Diffusion in Oxides –
here: Oxygen Ion Conductors

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Walther Nernst

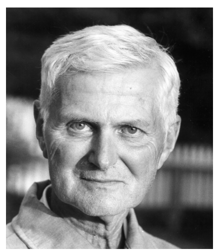
Nernst Glower
Deutsches Patent
Nr. 104872 vom 6.7.1897

filament

Filament (Nernstmasse)

Chalk, magnesia, zirconia, rare earths

Carl Wagner



Über den Mechanismus der elektrischen Stromleitung im Nernststift, *Naturwissenschaften* 31 (1943) 265.

Zr^{4+} Zr^{4+} Zr^{4+} Zr^{4+} Zr^{4+}
O^{2-} O^{2-} O^{2-} O^{2-} O^{2-}
O^{2-} O^{2-} O^{2-} O^{2-} O^{2-}
Zr^{4+} Zr^{4+} Zr^{4+} Zr^{4+} Zr^{4+}
O^{2-} O^{2-} O^{2-} O^{2-} O^{2-}
O^{2-} O^{2-} O^{2-} O^{2-} O^{2-}

+

Y^{3+}
Y^{3+}
O^{2-}
O^{2-}
O^{2-}

=

Zr^{4+} Zr^{4+} Zr^{4+} Zr^{4+} Zr^{4+} Y^{3+}
O^{2-} O^{2-} O^{2-} O^{2-} O^{2-} O^{2-}
O^{2-} O^{2-} O^{2-} O^{2-} O^{2-} □
Zr^{4+} Zr^{4+} Zr^{4+} Zr^{4+} Zr^{4+} Y^{3+}
O^{2-} O^{2-} O^{2-} O^{2-} O^{2-} O^{2-}
O^{2-} O^{2-} O^{2-} O^{2-} O^{2-} O^{2-}

Y'_{Zr}

$V_O^{\bullet\bullet}$

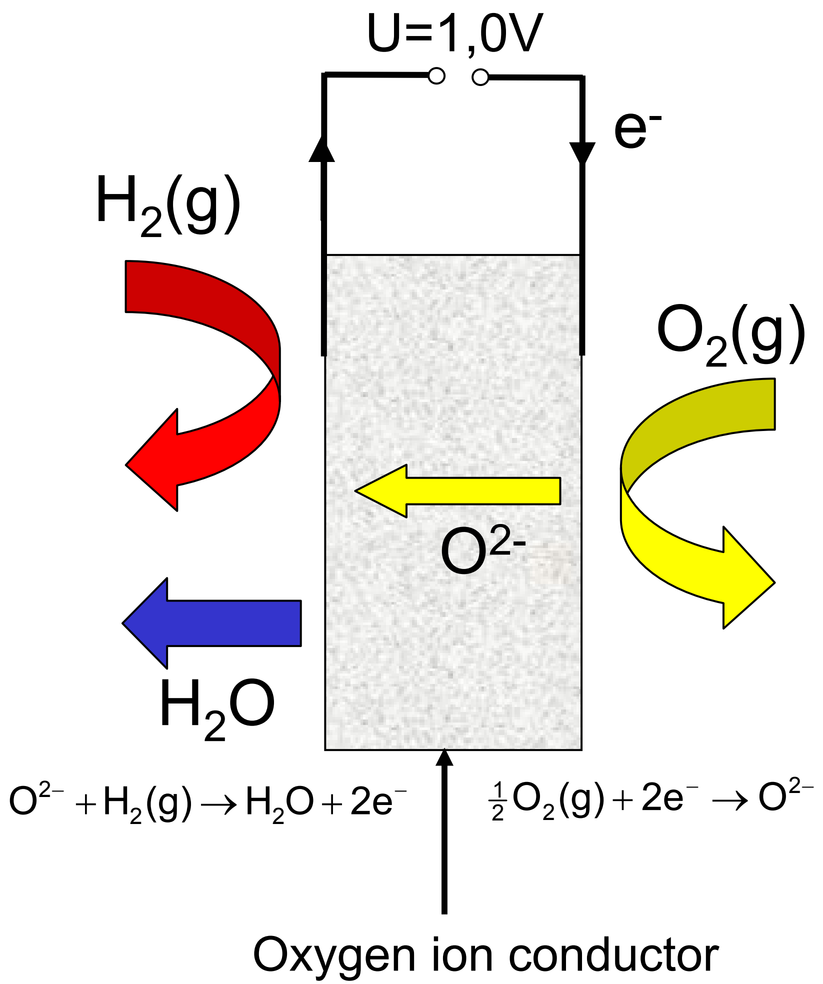
$$[Y'_{Zr}] = 2[V_O^{\bullet\bullet}]$$

Majority defects

Vacancies,

in Rome already known 27 BC

Solid Oxide Fuel Cell (SOFC)



800-1000°C

Ionic conductivities of oxide electrolytes: $\sigma \propto D_V \cdot c_V$

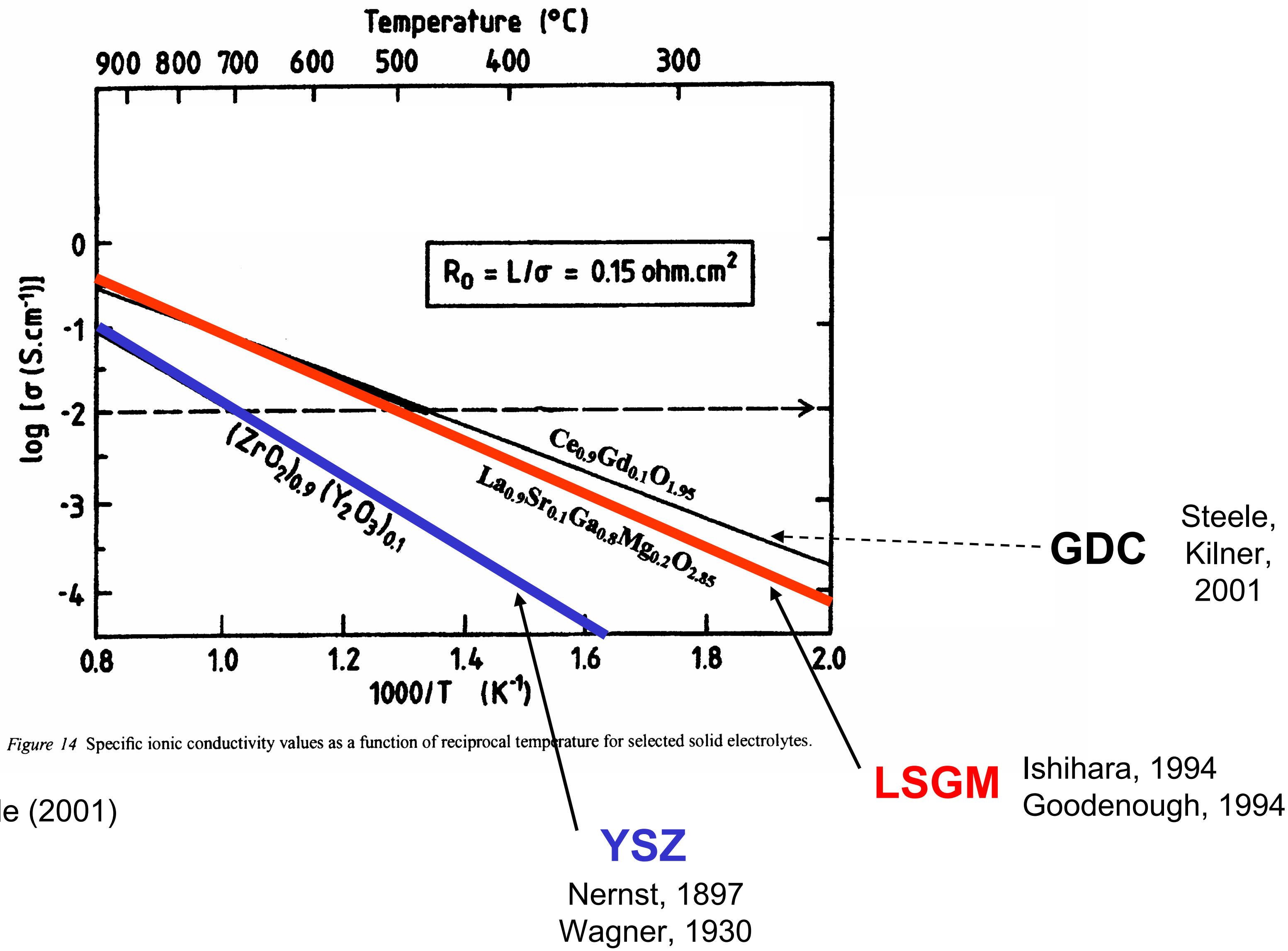
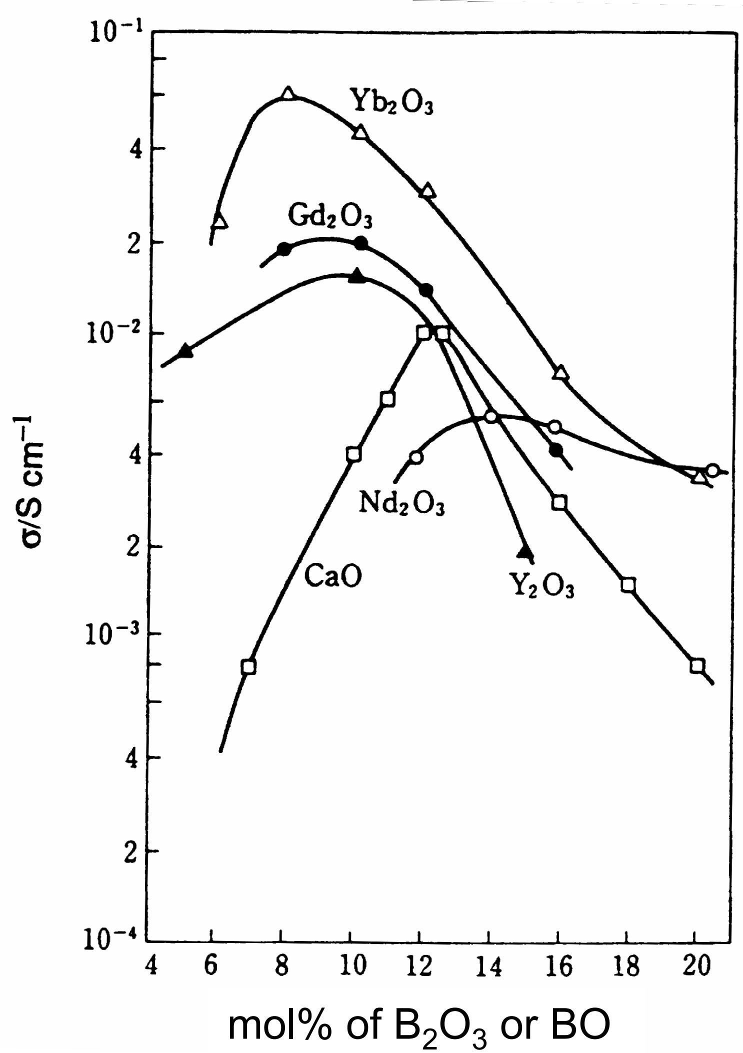


Figure 14 Specific ionic conductivity values as a function of reciprocal temperature for selected solid electrolytes.

B.C.H. Steele (2001)

Ionic conductivities of doped ZrO_2 : $\sigma \propto D_V \cdot c_V$



H. Tannenberger (1965)

Maximum due to:

- defect clusters
- defect ordering

→ number of mobile oxygen vacancies decreases

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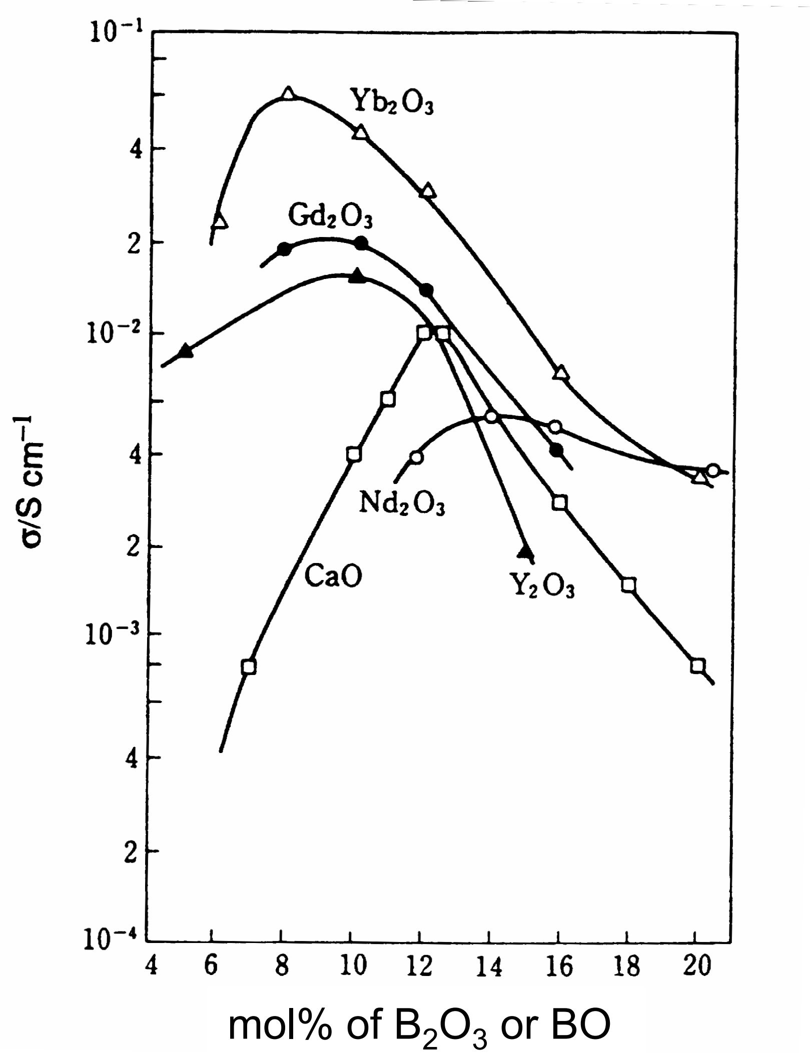
Ionic conductivities of doped ZrO_2 : $\sigma \propto D_V \cdot c_V$



H. Tannenberger (1965)

Maximum due to:

- defect clusters
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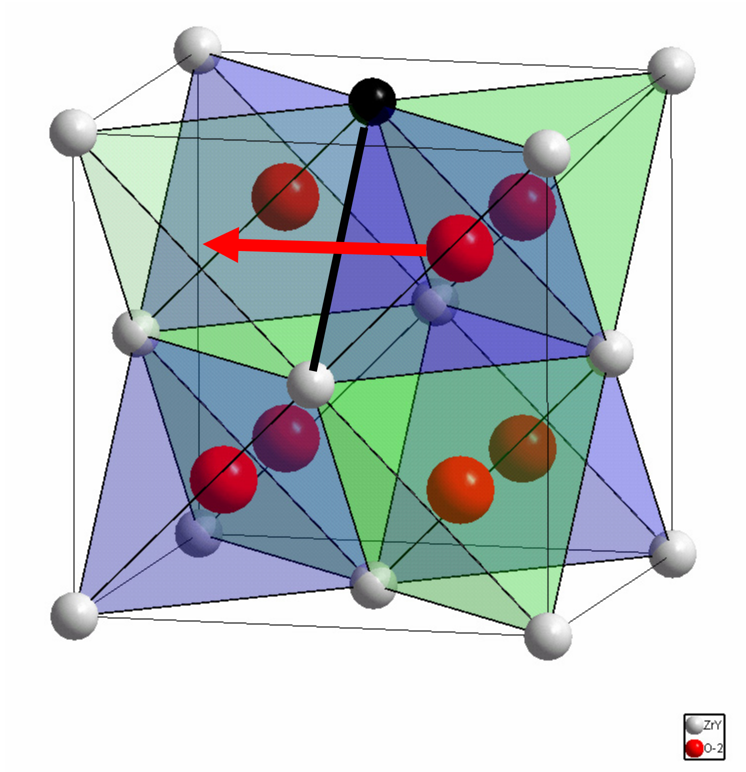
→ number of mobile oxygen vacancies decreases

$B'_A - V_O^{\bullet\bullet}$

- undersized cations: nn
- oversized cations: nnn

Cluster at 10 – 20 % dopant level ?

YSZ (fluorite structure)



Shimojo et al. (1992): MD

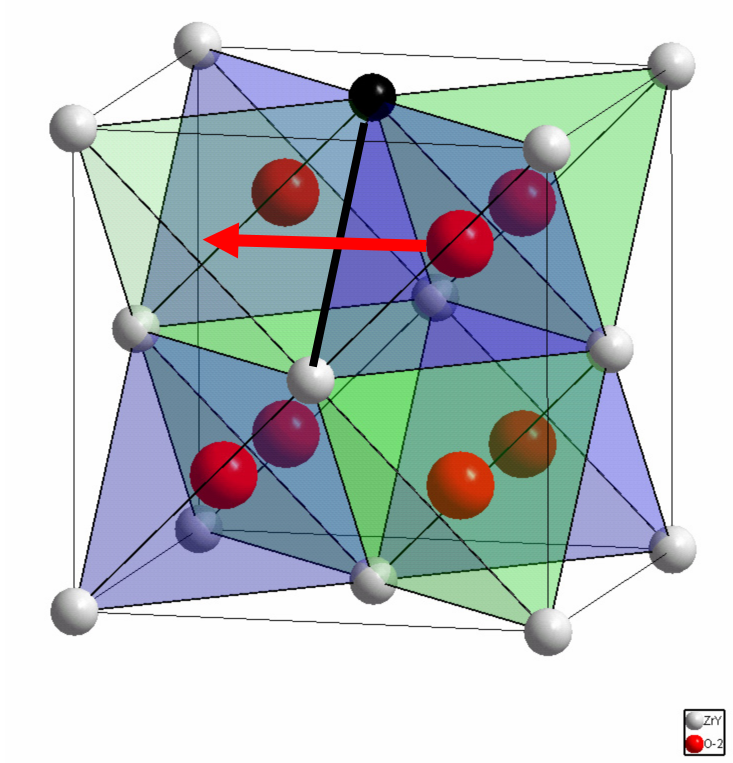
Krishnamurthy et al. (2004): DFT

Edge	E_{AB} / eV
Zr – Zr	0.58
Zr - Y	1.29
Y - Y	1.86

Y – Y edges are „blocking“

→ maximum in σ_{oxygen}

YSZ (fluorite structure)



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Edge	E_{AB} / eV
Zr – Zr	0.58
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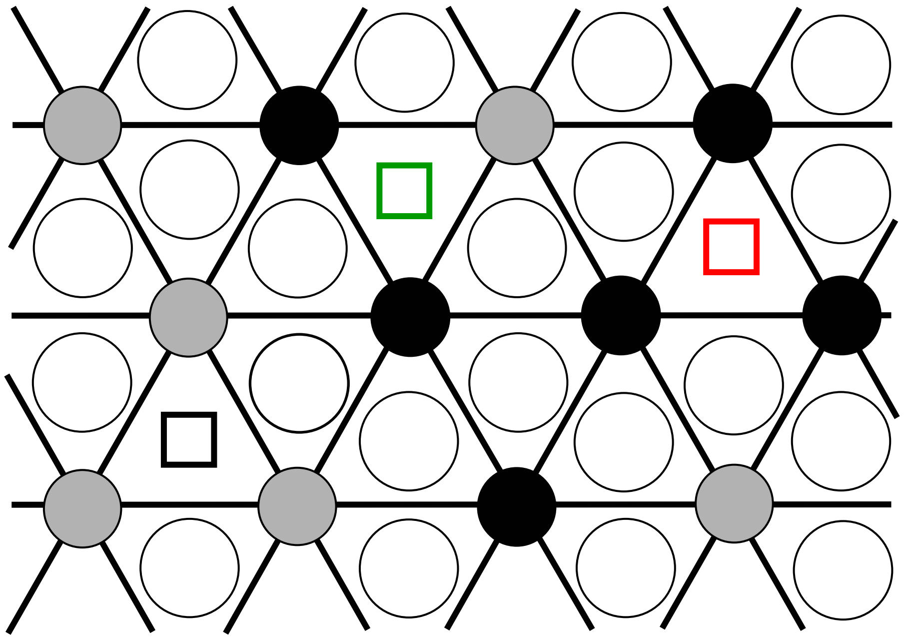
Y – Y edges are „blocking“

→ maximum in σ_{oxygen}

But: no Y-V_O interactions

random vacancy distribution

Concentrated solution of (A_A,B_A) and (O_O,V_O)



Only nearest neighbor interactions B_A-V_O

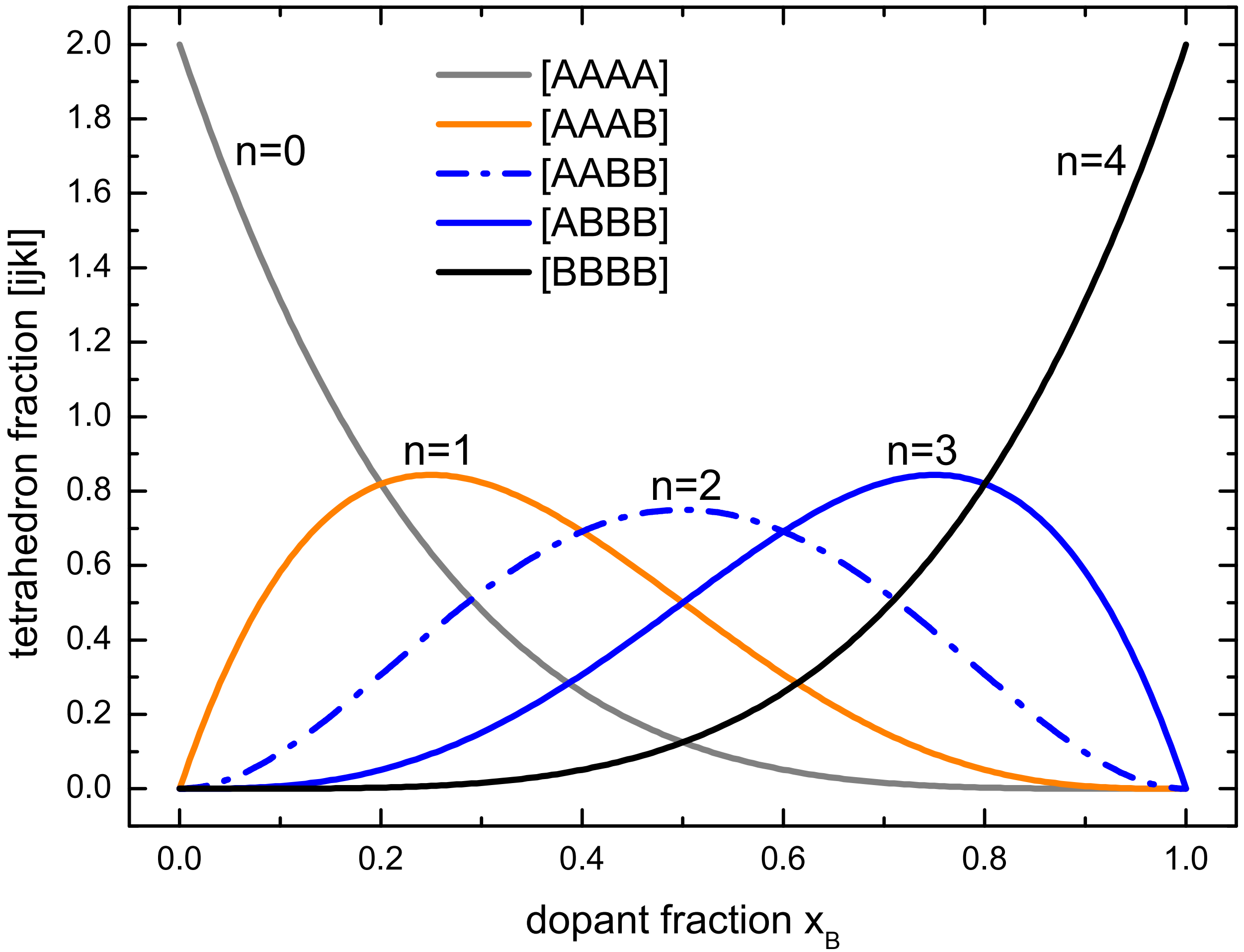
Simple model for the oxygen ion conductivity:

1. Random cation distribution, immobile cations
2. Oxygen vacancy distribution (random, non-random)
3. Vacancy jump types
4. Ionic conductivity

1. Random cation distribution

$$f_n(x_B) = 2\binom{4}{n} x_B^n (1 - x_B)^{4-n}$$

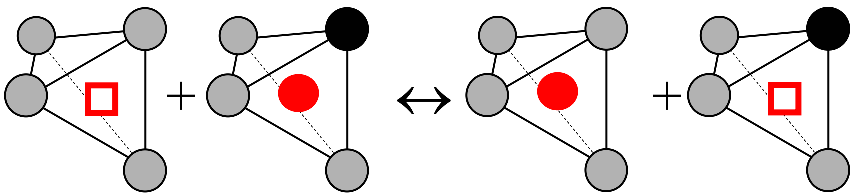
fraction of tetrahedra with n B-cations



2. Vacancy distribution: $(Zr^{4+}_{1-y}\,Y^{3+}_{y})O^{2-}_{2-x/2}$ or $(Zr^{x}_{1-y}\,Y'_{y})(O^{x}_{2-y/2}V^{\bullet\bullet}_{y/2})$

attractive

$$V_{AAAA} + O_{AAAB} \longleftrightarrow O_{AAAA} + V_{AAAB}$$



$$K_1 = \frac{[O_{AAAA}]\cdot[V_{AAAB}]}{[V_{AAAA}]\cdot[O_{AAAB}]} \qquad K_1 = \exp\left(-\frac{\Delta E_1}{kT}\right)$$

$$V_{AAAA} + O_{AABB} \longleftrightarrow O_{AAAA} + V_{AABB}$$

$$K_2 = \frac{[O_{AAAA}]\cdot[V_{AABB}]}{[V_{AAAA}]\cdot[O_{AAABB}]} \qquad K_2 = \exp\left(-\frac{\Delta E_2}{kT}\right)$$

$$V_{AAAA} + O_{ABBB} \longleftrightarrow O_{AAAA} + V_{ABBB} \qquad \cdots$$

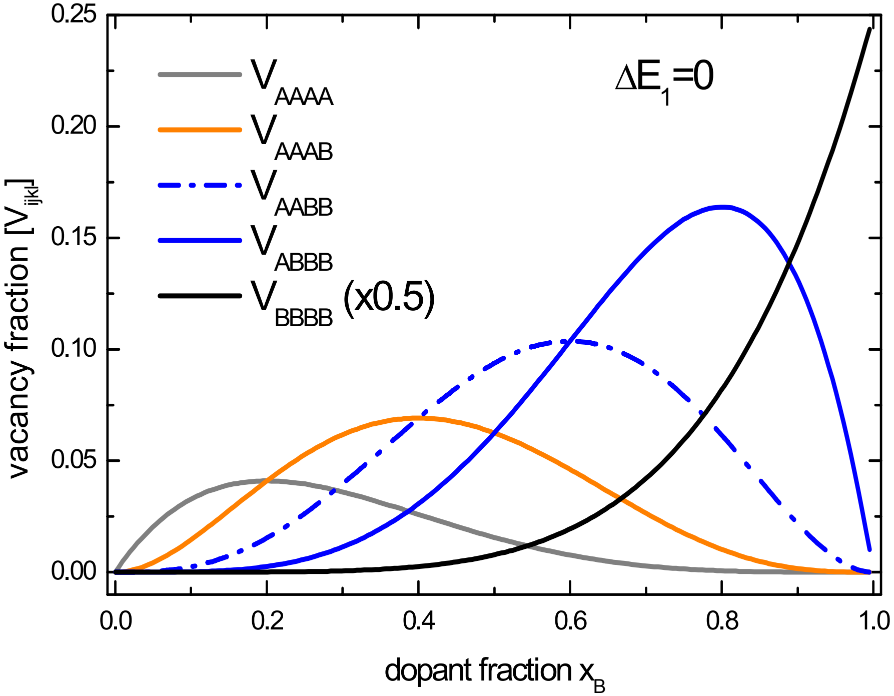
$$V_{AAAA} + O_{BBBB} \longleftrightarrow O_{AAAA} + V_{BBBB} \qquad \cdots$$

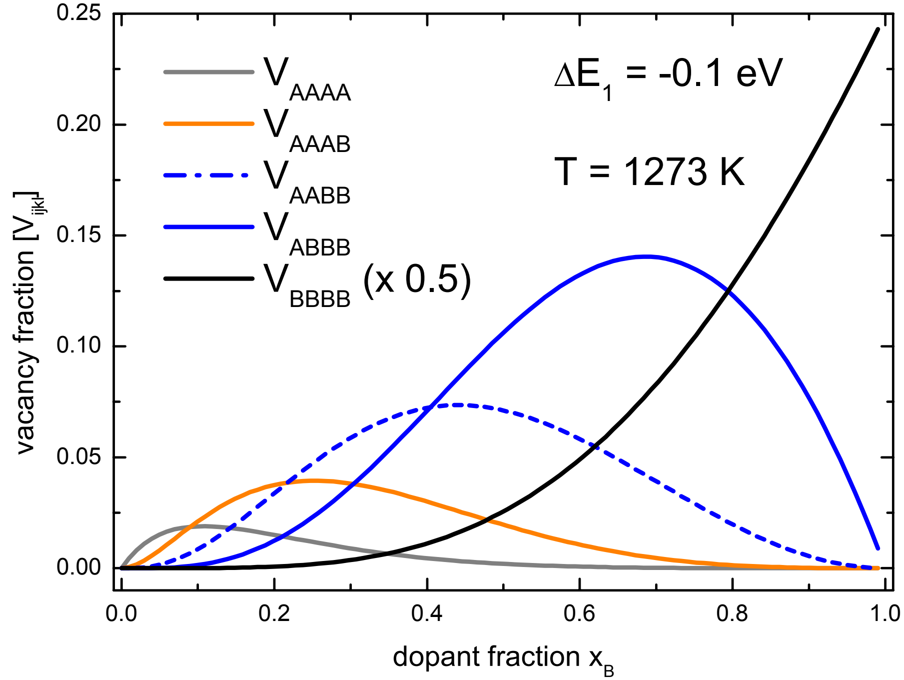
Charge neutrality

$$x_B = 2([V_{AAAA}] + [V_{AAAB}] + [V_{AABB}] + [V_{ABBB}] + [V_{BBBB}])$$

- no B-V interaction
- random vacancy distribution

- attractive B-V interaction
- non-random vacancy distribution

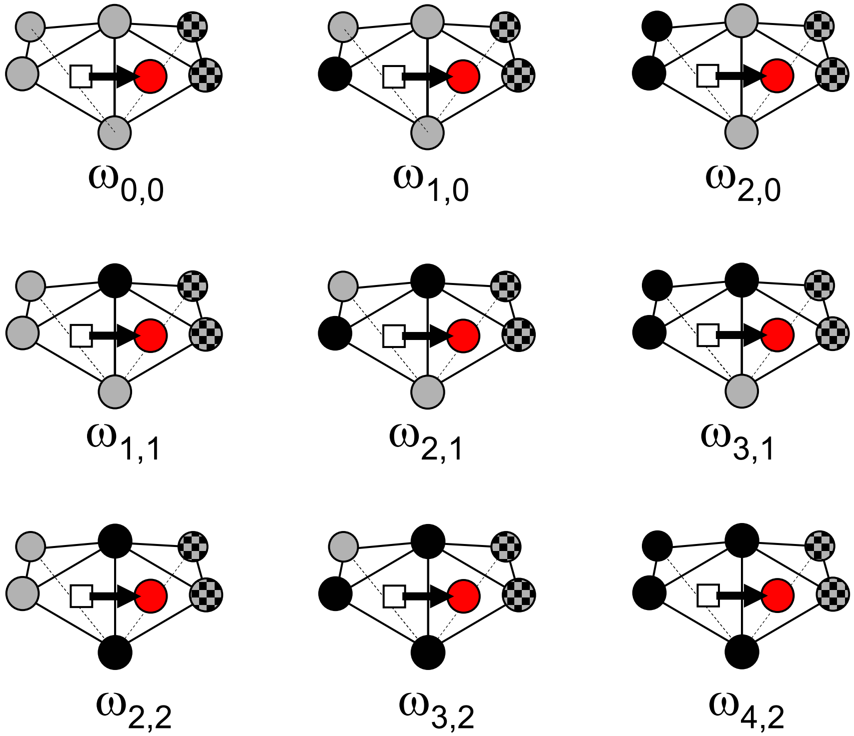




more vacancies in
B-containing tetrahedra

$$\Delta E_n = n \cdot \Delta E_1$$

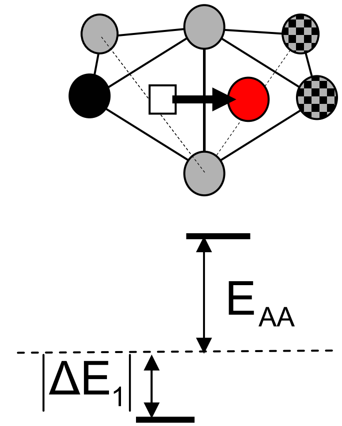
3. Jump types



Site energies

$$\Delta E_n = n \cdot \Delta E_1$$

$n = 0,1,2,3,4$

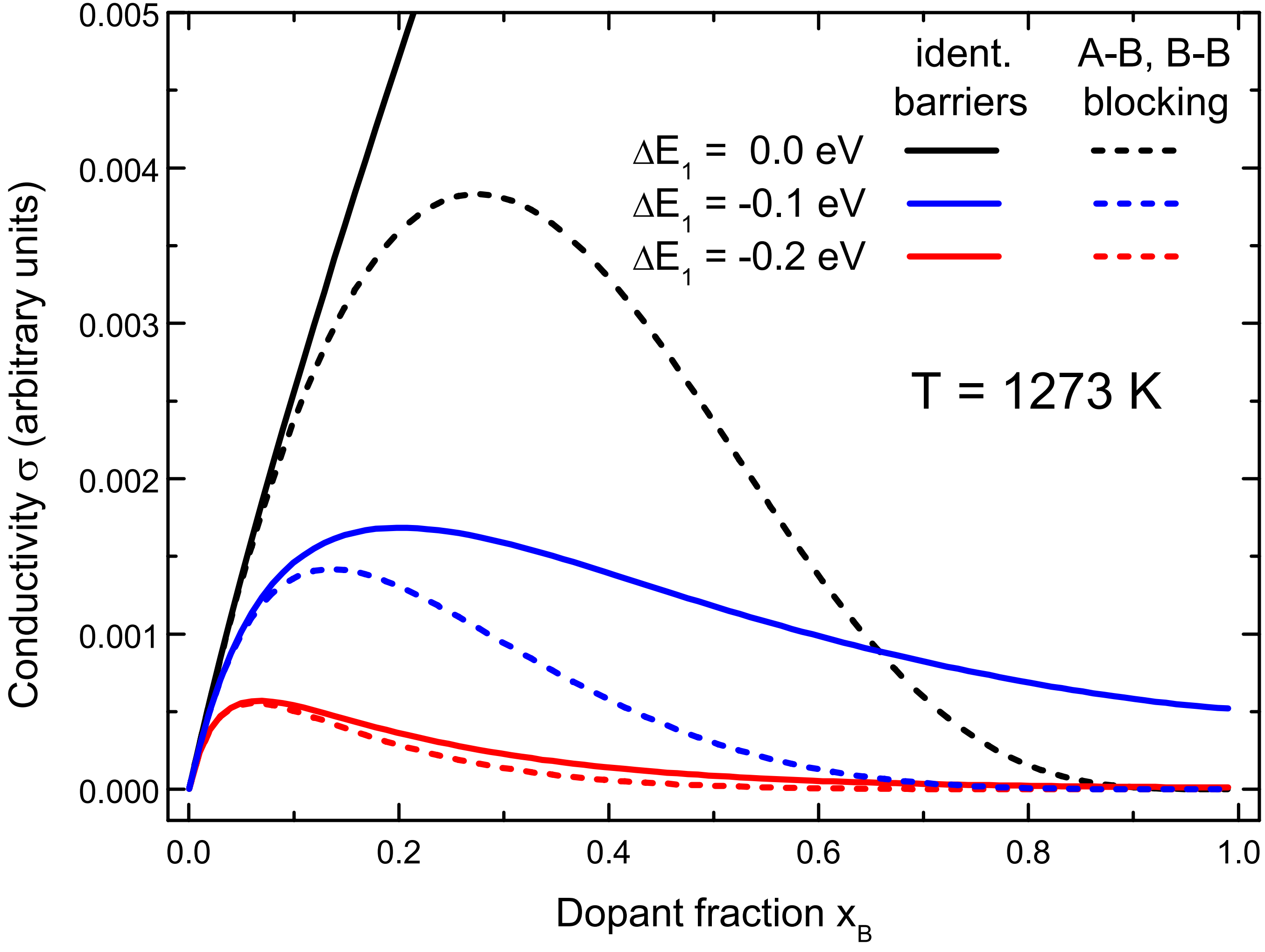


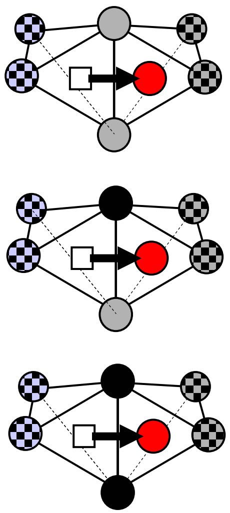
4. Oxygen ion conductivity

$$\begin{aligned}\sigma \propto \Big(& [V_{AAAA}] \cdot 6 \cdot \omega_{0,0} \cdot ([O_{AAAA}] + [O_{AAAB}] + [O_{AABB}]) \\ & + [V_{AAAB}] \cdot \{ 3 \cdot \omega_{1,0} \cdot ([O_{AAAA}] + [O_{AAAB}] + [O_{AABB}]) + 3 \cdot \omega_{1,1} \cdot ([O_{AAAB}] + [O_{AABB}] + [O_{ABBB}]) \} \\ & + [V_{AABB}] \cdot \left\{ \begin{array}{l} + \omega_{2,0} \cdot ([O_{AAAA}] + [O_{AAAB}] + [O_{AABB}]) + \omega_{2,2} \cdot ([O_{AABB}] + [O_{ABBB}] + [O_{BBBB}]) \\ + 4\omega_{2,1} \cdot ([O_{AAAB}] + [O_{AABB}] + [O_{ABBB}]) \end{array} \right\} \\ & + [V_{ABBB}] \cdot \{ 3 \cdot \omega_{3,2} \cdot ([O_{AABB}] + [O_{ABBB}] + [O_{BBBB}]) + 3 \cdot \omega_{3,1} \cdot ([O_{AAAB}] + [O_{AABB}] + [O_{ABBB}]) \} \\ & + [V_{BBBB}] \cdot 6 \cdot \omega_{4,2} \cdot ([O_{AABB}] + [O_{ABBB}] + [O_{BBBB}]) \Big)\end{aligned}$$

Correlated motion

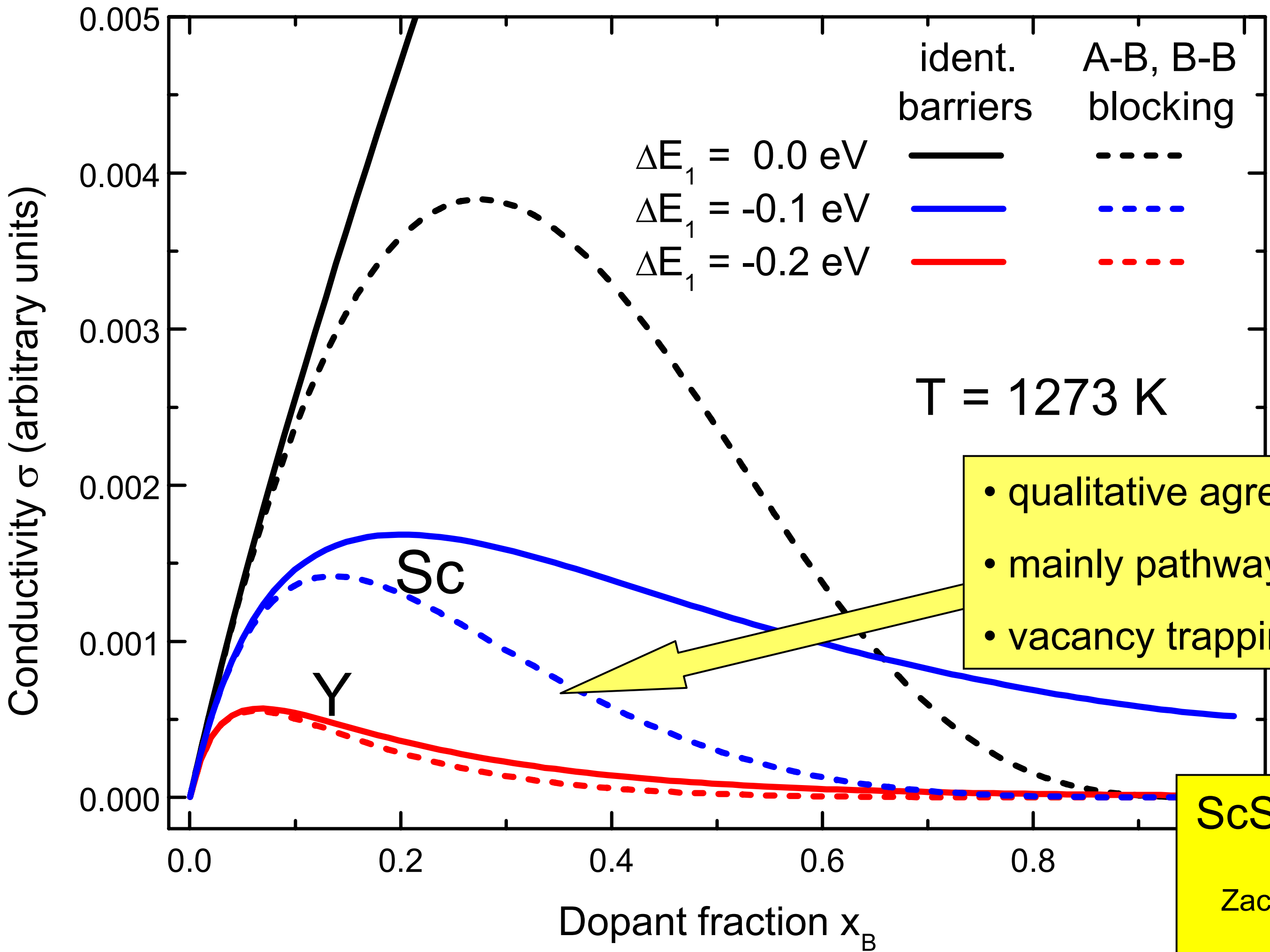
Ionic conductivity

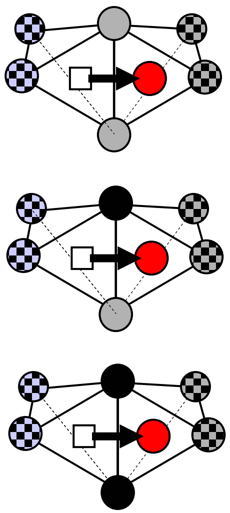




MM, J. Electroceram. 17 (2006) 765

Ionic conductivity





- qualitative agreement with exper.
- mainly pathways across Zr-Zr edges
- vacancy trapping in Y-tetrahedra

ScSZ: R(Sc) < R(Y)

Zacate $\Delta E_1(Sc) < \Delta E_1(Y)$

Badwal $\sigma(Sc) > \sigma(Y)$

MM, J. Electroceram. 17 (2006) 765

Ionic conductivities of oxide electrolytes

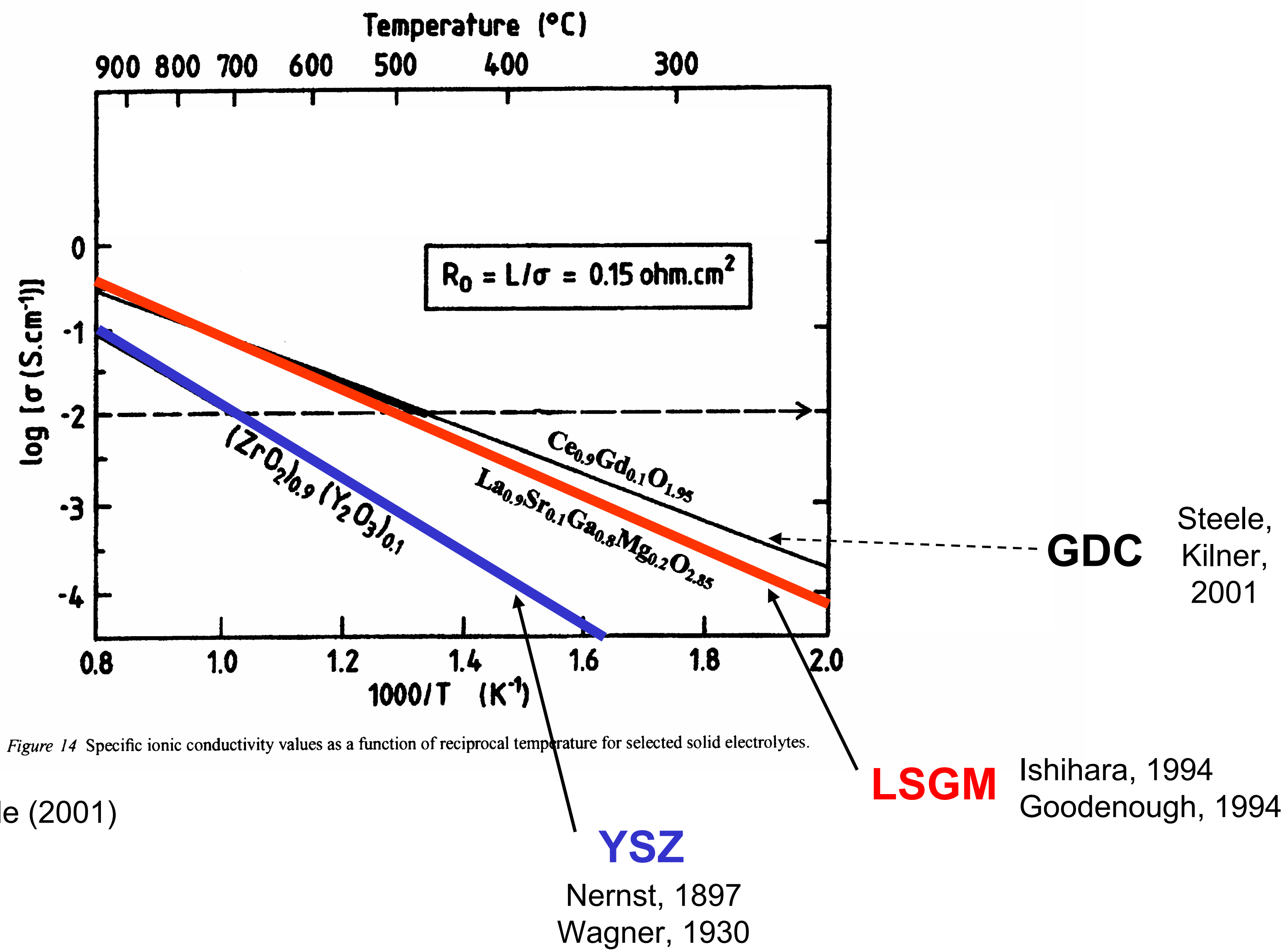


Figure 14 Specific ionic conductivity values as a function of reciprocal temperature for selected solid electrolytes.

B.C.H. Steele (2001)

Cation diffusion in oxygen ion conductors

- Why study cation diffusion in an oxygen ion conductor?

- Cations are the slowest species: $t_{cation} << t_e, t_h << t_O$

  10^{-10} 10^{-4} 1

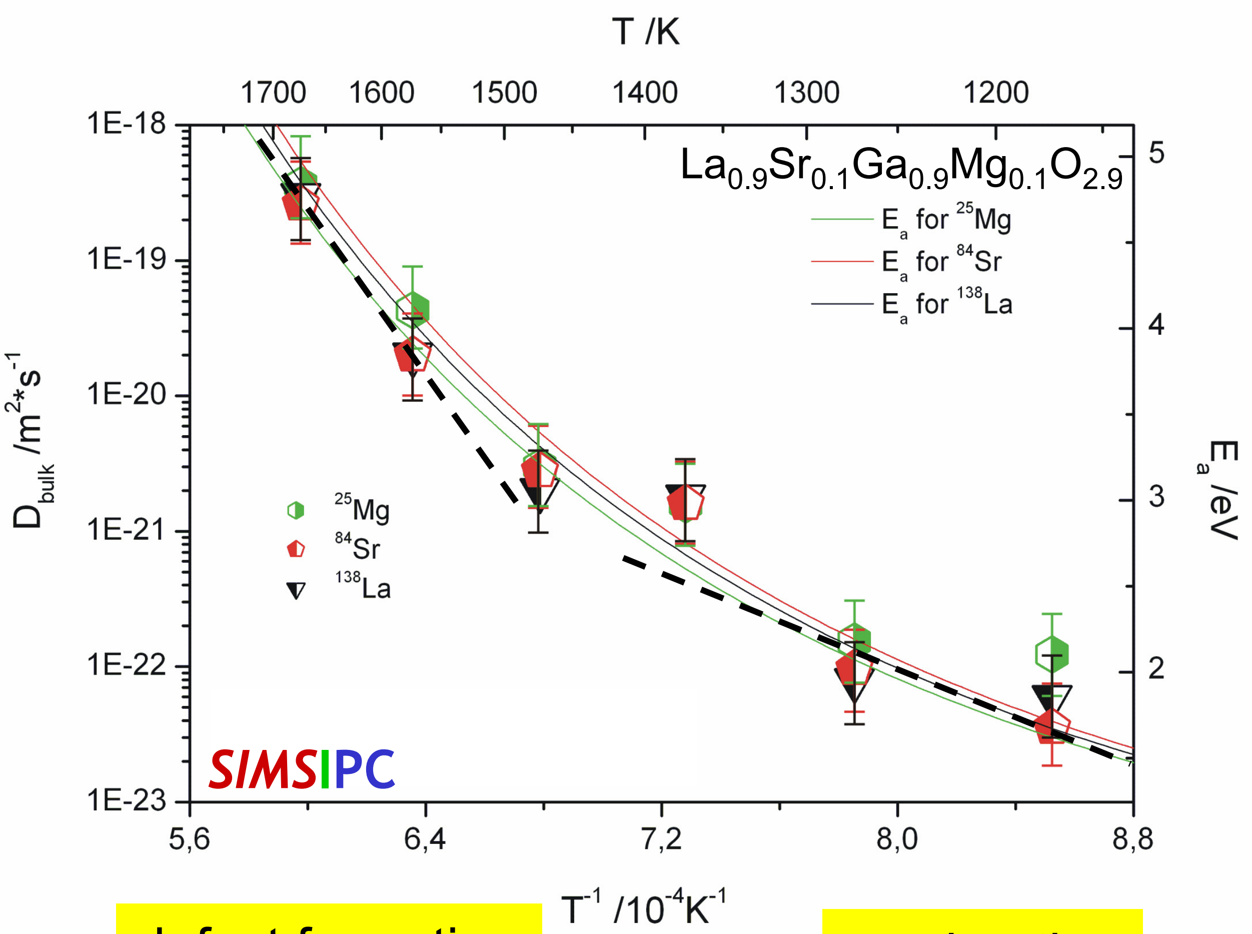
  ↑ Minority defects

- They determine the rates of:
  - defect equilibration
  - sintering, creep
  - interdiffusion (with electrodes)
  - kinetic demixing (of electrolyte)

Long term degradation effects

- Complicated diffusion mechanism

Cation self-diffusion in LSGM



- curvature

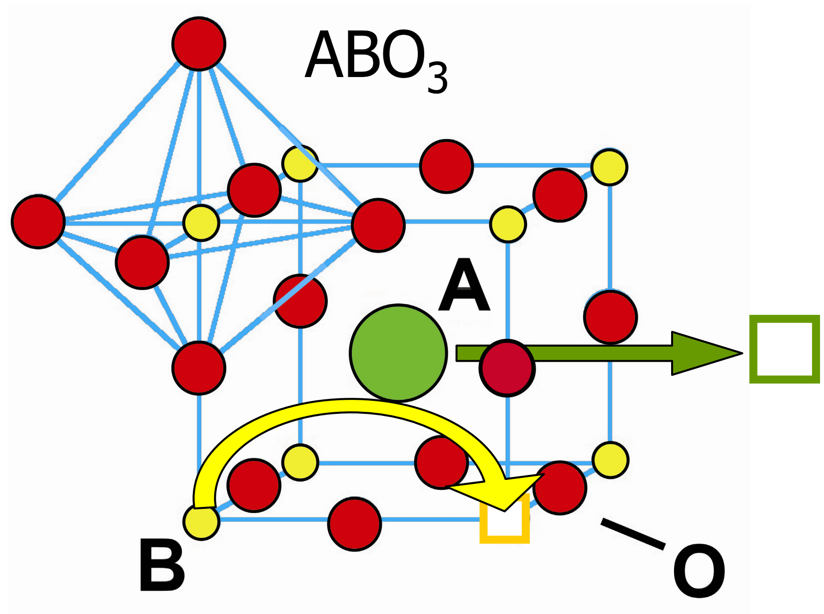
  frozen in defects at low temperatures

defect formation
+ migration
≈ 4.5 eV

migration
≈ 2 eV

O. Schulz, M. Martin et al., *PCCP* (2003)

Cation self-diffusion in LSGM



Experiment

- similar migration energies for all cations $\approx$ 2 eV
- similar diffusion coeff. for all cations

Ionic radii

A-site	**B-site**
La^{3+}: 106 pm	Ga^{3+}: 62 pm
Sr^{2+}: 118 pm	Mg^{2+}: 74 pm

Theory

$E^{mig}_{La} = 4.6\ eV$ $E^{mig}_{Ga} = 17\ eV$ Khan et al. (1998)

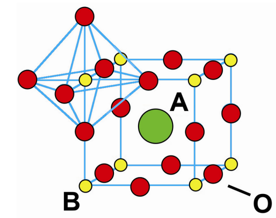
$E^{mig}_{Y} = 2.6\ eV$ $E^{mig}_{Cr} = 10\ eV$ De Souza, Maier (2002)

Simple cation vacancy mechanisms

More complicated diffusion mechanism ?

O. Schulz, M. Martin et al., *PCCP* (2003)

Cluster formation in LSGM

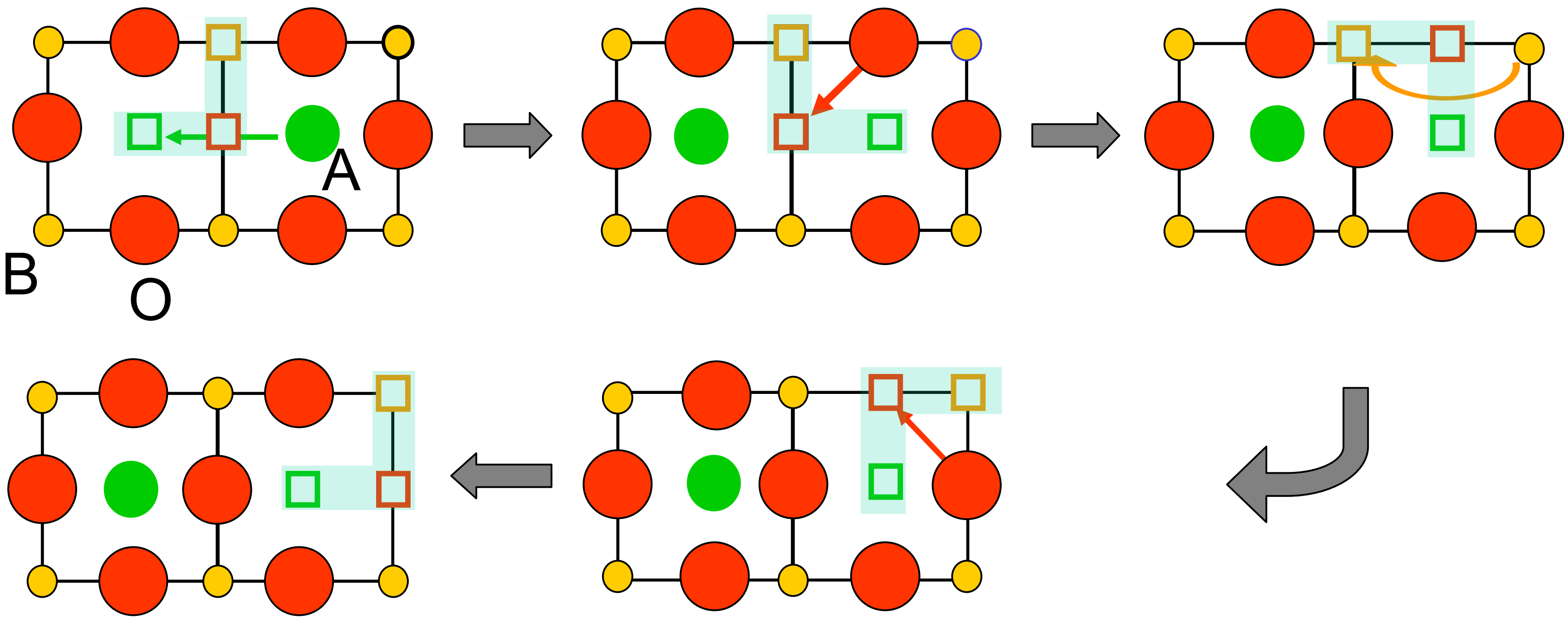


$$V_A''' + V_B''' + V_O^{\bullet\bullet} \leftrightarrow \underbrace{\left(V_A''', V_O^{\bullet\bullet}, V_B'''\right)}_{\text{cluster}}$$

Minority defects

$\Delta E_C \approx -7.5$ eV

(point charges)



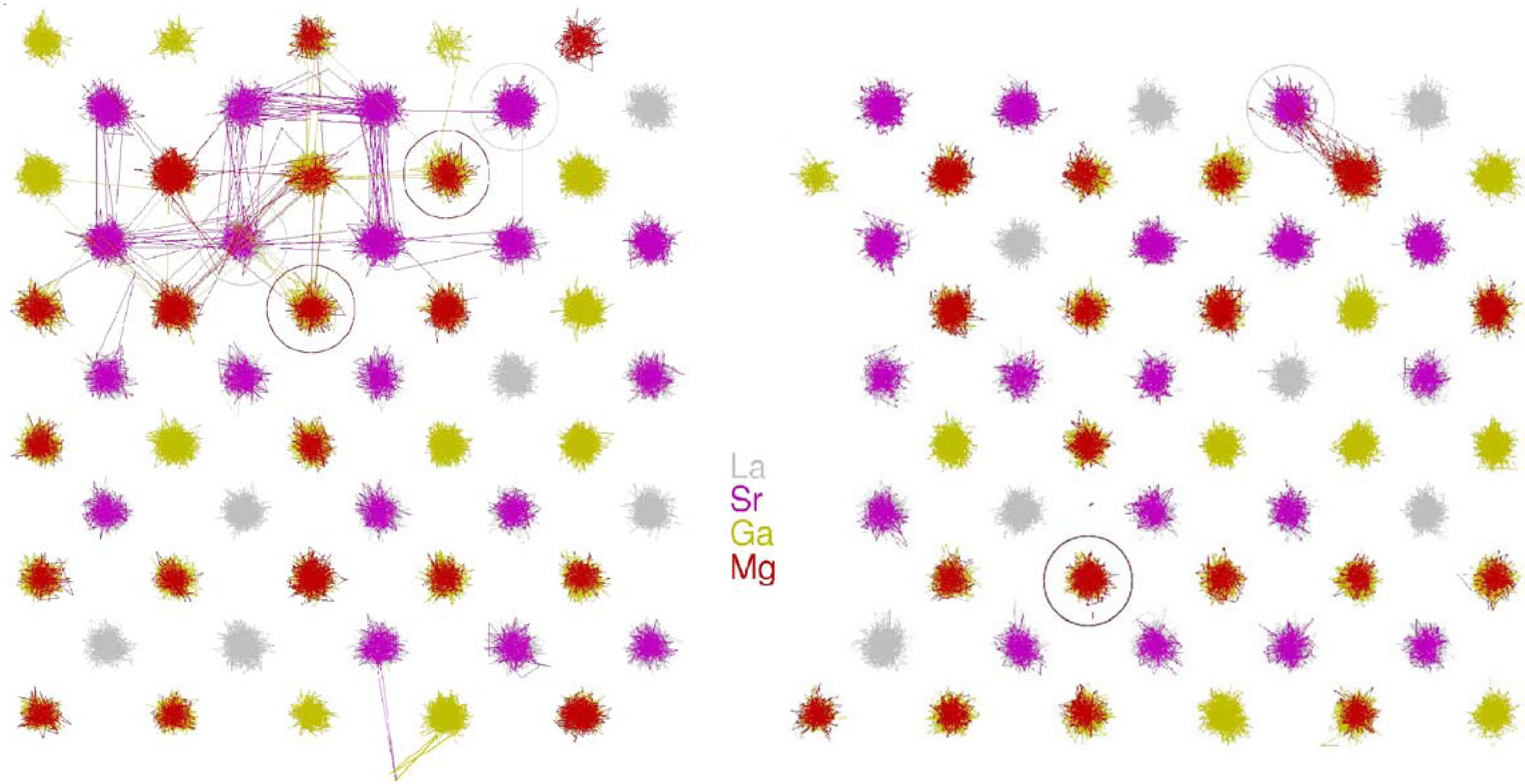
Correlated four jump cycle

$\omega_O >> \omega_A > \omega_B$

O. Schulz, M. Martin et al., *PCCP* (2003)

Molecular Dynamics

Vacancy pair: (V_A, V_B) | Separated vacancies V_A and V_B



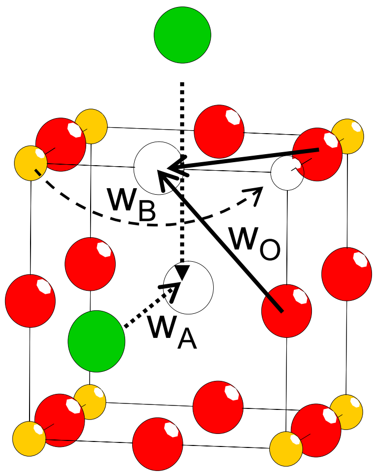
long range B-jumps via V_A | only forward-backwards jumps

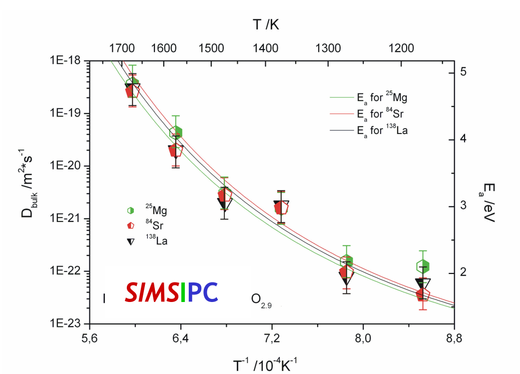
M. Kilo, M.A. Taylor, C. Argirusis, G. Borchardt, R.A. Jackson,
O. Schulz, M. Martin, M. Weller, *Solid State Ionics* 175 (2004) 823.

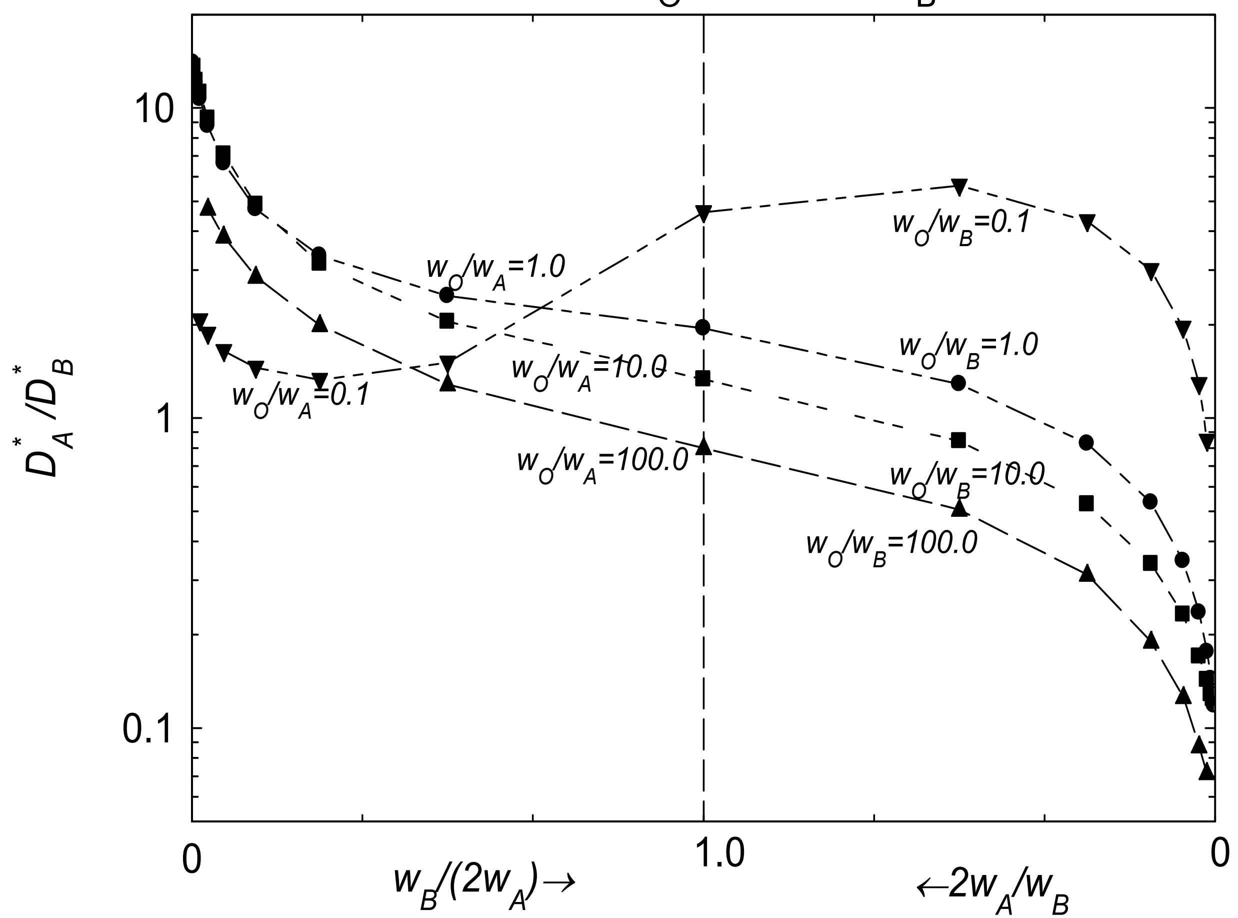
Cluster migration in ABO_3

Sum rule expressions for the transport coefficients L_{ij}, e.g.

$$L_{AA} + 2\frac{w_A}{w_O}L_{AO} + 2\frac{w_A}{w_B}L_{AB} = L_{AA}^{(0)}$$



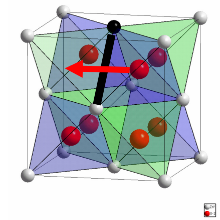


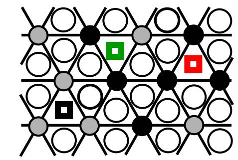


I.V. Belova, G.E. Murch, D. Samuelis, M. Martin, Defect and Diffusion Forum 263 (2007) 81-86

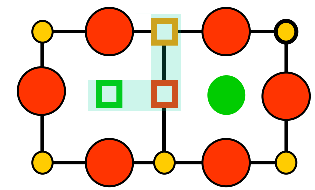
Conclusions

- Oxygen diffusion in YSZ (and LSGM):
  - jumps through edges <u>and</u> interactions
  - simple, analytical model for concentrated defects and conductivity maximum



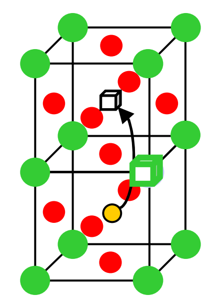


- Cation diffusion in LSGM (minority defects)
  - “identical” activation energies for all cations
  - “identical” diffusion coefficients for all cations
  - defect clustering
  - four-jump cycle
  - qualitative confirmation by GULP, MD and sum rules



- General mechanism for cation diffusion in perovskites ?

  $D_B \propto [V_B]\cdot[V_A]$



- Thanks: DFG (SPP 1060), CHF, Land NRW

Vacancies,

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