# Electrical properties of undoped CoO – a Debye–Huckel approach

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Thermopower and electrical conductivity data for both single crystal and polycrystalline undoped CoO are considered in terms of a defect disorder model based on doubly ionized cobalt vacancies as the predominant defects. The analysis, based on the Debye–Hückel theory for liquid electrolytes, aims at an evaluation of the interactions between defects such as doubly ionized cation vacancies. It was shown that, in the temperature range 1200–1700 K, the reciprocals of the partial pressure of oxygen $p(O_2)$ exponent of thermopower and electrical conductivity vary between $3.6 < n_\alpha < 4.2$ and $3.5 < n_\sigma < 3.8$, respectively. About 1300 K, both $n_\alpha$ and $n_\sigma$ are higher for single crystal than for the polycrystalline specimens. It was shown that closer agreement between the defect model and experimental data can be obtained by introducing defect activities instead of concentrations.

## 1. Introduction

It has been reported that strong interactions between defects must be taken into account in the construction of defects models for CoO [1–5]. These defect interactions can be considered in terms of the Debye–Hückel theory for strong electrolytes [4, 5].

It is documented that oxide crystals, such as CoO, exhibit different defect structures and related properties in the bulk phase compared to those of a boundary layer [6, 7]. The difference is caused by segregation-induced enrichment of the boundary layer with cation vacancies and other defects. One may, therefore, expect that this enrichment results in much stronger interactions between the defects within this layer than in the bulk phase. Accordingly, the electrical properties of polycrystalline materials should be analysed in terms of both the bulk phase component, corresponding to the bulk defect structure, and also the boundary layer component which corresponds to the local defect chemistry of the boundary region. One should, therefore, expect that a decrease in the grain size will result in an increase in the boundary layer component which is characterized by much stronger defect interactions than those corresponding to the interior of the crystallites.

Based on the ideal defect disorder it has been shown that the mobility of electron holes in CoO increases with the equilibrium oxygen partial pressure, $p(O_2)$ and thus with nonstoichiometry [8]. This effect is not understood since an increase in defect concentration should result in increasing interactions between the defects, including electronic defects.

The purpose of the present work is to analyse electrical conductivity and thermopower data for undoped CoO in terms of different transport models.

## 2. Definition of terms

At elevated temperatures the predominant defects in CoO are doubly ionized Co vacancies and electron holes which, according to the ideal defect model, are formed according to the following equilibrium:

$$1/2 O_2 \rightleftarrows V_{Co}'' + 2h^\bullet \qquad (1)$$
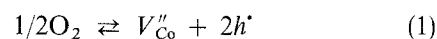
Assuming that the concentration of Co vacancies is equal to half that of the electron holes ($2[V_{Co}''] = [h^\bullet]$) the following relationship may be written between $[h^\bullet]$ and $p(O_2)$:

$$[h^\bullet] = (2K_1)^{1/3} p(O_2)^{1/6} \qquad (2)$$

where $[h^\bullet]$ is the concentration of electron holes and $K_1$ is the equilibrium constant of the reaction shown in Equation 1.

Considerations of defect models are usually based on the dependence of various crystal properties, such as electrical conductivity $(n_\sigma)$ or thermopower $(n_\alpha)$ on the oxygen partial pressure:

$$\frac{1}{n_z} = \left(\frac{\partial \log z}{\partial \log p(O_2)}\right) \quad (3)$$

where $z$ represents a crystal property such as in this case the concentration of electron carriers ($[e']$ or $[h^\cdot]$). In the case of a determination of $z$ from electrical conductivity or thermopower data then Equation 3 assumes the forms:

$$\frac{1}{n_\sigma} = \left(\frac{\partial \log \sigma}{\partial \log p(O_2)}\right) \quad (4)$$

$$\frac{1}{n_\alpha} = \frac{-1}{2.303}\left(\frac{\partial q\alpha}{\partial k \log p(O_2)}\right) \quad (5)$$

where $q$ is the elementary charge.

## 3. Postulation of the problem

Figure 1 illustrates both $n_\sigma$ and $n_\alpha$ versus temperature determined for both single crystal and polycrystalline specimens [8]. As seen the parameter $n_\alpha$ for both types of specimen is higher than $n_\sigma$ in the temperature range 1230–1470 K. It is also interesting to note that there is no essential difference in the value of these quantities between single crystal and polycrystalline CoO.

Based on the ideal defect model it has also been shown that the mobility of electron holes increases with equilibrium $p(O_2)$ [7]. This quantity is much higher for a single crystal than for a ceramic specimen.

The objective of this paper is to discuss a physical meaning of the oxygen pressure exponent determined by using thermopower $(n_\alpha)$ and electrical conductivity $(n_\sigma)$ and the reason of the observed discrepancy between them for CoO.

## 4. Thermopower versus electrical conductivity

A simple defect disorder requires that:

(i) the ideal approximation for the defects in the crystal is applicable,

(ii) one kind of ionic defect is predominant, and

(iii) the mobility of the defects is independent of the crystal composition.

In this case

$$n_\alpha = n_\sigma \quad (6)$$

Taking into account the requirements (i)–(iii) one may assume that a simple defect model for CoO may be considered when the predominant ionic defects are doubly ionized Co vacancies formed according to Equation 1. In the light of the results displayed in Fig. 1 the simple defect model is not valid for CoO. Thus, a more complex defect disorder must be considered involving either strong interactions between the defects or several types of defects present at comparable concentrations.
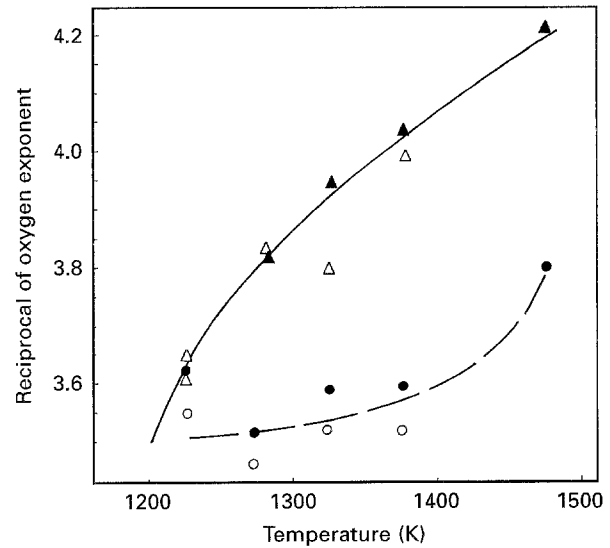


*Figure 1* Reciprocal of $p(O_2)$ exponent for single crystal (●) electrical conductivity $(n_\sigma)$ and (▲) thermopower $(n_\alpha)$ and also for; (○) $n_\sigma$ and (△) $n_\alpha$ for polycrystalline samples.

As seen from Fig. 1,

$$n_\alpha > n_\sigma \quad (7)$$

over the entire temperature range. This inequality may be considered in terms of the following effects:

(1) the mobility of electronic charge carriers depends on $p(O_2)$,

(2) the role of minority charge carriers in the conduction process cannot be ignored,

(3) the density of states, $N_h$, depends on $p(O_2)$

(4) interactions between the defects have an effect on the thermopower.

These items will be analysed below in more detail.

### 4.1. Dependence of the mobility of electron carriers on $p(O_2)$

This consideration is performed assuming that:

a) the predominant electronic defects are electron holes (pure p-type regime),

b) $N_h$ is independent of $p(O_2)$,

c) the ideal defect model is applicable.

Then the following relationships can be written:

$$\sigma = \text{const } [h^\cdot] \, \mu_h \quad (9)$$

where $\mu_h$ is the mobility of the electron holes. Then

$$1/n_\sigma = \partial \log \sigma / \partial \log p(O_2) = \partial \log[h^\cdot]/$$

$$\partial \log p(O_2) + \partial \log \mu_h / \partial \log p(O_2) \quad (10)$$

Therefore

$$1/n_\sigma = 1/n_h + 1/n_\mu \quad (11)$$

From the dependence

$$\alpha = k/q(\ln N_h/[h^\cdot] + A_h) \quad (12)$$

we have

$$1/n_\alpha = 1/n_h \quad (13)$$

therefore

$$1/n_\mu = 1/n_\sigma - 1/n_\alpha = (n_\alpha - n_\sigma)/n_\sigma n_\alpha \quad (14)$$

and

$$n_\mu = n_\sigma n_\alpha/(n_\alpha - n_\sigma) > 0 \quad (15)$$

The positive value of $n_\mu$ indicates that $\mu_h$ increases with $p(O_2)$. This is in agreement with the results reported for both single crystal and polycrystalline CoO [8]. This effect, however, is in conflict with the small polaron theory which has been postulated for CoO [8].

## 4.2. Effect of electrons as minority charge carriers

This consideration will be performed assuming that:
a) the mobilities of both electronic carriers are independent of $p(O_2)$,
b) the density of states, $N_h$, is independent of $p(O_2)$,
c) Equation 12 is valid.
In this case the following relationships must be considered

$$\sigma = q(\mu_e[e'] + \mu_h[h^\cdot]) \quad (16)$$

$$\alpha = (\alpha_e\sigma_n + \alpha_h\sigma_h)/(\sigma_e + \sigma_h) \quad (17)$$

where

$$\alpha_e = (- k/q) \ln(1/[e']) = k/q \ln[e'] \quad (18)$$

$$\alpha_h = k/q \ln(1/[h^\cdot]) = - k/q \ln[h^\cdot] \quad (19)$$

$$[e'] = K_i/[h^\cdot] \quad (20)$$

$$n_e = \partial\{\ln[e']\}/\partial\{\ln p(O_2)\} \quad (21)$$

and where $\mu_e$ is the mobility of electrons, $\sigma_n$ and $\sigma_h$ are the electrical conductivity components corresponding to electrons and electron holes, respectively, and $K_i$ is the equilibrium constant of intrinsic electronic equilibrium. Accordingly

$$\sigma = q\mu_h([h^\cdot] + \mu_e K_i/\mu_h[h^\cdot]) \quad (22)$$

$$\alpha = \frac{k}{q} \frac{- [h^\cdot]^2 \ln[h^\cdot] + K_i b \ln K_i - K_i b \ln[h^\cdot]}{[h^\cdot]^2 + bK_i} \quad (23)$$

where

$$b = \frac{\mu_e}{\mu_h} \quad (24)$$

Using the Debye–Hückel theory for strong electrolytes the equilibrium constant $K_1$ assumes the following form:

$$K_1^* = [h^\cdot]^3 f^6/2p(O_2)^{1/2} \quad (25)$$

where $f$ is a mean activity coefficient and $K_1^*$ is the equilibrium constant $K_1$ by assuming activities instead of concentrations.

Assuming that

$$S = \sigma/q\mu_h = ([h^\cdot] + bK_i/[h^\cdot]) \quad (26)$$

$$A = q\alpha/k = \frac{- [h^\cdot]^2 \ln[h^\cdot] - K_i b \ln[h^\cdot] + K_i b \ln K_i}{[h^\cdot]^2 + bK_i} \quad (27)$$

we obtain:

$$n_\sigma = \partial \ln p(O_2)/\partial \ln S \quad (28)$$

$$n_\alpha = \partial \ln p(O_2)/\partial \ln A \quad (29)$$

Based on the parameters $K_1^*$, $K_i$, $b$ and $f$ reported in references [4, 5] one may determine $[h^\cdot]$ and thus the parameters $S$ and $A$. Figs. 2–9 illustrate $S$, $A$ and $[h^\cdot]$ as functions of $p(O_2)$ at temperatures of 1273, 1473 and 1673 K. As can be seen at high $p(O_2)$, the parameter $n_\sigma$ is comparable to $n_\alpha$ while at lower $p(O_2)$:

$$n_\alpha > n_\sigma \quad (30)$$

For decreasing $p(O_2)$ the thermopower passes through a minimum ($n_\alpha = \infty$) and then

$$n_\alpha > n_\sigma \quad (31)$$

This indicates that thermopower is more sensitive to the presence of the minority charge carriers than the conductivity.

In this case the parameters $n_\alpha$, $n_\sigma$ and $n_h$ assume the following values:

1273 K: $n_\alpha = n_\sigma = n_h = 3.91$   (Fig. 5)

1473 K: $n_\alpha = n_\sigma = n_h = 3.91$   (Figs. 3 and 4)

1673 K: $n_\alpha = 4.63$;   (Fig. 6)
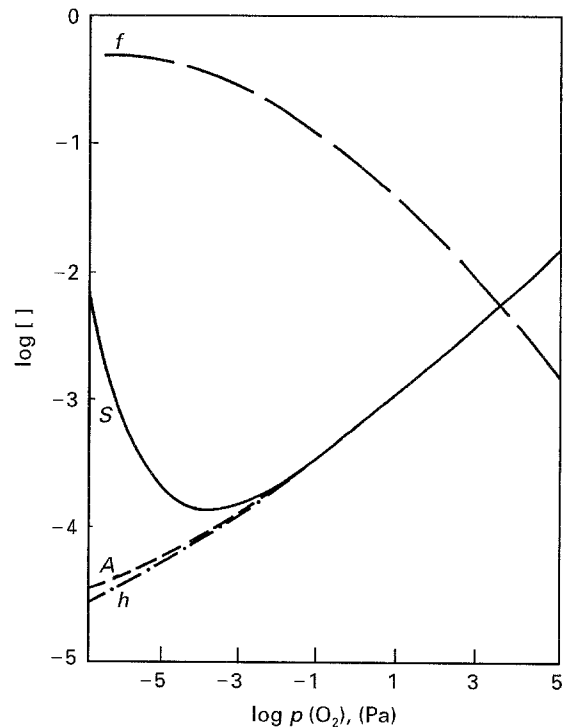
$n_\sigma = n_h = 4.16$   (Fig. 6)



*Figure 2* Plot of normalized thermopower (A) and electrical conductivity (S) as well as $[h^\cdot]$ and $f$ at 1273 K.
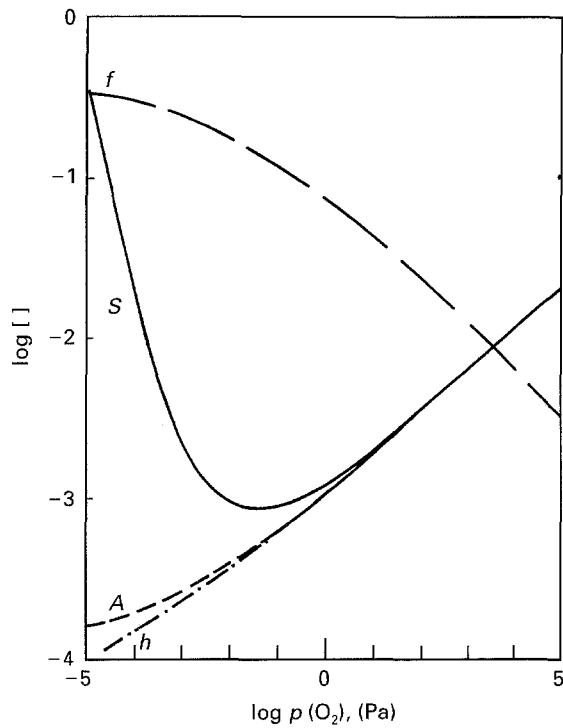
*Figure 3* Plot of normalized thermopower ($A$) and electrical conductivity ($S$) as well as $f$ and [$h^{\cdot}$] as a function of $p(O_2)$ at 1473 K.
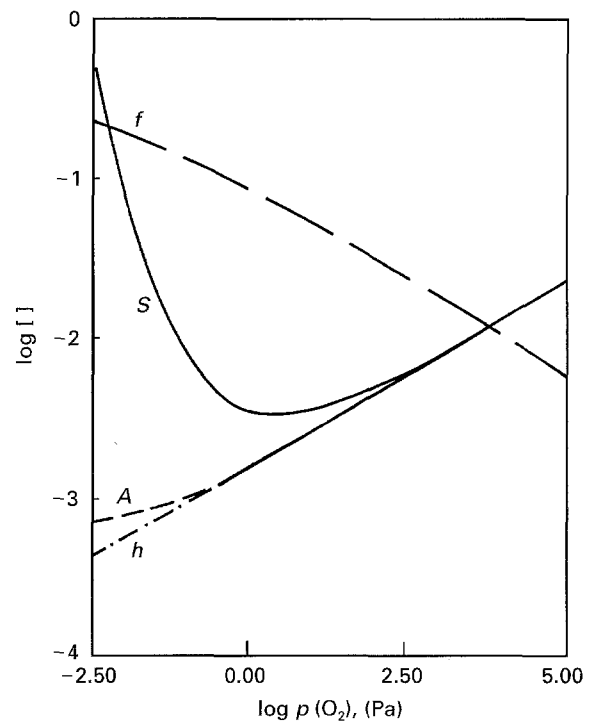


*Figure 5* Plot of normalized thermopower ($A$) and electrical conductivity ($S$) as well as $f$ and [$h^{\cdot}$] as a function of $p(O_2)$ at 1673 K.
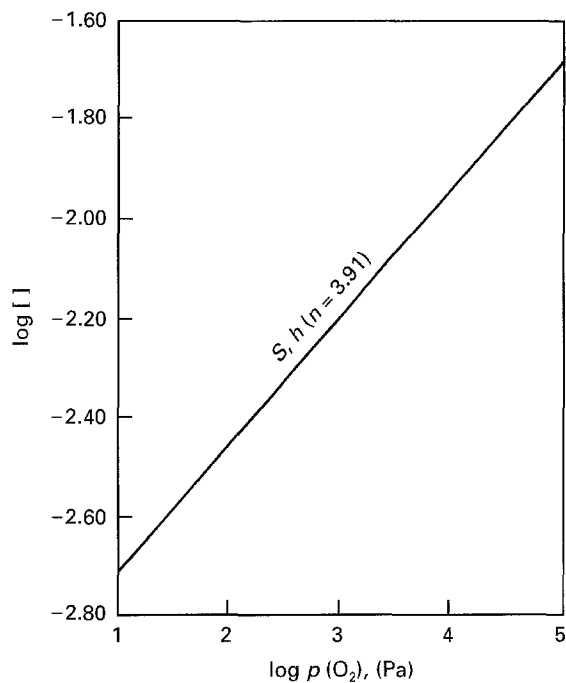


*Figure 4* Enlargement of both $S$ and [$h^{\cdot}$] versus $p(O_2)$ at 1273 K.



*Figure 6* Enlargement of both $S$ and $A$ at 1673 K.

As can be seen the role of the minority charge carriers is consistent with the relation:

$$n_\alpha > n_\sigma \qquad (32)$$

However, the difference between $n_\alpha$ and $n_h$ ($n_h = n_\sigma$) at the temperatures of 1273 and 1473 K (Figs. 2–4) and in the experimental $p(O_2)$ range is negligible. A difference between the two values can only be observed at 1673 K (Fig. 6). Accordingly, in the temperature range corresponding to the experimental data reported in reference [8] the effect of the minority charge carriers
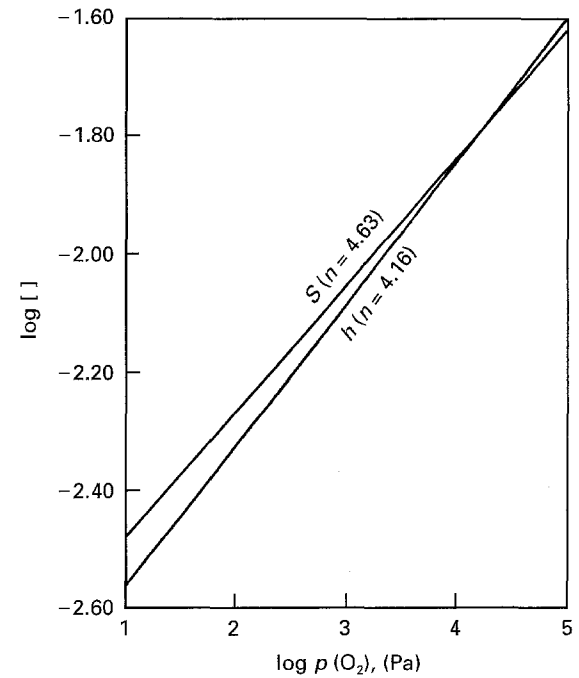
(electrons) on the $p(O_2)$ exponent can be neglected. Therefore, further considerations should be based on the assumption that electron holes are the predominant electronic defects.

## 4.3. Effect of the density of states on $p(O_2)$

This effect will be considered with the following assumptions:

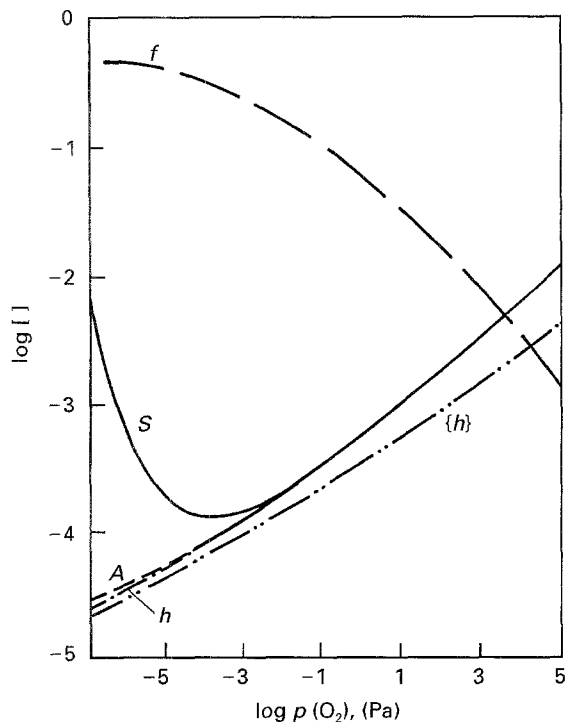a) the mobility of electron holes is independent of $p(O_2)$,

b) [$e'$] ≪ [$h^{\cdot}$],

*Figure 7* Plot of normalized thermopower ($A$) and electrical conductivity ($S$) as well as [$h^{\cdot}$], $\{h\}$ and $f$ at 1273 K.
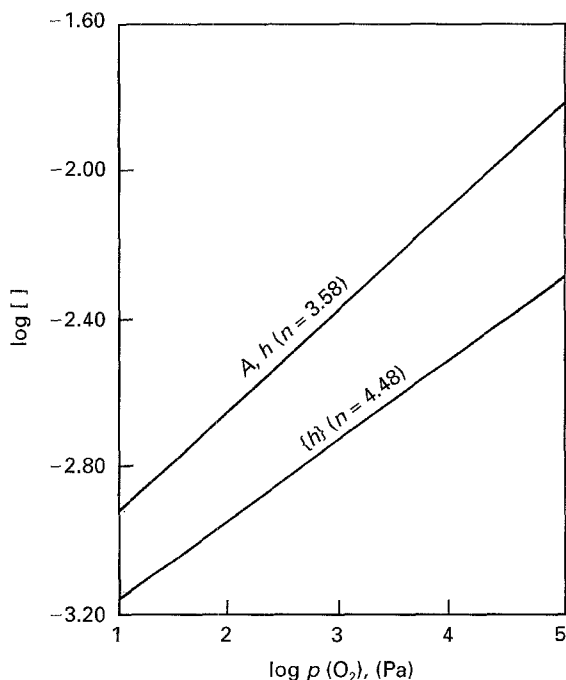


*Figure 8* Enlargement of $A$, [$h^{\cdot}$] and $\{h\}$ at 1273 K.

c) the ideal defect model is applicable.

The increase of $p(O_2)$ results in a decrease in the density of states. As seen from Equations 9 and 12 one should expect that:

$$n_\alpha < n_\sigma \qquad (33)$$

This inequality is not in agreement with the experimental values illustrated in Fig. 1. Accordingly, an effect of $p(O_2)$ on $N_h$ does not explain the discrepancy between $n_\sigma$ and $n_\alpha$ observed in Fig. 1.
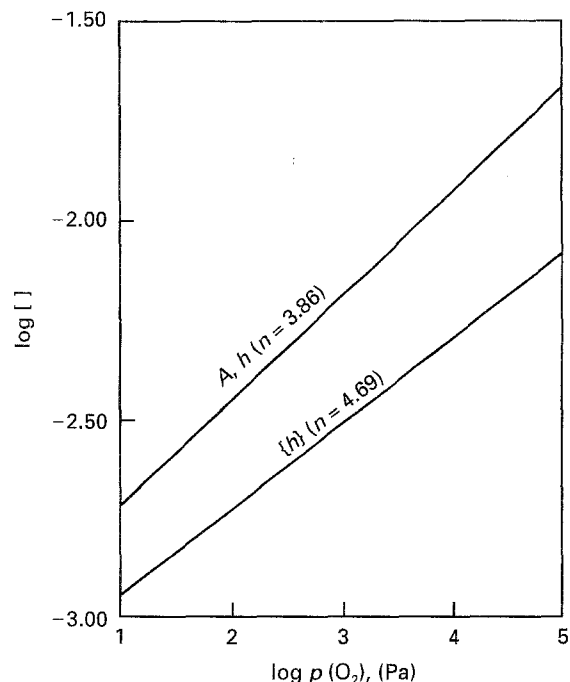


*Figure 9* Enlargement of $A$, [$h^{\cdot}$] and $\{h\}$ at 1473 K.

## 4.4. Effect of defect interactions on thermopower

Let us make the following assumptions:

a) $\mu_h$ is independent of $p(O_2)$,

b) [$e'$] $\ll$ [$h^{\cdot}$],

c) $N_h = $ const.

The dependence shown in Equation 12 results from quantum statistics assuming that interactions between defects are negligible. In the case that defect interactions are involved Equation 12 can still be applied, however, activities must be used instead of concentrations. Equation 23 then assumes the form:

$$\alpha = k/q \, \ln(N_h/\{h\} + A_h) \qquad (34)$$

where $\{h\}$ denotes activity of electron holes. Accordingly:

$$n_\alpha = n_{\{h\}} \qquad (35)$$

The evaluation of $n_\alpha$ from Equation 29 requires knowledge of the activity coefficient of electron holes. Based on the Debye–Huckel [4, 5] theory the activity of individual species cannot be determined and only average values are taken into account.

One should emphasize at this point that activity coefficients of various defects may differ substantially. However, there is a lack of information in this matter. Therefore, assuming that the character of interactions for species such as $V_{Co}''$ and [$h^{\cdot}$] are similar in nature one may write that:

$$f_{V_{Co}} = f_h^4. \qquad (36)$$

thus

$$f_h = (f\pm)^{1/2} = f \qquad (37)$$

Fig. 7 illustrates the dependence between $S$, $A$, $h$, $f$ and $\{h\}$ as a function of $p(O_2)$. As seen:

$$n_{\{h\}} > n_\sigma \qquad (38)$$

As can be seen from Figs 8–10 this inequality assumes substantial values in the experimental $p(O_2)$ range: $(10 > p(O_2) > 10^5$ Pa).

Fig. 11 illustrates the quantities such as $n_\sigma$ and $n_\alpha$ determined theoretically (by using the Debye–Hückel theory) and based on Equation 29 along with experimental data determined in the present work. As
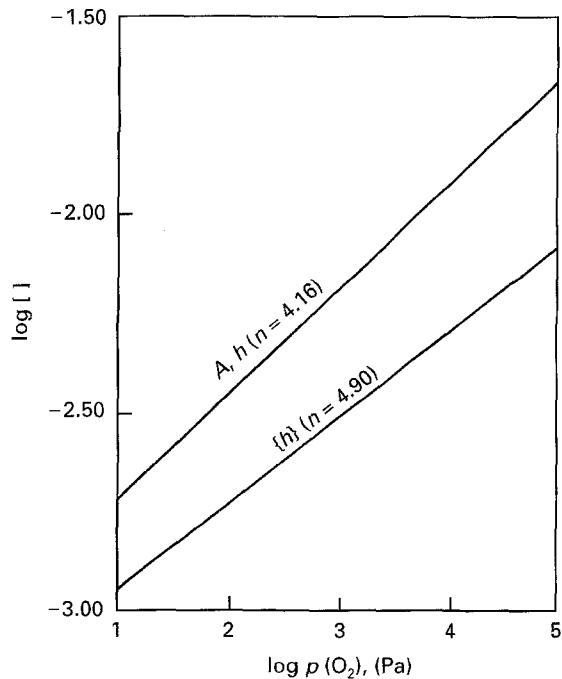


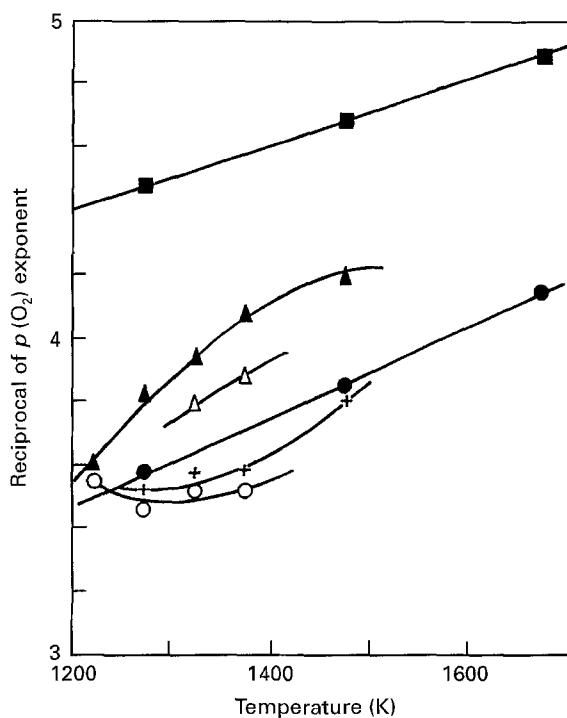Figure 10 Enlargement of $A$, $[h^\cdot]$ and $\{h\}$ at 1673 K.



Figure 11 Reciprocal of $p(O_2)$ exponent of electrical conductivity ( + ) $(n_\sigma)$ and (▲) thermopower $(n_\alpha)$ for single crystal (scr) and also (○) $n_\sigma$ and (△) $n_\alpha$ for polycrystalline CoO as a function of temperature [7] along with theoretical values (■) $(n_\alpha)_t$ and (●) $(n_\sigma)_t$ determined in this work.

seen, the parameter $n_\alpha$ determined from the Debye–Hückel theory is higher than those determined experimentally. This indicates that the activity coefficient of the electron holes is lower than that determined from Equation 31. Accordingly, assuming that the mobility of electron holes is independent of $p(O_2)$, both $n_\sigma$ and $n_\alpha$ should be identical. The observed difference between the two quantities may be explained by defect interactions. Introducing activities instead of concentrations (Equation 29) results in the increase of the parameter $n_\alpha$ in respect to $n_\sigma$ (Fig. 11). As can also be seen there is no difference between the parameters $n_\alpha$ for the single crystal and the ceramic specimen (one would expect that $n_\alpha$ for the polycrystalline specimen would be higher than that of the single crystal as a result of the grain boundary contribution).

## 5. Conclusions

It has been shown that there is a substantial discrepancy between the $p(O_2)$ exponent resulting from thermopower and electrical conductivity of undoped CoO. The reason for the discrepancy has been considered in term of several defect and transport models. Assuming that the predominant ionic defects in CoO are doubly ionized Co vacancies it was shown that the observed discrepancy between $n_\sigma$ and $n_\alpha$ may only be explained assuming substantial interactions between the defects in CoO. Under these circumstances defect activities should be taken into account instead of concentrations. The Debye–Hückel approach gives satisfactory results although this approach does not inform us of the nature of the interactions between defects.

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