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Thermodynamic Quantities and Defect Equilibrium in the Perovskite-Type Oxide Solid Solution $La_{1-x}Sr_xFeO_{3-\delta}$

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In order to clarify the relationship between the thermodynamic quantities and the defect equilibrium of the solid solution $La_{1-x}Sr_xFeO_{3-\delta}$, analysis and statistical thermodynamic calculations were made using the authors' previously reported nonstoichiometry data. From the δ–log P_{O_2}–T relationships, using the Gibbs–Helmholtz equation, the partial molar enthalpy $(h_O - h^\circ_O)$ and the partial molar entropy $(s_O - s^\circ_O)$ of oxygen in $La_{1-x}Sr_xFeO_{3-\delta}$ were determined as functions of x and δ. Here, the standard states of h_O and s_O, h°_O, and s°_O are in equilibrium with 1 atm oxygen gas. For $\delta < x/2$ and $\delta > x/2$, $(h_O - h^\circ_O)$ is essentially constant and $(s_O - s^\circ_O)$ increases with δ. Around $\delta = x/2$, drastic decreases in $(h_O - h^\circ_O)$ and $(s_O - s^\circ_O)$ are observed. Statistical thermodynamic calculations were made for the oxygen chemical potential, μ_O, the partial molar enthalpy, h_O, and the partial molar entropy, s_O, assuming random distribution of the defects, $V_O^{\cdot\cdot}$, Fe'_{Fe}, and $Fe^{\cdot}_{Fe}$, on each lattice site. Numerical calculations for $(h_O - h^\circ_O)$ and $(s_O - s^\circ_O)$ were made using the defect concentrations, the equilibrium constant, K_i, for the reaction of $2Fe^x_{Fe} = Fe'_{Fe} + Fe^{\cdot}_{Fe}$, and K_{ox} for the reaction of $\frac{1}{2}O_2(g) + V_O^{\cdot\cdot} + 2Fe^x_{Fe} = 2Fe^{\cdot}_{Fe} + O^x_O$. The calculated $(h_O - h^\circ_O)$ and $(s_O - s^\circ_O)$ vs δ relationships based on the statistical thermodynamic model agreed quite well with those determined from the experimental data using the Gibbs–Helmholtz equation.

1. Introduction

In the preceding paper (*1*), the present authors reported the nonstoichiometry δ of the perovskite-type oxide solid solution $La_{1-x}Sr_xFeO_{3-\delta}$ as a function of the oxygen partial pressure, P_{O_2}, temperature, T, and the A-site composition, x. The nonstoichiometry data for $LaFeO_{3-\delta}$ were interpreted by the defect equilibrium among Fe'_{Fe}, $Fe^{\cdot}_{Fe}$, $V_O^{\cdot\cdot}$, and V'''_{La}, where V'''_{La} is caused by the nonstoichiometric La/Fe ratio. For $La_{1-x}Sr_xFeO_{3-\delta}$ ($x \geq 0.1$), the data were explained by the equilibrium among Fe'_{Fe}, $Fe^{\cdot}_{Fe}$, $V_O^{\cdot\cdot}$, and Sr'_{La}. Calculations were made for the concentrations of the defects and the equilibrium constants, K_{ox} and K_i. Here,

$$K_{ox} = \frac{[O^x_O][Fe^{\cdot}_{Fe}]^2}{P_{O_2}^{1/2}[V_O^{\cdot\cdot}][Fe^x_{Fe}]^2} \quad (1)$$

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is the equilibrium constant for the reaction between the defects and the gas phase,

$$\tfrac{1}{2}O_2(g) + V_O^{\cdot\cdot} + 2Fe_{Fe}^{x} = O_O^{x} + 2Fe_{Fe}^{\cdot}, \quad (2)$$

and

$$K_i = \frac{[Fe_{Fe}^{\cdot}][Fe_{Fe}']}{[Fe_{Fe}^{x}]^2} \quad (3)$$

is the constant for the internal equilibrium of

$$2Fe_{Fe}^{x} = Fe_{Fe}' + Fe_{Fe}^{\cdot}. \quad (4)$$

In this paper, defects are expressed by the Kröger–Vink-type notations (*2*).

It was found that the equilibrium constants are essentially constant independent of δ. This finding may suggest that the point defects in $La_{1-x}Sr_xFeO_{3-\delta}$ can be described by the ideal solution approximation. However, there has been no further discussion of the thermodynamic properties of the solid solution, because our interest in the preceding paper (*1*) focused on the thermogravimetric measurement of nonstoichiometry, the determination of defect concentration, and the relationship between the defect concentration and the electrical properties.

The purpose of the present study is to clarify the relationship between the thermodynamic quantities and the internal defect equilibrium of the $La_{1-x}Sr_xFeO_{3-\delta}$ solid solution system. From the reported nonstoichiometry data (*1*), we calculate the partial molar enthalpy and the partial molar entropy of oxygen in the solid solution as a function of δ. Based on the statistical thermodynamics, we calculate the relationship between the partial molar quantities and the internal defect equilibrium. We then compare the thermodynamic quantities determined directly from the experimental results with those calculated based on the statistical thermodynamics, and discuss the relationships between the partial molar quantities and the defect equilibrium constants and the configurational entropy of the defects.

2. Partial Molar Enthalpy and Entropy of Oxygen

The nonstoichiometry, δ, of $La_{1-x}Sr_xFeO_{3-\delta}$ ($x = 0$, 0.1, 0.25, 0.4, and 0.6) was given as a function of T and P_{O_2} (*1*). The P_{O_2} values are related to the oxygen chemical potential, μ_O, in $La_{1-x}Sr_xFeO_{3-\delta}$ by the equation

$$\mu_O - \mu^{\circ}_O = 2.303RT \log P_{O_2}, \quad (5)$$

where μ°_O is the μ_O in $La_{1-x}Sr_xFeO_{3-\delta}$ in equilibrium with 1 atm $O_2(g)$. Using Eq. (5), the nonstoichiometry data of $La_{1-x}Sr_xFeO_{3-\delta}$ can be expressed as a function of μ_O.

The partial molar enthalpy, h_O, and the partial molar entropy, s_O, of oxygen are related to μ_O by the equation

$$\mu_O = h_O - Ts_O. \quad (6)$$

From Eqs. (5) and (6), using the Gibbs–Helmholtz equation, we obtain

$$h_O - h^{\circ}_O = \frac{R}{2}\left[\frac{\partial \ln P_{O_2}}{\partial(1/T)}\right]_{\delta,x} \quad (7)$$

and

$$s_O - s^{\circ}_O = -\frac{1}{2}\left[\frac{\partial(RT \ln P_{O_2})}{\partial T}\right]_{\delta,x}, \quad (8)$$

where h°_O and s°_O are the h_O and s_O, respectively, of $La_{1-x}Sr_xFeO_{3-\delta}$ in equilibrium with 1 atm $O_2(g)$. From the slopes of the plots of $\log P_{O_2}$ vs $1/T$ and $RT \log P_{O_2}$ vs T under constant δ and x, we can determine $(h_O - h^{\circ}_O)$ and $(s_O - s^{\circ}_O)$.

The nonstoichiometry data for $x = 0.4$ are shown in Fig. 1 in the $\log P_{O_2}$ vs $1/T$ plot, with δ as a parameter. In Fig. 2, the data for $x = 0.25$ are shown in the $RT \log P_{O_2}$ vs t(°C) plot. Because the results fall along a straight line, $(h_O - h^{\circ}_O)$ and $(s_O - s^{\circ}_O)$ are considered to be constant independent

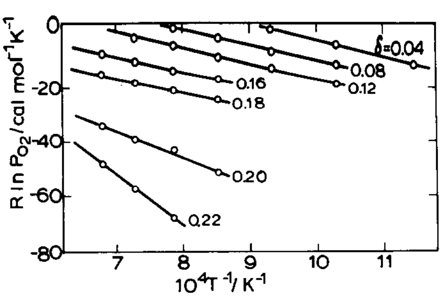

FIG. 1. Relations between the equilibrium P_{O_2} and T of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ of different δ in the plots of $R \ln P_{O_2}$ versus $1/T$.

of the temperature under the conditions in which our measurements were made (*1*). Figures 3 and 4 show the relationships between the calculated $(h_0 - h°_0)$ and δ for $LaFeO_{3-\delta}$ and $La_{1-x}Sr_xFeO_{3-\delta}$ ($x \geq 0.1$), respectively. Figures 5 and 6 give the relationships of the calculated $(s_0 - s°_0)$ to δ.

The values of $(h_0 - h°_0)$ are constant independent of δ for $\delta < x/2$ of $La_{1-x}Sr_xFeO_{3-\delta}$ ($x \geq 0.1$) and for $\delta > 0.003$ of $LaFeO_{3-\delta}$. For $\delta < x/2$ and $\delta > x/2$, $(s_0 - s°_0)$ increases gradually with increasing δ. The characteristic features of the plots are the remarkable decreases observed both in $(h_0 - h°_0)$ and in $(s_0 - s°_0)$ around $\delta = x/2$ for the compounds of $x \geq 0.1$ and around $\delta = 0.0015$ for $LaFeO_{3-\delta}$.

3. Statistical Thermodynamic Calculations

The Gibbs free energy, G, of $La_{1-x}Sr_xFeO_{3-\delta}$ can be expressed by using the standard state chemical potential of each quasi-chemical species (ions and defects) in the solid solution and the configurational entropy of the quasi-chemical species (*2*).

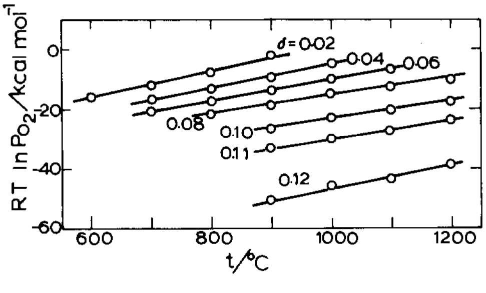

FIG. 2. Relations between the equilibrium P_{O_2} and T of $La_{0.75}Sr_{0.25}FeO_{3-\delta}$ of different δ in the plots of $RT \ln P_{O_2}$ versus t.

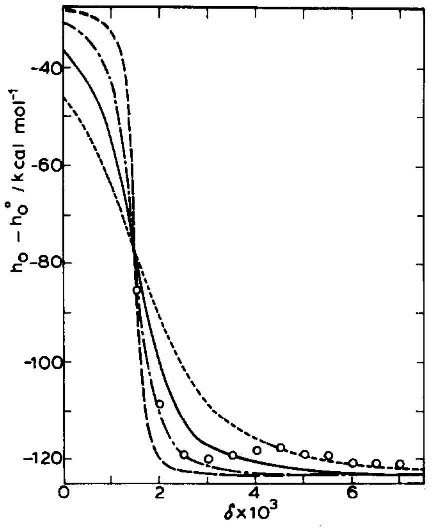

FIG. 3. Relation of $(h_0 - h°_0)$ to δ for $LaFeO_{3-\delta}$. Marked points are calculated by the Gibbs–Helmholtz equation. Curves are calculated by the statistical thermodynamic model described in Section 5: (——) 900°C; (–·–·–) 1000°C; (——) 1100°C; (---) 1200°C.

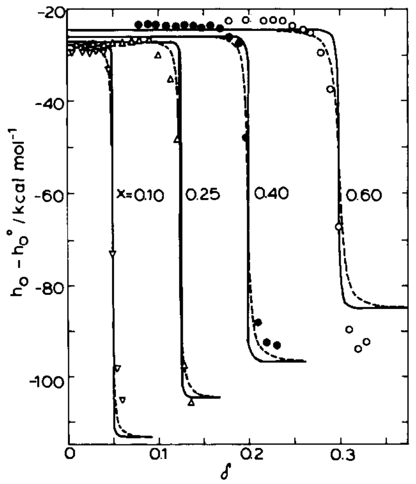

FIG. 4. Relation of $(h_0 - h°_0)$ to δ for $La_{1-x}Sr_xFeO_{3-\delta}$ ($x = 0.1$, 0.25, 0.4, and 0.6). Marked points are calculated by the Gibbs–Helmholtz equation. Curves are calculated by the statistical thermodynamic model described in Section 5: (——) 900°C; (---) 1200°C.

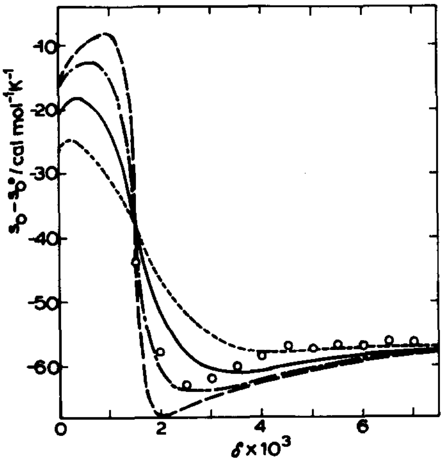

FIG. 5. Relation of $(s_0 - s^\circ_0)$ to δ for $\mathrm{LaFeO_{3-\delta}}$. Marked points are calculated by the Gibbs–Helmholtz equation. Curves are calculated by the statistical thermodynamic model described in Section 5: (—–) 900°C; (–·–·–) 1000°C; (——) 1100°C; (---) 1200°C.

Based on the results of the preceding papers (*1, 3, 4*), we assume that the major quasi-chemical species in $\mathrm{La_{1-x}Sr_xFeO_{3-\delta}}$ are $\mathrm{La_{La}^{x}}$, $\mathrm{Sr'_{La}}$, $\mathrm{Fe_{Fe}^{x}}$, $\mathrm{Fe'_{Fe}}$, $\mathrm{Fe^{\cdot}_{Fe}}$, $\mathrm{O_O^{x}}$, and $\mathrm{V_O^{\cdot\cdot}}$. Therefore, G can be expressed by the equation

$$\begin{aligned} G = G^\circ &+ (1-x)\mu^\circ(\mathrm{La_{La}^{x}}) + x\mu^\circ(\mathrm{Sr'_{La}}) \\ &+ [\mathrm{Fe^{\cdot}_{Fe}}]\mu^\circ(\mathrm{Fe^{\cdot}_{Fe}}) + [\mathrm{Fe_{Fe}^{x}}]\mu^\circ(\mathrm{Fe_{Fe}^{x}}) \\ &+ [\mathrm{Fe'_{Fe}}]\mu^\circ(\mathrm{Fe'_{Fe}}) + (3-\delta)\mu^\circ(\mathrm{O_O^{x}}) \\ &+ \delta\mu^\circ(\mathrm{V_O^{\cdot\cdot}}) - TS(\mathrm{conf}), \qquad (9) \end{aligned}$$

where μ° of each quasi-chemical species is taken as the chemical potential of each species in the stoichiometric $\mathrm{LaFeO_3}$. That is, the quasi-chemical species of $\mathrm{La_{La}^{x}}$, $\mathrm{Fe_{Fe}^{x}}$, and $\mathrm{O_O^{x}}$ are taken as "the solvents" and the other species are considered "the solutes." In Eq. (9), interaction energies between the quasi-chemical species are not shown explicitly but are included in the μ°'s of respective quasi-chemical species.

The configurational entropy, $S(\mathrm{conf})$, is given by the equation

$$\begin{aligned} S(\mathrm{conf}) = k\Bigg[&\ln\frac{N!}{(N(1-x))!(Nx)!} \\ &+ \ln\frac{N!}{(N[\mathrm{Fe'_{Fe}}])!(N[\mathrm{Fe^{\cdot}_{Fe}}])!(N[\mathrm{Fe_{Fe}^{x}}])!} \\ &+ \ln\frac{(3N)!}{(N(3-\delta))!(N\delta)!}\Bigg], \qquad (10) \end{aligned}$$

where N is the Avogadro constant. All three terms in the brackets show the configurational entropy for A, B, and O sites, respectively.

The oxygen chemical potential, μ_O, in $\mathrm{La_{1-x}Sr_xFeO_{3-\delta}}$ is calculated by differentiating G by the number of moles of oxygen atoms in the oxide, keeping the number of moles of other species (La, Sr, and Fe) constant. Since the number of moles of oxygen is $[\mathrm{O_O^{x}}] = (3-\delta)$, μ_O can be calculated from Eqs. (9) and (10) as

$$\begin{aligned} \mu_\mathrm{O} &= \frac{\partial G}{\partial[\mathrm{O_O^{x}}]} = \frac{\partial G}{\partial(3-\delta)} = -\frac{\partial G}{\partial\delta} \\ &= -\frac{\partial[\mathrm{Fe^{\cdot}_{Fe}}]}{\partial\delta}\mu^\circ(\mathrm{Fe^{\cdot}_{Fe}}) - \frac{\partial[\mathrm{Fe'_{Fe}}]}{\partial\delta}\mu^\circ(\mathrm{Fe'_{Fe}}) \\ &\quad - \frac{\partial[\mathrm{Fe_{Fe}^{x}}]}{\partial\delta}\mu^\circ(\mathrm{Fe_{Fe}^{x}}) \\ &\quad + \mu^\circ(\mathrm{O_O^{x}}) - \mu^\circ(\mathrm{V_O^{\cdot\cdot}}) - Ts_0(\mathrm{conf}), \qquad (11) \end{aligned}$$

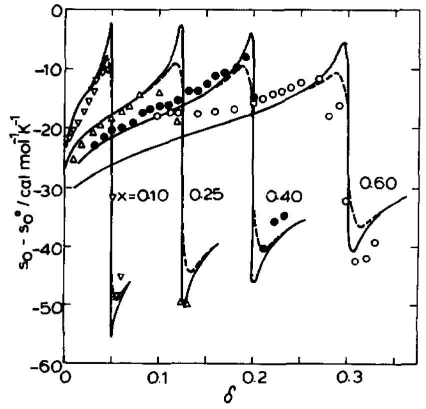

FIG. 6. Relation of $(s_0 - s^\circ_0)$ to δ for $\mathrm{La_{1-x}Sr_xFeO_{3-\delta}}$ (x = 0.1, 0.25, 0.4, and 0.6). Marked points are calculated by the Gibbs–Helmholtz equation. Curves are calculated by the statistical thermodynamic model described in Section 5: (——) 900°C; (---) 1200°C.

where we used the ideal solution approximation for the oxygen dissolution in $\mathrm{La_{1-x}Sr_xFeO_{3-\delta}}$. That is, we assumed that μ° of each quasi-chemical species does not change with δ. In Eq. (11), $s_0(\mathrm{conf})$ is the partial molar entropy of oxygen due to the configurational entropy, which is expressed by the equation

$$s_0(\mathrm{conf}) = -\frac{\partial S(\mathrm{conf})}{\partial \delta}. \qquad (12)$$

From Eqs. (10) and (12), Stirling's formula, and the relationship of $R = Nk$, we have

$$\begin{aligned} s_0(\mathrm{conf}) = R \Bigg[& \frac{\partial[\mathrm{Fe_{Fe}^{\cdot}}]}{\partial \delta} (\ln\,[\mathrm{Fe_{Fe}^{\cdot}}] + 1) \\ & + \frac{\partial[\mathrm{Fe_{Fe}^{x}}]}{\partial \delta} (\ln\,[\mathrm{Fe_{Fe}^{x}}] + 1) \\ & + \frac{\partial[\mathrm{Fe_{Fe}^{\prime}}]}{\partial \delta} (\ln\,[\mathrm{Fe_{Fe}^{\prime}}] \\ & + 1)\Bigg] + R \ln \frac{\delta}{3-\delta}. \qquad (12') \end{aligned}$$

The electroneutrality condition is given by

$$x + [\mathrm{Fe_{Fe}^{\prime}}] = 2\delta + [\mathrm{Fe_{Fe}^{\cdot}}], \qquad (13)$$

where x for $\mathrm{La_{1-x}Sr_xFeO_{3-\delta}}$ ($x \geq 0.1$) represents $[\mathrm{Sr_{La}^{\prime}}]$, while x for $\mathrm{LaFeO_{3-\delta}}$ represents $3[\mathrm{V_{La}^{\prime\prime\prime}}]$ because, in $\mathrm{LaFeO_{3-\delta}}$, the trivalent lanthanum vacancy $\mathrm{V_{La}^{\prime\prime\prime}}$ due to the nonstoichiometric La/Fe ratio is considered as a majority defect instead of $\mathrm{Sr_{La}^{\prime}}$ (*1*).

The number of moles in 1 mole $\mathrm{La_{1-x}Sr_xFeO_{3-\delta}}$ is unity. Therefore, we have

$$[\mathrm{Fe_{Fe}^{\cdot}}] + [\mathrm{Fe_{Fe}^{x}}] + [\mathrm{Fe_{Fe}^{\prime}}] = 1. \qquad (14)$$

The differentiations by δ of Eqs. (3), (13), and (14), respectively, are

$$\begin{aligned} \frac{2}{[\mathrm{Fe_{Fe}^{x}}]} \frac{\partial[\mathrm{Fe_{Fe}^{x}}]}{\partial \delta} = & \frac{1}{[\mathrm{Fe_{Fe}^{\cdot}}]} \frac{\partial[\mathrm{Fe_{Fe}^{\cdot}}]}{\partial \delta} \\ & + \frac{1}{[\mathrm{Fe_{Fe}^{\prime}}]} \frac{\partial[\mathrm{Fe_{Fe}^{\prime}}]}{\partial \delta}, \qquad (15) \end{aligned}$$

$$\frac{\partial[\mathrm{Fe_{Fe}^{\prime}}]}{\partial \delta} = 2 + \frac{\partial[\mathrm{Fe_{Fe}^{\cdot}}]}{\partial \delta}, \qquad (16)$$

and

$$\frac{\partial[\mathrm{Fe_{Fe}^{x}}]}{\partial \delta} + \frac{\partial[\mathrm{Fe_{Fe}^{\prime}}]}{\partial \delta} + \frac{\partial[\mathrm{Fe_{Fe}^{\cdot}}]}{\partial \delta} = 0. \qquad (17)$$

Using Eqs. (16) and (17), the differentiations $\partial[\mathrm{Fe_{Fe}^{x}}]/\partial\delta$ and $\partial[\mathrm{Fe_{Fe}^{\cdot}}]/\partial\delta$ can be expressed in terms of $\partial[\mathrm{Fe_{Fe}^{\prime}}]/\partial\delta$. Therefore, we can eliminate the terms $\partial[\mathrm{Fe_{Fe}^{x}}]/\partial\delta$ and $\partial[\mathrm{Fe_{Fe}^{\cdot}}]/\partial\delta$ from Eqs. (11) and (12'). Thus, we obtain

$$\begin{aligned} \mu_0 = {} & 2\mu^\circ(\mathrm{Fe_{Fe}^{\cdot}}) - 2\mu^\circ(\mathrm{Fe_{Fe}^{x}}) \\ & + \frac{\partial[\mathrm{Fe_{Fe}^{\prime}}]}{\partial \delta} [2\mu^\circ(\mathrm{Fe_{Fe}^{x}}) - \mu^\circ(\mathrm{Fe_{Fe}^{\cdot}}) \\ & - \mu^\circ(\mathrm{Fe_{Fe}^{\prime}})] + \mu^\circ(\mathrm{O_O^{x}}) - \mu^\circ(\mathrm{V_O^{\cdot\cdot}}) \\ & - Ts_0(\mathrm{conf}) \qquad (18) \end{aligned}$$

and

$$\begin{aligned} s_0(\mathrm{conf}) = R \Bigg(& \ln \frac{\delta[\mathrm{Fe_{Fe}^{x}}]^2}{(3-\delta)[\mathrm{Fe_{Fe}^{\cdot}}]^2} \\ & + \frac{\partial[\mathrm{Fe_{Fe}^{\prime}}]}{\partial \delta} \ln K_i \Bigg), \qquad (19) \end{aligned}$$

where Eq. (3) is also used. From Eqs. (3) and (13)–(17), we obtain

$$\begin{aligned} \frac{\partial[\mathrm{Fe_{Fe}^{\prime}}]}{\partial \delta} = {} & 1 \\ & + \frac{2\delta - x}{4K_i[\mathrm{Fe_{Fe}^{x}}] + [\mathrm{Fe_{Fe}^{\prime}}] + [\mathrm{Fe_{Fe}^{\cdot}}]}. \qquad (20) \end{aligned}$$

Equations (18)–(20) give the relationship between μ_0 and the chemical potential and concentration of the defects in $\mathrm{La_{1-x}Sr_xFeO_{3-\delta}}$.

4. Relationship between Thermodynamic Quantities and Defect Equilibrium

The standard Gibbs free energy change for the reaction of Eq. (2), $\Delta G^\circ_{\mathrm{ox}}$, is expressed by the reaction

$$\begin{aligned} -RT \ln K_{\mathrm{ox}} = \Delta G^\circ_{\mathrm{ox}} = {} & \mu^\circ(\mathrm{O_O^{x}}) - \mu^\circ(\mathrm{V_O^{\cdot\cdot}}) \\ & + 2(\mu^\circ(\mathrm{Fe_{Fe}^{\cdot}}) - \mu^\circ(\mathrm{Fe_{Fe}^{x}})) - \tfrac{1}{2}\mu^\circ(\mathrm{O_2(g)}), \\ & \qquad (21) \end{aligned}$$

where $\mu^\circ(\mathrm{O_2(g)})$ is the chemical potential of 1 atm oxygen gas, which is related to μ°_0 by

$$\mu^{\circ}(\mathrm{O_2(g)}) = 2\mu^{\circ}_{\mathrm{O}}. \quad (22)$$

The standard Gibbs free energy change for the reaction of Eq. (4), ΔG°_i, is given by

$$-RT \ln K_i = \Delta G^{\circ}_i = \mu^{\circ}(\mathrm{Fe}^{\cdot}_{\mathrm{Fe}}) + \mu^{\circ}(\mathrm{Fe}'_{\mathrm{Fe}}) - 2\mu^{\circ}(\mathrm{Fe}^{x}_{\mathrm{Fe}}). \quad (23)$$

Using Eqs. (21)–(23), Eq. (18) can be rewritten as

$$\mu_{\mathrm{O}} - \mu^{\circ}_{\mathrm{O}} = \Delta G^{\circ}_{\mathrm{ox}} - \frac{\partial[\mathrm{Fe}'_{\mathrm{Fe}}]}{\partial\delta}\Delta G^{\circ}_i - Ts_{\mathrm{O}}(\mathrm{conf}). \quad (24)$$

When we express the enthalpy and entropy terms of Eq. (24) separately, we obtain

$$h_{\mathrm{O}} - h^{\circ}_{\mathrm{O}} = \Delta H^{\circ}_{\mathrm{ox}} - \frac{\partial[\mathrm{Fe}'_{\mathrm{Fe}}]}{\partial\delta}\Delta H^{\circ}_i \quad (25)$$

and

$$s_{\mathrm{O}} - s^{\circ}_{\mathrm{O}} = \Delta S^{\circ}_{\mathrm{ox}} - \frac{\partial[\mathrm{Fe}'_{\mathrm{Fe}}]}{\partial\delta}\Delta S^{\circ}_i + s_{\mathrm{O}}(\mathrm{conf}). \quad (26)$$

Equations (24)–(26) give the relationships of the partial molar quantities to the parameters determined for the defect equilibrium in $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{FeO}_{3-\delta}$.

5. Partial Molar Quantities Calculated from the Statistical Thermodynamic Model

In the preceding paper (*1*), the parameters K_{ox}, $\Delta H^{\circ}_{\mathrm{ox}}$, $\Delta S^{\circ}_{\mathrm{ox}}$, K_i, ΔH°_i, and ΔS°_i were determined as functions of x. When δ and x are given, we can calculate the concentrations of $[\mathrm{Fe}^{x}_{\mathrm{Fe}}]$, $[\mathrm{Fe}'_{\mathrm{Fe}}]$, and $[\mathrm{Fe}^{\cdot}_{\mathrm{Fe}}]$ by using the K_i values and Eqs. (3), (13), and (14).

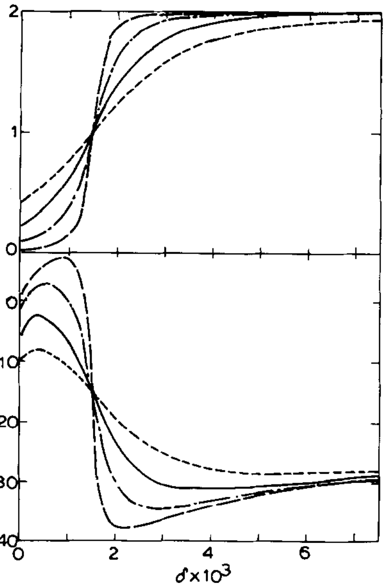

FIG. 7. Relation of $\partial[\mathrm{Fe}'_{\mathrm{Fe}}]/\partial\delta$ and $s_{\mathrm{O}}(\mathrm{conf})$ to δ for $\mathrm{LaFeO}_{3-\delta}$ calculated by the statistical thermodynamic model described in Section 5: (– – –) 900°C; (–·–·–) 1000°C; (——) 1100°C; (- - -) 1200°C.

Using the given parameters and the defect concentrations, numerical calculations are made, as functions of δ and x, for $\partial[\mathrm{Fe}'_{\mathrm{Fe}}]/\partial\delta$ from Eq. (20) and for $s_{\mathrm{O}}(\mathrm{conf})$ from Eqs. (19) and (20). Figure 7 shows the calculated $\partial[\mathrm{Fe}'_{\mathrm{Fe}}]/\partial\delta$ and $s_{\mathrm{O}}(\mathrm{conf})$ for $\mathrm{LaFeO}_{3-\delta}$ ($[\mathrm{V}'''_{\mathrm{La}}] = 0.001$ and $x = 0.003$ (*1*)), and those for $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{FeO}_{3-\delta}$ ($x \geq 0.1$) are shown in Fig. 8. It is seen that $\partial[\mathrm{Fe}'_{\mathrm{Fe}}]/\partial\delta$ changes abruptly around $x/2$. For $\delta < x/2$, $\partial[\mathrm{Fe}'_{\mathrm{Fe}}]/\partial\delta$ is close to zero, while for $\delta > x/2$, it is close to 2. The value of $s_{\mathrm{O}}(\mathrm{conf})$ also changes abruptly around $x/2$ due to the term $R(\partial[\mathrm{Fe}'_{\mathrm{Fe}}]/\partial\delta) \ln K_i$ in Eq. (19). For $\delta < x/2$, $s_{\mathrm{O}}(\mathrm{conf})$ is essentially determined by $[\mathrm{Fe}^{x}_{\mathrm{Fe}}]$, $[\mathrm{Fe}^{\cdot}_{\mathrm{Fe}}]$, and $\mathrm{V}^{\cdot\cdot}_{\mathrm{O}}]$ ($= \delta$), while it is determined by $[\mathrm{Fe}^{x}_{\mathrm{Fe}}]$, $[\mathrm{Fe}'_{\mathrm{Fe}}]$, and $[\mathrm{V}^{\cdot\cdot}_{\mathrm{O}}]$ for $\delta > x/2$. The changes of $\partial[\mathrm{Fe}'_{\mathrm{Fe}}]/\partial\delta$ and $s_{\mathrm{O}}(\mathrm{conf})$ around $\delta = x/2$ are more drastic with decreasing temperature. This is because the K_i value becomes smaller with decreasing temperature.

The curves in Figs. 3 and 4 are calculated using Eq. (25) and the given parameters. Those in Figs. 5 and 6 are calculated using Eq. (26). The curves and the points of experimentally based results agreed with each other. Around $\delta = x/2$, the curves change with temperature, showing the changes in

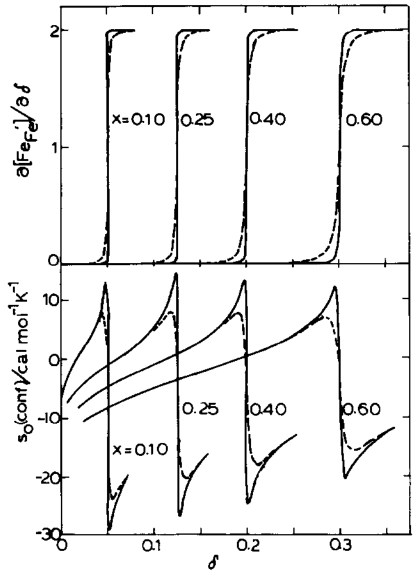

FIG. 8. Relation of $\partial[Fe_{Fe}']/\partial\delta$ and s_0(conf) to δ for $La_{1-x}Sr_xFeO_{3-\delta}$ ($x = 0.1, 0.25, 0.4$, and 0.6) calculated by the statistical thermodynamic model described in Section 5: (——) 900°C; (---) 1200°C.

($h_0 - h^\circ_0$) and ($s_0 - s^\circ_0$) around $\delta = x/2$ with temperature. Experimentally, the changes may appear in Figs. 1 and 2 as the deviations of the experimental points for $\delta \sim x/2$ from the straight lines. However, the deviations expected from the changes of calculated $h_0 - h^\circ_0$ and $s_0 - s^\circ_0$ with temperature were too small to be detected on the plots in Figs. 1 and 2.

The agreement between the experimentally based results and the theoretical curves in Figs. 3–6 proves that by using the statistical thermodynamic calculations in Sections 3 and 4, we properly interpreted the relationships between the thermodynamic quantities and the nonstoichiometry and defect structure of $La_{1-x}Sr_xFeO_{3-\delta}$: The point defects $V_O^{\cdot\cdot}$, Fe_{Fe}', and $Fe_{Fe}^{\cdot}$ are distributed randomly on each lattice site, and are described essentially by the ideal solution approximation. The remarkable decrease in h_0 around $\delta = x/2$ is related to the internal defect equilibrium among $Fe_{Fe}^{\times}$, Fe_{Fe}', and $Fe_{Fe}^{\cdot}$. The decrease in h_0 is approximately $2\Delta H^\circ_i$, twice the pseudo-bandgap (*1, 3, 4*). The sharp decrease in s_0 around $\delta = x/2$ is essentially due to the decrease in s_0(conf).

Among the given parameters of ΔH°_{ox}, ΔS°_{ox}, ΔH°_i, and ΔS°_i, the x dependences of ΔH°_{ox}, ΔS°_{ox}, and ΔS°_i are very small and are almost less than the experimental error (*1*). That is, ΔH°_{ox} (= −26 kcal/mol), ΔS°_{ox} (= −17 cal/K mol), and ΔS°_i (= 3 cal/K mol) are essentially constant independent of x. Only ΔH°_i depends remarkably on x (45 kcal/mol for $x = 0$ and 30 kcal/mol for $x = 0.6$). In the region of $\delta < x/2$, $[Fe_{Fe}^{\cdot}] \gg [Fe_{Fe}']$ holds and, therefore, the nonstoichiometry in $La_{1-x}Sr_xFeO_{3-\delta}$ is determined by ΔH°_{ox} and ΔS°_{ox}. Because ΔH°_{ox} and ΔS°_{ox} are almost independent of x, the ideal solution approximation holds not only for the oxygen nonstoichiometry but also for the Sr distribution in $La_{1-x}Sr_xFeO_{3-\delta}$ for the region of $\delta < x/2$, in which the valence states of Fe ions are 3+ and 4+. Because ΔH strongly depends on x, the ideal solution approximation cannot be applied to the Sr concentration change in the region of $\delta > x/2$, in which the predominant Fe valence states are 3+ and 2+.

The nonstoichiometry data for the perovskite-type $La_{1-x}Sr_xCrO_{3-\delta}$ (*5*) and $La_{1-x}Sr_xCoO_{3-\delta}$ (*6*) suggest that the ΔH_{ox} of these solid solutions strongly depends on x and δ. The x dependences of ΔS_{ox} are also observed. The difference in the x and δ dependences of the thermodynamic parameters between these solid solutions, and $La_{1-x}Sr_xFeO_{3-\delta}$ may be attributed to the difference in the electronic state of *B*-site ions.

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