

# Estimating off-stoichiometry using density functional theory based calculations and the sub-lattice formalism

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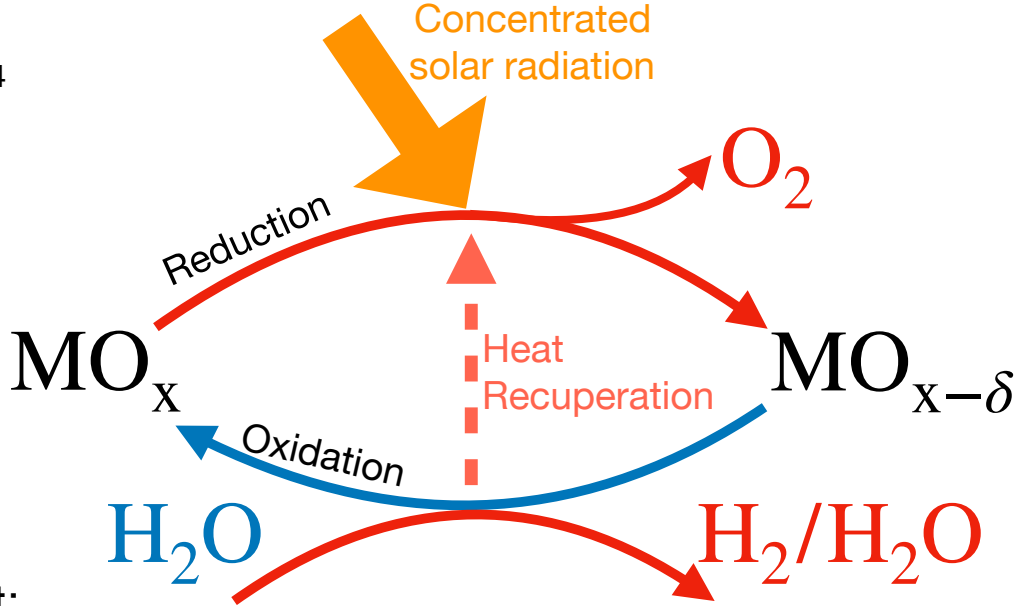
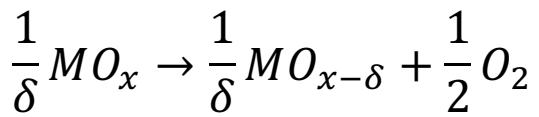
PHYS: New frontiers in the confluence of experimental thermodynamics, structural investigation & theory/computation, American Chemical Society Spring Meeting

Apr 3, 2019

# Solar thermochemical (STC) production of H<sub>2</sub> and/or CO

Candidates so far:

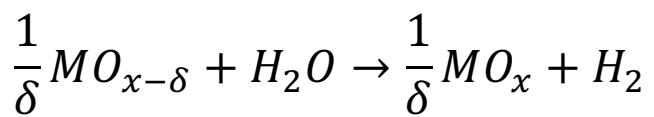
- CeO<sub>2</sub>
- Fe(Fe,X)<sub>2</sub>O<sub>4</sub>
- (A,A')BO<sub>3</sub>



Thermal reduction (TR)  
High T (1673 K)  
~vacuum ( $p_{O_2} = 10$  Pa)

Water splitting (WS)  
Low T (873 K)  
High H<sub>2</sub> yield ( $\frac{p_{H_2O}}{p_{H_2}} = 9$ )

State-of-the-art:  
Pure and doped  
fluorite-CeO<sub>2</sub>



Needs “good” materials!

- Durability (withstand high TR and low WS temperatures)
- Capacity (tolerate high degrees of oxygen off-stoichiometry)
- Stability (no undesired phase transformations)

Can we theoretically screen for better candidates?

Siegel *et al.*, *Ind. Eng. Chem. Res.* **2013**, *52*, 3276  
Carillo and Scheffe, *Sol. Energy* **2017**, *156*, 3

# Thermodynamics of STC water-splitting: Reduction energetics



The reduction reaction is favorable if the Gibbs energy of the reaction is negative

$$\Delta G_{reduction} = G^{MO} + \left(\frac{1}{2}\right) G^{O_2} - G^{MO_2} \leq 0$$

Rearrangement of terms

$$\left(\frac{1}{2}\right) G^{O_2} \leq G^{MO_2} - G^{MO}$$

Chemical potential of oxygen in gas stream

$$\mu_{O_2, gas} = \left(\frac{1}{2}\right) G^{O_2} = \frac{1}{2} (H^{O_2} - TS^{O_2} + RT \ln pO_2)$$

$$\text{Or, } \mu_{O_2}^{gas} = \frac{dG^{gas}}{dx_O}$$

$H, S$  are  $T$  dependent

Chemical potential of oxygen in solid

$$\begin{aligned} \mu_{O_2}^{MO_2-MO, solid} &= G^{MO_2} - G^{MO} \equiv \frac{dG^{solid}}{dx_O} \\ &= H^{MO_2} - H^{MO} - T(S^{MO_2} - S^{MO}) \\ &\approx \Delta H_f^{MO_2} - \Delta H_f^{MO} - T(S^{MO_2} - S^{MO}) \end{aligned}$$

Main  $T$  dependence is from  $S$  terms

Reduction is spontaneous, if  $\mu_{O_2, gas} \leq \mu_{O_2}^{MO_2-MO, solid}$

Note:  $\Delta H_f$  terms are at 298 K, 1 atm

# Thermodynamics of STC water-splitting: Reduction energetics



Water-splitting is spontaneous, if  $\mu_O^{MO_2-MO,solid} \leq \mu_O^{H_2O-H_2,gas}$

Oxygen chemical potential is the quantity to estimate

Chemical potentials in gas phases ( $H_2$ ,  $O_2$ ,  $H_2O$ ) can be calculated from experimental data (e.g., from National Institute of Standards and Technology)

How to estimate chemical potentials (i.e., Gibbs energies) in solids?  
Validate for  $CeO_x$ ?

$$\text{Or, } \mu_O^{gas} = \frac{dG^{gas}}{dx_O}$$

$H$ ,  $S$  are  $T$  dependent

$$\begin{aligned} &= H^{MO_2} - H^{MO} - T(S^{MO_2} - S^{MO}) \\ &\approx \Delta H_f^{MO_2} - \Delta H_f^{MO} - T(S^{MO_2} - S^{MO}) \end{aligned}$$

Main  $T$  dependence is from  $S$  terms

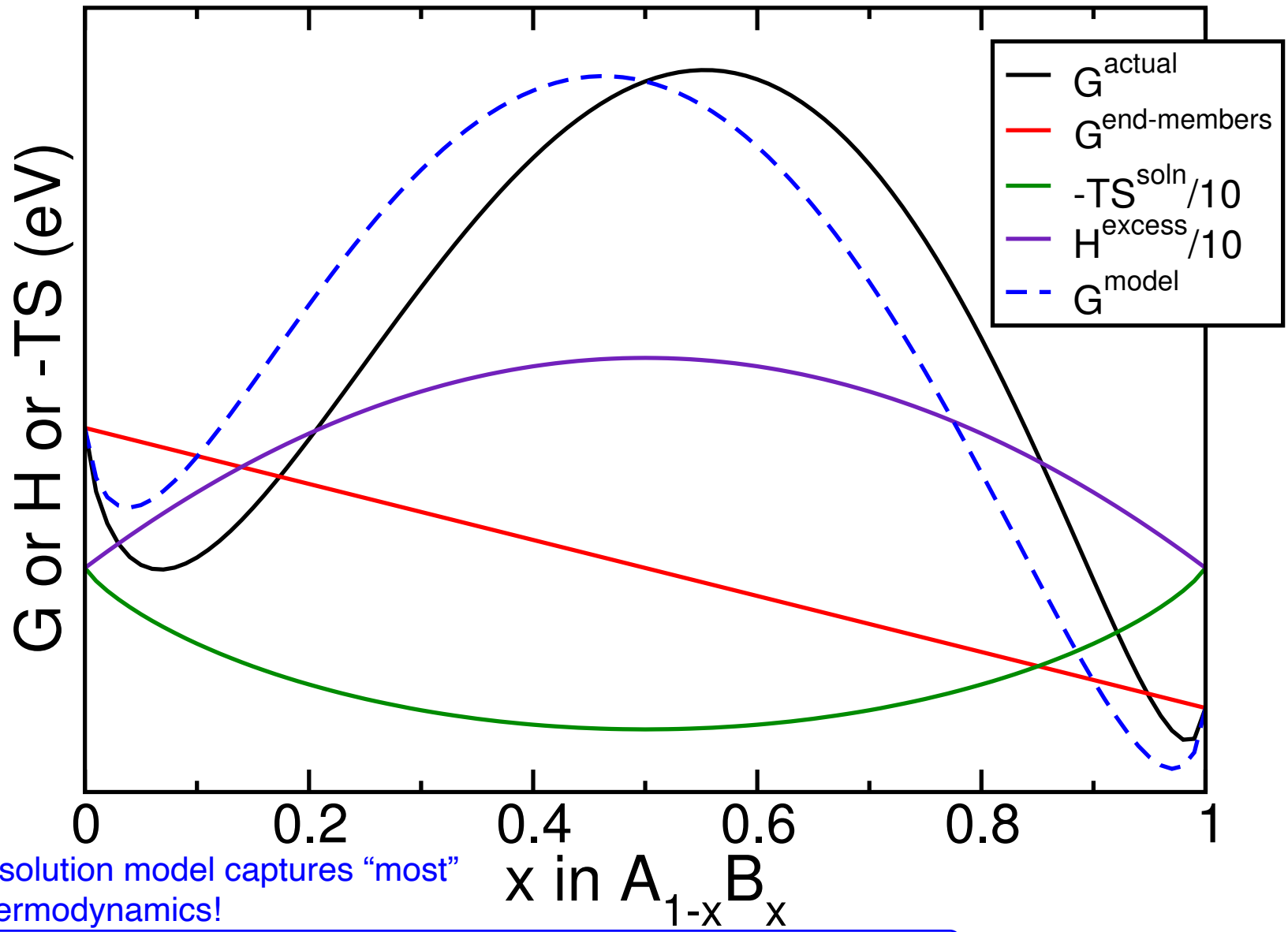
Reduction is spontaneous, if  $\mu_O^{O_2,gas} \leq \mu_O^{MO_2-MO,solid}$

Note:  $\Delta H_f$  terms are at 298 K, 1 atm

# Thermodynamics of solid solution phases

Or how to describe fluorite-CeO<sub>x</sub>?

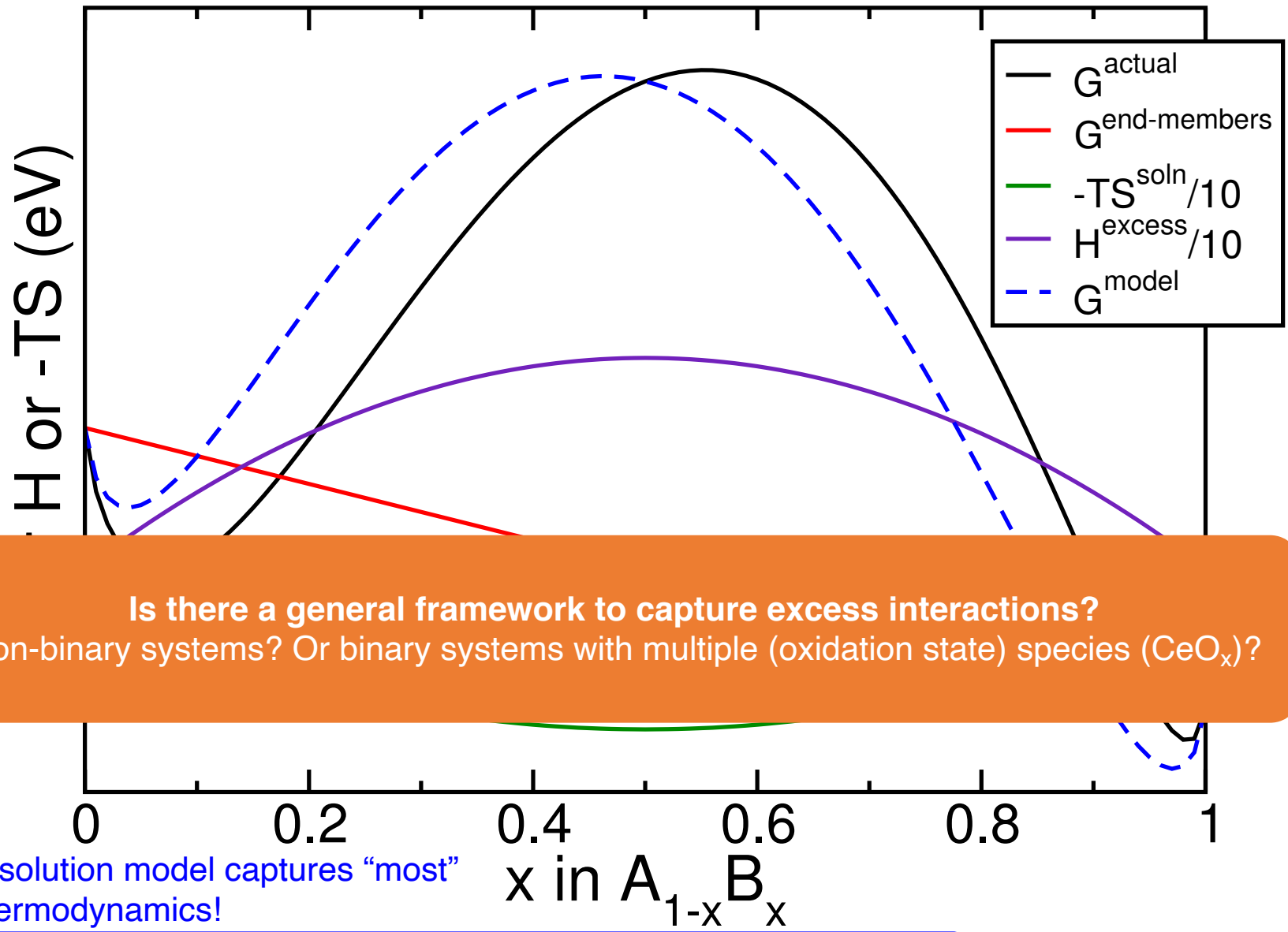
# Modeling $G$ for simple $A_{1-x}B_x$ binary



Regular solution model captures “most” of the thermodynamics!

$$G^{actual} = (1-x)G_A + xG_B + RT(x \ln x + 1-x \ln 1-x) + L_0x(1-x) + L_1x(1-x)(1-2x)$$

# Modeling $G$ for simple $A_{1-x}B_x$ binary



**Is there a general framework to capture excess interactions?**  
 Non-binary systems? Or binary systems with multiple (oxidation state) species ( $CeO_x$ )?

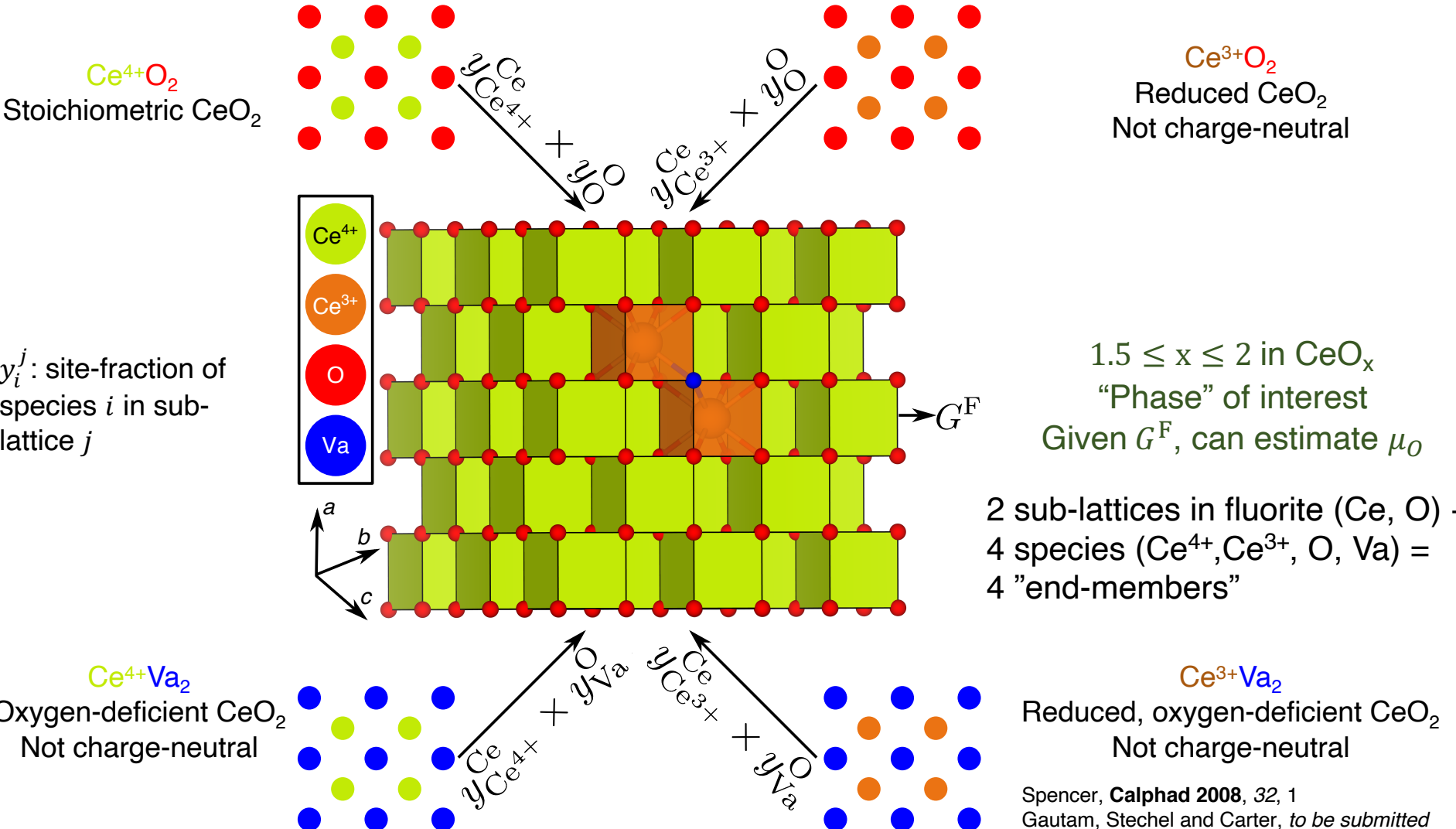
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$$G^{actual} = (1-x)G_A + xG_B + RT(x \ln x + 1-x \ln 1-x) + L_0x(1-x) + L_1x(1-x)(1-2x)$$

# “Sub-lattice” formalism:

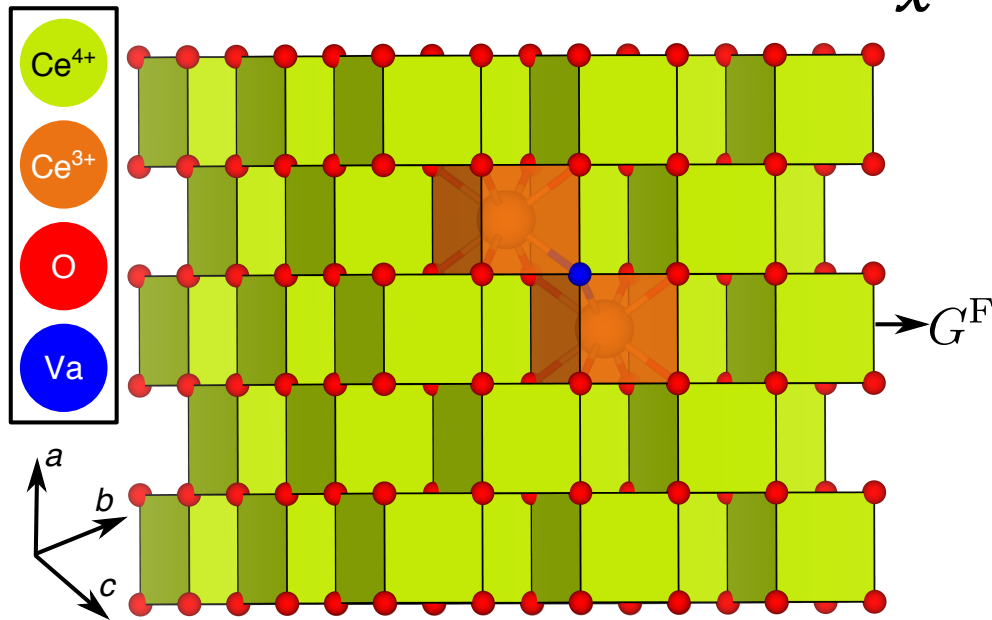
Or how to describe off-stoichiometric compounds?

Example of fluorite-CeO<sub>x</sub>; describe G(fluorite phase) = f(x,T)?





# Gibbs energy function ( $G_{CeO_x}^F$ )



$$G_{CeO_x}^F = y_{Ce^{4+}}^{Ce} y_O^O G_{Ce^{4+};O} + y_{Ce^{3+}}^{Ce} y_O^O G_{Ce^{3+};O} + y_{Ce^{4+}}^{Ce} y_{Va}^O G_{Ce^{4+};Va} + y_{Ce^{3+}}^{Ce} y_{Va}^O G_{Ce^{3+};Va} - TS_{config} + G_{excess}$$

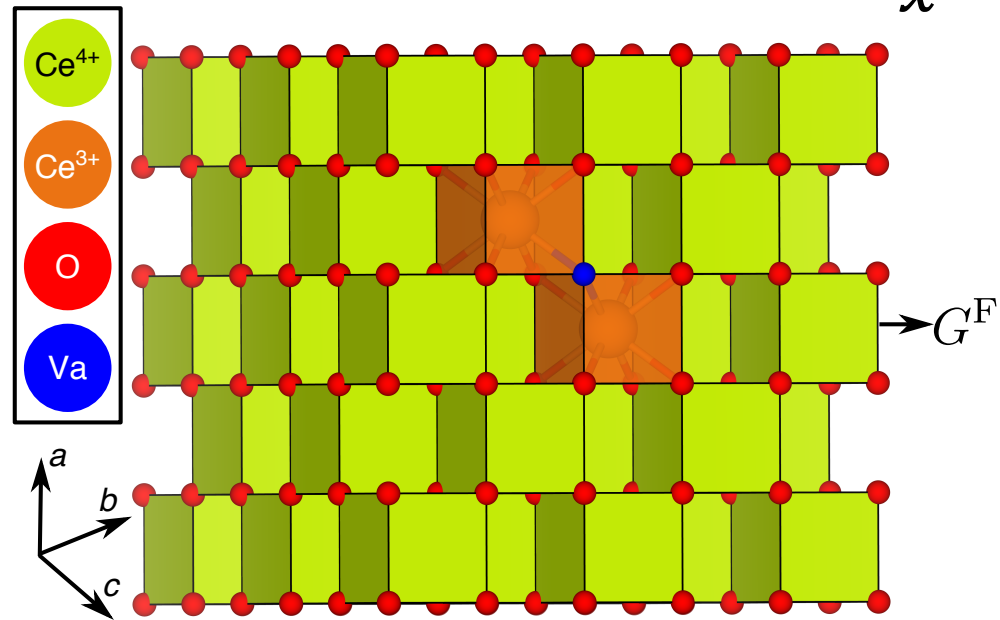


End-member Gibbs energies

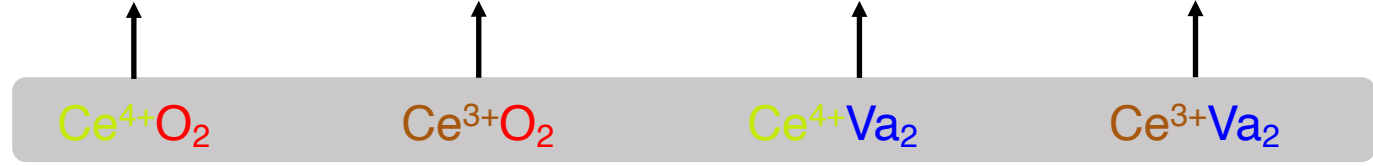
$$S_{config} = -R \left[ n^{Ce} \left( y_{Ce^{4+}}^{Ce} \ln y_{Ce^{4+}}^{Ce} + y_{Ce^{3+}}^{Ce} \ln y_{Ce^{3+}}^{Ce} \right) + n^O \left( y_O^O \ln y_O^O + y_{Va}^O \ln y_{Va}^O \right) \right]$$

$G_{excess}$  : everything not captured by end-member Gibbs energies and configurational entropy

# Gibbs energy function ( $G_{CeO_x}^F$ )



$$G_{CeO_x}^F = y_{Ce^{4+}}^{Ce} y_O^O G_{Ce^{4+}:O} + y_{Ce^{3+}}^{Ce} y_O^O G_{Ce^{3+}:O} + y_{Ce^{4+}}^{Ce} y_{Va}^O G_{Ce^{4+}:Va} + y_{Ce^{3+}}^{Ce} y_{Va}^O G_{Ce^{3+}:Va} - TS_{config} + G_{excess}$$



End-member Gibbs energies

How do we estimate end-member Gibbs energies? Excess terms?

# Reference states and reciprocal relations

$$G_{CeO_x}^F = y_{Ce^{4+}}^{Ce} y_O^O G_{Ce^{4+}:O} + y_{Ce^{3+}}^{Ce} y_O^O G_{Ce^{3+}:O} + y_{Ce^{4+}}^{Ce} y_{Va}^O G_{Ce^{4+}:Va} + y_{Ce^{3+}}^{Ce} y_{Va}^O G_{Ce^{3+}:Va} - TS_{config} + G_{excess}$$

$G_{Ce^{4+}:O}$	= Stoichiometric CeO <sub>2</sub> = $G_{CeO_2}^F$
$G_{Ce^{4+}:Va}$	=Oxygen deficient CeO <sub>2</sub> Not charge-neutral
$G_{Ce^{3+}:O}$	=Stoichiometric, reduced CeO <sub>2</sub> Not charge-neutral
$G_{Ce^{3+}:Va}$	=Reduced, oxygen deficient CeO <sub>2</sub> Not charge-neutral

Gibbs energy experimentally known.  
Can be theoretically calculated.

Difficult to get energy. Define reference state.  
 $G_{Ce^{4+}:Va} = G_{CeO_2}^F - G_{O_2}(g)$

Difficult to get energy.  
Define reference state + reciprocal relation

Ce<sub>2</sub>O<sub>3</sub> or CeO<sub>1.5</sub>: charge-neutral compound with **hexagonal** ground-state

- But  $G$  for **metastable** fluorite-CeO<sub>1.5</sub> can be theoretically/experimentally estimated

Reference state:  $G_{CeO_{1.5}}^F = \frac{3}{4} G_{Ce^{3+}:O} + \frac{1}{4} G_{Ce^{3+}:Va} + 2RT \left( \frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right)$

Reciprocal relation:  $G_{Ce^{4+}:O} - G_{Ce^{4+}:Va} = G_{Ce^{3+}:O} - G_{Ce^{3+}:Va}$  ( $G_{O_2}(g) = G_{O_2}(g)$ )

4 variables and 4 equations

Actual values can be fit to experimental data (*classic* thermodynamic assessments) or calculated using theory (this work)

# Excess terms

- Typically written as a Redlich-Kister<sup>1</sup> polynomial series, with as few terms used as possible

- $$G_{excess}^F(\text{CeO}_x) = y_{\text{Ce}^{3+}}^{\text{Ce}} y_{\text{Ce}^{4+}}^{\text{Ce}} y_{\text{O}}^{\text{O}} \left( L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}: \text{O}} + \left( y_{\text{Ce}^{3+}}^{\text{Ce}} - y_{\text{Ce}^{4+}}^{\text{Ce}} \right) L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}: \text{O}} \right) + y_{\text{Ce}^{3+}}^{\text{Ce}} y_{\text{Ce}^{4+}}^{\text{Ce}} y_{\text{Va}}^{\text{O}} \left( L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}: \text{Va}} + \left( y_{\text{Ce}^{3+}}^{\text{Ce}} - y_{\text{Ce}^{4+}}^{\text{Ce}} \right) L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}: \text{Va}} \right) + \dots$$
 (analogous binary interaction terms) + (ternary interaction terms) + ...

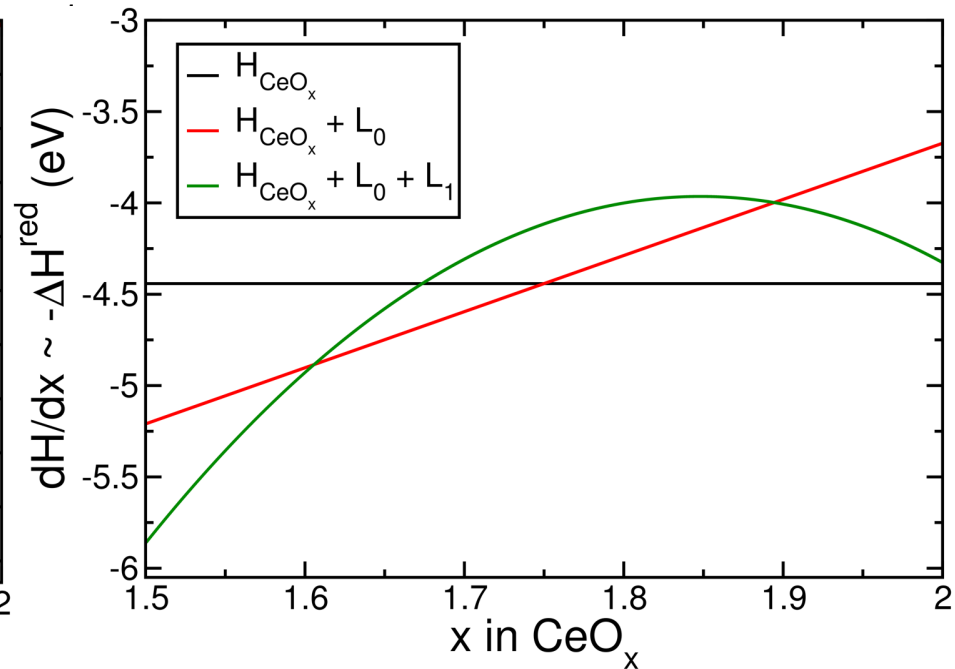
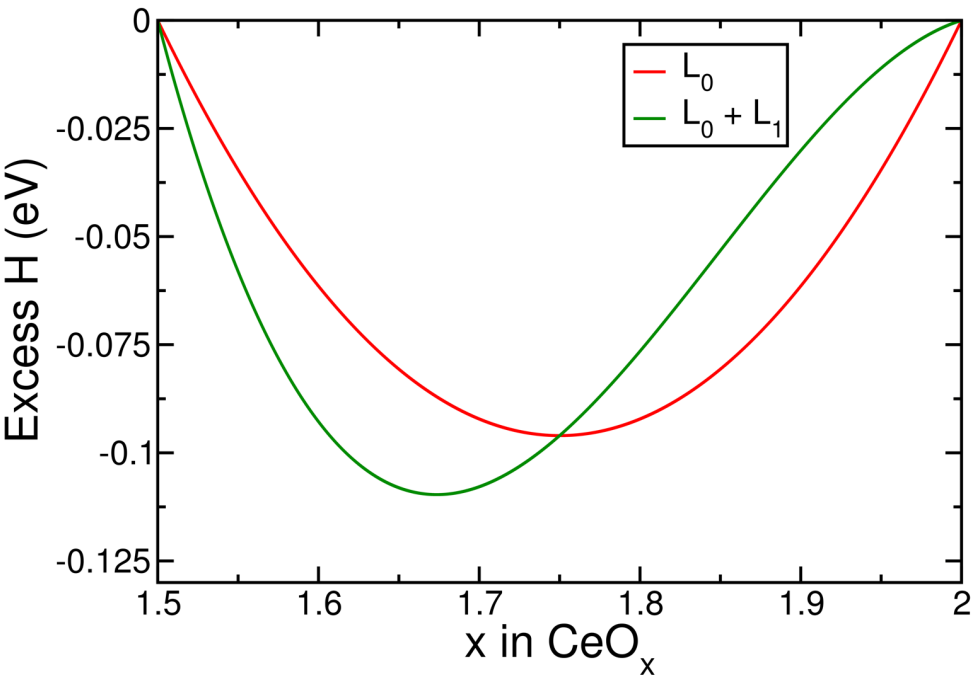
- Excess terms contribute a polynomial dependence on composition ( $y$ ) instead of a logarithmic dependence (like entropy)

- Excess terms  $\sim$  enthalpic, although errors from non-ideal/non-configurational entropy contributions are compensated

- Two excess terms used in the sub-lattice model fit to experimental data for  $\text{CeO}_x$ <sup>2</sup>

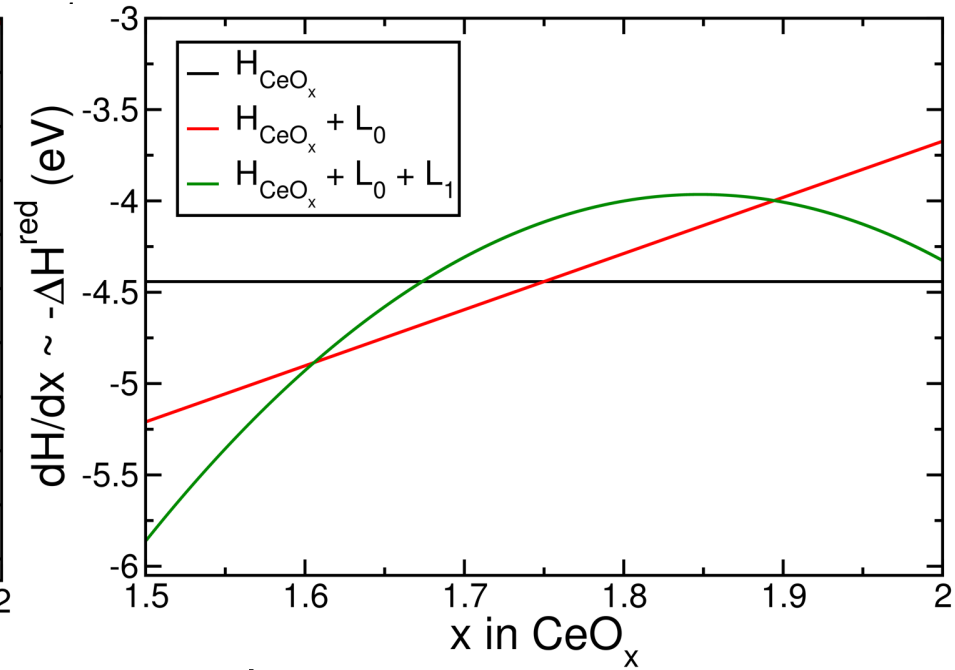
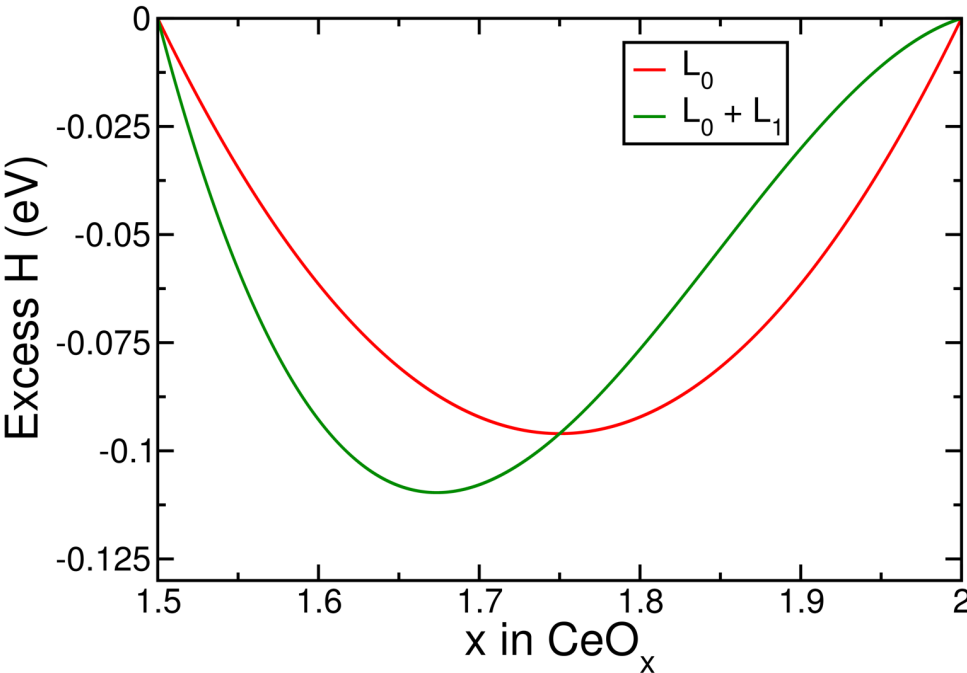
- $L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}: \text{O}} = L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}: \text{Va}} = L_0$
- $L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}: \text{O}} = L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}: \text{Va}} = L_1$

# Excess terms



- Two excess terms used in the sub-lattice model fit to experimental data for  $\text{CeO}_x^2$ 
  - $L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}:0} = L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}:va} = L_0$
  - $L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}:0} = L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}:va} = L_1$
- Physically,  $L_0$  = stabilization of an isolated vacancy,  $L_1$  = vacancy-vacancy interactions

# Excess terms



- Two excess terms used in the sub-lattice model fit to experimental data for  $\text{CeO}_x^2$ 
  - $L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}:0} = L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}:va} = L_0$
  - $L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}:0} = L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}:va} = L_1$

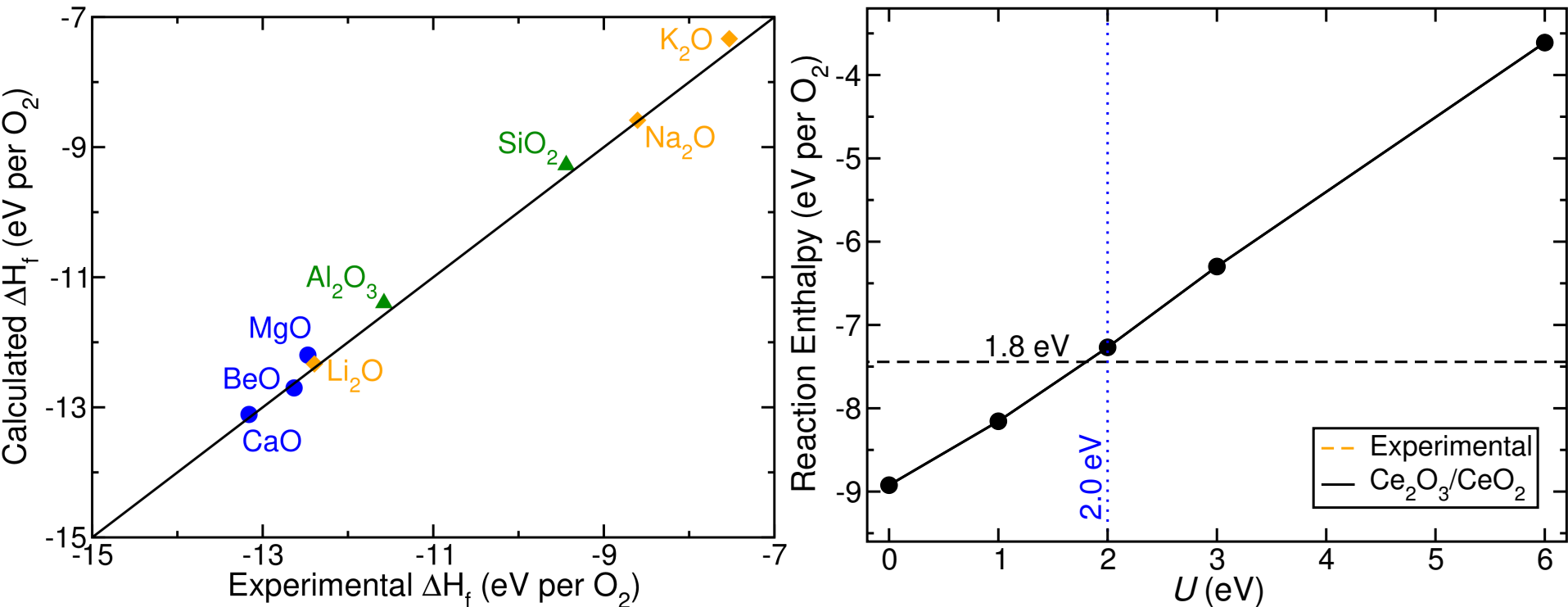
Use  $G_{\text{end-members}}$ ,  $S_{\text{config}}$  and  $G_{\text{excess}}$ , obtained theoretically, to predict overall  $G_{\text{CeO}_x}^F$  and  $\mu_0^{\text{solid}}$  as  $f(x, T)$

# Density functional theory calculations

# SCAN+ $U$ calculations

Strongly constrained and appropriately normed (SCAN) functional is used to describe electronic exchange-correlation within Density Functional Theory (DFT)

- SCAN satisfies 17 known constraints on the behavior of an exchange-correlation functional
- Hubbard  $U$  correction of 2 eV added to Ce's 4f orbitals
  - To reduce self-interaction errors



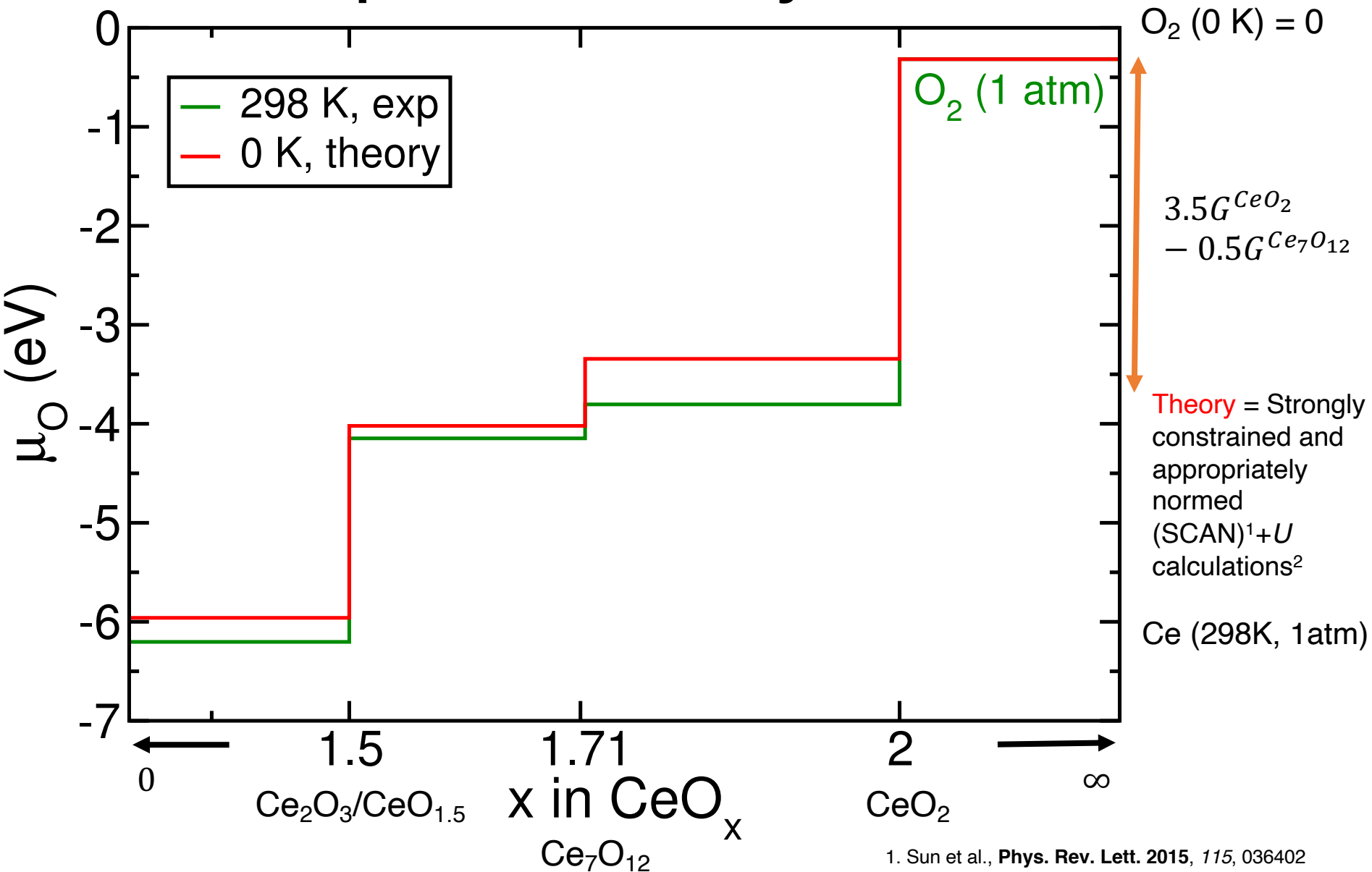
Sun et al., **Phys. Rev. Lett.** 2015, 115, 036402; Anisimov et al., **Phys. Rev. B** 1991, 44, 943

Gautam and Carter, **Phys. Rev. Mater.** 2018, 2, 095401



How does theory describe  $\text{CeO}_x$ ?

# Ce-O: exp. vs. theory, 298 K

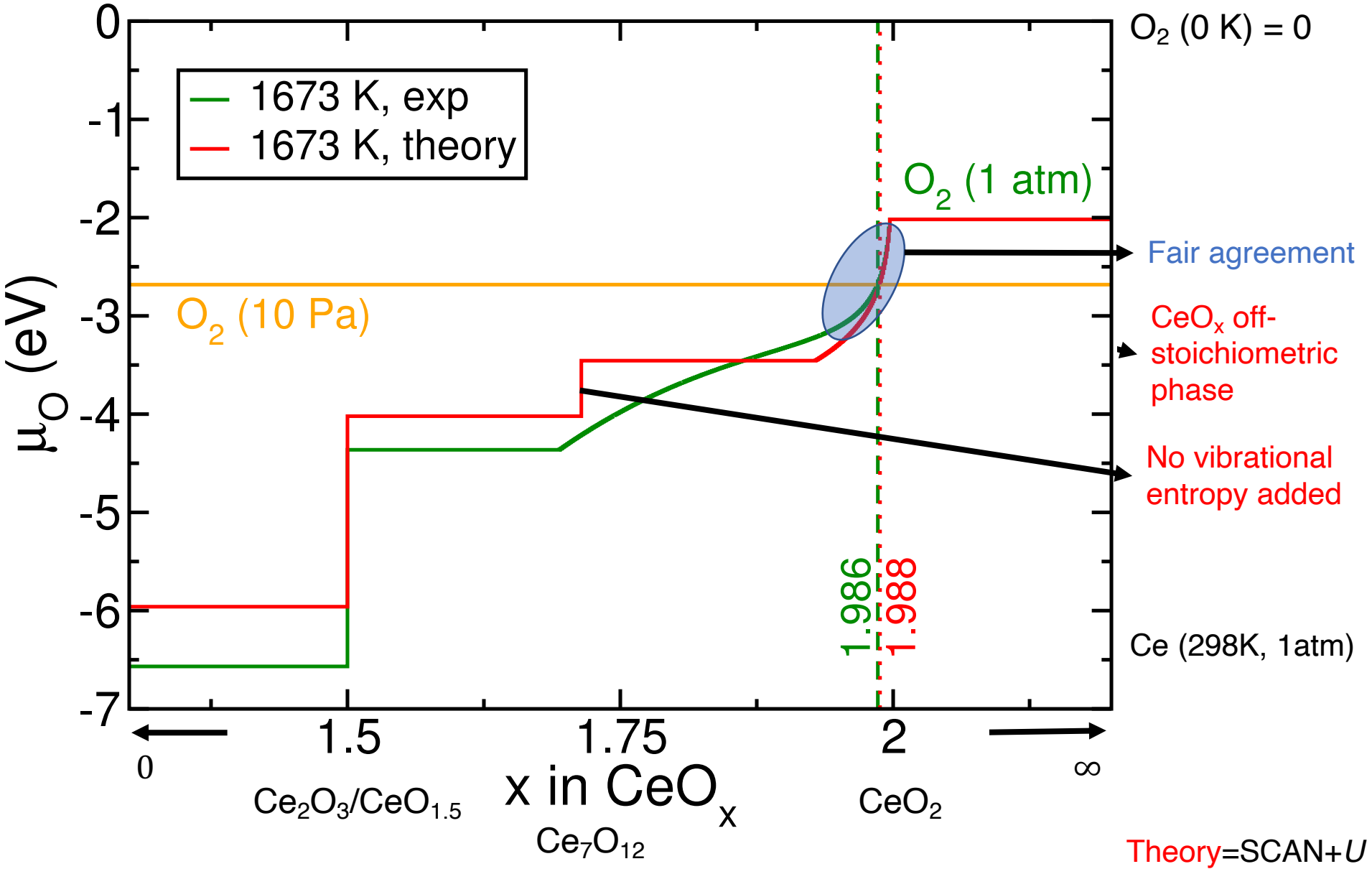


1. Sun et al., **Phys. Rev. Lett.** **2015**, *115*, 036402

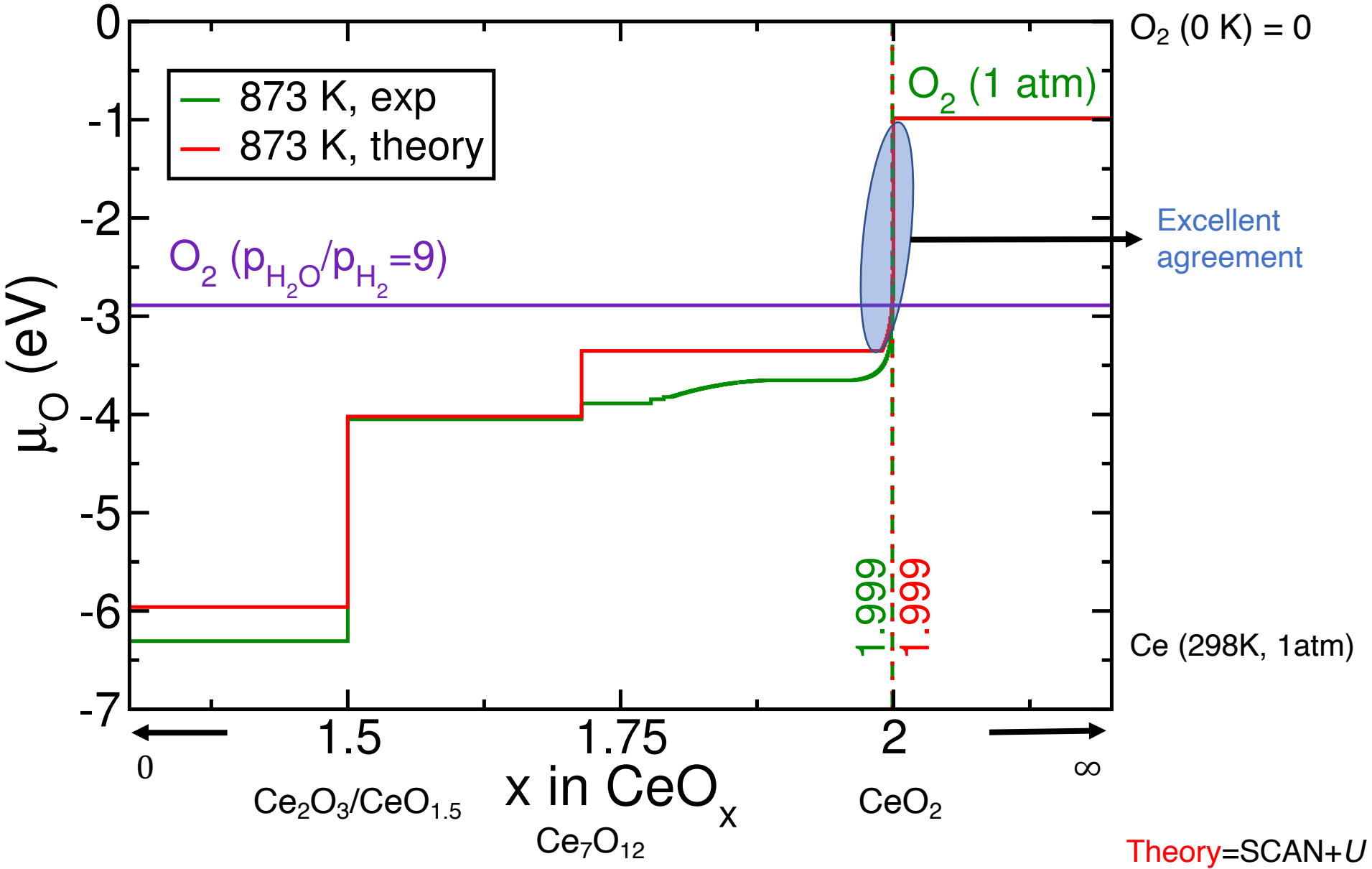
2. [Gautam](#), and Carter, **Phys. Rev. Mater.** **2018**, *2*, 095401

[Gautam](#), Stechel and Carter, *to be submitted*

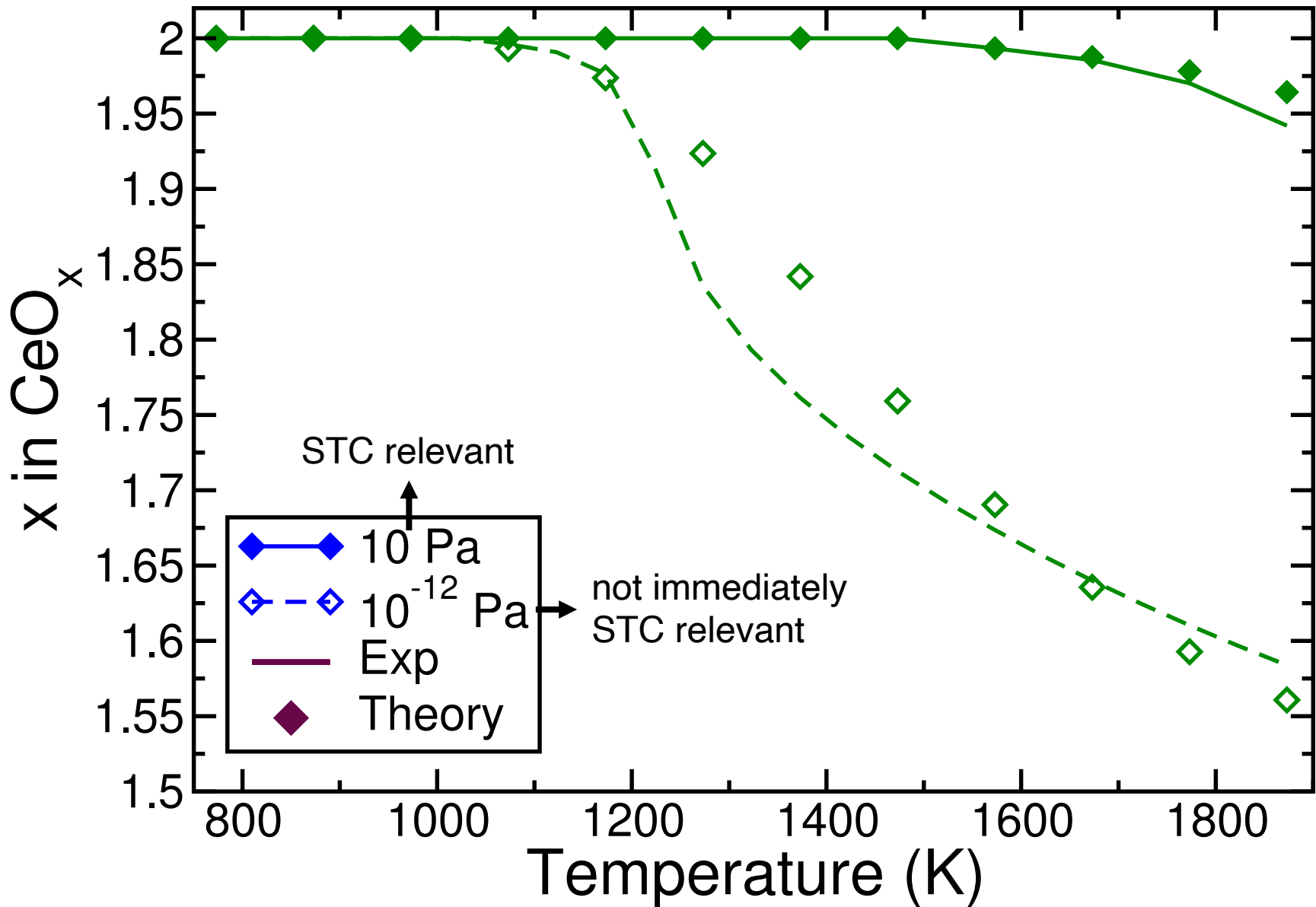
# Ce-O: exp. vs. theory, 1673 K (TR)



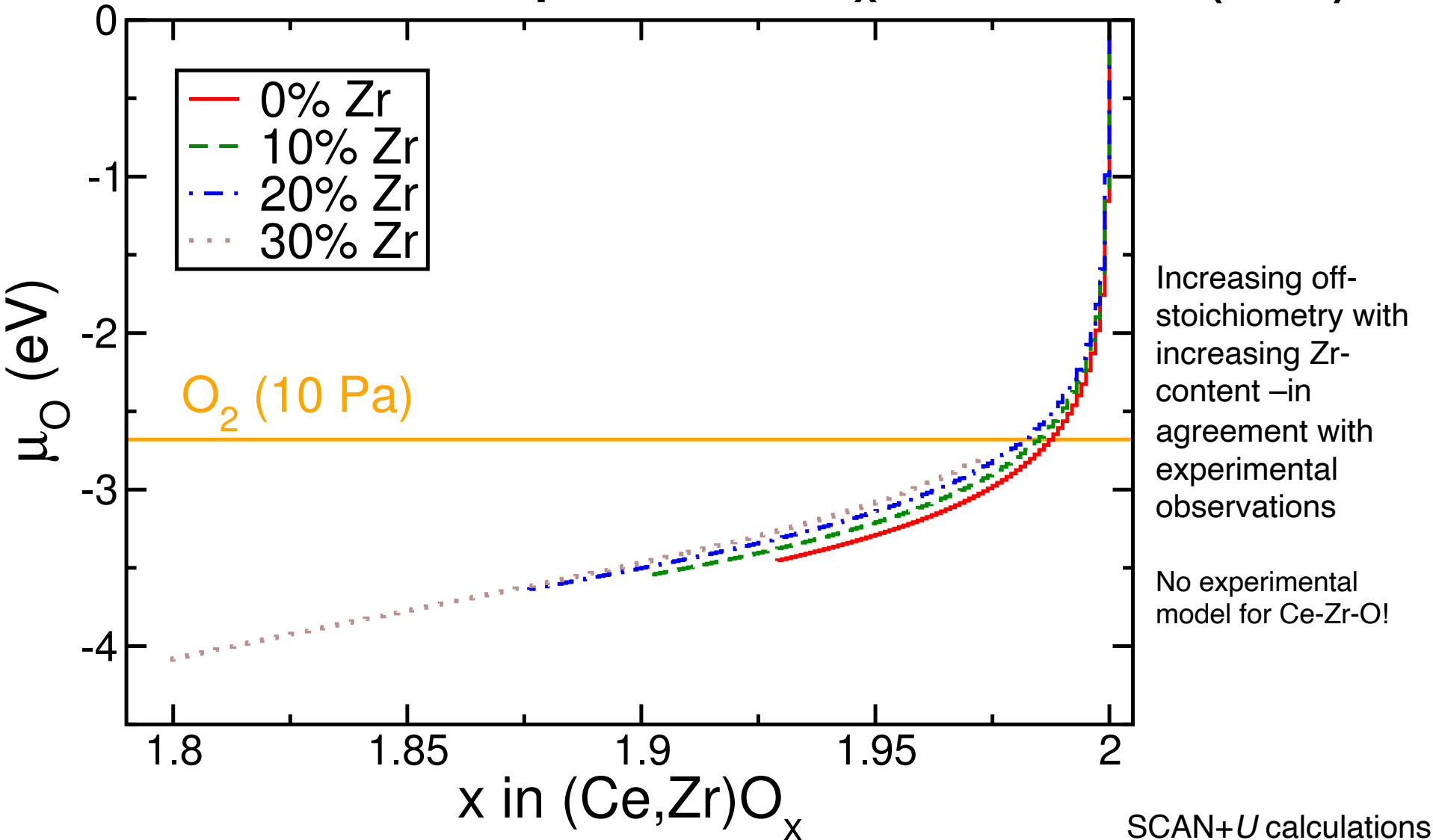
# Ce-O: exp. vs. theory, 873 K (WS)



# x in CeO<sub>x</sub>, exp. vs. theory



# Extension of theoretical sub-lattice model to Zr-doped $\text{CeO}_x$ ; 1673 K (TR)

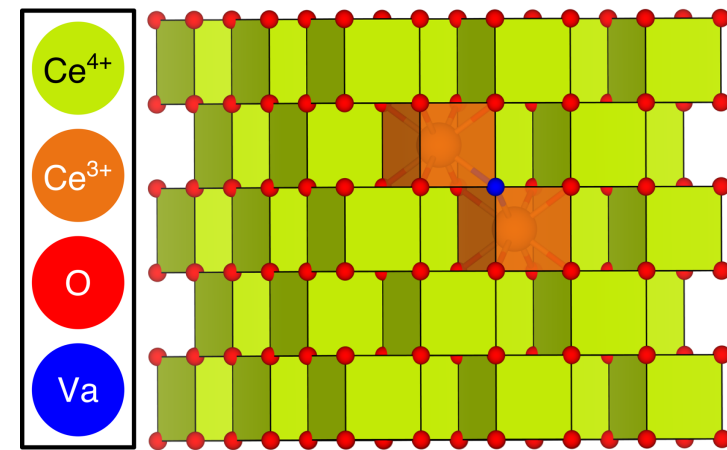


Gautam, Stechel and Carter, *to be submitted*

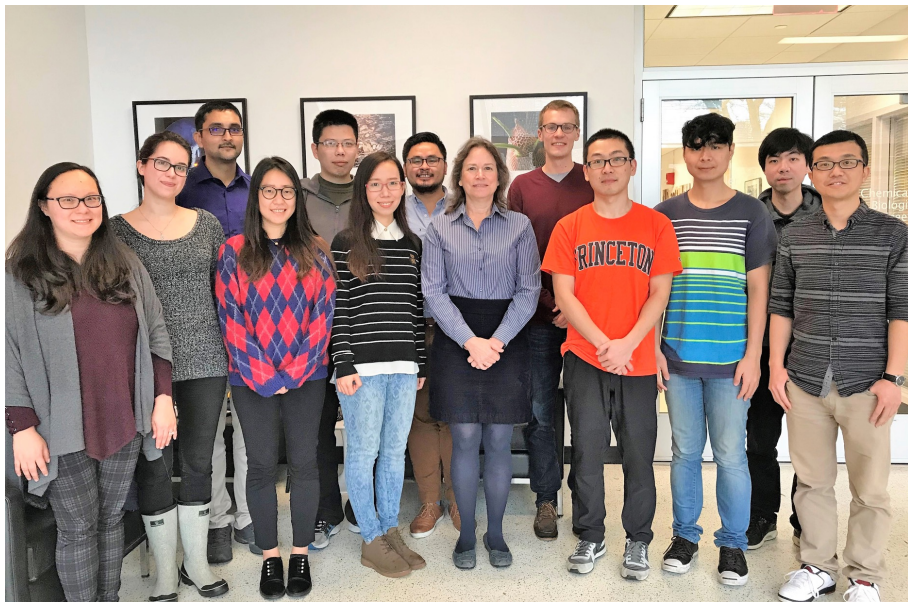
Exp. observations: Le Gal and Abanades, *J. Phys. Chem. C* 2012, 116, 13516; Hao *et al.*, *Chem. Mater.* 2014, 26, 6073

# Summary and outlook

- Need better materials for STC-water splitting
  - Durability, Capacity and Stability
- $\text{CeO}_2$ , oxide spinels, and oxide perovskites have been studied as candidates
  - Opportunity to test theoretical models
  - Understand unique features of these materials to predict new candidates
- Testing theoretical frameworks: DFT-based sub-lattice formalism indicates promise!
  - Sub-lattice models are conventionally used to build phase diagrams based on experimental data (such as CALPHAD-style modeling)
  - Predictions on  $\text{CeO}_2$ , and Zr-doped  $\text{CeO}_2$  are reasonable
  - Need to generalize for systems with higher (quaternary/quinary) components
- Screening materials: need a descriptor
  - In progress: sub-lattice formalism can be used to predict redox capacities of candidates



# Acknowledgments



Prof. Emily A. Carter



Dr. Ellen B. Stechel



“A first-principles-based sub-lattice formalism for predicting off-stoichiometry in materials”,  
G.S. Gautam, E.B. Stechel and E.A. Carter, *to be submitted*

“Evaluating transition metal oxides within DFT-SCAN and SCAN+ $U$  frameworks for solar thermochemical applications”, G.S. Gautam, and E.A. Carter, *Phys. Rev. Mater.* **2018**, *2*, 095401



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