

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

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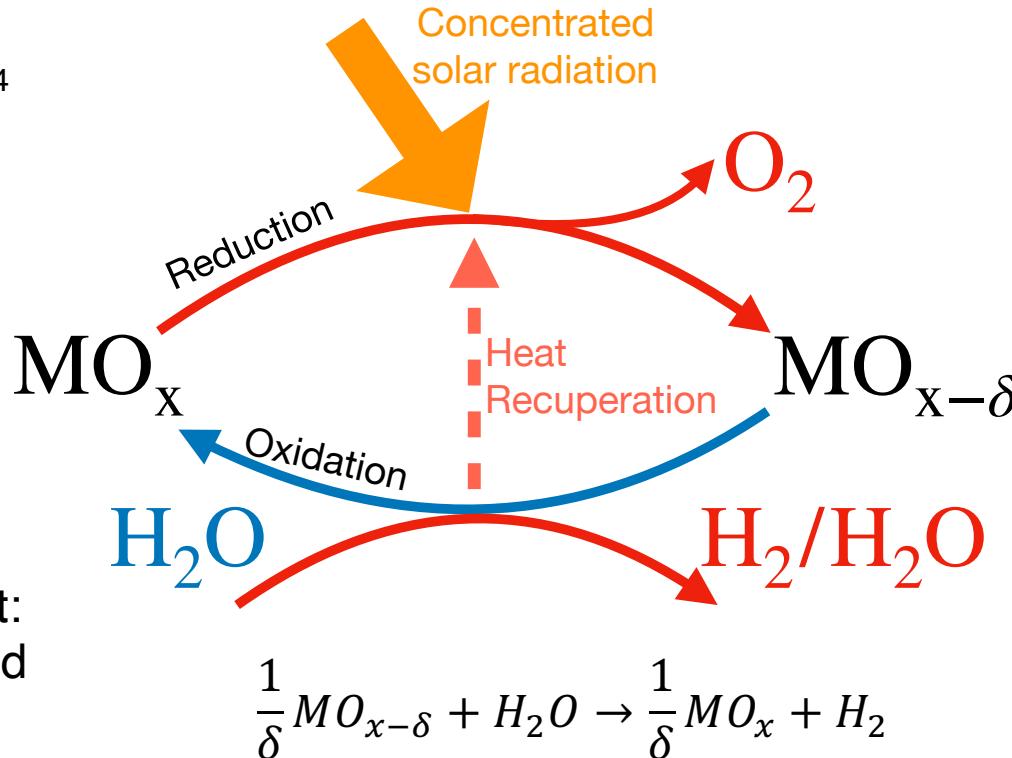
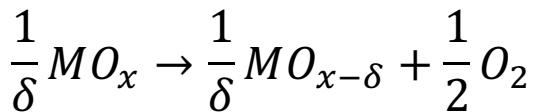
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PHYS: New frontiers in the confluence of experimental thermodynamics, structural investigation & theory/computation, American Chemical Society Spring Meeting
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Solar thermochemical (STC) production of H₂ and/or CO

Candidates so far:

- CeO₂
- Fe(Fe,X)₂O₄
- (A,A')BO₃



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

Water splitting (WS)
Low T (873 K)
High H₂ yield ($\frac{p_{H_2O}}{p_{H_2}} = 9$)

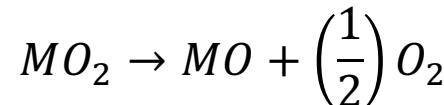
State-of-the-art:
Pure and doped
fluorite-CeO₂

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?

Thermodynamics of STC water-splitting: Reduction energetics



Target T: 1673 K, pO₂: 10 Pa

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

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

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

H, S are T dependent

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

Chemical potential of oxygen in solid

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

Main T dependence is from S terms

Note: ΔH_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 ?

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

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

H , S are T dependent

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

$$= H^{MO_2} - H^{MO} - T(S^{MO_2} - S^{MO})$$

$$\approx \Delta H_f^{MO_2} - \Delta H_f^{MO} - T(S^{MO_2} - S^{MO})$$

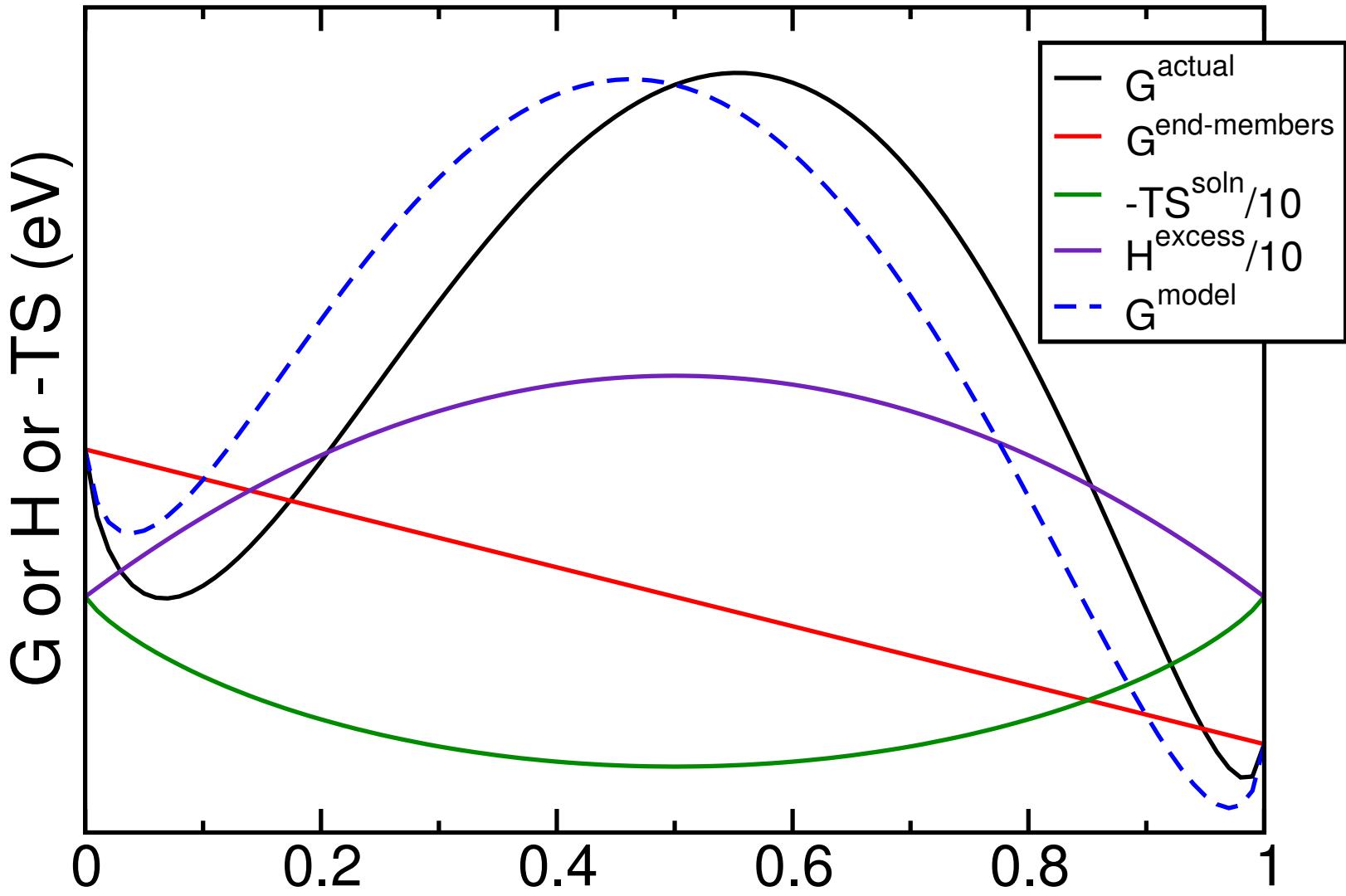
Main T dependence is from S terms

Note: ΔH_f terms are at 298 K, 1 atm

Thermodynamics of solid solution phases

Or how to describe fluorite- CeO_x ?

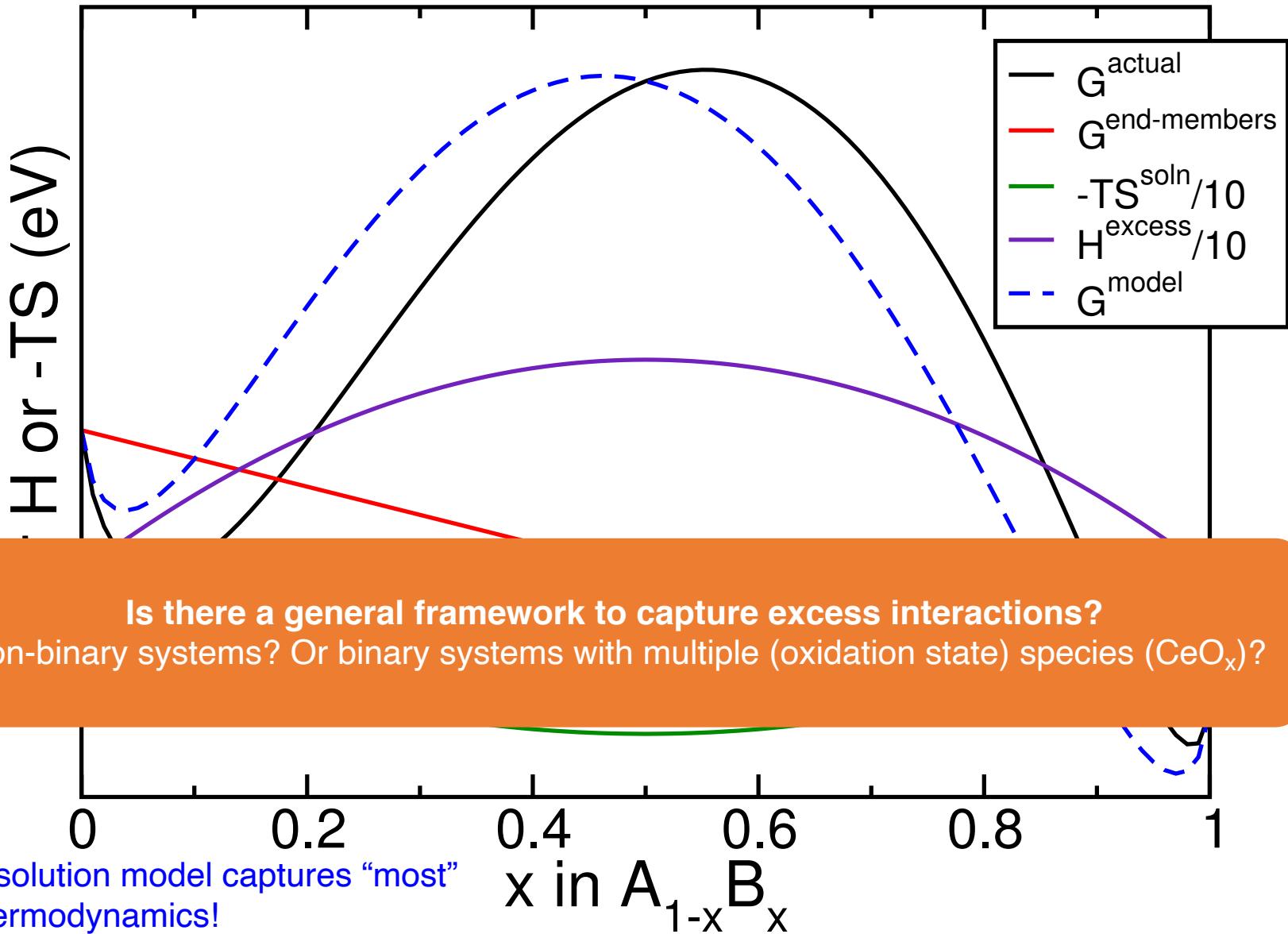
Modeling G for simple $A_{1-x}B_x$ binary



Regular solution model captures “most”
of the thermodynamics!

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

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

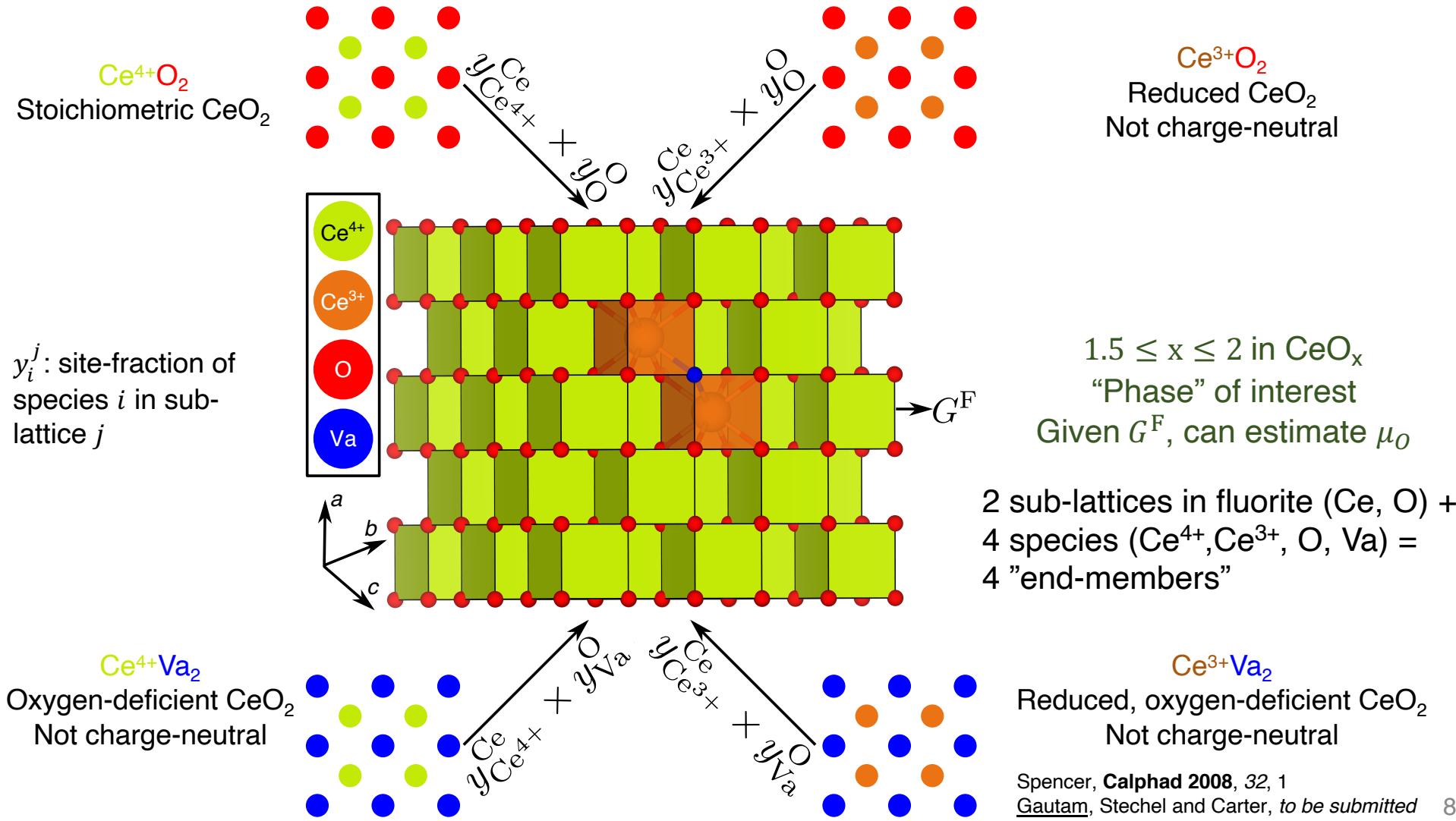


$$G^{\text{actual}} = (1 - x)G_A + xG_B + RT(x \ln x + 1 - x \ln 1 - x) + L_0x(1 - x) + L_1x(1 - x)(1 - 2x)$$

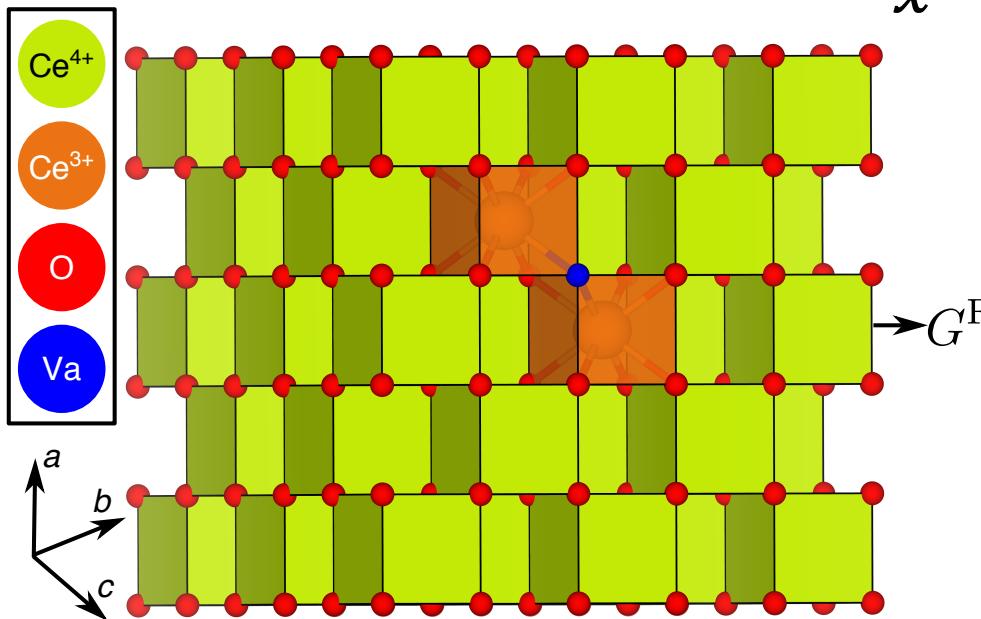
“Sub-lattice” formalism:

Or how to describe off-stoichiometric compounds?

Example of fluorite- CeO_x ; describe $G(\text{fluorite phase}) = f(x, T)$?



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



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

\uparrow

$Ce^{4+}O_2$

\uparrow

$Ce^{3+}O_2$

\uparrow

$Ce^{4+}Va_2$

\uparrow

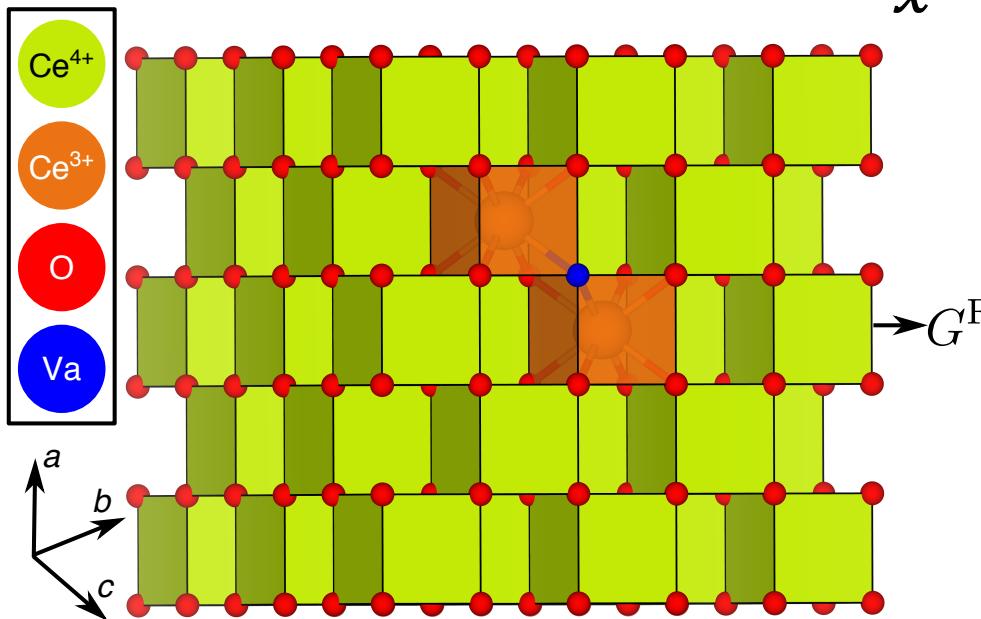
$Ce^{3+}Va_2$

End-member Gibbs energies

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

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

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



$$G_{CeO_x}^F = y_{Ce^{4+}}^{Ce} y_O^0 G_{Ce^{4+}:O} + y_{Ce^{3+}}^{Ce} y_O^0 G_{Ce^{3+}:O} + y_{Ce^{4+}}^{Ce} y_{Va}^0 G_{Ce^{4+}:Va} + y_{Ce^{3+}}^{Ce} y_{Va}^0 G_{Ce^{3+}:Va} - TS_{config} + G_{excess}$$

\uparrow
Ce⁴⁺O₂

\uparrow
Ce³⁺O₂

\uparrow
Ce⁴⁺Va₂

\uparrow
Ce³⁺Va₂

End-member Gibbs energies

S_{config})]

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

G_{excess} entropy

Reference states and reciprocal relations

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

$G_{Ce^{4+}:O}$	= Stoichiometric CeO ₂ = $G_{CeO_2}^F$	Gibbs energy experimentally known. Can be theoretically calculated.
$G_{Ce^{4+}:Va}$	=Oxygen deficient CeO ₂ Not charge-neutral	Difficult to get energy. Define reference state. $G_{Ce^{4+}:Va} = G_{CeO_2}^F - G_{O_2}(g)$
$G_{Ce^{3+}:O}$	=Stoichiometric, reduced CeO ₂ Not charge-neutral	Difficult to get energy. Define reference state + reciprocal relation
$G_{Ce^{3+}:Va}$	=Reduced, oxygen deficient CeO ₂ Not charge-neutral	

Ce₂O₃ or CeO_{1.5}: charge-neutral compound with **hexagonal** ground-state

- But G for **metastable** fluorite-CeO_{1.5} can be theoretically/experimentally estimated

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

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

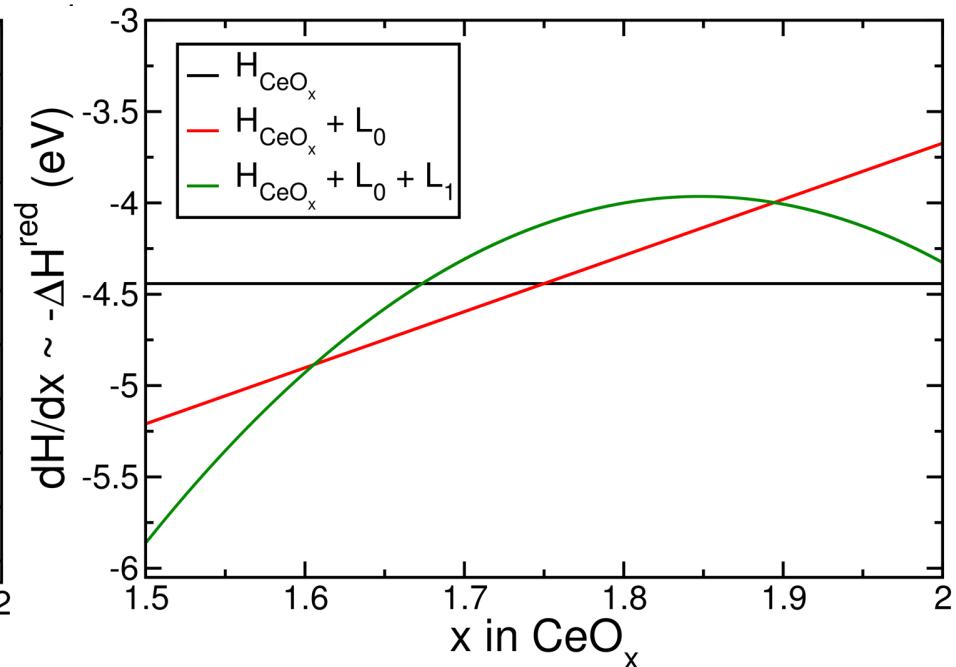
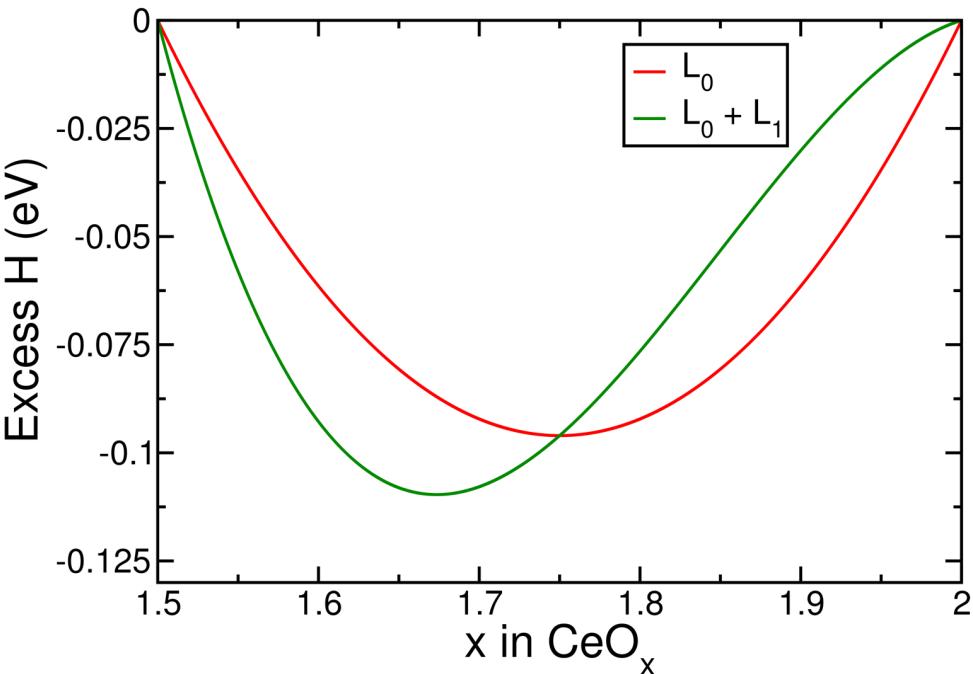
4 variables and 4 equations

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

Excess terms

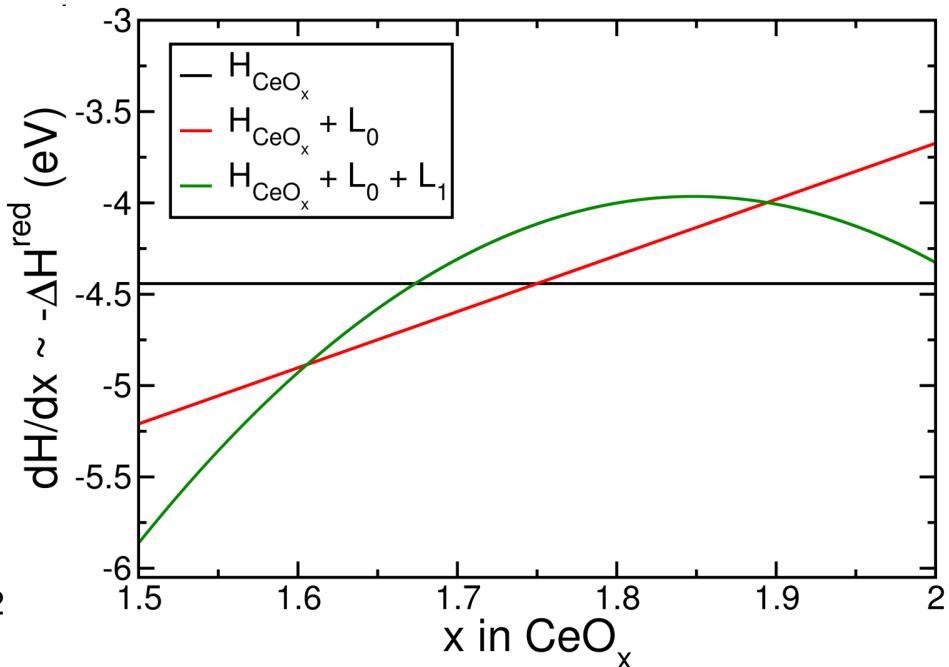
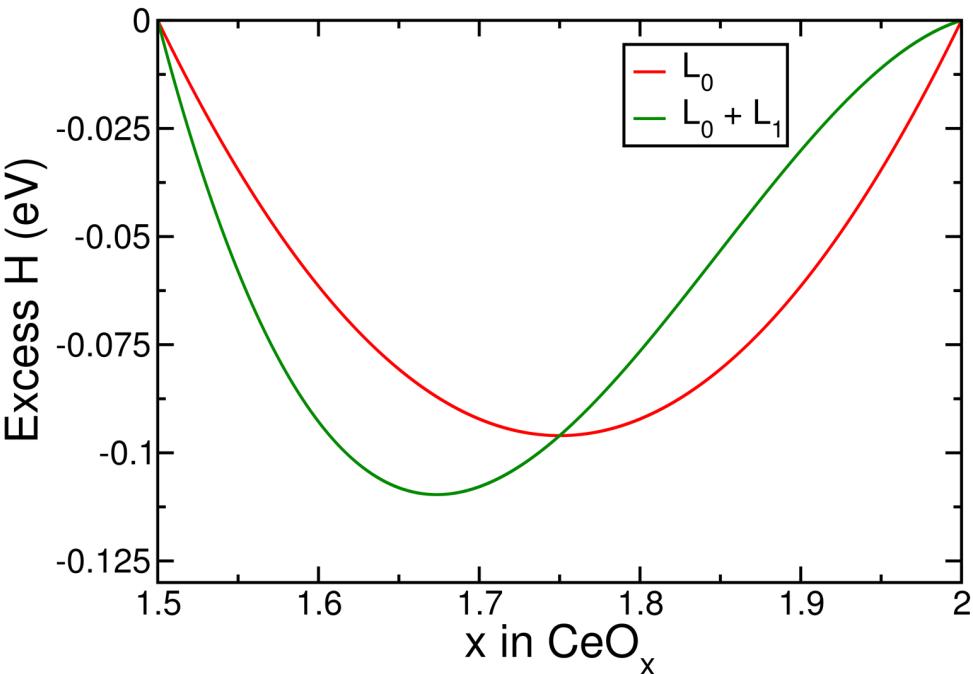
- Typically written as a Redlich-Kister¹ polynomial series, with as few terms used as possible
- $G_{excess}^F(\text{CeO}_x) = y_{\text{Ce}^{3+}}^{\text{Ce}} y_{\text{Ce}^{4+}}^{\text{Ce}} y_O^O \left(L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}:O} + (y_{\text{Ce}^{3+}}^{\text{Ce}} - y_{\text{Ce}^{4+}}^{\text{Ce}}) L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}:O} \right) + y_{\text{Ce}^{3+}}^{\text{Ce}} y_{\text{Ce}^{4+}}^{\text{Ce}} y_{Va}^O \left(L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}:Va} + (y_{\text{Ce}^{3+}}^{\text{Ce}} - y_{\text{Ce}^{4+}}^{\text{Ce}}) L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}:Va} \right) + \dots \text{ (analogous binary interaction terms)} + \text{ (ternary interaction terms)} + \dots$
- 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 CeO_x ²
 - $L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}:O} = L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}:Va} = L_0$
 - $L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}:O} = L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}:Va} = L_1$

Excess terms



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

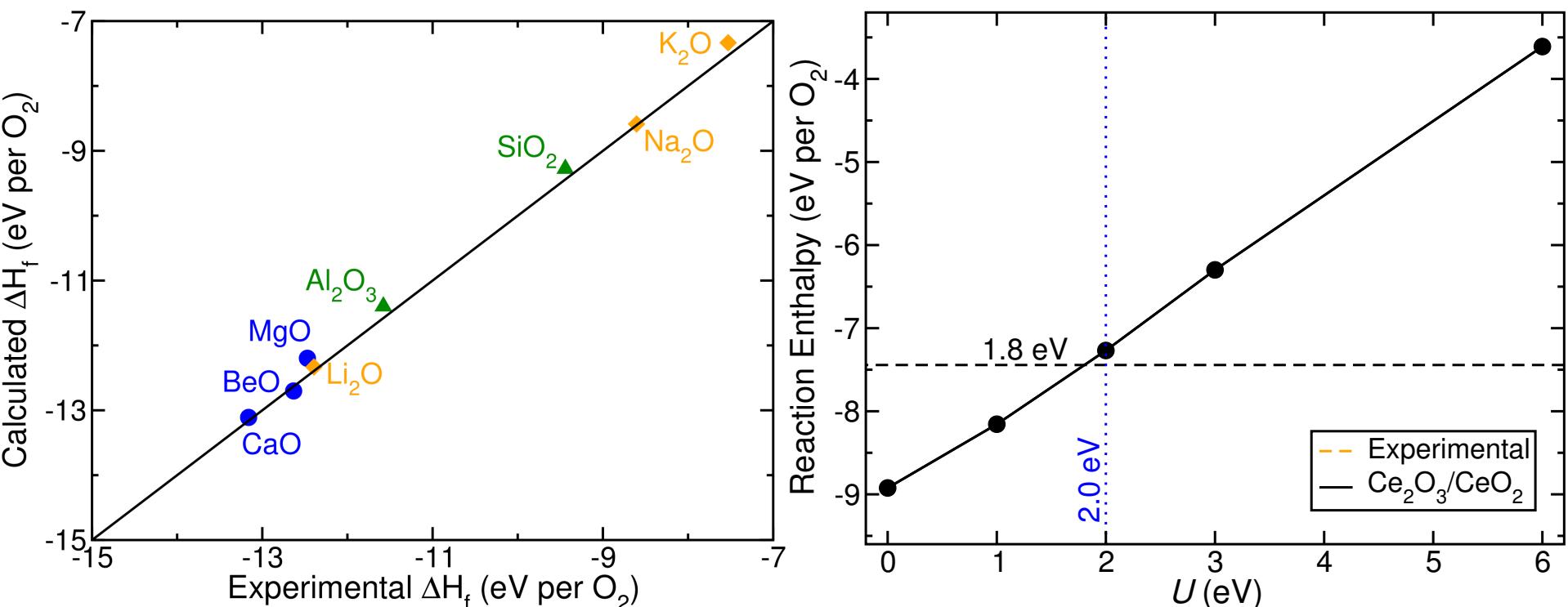
Use $G_{end-members}$, S_{config} and G_{excess} , obtained theoretically, to predict overall $G_{CeO_x}^F$ and μ_O^{solid} as $f(x, T)$

Density functional theory calculations

SCAN+ U calculations

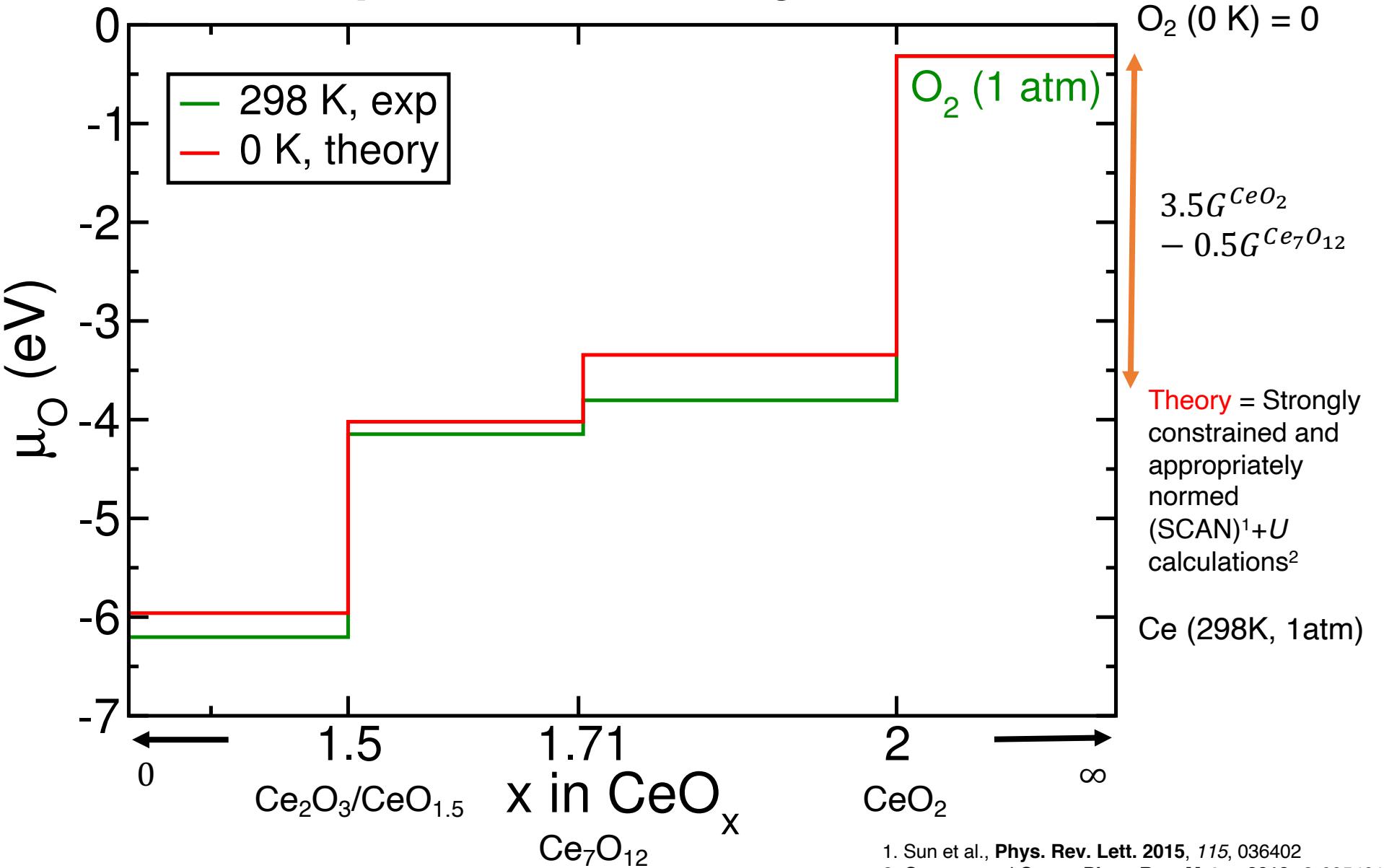
Strongly constrained and appropriately normed (SCAN) functional is used to describe electronic exchange-correlation within Density Functional Theory (DFT)

- 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

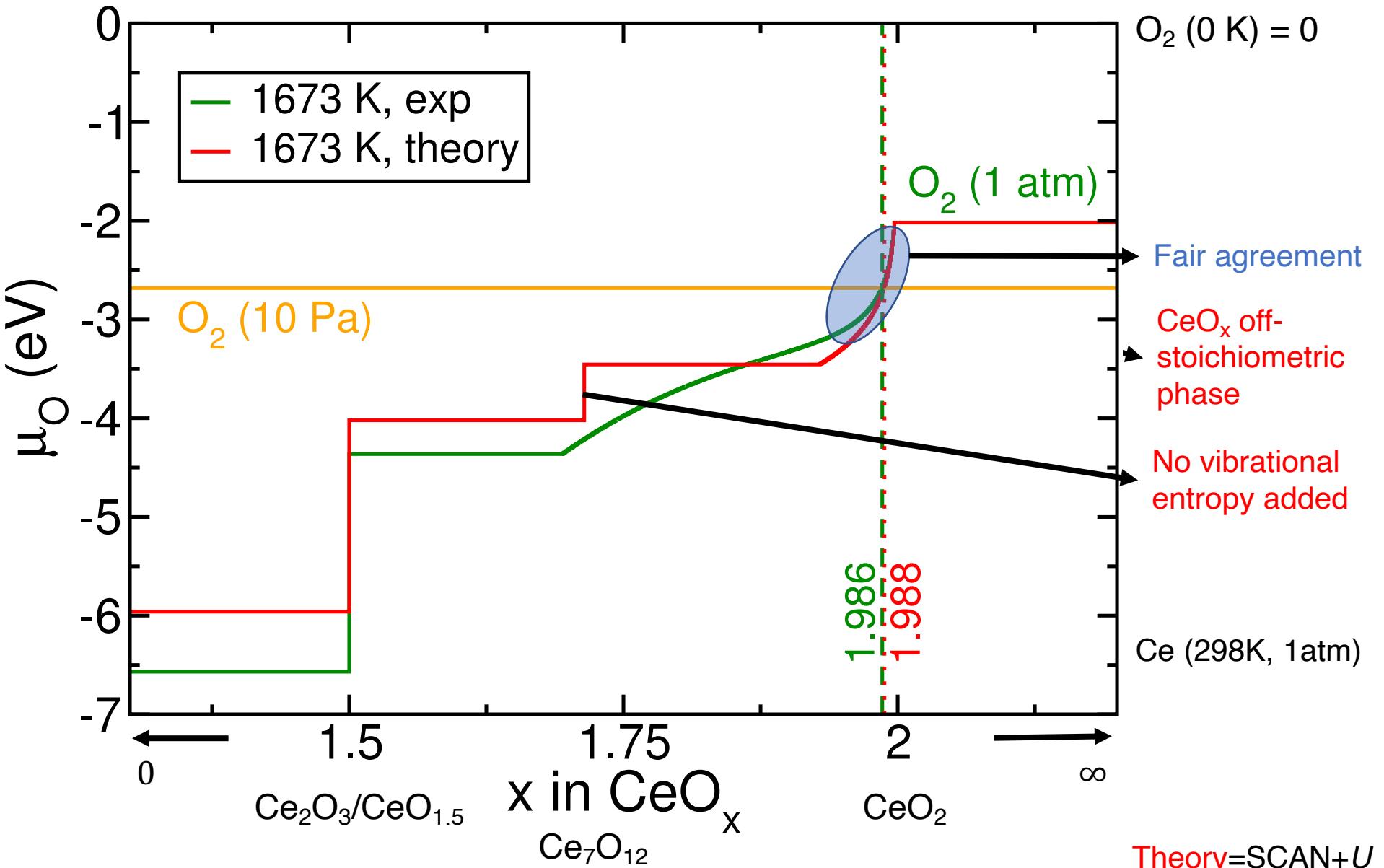


How does theory describe CeO_x?

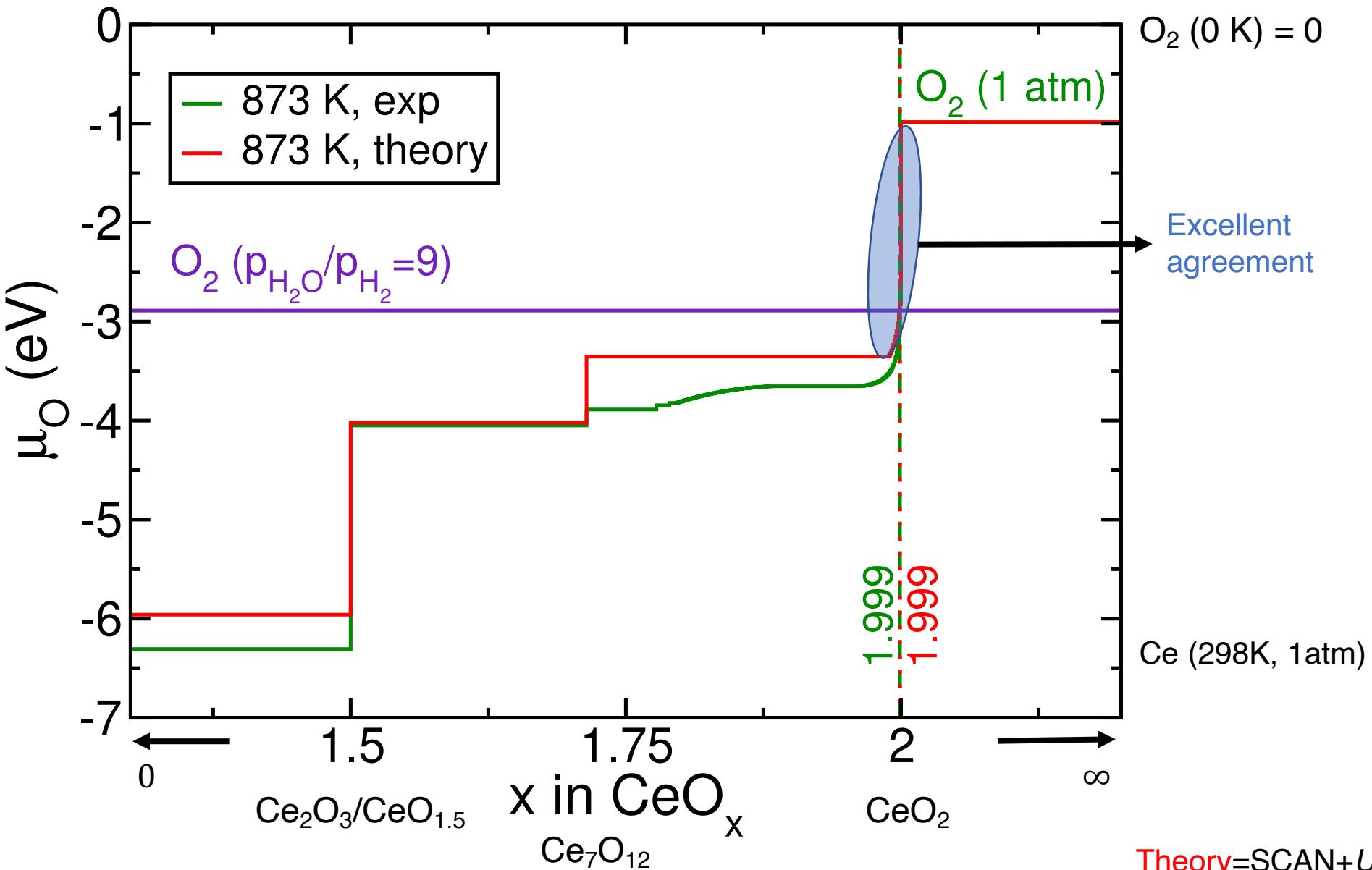
Ce-O: exp. vs. theory, 298 K



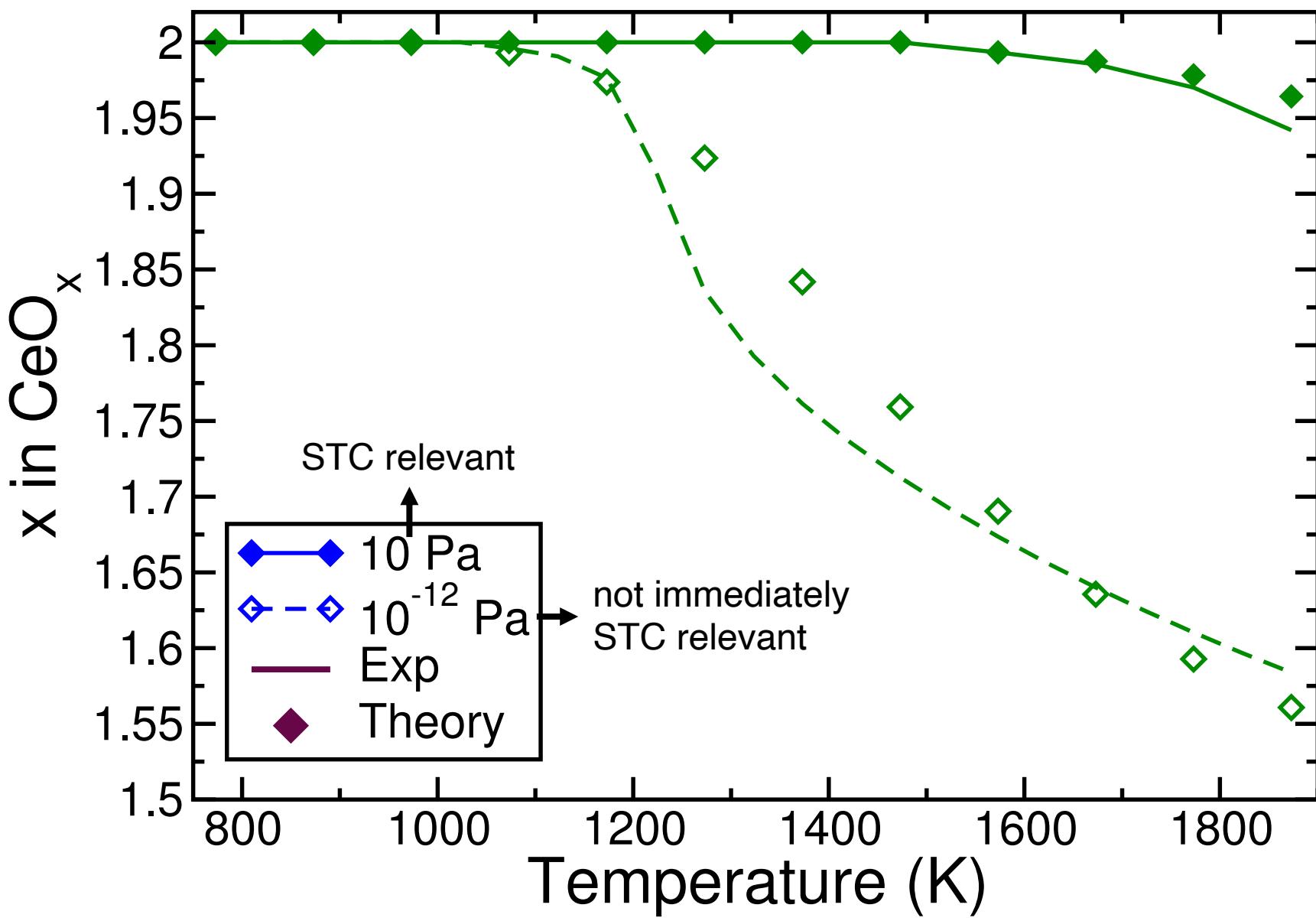
Ce-O: exp. vs. theory, 1673 K (TR)



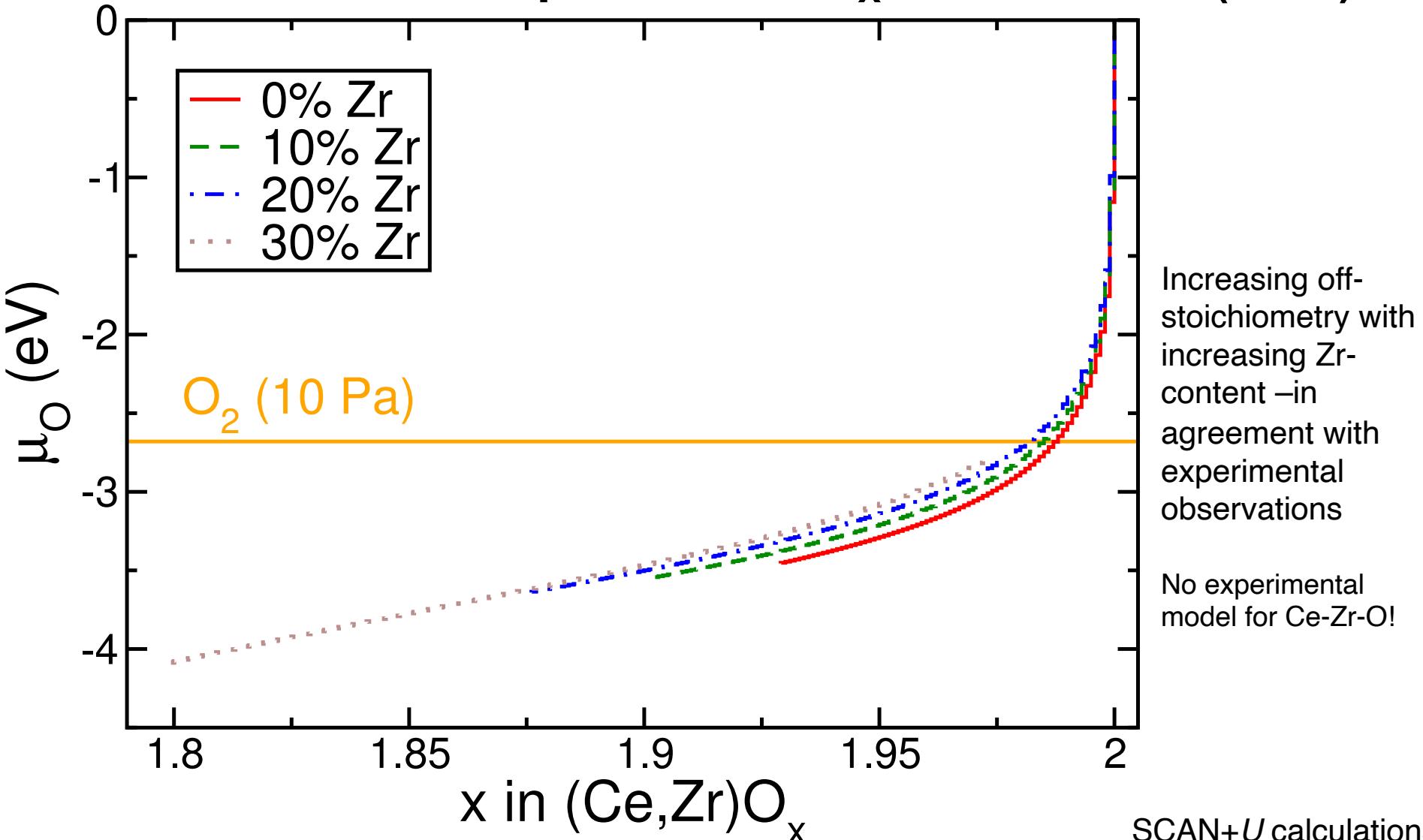
Ce-O: exp. vs. theory, 873 K (WS)



x in CeO_x , exp. vs. theory

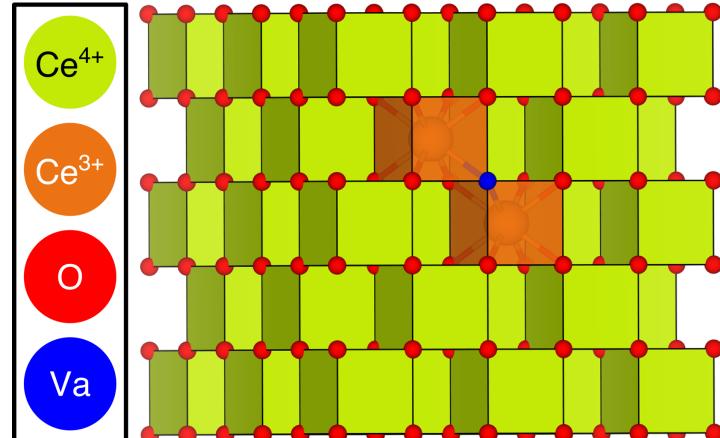


Extension of theoretical sub-lattice model to Zr-doped CeO_x; 1673 K (TR)

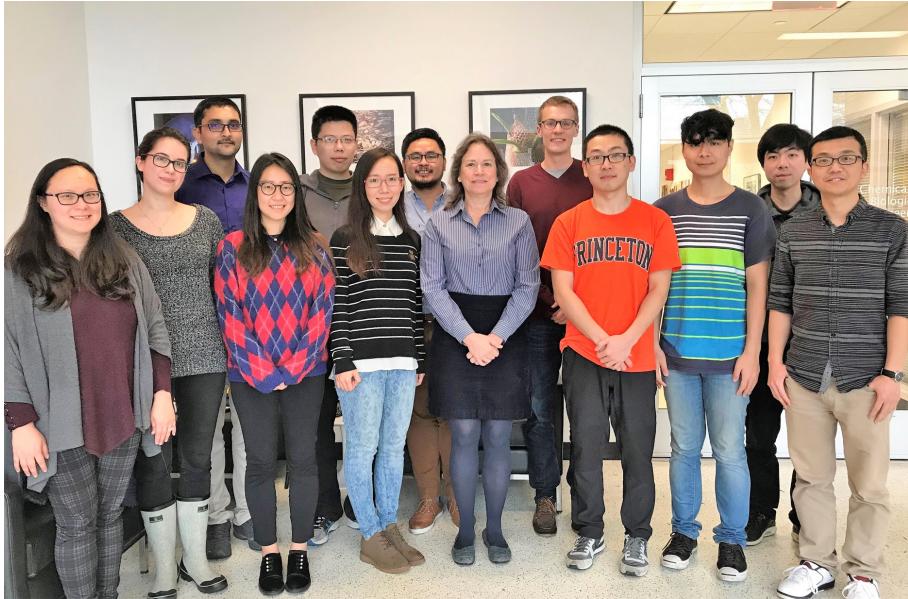


Summary and outlook

- Need better materials for STC-water splitting
 - Durability, Capacity and Stability
- 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 CeO_2 , and Zr-doped 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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