Atomic-Scale Insights into Long-Range Charge Transfer in Lanthanum Strontium Ferrite

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1. Introduction

- In mixed ionic electronic materials (MIEC) the bulk oxygen vacancy concentration is altered by changing cation oxidation states.[1]
- For MIEC material like lanthanum strontium ferrite (LSF) this can be summarized as:[2]

$$2Fe_{Fe}^{\bullet} + O_O^x \rightarrow \tfrac{1}{2}O_{2(g)} + V_O^{\bullet\bullet} + 2Fe_{Fe}^x \qquad [1]$$
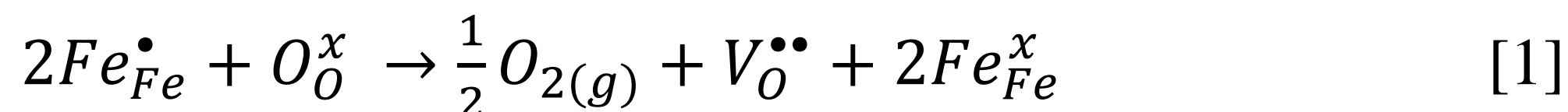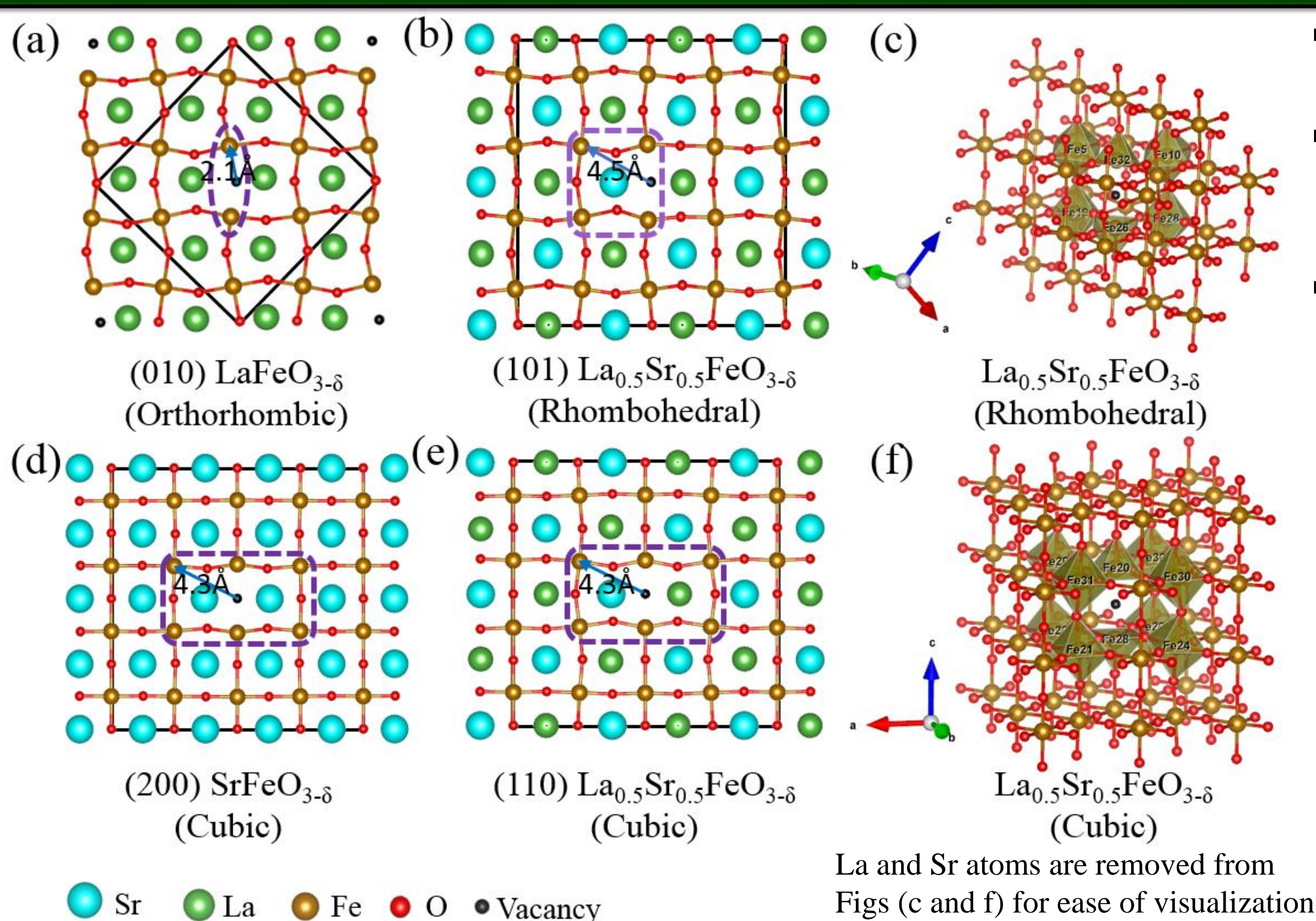
however, the localized or distributed nature of the electrons generated from the oxygen vacancy ($V_O^{\bullet\bullet}$) formation reaction (Eqn. 1) remains unknown.
- Further, in $La_{1-x}Sr_xFeO_{3-\delta}$ the La/Sr ratio producing the highest $V_O^{\bullet\bullet}$ concentration remains unknown.
- Therefore, the objective of this work is to determine 1) how the electron distribution impacts the location and energetics of $V_O^{\bullet\bullet}$ formation, and 2) the temperature and La/Sr ratios that maximize the $V_O^{\bullet\bullet}$ concentration.

2. Computational Approach

- Computational studies were performed using Density Functional Theory (DFT) and Thermodynamics.
- U = 3 was selected to give $LaFeO_3$ and $SrFeO_3$ magnetic moments and lattice parameters comparable to the experimentally measured values.
- DFT+U was used to calculate the oxygen vacancy formation energy in supercells with varying size and a single oxygen vacancy, mimicking a broad range of oxygen nonstoichiometry.
- The long-range charge transfer polaron volume was predicted in a dilute (non-interacting) oxygen vacancy scenario.
- A thermodynamic model was developed to predict oxygen vacancy site fraction (X) as a function of temperature for both interacting and non-interacting vacancies.
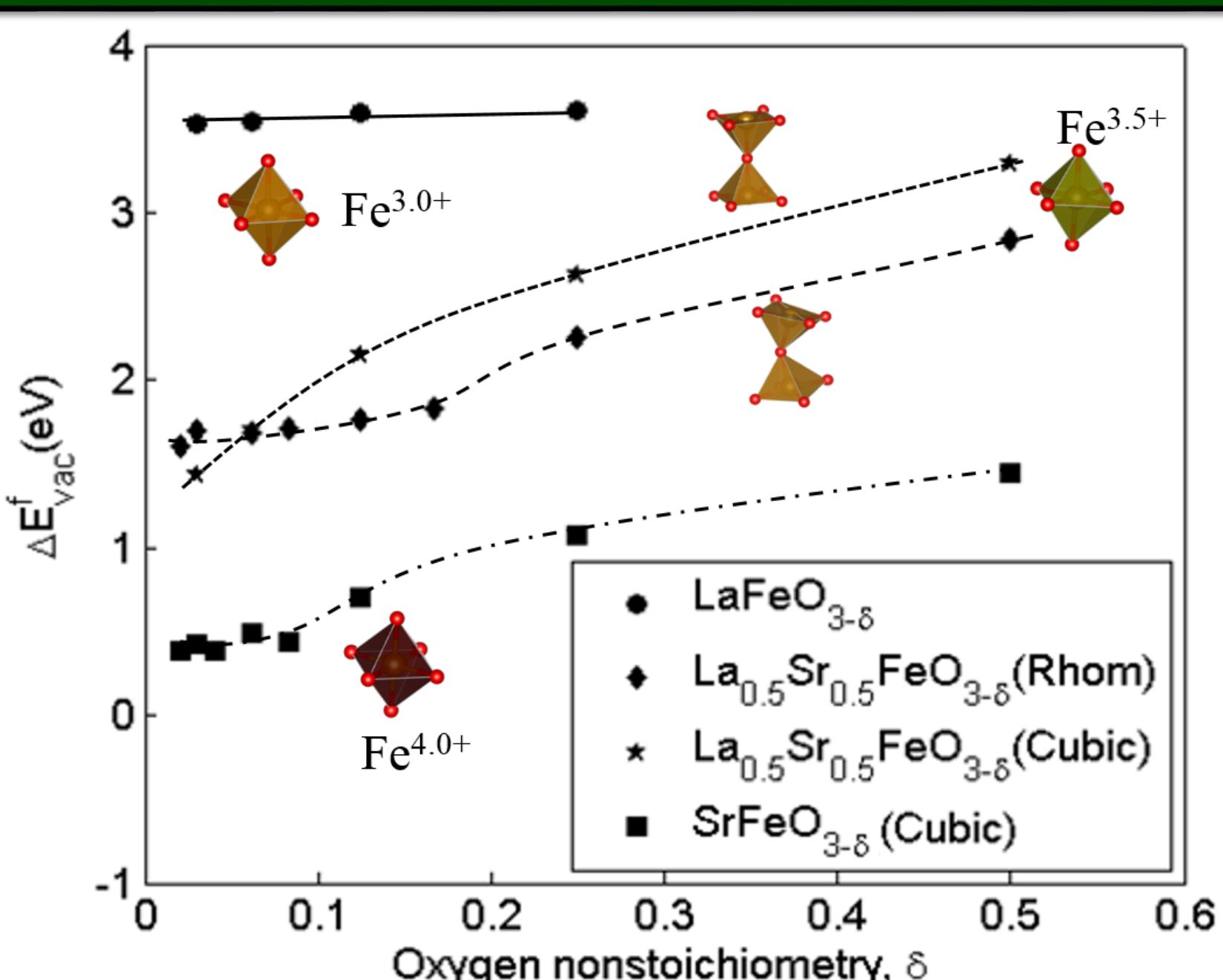
3. Long Range Charge Transfer in $La_{1-x}Sr_xFeO_{3-\delta}$

(a) (010) LaFeO$_{3-\delta}$ (Orthorhombic)
(b) (101) La$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ (Rhombohedral)
(c) La$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ (Rhombohedral)
(d) (200) SrFeO$_{3-\delta}$ (Cubic)
(e) (110) La$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ (Cubic)
(f) La$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ (Cubic)

● Sr ● La ● Fe ● O • Vacancy

La and Sr atoms are removed from Figs (c and f) for ease of visualization

- In LaFeO$_{3-\delta}$, oxygen vacancies alter the oxidation state of the first nearest neighboring Fe atoms. The shape of polaron is ellipsoidal, as shown in Fig (a).
- In rhombohedral LSF55, oxygen vacancies alter the oxidation state of four second nearest neighboring Fe atoms. The polaron forms a quarter of a "pan-cake", as shown in the Figs (b-c).
- In SrFeO$_{3-\delta}$ and cubic La$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ (LSF55), oxygen vacancies alter the oxidation state of all the second nearest neighboring Fe atoms. The shape of polaron is "pan-cake" like, as shown in Figs (d-f).

(g) (h) (i)

- Fe d-orbital splitting explains why the extra electrons generated by Eqn. [1] cause the Fe polyhedra to adopt the shapes shown in (g), (h), and (i) for LaFeO$_{3-\delta}$ (5 unpaired e), SrFeO$_{3-\delta}$ (4 unpaired e), and LSF55 (4.5 unpaired e).

4. $\Delta E_{vac}^f \uparrow$ with $\downarrow x+$ on Fe^{x+}

- In LaFeO$_{3-\delta}$, due to charge localization on Fe after $V_O^{\bullet\bullet}$ formation, vacancies do not interact and $V_O^{\bullet\bullet}$ formation energy (ΔE_{vac}^f) remains constant.
- In SrFeO$_{3-\delta}$ and LSF55, due to long-range charge transfer, vacancies interact at higher $V_O^{\bullet\bullet}$ concentrations. As a result the $V_O^{\bullet\bullet}$ formation energy increases.
- In rhombohedral LSF55, a relatively lower $V_O^{\bullet\bullet}$ formation energy occurs due to tilt among Fe-O square-pyramids.

5. Thermodynamic Extension to High Temp from DFT Calc Energy

- To account for SOFC operating conditions, the following thermodynamic extension was used:[3,4]

$$\Delta G_{f,vac} = E_{vac}^f + \frac{1}{2}\Delta\mu_{O_2}(T,p)$$

$$\Delta G_{f,vac} = E_{defective} - E_{perfect} + \frac{1}{2}\mu_{O_2}$$

$$\mu_{O_2}(T,p) = E_{O_2}^{DFT} + \Delta\mu_{O_2}^0(T_r) + \int_{T_r}^{T} C_p\,dT - T\int_{T_r}^{T} {C_p}/{T}\,dT - (T-T_r)S_r + kT\ln p_{O_2}$$

$E_{perfect}$ = energy of a perfect crystal structure

$E_{defective}$ = energy of a crystal structure with one oxygen vacancy

$\mu_{O_2}(T,p)$ = chemical potential of oxygen at SOFC operating conditions.[5,6]

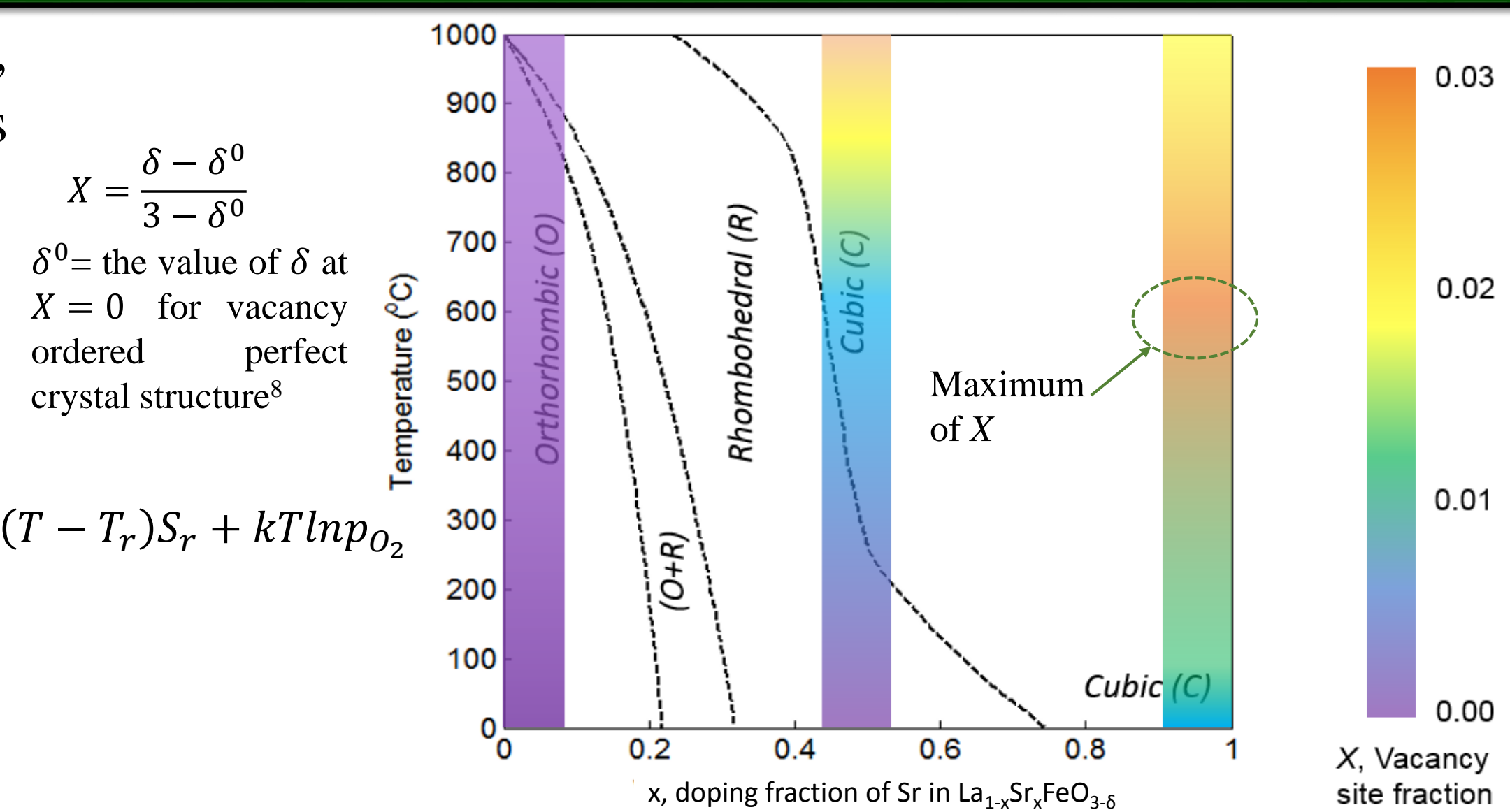$E_{O_2}^{DFT}$ = DFT calculated energy of a single oxygen molecule

$\Delta\mu_{O_2}^0(T_r)$ = connection energy of oxygen from 0 K, isolated molecule to standard state

T_r = standard state temperature (298.15K)

S_r = entropy of oxygen molecule at standard state.

- The dilute and non-dilute $V_O^{\bullet\bullet}$ site fractions (X) were calculated as a function of temperature, pressure and vacancy formation energy via:[7]

$$\frac{X}{1-X} = \exp\left(-\frac{\Delta G_{f,vac}(T,p,X)}{RT}\right)$$

$$X = \frac{\delta - \delta^0}{3 - \delta^0}$$

δ^0 = the value of δ at $X = 0$ for vacancy ordered perfect crystal structure[8]

6. Conclusions

- Long-range charge transfer in LSF explains $V_O^{\bullet\bullet}$ interaction at high $V_O^{\bullet\bullet}$ concetrations.
- d-orbital splitting due to varying Fe-O coordination explains electron transfer to the second nearest neighbor Fe.
- Among the different LSF phases, SrFeO$_{3-\delta}$ has highest oxygen vacancy concentration. This occurs around 600ºC. Above 600ºC, a vacancy ordered phase transition reduces the oxygen vacancy site fraction.
- This work is summarized in Das et al.[8]

References: [1] Yang et al., Solid State Ionics, 249, 123 (2013) [2] Mizusaki et al., J. Solid State Chem., 58, 257-266 (1985) [3] Lee et. al., Phys. Rev. B, 80, 224101 (2009) [4] Sholl et al., Density Functional Theory: A Practical Introduction, p. 169, Wiley, New Jersy (2009) [5] Zhang et. al., Phys. Rev. B, 70, 024103 (2004) [6] Guo et al., Appl. Phys. Lett. 92, 241921 (2008) [7] C. Kittel, Introduction to Solid State Physics, p. 541, Wiley, New York (1996) [8] Das et al., Chem. Mater, Submitted, (2016)