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Importance of electronic band structure to nonstoichiometric behaviour of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$

Martijn H.R. Lankhorst, H.J.M. Bouwmeester*, H. Verweij

University of Twente, Department of Chemical Technology, Laboratory of Inorganic Materials Science, P.O. Box 217, 7500 AE Enschede, The Netherlands

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Abstract

The partial energy and entropy involved in the process of oxygen incorporation into the mixed oxygen ion and electronic conducting $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ was measured by oxygen coulometric titration. The partial entropy can be assigned to the configurational entropy of randomly distributed oxygen vacancies. The partial energy decreases linearly with increasing oxygen nonstoichiometry. These observations can be explained assuming that electrons, created during vacancy formation, gradually fill electron states in a wide band resulting in a corresponding increase of the Fermi level.

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1. Introduction

Many of the 3d transition metal perovskite-type oxides are characterized by increased lattice oxygen vacancy formation at high temperatures, which results in substantial departures from ideal oxygen stoichiometry. Vacancy formation is accompanied by a proportional change in the effective valence of either the transition metal or oxygen ions. The relatively high vacancy mobility in conjunction with the metallic-like electronic conductivity cause these materials to be permeable for oxygen gas, which is of interest for various applications [1]. In addition, many of the 3d transition metal perovskites are

studied for the occurrence of special electronic and magnetic transitions as a function of temperature and composition [2,3]. The complicated electronic structure of these oxides is a direct consequence of the competition between charge disproportionation and charge transfer [4]. Although charge disproportionation was not observed in LaCoO_3 by XAS [2], Sarma et al. [3] state that for this material the influence of both types of charge fluctuations are of the same order of magnitude leading to a very mixed character of the ground state. Charge disproportionation was used to model data from oxygen nonstoichiometry [5] and Seebeck measurements [6] of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. In both cases, however, the best fit implied the simultaneous presence of unrealistically high concentrations of Co^{2+} and Co^{4+} . In Sr-doped LaCoO_3 , significant spectral intensities at the

*Corresponding author. Tel.: (31-53) 4892202; fax: (31-53) 4894683; e-mail: h.j.m.bouwmeester@ct.utwente.nl

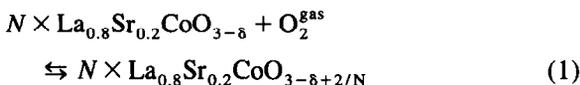
Fermi-energy have been observed by Sarma et al. [3] using UPS and Bremsstrahlung Isochromat Spectroscopy. They concluded that electron hole states, created by substitution of La by Sr, overlap the top of the wide oxygen 2p band giving rise to a mixed-valency metallic compound. Furthermore, Seebeck and conductivity measurements [6] at high temperatures also indicate metallic-like properties for Sr-doped LaCoO_3 . It is therefore believed that in the latter compounds electrons, created during vacancy formation, occupy delocalized electron states near the Fermi level in a broad electron band.

In this study, the oxygen incorporation thermodynamics of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ is studied by high-temperature coulometric titration. Here the oxide sample is enclosed in a sealed electrochemical cell; its oxygen stoichiometry is adjusted by electrochemically pumping oxygen into or out of the cell. The oxygen partial pressure inside the cell is determined from the EMF that can be measured when using identical metallic probes.

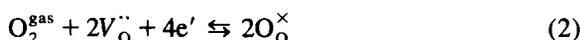
Since the concentration of conduction electrons is coupled directly to that of oxygen vacancies, their concentration can be controlled in situ by electrochemical titration. Analysis of the oxygen partial pressure and temperature dependence of the oxygen stoichiometry permits evaluation of thermodynamic quantities concerning both oxygen vacancies and electrons.

2. Theory

The oxygen pumped into the cell equilibrates with the oxide and this reaction can be represented as



where N represents the number of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ units and δ is the oxygen nonstoichiometry parameter. The latter is directly related to the number of oxygen vacancies in the lattice. Oxygen molecules are being incorporated as two regular lattice oxygen ions (O_O^\times), at the expense of two lattice oxygen vacancies ($\text{V}_\text{O}^\ddot{\cdot}$) and four electrons (e'),



where the Kröger Vink notation [7] is used. From Eq. (2), it is seen that electrochemically pumping of oxygen into the cell leads to an adjustment of the concentration of both lattice oxygen vacancies and electrons. The equilibrium condition for the reaction of Eq. (2) reads

$$\mu_{\text{O}_2} = -2(\mu_{\text{V}_\text{O}^\ddot{\cdot}} - \mu_{\text{O}_\text{O}^\times}) - 4\mu_{e'} \quad (3)$$

where μ_i denotes the chemical potential of species i . In the following, expressions will be derived for both $(\mu_{\text{V}_\text{O}^\ddot{\cdot}} - \mu_{\text{O}_\text{O}^\times})$ and $\mu_{e'}$.

The calculation of $(\mu_{\text{V}_\text{O}^\ddot{\cdot}} - \mu_{\text{O}_\text{O}^\times})$ requires evaluation of the change in the free energy of the oxide F^{oxide} upon adding a single vacancy. To a first order of approximation, the energy required to create $N_{\text{V}_\text{O}^\ddot{\cdot}}$ vacancies in the oxide, is given by

$$E^{\text{oxide}} = N_{\text{V}_\text{O}^\ddot{\cdot}} \epsilon_{\text{V}}^0 \quad (4)$$

where ϵ_{V}^0 represents the formation energy per vacancy. In principle, we have neglected coulombic interactions between oxygen vacancies that may give rise to an energy part of $(\mu_{\text{V}_\text{O}^\ddot{\cdot}} - \mu_{\text{O}_\text{O}^\times})$ being a function of the vacancy concentration [8]. The latter effect has not been observed, however, in the related structure $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ [9]. Since the electronic conduction [10] of $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ is substantially lower than that of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ [6], screening of coulombic interactions is expected to be even more effective in the cobaltite perovskite. The associated entropy can be calculated by assuming that the $N_{\text{V}_\text{O}^\ddot{\cdot}}$ oxygen vacancies and $N_{\text{O}_\text{O}^\times}$ regular lattice oxygen ions are randomly distributed over the $3N$ available sites in the perovskite lattice. This assumption implies that all lattice oxygen vacancies are equivalent, which is in agreement with data of oxygen permeation through these materials as measured by Van Doorn et al. [11]. These latter authors showed that the rate of oxygen permeation through $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ is proportional to the extent of oxygen nonstoichiometry, from which it can be concluded that all oxygen vacancies are involved in the total transport of oxygen. The latter conclusion also rules out the possibility that vacancies are partially associated to Sr'_{La} centers. Using $S^{\text{oxide}} = k_{\text{B}} \ln(\Omega)$, where Ω is the total number of configurations, one finds

$$S^{\text{oxide}} = k_B \ln \left(\frac{(3N)!}{N_{V_{\text{O}}}! N_{\text{O}_{\text{O}}}!} \right). \quad (5)$$

Differentiating Eqs. (4) and (5) with respect to $N_{V_{\text{O}}}$ using $N_{V_{\text{O}}} + N_{\text{O}_{\text{O}}} = 3N$ and $\delta = N_{V_{\text{O}}}/N$ leads to the following expression for $(\mu_{V_{\text{O}}} - \mu_{\text{O}_{\text{O}}})$:

$$(\mu_{V_{\text{O}}} - \mu_{\text{O}_{\text{O}}}) = \mu_V^0 - T \left[k_B \ln \left(\frac{3-\delta}{\delta} \right) \right] \quad (6)$$

where μ_V^0 contains ϵ_V^0 in addition to constant energy and entropy terms originating from vibrational contributions [8]. The term between square brackets in Eq. (6) is the *configurational entropy* of randomly distributed oxygen vacancies.

Next, an expression will be derived relating $\mu_{e'}$ to the electron occupancy $n = N_{e'}/N$, where $N_{e'}$ is the total number of conduction electrons. Within the one-electron approximation, n may be evaluated by integrating the Fermi–Dirac distribution function, $f(\epsilon)$, multiplied by the density of states, $g(\epsilon)$, over the total bandwidth,

$$n = \int_{\epsilon = \epsilon_b}^{\epsilon = \epsilon_t} g(\epsilon) f(\epsilon) d\epsilon \approx \int_{\epsilon = \epsilon_b}^{\epsilon = \epsilon_F} g(\epsilon) d\epsilon \quad (7)$$

where ϵ_b and ϵ_t are the energies at the bottom and top of the band, respectively. Note that the approximation made in Eq. (7) is based on the assumption that only electron states below the Fermi level ϵ_F are occupied while those above are empty. In practice, however, electron states within a few $k_B T$ of ϵ_F are partially filled, but this effect can be neglected in the case where the bandwidth is large compared with $k_B T$. The overall electron entropy thus has a negligible influence on $\mu_{e'}$. Using the first-order Taylor expansion of Eq. (7), the electron chemical potential $\mu_{e'}$ (or the Fermi level ϵ_F) can be expressed in terms of n and $g(\epsilon_F)$

$$\mu_{e'} = \epsilon_F \approx \epsilon_F(n^0) + \frac{(n - n^0)}{g(\epsilon_F)} \quad (8)$$

where n^0 is defined as the electron occupancy at zero vacancy concentration in LaCoO_3 . When Eq. (8), in conjunction with the requirement of charge neutrality, i.e. $n - n^0 = 2\delta - x$, is used to calculate variations in $\mu_{e'}$ with changing vacancy concentration, it

is implicitly assumed that the shape of the band is unchanged.

The values of the energy and entropy part of both $(\mu_{V_{\text{O}}} - \mu_{\text{O}_{\text{O}}})$ and $\mu_{e'}$ can not be measured by direct means. It is however possible to measure the partial energy ϵ_{O_2} and entropy s_{O_2} of oxygen incorporation. These latter parameters include both energy and entropy of lattice oxygen vacancies and conduction electrons: $\epsilon_{\text{O}_2} = -2(\epsilon_{V_{\text{O}}} - \epsilon_{\text{O}_{\text{O}}}) - 4\epsilon_{e'}$ and $s_{\text{O}_2} = -2(s_{V_{\text{O}}} - s_{\text{O}_{\text{O}}}) - 4s_{e'}$. Values of ϵ_{O_2} and s_{O_2} can be evaluated from measurement of μ_{O_2} as a function of temperature T at constant oxygen stoichiometry of the sample [8],

$$\epsilon_{\text{O}_2} = \left(\frac{\partial \mu_{\text{O}_2} / T}{\partial 1/T} \right)_{\delta}, \quad (9)$$

$$s_{\text{O}_2} = - \left(\frac{\partial \mu_{\text{O}_2}}{\partial T} \right)_{\delta}. \quad (10)$$

3. Experimental

Measurements were performed using the electrochemical cell shown in Fig. 1. A cylindrical disc of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ was placed in a small cylindrical

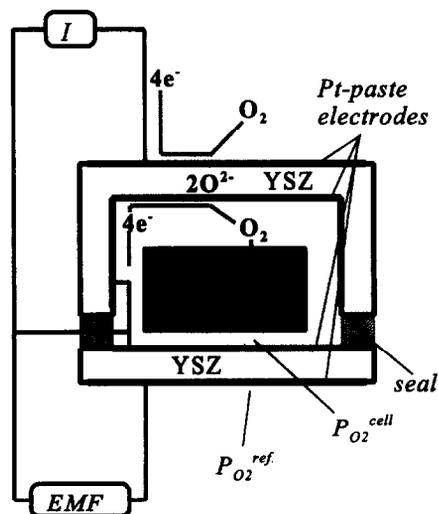


Fig. 1. Electrochemical cell used for oxygen titration experiments on $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. Two ZY13 solid electrolytes are used. One is used to measure the P_{O_2} in the cell, cf. Eq. (11), and the other to pump oxygen into or out of the cell.

ZY13 ($\text{Zr}_{0.87}\text{Y}_{0.13}\text{O}_{1.935}$) crucible, which was sealed to a ZY13 disc by a Pyrex glass ring. Pt-based electrodes were painted on both sides of the disc and the crucible. The inner electrodes were connected to a thin Pt tape which led to the exterior of the cell via the Pyrex glass ring. In the cell arrangement, as shown in Fig. 1, the ZY13 disc is used to measure the EMF of the cell. The latter is related to the gradient in oxygen chemical potential imposed across the ZY13 disc, $\Delta\mu_{\text{O}_2}$, according to

$$\text{EMF} = \Delta\mu_{\text{O}_2}/4e = (k_{\text{B}}T/4e) \ln(P_{\text{O}_2}^{\text{ref.}}/P_{\text{O}_2}^{\text{cell}}) \quad (11)$$

where k_{B} is Boltzmann's constant, T the temperature, e the elementary charge and $P_{\text{O}_2}^{\text{ref.}}$ and $P_{\text{O}_2}^{\text{cell}}$ are the oxygen partial pressure at the positive and negative electrode, respectively. The ZY13 crucible is used for electrochemical pumping of oxygen into or out of the cell. The current measured is related to the oxygen pumping rate in accordance with Faraday's law. Further experimental details were discussed elsewhere [12].

The δ - P_{O_2} curves were measured at various temperatures by numerical integration of the current decay after a step-wise change in the cell voltage. Voltage steps of typically 25 mV were applied between 0 and 200 mV. These measurements, henceforth referred to as the *voltage step measurements*, were performed at 700, 750, 800, 850, 900, 950 and

1000°C. The relative positions of the resulting δ - P_{O_2} lines were determined by measuring the open cell EMF while changing the temperature. To measure the energy and entropy of oxygen incorporation, the open cell EMF was monitored as a function of temperature at constant oxygen nonstoichiometry. These *temperature step measurements* were performed in the range $0.01 < \delta < 0.085$. Between two temperature steps, the oxygen stoichiometry of the sample was adjusted by electrochemically pumping oxygen into or out of the cell.

4. Results and discussion

In Fig. 2, $\log(\delta)$ is plotted against $\log(P_{\text{O}_2})$ at various temperatures, as obtained from the *voltage step measurements*. The oxygen stoichiometry at 800°C in air, as measured by Mizusaki et al. [13] was taken as the reference stoichiometry. The curves in Fig. 2 are almost linear with slope, γ , equal to -0.23 ± 0.02 . This observation is in good agreement with the results obtained from the thermogravimetric study by Mizusaki et al. [13].

Fig. 3 shows that the entropy of oxygen incorporation s_{O_2} increases with increasing δ . Neglecting the entropy of the conduction electrons, changes in s_{O_2} are determined only by the configurational entropy of the vacancies in the oxygen sublattice.

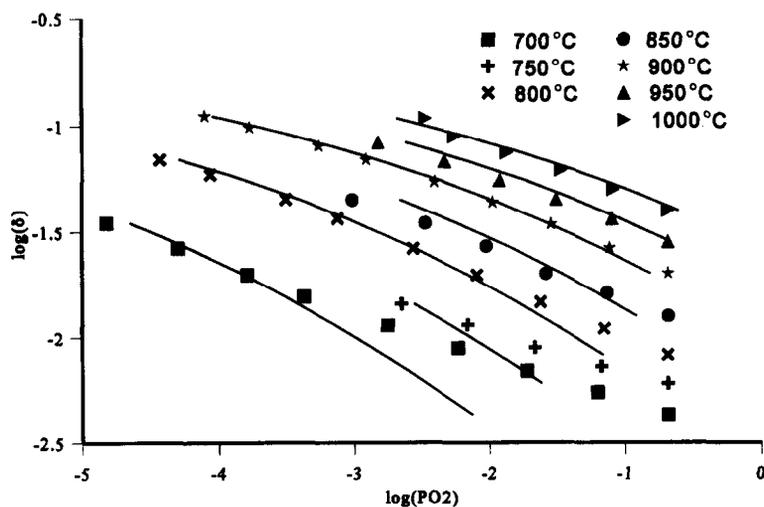


Fig. 2. Plot of $\log(\delta)$ as a function of $\log(P_{\text{O}_2})$. Experimental data was determined from the *voltage step measurements*. The theoretical values are calculated from Eq. (15).

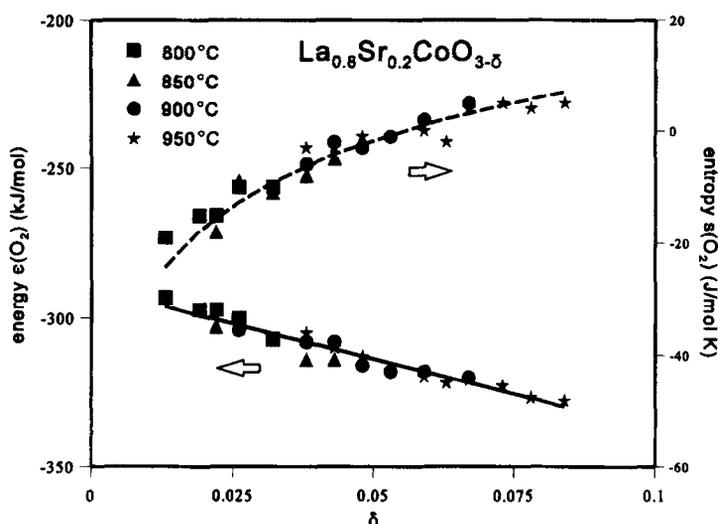


Fig. 3. Plot of the partial energy (ϵ_{O_2}) and entropy (s_{O_2}) as a function of oxygen non-stoichiometry, δ . Data was determined from the temperature step measurements. Dashed and solid lines indicates fits to Eq. (12) and Eq. (13), respectively.

$$s_{O_2} = s^0 + 2k_B \ln \left(\frac{\delta}{3 - \delta} \right) \quad (12)$$

where s^0 is a constant. Fig. 3 shows that the experimental data for s_{O_2} , evaluated at four different temperatures, can be fitted well to Eq. (12). The value of s^0 was refined to $s^0 = 7.12 \times 10^{-4} \text{ eV K}^{-1}$ ($68.7 \text{ J mol}^{-1} \text{ K}^{-1}$). The agreement noted with the configurational entropy of oxygen vacancies favours the assumption of randomly distributed oxygen vacancies and that of negligibly small contribution of the entropy of electrons.

Fig. 3 shows that ϵ_{O_2} decreases almost linearly with increasing nonstoichiometry, but is almost temperature independent. Combining Eqs. (3), (6) and (8) leads to the following expression relating ϵ_{O_2} to δ and the density of states at the Fermi level $g(\epsilon_F)$

$$\epsilon_{O_2} = \epsilon^0 - \frac{4(2\delta - x)}{g(\epsilon_F)} \quad (13)$$

where ϵ^0 is a constant. Values of ϵ^0 and $g(\epsilon_F)$ obtained from fitting the data shown in Fig. 3 to Eq. (13) are -3.43 eV (-331 kJ mol^{-1}) and 1.9 eV^{-1} ($0.0198 \text{ mol kJ}^{-1}$), respectively. The value of $g(\epsilon_F)$ is of the same order of magnitude as the 1.0, 1.3 and 1.5 eV^{-1} obtained from the shift in the O-2p band

towards the Fermi level with increasing Sr content as measured using XPS by different authors [3,14,15].

McKinnon and Selwyn [16] criticized the use of the so-called *electron gas rigid band model* in which the Fermi level raises when the band is filled due to ionization of added impurities. With reference to the *screened impurity rigid band model* developed by Friedel [17], these authors assume that due to the presence of the ionized impurities the entire electron band shifts due to the perturbation constituted by the screened impurity potential. Since the latter shift is exactly opposite to that of the Fermi level relative to the band edges, the Fermi level on an absolute energy scale remains unaltered. This model can not, however, explain the good correlation found between the measured chemical potential variations for alkali metal intercalated transition metal dichalcogenides and the corresponding density of states calculations [18] and data from X-ray absorption measurements [19]. A constant Fermi level might not either explain the observed decrease in ϵ_{O_2} with increasing δ . For $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ it seems that screening of oxygen vacancies only partly balances the upwards shift in the Fermi level with increasing electron occupancy. This would also explain why the value of $g(\epsilon_F)$ determined from this study is somewhat larger than those obtained with XPS.

The exchange reaction given by Eq. (2) is com-

monly analyzed using a traditional formalism that has been discussed in length by Kröger [20]. In this approach point defects are assumed to be ideally diluted and corresponding chemical potentials are derived using Maxwell–Boltzmann statistics. Such an analysis typically leads to mass-action type equations. In the present case this leads to

$$P_{\text{O}_2} \left(\frac{\delta}{3-\delta} \right)^2 \left(\frac{n}{1-n} \right)^4 = \exp \left(\frac{-\Delta F^0}{k_B T} \right) \quad (14)$$

where ΔF^0 is a Helmholtz free energy, the value of which depends on temperature only. In deriving Eq. (14), it is implicitly assumed that ϵ_{O_2} is constant, while s_{O_2} is a function of the concentration of both lattice oxygen vacancies and conduction electrons. Both assumptions do not agree with the results of this study. By utilizing Eqs. (12) and (13), the mass action type of equation in Eq. (14) can be modified into

$$P_{\text{O}_2} \left(\frac{\delta}{3-\delta} \right)^2 = \exp \left(\frac{-\Delta F^0 - 4(2\delta - x)/g(\epsilon_F)}{k_B T} \right) \quad (15)$$

where ΔF^0 is equal to $(3.70 - 0.00184 \times T)$ eV or $(358 - 177 \times T)$ kJ mol⁻¹. From Fig. 2, we see that the experimental data obtained with the *voltage step measurements* are in fair agreement with those predicted by Eq. (15). The agreement noted implies that the results of the *voltage step measurements* are consistent with those obtained from the *temperature step measurements*.

The value of γ corresponds with the slope in the double logarithmic plot of δ versus P_{O_2} . Taking the logarithm of Eq. (15), partial differentiation with respect to $\log(\delta)$ shows that γ is a function of δ and the density of states at the Fermi level,

$$\gamma = - \left(2 \left(\frac{3}{3-\delta} \right) + \frac{8\delta}{k_B T g(\epsilon_F)} \right)^{-1} \quad (16)$$

Substituting the value for $g(\epsilon_F)$, taking an average value of δ equal to 0.05 and T in the range 973–1223 K yields $\gamma = 0.24 \pm 0.02$, which fairly agrees with the overall value obtained from the *voltage step measurement*, shown in Fig. 2.

5. Summary

The entropy associated with the incorporation of oxygen into $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ is related to δ in agreement with that calculated from the configurational entropy of randomly distributed oxygen vacancies. No influence of the change in electron entropy was observed in the experimental data. The energy of oxygen incorporation decreases almost linearly with increasing oxygen nonstoichiometry. Both energy and entropy data can be explained with a model which assumes that electrons are placed in a broad electron band. The model implies that changes in the value of ϵ_{O_2} are directly related to changes in the value of the Fermi level, and as a result, they are also related to the electron density of states at the Fermi level. An expression is presented, relating oxygen nonstoichiometry to temperature and oxygen partial pressure, which clearly deviates from a conventional mass-action type of law.

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