

2005 TMS Annual Meeting

Multicomponent Multiphase Diffusion Symposium in Honor of J. E. MORRAL
San Francisco, CA, February 13-17, 2005

Oxygen Diffusivity in CeO_{2-x}

P. Cristea and M. Stan

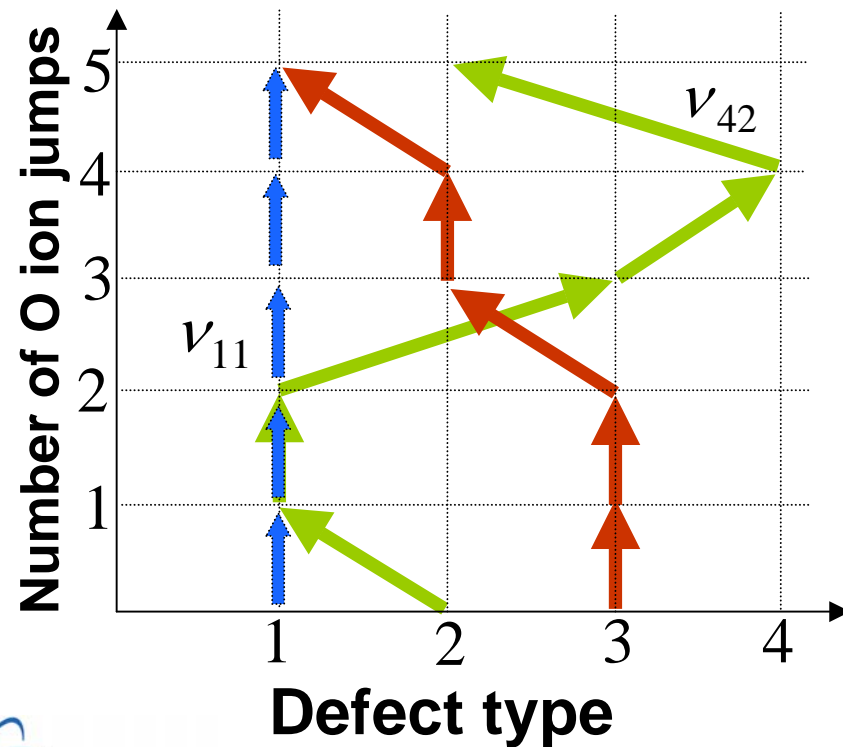
Los Alamos National Laboratory, NM, U.S.A.

Outline

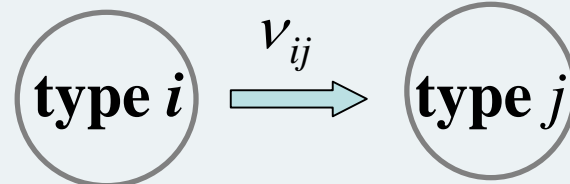
- Background and definitions
- Jumping Scenario
- Model of Diffusivity
- Results
- Conclusions and Future Work

Background

The diffusion jumps change the identity of point defects



JUMP FREQUENCIES



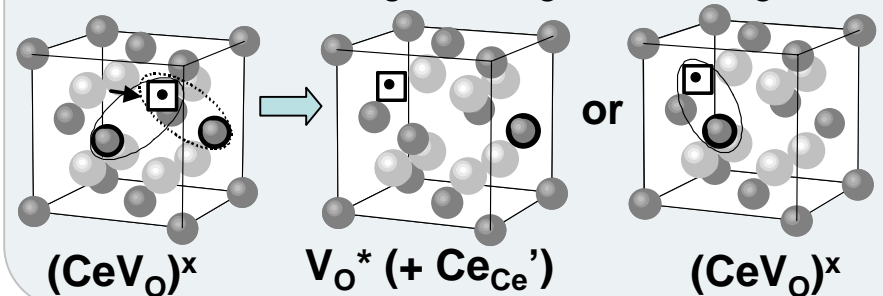
Arrhenius type dependency

$$v_{ij} = v_{0,ij} \exp(-E_{m,ij} / k_B T)$$

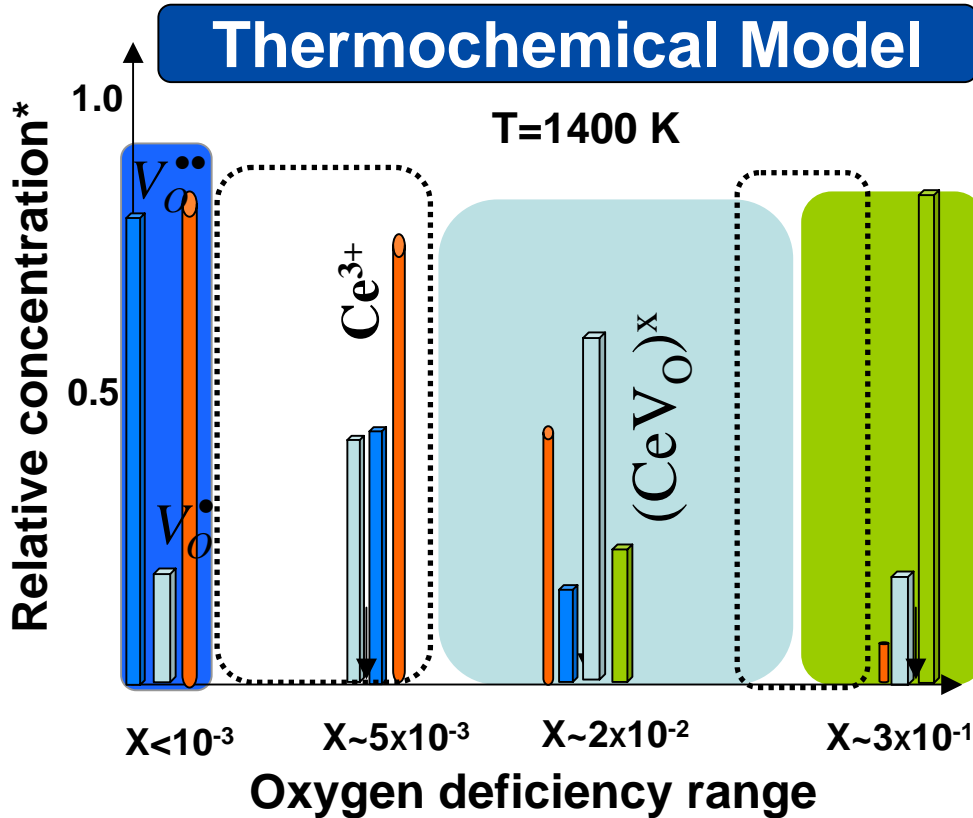
MIGRATION ENERGIES

$$E_{m,ij} = E_{m,ij}(T, x)$$

Example: $(\text{CeV}_\text{O})^x \rightarrow \text{V}_\text{O}^* \text{ or } (\text{CeV}_\text{O})^x$



Jumping Scenario



*NOTE: the scale for Ce^{3+} concentration is different

Jumping Scenario

Defect site	Jumping Ion	
	O^{1-}	O^{2-}
V_O^{\bullet}	$V_O^{\bullet}, (CeV_O)^x$	$V_O^{\bullet\bullet} \oplus Ce', (CeV_O)^{\bullet}$
$V_O^{\bullet\bullet}$	$V_O^{\bullet}, (CeV_O)^x$	$V_O^{\bullet\bullet}, (CeV_O)^{\bullet}$
$(CeV_O)^{\bullet}$	$V_O^{\bullet}, (CeV_O)^x$	$V_O^{\bullet\bullet} \oplus Ce', (CeV_O)^{\bullet}$
$(CeV_O)^x$	$V_O^{\bullet} \oplus Ce', (CeV_O)^x$	$V_O^{\bullet\bullet} \oplus 2Ce', (CeV_O)^{\bullet} \oplus Ce'$

Conclusion

- O^{2-} ions mediate the oxygen diffusion close to the stoichiometric range only;
- O^{1-} ions control the oxygen diffusion in the intermediate and high nonstoichiometry region.

Model of Oxygen Self-Diffusivity

❑ DIFFICULTIES

- **Extensive atomistic calculations** are required to evaluate the formation and the migration of oxygen defect species;
- **The short time involved** in such calculations (hundreds of ps, at the most) may lead to uncertainties in calculated self-diffusivities.

❑ WORKING AROUND

- Define an *average jumping frequency*:

$$v(x, T) = v_0 \exp\left(-\frac{E_m}{k_B T}\right) \exp\left[-\frac{E_f(x, T)}{k_B T}\right]$$

❑ The *average formation energy* $E_f(x, T)$ was numerically calculated using a thermo-chemical approach;

❑ An *average migration energy* $E_m = 0.55$ eV (atomistic modeling) was used in calculations ($v_0 = 3 \times 10^{13} \text{ s}^{-1}$)

Model of Oxygen Self-Diffusivity (Continued)

□ The oxygen self-diffusivity:

$$D_s(x, T) = (a_o^2 / 24)v(x, T)f_{av}(x)$$



lattice constant = 5.4 Å

average correlation factor

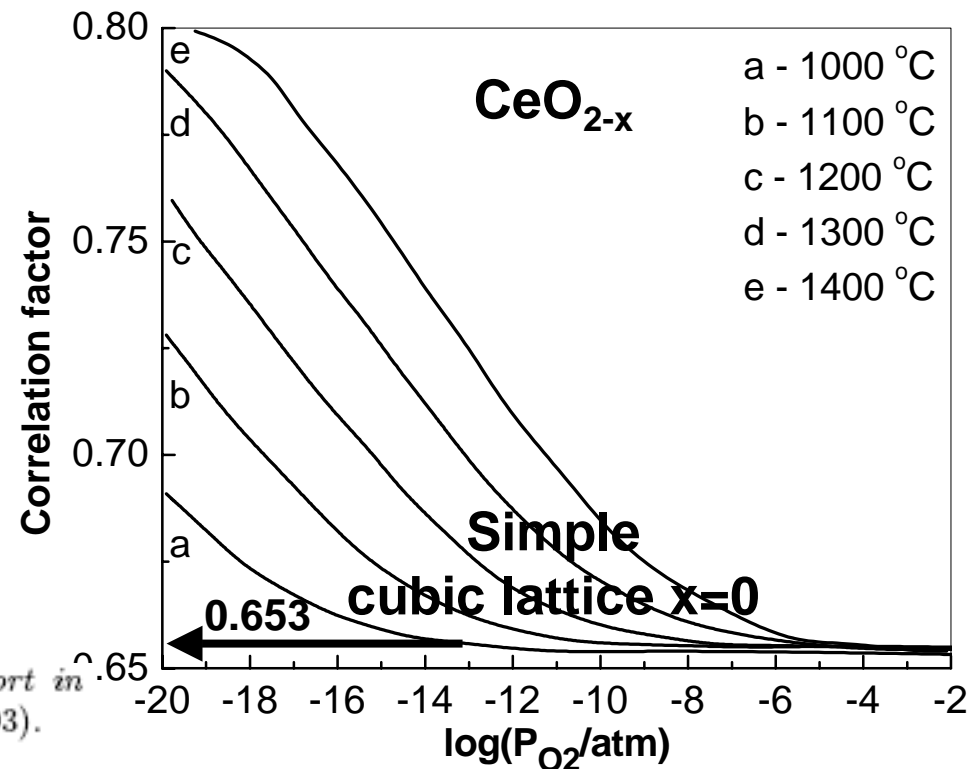
$$f_{av}(x) = \sum_{\alpha} (x_{\alpha} / x) f(x_{\alpha})$$

$$f(x_{\alpha}) = \frac{1}{1 + \frac{[1 - (x_{\alpha} / 2)](1 - f_o)}{[1 + (x_{\alpha} / 2)]f_o}}$$



A. R. Allnatt and A. B. Lidiard, *Atomic Transport in Solids* (Cambridge University Press, Cambridge, 1993).

Calculated Correlation Factor



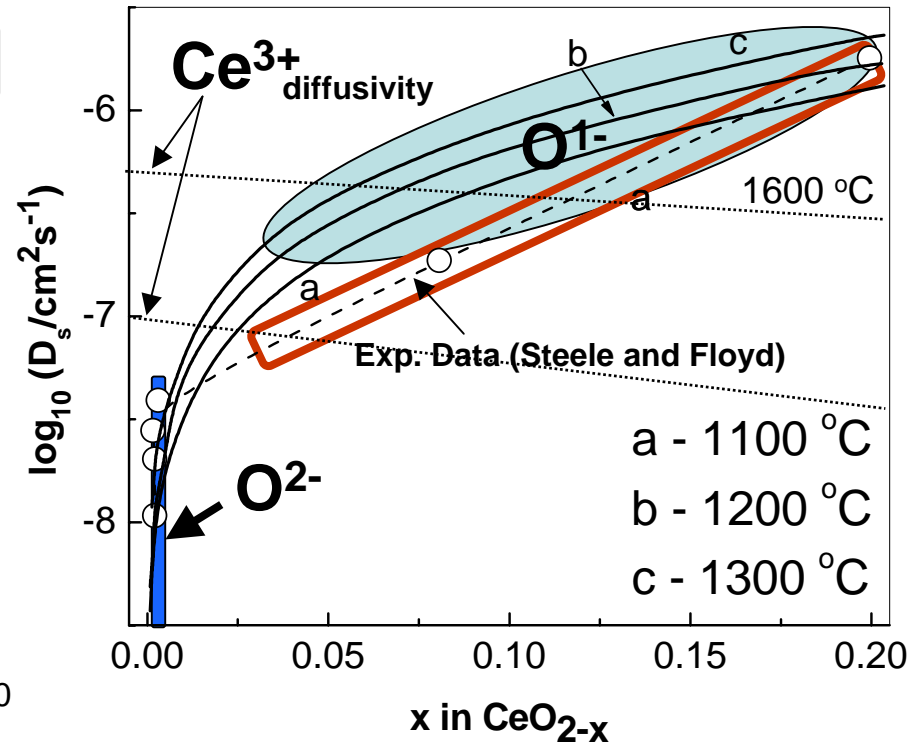
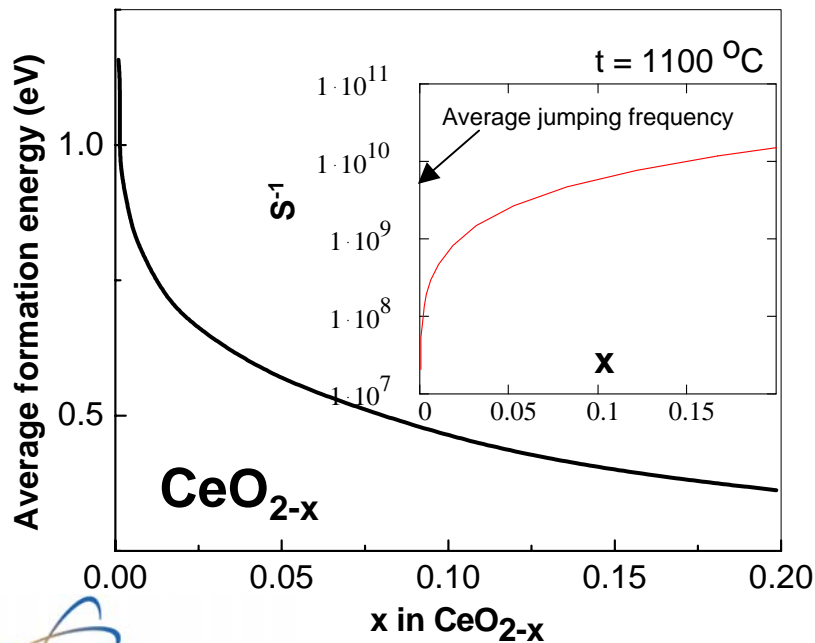
Model of Oxygen Self-Diffusivity (Continued)

□ The oxygen self-diffusivity:

$$D_s(x, T) = (a_o^2 / 24)v(x, T)f_{av}(x)$$

Calculated Self-Diffusivities

Average Formation Energy



Conclusions and Future Work

- ❑ The average formation energy decreases with increasing the nonstoichiometry from **1.3 eV close to $x=0$, to 0.4 eV, close to $x=0.2$** ; the temperature has only little influence on this trend;
- ❑ **The O^{2-} ions control the self-diffusivity close to the stoichiometric domain; the intermediate and the high nonstoichiometric domain is controlled by the O^{1-} ions.**
This conclusion follows from the particular assumption about the nature of the defect species in ceria.
- ❑ **A first principles based calculation of self-diffusivity in ceria still represents a very difficult problem due to the complex nature of defect species.**

FUTURE WORK

- ❑ Extend the calculations to similar lattices, such as PuO_{2-x} and $UO_{2\pm x}$.
- ❑ Retrieve the free energy of defect migration and defect formation from electronic structure and atomistic calculations.