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Thermopower and Electrical Conductivity of Single Crystal and Polycrystalline CoO

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Abstract

Comparative studies of both electrical conductivity and thermopower (Seebeck effect) were carried out for undoped $Co_{1-y}O$ *involving both single crystal and polycrystalline specimens within the temperature range 1223–1473 K and under oxygen partial pressure range* 10–10^5 *Pa.*

It was observed that the reciprocal of oxygen pressure exponent determined by thermopower (n_α) *and electrical conductivity* (n_σ) *for both single crystal and polycrystalline CoO increases with temperature. The parameter* n_α *assumes much higher values than* n_σ *for both specimens.*

The mobility of electron holes increases with non-stoichiometry (y) for both the single crystal and the polycrystalline specimen.

Based on the electrical conductivity data on temperatures it was concluded that conduction in CoO occurs according to the hopping model rather than the band model.

The effect of $p(O_2)$ *on the exponent of the oxygen pressure dependence have been considered in terms of interactions between the defects in this region.*

Die elektrische Leitfähigkeit und die Thermokraft (Seebeck-Effekt) von undotierten $Co_{1-y}O$*-Ein- und Vielkristallproben wurden für den Temperaturbereich 1223–1473 K bei einem Sauerstoffpartialdruck zwischen* 10–10^5 *Pa untersucht.*

Dabei zeigte sich, daß der Kehrwert des Sauerstoffdruckexponenten, bestimmt aus der Thermokraft (n_α) *und der elektrischen Leitfähigkeit* (n_σ), *sowohl für CoO-Ein- als auch für CoO-Vielkristallproben mit der Temperatur zunimmt. Für beide Probenarten erreicht der Parameter* n_α *wesentlich höhere Werte als* n_σ.

Die Mobilität der Elektronenfehlstellen nimmt mit der Nichtstöchiometrie (y) sowohl für Ein- als auch für Vielkristallproben zu.

Augrund der Variation der elektrischen Leitfähigkeit mit der Temperatur wurde geschlossen, daß die Leitfähigkeit in CoO entsprechend dem 'hopping' Modell und nicht dem 'band' Modell erfolgt.

Der Effekt von $p(O_2)$ *auf den Exponenten des Sauerstoffdruckes wurde bezüglich der Wechselwirkung zwischen den Defekten diskutiert.*

Nous avons procédé à une étude comparative d'échantillons mono et polycristallins de $Co_{1-y}O$, *non dopés, du point de vue de la conductivité électrique et du comportement thermoélectrique (effect Seebeck), dans la gamme de températures 1223–1473 K et sous une pression partielle d'oxygène variant de 10 à* 10^5 *Pa.*

Nous avons observé que l'inverse de l'exposant de la pression d'oxygène, determiné par la constante thermoélectrique (n_α) *et la conductivité électrique* (n_σ) *pour les échantillons monocristallins ou polycristallins augmente avec la température. Le paramètre* n_α *suppose des valeurs plus élevées que le paramètre* n_σ, *ceci pour les deux types d'échantillons.*

La mobilité des trous d'électrons augmente avec l'écart à la stoechiométrie (y) pour les deux catégories.

La variation de la conductivité avec la température nous conduit à penser que la conduction dans CoO est une conduction par sauts plutôt qu'une conduction de bande.

L'effet de $p(O_2)$ *sur la mobilité des trous, aussi bien que sur l'exposant de la variation de la pression d'oxygène est examiné en termes des interactions entre les défauts.*

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1 Introduction

Significant experimental and theoretical material has been reported on the defect structure of CoO[1–12] and its transport properties.[11–19] It has been documented that CoO is a metal-deficient oxide exhibiting cation vacancies as the predominant defects.

In thermodynamic equilibrium the concentration of Co vacancies in CoO can be expressed as the following function of $p(O_2)$ and temperature:

$$y = [V_{\mathrm{Co}}^{-z}] = \text{const.}\ p(O_2)^{1/n} \times \exp\left\{\left(-\frac{1}{z+1}\Delta H_f\right)/RT\right\} \quad (1)$$

where y is the deviation from stoichiometry, z is the ionization degree of defects, n is the parameter depending on the valency of defects, ΔH_f is the enthalpy of defects formation, R is the gas constant and T is the absolute temperature. The following relation can be written between z and n:

$$n = 2(z+1) \quad (2)$$

It has been shown that defects in CoO can be considered within an ideal defect model only at low nonstoichiometry.[3,20] At higher defect concentrations strong interactions between the defects must be considered. Then either the Debye–Huckel model[21] or the cluster model[22] can be applied rather than an ideal model.

There are conflicting reports on transport properties of CoO involving mobility of ionic and electronic defects. On one hand Fryt *et al.*[23] report that chemical diffusion in CoO is independent of the oxide composition. This phenomenon is typical for ideal solid solutions of defects in crystal. On the other hand, Nowotny & Sadowski[6] as well as Morin[15] have shown that the mobility of ionic defects in CoO strongly depends on their concentration. The variation of defects mobility has been considered in terms of interaction between the defects. Also theoretical studies have shown that strong defect interactions must be taken into account at higher deviations from stoichiometry of CoO.[9]

Conflicting data were also reported on the mobility of electron holes.[5,7] Nowotny *et al.*[5] have observed that the mobility in polycrystalline CoO increases with equilibrium $p(O_2)$ and related nonstoichiometry. On the other hand, the studies of Petot-Ervas *et al.*[7] did not confirm this effect for a CoO single crystal. Thus the following question may arise: is this an apparent discrepancy related to different nature of materials used (single crystal on one side and a ceramic material on the other side) and should it be considered as an effect of interfaces or is there another reason for the conflicting reports? Therefore, it seems of interest to perform comparative studies for both single crystal and polycrystalline CoO in the same experimental conditions by using the same set of equipment.

Another important effect, which requires experimental verification, involves the effect of impurities. It has been documented that aliovalent impurities may cause substantial changes in CoO electrical properties already at the level of 10 ppm.[20] Unfortunately, detailed analysis of this problem is awkward because information about the impurity level is not available in most of reports on the electrical properties of CoO.

Studies performed by Osburn & Vest[24] for NiO have confirmed a substantial effect of aliovalent ions on the oxygen pressure exponent of electrical conductivity which varies between 1/6 for a very pure specimen and 1/4 for a specimen involving trivalent cation impurities. This effect was later confirmed by Parlinska.[25]

Assuming that there is a substantial difference between the defect structure of the bulk phase and of the boundary region, properties of polycrystalline specimens, such as electrical and transport properties, should be considered in terms of two components, such as bulk phase component and the grain boundary component. The effect of segregation on the surface versus bulk electrical properties has been considered for NiO and ZrO_2 in Refs 26 and 27. Therefore, one may expect that ceramic materials, involving a high density of grain boundaries, will exhibit different electrical properties to single crystals. So far, however, regular comparative studies on defect-related properties for both single crystals and polycrystalline specimens have not been performed.

As results from this consideration, a comparison between literature data reported for the different natures of oxide specimens involving single crystals and polycrystals of different microstructure may lead to misleading conclusions, if the effect of interface on measured property predominates.

The objective of the present work was to perform comparative studies of electrical properties for both single crystal and a polycrystalline specimen of CoO in order to determine the effect resulting from grain boundaries. The studies are based on both electrical conductivity and thermopower methods performed in equilibrium with the gas phase of controlled oxygen activity and determined in the same experimental conditions.

2 Experimental

Polycrystalline specimens of undoped CoO were prepared by decomposition of high purity cobalt carbonate at 1273 K for 5 h in an alumina tube. The thus obtained CoO powder was pressed into rectangularly shaped pellets under 200 MPa. The pellets were sintered at 1370 K for 4h. The thus prepared CoO consists of individual particles of average grain size 10^{-7} m. According to spectral analysis the concentration of aliovalent impurities such as Si, Sn and Al was of the order of 50 ppm.

The CoO single crystal was prepared by the Verneuille method. Rectangular samples (1 × 1·5 × 10 mm) were cut by natural cleavage from a single crystal boule. The main impurity in both single crystal and polycrystalline CoO was Ni (up to 1 at.%). The concentration of aliovalent elements was lower than 20 ppm.

Both electrical conductivity and thermopower were measured as a function of temperature and oxygen partial pressure. The classical four-probe conductivity method was applied using 5–20 mA of DC current. Thermopower was determined from at least seven temperature gradients. The maximum gradient of ΔT was 3 K. Both electrical conductivity and thermopower were measured simultaneously for the same oxide specimen in identical conditions of T and $p(O_2)$. Details of the experimental set-up of both methods are described in Ref. 5.

Studies were performed in the temperature range 1223–1473 K under oxygen partial pressure between 10 and 10^5 Pa. The required $p(O_2)$ was imposed by the Ar–O_2 gas mixture flowing through the reaction chamber. Oxygen activity was controlled by a zirconia oxygen gauge.

The equilibration kinetics of the studied gas–solid system were monitored by electrical conductivity. The kinetics were measured isothermally for oxidation runs after oxygen activity in the gas phase was suddenly changed to a new value.

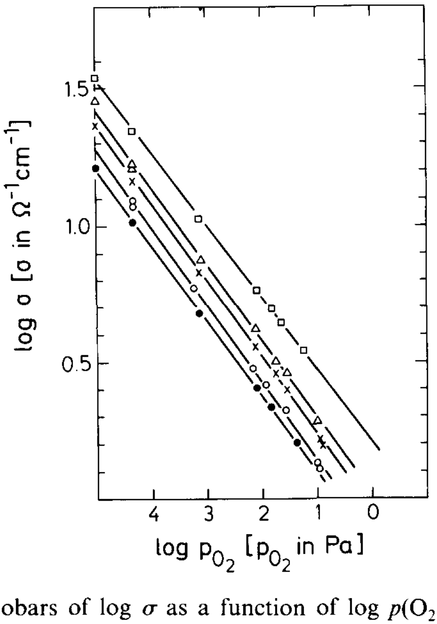

Fig. 1. Isobars of log σ as a function of log $p(O_2)$ for CoO single crystal. ●, 950°C; ○, 1000°C; ×, 1050°C; Δ, 1100°C; □, 1200°C.

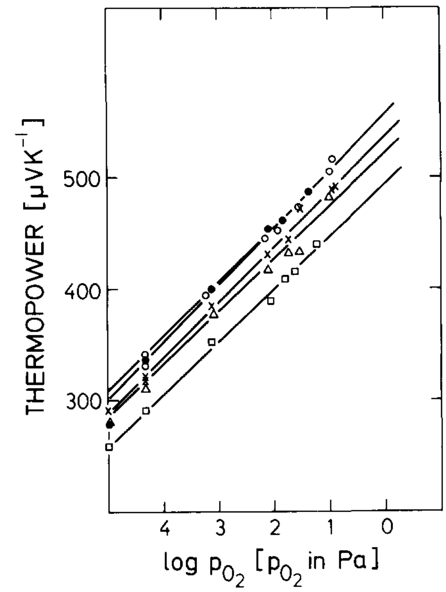

Fig. 2. Isotherms of thermopower (α) as a function of log $p(O_2)$ for CoO single crystals. ●, 950°C; ○, 1000°C; ×, 1050°C; Δ, 1100°C; □, 1200°C.

3 Results and Discussion

3.1 CoO single crystal

Experimental data of electrical conductivity (σ) and thermopower (α) as a function of log $p(O_2)$ are shown in Figs 1 and 2, respectively. The experimental error was below 8% and 3% for σ and α, respectively. The parameters n_σ and n_α were determined from the following relationships:

$$1/n_\sigma = \{[\partial \log \sigma]/[\partial \log p(O_2)]\}_T \qquad (3)$$

$$1/n_\alpha = \{-q/k\{\partial\alpha/[\ln p(O_2)]\}_T \qquad (4)$$

where q is the elementary charge and k is the Boltzmann constant. The determined values of the parameters n_σ and n_α are shown in Table 1. As seen, the parameter n_α assumes much higher values (3·6–4·2) than n_σ (3·5–3·8). Also n_α increases much more strongly, with temperatures than n_σ (Fig. 3).

Based on the ideal defect model one may assume that the oxygen pressure exponent close to four corresponds to singly ionized cobalt vacancies. However, the observed decrease of both n_σ and n_α below 4 at lower temperatures (below 1400 K) is not consistent with the ideal defect model. This

Table 1. Parameters n_σ and n_α for single crystal CoO

T (K)	n_σ	n_α	$n_\sigma - n_\alpha$
1 223	3·63 ∓ 0·04	3·61 ∓ 0·22	0·02 ∓ 0·26
1 273	3·52 ∓ 0·07	3·83 ∓ 0·11	−0·31 ∓ 0·18
1 323	3·58 ∓ 0·04	3·95 ∓ 0·10	−0·37 ∓ 0·14
1 373	3·59 ∓ 0·05	4·09 ∓ 0·17	−0·50 ∓ 0·22
1 473	3·81 ∓ 0·04	4·21 ∓ 0·14	−0·40 ∓ 0·18

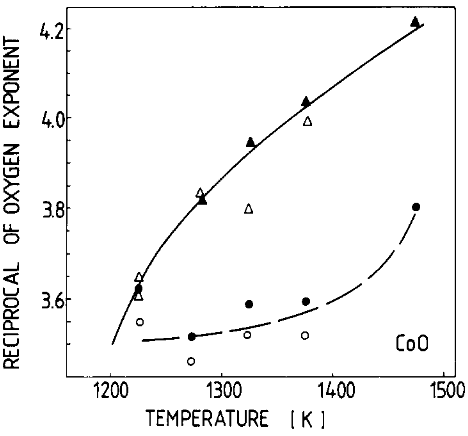

Fig. 3. Reciprocal of $p(O_2)$ exponent of electrical conductivity (n_σ; ●, ○) and thermopower (n_α; ▲, △) as a function of temperature for both single crystal (●▲) and polycrystalline (○△) CoO.

effect can be explained by assuming strong interactions between the defects for CoO as has already been indicated in Refs 3 and 20.

Assuming that interactions between the defects is much stronger in the grain boundary region, where the local nonstoichiometry assumes much higher values, the comparison between n_α and n_σ indicates that the electrical conductivity is more sensitive for the sample microstructure than thermopower. This may be caused by grain boundary weak links in the determination of electrical conductivity. On the other hand, thermopower is determined by the temperature gradient across the entire crystal and, therefore, is less sensitive for grain boundaries.

The electrical conductivity of CoO can be expressed as

$$\sigma = q[\mathrm{h}^\cdot]\mu_\mathrm{h} \qquad (5)$$

where $[\mathrm{h}^\cdot]$ denotes the concentration of electron holes in cm^{-3} and μ_h is their mobility. On the other hand, the following relationship can be written between α and $[\mathrm{h}^\cdot]$:

$$\alpha = (k/q)\{\ln(N_\mathrm{h}/[\mathrm{h}^\cdot]) + A\} \qquad (6)$$

where N_h is the density of states and A is the kinetic term. As can be seen, knowledge of several parameters such as μ_h, A and N_h is required to solve eqns (5) and (6). In the case of the band model the parameter A may vary between 2 and 4 depending on the scattering mechanism.[4,28] On the other hand, for the small polaron mechanism:[29]

$$N_\mathrm{h} = \beta D \qquad (7)$$

$$A_\mathrm{h} = \Delta S/k \qquad (8)$$

where β is the parameter involving the spin and orbital degeneracy, D is the concentration of donors and ΔS is the vibrational entropy term associated with the polaron environment on a given ion site.

The absolute value of the mobility term μ_h may serve as a certain criterion concerning the conductivity mechanism. Bosman & van Daal[30] have claimed that for the small polaron model and the narrow band model, respectively:

$$\mu_\mathrm{h} \ll 0{\cdot}1\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$$

and

$$\mu_\mathrm{h} > 0{\cdot}5\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$$

It has been argued that the band model requires the following dependence:[4]

$$\{(\partial \ln \sigma)/\partial(1/T)\}_\alpha = 0 \qquad (9)$$

On the other hand, the polaron model involves the following dependence of μ_h on temperature:

$$\mu_\mathrm{h} = \{[(1 - c)qa^2\nu_0]/kT\} \exp(-E_\mu/kT) \qquad (10)$$

where a is the lattice parameter, c is the ratio of occupied sites, ν_0 is the vibration frequency of phonons and E_μ is the jump activation energy. Therefore:

$$\{(\partial \ln \sigma)/\partial(1/T)\}_\alpha = T - E_\mu/k \qquad (11)$$

Chen & Mason[3] have reported that eqn (9) is valid for CoO. For the polaron mechanism:

$$E_\mu = kT \qquad (12)$$

Petot-Ervas *et al.*[7] have recently reported that eqn (9) is not valid for CoO:

$$k(\partial \ln \sigma)/\partial(1/T)_\alpha = \sim -0{\cdot}1\ \mathrm{eV} \qquad (13)$$

Figure 4 illustrates slopes of $\ln \sigma$ versus $1/T$ at α = const. from the results obtained in the present work (Table 2). These values are about one order of magnitude smaller than those reported in Ref. 4. In contrast to experimental data reported in

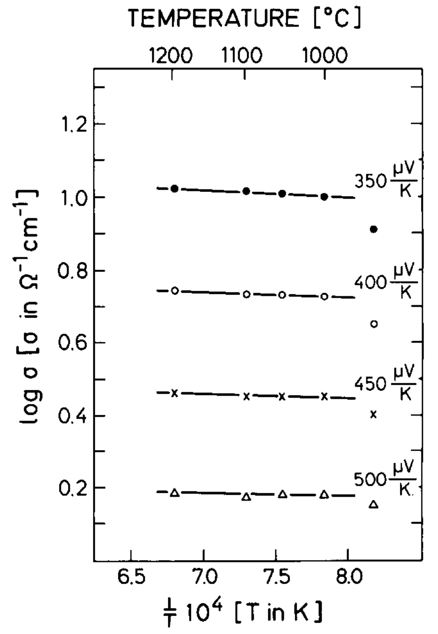

Fig. 4. Log σ as a function of $1/T$ at constant for CoO single crystal.

Table 2. Temperature dependences of σ at α = constant

α ($\mu V K^{-1}$)	$k(\partial \ln \sigma/\partial(1/T))$ (eV)
350	−0·038
400	−0·029
450	−0·022
500	−0·013

Refs. 4 and 7, the present measurements of both σ and α were performed simultaneously for the same specimen.

Application of eqn (11) to describe the experimental data (Fig. 4) indicates that

$$T - E_\mu/k \approx 0 \qquad (14)$$

Therefore, in the temperature and composition ranges under study

$$0{\cdot}11 < E_\mu < 0{\cdot}13 \text{ eV} \qquad (15)$$

These values are close to those reported before (0·09–0·3 eV).[21]

Based on these considerations one may suppose that the charge transport in CoO occurs according to the small polaron mechanism.

Assuming the ideal defect structure model and the polaron conductivity mechanism Petot-Ervas *et al.*[7] have determined that for y = 0·01 the following relation can be written:

$$n_\sigma - n_\alpha = 0{\cdot}20 \qquad (16)$$

Negative values of the difference between n_σ and n_α obtained in this work (Table 1) are in obvious conflict with the model reported in Ref. [7], which is constructed assuming an ideal solid solution of defects in CoO. As has been shown before[20] the validity of the ideal model is limited to very low values of the deviation from stoichiometry close to the Co/CoO phase boundary. At higher values of y the ideal defect model is not valid.

Table 3. The mobility of electron holes for single crystal CoO

T (K)	$p(O_2)$ (Pa)	μ ($cm^2\ V^{-1}\ s^{-1}$)
1273	$2{\cdot}1 \times 10^4$	0·367
	$1{\cdot}7 \times 10^3$	0·341
	$1{\cdot}5 \times 10^2$	0·320
	83	0·300
	10	0·284
1373	10^5	0·462
	$2{\cdot}1 \times 10^4$	0·423
	$1{\cdot}2 \times 10^3$	0·366
	$1{\cdot}3 \times 10^2$	0·340
	52	0·311
1473	10^5	0·473
	$2{\cdot}1 \times 10^4$	0·441
	$1{\cdot}3 \times 10^3$	0·392
	$1{\cdot}2 \times 10^2$	0·367
	65	0·359
	43	0·348
	17	0·334

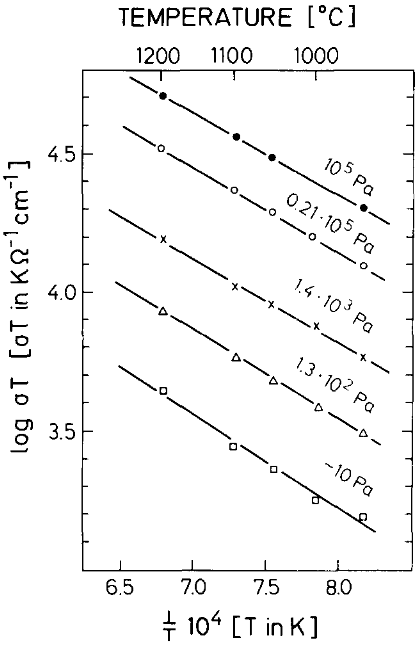

Fig. 5. Isobars of log σT as a function of $1/T$ for CoO single crystal.

Based on concentration values reported by Dieckmann[12] the mobility term μ_h has been determined and is shown in Table 3. As can be seen the mobility increases with temperature, in disagreement with the band model, which requires that:[28]

$$\mu_h \sim T^{3/2} \qquad (17)$$

It is interesting to note that the mobility of electron holes increases with equilibrium $p(O_2)$ and, accordingly, with oxide nonstoichiometry. This is in agreement with previous studies[5] but in a disagreement with the results of Petot-Ervas *et al.*[7]

Changes of the electrical conductivity as a function of temperature can be expressed as

$$\{\partial \ln (\sigma T)/\partial(1/T)\}_{p(O_2)} = -E_\sigma/k \qquad (18)$$

Figure 5 illustrates the dependence of log (σT) versus $1/T$ which is linear. The product σT and the activation energy are listed in Table 4. Figure 6 illustrates the dependence between log [h˙] and log $p(O_2)$.

Table 4. Parameters of eqn (18) for CoO single crystal

p_{O_2} (Pa)	$\ln \sigma T$	E_σ (eV)
10^5	$15{\cdot}45\ (\mp 0{\cdot}03) - 6780\ (\mp 40)T^{-1}$	$0{\cdot}58 \mp 0{\cdot}01$
$2{\cdot}1 \times 10^4$	$15{\cdot}15\ (\mp 0{\cdot}12) - 7010\ (\mp 150)T^{-1}$	$0{\cdot}60 \mp 0{\cdot}02$
$1{\cdot}4 \times 10^3$	$14{\cdot}37\ (\mp 0{\cdot}21) - 6970\ (\mp 275)T^{-1}$	$0{\cdot}60 \mp 0{\cdot}03$
$1{\cdot}3 \times 10^2$	$14{\cdot}03\ (\mp 0{\cdot}10) - 7316\ (\mp 122)T^{-1}$	$0{\cdot}63 \mp 0{\cdot}02$
10	$13{\cdot}59\ (\mp 0{\cdot}47) - 7711\ (\mp 615)T^{-1}$	$0{\cdot}66 \mp 0{\cdot}06$

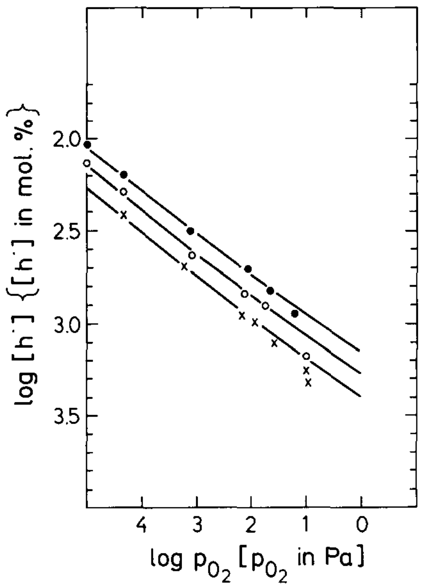

Fig. 6. Isotherms of log [$h^{\cdot}$] as a function of log $p(O_2)$ for CoO single crystal. ×, 1000°C; ○, 1100°C; ●, 1200°C.

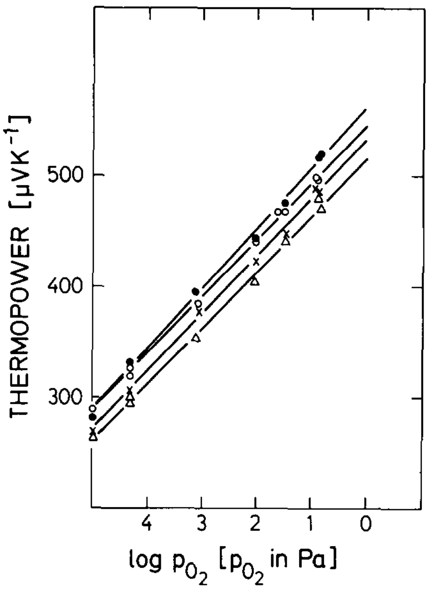

Fig. 8. Isotherms of thermopower as a function of log $p(O_2)$ for polycrystalline CoO. ●, 950°C; ○, 1000°C; ×, 1050°C; Δ, 1100°C.

3.2 Polycrystalline CoO

Figures 7 and 8 illustrate the experimental dependences of both log σ and α as a function of log $p(O_2)$. The slopes of these dependences (eqns (3) and (4)) are shown in Fig. 3. As can be seen, the values of both n_α and n_σ for the polycrystalline specimen are comparable to respective values determined for the single crystal. The character of their temperature dependence is essentially the same for both specimens; however, the values of n_α and n_σ for the polycrystalline CoO are slightly lower than those for the single crystal (Table 5). This effect is apparently related to the effect of grain boundaries. Again in both cases the two parameters (n_α and n_σ) assume values lower than 4. This is in an agreement with the assumption that strong interactions between the defects are involved. The extent of the interactions increases with the decrease of temperature and with the increase of nonstoichiometry. This effect is confirmed in the present studies.

Comparison between the dependence of n_α and n_σ on temperature suggests that interactions between defects results in changes of the mobility term rather than in the ionization degree of Co vacancies.

Figure 9 illustrates plots of the log σT versus $1/T$ dependence. The thus determined activation energy is practically independent of oxide composition and is the same for both single crystals (Table 4) and polycrystals (Table 6).

According to Tables 3 and 7 the mobility of electron holes increases with oxide nonstoichiometry. This effect indicates that the increase in the concentration of Co vacancies results in a faster displacement of electron holes. It is surprising that this effect is the same for both the single crystal and the ceramic material.

3.3 Chemical diffusion

After oxygen activity is suddenly changed over a CoO crystal then a new nonstoichiometry is imposed at the surface while the nonstoichiometry of the bulk phase is not equilibrated. The equili-

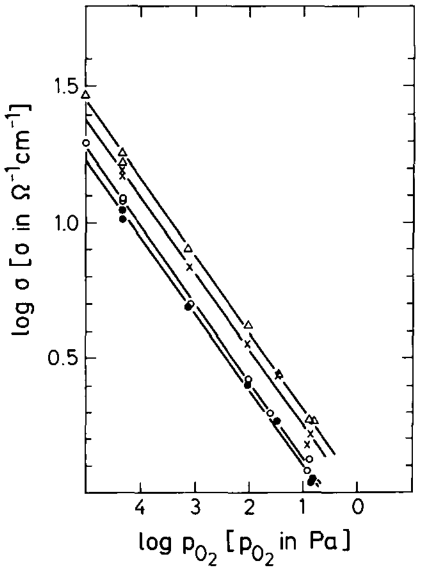

Fig. 7. Isotherms of log σ as a function of log $p(O_2)$ for polycrystalline CoO. ●, 950°C; ○, 1000°C; ×, 1050°C; Δ, 1100°C.

Table 5. The parameters n_σ and n_α for polycrystalline CoO

T (K)	n_σ	n_α
1223	3·55 ∓ 0·07	3·65 ∓ 0·09
1273	3·46 ∓ 0·06	3·83 ∓ 0·06
1323	3·52 ∓ 0·10	3·80 ∓ 0·10
1373	3·52 ∓ 0·06	3·89 ∓ 0·11

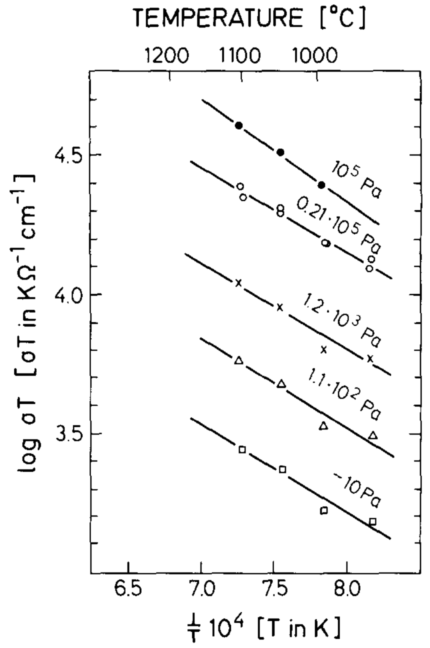

Fig. 9. Isobars of log σT as a function of log $1/T$ for polycrystalline CoO.

bration involves a propagation of the new nonstoichiometry gradient from the surface into the bulk. The propagation rate is controlled by chemical diffusion. Therefore, by monitoring the equilibration kinetics of the oxide/oxygen system, one may determine the diffusion coefficient for the oxide crystal.

The electrical conductivity has been applied to monitor the rate of the re-equilibration of the studied CoO single crystal. The experiments involved isothermal oxidation runs. The experimental data were analysed by using the approximate solution reported by Price & Wagner:[31]

$$\tilde{D} = -\frac{0{\cdot}934}{t[(1/a^2) + (1/b^2) + (1/c^2)]} \times \log \frac{0{\cdot}533}{[1 - (\Delta\sigma_t/\Delta\sigma_\infty)]} \qquad (19)$$

where $\tilde{D}$ is the chemical diffusion coefficient, $2a$, $2b$ and $2c$ are sample dimensions and $\Delta\sigma_t$ and $\Delta\sigma_\infty$ denote the change of the electrical conductivity after time t and the total change of σ between the two equilibrium states, respectively. Equation (19) was applied only at the condition that:[31]

$$\Delta\sigma_t/\Delta\sigma_\infty > 0{\cdot}75 \qquad (20)$$

Table 6. Parameters log σT and $E\sigma$ for polycrystalline CoO

p_{O_2} (Pa)	log σF	E_σ (eV)
10^5	$16{\cdot}77\ (\mp 0{\cdot}53) - 8478\ (\mp 708)T^{-1}$	$0{\cdot}73 \mp 0{\cdot}07$
$2{\cdot}1 \times 10^4$	$15{\cdot}15\ (\mp 0{\cdot}35) - 6969\ (\mp 462)T^{-1}$	$0{\cdot}60 \mp 0{\cdot}04$
$1{\cdot}2 \times 10^3$	$11{\cdot}65\ (\mp 1{\cdot}02) - 7348\ (\mp 1323)T^{-1}$	$0{\cdot}63 \mp 0{\cdot}12$
$1{\cdot}1 \times 10^2$	$13{\cdot}89\ (\mp 0{\cdot}97) - 7207\ (\mp 1264)T^{-1}$	$0{\cdot}62 \mp 0{\cdot}11$
10	$13{\cdot}13\ (\mp 0{\cdot}33) - 7128\ (\mp 1135)T^{-1}$	$0{\cdot}61 \mp 0{\cdot}10$

Table 7. The mobility of electron holes for polycrystalline CoO

T (K)	$p(O_2)$ (Pa)	σ (Ω^{-1} cm^{-1})	μ_h (cm^2 V^{-1} s^{-1})
1273	10^5	19·61	0·442
	$2{\cdot}1 \times 10^4$	12·05	0·396
	$1{\cdot}3 \times 10^3$	5·03	0·317
	$1{\cdot}1 \times 10^2$	2·68	0·294
	43·6	1·99	0·269
	32·6	1·85	0·267
	7·9	1·34	0·261
	8·6	1·21	0·230
1373	10^5	29·41	0·501
	$2{\cdot}1 \times 10^4$	16·39	0·407
	$1{\cdot}3 \times 10^3$	8·06	0·377
	$1{\cdot}1 \times 10^2$	4·22	0·344
	30	2·73	0·272
	6	1·84	0·268

Figure 10 illustrates the Arrhenius plot of the chemical diffusion coefficient at three different intervals of $p(O_2)$. The thus obtained activation energy (126 kJ mol^{-1}) is in excellent agreement with the value reported before.[6] The thus determined diffusion data were used to evaluate the time required to achieve equilibrium in the studied system.

4 Conclusions

The reciprocal of the oxygen pressure exponent (n_α) determined by thermopower is higher than that determined by the conductivity method (n_σ). This indicates a substantial effect of the mobility term on the discrepancy between the two parameters.

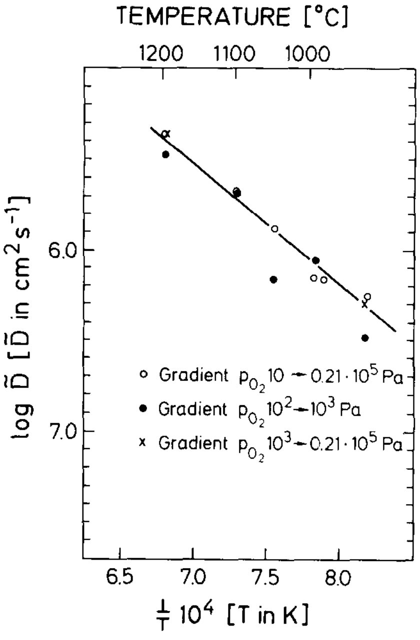

Fig. 10. Arrhenius-type plot of the chemical diffusion coefficient for CoO single crystal.

Except n_α values at higher temperatures, when n_α is close to four, both n_α and n_σ assume values much lower than four. This is in agreement with the CoO defect model involving strong interactions between defects.[32,33]

It is observed that n_σ values are slightly lower for the polycrystalline specimen (Fig. 3). The difference indicates an effect of grain boundaries on measured electrical conductivity (in the case of thermopower this effect is not observed). The observed effect is consistent with higher nonstoichiometry for the grain boundary region (as a result of segregation of Co vacancies) and resulting stronger interactions between defects in this region than those in the bulk phase.

The present study confirms that the mobility of electron holes increases substantially with equilibrium $p(O_2)$ and related deviation from stoichiometry in CoO. This study confirms the result of previous studies.[5] The nature of this effect, which is observed for both ceramic and single crystal specimens, is not clear. A possible explanation involves the apparent effect of defect concentration on the scattering mechanism. Unfortunately, the substantial scatter of data does not allow a distinction of the extent of the effect between the single crystal and the ceramic material. Further studies are required to clarify this matter.

The observed change in the mobility of electronic carriers with temperature indicates that the conductivity occurs according to the hopping mechanism.

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