes was measured with an electrometer.

The experiments were carried out in the temperature range 950 to 1200° C and in the oxygen pressure range from 1 to 0.3 × 10^{-3} atm. The electrical conductivity at a given oxygen partial pressure was measured at different temperatures in steps of 50° C. The oxygen pressure was then changed and the temperature dependence of the conductivity was again registered. To make sure that the measured value corresponded to the thermodynamic equilibrium, the temperature dependence of the conductivity was measured for each sample on cooling and on heating. The same values of the conductivity obtained in these two series of measurements, indicated that the values registered were the equilibrium values.

It should be noted that in the case of single crystals, thermodynamic equilibrium was established after a considerably longer time than that required for polycrystalline samples. For example, the stationary value of σ at 1200° C was reached, in the case of single crystals, after 8 h and at 950° C after 25 h. The respective times for polycrystalline samples were several minutes and ~ 15 min respectively.
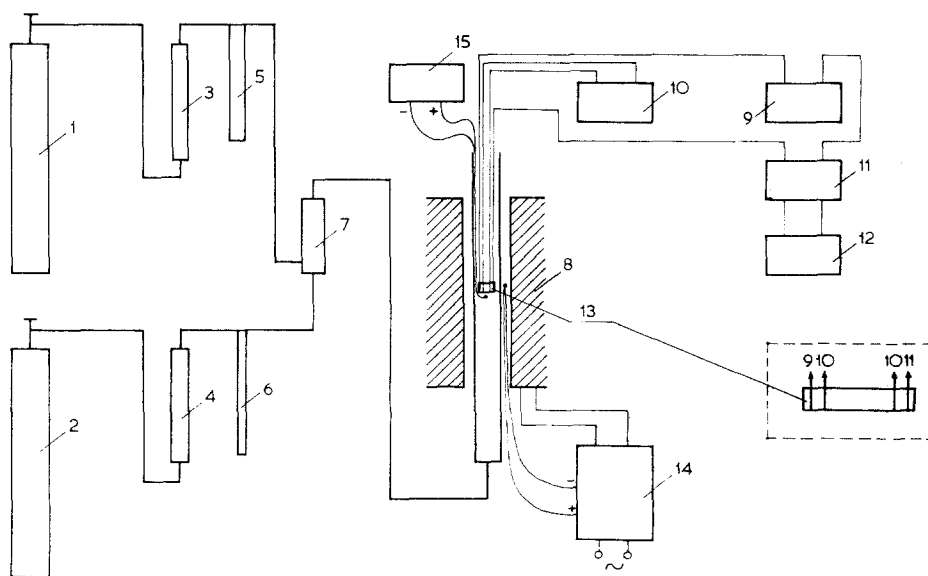
In Fig. 2 the results of the conductivity studies

Figure 1 Schematic diagram of the apparatus for electrical conductivity measurements; 1 – oxygen cylinder; 2 – argon cylinder; 3, 4 – bubblers; 5, 6 – flowmeters; 7 – mixer; 8 – oven; 9 – milliampmeter; 10 – electrometer; 11 – voltage divider; 12 – source of constant voltage; 13 – sample and four probes; 14 – thermoregulator; 15 – thermocouple set up.

are plotted as a function of log σ versus $1/T$ for a number of oxygen pressures. The continuous lines pertain to polycrystalline preparations and broken lines to single crystals. In Fig. 3 the function $\log \sigma = f(\log p_{O_2})$ is plotted for different temperatures. It follows from Fig. 3 that the values of electrical conductivity obey the Arrhenius equation in the whole range of temperatures and oxygen pressures. It should be particularly noted that the absolute values of σ for single crystals are practically the same as those obtained for polycrystalline material. This indicates, that in contrast to the present viewpoints, no scattering of current carriers on grain boundaries occurs at high temperatures.

It follows from Fig. 2 that the activation energy of conductivity is independent of oxygen pressure and amounts to 19.8 kcal mol^{-1}. This result is in good agreement with the most recent literature data (cf. Table I).

The plot shown in Fig. 3 implies that the character of dependence of electrical conductivity on oxygen pressure does not change with temperature in the range under study. The exponent $1/n$ of Equations 11 or 12 derived from this plot amounts to 1/5. Identical results were obtained on polycrystalline NiO prepared by decomposition of nickel hydroxide.
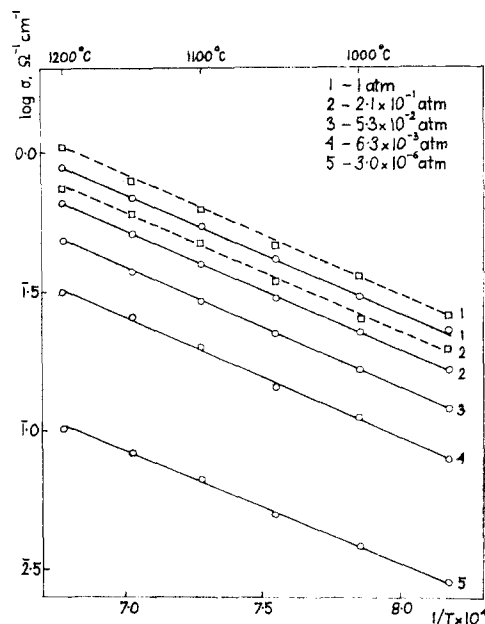

Figure 2 Logarithm of electrical conductivity of single and polycrystalline NiO as a function of reciprocal temperature at various oxygen partial pressures.

The dependence of electrical conductivity of mono- and polycrystalline nickel oxide, on
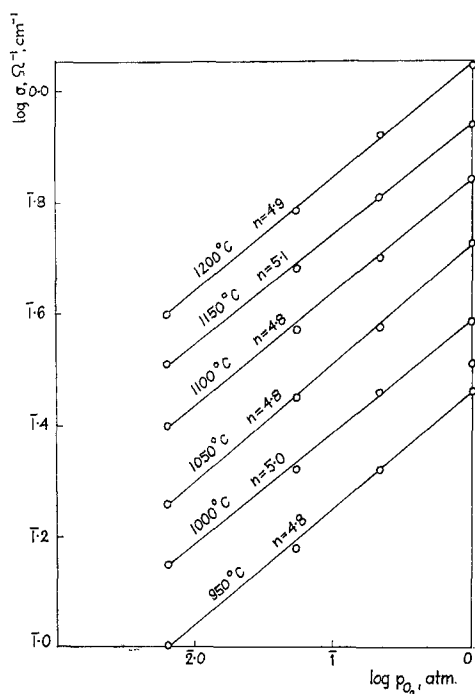
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Figure 3 Logarithm of electrical conductivity of poly-crystalline NiO as a function of the logarithm of oxygen partial pressure at various temperatures.

temperature and oxygen pressure, can be then described by the following empirical equations:

$$\sigma_{mono} = p_{O_2}^{\frac{1}{6}} 1 \cdot 10^3 \exp\left(-\frac{19.8}{RT}\right) \quad (23)$$

and

$$\sigma_{poly} = p_{O_2}^{\frac{1}{6}} .8 \cdot 10^2 \exp\left(-\frac{19.8}{RT}\right). \quad (24)$$

7. Results of measurements of chemical diffusion

The measurements of chemical diffusion coefficients, D_{chem}, were carried out on the same samples and with the same apparatus as in the studies of electrical conductivity. The principle of the measurement was also the same as that in the case of determination of the equilibrium values of σ, and consisted in measuring the electrical conductivity of nickel oxide at different temperatures with the four-probe method. The changes of electrical conductivity with time occurring at rapid changes of partial pressure of oxygen, were followed at constant temperature. The determination of D_{chem} was based on the Price and Wagner's method [24] consisting in measuring kinetics of changes of σ, during

transition of a crystal from one state of thermo-dynamic equilibrium to another. Under these conditions there exists in a crystal a gradient of defect concentration which leads to their diffusion until a new defect equilibrium is established. Since changes in concentration of cationic vacancies are accompanied by changes of hole concentration, the value of the chemical diffusion coefficient may be determined from the measurements of electrical conductivity changes. It is necessary, however, to assume that hole mobility is independent of hole concentration [24, 34, 35]. Only in this case the changes of σ are the measure of changes of current carrier concentration. Also, the crystal should not contain non-ionized cationic vacancies or defect complexes. In other words, the determination of chemical diffusion coefficients from indirect measurements yields correct results only when the defect situation in a crystal is relatively simple and is given by Equations 2 and 3.

The results of studies on mobility of current carriers in nickel oxide [6] and on defect equilibria [7, 16-23, 31] show that in the case under discussion both of the above assumptions are obeyed.

The chemical diffusion coefficients were calculated from the formula derived by Price and Wagner [24] for rectangular samples

$$D_{chem} = \frac{0.934}{t\left(\frac{1}{a} + \frac{1}{b} + \frac{1}{c}\right)} \log \frac{0.533}{1 - \frac{\Delta\sigma_t}{\Delta\sigma_\infty}} \quad (25)$$

where $2a$, $2b$, $2c$ are lengths of sides of the samples, $\Delta\sigma_t = \sigma_t - \sigma_i$; $\Delta\sigma_\infty = \sigma_2 - \sigma_1$; σ_1 and σ_2 are equilibrium electrical conductivities of the crystal at two different partial pressures of oxygen, and σ_t is the conductivity at non-equilibrium conditions after time t, taken from the moment of change of the partial pressure of oxygen in the reaction space.

In the method applied it is indifferent whether the crystal is equilibrated at higher pressure of oxygen, the pressure rapidly decreased and the changes of σ followed, or whether conversely the initial state of the crystal corresponds to the lower partial pressure of oxygen. In our studies [8], the second variant was employed: the crystal was heated initially in the argon-oxygen mixture of the partial oxygen pressure of 3×10^{-6} atm until the constant value of σ was established. The flow of oxygen was then stopped and air was admitted to the reaction space.

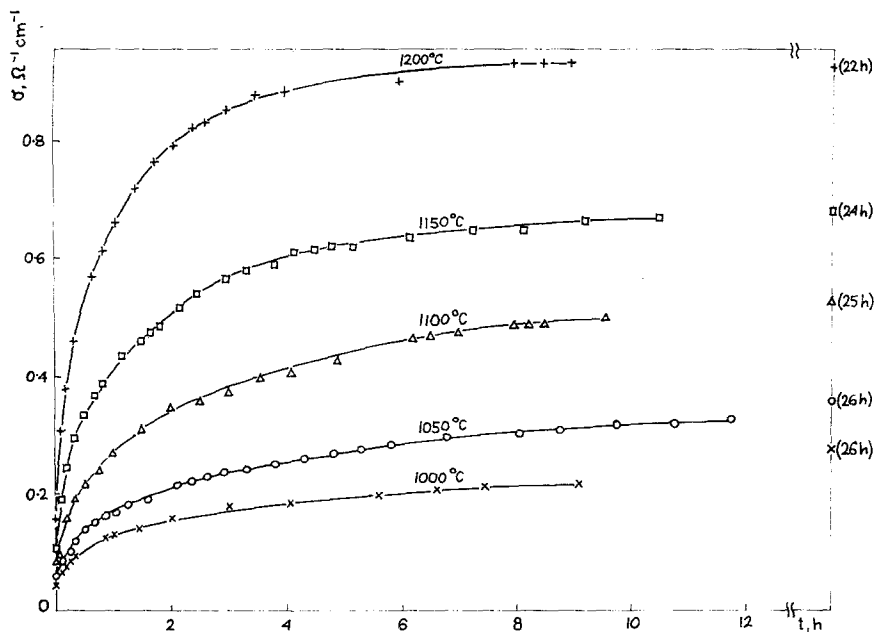In order to realize rapid exchange of gases and

Figure 4 Electrical conductivity of a NiO single crystal in air as a function of time at various temperatures.

establishment of partial oxygen pressure at a new level, the flow rate of air in the first minute was six times higher, amounting to 1.3 cm sec^{-1}. The stationary value of oxygen partial pressure of 0.21 atm was established within 3 min.

After admitting air to the reaction space, electrical conductivity was measured until the new constant value of σ corresponding to thermodynamic equilibrium in these conditions, was established. The measurements were carried out at various temperatures in the range 1000 to 1200°C. The selected results of these studies obtained on monocrystalline sample are presented in Fig. 4. It follows from this Figure that the time necessary for establishing a new thermodynamic equilibrium for the sample of above given dimensions was, depending on temperature of the measurement, from several to several tens of hours. Thus, the function of σ versus me could be determined with sufficient accuracy, and value of D_{chem} could be calculated.

We could not obtain this effect for polycrystalline material. In this case, new thermodynamic equilibrium in the gas-sample system was established within several minutes. The measurements here, require modification of the apparatus enabling rapid exchange of gases. Our polycrystalline sample contained NiO grains of the average size of 0.1 mm. In spite of the fact

that the sample was annealed at relatively high temperature (1600°C), and the preparation obtained was apparently microscopically compact, oxygen could penetrate the sample relatively quickly and the equilibrium was reached with the rate proportional to the size of individual grains and not to the size of the whole sample. This unexpected observation implies that diffusion of oxygen into the bulk of the sample occurs along the grain boundaries, though the polycrystalline material was relatively well sintered. This is proved by practically the same values of σ for poly- and mono-crystalline samples. It is generally recognized that activation energy of intergranular diffusion is considerably lower than the activation energy of lattice diffusion [32, 33] and hence at the high temperatures at which the experiments were performed, the intergranular diffusion of oxygen should play only a minor role. The authors believe then that the compactness of polycrystalline material was only apparent and oxygen could migrate to the bulk of the sample at the high rate through canals of considerably higher diameters than the grain boundaries of the real polycrystallite. To check this hypothesis, the experiments should be performed on polycrystalline material without any discontinuities.
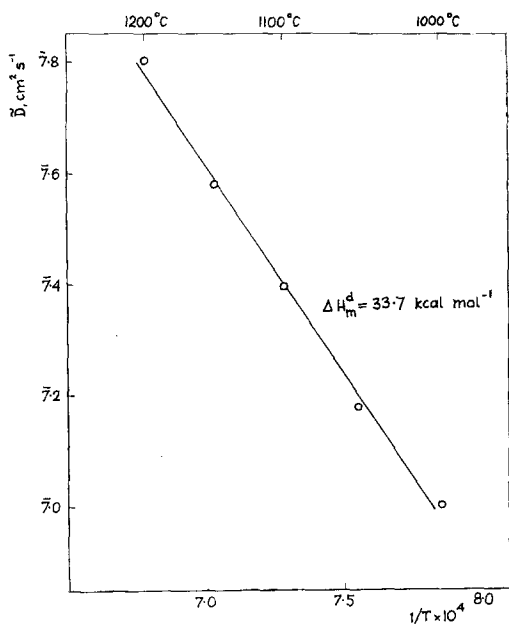
Owing to the difficulties in measuring the

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Figure 5 Logarithm of the chemical diffusion coefficient as a function of reciprocal temperature.

chemical diffusion coefficients of polycrystallites mentioned above, the values of D_{chem} were determined only for monocrystalline samples. The results of these studies are shown in Fig. 5. It follows from this Figure that the dependence of log D_{chem} on reciprocal temperature, is linear. The activation energy of diffusion of cationic vacancies ΔH_m^d calculated from this plot amounts to 33.7 kcal mol^{-1} which is consideraby higher than the value reported by Price and Wagner [24]. The results obtained in these studies can be described by the following empirical equation:

$$D_{\text{chem}} = 5.45 \cdot 10^{-2} \exp\left(-\frac{33.7}{RT}\right). \quad (26)$$

The respective equation derived by Price and Wagner [24] has the form:

$$D_{\text{chem}} = 7.52 \cdot 10^{-4} \exp\left(-\frac{21.9}{RT}\right). \quad (27)$$

8. Discussion of the results

The results of the studies on electrical conductivity and the data on mobility and activation energy of motion of cationic vacancies in nickel oxide, allow some new conclusions to be formulated about the defect structure in this
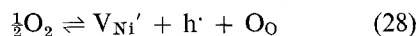
oxide and provide further quantitative information about its transport and electrical properties.

The results of studies of electrical conductivity obtained on poly- and monocrystalline material seem to solve the problem of the value of the exponent $1/n$ (Equation 11) in favour of the data reported by Cox and Quinn [22] (Table I). It should be noted that this value was obtained on two series of polycrystalline samples.
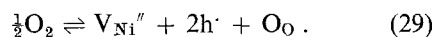
The results obtained do not fully agree with the recent data of Osburn and Vest [31], who assume the value of $1/n$ to be equal to 1/6. Their data obtained for the purest preparation of NiO with a thermogravimetric method, however, yield values of $n = 5.26$, very close to that obtained in the present studies. The value of $\frac{1}{6}$ accepted by them is based on the values of $n = 5.7$ obtained in studies of electrical conductivity. Although the conclusion that the value of $\frac{1}{4}$ is obtained when experiments are performed on contaminated material, seems to be conclusive, the comparison of analysis of preparations employed by Osburn and Vest and those used in the present studies shows practically the same purity of the material in the both cases. No effect of temperature on the value of n, which is characteristic of contaminated samples, was observed in the present studies.

In view of the above considerations we believe that in both cases nickel oxide contains both singly- and doubly-ionized cationic vacancies. The differences in the values of n are most probably due to the small differences in qualitative composition of the addition.

The conclusion of comparable concentrations of singly- and doubly-ionized vacancies in our samples can be derived from the following considerations on defect equilibria [8]. If we assume that in the discussed conditions, practically all cationic vacancies are ionized, half of them being doubly-ionized, then defect equilibria can be described by the following equations:

$$\tfrac{1}{2}O_2 \rightleftharpoons V_{\text{Ni}}' + h^{\cdot} + O_O \quad (28)$$

and

$$\tfrac{1}{2}O_2 \rightleftharpoons V_{\text{Ni}}'' + 2h^{\cdot} + O_O. \quad (29)$$

Adding the sides of the above partial equilibria we obtain the overall reaction of formation of singly- and doubly-ionized vacancies and of the equivalent number of electron holes:

$$O_2 \rightleftharpoons V_{\text{Ni}}' + V_{\text{Ni}}'' + 3h^{\cdot} + 2O_O. \quad (30)$$
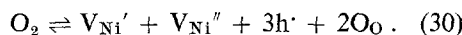
Bearing in mind the assumption mentioned above, it follows from Equation 30 that

$$[V_{\text{Ni}}'] = [V_{\text{Ni}}'']. \quad (31)$$

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The electroneutrality condition therefore assumes the form:

$$[V_{Ni}'] + [V_{Ni}''] = \tfrac{2}{3}[h^{\cdot}] . \qquad (32)$$

Applying the law of mass action to Equilibrium 30 and taking into account Equations 31 and 32, one obtains the following relationship between the concentration of electron hole and oxygen pressure:

$$[h^{\cdot}] = const . p_{O_2}^{\tfrac{1}{6}} . \qquad (33)$$

Equation 33 can be further transformed into the form:

$$[h^{\cdot}] = const \cdot p_{O_2}^{\tfrac{1}{6}} \exp\left(= \frac{\tfrac{1}{6}\Delta H_f^s}{RT} \right) \qquad (34)$$

where ΔH_f^s is the total enthalpy of formation of one mole of singly- and doubly-ionized cationic vacancies according to Equation 30. The constant contains the entropy term of this process. Using Equations 9, 10 and 34 we obtain finally the relationship between electrical conductivity of the studied material and oxygen pressure:

$$\sigma = const . p_{O_2}^{\tfrac{1}{6}} \exp\left(- \frac{\tfrac{1}{6}\Delta H_f^s + \Delta H_m^{h^{\cdot}}}{RT} \right). \qquad (35)$$

Comparison of this relationship with empirical Equations 23 and 24, shows the correctness of the assumptions concerning defect structure in the crystalline lattice of NiO in the studied range of temperatures and oxygen pressures.

Accepting the model of the defect structure given above, one may calculate the total enthalpy of formation of singly- and doubly-ionized cationic vacancies using the activation energy of electrical conductivity derived in the present work (Equations 23 or 24) and the values of $\Delta H_m^{h^{\cdot}}$ quoted in the literature. From all the data on activation energy of motion of electron holes in nickel oxide, the values given by Mitoff [16] seem to be the most conclusive ones since the value of $\Delta H_m^{h^{\cdot}}$ reported by this author is in good agreement with the value of activation energy of highly-doped nickel oxide [27]. The solid solution $Li_xNi_{1-x}O$ of high Li- concentration, shows that the concentration of holes is independent of temperature and hence that the activation energy of electrical conductivity is directly equal to $\Delta H_m^{h^{\cdot}}$. In view of this fact, the value of $\Delta H_m^{h^{\cdot}} = 5.5$ kcal mol^{-1} obtained by Mitoff [16] was used in calculations of ΔH_f^s. From Equations 35 and 23 or 24 we obtain:

$$\Delta H_f^s = 71.5 \text{ kcal mol}^{-1} . \qquad (36)$$

The above value of the enthalpy of formation of cationic vacancies in the material under study

was calculated under the defined assumptions concerning the defect structure. Since the value of ΔH_m^d was determined in the studies on chemical diffusion, the attempt has been made to verify the proposed model of defect structure in crystalline lattice of NiO. Using Equations 30 to 32 and general relationships 14 and 15, the temperature dependence of self-diffusion coefficient could be derived and on the basis of ΔH_f^s and ΔH_m^d values of activation energy E_D could be calculated. Then this value of E_D could be compared with experimental value obtained by a number of authors with the use of a radioactive isotope of nickel and the high-temperature oxidation method [11-13, 15, 28, 29].

Applying the law of mass action to Equilibrium 30 and using electroneutrality condition 32 and Equation 31, one obtains the following relationships between concentration of cationic vacancies and oxygen pressure:

$$[V_{Ni}]_{total} = \left(\frac{K}{18}\right)^{\tfrac{1}{6}} p_{O_2}^{\tfrac{1}{6}} \qquad (37)$$

where $[V_{Ni}]_{total} = [V_{Ni}'] + [V_{Ni}'']$ is the total concentration of cationic vacancies, K is the equilibrium constant of reaction 30. Eliminating K, we obtain finally, the expression analogous to Equation 34

$$[V_{Ni}]_{total} = const . p_{O_2}^{\tfrac{1}{6}} \exp\left(- \frac{\tfrac{1}{6}\Delta H_f^s}{RT^2} \right). \qquad (38)$$

The constant has obviously different physical meaning than that in Equation 34. Substituting the above equation into Equation 14 and using Equation 15 we obtain:

$$D_{Ni} = const . p_{O_2}^{\tfrac{1}{6}} \exp\left(- \frac{\tfrac{1}{6}\Delta H_f^s + \Delta H_m^d}{RT} \right) . \\ \dots\dots (39)$$

Substituting into this equation, the value of $\Delta H_f^s = 71.5$ kcal mol^{-1} calculated from the measurements of electrical conductivity and the value of $\Delta H_f^s = 33.7$ kcal mol^{-1} determined in the measurements of chemical diffusion, we obtain $E_D = 47.9$ kcal mol^{-1}. Table III gives the values of E_D determined by various authors in the studies of self-diffusion of nickel in poly- and monocrystalline material as well as in the studies on kinetics of high-temperature oxidation of nickel. As seen from the table the value of E_D obtained by various authors vary from 44.2 to 60.8 kcal mol^{-1}. The value of E_D obtained in the present investigation is contained in this range, being very close to the five out of seven values

TABLE III Activation energy, E_D, of self-diffusion of nickel in nickel oxide obtained by various authors using tracer and oxidation methods

Reference	Temperature range [°C]	Oxygen partial-pressure range [atm]	Investigated material	Methods	E_D [kcal mol^{-1}]
[11]	1182 – 1762	$10^{-7} – 1$	Monocrystalline	Tracer	60.8 ± 0.6
[12]	1000 – 1400	0.2	Monocrystalline	Tracer	45.6 ± 2
[13]	900 – 1400	0.2	Polycrystalline	Kinetic	48.4
[15]	900 – 1400	$10^{-7} – 1$	Polycrystalline	Kinetic	50.3 ± 0.2
[28]	1000 – 1400	0.2	Polycrystalline	Tracer	44.2 ± 0.6
[28]	1000 – 1400	0.2	Monocrystalline	Tracer	44.2 ± 0.2
[29]	740 – 1400	0.2	Polycrystalline	Tracer	56.0

quoted in Table III. This fact could be taken as proof of the accuracy of the model of structure proposed above.

It follows from this model that the mean degree of ionization of cationic vacancies in nickel oxide – i.e., the absolute value of z in Equation 18 – is equal to 1.5. Using this value and the values of chemical diffusion coefficients, the coefficient of self-diffusion of cationic vacancies D_V as dependent on temperature, was calculated from Equation 18. The results can be described by the following empirical equation:

$$D_V = 2.18 . 10^{-2} \exp\left(-\frac{33.7}{RT}\right) . \quad (40)$$

This dependence and the value of D_{Ni} were then employed to calculate (from Equation 14) the concentration of cationic vacancies in nickel
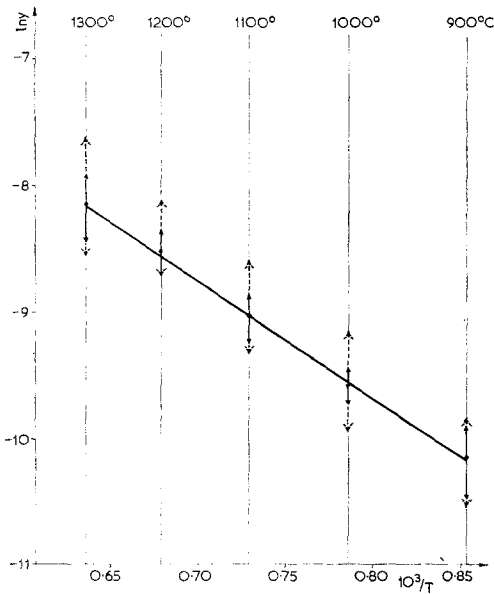
oxide for several temperatures and at the oxygen pressure of 1 atm. The results of these calculations are listed in Table IV in which the values determined in direct measurements of deviations from stoichiometry in nickel oxide with gravimetric method [11, 16, 31], and by coulometric titration are also shown for comparison [17, 18]. It turns out that the temperature dependence of cationic vacancies calculated from the values of Wagner [15], Klotzman [13], and Volpe [11] and from the data determined by Mitoff [16], Sockel and Schmalzried [18], Tripp [30] and Osburn [31] can be represented by the straight line in Fig. 6. The deviation, marked by arrows, was calculated at the confidence level of 0.05. Taking into account the data reported by Lindner [29] one obtains a similar dependence, the accuracy of determination of the parameter under study being, however, smaller (the broken arrows). The dependence $y = f(T)$ can be described by the formula:

$$y = 0.1093 \exp\left(-\frac{18\,525}{RT}\right) . \quad (41)$$

Essentially different results were obtained only by Tretakiow and Rapp [17] and Shim and Moore [28].

9. Conclusions

The results of measurements of electrical conductivity of nickel oxide carried out in the conditions of thermodynamic equilibrium at different temperatures and oxygen pressures and studies of chemical diffusion coefficients, allow the following conclusions to be formulated about the structure of point defects and their mobility in this material.

1. At high temperatures ($> 900°C$) and relatively high oxygen pressures ($10^{-3} – 1$ atm) the crystal lattice of NiO contains both singly- and doubly-ionized cationic vacancies.

Figure 6 Logarithm of cationic vacancies $y = [V_{Ni}]$ concentration as a function of reciprocal temperature.

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TABLE IV Concentration of cationic vacancies in NiO (by p_{O_2} = 1 atm) calculated for temperatures 900 to 1300°C from the values of D_c^1em and D_{Ni} and determined with coulometric titration and gravimetric methods

Temperature [°C]	Concentration of cation vacancies in $Ni_{1-y}O$, mole fraction $y = [V_{Ni}]$									
	Calculated from D_{Ni} values, which were determined by [11, 13, 15, 28, 29]					Determined by [16–18, 30, 31]				
	[11]	[13]	[15]	[28]	[29]	[16]	[17]	[18]	[30]	[31]
900	0.20×10^{-4}	0.40×10^{-4}	0.41×10^{-4}	1.97×10^{-4}	0.54×10^{-4}	0.52×10^{-4}	1.49×10^{-4}	—	0.34×10^{-4}	0.45×10^{-4}
1000	0.50×10^{-4}	0.66×10^{-4}	0.72×10^{-4}	2.83×10^{-4}	1.16×10^{-4}	0.97×10^{-4}	2.82×10^{-4}	—	0.67×10^{-4}	0.70×10^{-4}
1100	1.08×10^{-4}	1.00×10^{-4}	1.16×10^{-4}	3.81×10^{-4}	2.19×10^{-4}	1.66×10^{-4}	4.86×10^{-4}	—	1.19×10^{-4}	1.19×10^{-4}
1200	2.14×10^{-4}	1.45×10^{-4}	1.75×10^{-4}	4.93×10^{-4}	3.83×10^{-4}	2.51×10^{-4}	7.83×10^{-4}	2.50×10^{-4}	1.93×10^{-4}	1.89×10^{-4}
1300	3.70×10^{-4}	1.92×10^{-4}	2.41×10^{-4}	6.01×10^{-4}	5.99×10^{-4}	3.69×10^{-4}	11.70×10^{-4}	—	2.92×10^{-4}	2.84×10^{-4}

2. Theoretical considerations show that concentrations of singly- and doubly-ionized cationic vacancies are comparable in these conditions.

3. Both the magnitude and the activation energy of electrical conductivity show the same values for poly- and monocrystalline material. This leads to the conclusion that at high temperatures, current carriers (electron holes) are not scattered at all at the grain boundaries.

4. The activation energy of diffusion of cationic vacancies in nickel oxide determined, is in keeping with the model of defect structure of this oxide proposed on the basis of electrical conductivity studies. The activation energy determined in this work is markedly higher than that reported by Price and Wagner [24].

5. On the basis of results obtained in studies of chemical diffusion and the knowledge of the mean degree of ionization of cationic vacancies, the diffusion coefficients of the vacancies in nickel oxide were calculated. Making use of these data and of the results of studies on self-diffusion of nickel in poly- and monocrystalline nickel oxide, the concentration of cationic vacancies in NiO was calculated for several temperatures. The results of these calculations remain in full agreement with experimental data.

6. It has been found that the time of homogenization of apparently compact, polycrystalline nickel oxide sintered at 1600°C, is several times shorter than for a single crystal of similar size. It has been assumed, as a working hypothesis, that in spite of apparent compactness, the polycrystalline material contains micropores, through which oxygen may rapidly migrate. This latter problem, however, requires further study.

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