Diffusion in multicomponent solids

Anton Van der Ven
Department of Materials Science and Engineering
University of Michigan
Ann Arbor, MI

Coarse graining time
Diffusion in a crystal

Two levels of time coarse graining

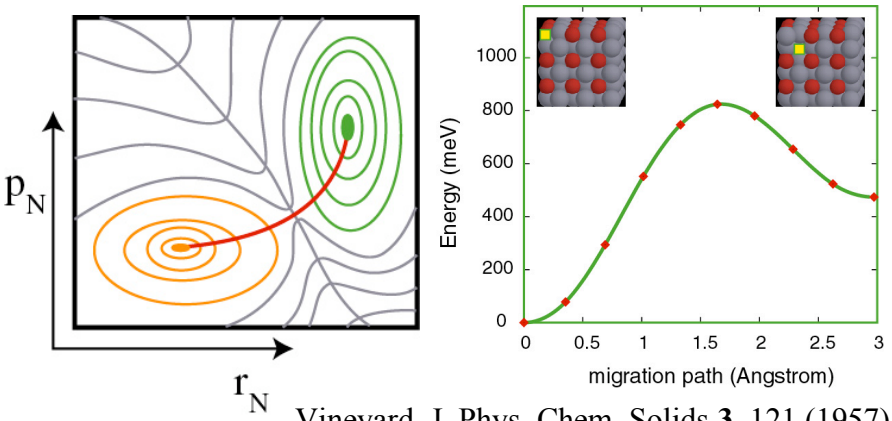
Coarse graining time
Diffusion in a crystal

Two levels of time coarse graining

Short-time coarse graining: transition state theory

$$\Gamma = \nu * \exp\left(\frac{-\Delta E_B}{kT}\right)$$

- MD simulations
- Harmonic approximation



Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

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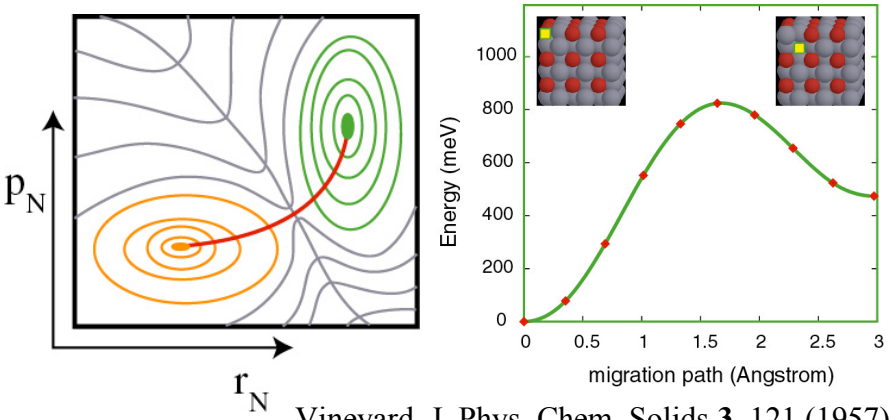


Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

A second level of coarse graining that leads to Fick's law

$$J = -D\nabla C$$

Green-Kubo

Kinetic coefficients derived from fluctuations **at equilibrium**

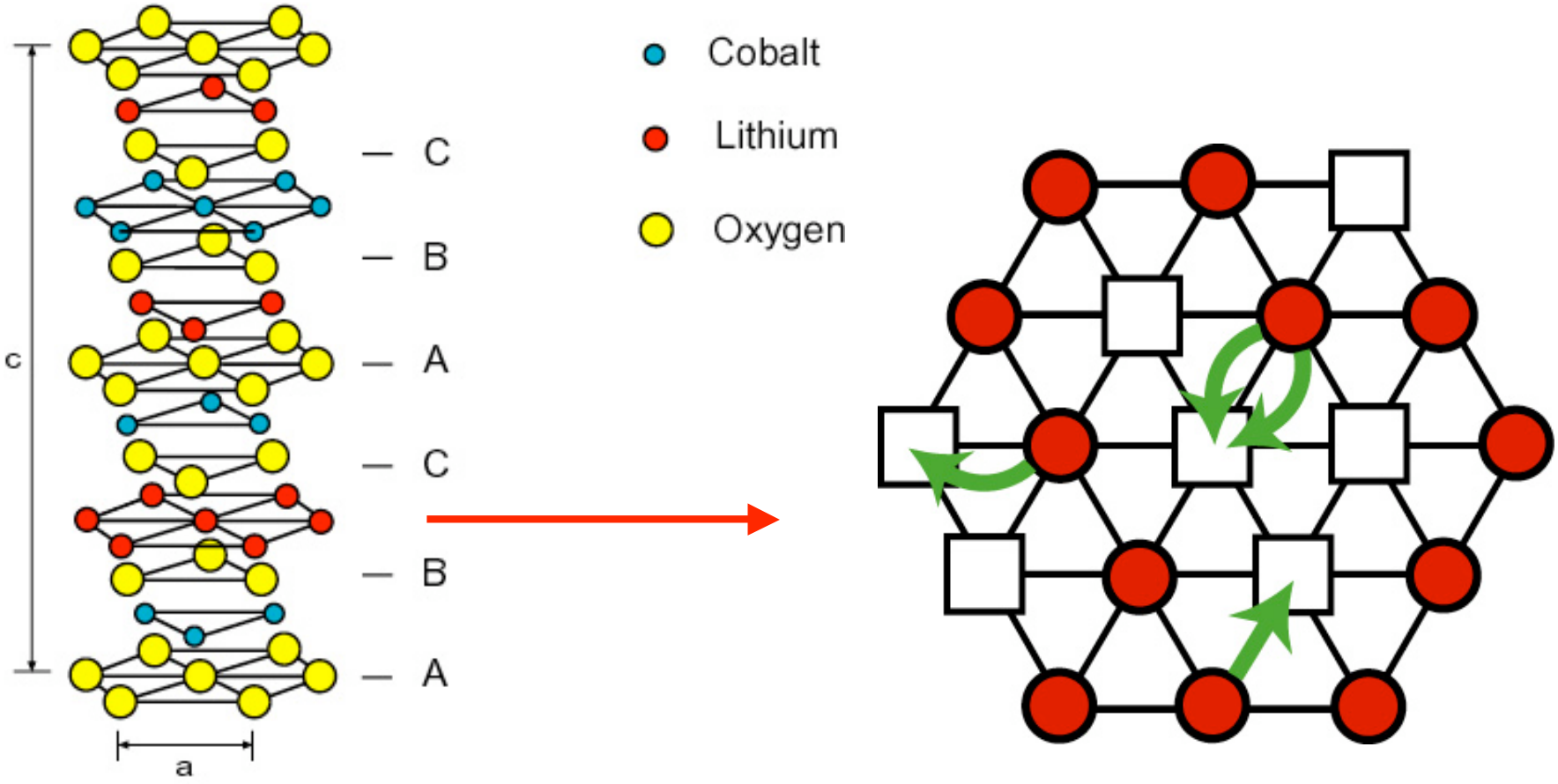
Zwanzig, Annu. Rev. Phys. Chem. **16**, 67 (1965).

Interstitial diffusion

- C diffusion in bcc Iron (steel)
- Li diffusion in transition metal oxide host
- O diffusion on Pt-(111) surface

In all examples, diffusion occurs on a rigid lattice which is externally imposed by a host or substrate

Example of interstitial diffusion



Irreversible thermodynamics: interstitial diffusion of one component

$$J = -L\nabla\mu$$

$$D = L\frac{d\mu}{dC}$$

$$J = -D\nabla C$$

Notation

M = number of lattice sites

N = number of diffusing atoms

v_s = volume per lattice site

x = N/M

$C=x/v_s$

Interstitial diffusion: one component

Kubo-Green relations
(linear response statistical mechanics)

$$D = L \cdot \Theta$$

Thermodynamic factor

$$\Theta = \frac{\partial \mu}{\partial C}$$

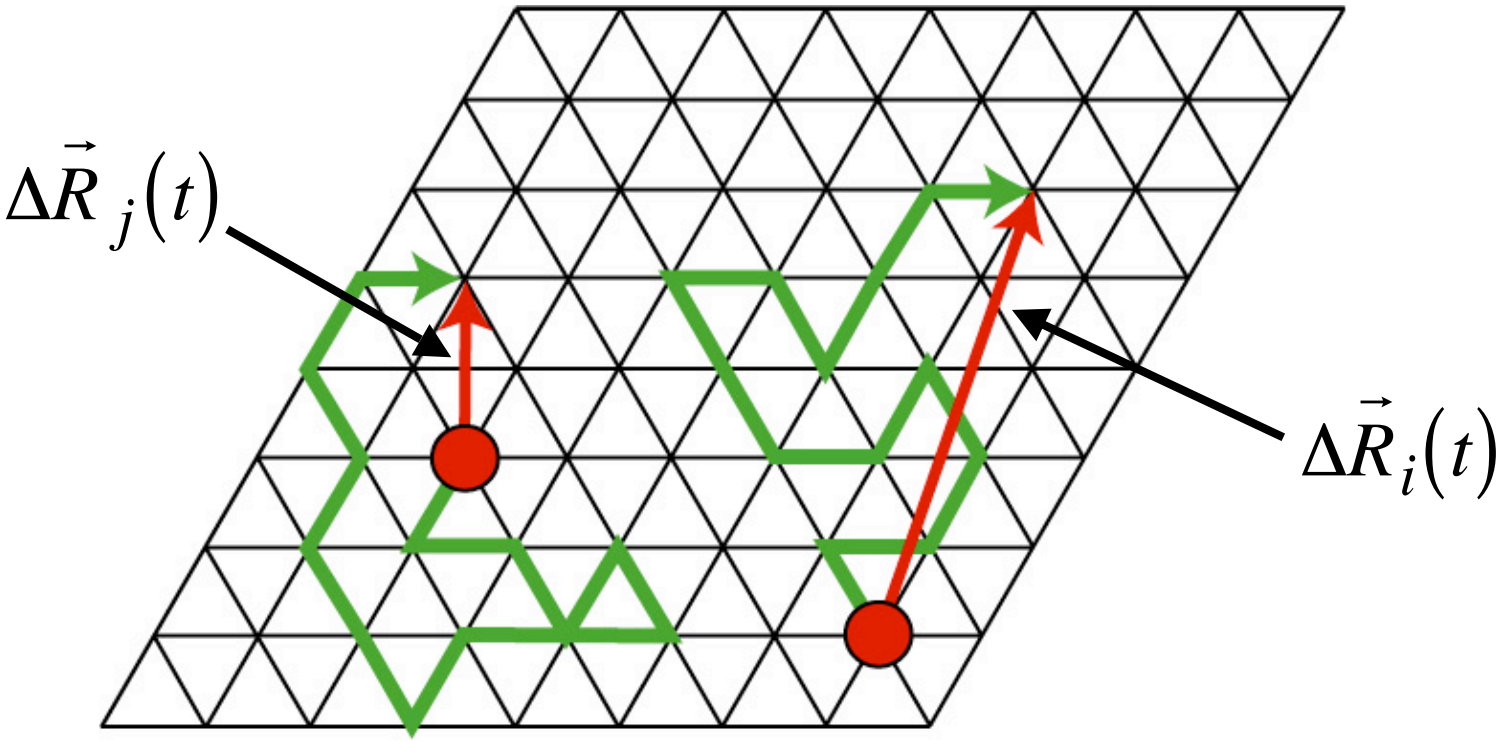
Kinetic coefficient

$$L = \frac{1}{(2d)tMv_s kT} \left\langle \left(\sum_{i=1}^{N} \Delta \vec{R}_i(t) \right)^2 \right\rangle$$

R. Gomer, Rep. Prog. Phys. **53**, 917 (1990)/

A. Van der Ven, G. Ceder, Handbook of Materials Modeling, chapt. 1.17, Ed. S. Yip, Springer (2005).

Trajectories



$$D_J = \frac{1}{(2d)t}\left\langle \frac{1}{N}\left(\sum_{i=1}^{N}\Delta\vec{R}_i(t)\right)^2\right\rangle$$

More familiar form

$$D = D_J \cdot \tilde{\Theta}$$

Thermodynamic factor

$$\tilde{\Theta} = \frac{\partial\left(\frac{\mu}{kT}\right)}{\partial \ln x}$$

Self diffusion coefficient

$$D_J = \frac{1}{(2d)t}\left\langle \frac{1}{N}\left(\sum_{i=1}^{N} \Delta\vec{R}_i(t)\right)^2 \right\rangle$$

R. Gomer, Rep. Prog. Phys. **53**, 917 (1990)/

Common approximation

$$D = D^* \cdot \tilde{\Theta}$$

Thermodynamic factor

$$\tilde{\Theta} = \frac{\partial\left(\frac{\mu}{kT}\right)}{\partial \ln x}$$

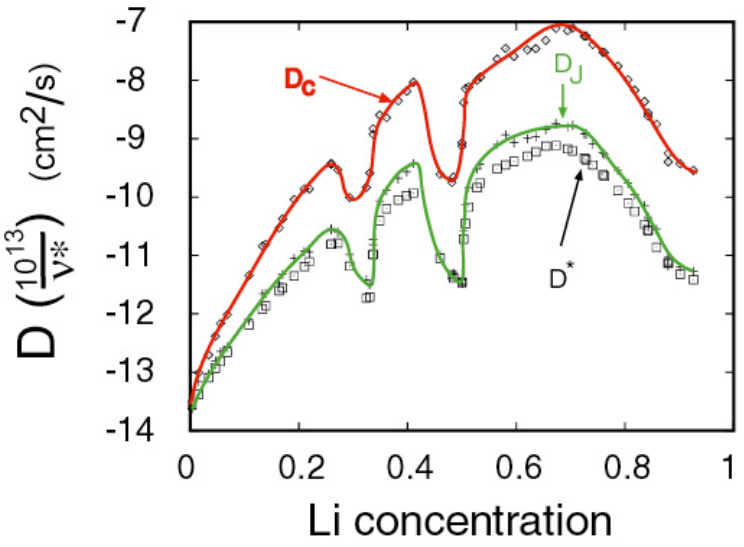
Tracer diffusion coefficient

$$D^* = \frac{\left\langle \left(\Delta R_i(t)\right)^2 \right\rangle}{(2d)t}$$

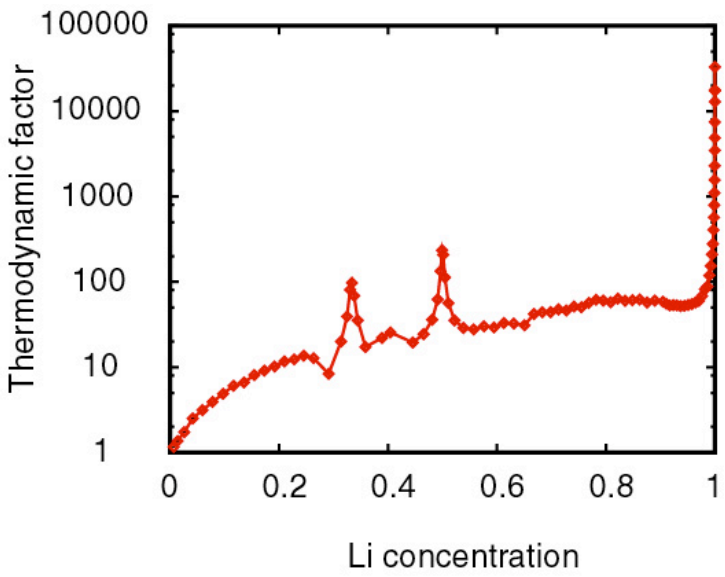
R. Gomer, Rep. Prog. Phys. **53**, 917 (1990)/

$$D = D_J \cdot \tilde{\Theta}$$

Diffusion coefficient at 300 K



Thermodynamic factor Θ



A. Van der Ven, G. Ceder, M. Asta, P.D. Tepesch, Phys Rev. B 64 (2001) 064112

Interstitial diffusion (two components)

- C & N diffusion in bcc Iron (steel)
- Li & Na diffusion in transition metal oxide host
- O & S diffusion on Pt-(111) surface

In all examples, diffusion occurs on a rigid lattice which is externally imposed by a host or substrate

Diffusion of two species on a lattice

$$J_A = -L_{AA}\nabla\mu_A - L_{AB}\nabla\mu_B$$

$$J_B = -L_{BA}\nabla\mu_A - L_{BB}\nabla\mu_B$$

$$D = L \cdot \Theta$$

$$\begin{pmatrix} D_{AA} & D_{AB} \\ D_{BA} & D_{BB} \end{pmatrix} = \begin{pmatrix} L_{AA} & L_{AB} \\ L_{BA} & L_{BB} \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial \mu_A}{\partial C_A} & \frac{\partial \mu_A}{\partial C_B} \\ \frac{\partial \mu_B}{\partial C_A} & \frac{\partial \mu_B}{\partial C_B} \end{pmatrix}$$

$$J_A = -D_{AA}\nabla C_A - D_{AB}\nabla C_B$$

$$J_B = -D_{BA}\nabla C_A - D_{BB}\nabla C_B$$

Alternative factorization

$$\begin{pmatrix} D_{AA} & D_{AB} \\ D_{BA} & D_{BB} \end{pmatrix} = \begin{pmatrix} \tilde{L}_{AA} & \tilde{L}_{AB} \\ \tilde{L}_{BA} & \tilde{L}_{BB} \end{pmatrix} \cdot \begin{pmatrix} \dfrac{\partial\left(\dfrac{\mu_A}{kT}\right)}{\partial x_A} & \dfrac{\partial\left(\dfrac{\mu_A}{kT}\right)}{\partial x_B} \\ \dfrac{\partial\left(\dfrac{\mu_B}{kT}\right)}{\partial x_A} & \dfrac{\partial\left(\dfrac{\mu_B}{kT}\right)}{\partial x_B} \end{pmatrix}$$

Kubo-Green

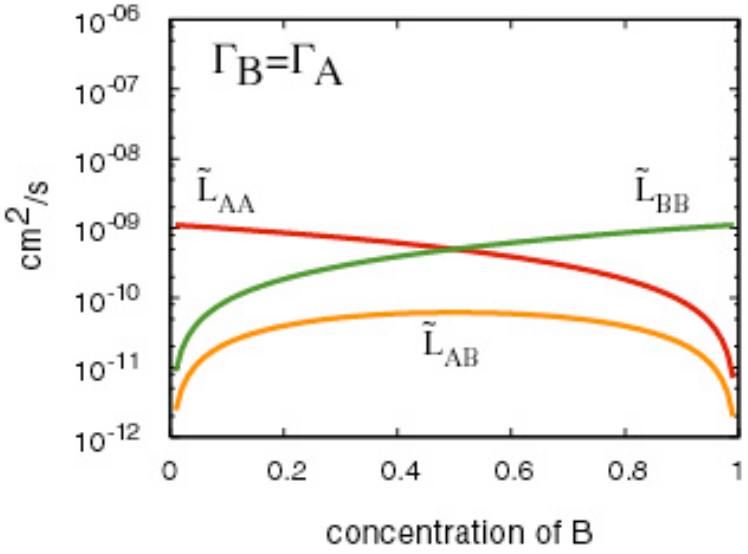
$$\tilde{L}_{ij} = \frac{\left\langle \left(\sum_{\varsigma} \Delta \vec{R}_{\varsigma}^{\,i}(t) \right) \cdot \left(\sum_{\xi} \Delta \vec{R}_{\xi}^{\,j}(t) \right) \right\rangle}{(2d)tM}$$

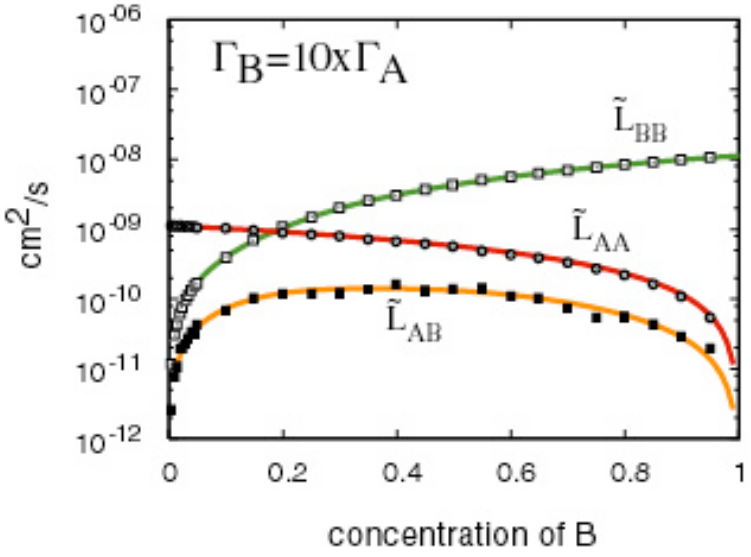
A. Van der Ven, G. Ceder, Handbook of Materials Modeling, chapt. 1.17, Ed. S. Yip, Springer (2005).

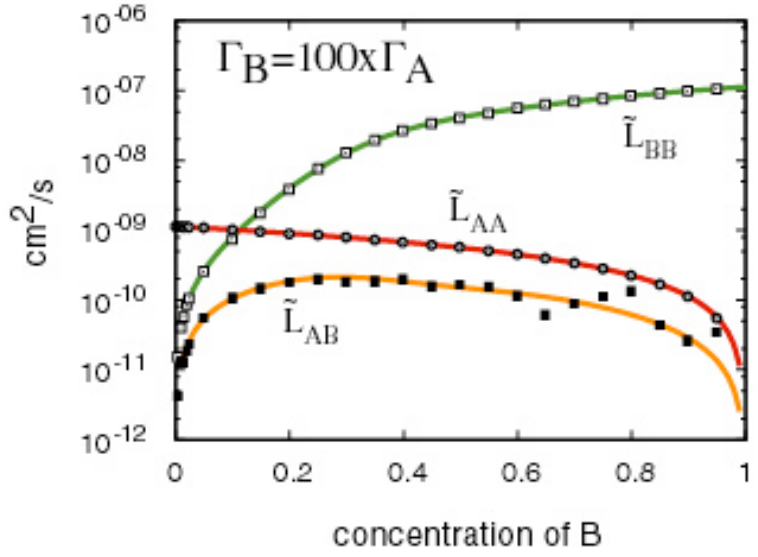
A.R. Allnatt, A.B. Lidiard, *Atomic Transport in Solids* (Cambridge Univ. Press, 1993).

Kinetic coefficients
(fcc lattice in dilute vacancy limit, ideal solution)

$$\tilde{L}_{ij} = \frac{\left\langle \left(\sum_{\varsigma} \Delta \vec{R}_{\varsigma}^{i}(t) \right) \cdot \left(\sum_{\xi} \Delta \vec{R}_{\xi}^{j}(t) \right) \right\rangle}{(2d)tM}$$





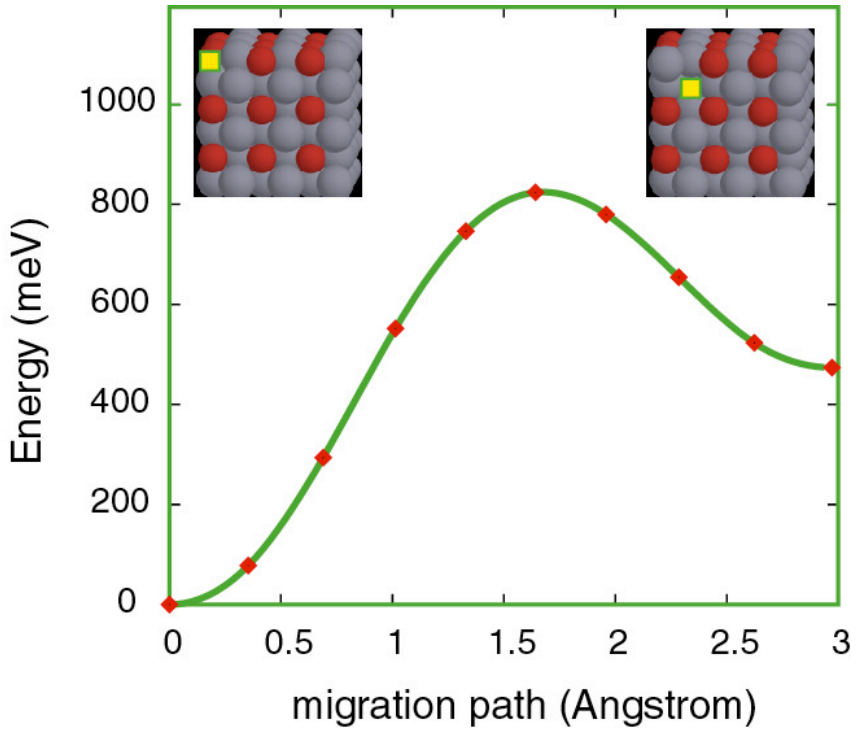


Diffusion in an alloy: substitutional diffusion

Not interstitial diffusion

Instead, diffusing atoms form the lattice

Dilute concentration of vacancies

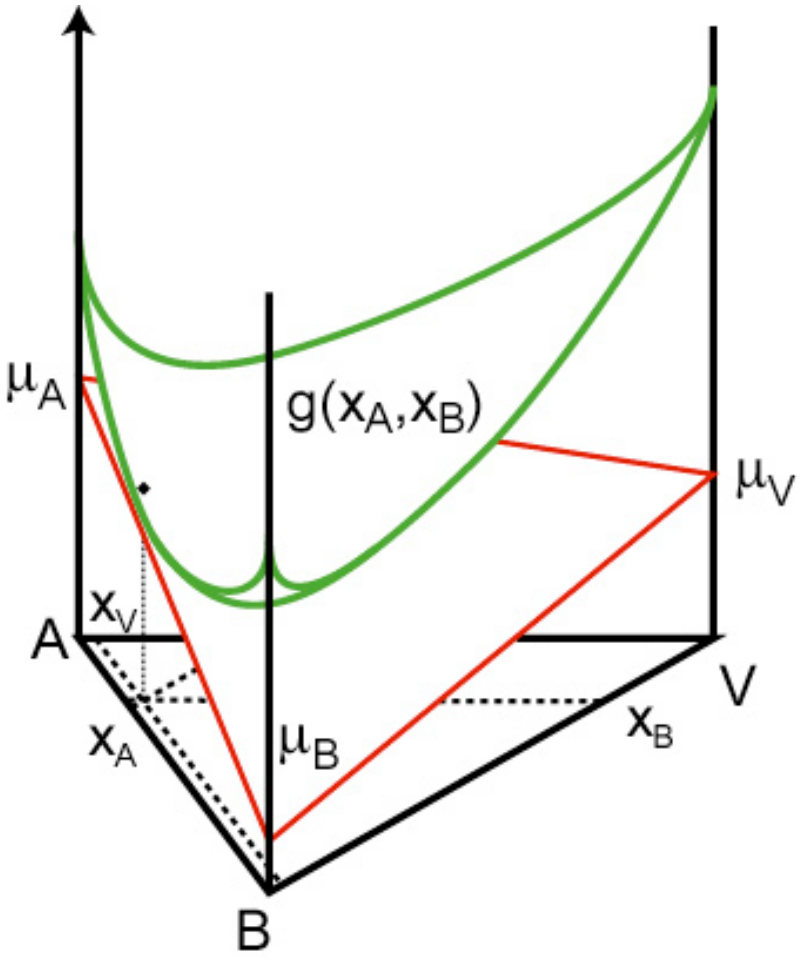


Thermodynamic driving forces for substitutional diffusion

$$J_A = -L_{AA}\nabla\tilde{\mu}_A - L_{AB}\nabla\tilde{\mu}_B$$

$$J_B = -L_{BA}\nabla\tilde{\mu}_A - L_{BB}\nabla\tilde{\mu}_B$$

$$\tilde{\mu}_A = \mu_A - \mu_V$$
$$\tilde{\mu}_B = \mu_B - \mu_V$$



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Textbook treatment of substitional diffusion

Not Rigorous

$$J_A = -L_{AA}\nabla\tilde{\mu}_A - L_{AB}\nabla\tilde{\mu}_B$$

$$J_B = -L_{BA}\nabla\tilde{\mu}_A - L_{BB}\nabla\tilde{\mu}_B$$

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$$J_B = -L_{BA}\nabla\tilde{\mu}_A - L_{BB}\nabla\tilde{\mu}_B$$

Traditional

Assume vacancy concentration in equilibrium everywhere

$$\mu_V = 0 \qquad d\mu_V = 0$$

Gibbs-Duhem ↓ $x_A d\mu_A + x_B d\mu_B = 0$

$$J_A = -D_A\nabla C_A$$
$$J_B = -D_B\nabla C_B$$

Textbook treatment of substitional diffusion
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Rigorous

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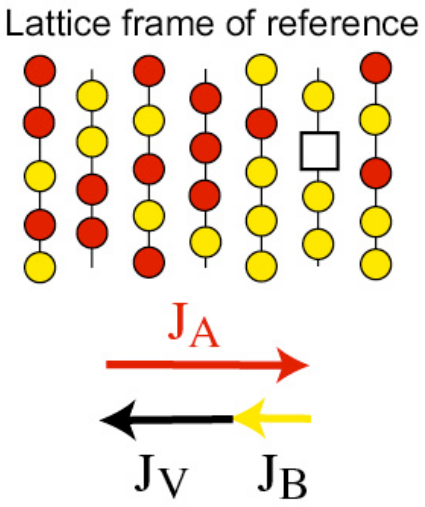
Lattice frame and laboratory frame of reference



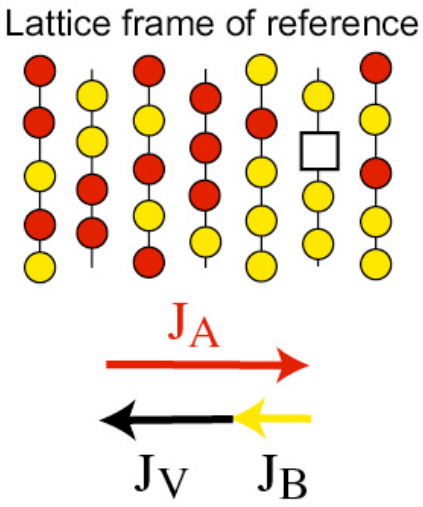
$$v_{lattice} = V_m \cdot J_V = -V_m \cdot (J_A + J_B)$$

Fluxes in the laboratory frame

$$\tilde{J}_A = J_A + x_A J_V$$

$$\tilde{J}_B = J_B + x_B J_V$$

Lattice frame and laboratory frame of reference



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Fluxes in the laboratory frame

$$\tilde{J}_A = J_A + x_A J_V$$

$$\tilde{J}_B = J_B + x_B J_V$$

$$J_V = -\tilde{W} \nabla C_B$$

$$J_B + x_B J_V = -\tilde{D} \nabla C_B$$

Drift

$$\tilde{W} = D_A - D_B$$

Interdiffusion

$$\tilde{D} = x_B D_A + x_A D_B$$

Rigorous treatment

$$J_A = -D_{AA}\nabla C_A - D_{AB}\nabla C_B$$
$$J_B = -D_{BA}\nabla C_A - D_{BB}\nabla C_B$$

Rigorous treatment

$$J_A = -D_{AA}\nabla C_A - D_{AB}\nabla C_B$$
$$J_B = -D_{BA}\nabla C_A - D_{BB}\nabla C_B$$

Diagonalize the D-matrix

Yields a mode corresponding to
(a) density relaxation
(b) interdiffusion

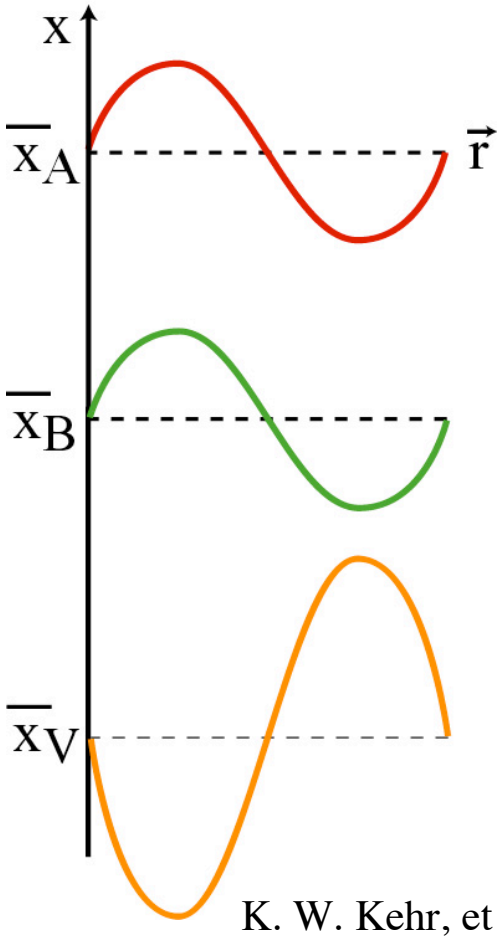
$$\begin{pmatrix} D_{AA} & D_{AB} \\ D_{BA} & D_{BB} \end{pmatrix} = E \cdot \begin{pmatrix} \lambda^+ & 0 \\ 0 & \lambda^- \end{pmatrix} \cdot E^{-1}$$

K. W. Kehr, et al, Phys. Rev. B **39**, 4891 (1989)

Physical meaning of modes λ^+ and λ^-

Physical meaning of modes λ^+ and λ^-

Density fluctuations relax with a time constant of λ^+



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Physical meaning of modes λ^+ and λ^-

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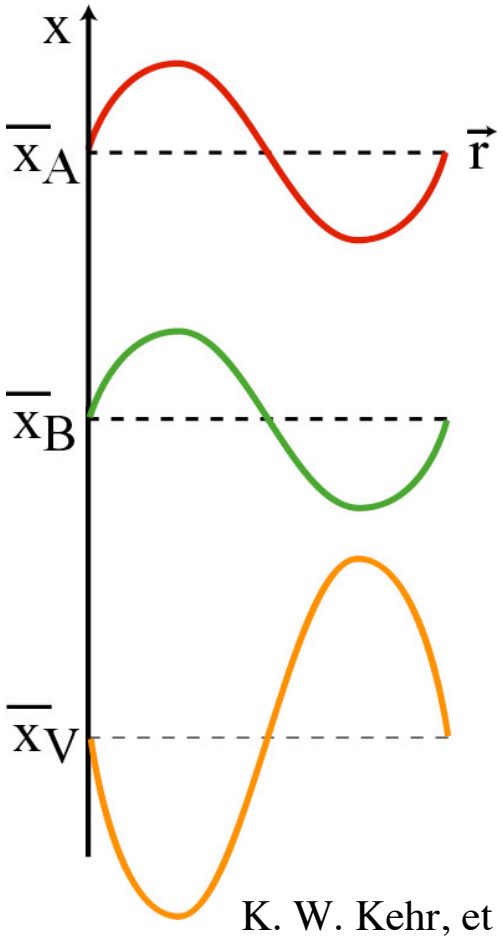
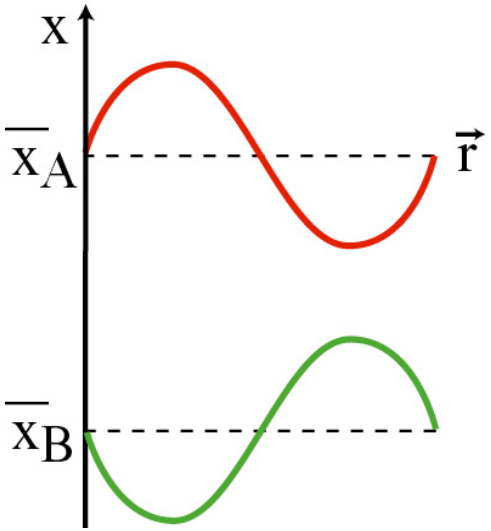


Compositional inhomogeneities decay with a time constant of λ^-



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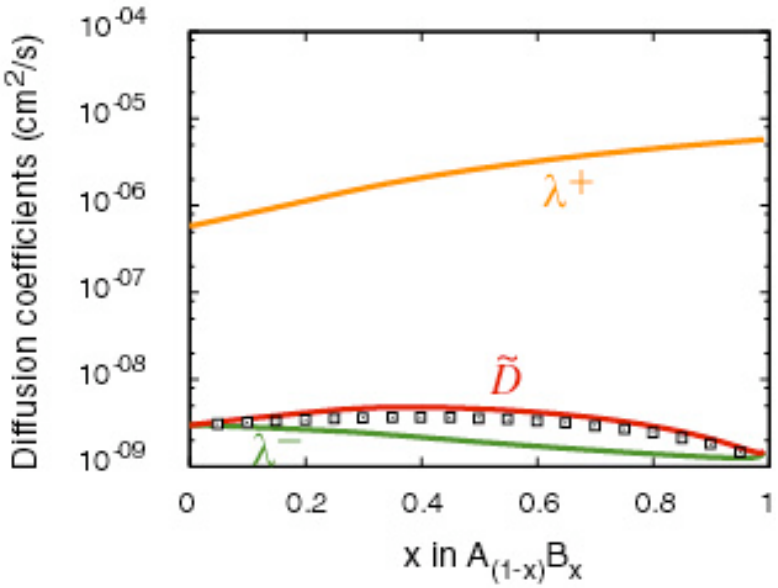
Comparisons of different treatments

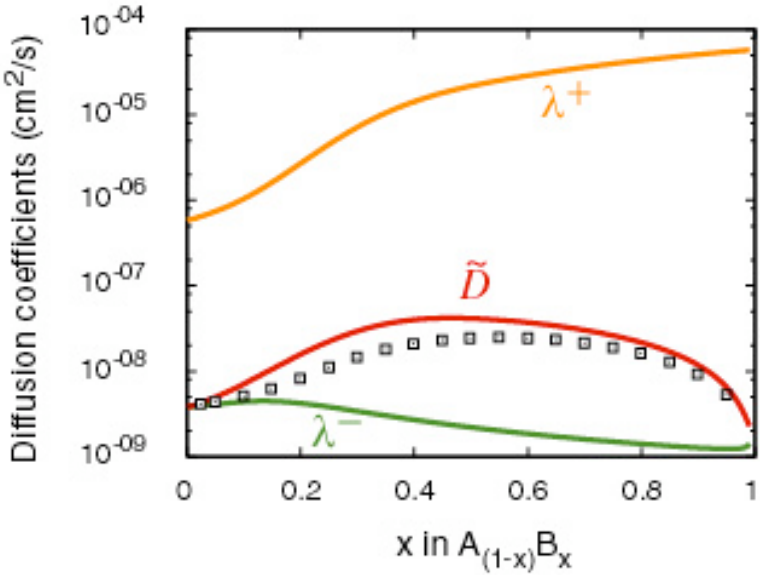
Random alloy

Traditional and rigorous treatment are equivalent only when $\Gamma_B=\Gamma_A$

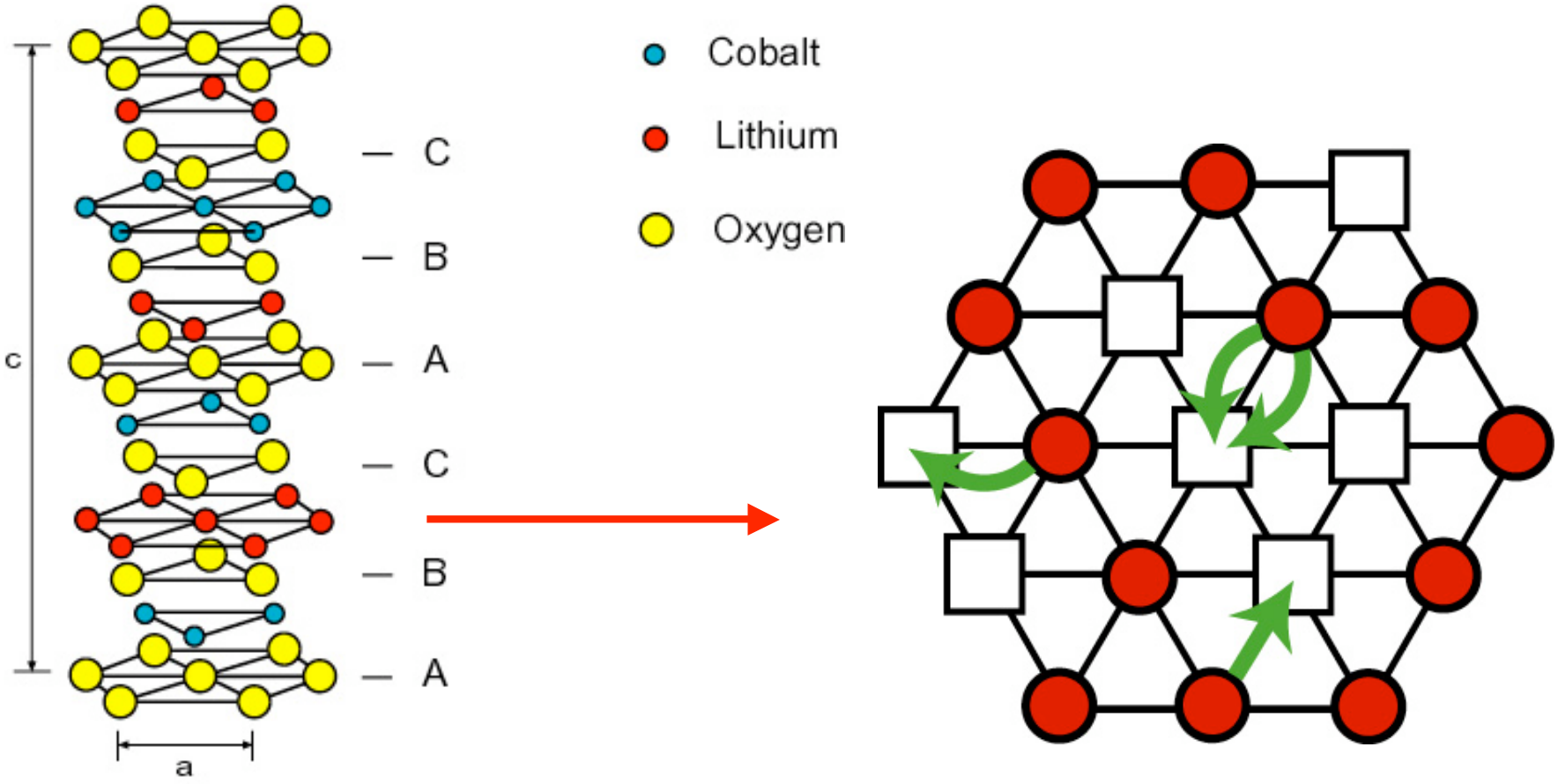
$\Gamma_B=10x\Gamma_A$



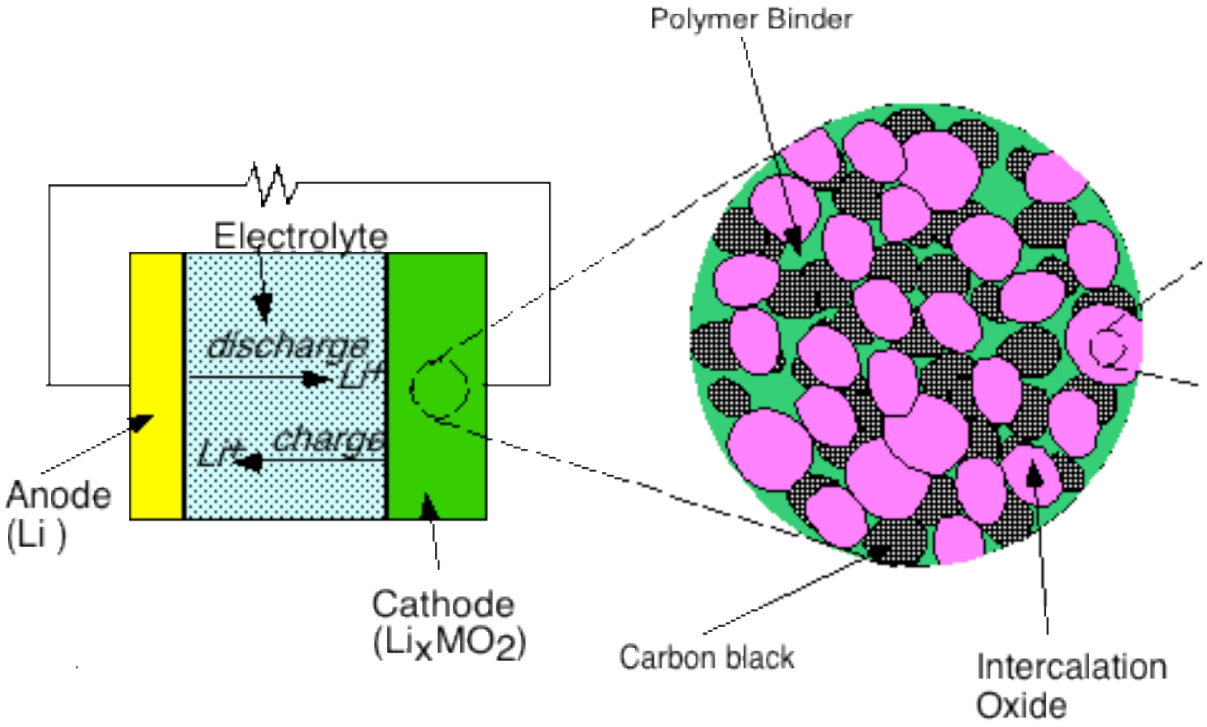
$\Gamma_B=100x\Gamma_A$

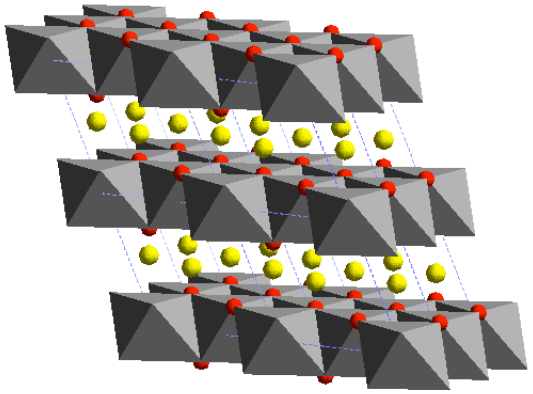


Example: Li_xCoO_2



Intercalation Oxide as Cathode in Rechargeable Lithium Battery





Li_xCoO_2

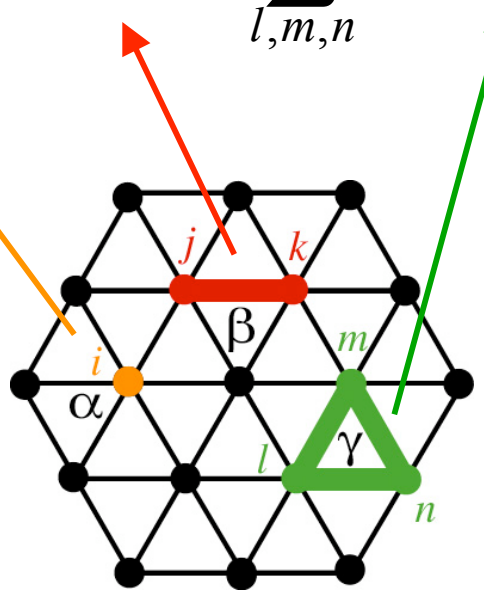
First-Principles (Density Functional Theory)

↓

Cluster Expansions

Fit V_α, V_β, V_γ, …
to first-principles energies

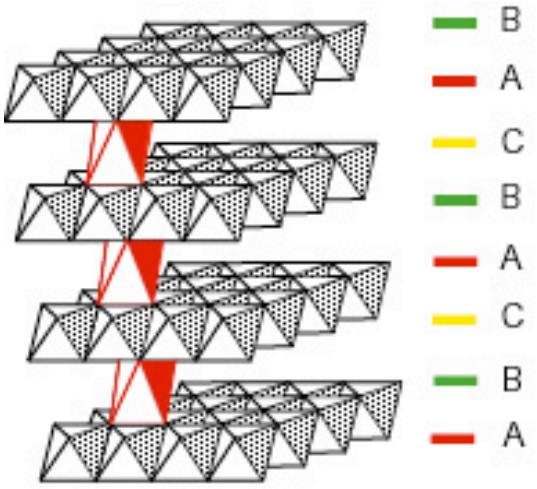
$$F(\sigma) = V_o + \sum_i V_\alpha \sigma_i + \sum_{j,k} V_\beta \sigma_j \sigma_k + \sum_{l,m,n} V_\gamma \sigma_l \sigma_m \sigma_n + \ldots$$



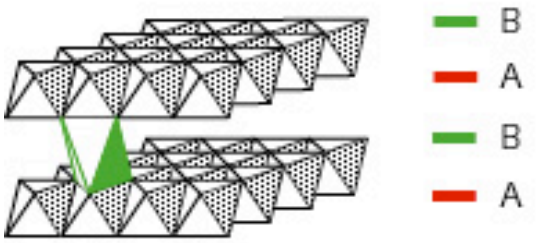
Monte Carlo

↓

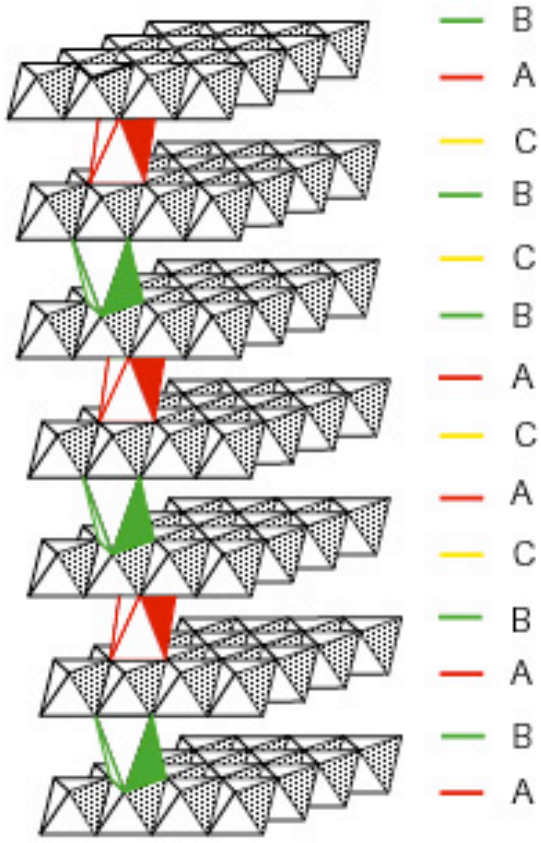
$$Z = \sum_\sigma \exp\left(-\frac{F(\sigma)}{k_B T}\right)$$



O3 host



O1 host



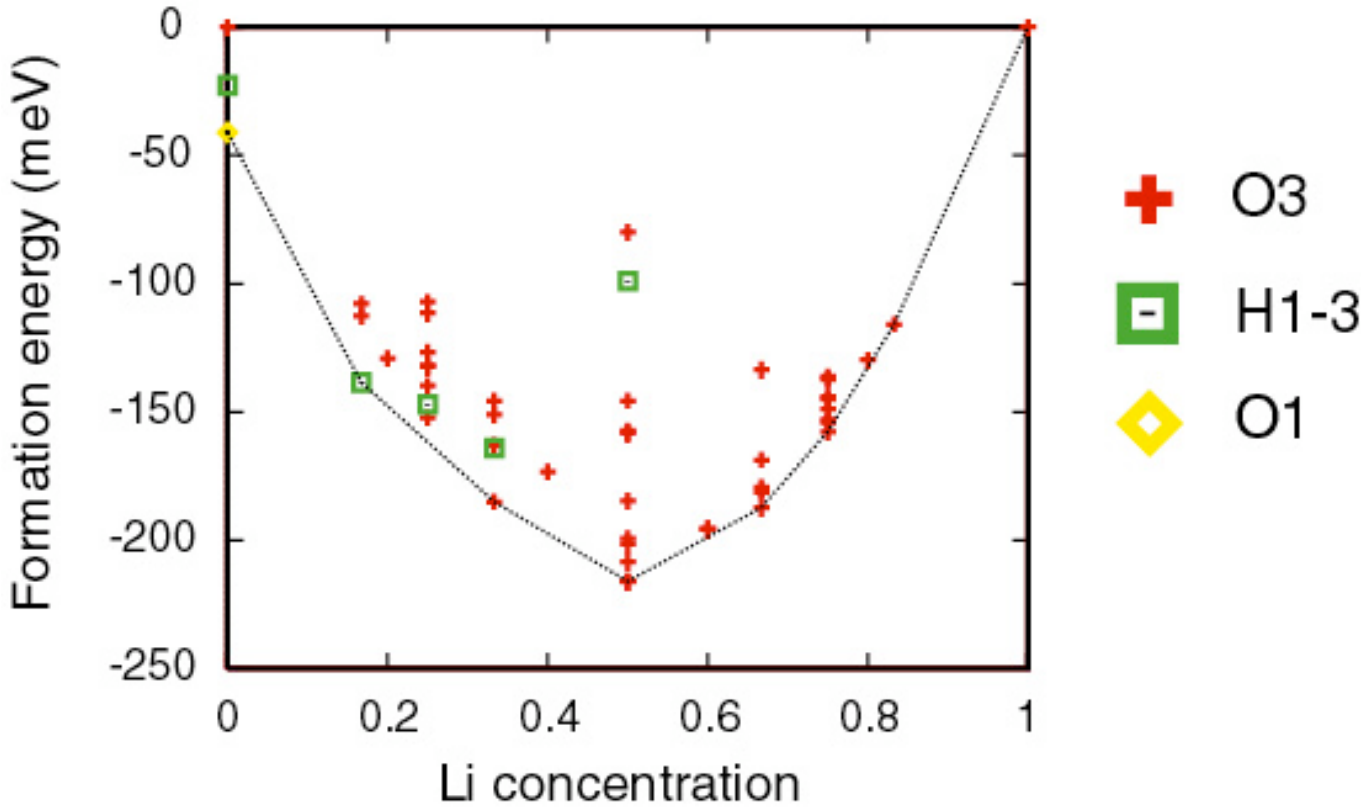
H1-3 host

O octahedra surrounding Co

Edge sharing O octahedra in Li

Face sharing O octahedra in Li plane

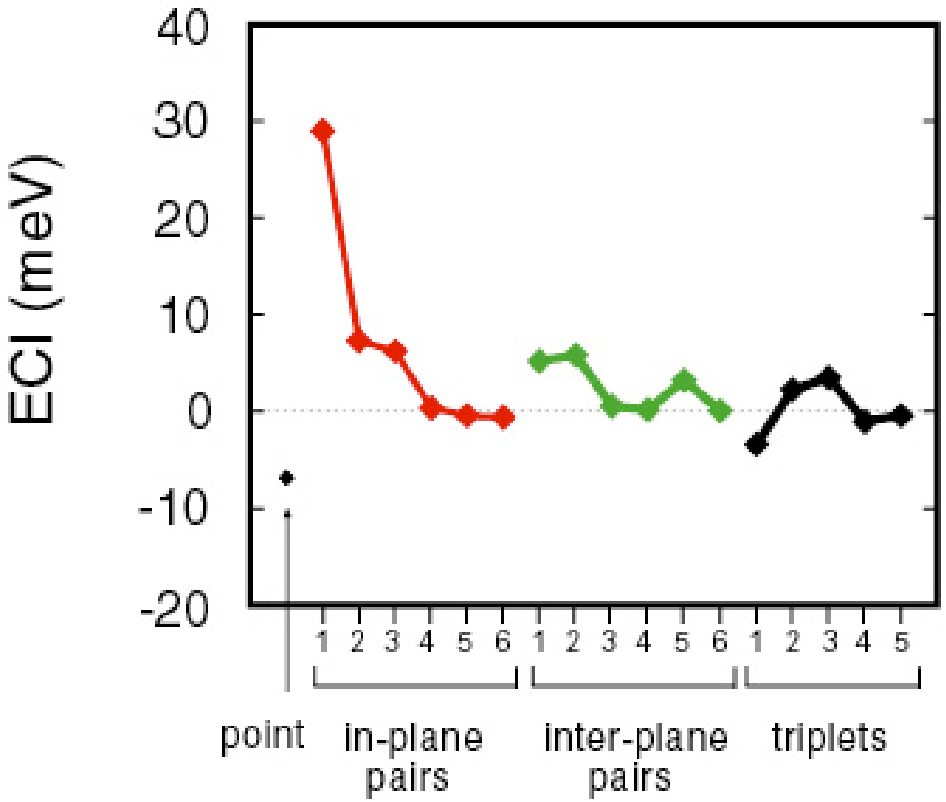
First principles energies (LDA) of different lithium-vacancy configurations

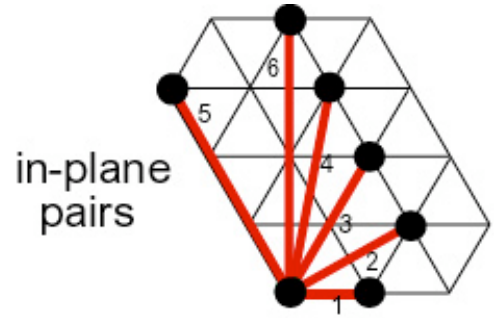


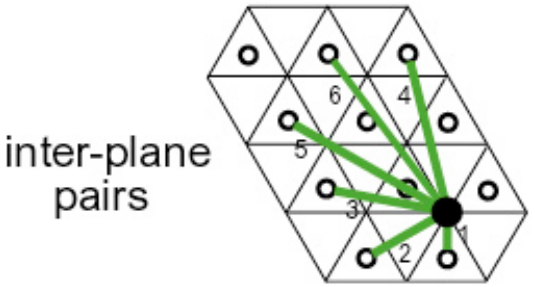
A. Van der Ven, et al, Phys. Rev. B 58 (6), p. 2975-87 (1998).

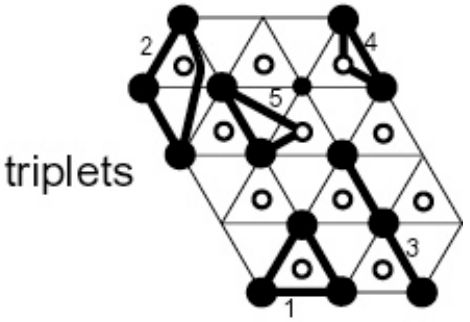
Cluster expansion for Li_xCoO_2

$$E(\sigma) = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$









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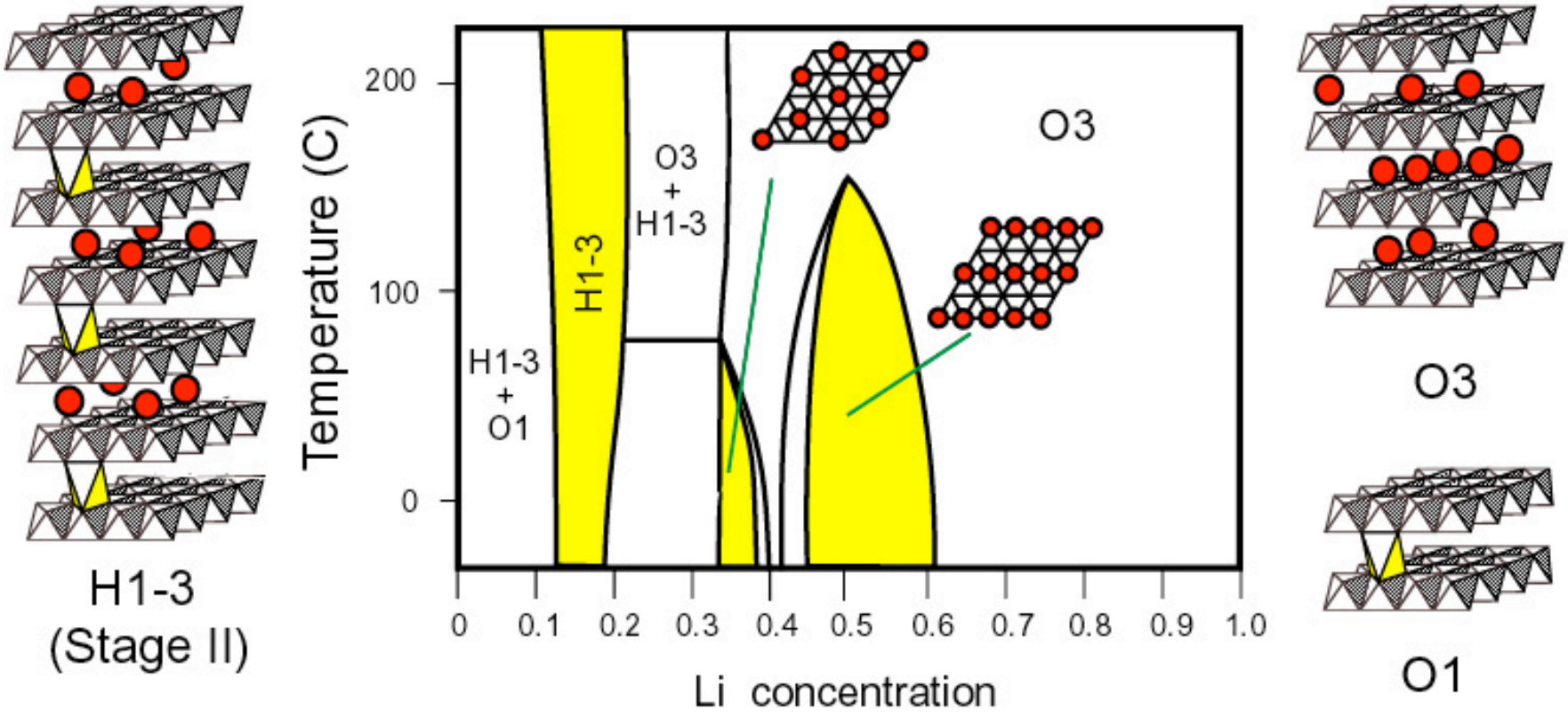
Calculated Li_xCoO_2 phase diagram



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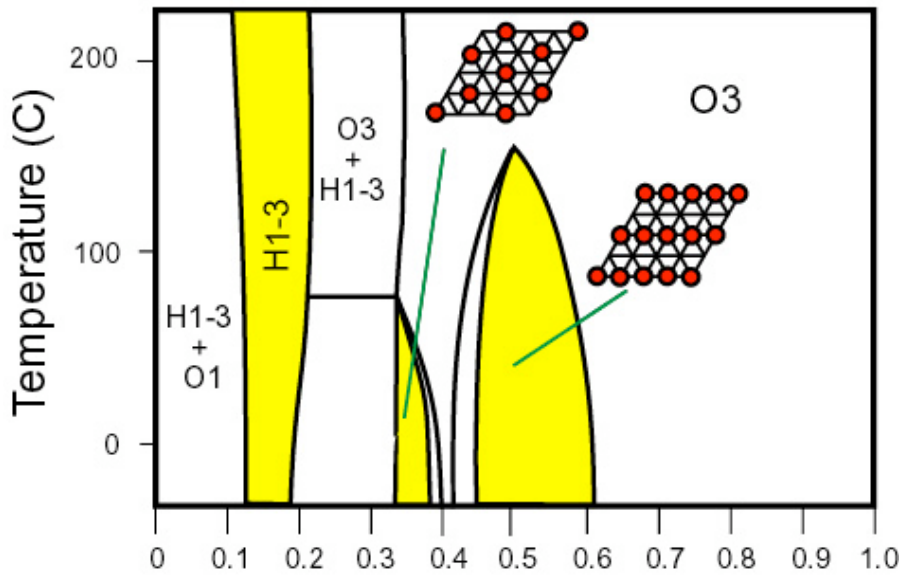
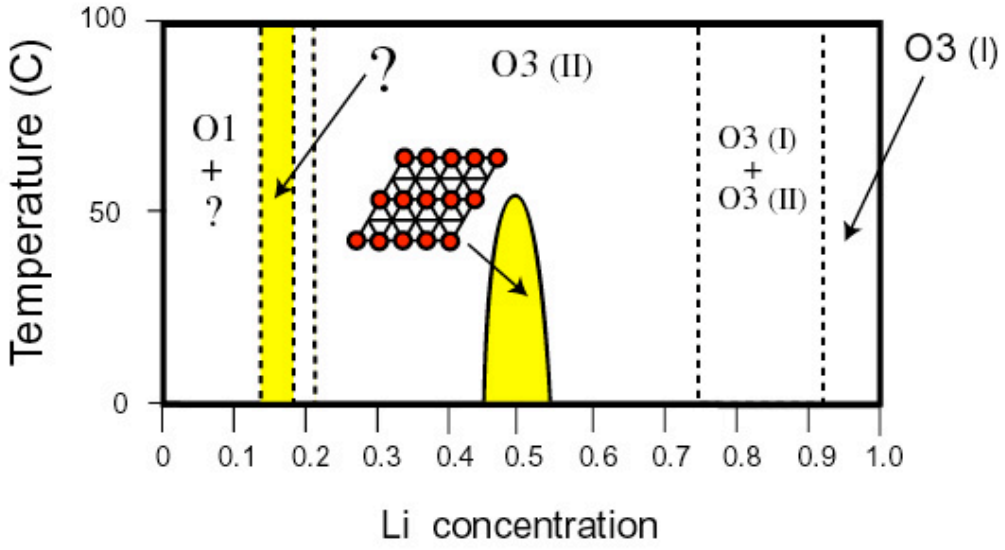
Calculated phase diagram

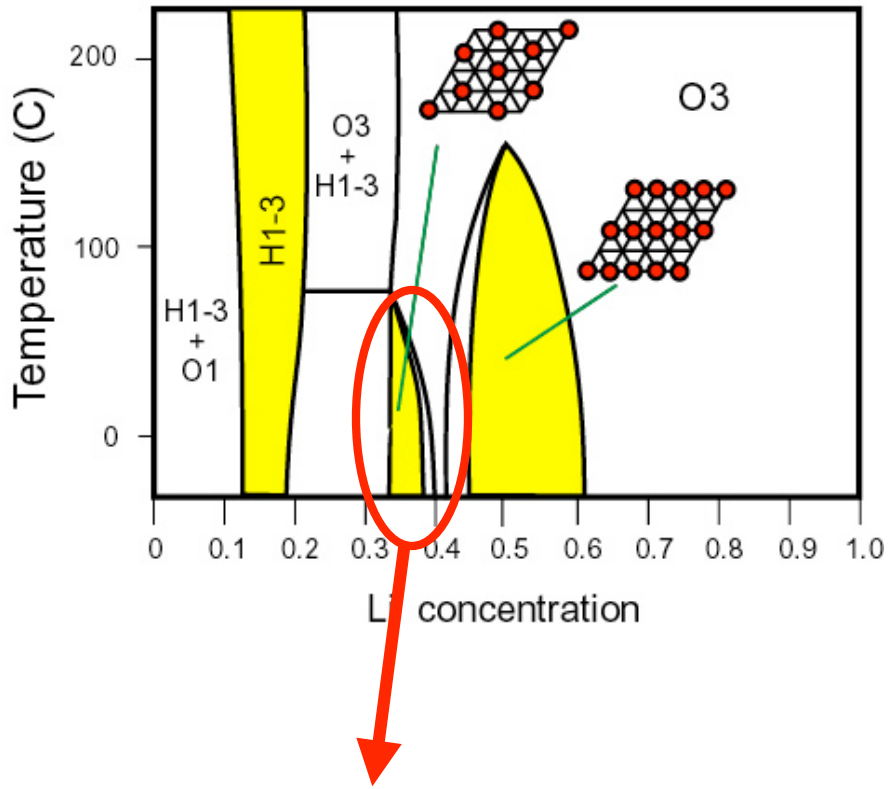


Experimental phase diagram



Reimers, Dahn, J.Electrochem. Soc, (1992)
Ohzuku, Ueda, J. Electrochem. Soc. (1994)
Amatucci et al, J. Electrochem. Soc. (1996)

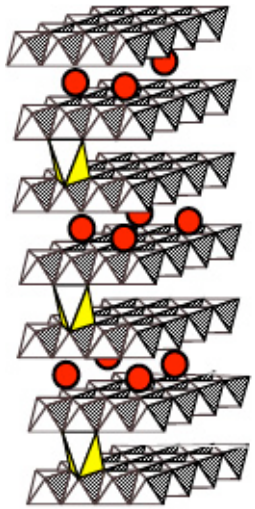
Predicted phases confirmed experimentally



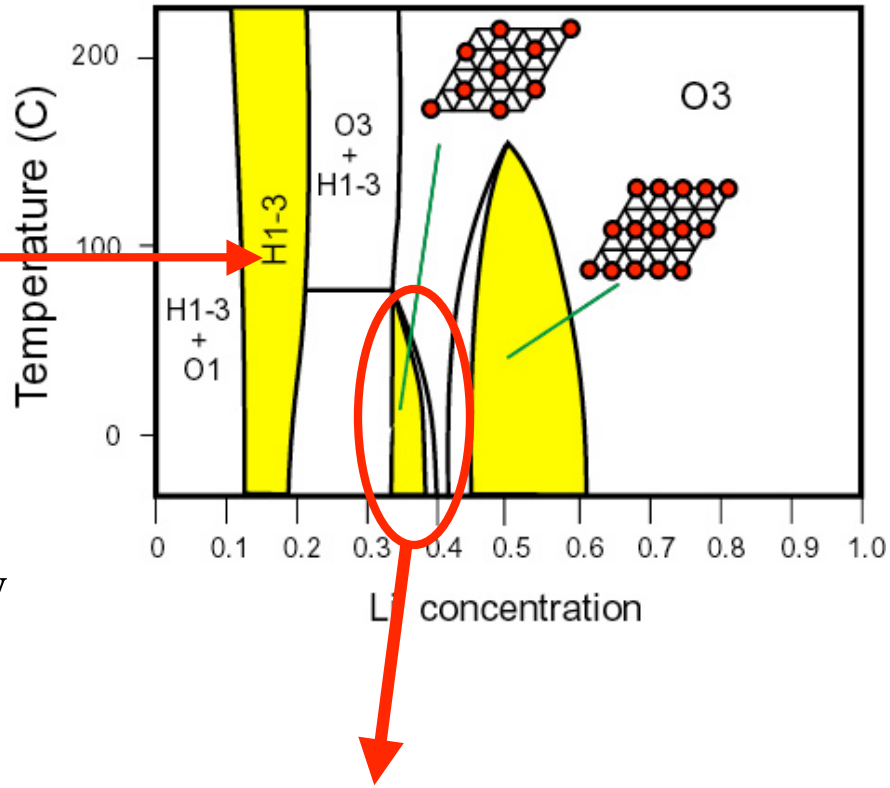
Confirmed experimentally with TEM

Y. Shao-Horn, S. Levasseur, F. Weill, C. Delmas, J. Electrochem. Soc. **150** (2003), A 366

Predicted phases confirmed experimentally



H1-3
(Stage II)



Confirmed experimentally by

Z. Chen, Z. Lu, J.R. Dahn J.
Electrochem. Soc. 149, A1604 (2002)

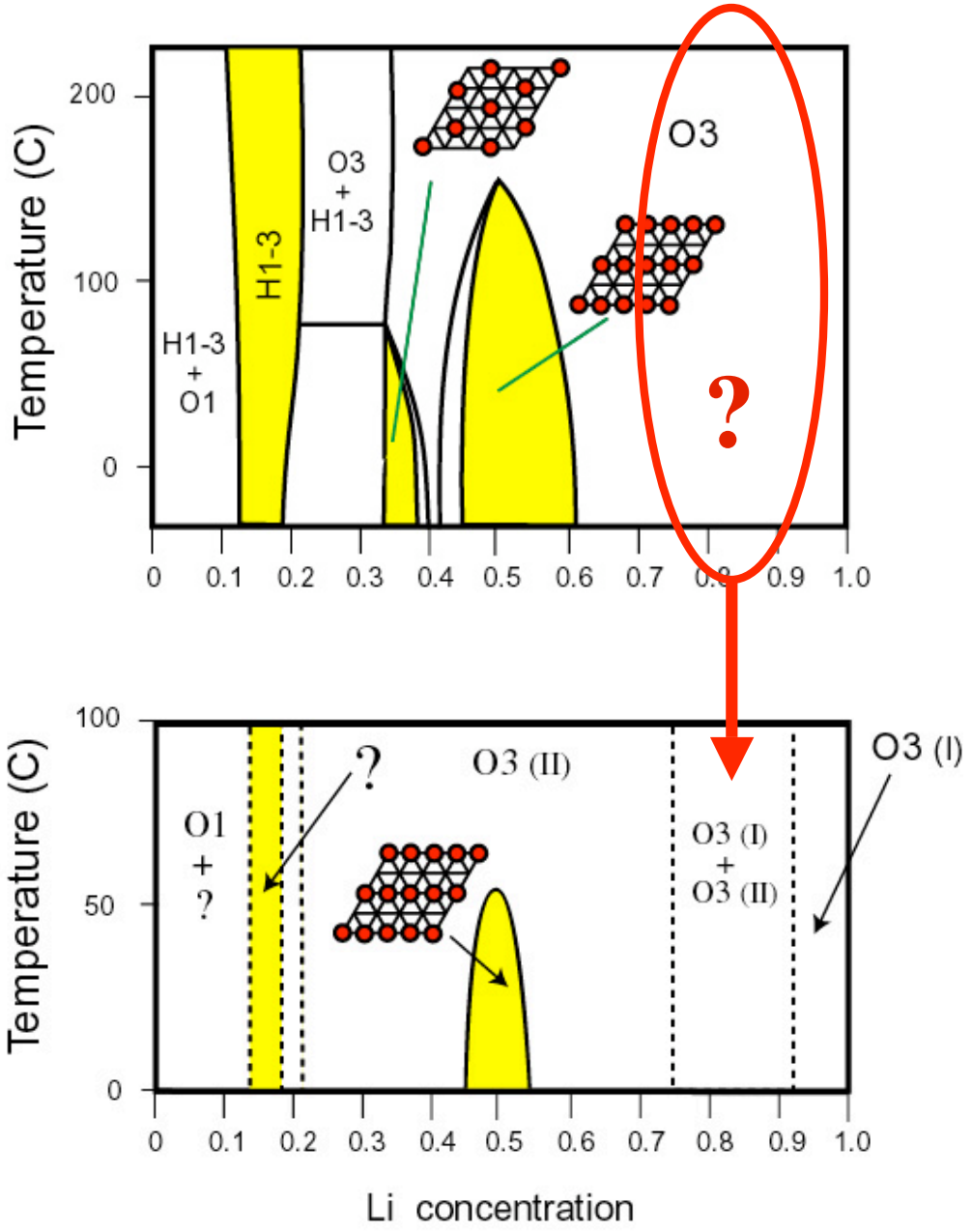
Confirmed experimentally with TEM

Y. Shao-Horn, S. Levasseur, F. Weill, C. Delmas, J. Electrochem. Soc. **150** (2003), A 366

Calculated phase diagram

Experimental phase diagram

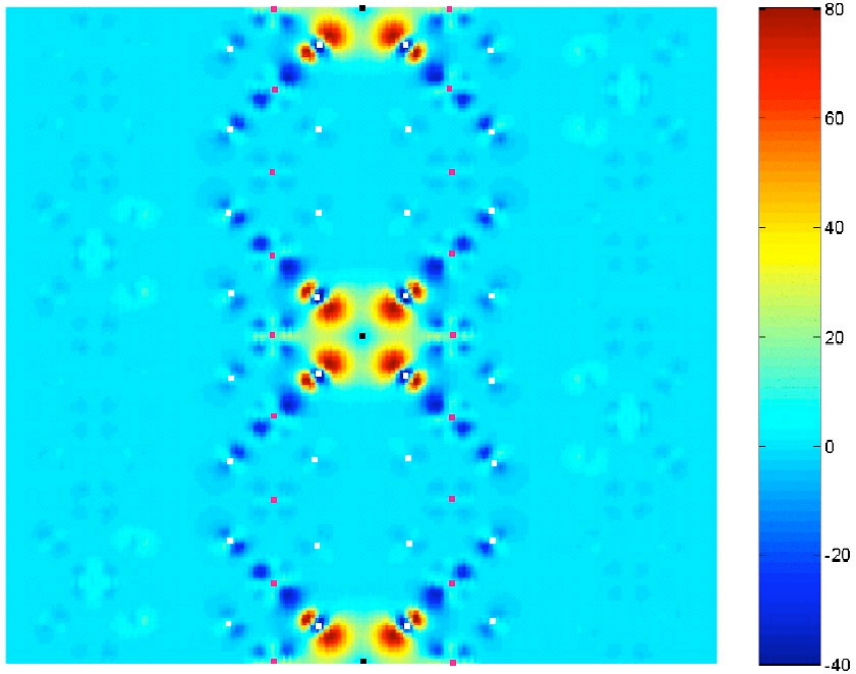
Reimers, Dahn, J.Electrochem. Soc, (1992)
Ohzuku, Ueda, J. Electrochem. Soc. (1994)
Amatucci et al, J. Electrochem. Soc. (1996)



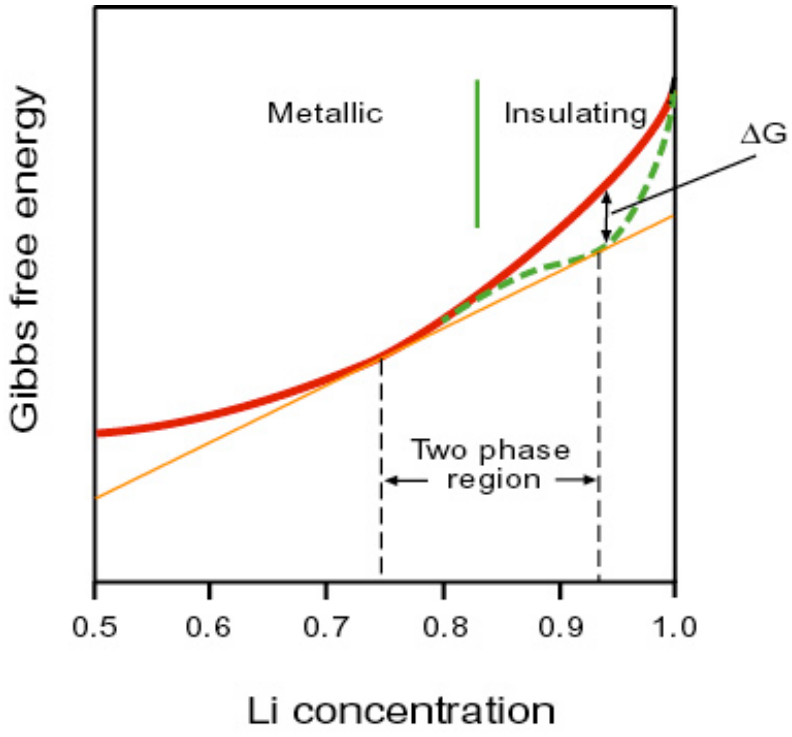
M. Menetrier et al J. Mater Chem. 9, 1135 (1999)

Effect of metal insulator transition

Holes in the valence band
localize in space

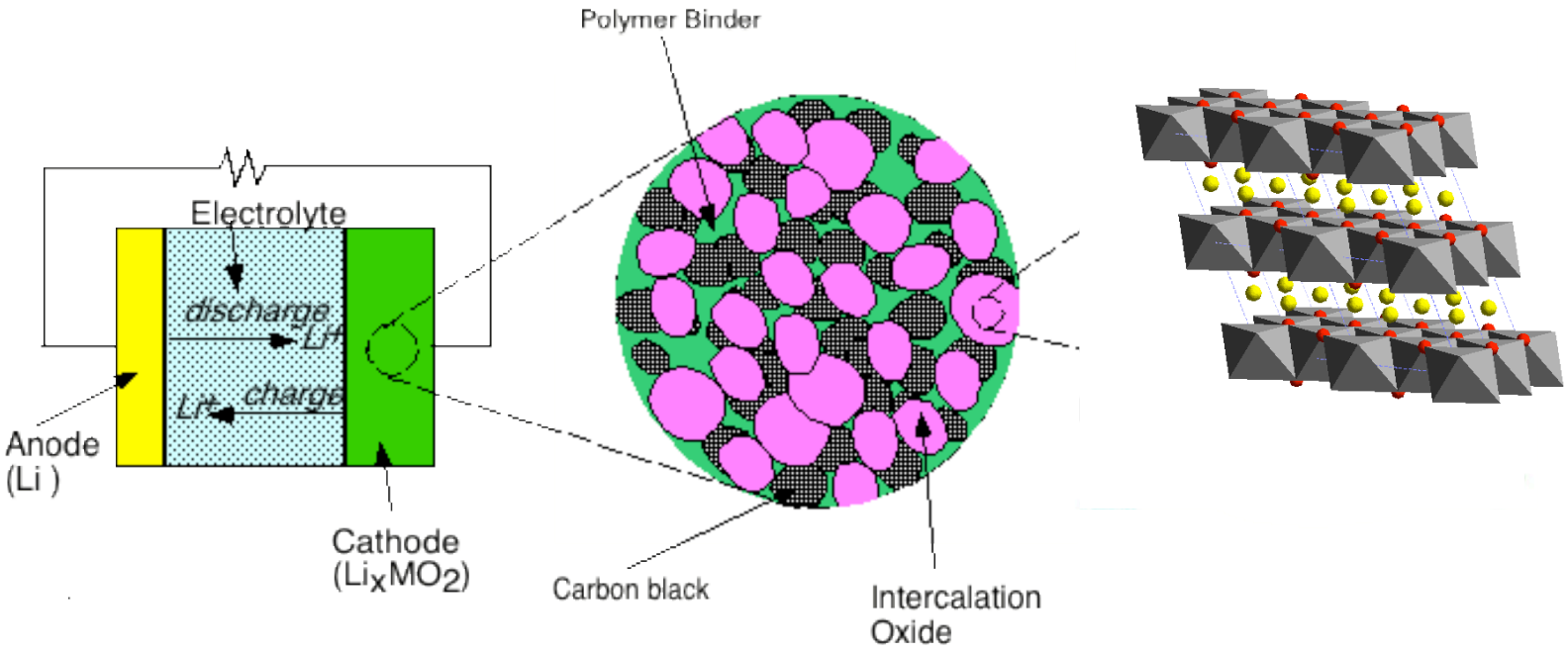


C. A. Marianetti et al, Nature Materials, 3, 627 (2004).



LDA & GGA fails to accurately describe localized electronic states

Diffusion



Fick's Law

$$J = -D\nabla C$$

Interstitial diffusion and configurational disorder

Kubo-Green relations

$$D = D_J \cdot \tilde{\Theta}$$

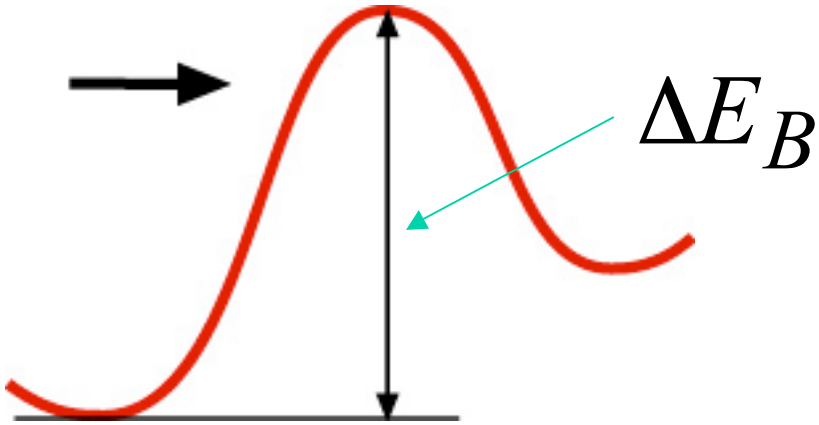
Thermodynamic factor

$$\tilde{\Theta} = \frac{\partial\left(\frac{\mu}{kT}\right)}{\partial \ln x}$$

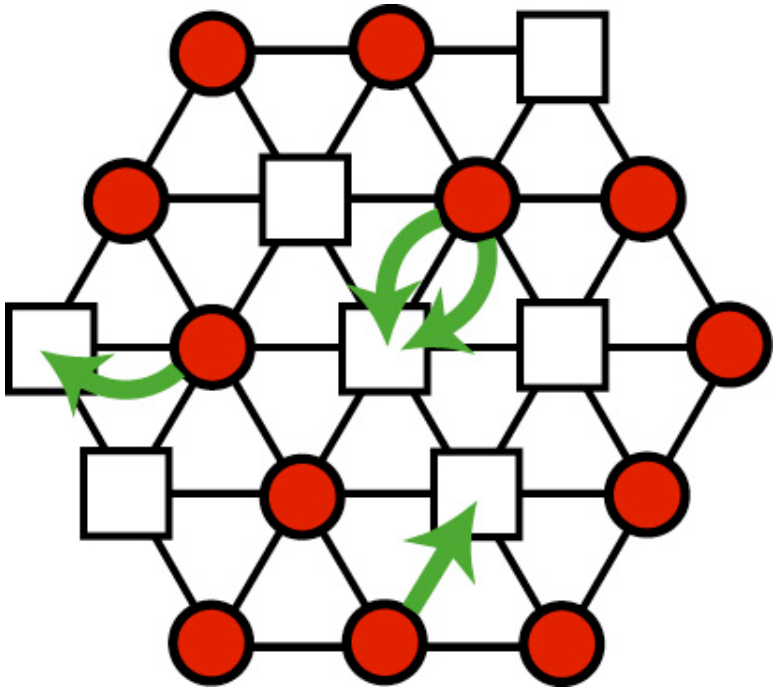
Self diffusion coefficient

$$D_J = \frac{1}{(2d)t}\left\langle \frac{1}{N}\left(\sum_{i=1}^{N} \Delta\vec{R}_i(t)\right)^2 \right\rangle$$

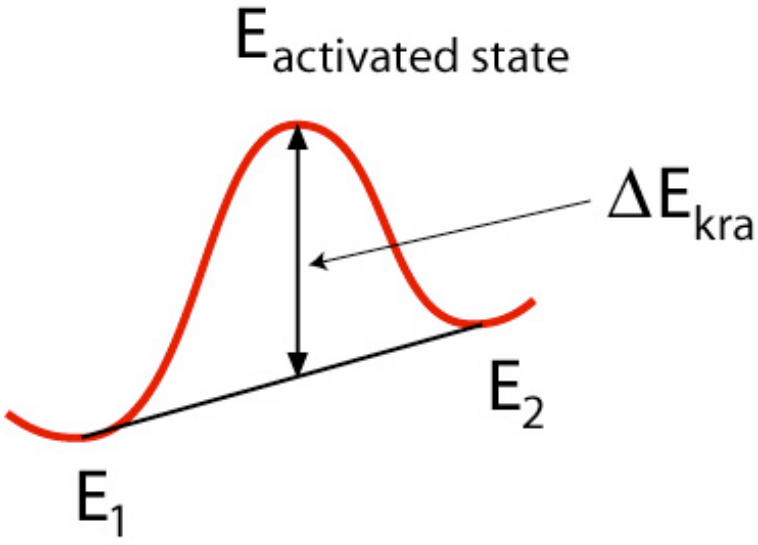
Individual hops: Transition state theory



$$\Gamma = \nu * \exp\left(\frac{-\Delta E_B}{kT}\right)$$



Kinetically resolved activation barrier

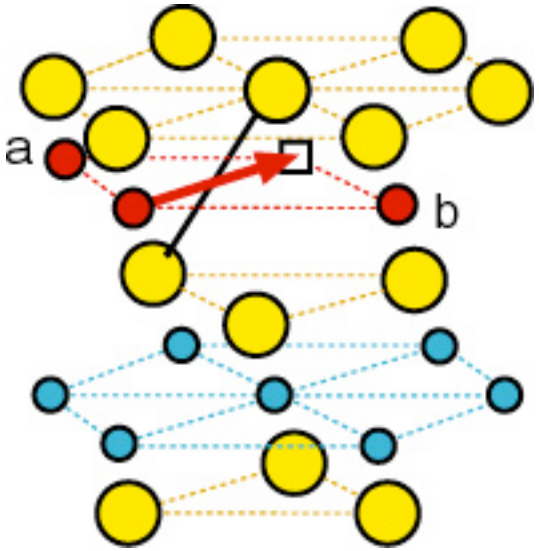


$$\Delta E_{kra} = E_{activated-state} - \frac{1}{2}\left(E_1 + E_2\right)$$

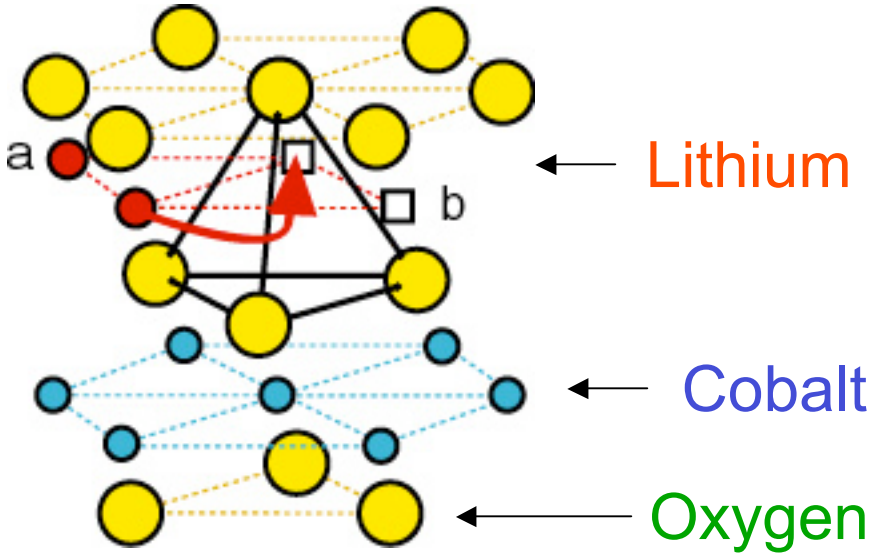
$$\Delta E_{barrier} = \Delta E_{kra} + \frac{1}{2}\left(E_{final} - E_{initial}\right)$$

A. Van der Ven, G. Ceder, M. Asta, P.D. Tepesch, Phys Rev. B 64 (2001) 064112

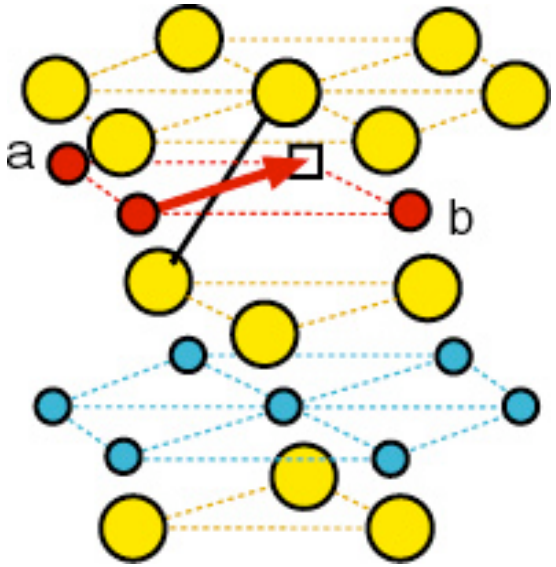
Migration mechanism in Li_xCoO_2

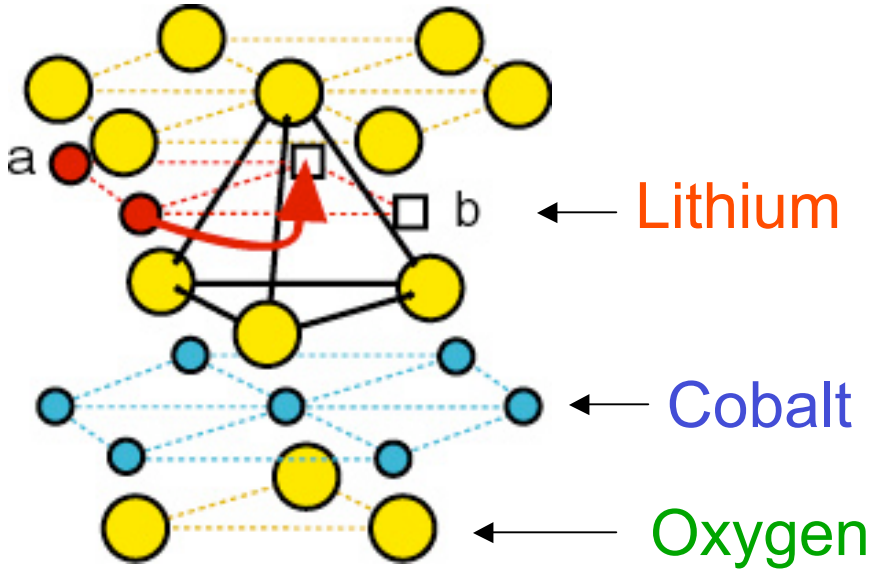


Single vacancy hop mechanism



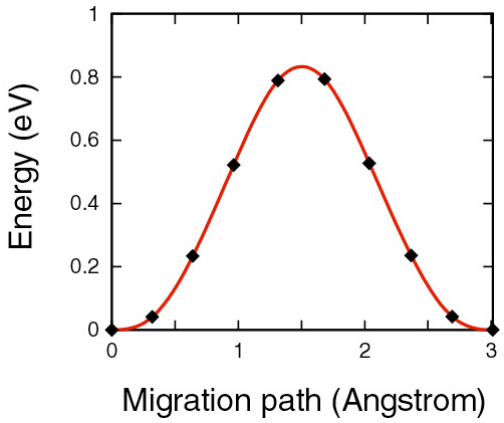
Divacancy hop Mechanism

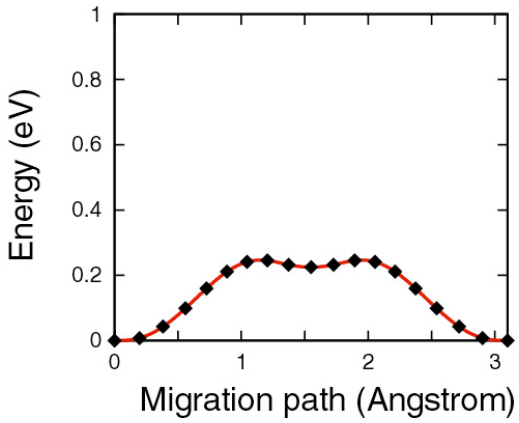




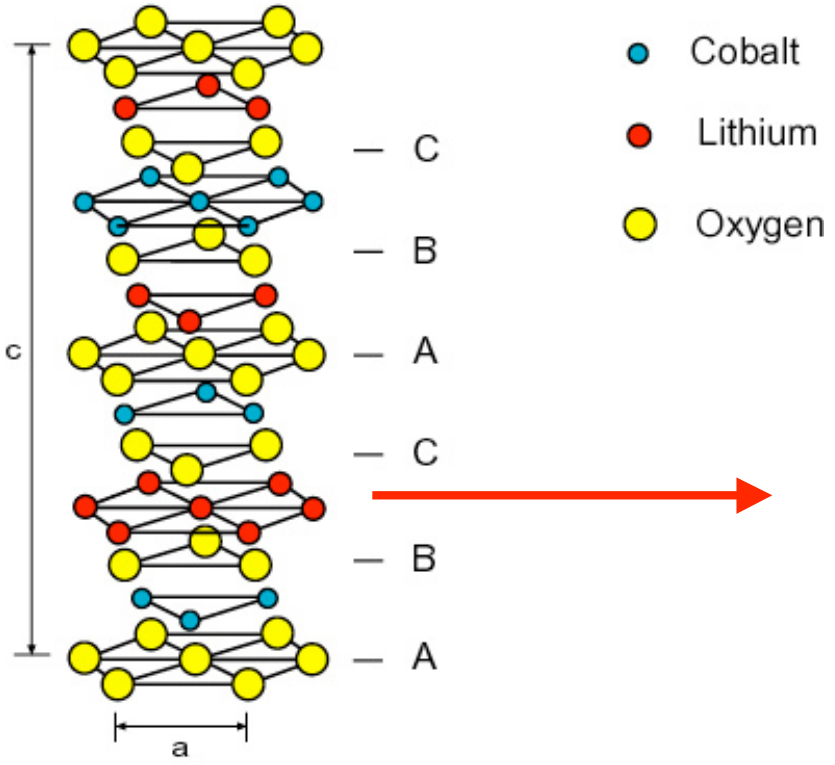
Single vacancy hop

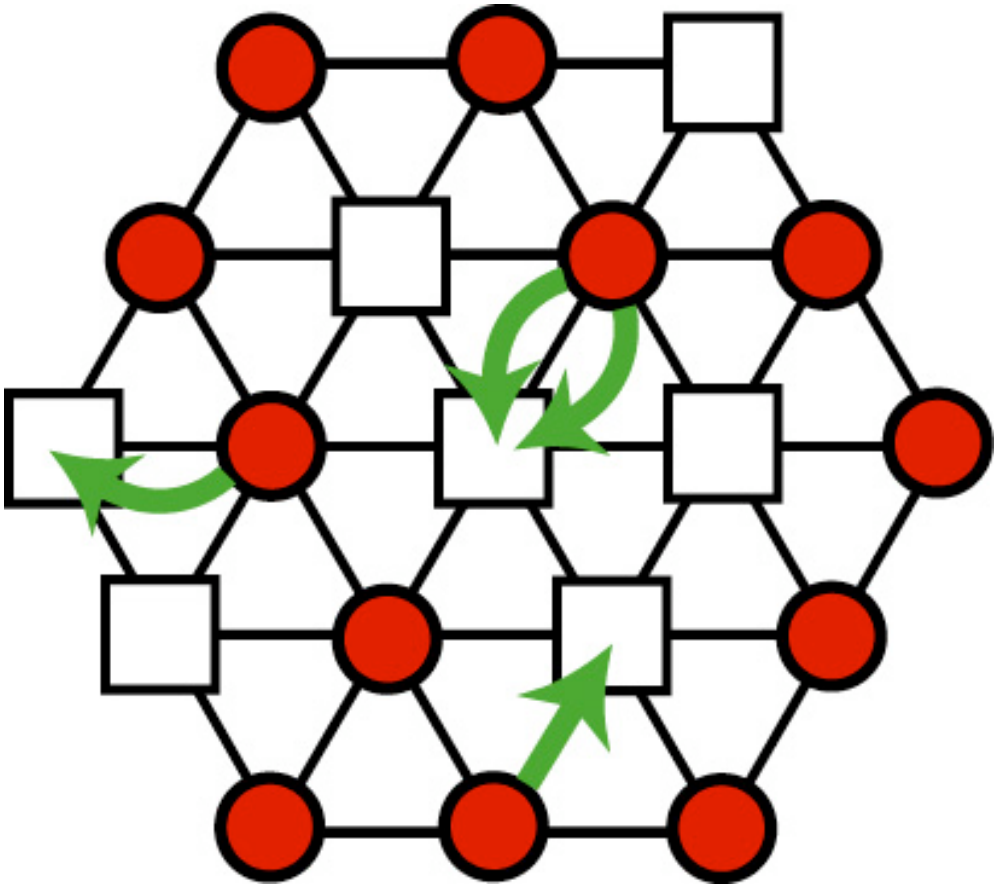
Divacancy hop



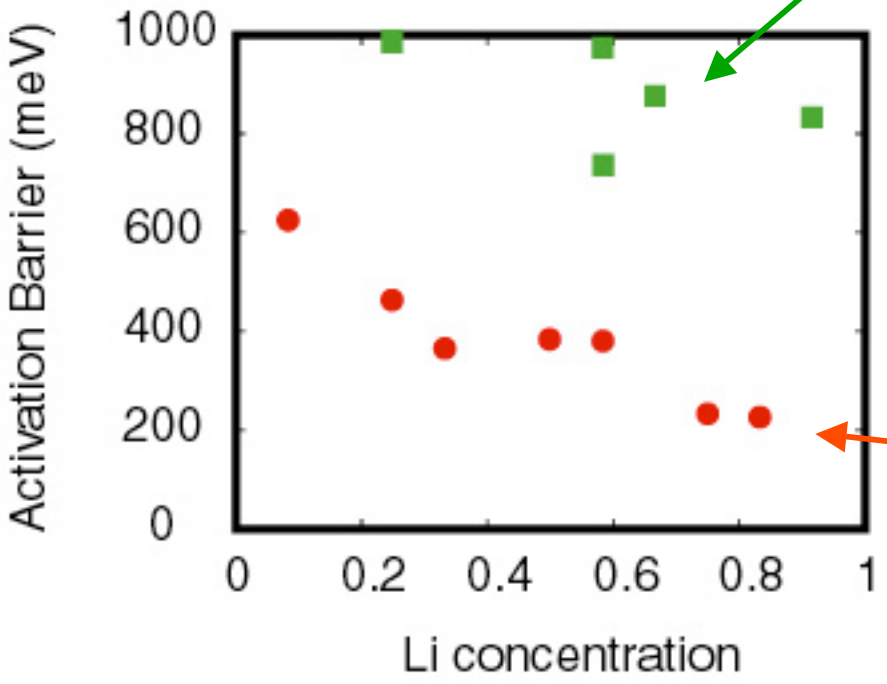


Many types of hop possibilities in the lithium plane

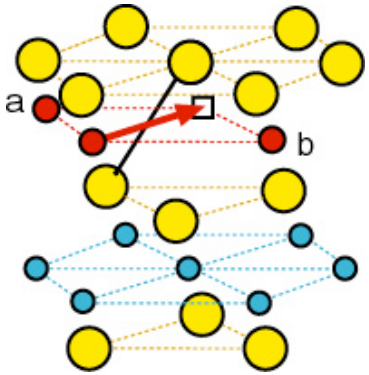




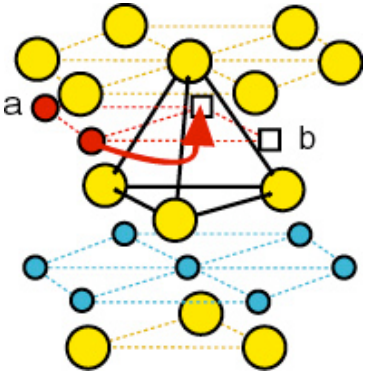
Migration barriers depend configuration and concentration



Single-vacancy mechanism

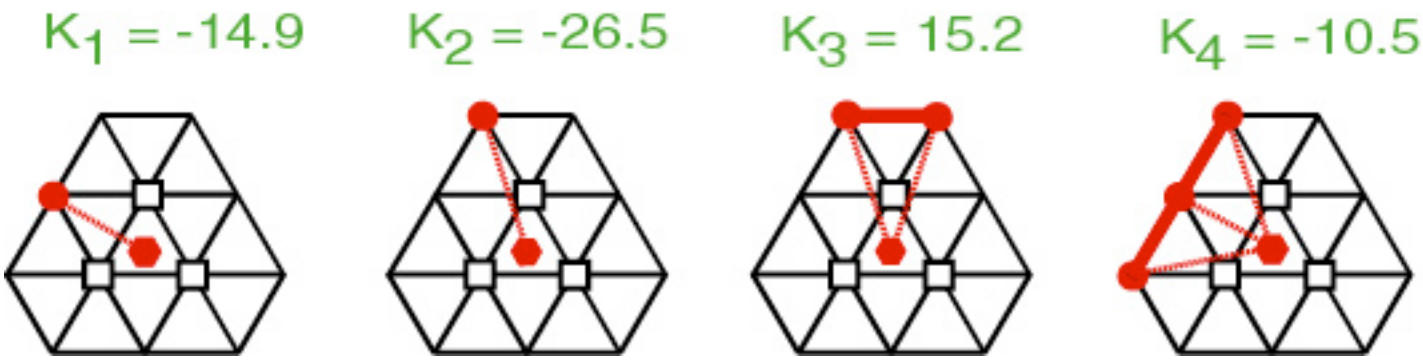


Divacancy mechanism



Local Cluster expansion for divacancy migration barrier

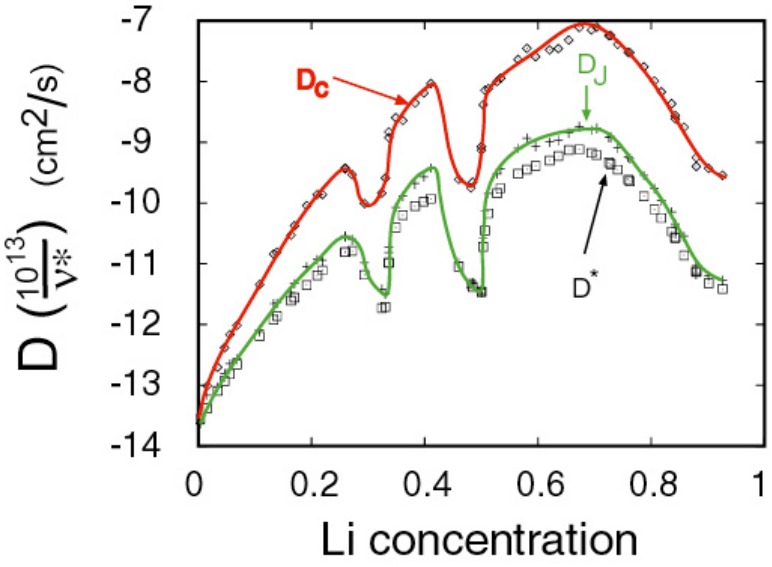
$K_0 = 411$ meV



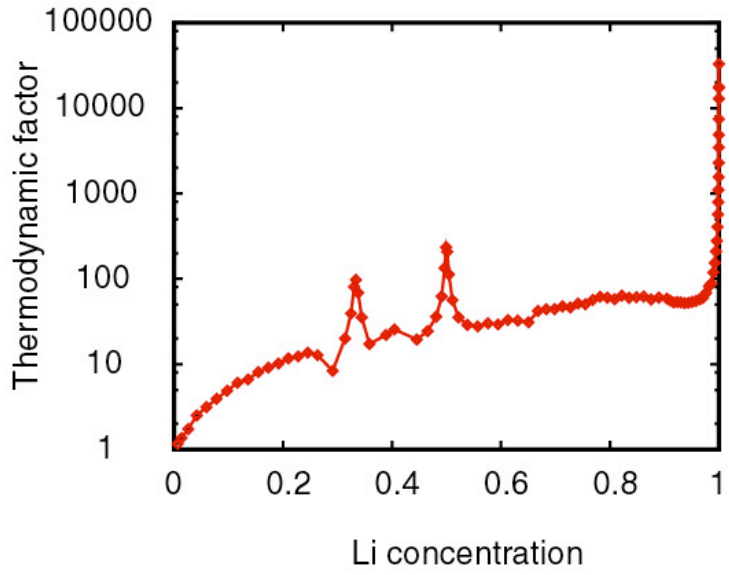
Calculated diffusion coefficient
(First Principles cluster expansion + kinetic Monte Carlo)

$$D = \Theta \cdot D_J$$

Diffusion coefficient at 300 K



Thermodynamic factor Θ



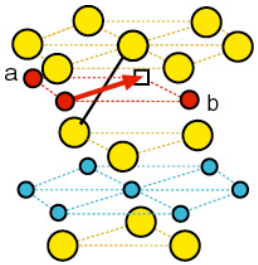
A. Van der Ven, G. Ceder, M. Asta, P.D. Tepesch, Phys Rev. B 64 (2001) 064112

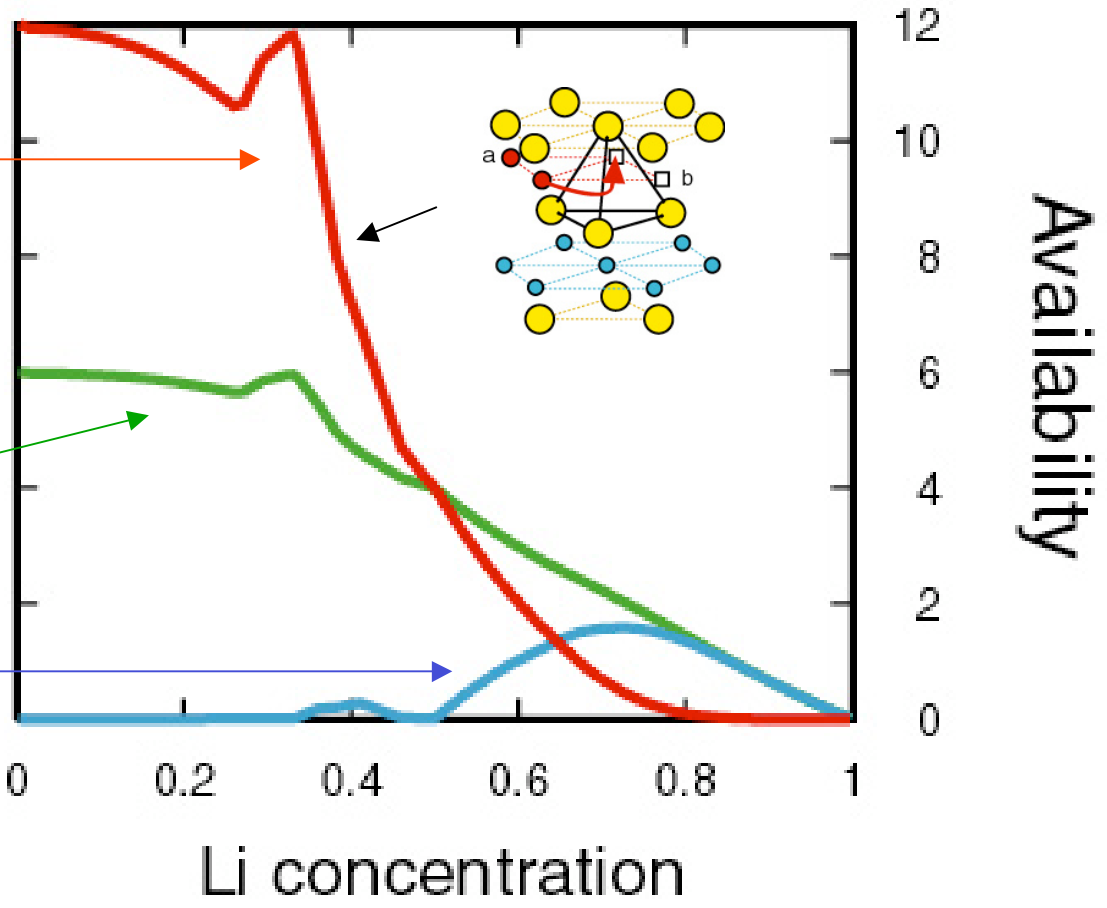
Available migration mechanisms for each lithium ion

Channels into a divacancy

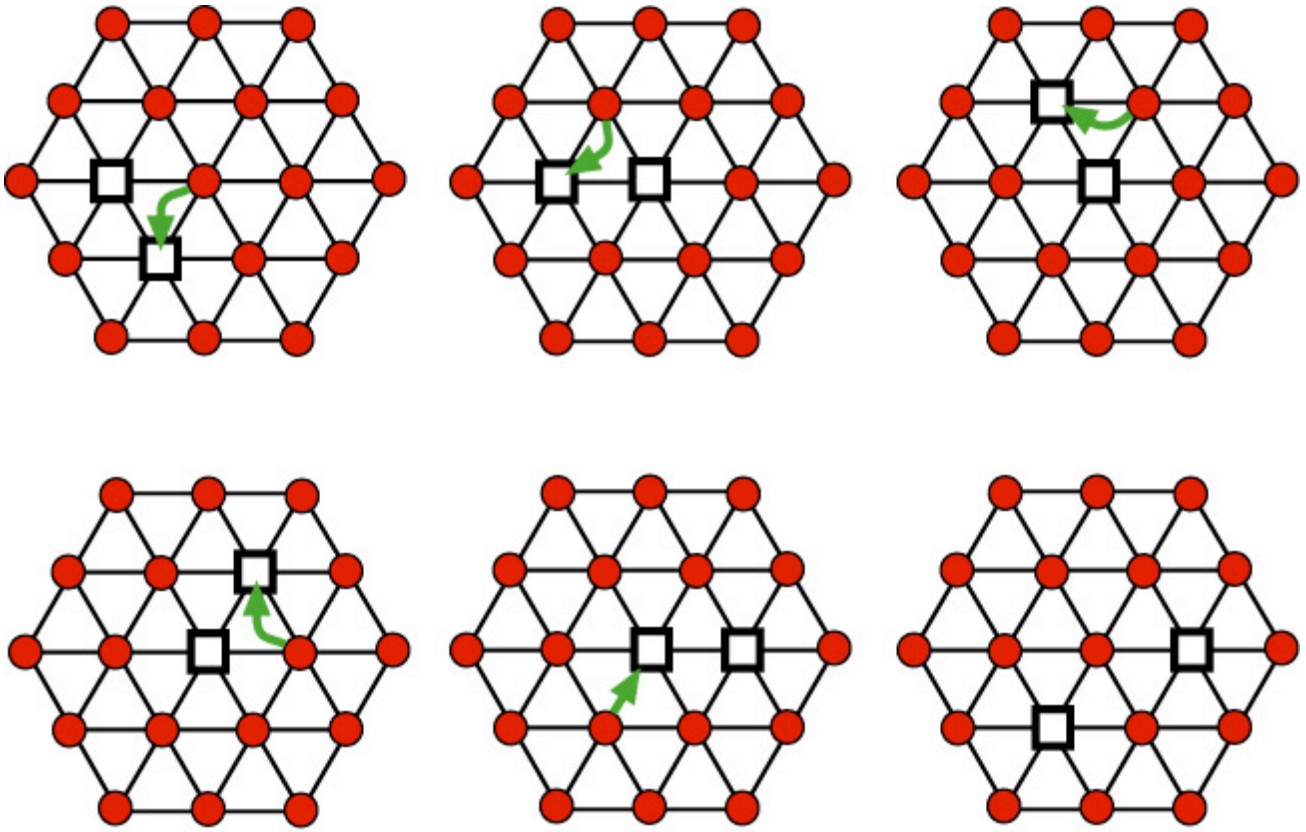
Number of vacancies around lithium

Channels into isolated vacancies

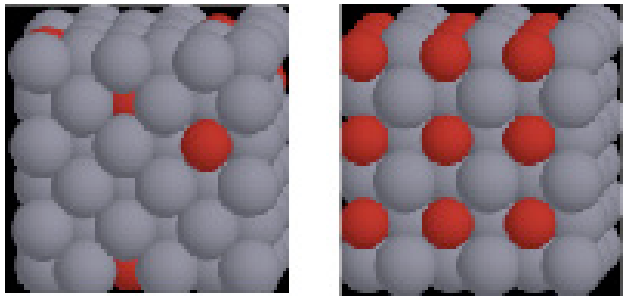


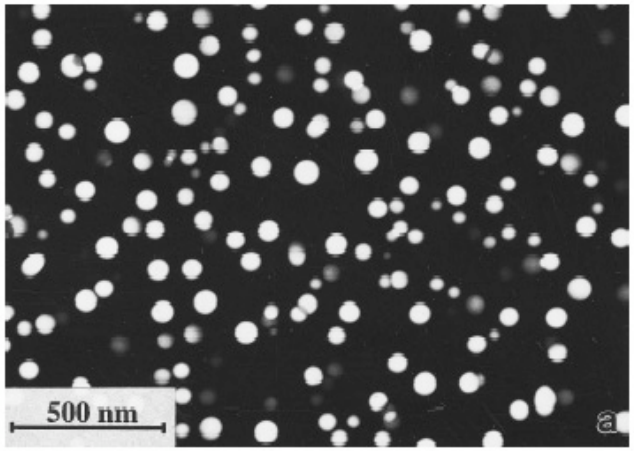


Diffusion occurs with a divacancy mechanism

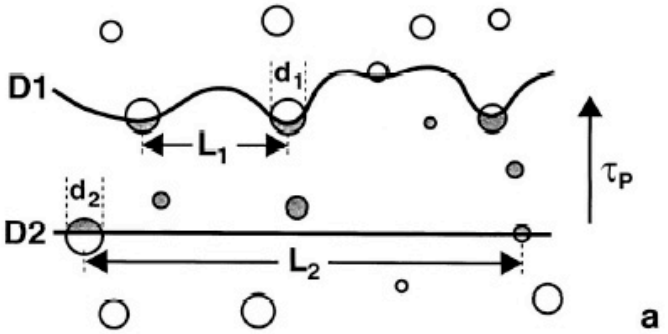


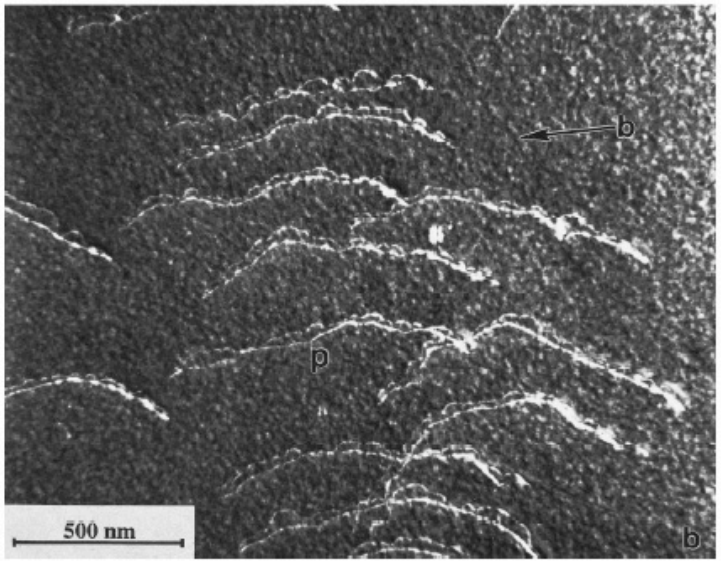
Diffusion and phase transformations in Al-Li alloys





Dark field TEM
A. Kalogeridis, J. Pesieka, E. Nembach, Acta Mater 47 (1999) 1953

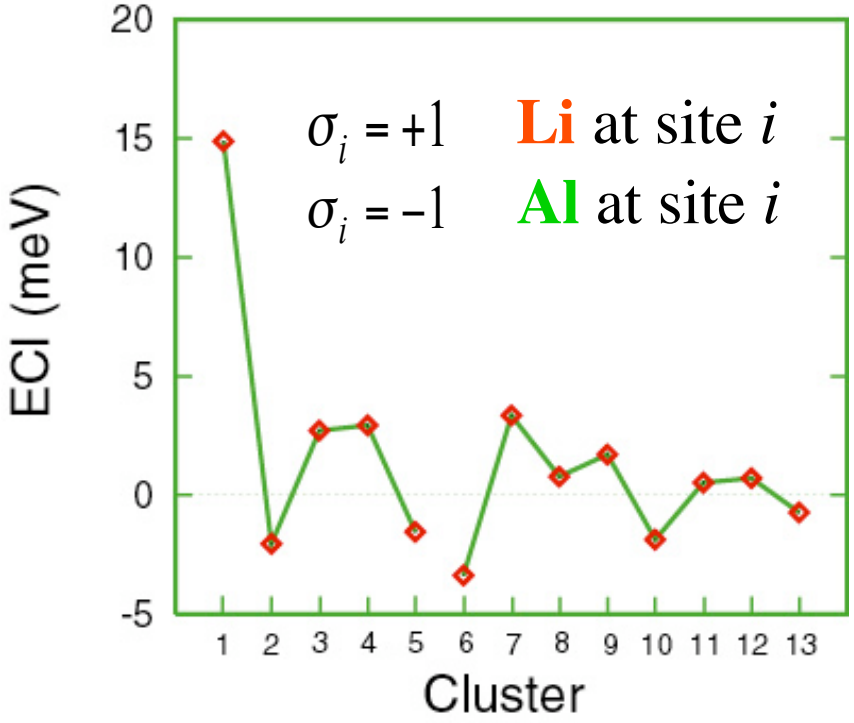


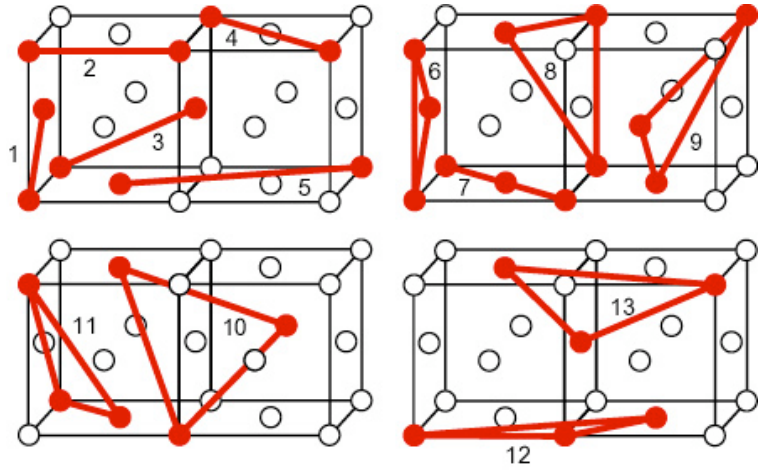


Dark field in situ TEM, peak aged Al-Li specimen under full load
H. Rosner, W. Liu, E. Nembach, Phil Mag A, 79 (1999) 2935

fcc Al-Li alloy

Binary cluster expansion





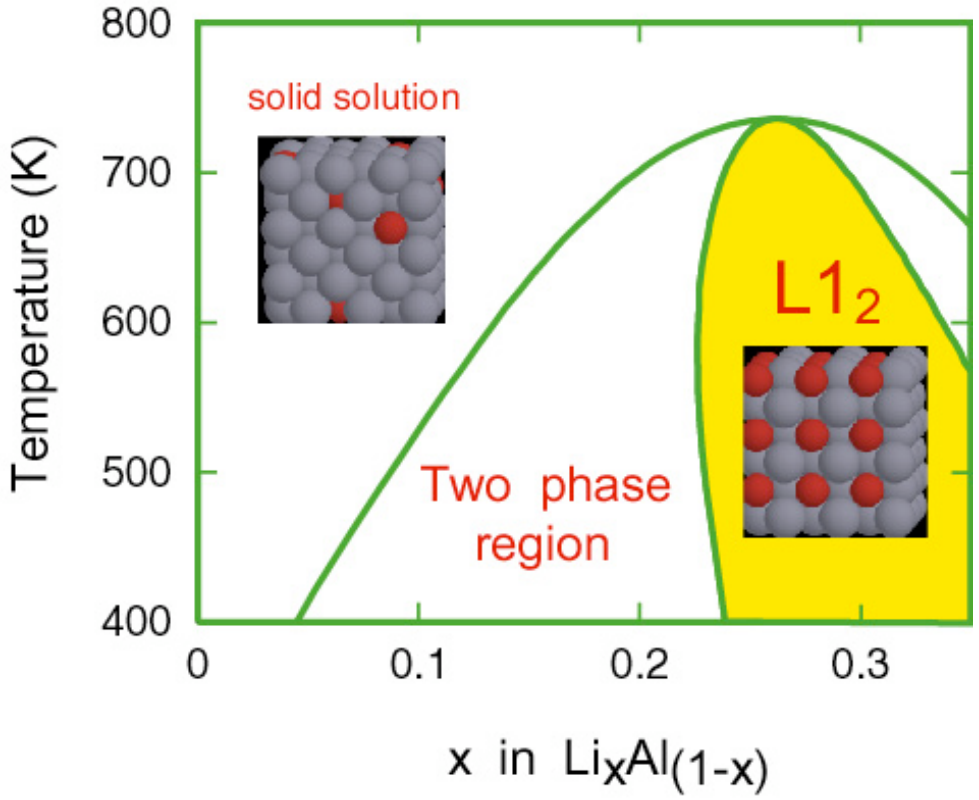
Fit to LDA energies of 70 different Al-Li arrangements on fcc

$$E(\sigma) = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$

A. Van der Ven, G. Ceder, Phys. Rev. B**71**, 054102(2005)

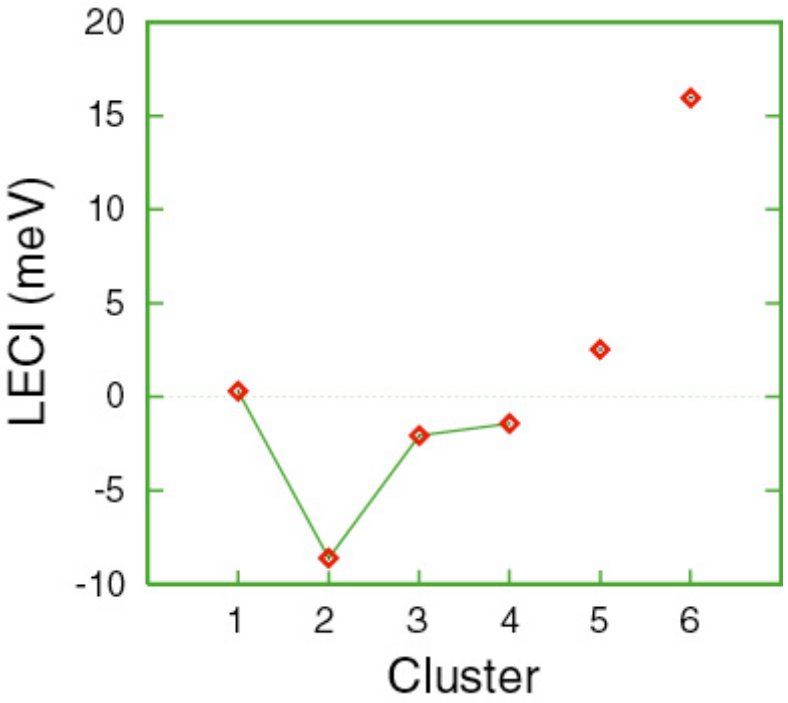
Calculated thermodynamic and kinetic properties of Al-Li alloy

First principles cluster expansion + Monte Carlo



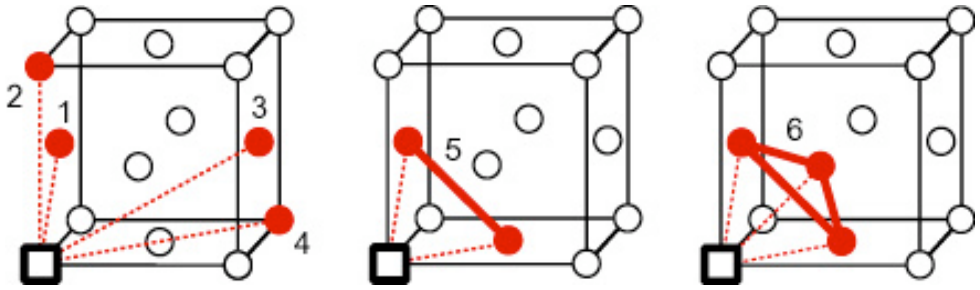
A. Van der Ven, G. Ceder, Phys. Rev. B**71**, 054102(2005)

Expand environment dependence of vacancy formation energy



Local cluster expansion*
(perturbation to binary cluster expansion)

Fit to 23 vacancy LDA formation energies in different Al-Li arrangements
(107 atom supercells).

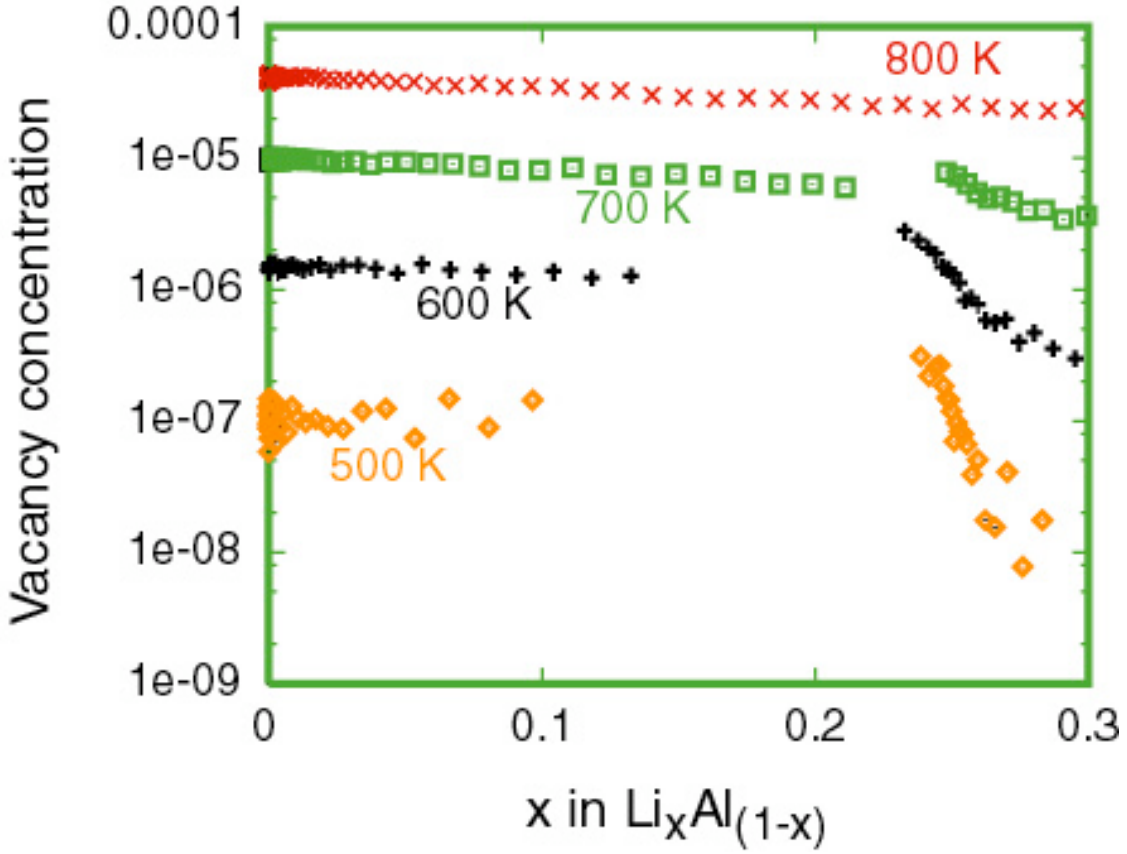


$\sigma_i = +1$ **Li** at site i

$\sigma_i = -1$ **Al** at site i

A. Van der Ven, G. Ceder, Phys. Rev. B**71**, 054102(2005)

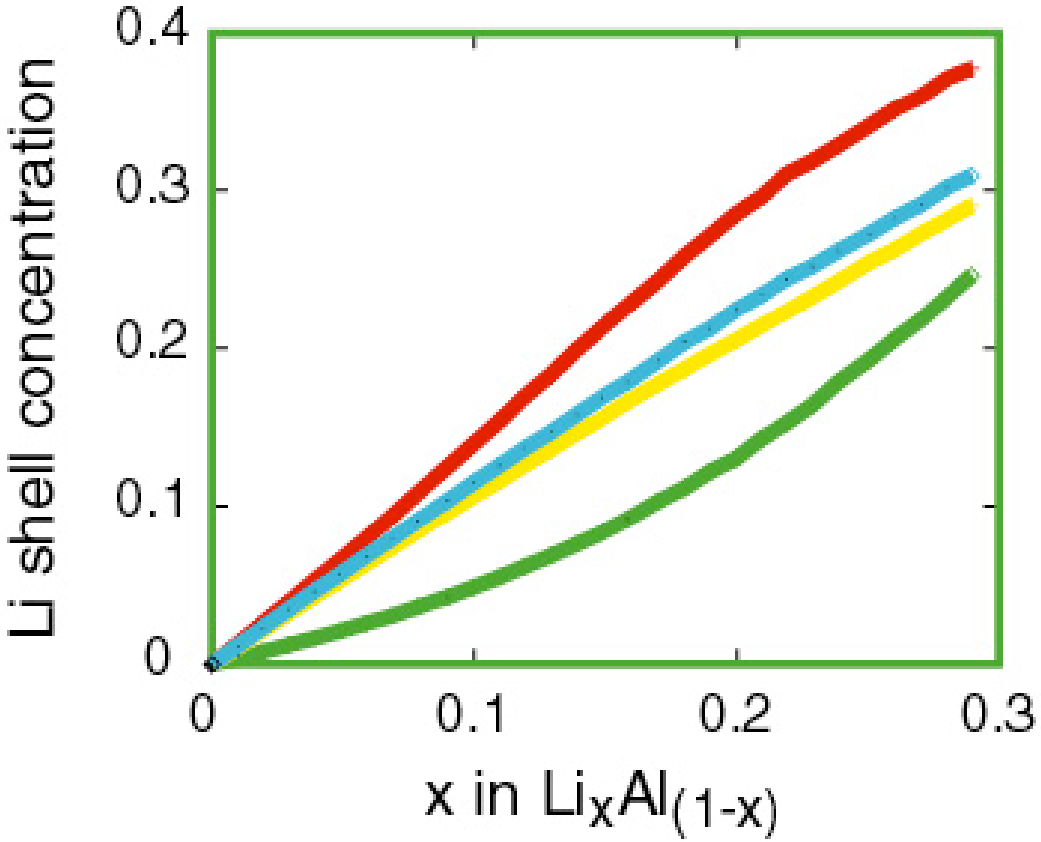
Equilibrium vacancy concentration
(Monte Carlo applied to cluster expansion)

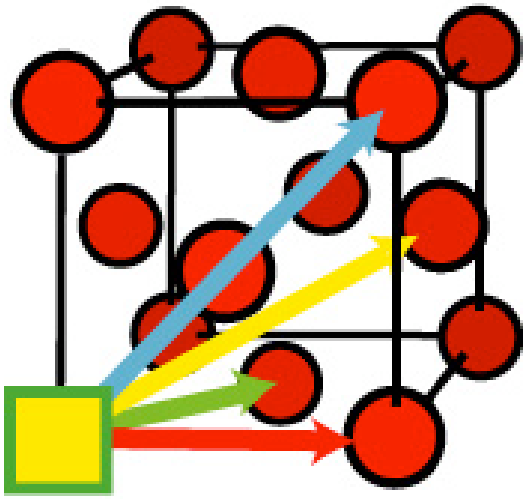


A. Van der Ven, G. Ceder, Phys. Rev. B**71**, 054102(2005)

Vacancy surrounds itself by Al
Short range order around a vacancy

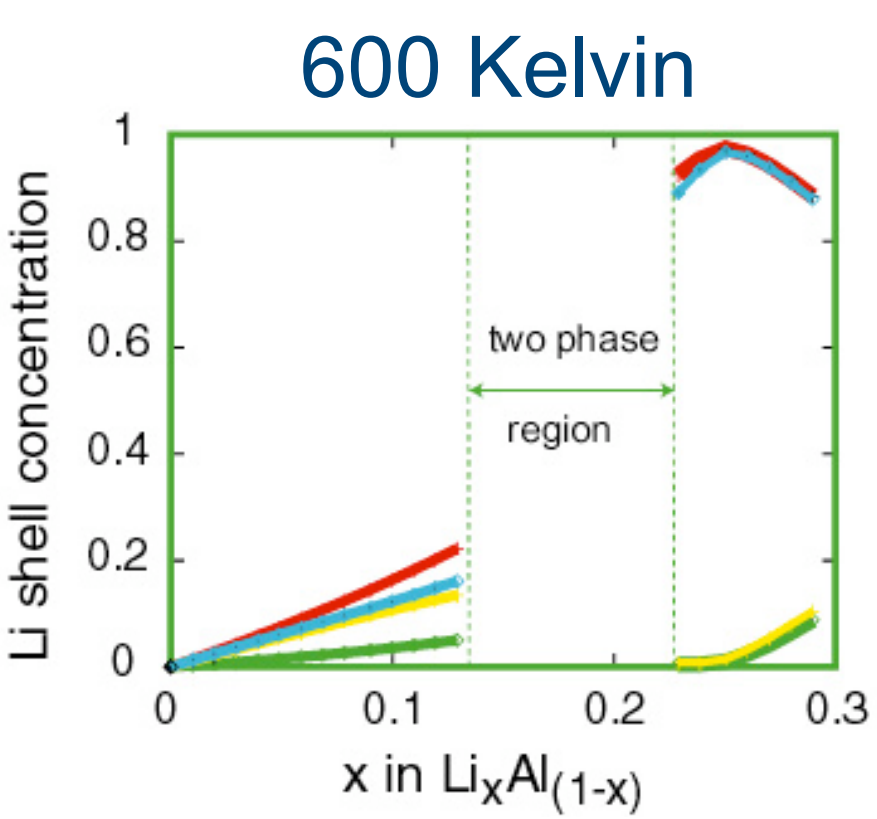
750 Kelvin

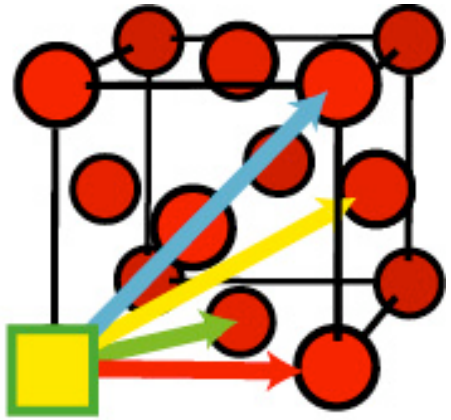


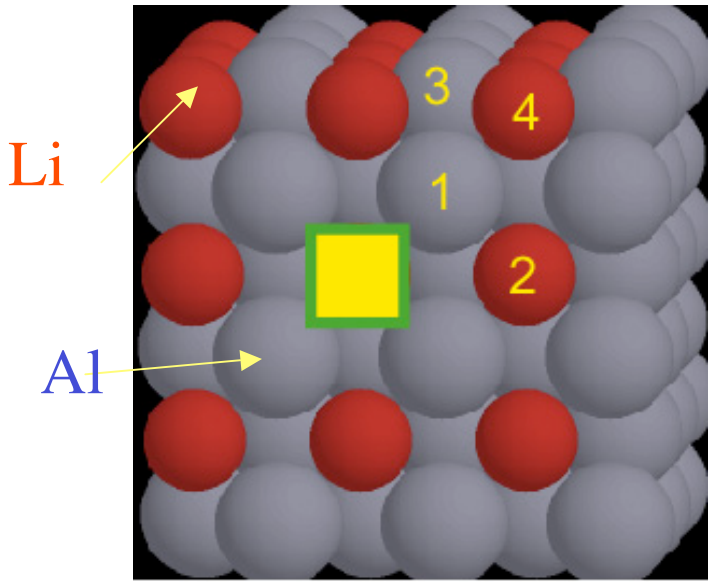


A. Van der Ven, G. Ceder, Phys. Rev. B**71**, 054102(2005)

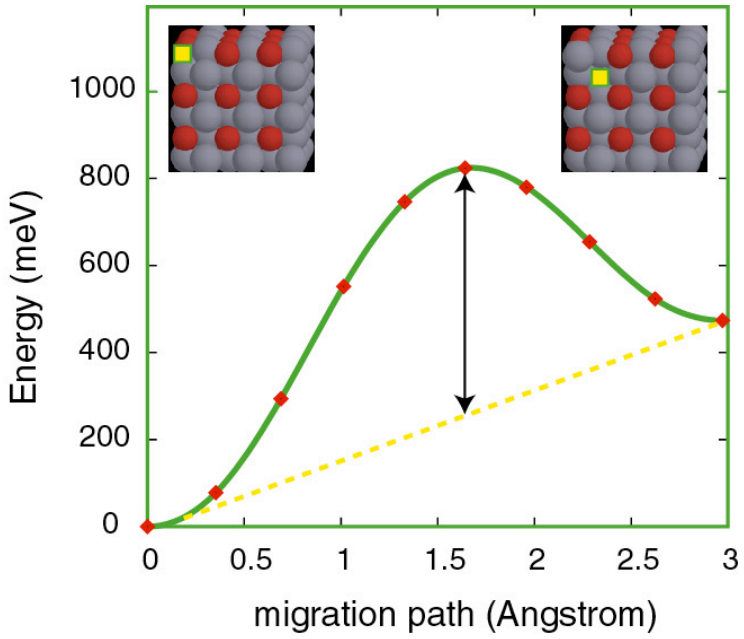
Vacancies reside on lithium sublattice in L12

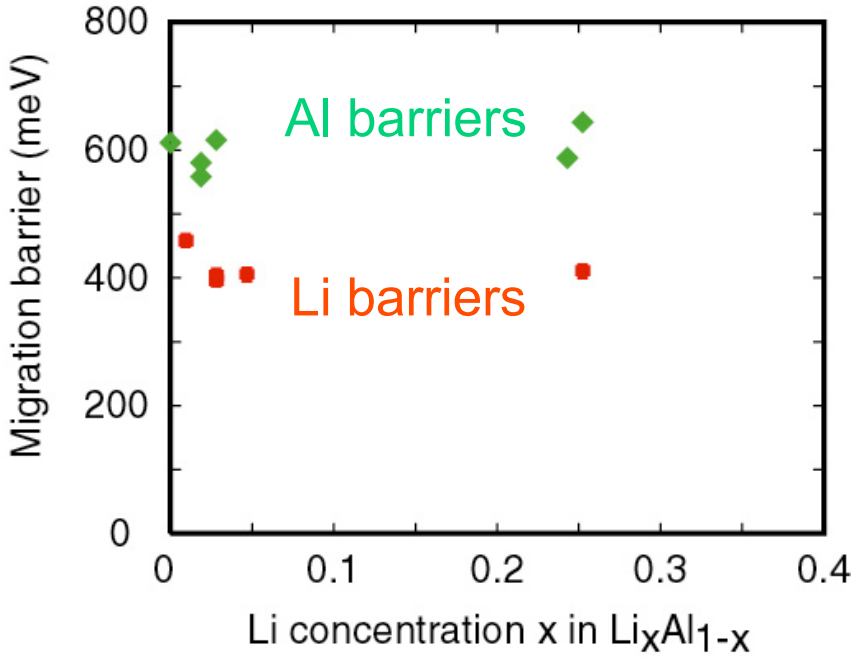






Migration barriers for lithium and aluminum differ by ~150 meV



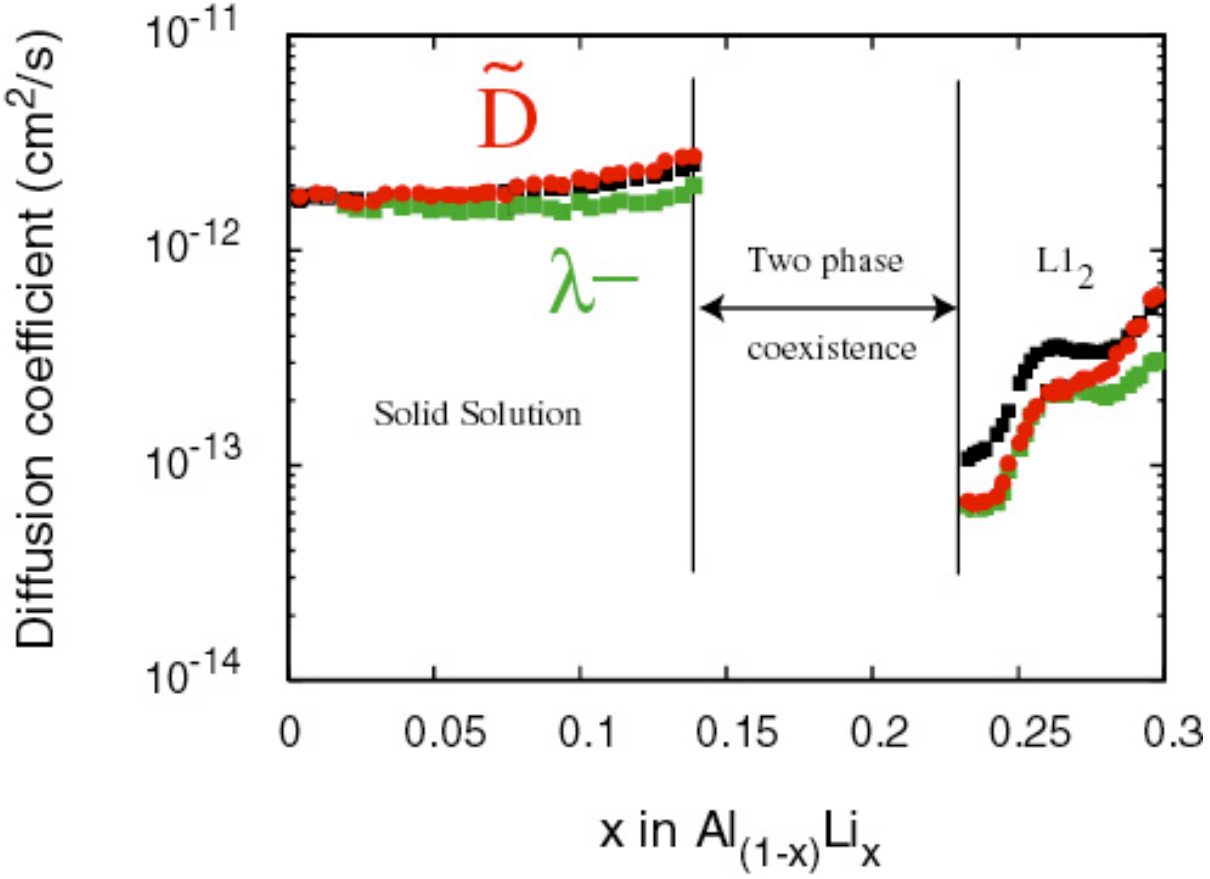


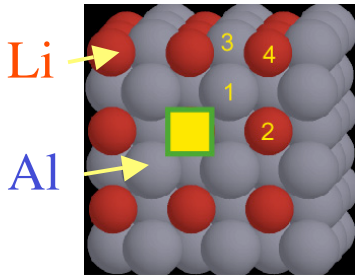
Calculated (LDA) in 107 atom supercells

$$\nu^*_{Al} \approx 4.5 \times 10^{13}\, Hz$$

$$\nu^*_{Li} \approx 7 \times 10^{13}\, Hz$$

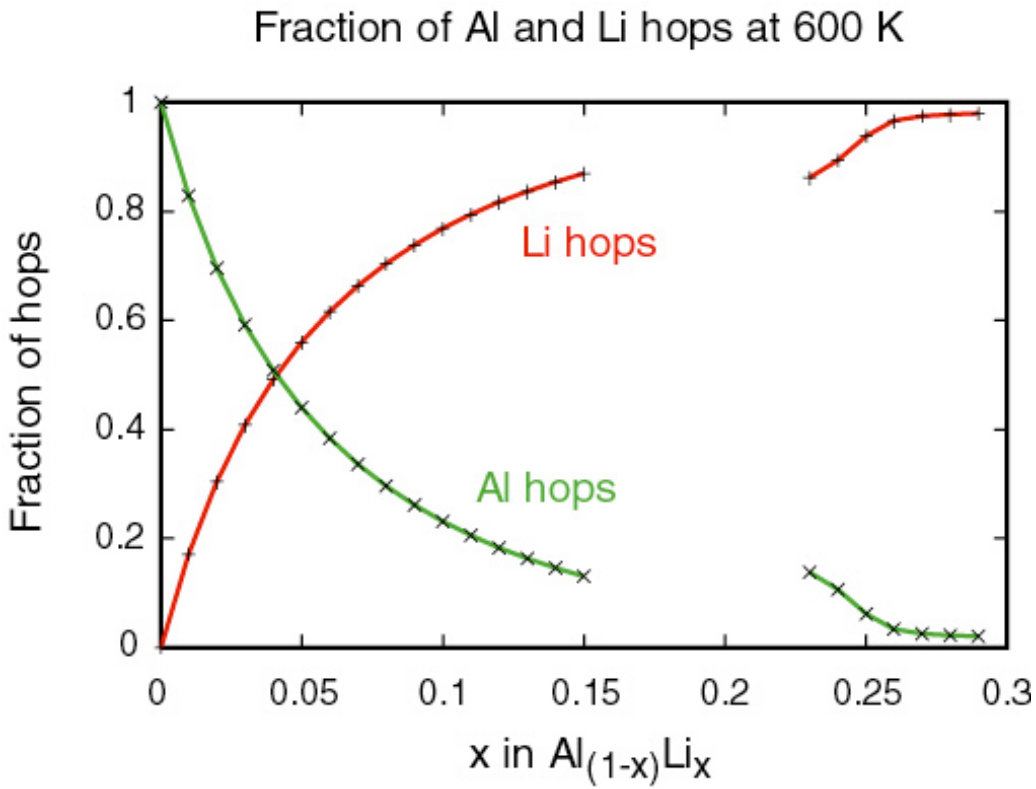
Calculated interdiffusion coefficient



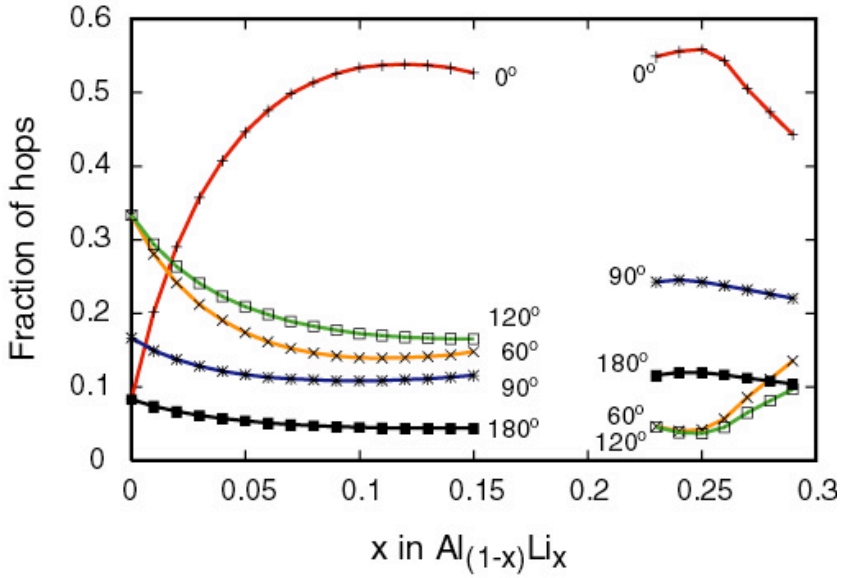


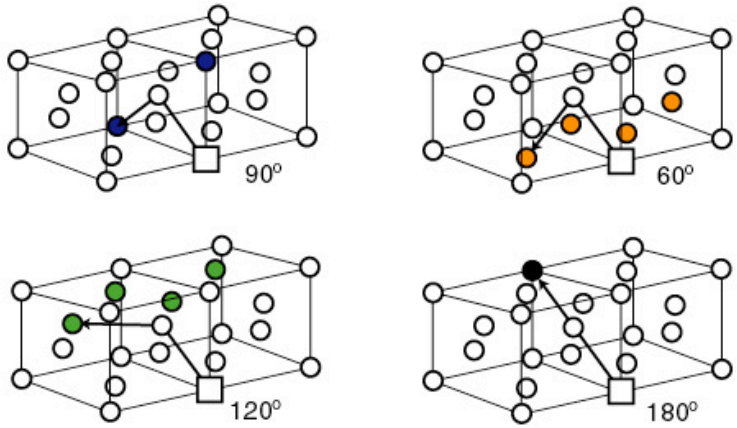
A. Van der Ven, G. Ceder, Phys. Rev. Lett. **94**, 045901 (2005).

Hop mechanisms



Frequency of hop angles between successive hops





A. Van der Ven, G. Ceder, Phys. Rev. Lett. **94**, 045901 (2005).

Conclusion

- Green-Kubo formalism yields rigorous expressions for diffusion coefficients
- Discussed diffusion formalism for both interstitial and substitutional diffusion
- Intriguing hop mechanisms in multi-component solids that can depend on ordering
- Thermodynamics plays a crucial role!