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Thermochemical Modeling of Urania-Rare Phases

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MMSNF
Materials Modeling and Simulation for Nuclear Fuels
October 14-16, 2013 -- Chicago, Illinois USA

Contents

- **My apologies for being unable to attend the meeting and present the intended paper**
- **Thank you to Marius for offering to give this abbreviated presentation**
- **This presentation discusses**
  - Extending the compound energy formalism application of C. Gueneau, et al. for urania to include rare earth elements dissolved in the fluorite structure phase
  - Modeling the non-fluorite structure phases for the pseudobinaries to reproduce phase equilibria
  - The need for inclusion of the U^{6+} valence cation in order to reproduce observed fluorite structure phase equilibria for high concentration trivalent rare earths dissolved with urania
  - However, for pure urania U^{6+} concentration is always negligible
  - Results for modeling urania-gadolinia so far without U^{6+}
  - Results for modeling urania-lanthana utilizing U^{6+} containing species

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Compound Energy Formalism (CEF) for $U_{1-y}Gd_yO_{2\pm x}$

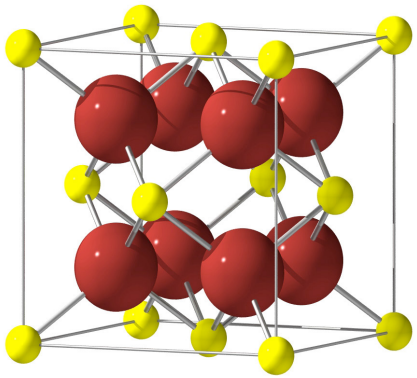
Three Sublattice Model

$$(U^{3+},U^{4+},U^{5+},Gd^{3+})_1(O^{2-},Va^0)_2(O^{2-},Va^0)_1$$

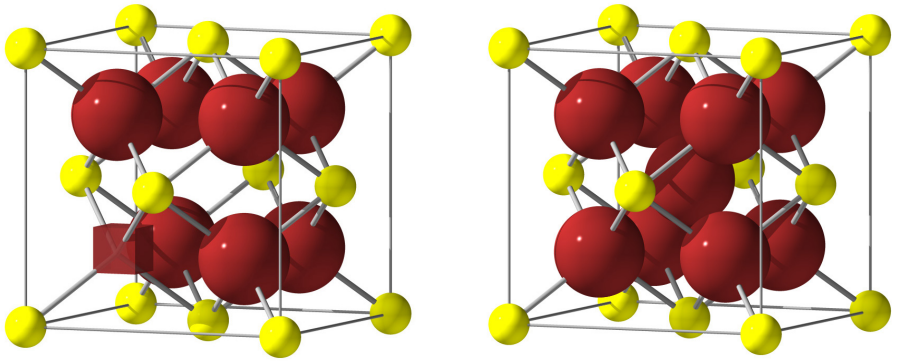
$U_{1-y}Gd_yO_{2\pm x}$ end-members

C. Gueneau et al., Journal of Nuclear Materials 304 (2002) 161–175

- $U^{3+}:O^{2-}:O^{2-}$
- $U^{3+}:O^{2-}:VA$
- $U^{3+}:VA:O^{2-}$
- $U^{3+}:VA:VA$
- $U^{4+}:O^{2-}:O^{2-}$
- $U^{4+}:O^{2-}:VA$
- $U^{4+}:VA:O^{2-}$
- $U^{4+}:VA:VA$
- $U^{5+}:O^{2-}:O^{2-}$
- $U^{5+}:O^{2-}:VA$
- $U^{5+}:VA:O^{2-}$
- $U^{5+}:VA:VA$
- **$Gd^{3+}:O^{2-}:O^{2-}$**
- **$Gd^{3+}:O^{2-}:VA$**
- **$Gd^{3+}:VA:O^{2-}$**
- **$Gd^{3+}:VA:VA$**

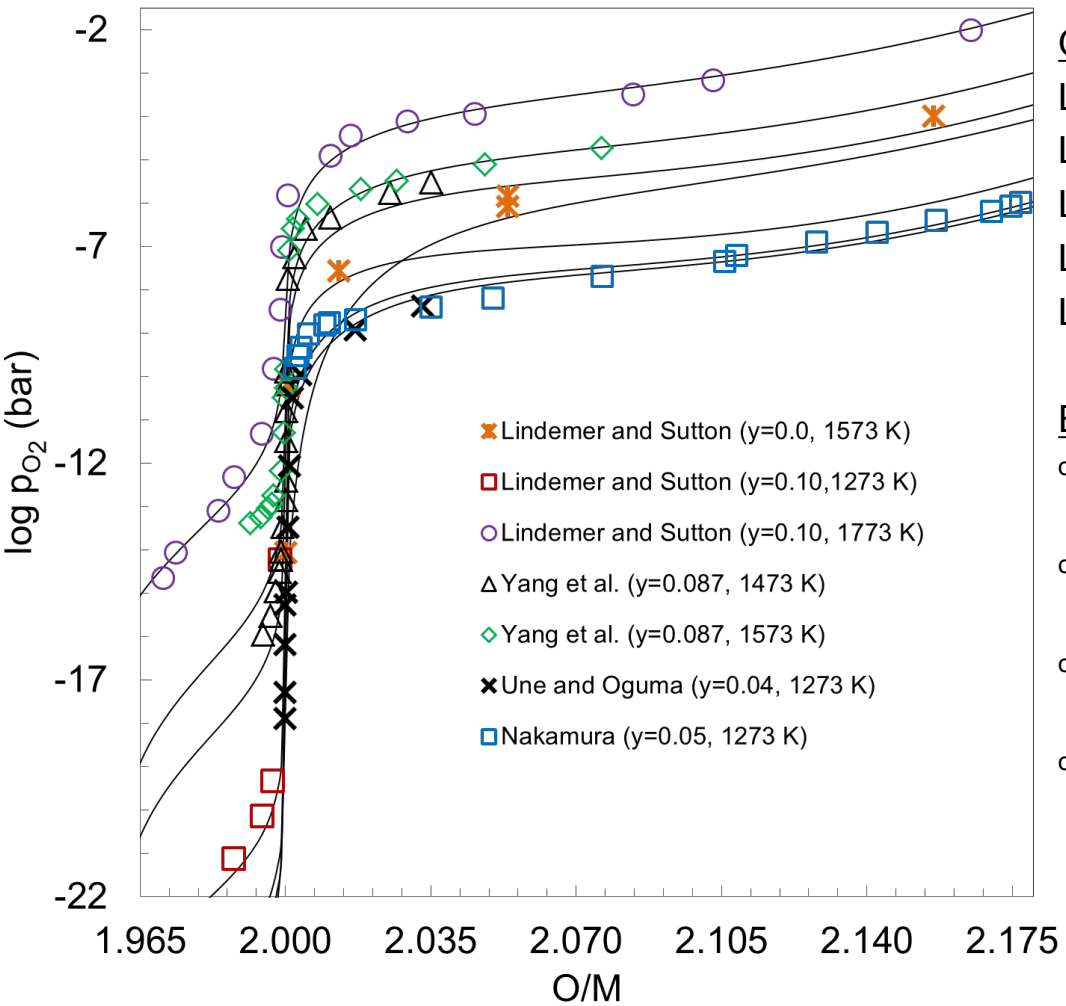


Current CEF for $UO_{2\pm x}$ considers only U^{3+} and U^{5+} uranium valencies and neglects clustering



Sickafus et al., Nature Materials 6 (2007)

Equilibrium oxygen pressures over $U_{1-y}Gd_yO_{2\pm x}$



<u>Optimized Parameters (J/mole)</u>

$L^0(U^{4+}\cdot Gd^{3+}:Va:Va) = -472289.19$

$L^0(U^{4+}\cdot Gd^{3+}:O:Va) = -48475.99$

$L^0(U^{5+}\cdot Gd^{3+}:O:O) = -427375.75$

$L^0(U^{5+}\cdot Gd^{3+}:Va:Va) = -786388.51 - 217.15\times T$

$L^0(U^{5+}\cdot Gd^{3+}:O:Va) = -62000.00$

<u>End-member adjustments</u>

$^oG_{Gd^{3+}:Va^0:Va^0} = \frac{1}{2}\,^oG_{Gd_2O_3} - 3/4\ O_2 + \Delta G^{CaF_2\text{-}Gd_2O_3} + 583600.31 - 34.68\times T$

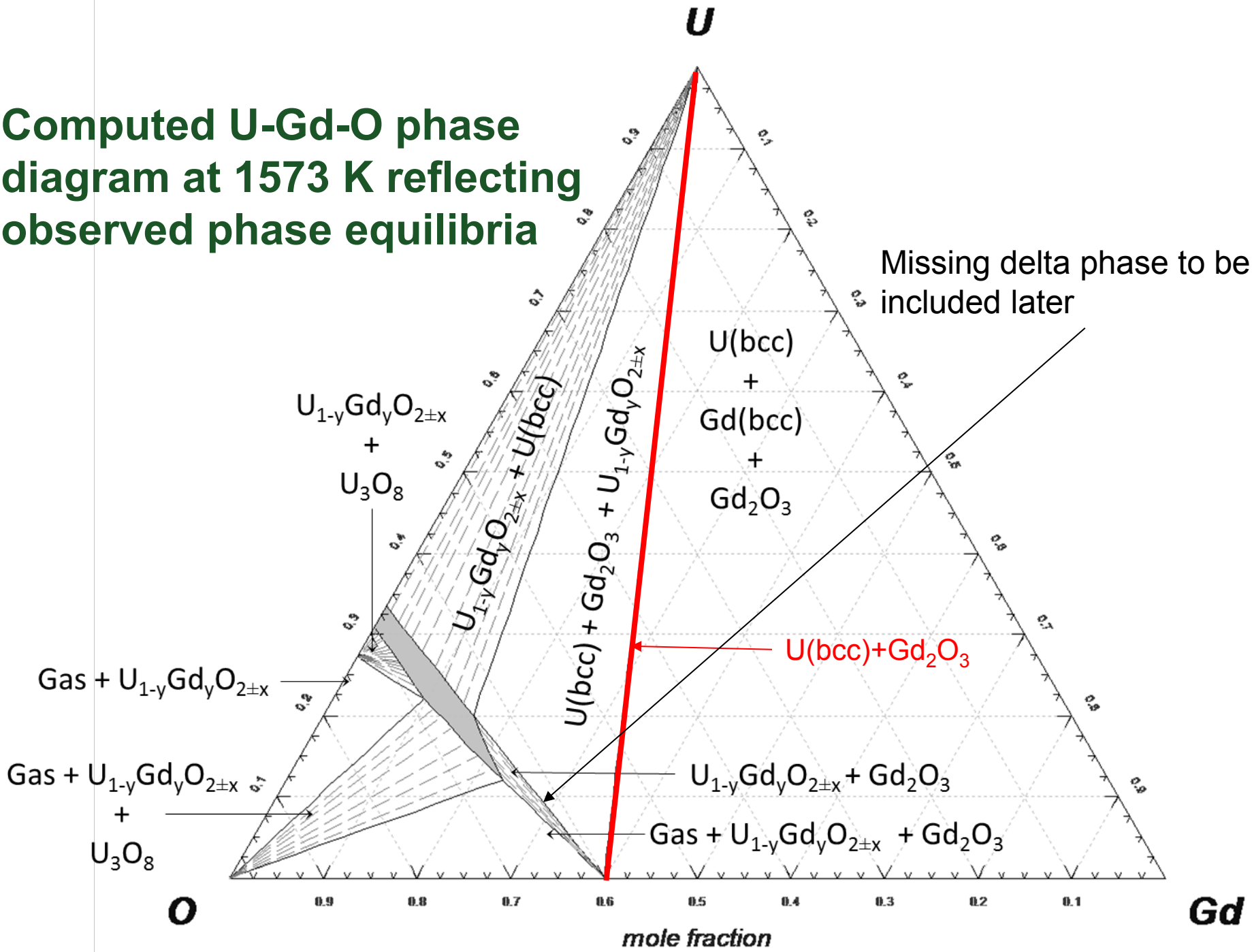
$^oG_{Gd^{3+}:O^{2-}:Va^0} = \frac{1}{2}\,^oG_{Gd_2O_3} + \frac{1}{4}\ O_2 + \Delta G^{CaF_2\text{-}Gd_2O_3} + 5080.00 - 287.68\times T$

$^oG_{Gd^{3+}:O^{2-}:O^{2-}} = \frac{1}{2}\,^oG_{Gd_2O_3} + 3/4\ O_2 + \Delta G^{CaF_2\text{-}Gd_2O_3} + 88469.00 - 359.68\times T$

$^oG_{Gd^{3+}:Va^0:Va^0} = +100000$

Points are reported experimental results and lines are from fitted model

Computed U-Gd-O phase diagram at 1573 K reflecting observed phase equilibria



The CEF for $U_{1-y}La_yO_{2\pm x}$

$U_{1-y}Gd_yO_{2\pm x}$ end-members

$U^{3+}:O^{2-}:O^{2-}$
$U^{3+}:O^{2-}:VA$
$U^{3+}:VA:O^{2-}$
$U^{3+}:VA:VA$
$U^{4+}:O^{2-}:O^{2-}$
$U^{4+}:O^{2-}:VA$
$U^{4+}:VA:O^{2-}$
$U^{4+}:VA:VA$
$U^{5+}:O^{2-}:O^{2-}$
$U^{5+}:O^{2-}:VA$
$U^{5+}:VA:O^{2-}$
$U^{5+}:VA:VA$
$U^{6+}:O^{2-}:O^{2-}$
$U^{6+}:O^{2-}:VA$
$U^{6+}:VA:O^{2-}$
$U^{6+}:VA:VA$
$La^{3+}:O^{2-}:O^{2-}$
$La^{3+}:O^{2-}:VA$
$La^{3+}:VA:O^{2-}$
$La^{3+}:VA:VA$

$$(U^{3+},U^{4+},U^{5+},U^{6+},La^{3+})_1(O^{2-},Va^0)_2(O^{2-},Va^0)_1$$

The U^{6+} uranium cation was added to better represent the reported phase equilibria.

U6+ containing end-member energies

$${}^oG_{U^{6+}:Va^0:Va^0} = {}^oG_{UO_2} - 3/4\ O_2 - 570600.52 + 43.38\times T$$

$${}^oG_{U^{6+}:O^{2-}:Va^0} = {}^oG_{UO_2} - 25390.31 + 77.42\times T$$

$${}^oG_{U^{6+}:O^{2-}:O^{2-}} = {}^oG_{UO_2} + 3/4\ O_2 - 25390.43 + 45.94\times T$$

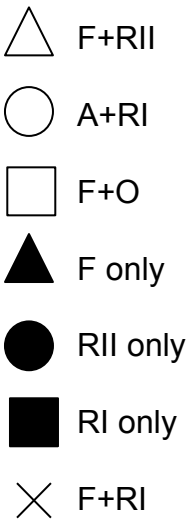
$${}^oG_{U^{6+}:Va^0:O^{2-}} = 10^6 + 0\times T$$

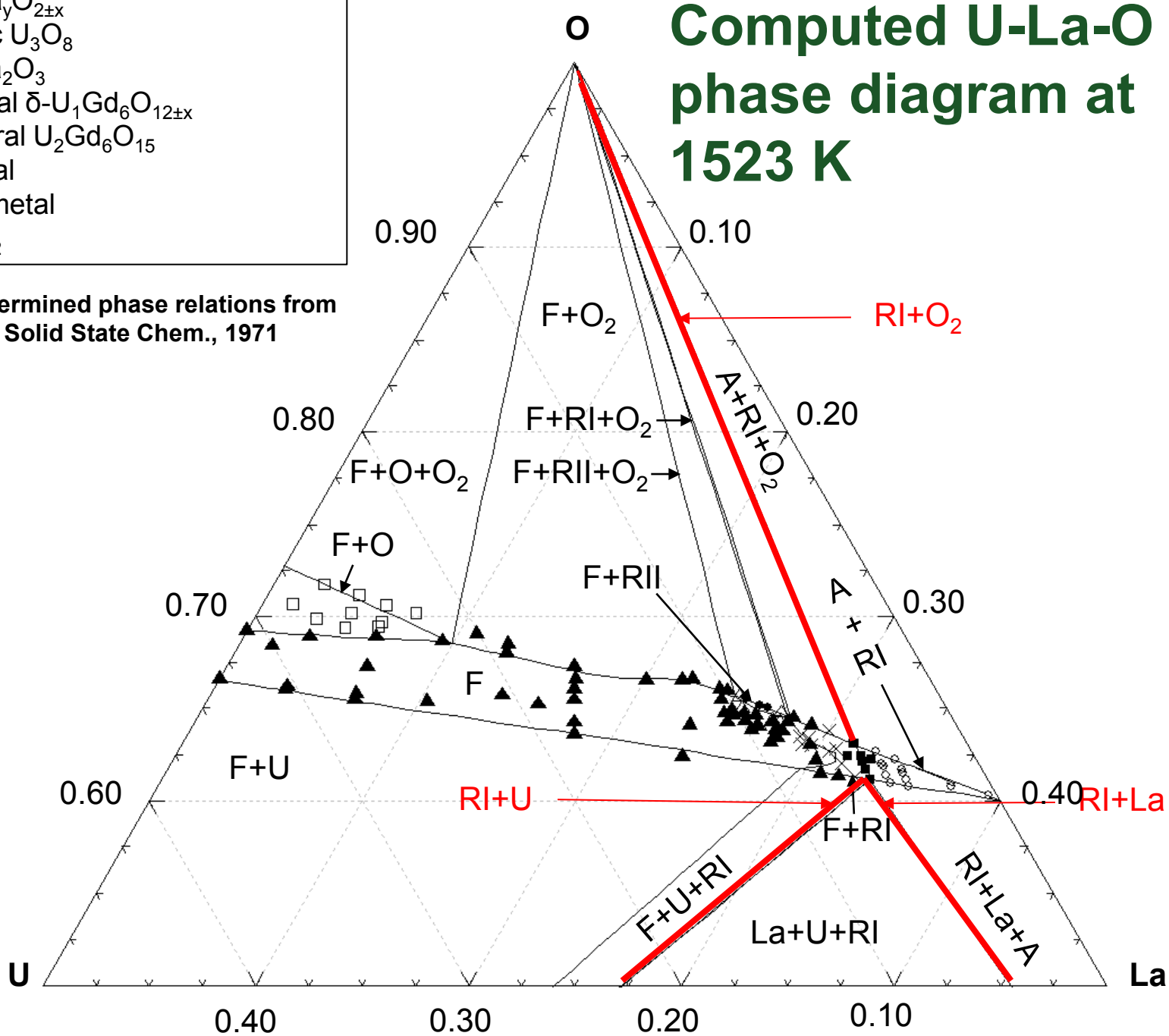
Note: For pure fluorite urania the U^{6+}, concentration will remain negligible under all conditions.

Computed U-La-O phase diagram at 1523 K

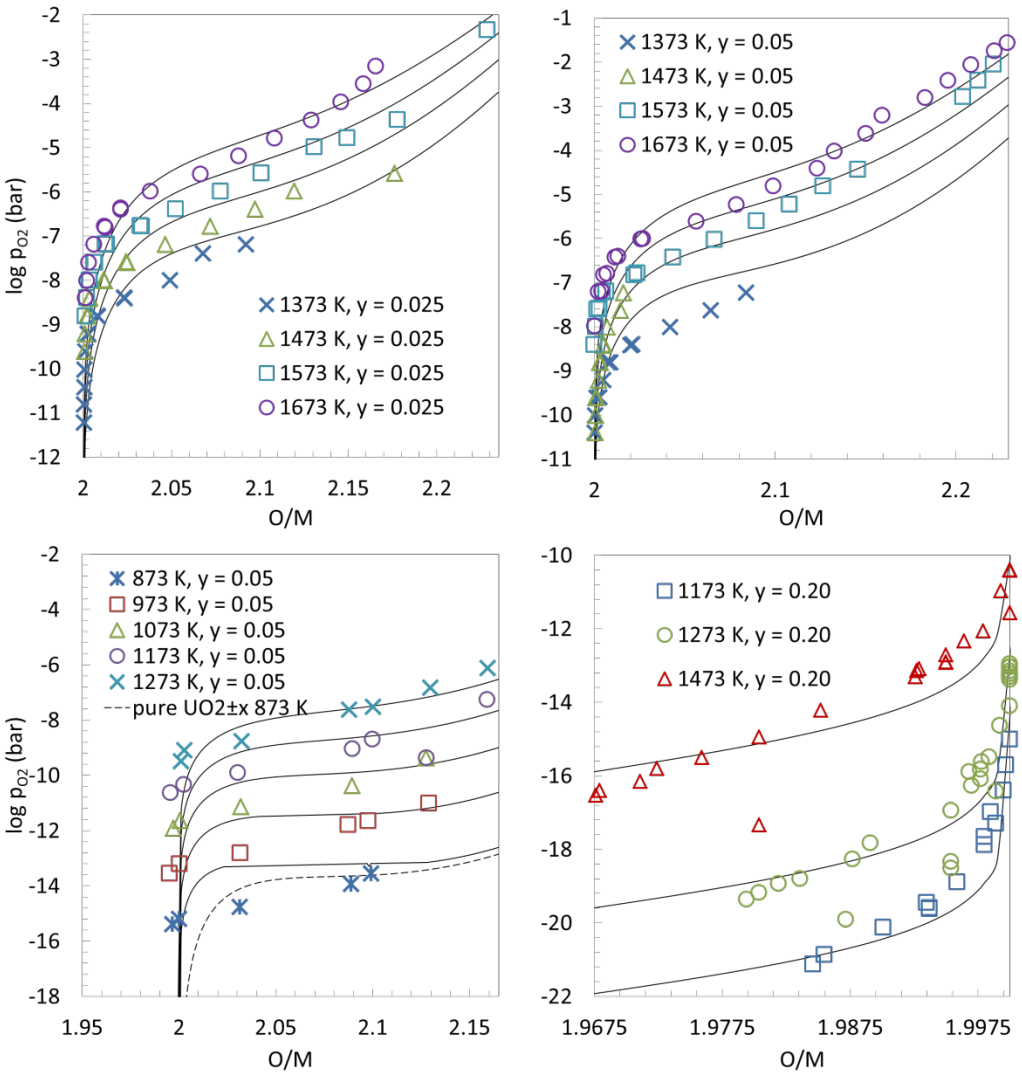
F = fluorite $U_{1-y}La_yO_{2\pm x}$
O = orthorhombic U_3O_8
A = hexagonal La_2O_3
RI = rhombohedral δ-$U_1Gd_6O_{12\pm x}$
RII = rhombohedral $U_2Gd_6O_{15}$
U = uranium metal
La = lanthanum metal
O_2 = ideal gas O_2

Experimentally determined phase relations from Diehl and Keller, J. Solid State Chem., 1971





Equilibrium oxygen pressures over $U_{1-y}La_yO_{2\pm x}$



Optimized Parameters (J/mole)

$L^0(U^{4+}\cdot La^{3+}:O:Va) = -48198.70$

$L^0(U^{4+}\cdot La^{3+}:Va:Va) = -472248.79$

$L^0(U^{5+}\cdot La^{3+}:O:O) = -427681.07$

$L^0(U^{5+}\cdot La^{3+}:O:Va) = -9350.00 - 50.00\times T$

$L^0(U^{5+}\cdot La^{3+}:Va:Va) = -786023.31 - 217.00\times T$

$L^0(U^{6+}\cdot La^{3+}:O:Va) = -75000.000$

End-member adjustments

$^oG_{La^{3+}:Va^0:Va^0} = \frac{1}{2}\,^oG_{La_2O_3} - 3/4\ O_2 + \Delta G^{CaF_2\text{-}La_2O_3} + 472436.32 - 58.94\times T$

$^oG_{La^{3+}:O^{2-}:Va^0} = \frac{1}{2}\,^oG_{La_2O_3} + \frac{1}{4}\ O_2 + \Delta G^{CaF_2\text{-}La_2O_3} + 12482.59 - 103.92\times T$

$^oG_{La^{3+}:O^{2-}:O^{2-}} = \frac{1}{2}\,^oG_{La_2O_3} + 3/4\ O_2 + \Delta G^{CaF_2\text{-}La_2O_3} + 12360.69 - 33.27\times T$

$^oG_{La^{3+}:Va^0:O^{2-}} = 10^6 + 0\times T$

Points are reported oxygen potential data from Hagemark and Broli, Stadlebauer et al., and Yoshida et al. Lines are computed from the model

Summary

- **Although U^{6+} is present in trivalent doped urania, negligible concentration seen in pure urania, which is supported by reported first principles calculations**
- **$U_{1-y}Gd_yO_{2\pm x}$ so far treated without U^{6+}, but issue will be addressed**
  - $(U^{3+},U^{4+},U^{5+},U^{6+},Gd^{3+})_1(O^{2-},Va^0)_2(O^{2-},Va^0)_1$
- **$U_{1-y}La_yO_{2\pm x}$ modeled with U^{6+}, to address phase diagram issues**
  - $(U^{3+},U^{4+},U^{5+},U^{6+},La^{3+})_1(O^{2-},Va^0)_2(O^{2-},Va^0)_1$
- **The rhombohedral phases δ-$U_1La_6O_{12-x}$ and $U_2La_6O_{15}$ were given Gibbs energies that best reproduce phase equilibria at 1523 K as an expedient until homogeneity range can be represented by a solution**