ELECTRICAL PROPERTIES OF NiO AT HIGH TEMPERATURES

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The high-temperature electrical properties, deviation from the stoichiometric composition and the defect structure of NiO are discussed. A detailed analysis of these data is carried out in order to explain the mechanism of electrical transport phenomena in NiO at temperatures above 1200 K. It has been found that in the 1200–1800 K range the charge carrier mobility u in nickel oxide is almost independent of temperature. The obtained values of u change from (0.27 ± 0.15) to (0.54 ± 0.15) cm²/Vs for different assumed degrees of ionization of nickel vacancies. It has been ascertained that this is not evidence of small-polaron conduction in NiO at high temperatures. Rather, it seems that the charge carrier transport phenomena in this oxide can be explained by the large-polaron theory, or else NiO has transitional electrical properties which may be exactly explained on the basis of a new intermediate model between the large and small polaron models.

1. Introduction

The transition metal oxides, such as NiO, are very interesting because for them the Bloch-Wilson theory of electrical conduction fails. According to this theory the structure of these oxides would at first indicate a metallic $3d$ band, whereas, e.g., pure and nearly stoichiometric nickel oxide as an insulator at low temperatures. Thus, the explanation of electrical transport phenomena in this oxide is not so simple and is still attracting a great deal of attention.

As is well known, nickel oxide usually exhibits p-type conductivity resulting from nonstoichiometry and also from the existence of univalent foreign atoms (e.g., Li) in its crystal lattice. The homogeneity range of NiO includes excess oxygen only [1]. Occasionally n-type NiO has been obtained [2], resulting probably from a predominance of trivalent metallic impurities. For the past twenty years the charge carrier transport phenomena in this oxide have been the subject of intensive researches, both experimental and theoretical. The results of investigations carried out at temperatures lower than about 1200 K were summarized in several excellent papers [3–6] and the results obtained also at temperatures higher than 1200 K have been reviewed recently by the author of this work [7].

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However, the energy level structure of NiO has been not elucidated till now and is still a matter for discussion. Some authors [1, 4, 5, 8] assume that the nickel 3d levels are the only states in the vicinity of the Fermi energy in NiO, and form either localized states or a narrow 3d band because the ions are relatively far apart and there is electrostatic repulsion between the 3d electrons. This suggests that in nickel oxide the 3d level conduction is due to small polarons [3, 8–12]. On the other hand, many investigators [6, 13–17] consider NiO to be a band semiconductor. Here, it is suggested that the oxygen 2p band is primarily responsible for the electrical transport phenomena in this compound [16–18]. Taking into account the polar bonding in NiO, large-polaron conduction may be expected in this oxide [3].

Recently, Bosman and Van Daal [6] have shown that in the temperature range of 100 to 1200 K the electrical properties of the oxide under consideration are difficult to explain on the grounds of the theory of small polarons. Instead, these authors believe that the properties of this oxide are in accordance with the theory of large-polaron band conduction. Adler and Feinleib [16] arrived at a similar conclusion in the case of the temperature range 200 to 1000 K. On the base of calculations of the latter authors it seems that in the case of NiO large-polaron conduction in the oxygen 2p band is more probable than the small-polaron mechanism in the 3d levels of this oxide.

Notwithstanding at high temperatures, over 1200 K, the hopping mechanism of electrical conduction is still unanimously assumed to be valid for NiO [19–24]. Such an interpretation of experimental data on NiO obtained at temperatures higher than 1200 K can indeed be reconciled with the small-polaron theory, but it is incompatible with the model of large-polaron conduction [3].

Therefore, it would seem proper to carry out a detailed analysis of the latest data and make an attempt to choose a model of charge carrier transport in this oxide, which would explain its properties in the whole range of temperatures.

Information on the mechanism of electrical conduction in oxides at high temperatures is usually obtained solely from the temperature dependence of charge carrier mobility. In the case of small-polaron conduction theory predicts [3, 9] the following temperature dependence of mobility u:

$$u = \frac{u_0}{T^{\frac{3}{2}}} \exp\left(-\frac{E_u}{kT}\right) \tag{1}$$

where u_0 is a constant, E_u is the hopping energy, and other symbols have conventional meanings. This relation is valid for $T > \frac{1}{2}\Theta$ where Θ denotes the characteristic temperature of longitudinal optical phonons.

On the other hand, the temperature dependence of large-polaron mobility is given by [3]

$$u = \frac{u_0'}{T^{\frac{1}{2}}} \quad \text{for} \quad T \gg \Theta \tag{2}$$

where u_0' is a constant. For NiO, $\Theta = 870$ K.

In the case of nickel oxide the high temperature Hall coefficient is negative [6, 14, 25] whereas as is well known, the electrical conduction is due to the motion of positive holes. This interesting phenomenon has not yet been explained satisfactorily.

At high temperatures the behaviour of mobility, obtained from electrical conductivity σ and Seebeck coefficient α, is found to depend on the density of states N_v and the heat of transfer in the formula for α [26]. Namely, if N_v is assumed to be a constant (hopping model), then the mobility increases with temperature, and if it is accepted that $N_v \sim T^{3/2}$ (band model), then the mobility decreases with increasing temperature [6, 13]. Thus, on the basis of the behaviour of σ and α it is impossible to resolve which mechanism of electrical conduction is present in NiO at high temperatures.

For temperatures at which thermodynamic equilibrium between the crystal and ambient oxygen is achievable, the investigations of the temperature dependence of mobility can be carried out on the basis of measurements of electrical conductivity and deviation from the stoichiometric composition y defined by the chemical formula $Ni_{1-y}O$. This possibility has been utilized in this work.

2. Calculation of mobility

The equilibrium electrical conductivity of NiO at high temperatures can be given by the following expression:

$$\sigma = \sigma_0 P_{O_2}^{1/n} \exp\left(-\frac{E_c}{kT}\right) \tag{3}$$

where σ_0 is a pre-exponential factor only slightly depending on temperature, P_{O_2} is oxygen pressure in atm, E_c may be called the activation energy of conductivity, and n denotes a small number, dependent on the defect structure in this oxide. The values of n and E_c obtained by different authors are given in Table I, and the values of σ (at $P_{O_2} = 1$ atm) as a function of temperature, compiled from five papers, are shown in Fig. 1.

As can be seen from Table I, the value of n varies from 4 to 6, and the value of E_c at $P_{O_2} = 1$ atm from 0.81 eV to 1.01 eV, depending on the author. There is, however, good agreement between the values of electrical conductivity of NiO obtained by different authors at this oxygen pressure, except for that of Bransky and Tallan [22]. The values of σ found by the latter, are much lower than the values of conductivity quoted in the remaining four papers; therefore, their result is assumed to be erroneous and is not considered in the estimation of mobility in nickel oxide.

The deviation from the stoichiometric composition y in NiO may be given by a formula similar to equation (3), namely,

$$y = y_0 P_{O_2}^{1/n} \exp\left(-\frac{E_y}{kT}\right) \tag{4}$$

where y_0 is a constant and E_y may be called the activation energy for deviation from the stoichiometric composition. The values of n, y_0 and E_y obtained by different authors are given in Table II.

Electrical conductivity of NiO at high temperatures

TABLE I

Year	Authors	Comments	Temperature range [K]	Oxygen pressure range [atm]	$\frac{1}{n}$	E_c[eV] at $P_{O_2} \approx 1$ atm	Conclusion drawn by the authors
1934	Baumbach, Wagner [27]	sample obtained by oxidation of nickel foil	070–2270	$10^{-3}-1$	$\frac{1}{4}$	—	singly ionized nickel vacancies
1961	Mitoff [19]	single crystals obtained by Verneuil technique	1170–1620	$10^{-4}-1$	$\frac{1}{6}$	1.01	doubly ionized nickel vacancies, hopping mechanism of conduction
1967	Pizzini, Morlotti [20]	sintered sample having various impurities	1070–1370	$10^{-2}-10^{-1}$	$\frac{1}{6}$	0.81 to 1.81 depending on impurities	doubly ionized nickel vacancies; $(V_{Ni}Ni_iV_{Ni})'$ complexes at $P_{O_2} > 10^{-1}$ atm
1967	Uno [21]	single crystal grown by Verneuil technique	1270–1520	$10^{-2}-1$	$\frac{1}{4}$	0.96	singly ionized nickel vacancies; hopping mechanism; E_c increases with decrease of P_{O_2}
1968	Bransky, Tallan [22]	single crystals grown by decomposition of $NiBr_2$ in oxygen atmosphere; polycrystalline samples obtained by oxydation of nickel foil	1270–1870	$10^{-6}-10^{-3}$ $10^{-3}-1$	$<\frac{1}{4}$ $\frac{1}{4}$	0.92	singly ionized nickel vacancies or doubly ionized vacancies controlled by trivalent impurities; hopping mechanism
1969	Eror, Wagner [23]	two different single crystals	1220–1470	$10^{-4}-1$	$\frac{1}{4}$	0.94 0.98	single ionized nickel vacancies; hopping mechanism, activation energy of motion of holes obeys the "Meyer-Neldel" relationship
1969	Cox, Quinn [28]	sintered samples	1220–	$10^{-2}-750$	$\frac{1}{5}$	—	singly ionized nickel vacancies

| 1970 | Volpe, Reddy [24] | single crystals grown by Verneuil technique | 1450–2030 | $5\times10^{-7}-1$ | $\frac{1}{5}$ | 0.96 | singly and doubly ionized nickel vacancies; hopping mechanism, activation energy E_c increases with decrease of oxygen pressure; both $3d$ band and $2p$ band holes influence conductivity |
| 1970 | Tripp, Tallan [29] | sintered samples | 1070–1370 | $10^{-4}-10^{-1}$ | $\frac{1}{5}$ | — | doubly ionized nickel vacancies controlled by trivalent impurities |
| 1971 | Dereń, Jarzębski, Mrowec, Walec [32] | single crystals grown by Vernouil technique and sintered material | 1220–1470 | $10^{-3}-1$ | $\frac{1}{5}$ | 0.86 | singly and doubly ionized nickel vacancies having comparable concentrations |
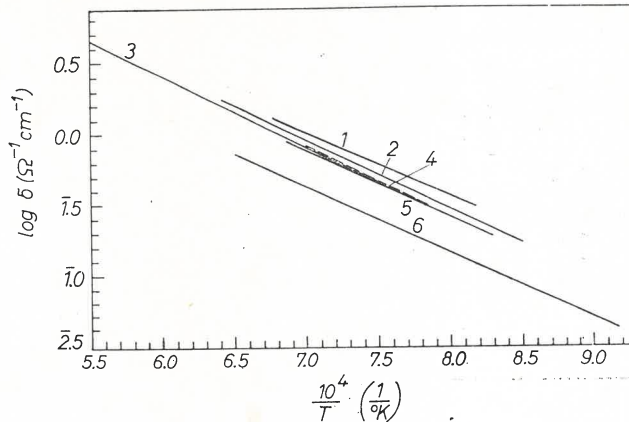
Fig. 1. Logarithm of high temperature electrical conductivity of NiO *versus* reciprocal temperature at oxygen pressure of 1 atm according to different authors. The curves are taken: *1* — from Ref. [32], *2* — from Ref. [19], *3* — from Ref. [24], *4* and *5* — from Ref. [23], *6* — from Ref. [22]

TABLE II

Deviation from the stoichiometric composition in NiO

Year	Authors	Samples and methods	Temperature range [K]	Oxygen pressure range [atm]	$\frac{1}{n}$	y_0	E [eV]
1961	Mitoff [19]	single crystals; thermogravimetry	1400–1800	1	—	0.77	1.04 ± 0.35
1968	Sockel, Schmalzried [31]	polycrystalline; coulometric titration	1470	$10^{-6} - 10^{-3}$	$\frac{1}{6}$	—	—
1969	Tretyakov, Rapp [30]	polycrystalline; coulometric titration	1100–1370	$10^{-4} - 1$	$\frac{1}{6}$	$0.51 \substack{+0.21 \\ -0.15}$	0.83 ± 0.4
1970	Tripp, Tallan [29]	polycrystalline thermogravimetry	1070–1370	$10^{-4} - 10^{-1}$	$\frac{1}{5}$	0.168	0.86 ± 0.15

It is generally assumed that nickel vacancies, resulting from deviation from the stoichiometric composition, are predominating native defects (acceptors) in NiO. The total concentration of these vacancies $[V_{Ni}]$ in nickel oxide is equal $y N$, where $N = 5.5 \times 10^{22}$ cm^{-3}

denotes the number of sites per cm³ in the nickel sublattice. The compiled data on the temperature dependence of the total concentration of nickel vacancies in NiO at an oxygen pressure of 1 atm, are shown in Fig. 2. Curve *1* in Fig. 2 corresponds to the equation $y = 0.51 \exp(-0.83 \text{ eV}/kT)$, obtained by Tretyakov and Rapp [30] (*cf.* Table II) by
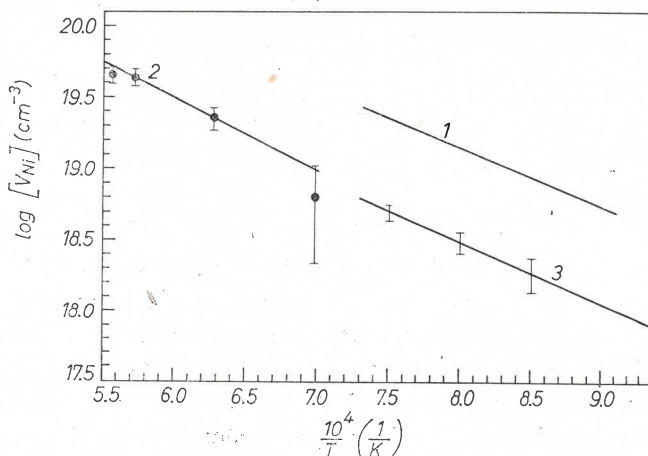

Fig. 2. Logarithm of equilibrium concentration of nickel vacancies in NiO *versus* reciprocal temperature at oxygen pressure of 1 atm according to different authors. The curves are taken: *1* — from Ref. [30], *2* — from Ref. [19], *3* — from Ref. [29]

the coulometric titration method. Taking into account the large errors involved in such measurements and the fact that the values of y found by these authors are considerably higher than those obtained by the more accurate thermogravimetric method (curve *2* and *3* in Fig. 2), the data of Tretyakov and Rapp are not taken into account in the calculation of high temperature mobility in NiO. Curve *2* and experimental points with the limits of accuracy are exactly reproduced from Mitoff's work [19]. Finally, curve *3* corresponds to the equation $y = 0.168 \exp(-0.86 \text{ eV}/kT)$ given by Tripp and Tallan [29]. The vertical lines on this curve indicate the limits of accuracy estimated from the data published by the authors. These vertical lines are given only for the few points which were taken for the calculation of mobility.

The degree of ionization of the vacancies is a matter for discussion, however. Both singly ionized [21–23, 27, 28] and doubly ionized [19, 20, 30, 31] nickel vacancies have been proposed. It has been suggested also that in NiO both singly and doubly ionized nickel vacancies exist simultaneously [24, 32, 33].

Therefore, the concentration of holes p in the oxide under consideration, may be given by $p = a[V_{Ni}]$, where a may vary from unity if singly ionized nickel vacancies predominate in NiO, to two if doubly ionized nickel vacancies prevail in this oxide. In the special case, if both singly and doubly ionized nickel vacancies exist having approximately comparable concentrations, then $a = 3/2$.

When calculating carrier mobility in NiO it is assumed that all charge carriers in this oxide, created by the ionization of nickel vacancies, belong to one band (have the same

mobility). As was mentioned in the introduction to this paper, recent results [16–18] show that 3d levels overlap the 2p band. Therefore, it seems reasonable to consider only the charge carriers in the last band, if we accept the band model. On the other hand, if we assume the small-polaron model holes should exist in 3d levels which either form a narrow 3d band or are localized. Thus, the mobility u can be given by the following formula:

$$u = \frac{\sigma}{ae[V_{Ni}]} \tag{5}$$

where e is electronic charge.

As can be seen from Tables I and II the activation energy E_c given in Ref. [32] is the same as the value of E_y obtained by Tripp and Tallan [29]. Hence, by substituting the measured values of σ and y given in the two last papers into formula (5) and taking into account expression (1) one can conclude that the results mentioned above are in conflict with the small-polaron model. Therefore, for further analysis of the high temperature behaviour of charge carrier mobility in NiO the results of measurements of electrical conductivity obtained by Mitoff [19], Volpe and Reddy [24] and Eror and Wagner [23], and the values of y given by Mitoff [19] and Tripp and Tallan [29] are taken into account. It is accepted that $a = 3/2$.

In the temperature range of 1400 to 1800 K the values of mobility have been calculated on the basis of thermogravimetric measurements of y given by Mitoff [19] and interpolated values of σ, obtained by Volpe and Reddy [24], whereas in the 1170 to 1400 K range on the basis of values of y obtained from the formula

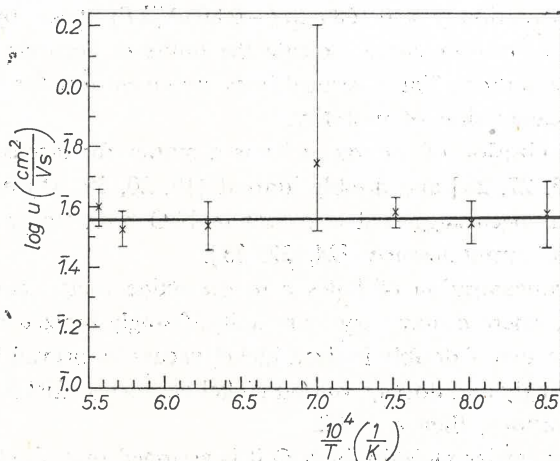$$y = 0.168 P_{O_2}^{1/5} \exp\left(-\frac{0.86\,eV}{kT}\right) \tag{6}$$

Fig. 3. Logarithm of mobility of charge carriers in NiO at high temperatures *versus* reciprocal temperature

(for $P_{O_2} = 1$ atm), given by Tripp and Tallan [29], and interpolated values of σ taken from the data given by Eror and Wagner [23] and Mitoff [19] (the last point in Fig. 3). All of these calculations concern nickel oxide in thermodynamic equilibrium with ambient oxygen at 1 atm. The obtained values of mobility are given in Fig. 3. The vertical lines in Fig. 3 indicate the limits of accuracy of mobility determinations due to the measurement errors of y only (*cf.* Fig. 2). The measurement errors of σ have been neglected here, as they are about an order of magnitude smaller than the errors of y.

As can be seen from Fig. 3, there is good conformity between the values of mobility of charge carriers in NiO at high temperatures calculated on the basis of experimental results of different authors. In the temperature range of 1200 to 1800 K the mobility is found to be (0.36 ± 0.15) cm²/Vs, and it slightly decreases with temperature. If it is assumed that $a = 1$, then $u = (0.54 \pm 0.15)$ cm²/Vs. On the other hand, if it is accepted that $a = 2$, then $u = (0.27 \pm 0.15)$ cm²/Vs.

3. Discussion and conclusions

On the basis of the considerations presented in this work it may be concluded that in the case of NiO there is no evidence that above 1200 K the mobility of charge carriers increases exponentially with temperature, at least with an activation energy higher than about 0.1 eV. (Taking into account the large errors involved in the measurements of deviation from the stoichiometric composition, one can not exclude the exponential dependence of mobility in NiO on temperature with an activation energy lower than about 0.1 eV.) This conclusion, drawn on the basis of an analysis of the data given by many authors, has been recently supported by the experimental results (electrical conductivity and deviation from the stoichiometric composition) obtained by Osburn and Vest [34]. In the 1170 to 1670 K range these authors found that for the very pure NiO samples $E_c = E_y = (0.81 \pm 0.04)$ eV. They also ascertained that the mobility in NiO in the studied temperature range is almost independent of temperature and equals 0.53 cm²/Vs.

Hence, the values of u calculated in the present paper are approximately equal to the value obtained by Osburn and Vest [34] by the same method. Moreover, they are compatible with the value of u determined by Bosman and Van Daal [6] for temperatures over 1200 K on the basis of measurements of σ and α, assuming that $N \sim T$ (see Fig. 14 in [6].

Mitoff [19] states that the activation energy of the motion of holes in NiO is equal to 0.24 eV. But his interpretation of the results of electrical conductivity measurements is based on the *a priori* acceptance that at temperatures lower than 1170 K, at which atomic defects in NiO may be considered to be frozen in the crystal lattice, the charge carriers concentration $p = $ const, and the temperature dependence of conductivity stems solely from the temperature dependence of mobility. Thus, according to such an interpretation of the $\sigma(T)$ function at temperatures lower than 1170 K, $E_c = E_u$. Proceeding along similar lines, Eror and Wagner [23] obtained values of activation energy of motion of holes at high temperatures contained within the limits from 0.25 eV to 1.46 eV, depending on the oxygen pressure under which defects in the oxide were frozen. In our opinion, however, it seems that in the temperature range where the atomic defects (foreign atoms

and native defects) are frozen [35], p increases exponentially with T because these defects become ionized, and the function $\sigma(T)$ is related mainly to the function $p(T)$ and not $u(T)$. This opinion is supported by the data published in papers [6, 13, 16].

Uno [21] assumes that in NiO the holes move by the hopping process, considering the fact that the ratio $\dfrac{uT}{u_{1270} \cdot 1270\ \mathrm{K}}$, estimated by him, increases with temperature. However, the ratio $\dfrac{u}{u_{1270}}$, estimated also by this author, decreases with increasing temperature.

Bransky and Tallan [22] suggest on the basis of conductivity and Seebeck coefficient measurements the following temperature dependence of mobility in NiO: $u = 5959/T \exp(-0.37\ \mathrm{eV}/kT)$. However, the experimental results obtained by these authors have been questioned by Bosman and Van Daal [6]. Furthermore, the value of $E_y = 0.66$ eV, obtained by Bransky and Tallan from the temperature dependence of the Seebeck coefficient assuming that $N_v = \mathrm{const}$, is in disagreement with values obtained by other authors and by means of other methods (see Table II).

Volpe and Reddy [24] assume the activation energy of mobility in NiO to be 0.3 eV, but do not back this value in any way.

The mobility of charge carriers in NiO has also been calculated on the basis of measurements of y made by Tretyakov and Rapp [30] and measurements of σ by various authors. In this case the values of activation energy of motion of holes are found to be considerably lower contained in the limits from 0.04 to 0.19 eV, depending on the activation energy of conductivity [36].

From the experimental data and discussion presented in this paper one can conclude that there are no grounds for accepting the small-polaron conduction model (hopping mechanism) in NiO at high temperatures. This conclusion has been drawn mainly on the base of two facts, namely:

1. in the large range of temperatures from 1200 to 1800 K the charge carrier mobility in NiO is almost independent of temperature, and

2. the obtained values of u, varying from (0.27 ± 0.15) to (0.54 ± 0.15) cm²/Vs for different assumptions regarding the degree of ionization of the nickel vacancies, are too large for typical hopping conduction, for which u should be much smaller than 0.1 cm²/Vs.

As had already been mentioned, a similar conclusion has been drawn recently by Bosman and Van Daal [6] regarding the situation in the temperature range 100 to 1200 K, Adler and Feinleib [16] in the range 200 to 1000 K, and Osburn and Vest in the ranges 570 to 1270 K [37] and 1170 to 1670 K [34]. Thus, in the whole range of temperatures in which investigations on NiO have been carried out, no proof has yet been revealed that small-polarons are the charge carriers in nickel oxide. Therefore, it rather appears that NiO can be considered to be a large-polaron band semiconductor. However, taking into account the comparatively small values of mobility in this compound, it is possible also that nickel oxide has transitional electrical properties which would be exactly explained by a new intermediate model between the large and small polaron models.

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