Cluster Expansions for Thermodynamics and Kinetics of Mixtures on fixed lattices

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Outline

- Alloy thermodynamics from 1st-principles
  - Cluster expansions
  - Phase diagrams, phase stability
- Alloy kinetics from 1st-principles
  - Impurity diffusion (in aluminum)
  - Diffusion in alloys
  - Clustering, initial stages of precipitation

Why first-principles?

- Scientifically the correct starting point
- predictive
- oftentimes as accurate as experiment
- “inexpensive”
- stable/metastable/hypothetical => trends & insight
- underlying physics => insight
- unified picture (thermodynamics, kinetics, upscaling to macroscopic scale) challenge of modeling realistic materials under realistic conditions – empirical modeling succumbs to piling up of assumptions, unknown parameters

Trends:

0K structures of the transition metals

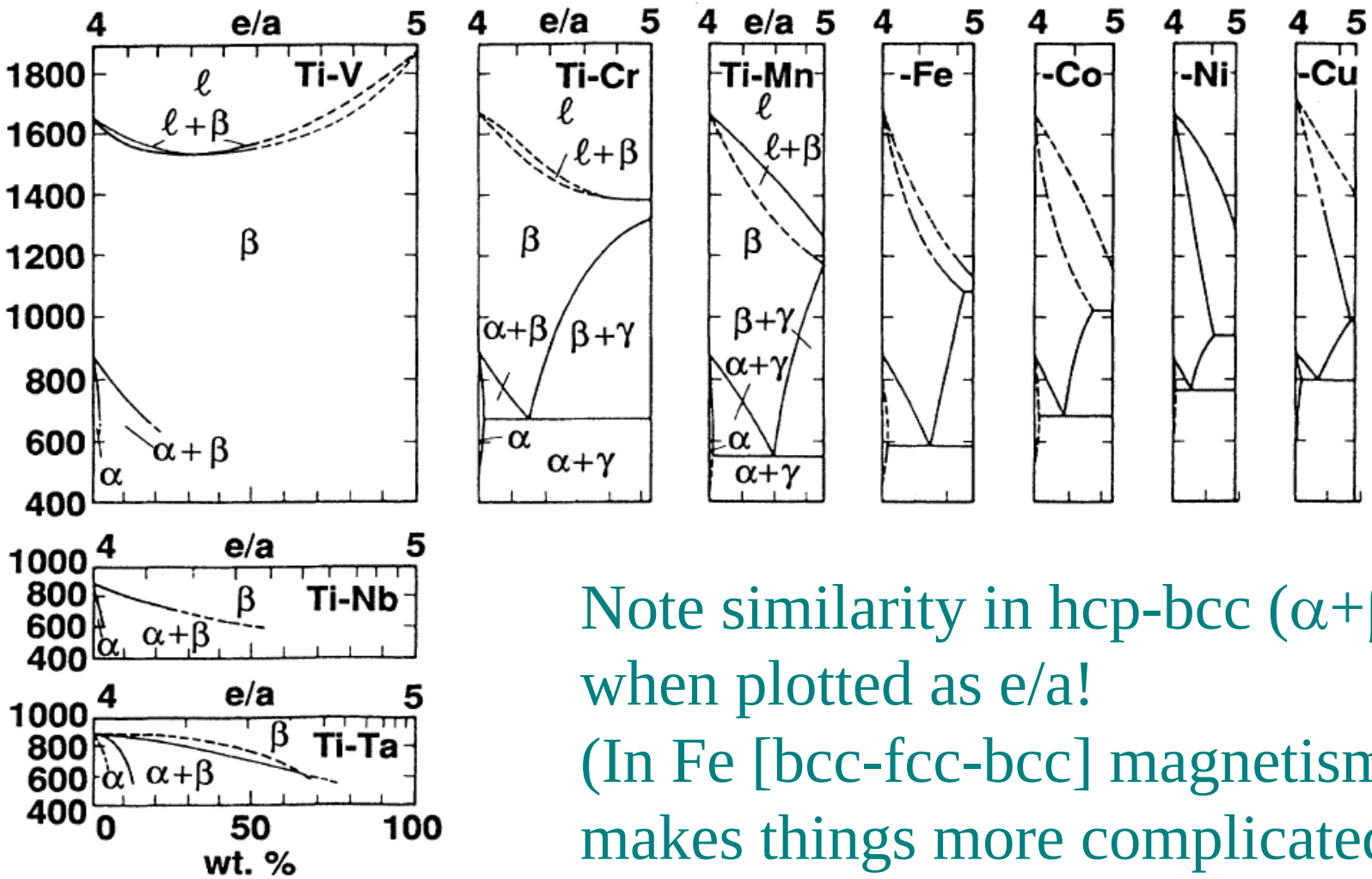
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1660	1890	1857	1245	1535	1495	1453	1083	419.58
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
1852	2468	2617	2200	2250	1966	1552	961.93	320.9
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
2150	2996	3410	3180	3045	2410	1772	1064.43	-38.87

bcc, hcp, fcc

Obvious trends with #valence electrons, not so much with atomic size etc.

a little disturbed by magnetism

Trends:
effect of alloying elements in hcp-bcc Ti



Note similarity in hcp-bcc (α+β) when plotted as e/a!
(In Fe [bcc-fcc-bcc] magnetism makes things more complicated)

From PRB 43, 12251 (1991)

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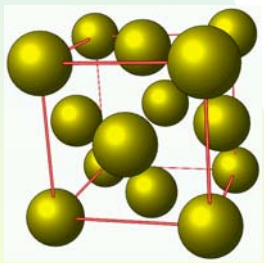
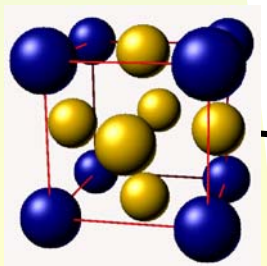
Ab initio alloy thermodynamics

Predict and explain, qualitatively& quantitatively

- Alloy phases
  - Al_3Li, AlLi, NiAl, Fe_3C
- Alloy structures
- Alloy properties





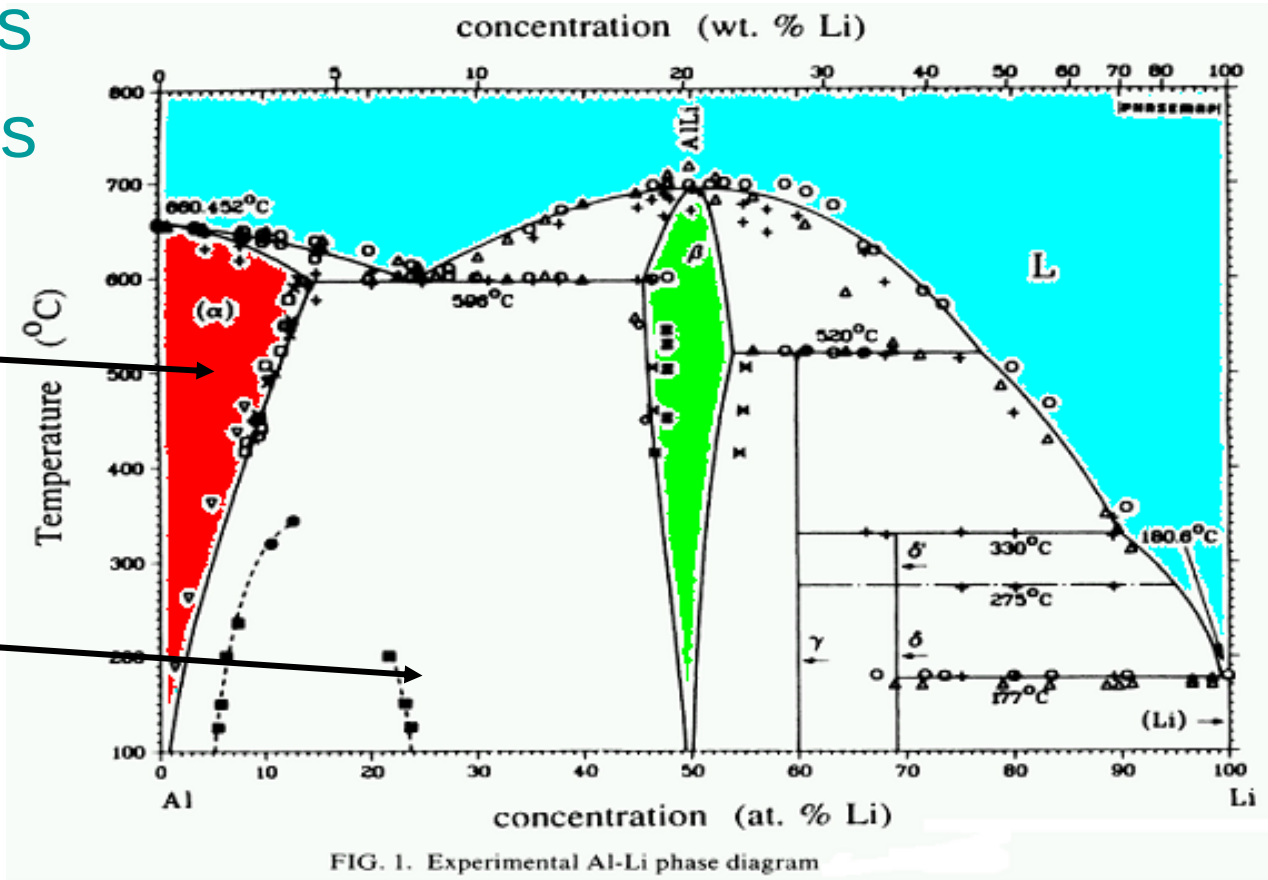
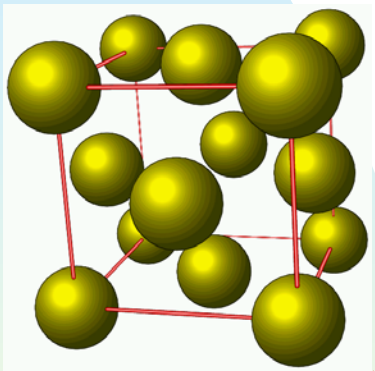


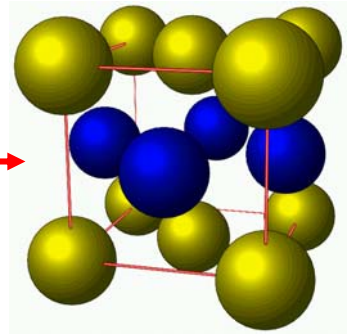
FIG. 1. Experimental Al-Li phase diagram

(ordered) structures

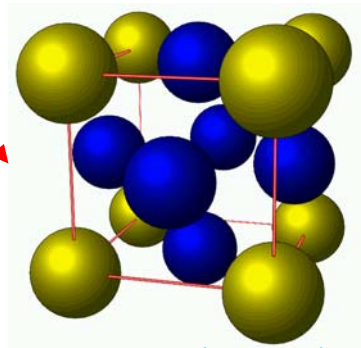
Predict and explain, qualitatively& quantitatively

- Alloy structures



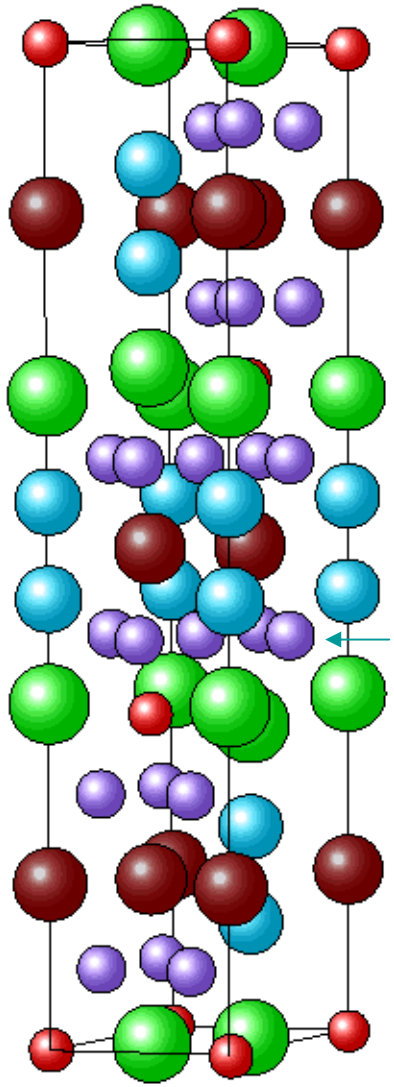


Parent structure



(ordered) superstructures

“complex struct.”



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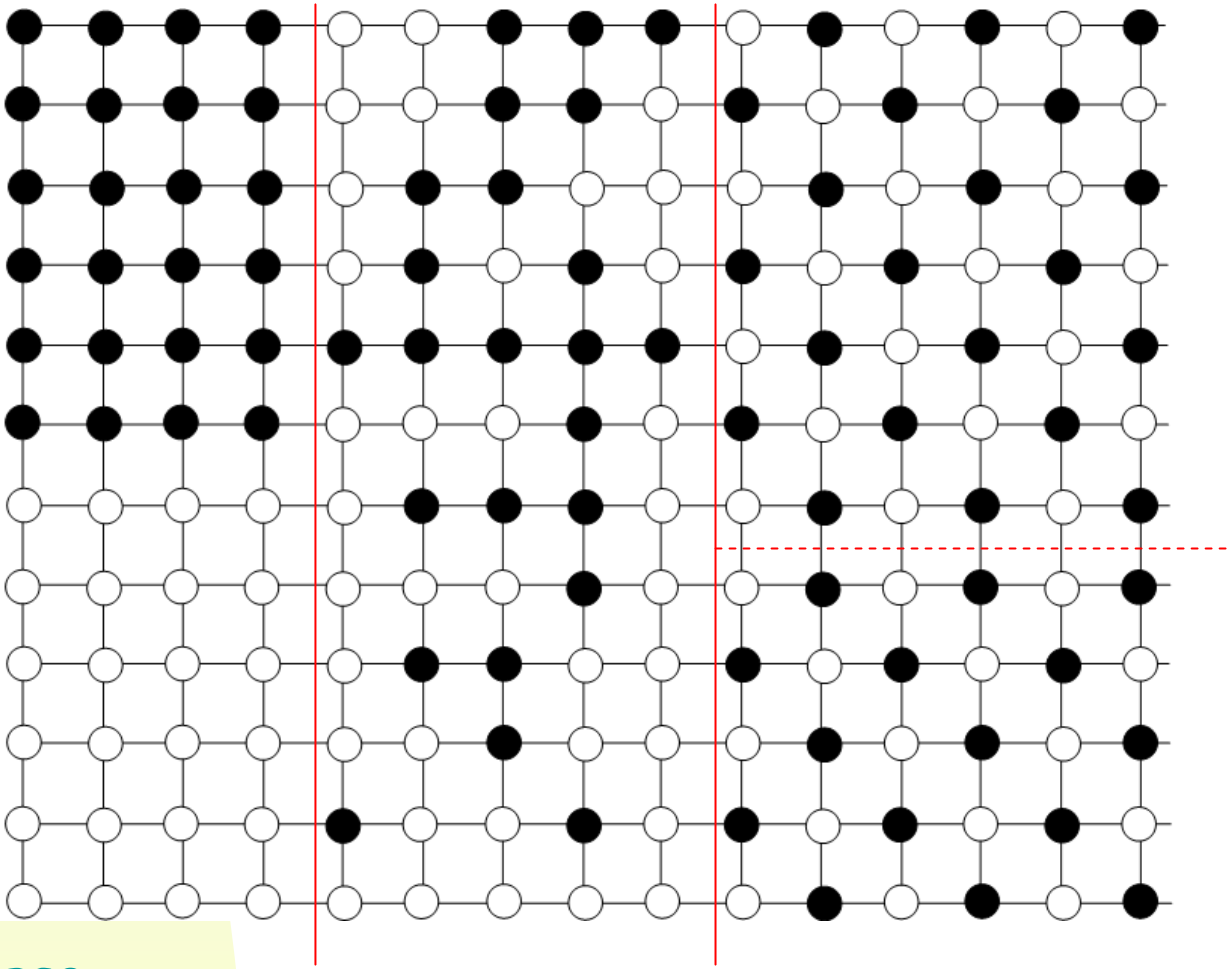
Order-Disorder / Partial Order



Phase separation segregation

Solid solution

superstructure Long range periodicity

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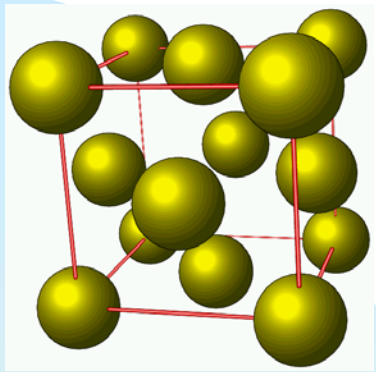
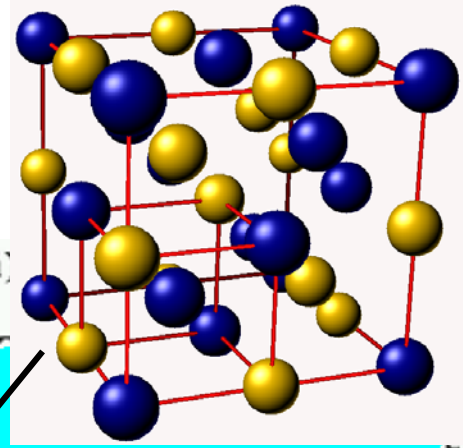
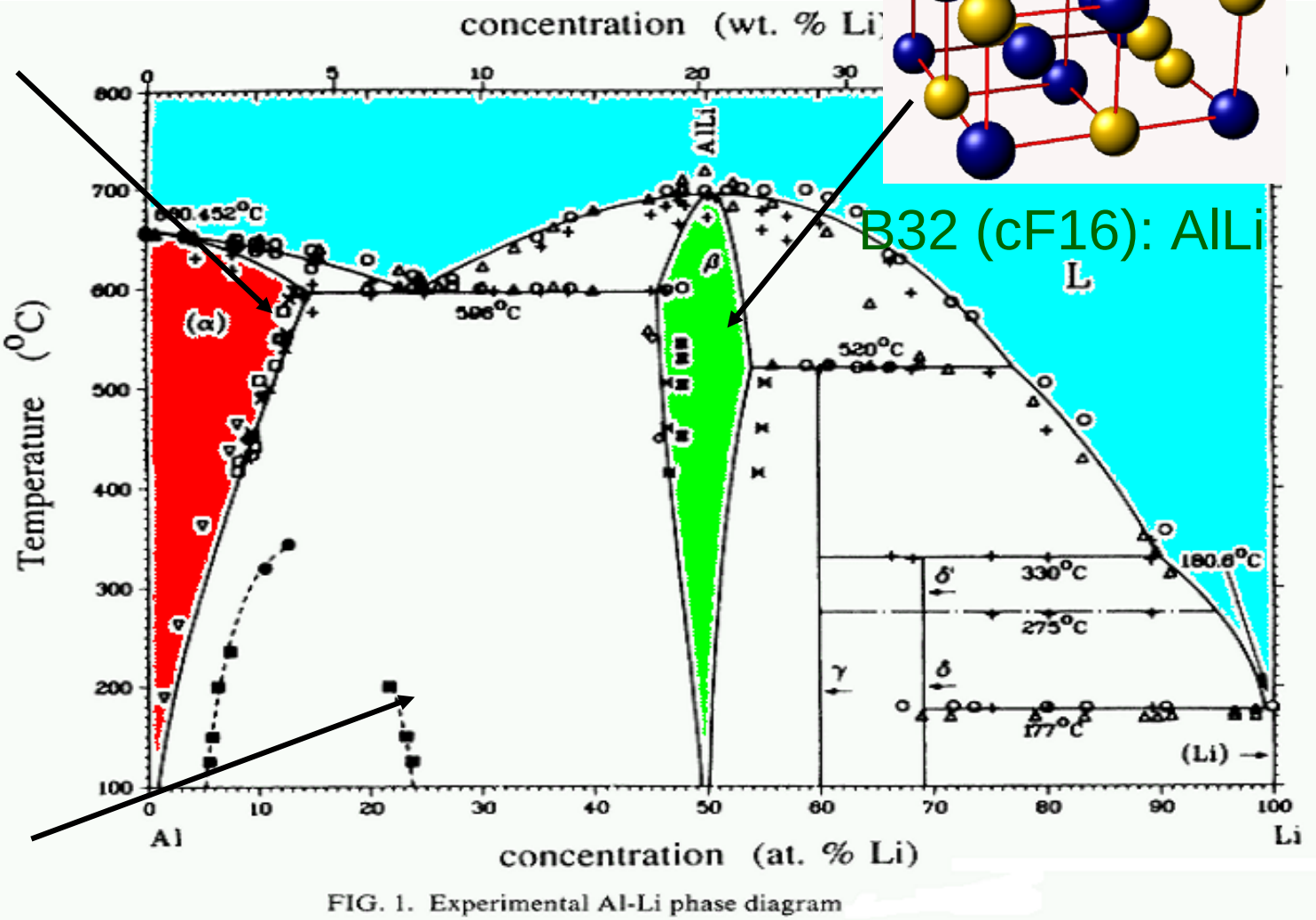
Al-Li system (1)



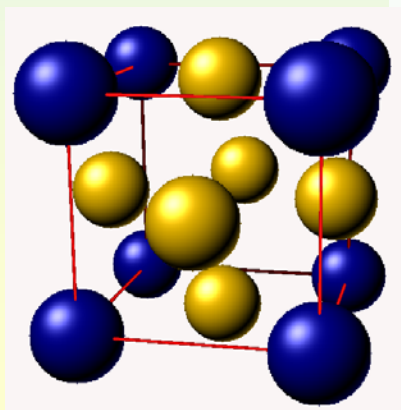
fcc (cF4): Al





B32 (cF16): AlLi

FIG. 1. Experimental Al-Li phase diagram



$L1_2$ (cP4): Al_3Li

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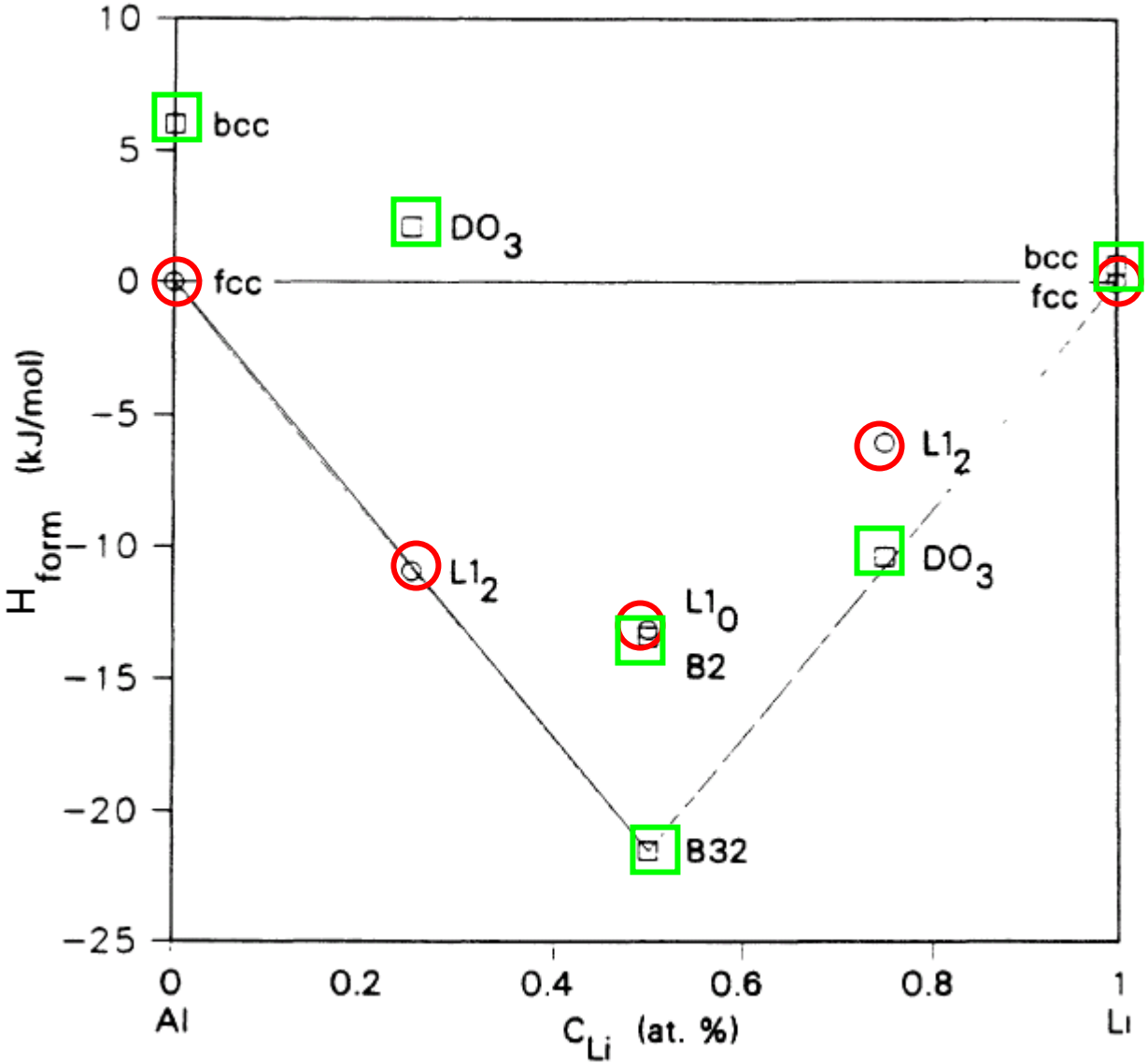
Al-Li system (2)

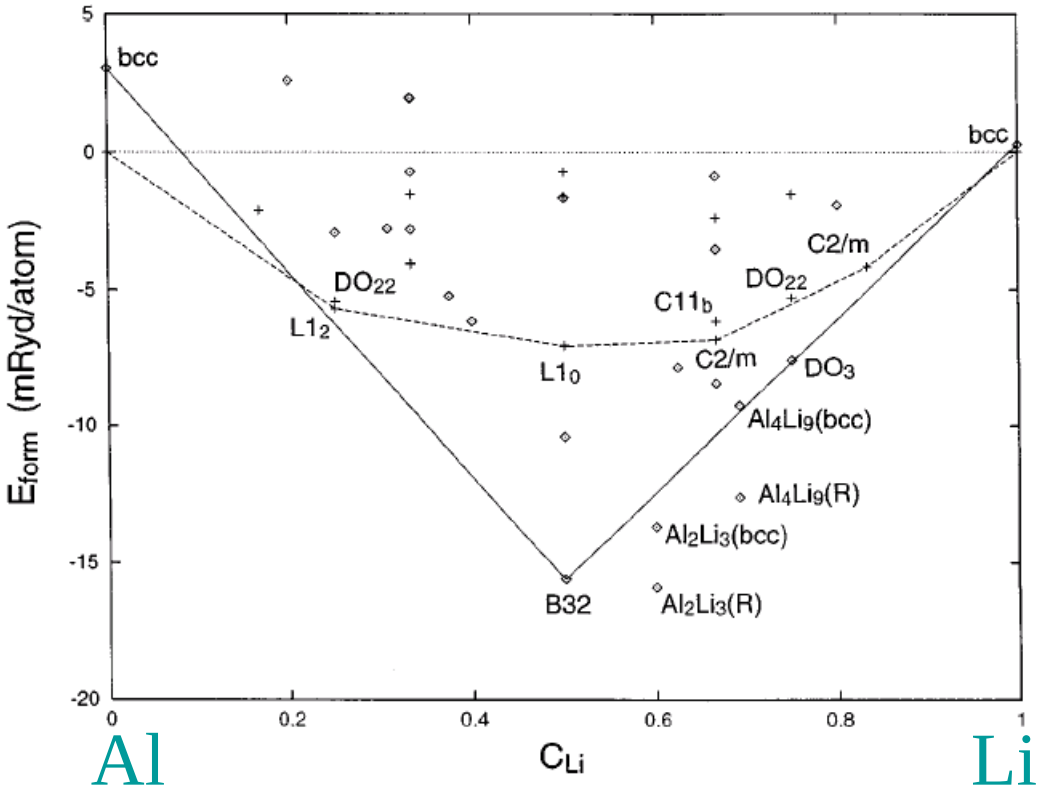


Electronic DFT calculations of some ordered structures in Al-Li
Now, can understand metastability of Al_3Li

Soon learned: need a lot of structures!

PRB42 10460 (1990)

Al-Li (3)



Al Li

Enthalpy of formation at P=0 for Al-Li alloys

basic picture of alloy phase stability!

1) fcc Al << bcc Al, fcc Li ≅ bcc Li

2) B32 AlLi very stable

3) Al_3Li metastable wrt fcc Al and B32 AlLi

4) no fcc/bcc ordered phases at Li-rich side, but other strs.

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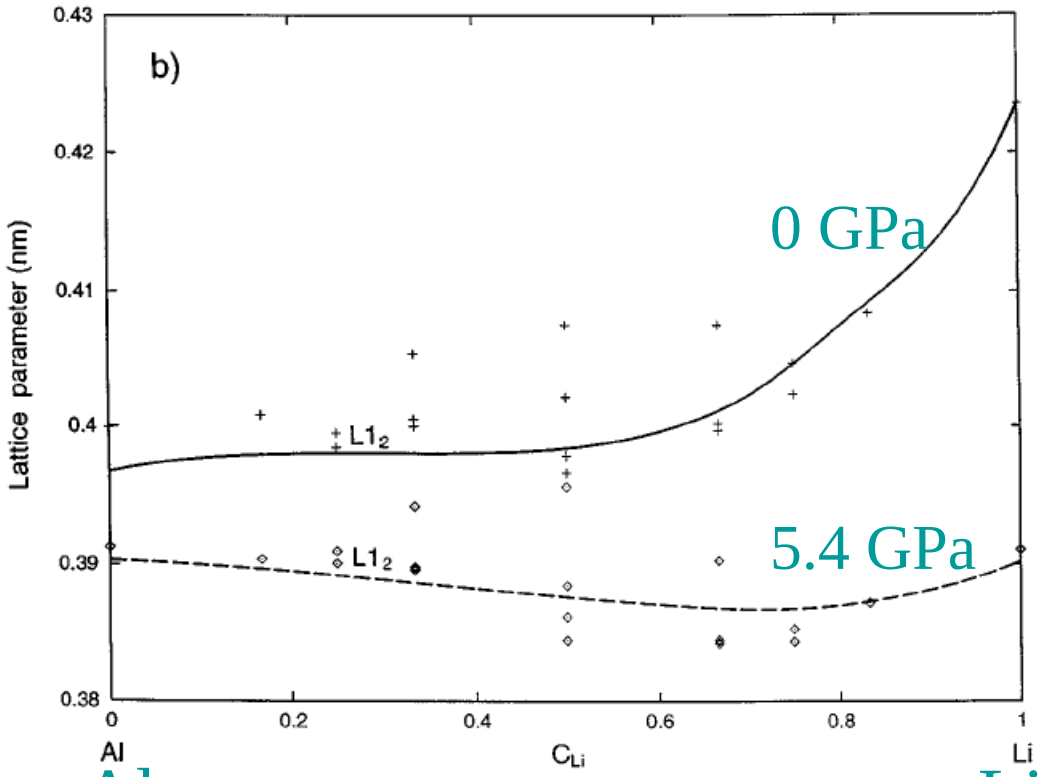
Al-Li (4)



Al Li

Not just energetics & thermodynamics

1) $L1_2$ and fcc solid solution lattice matched
2) $L1_2$ and fcc remain lattice matched under pressure

3) Li much more compressible
=> under hydrostatic pressure very different Li-rich alloy

(PRB **53**, 6137, 1996)

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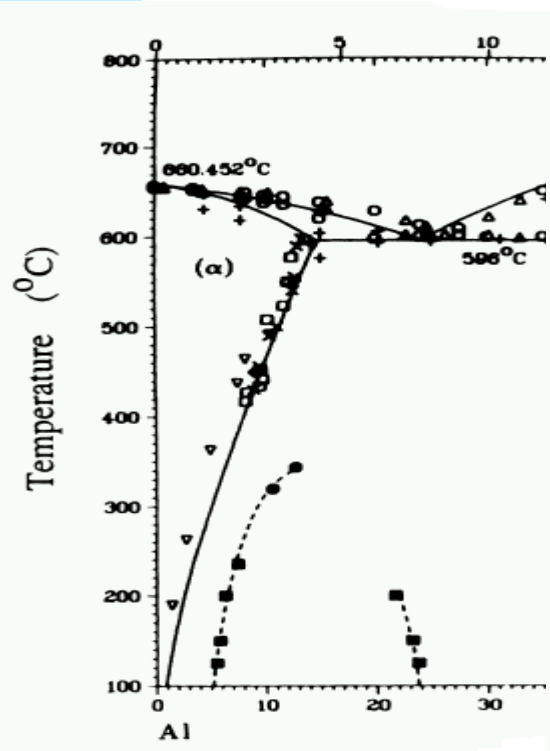
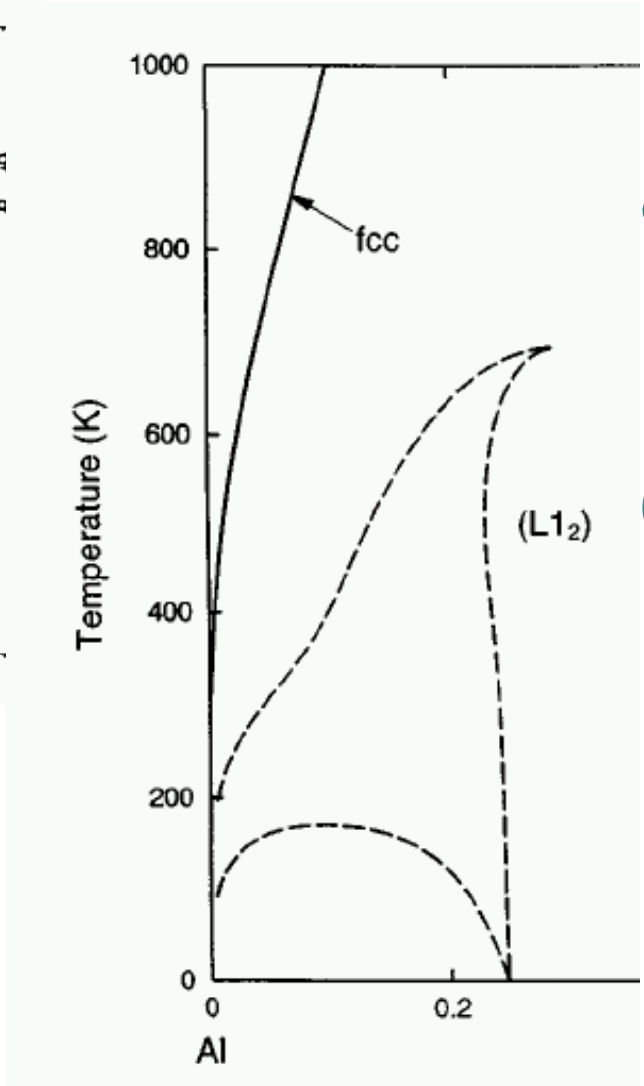
Al-Li system (5)

Detailed view





agreement
rather good
no experimental
data used!

How it was done: Cluster Expansion (1)

- Formation enthalpy of an organic molecule:

e.g. CH_4 from diamond and H_2 gas

$$CH_4 \Leftrightarrow C + 2H_2$$

4 C-H bonds formed

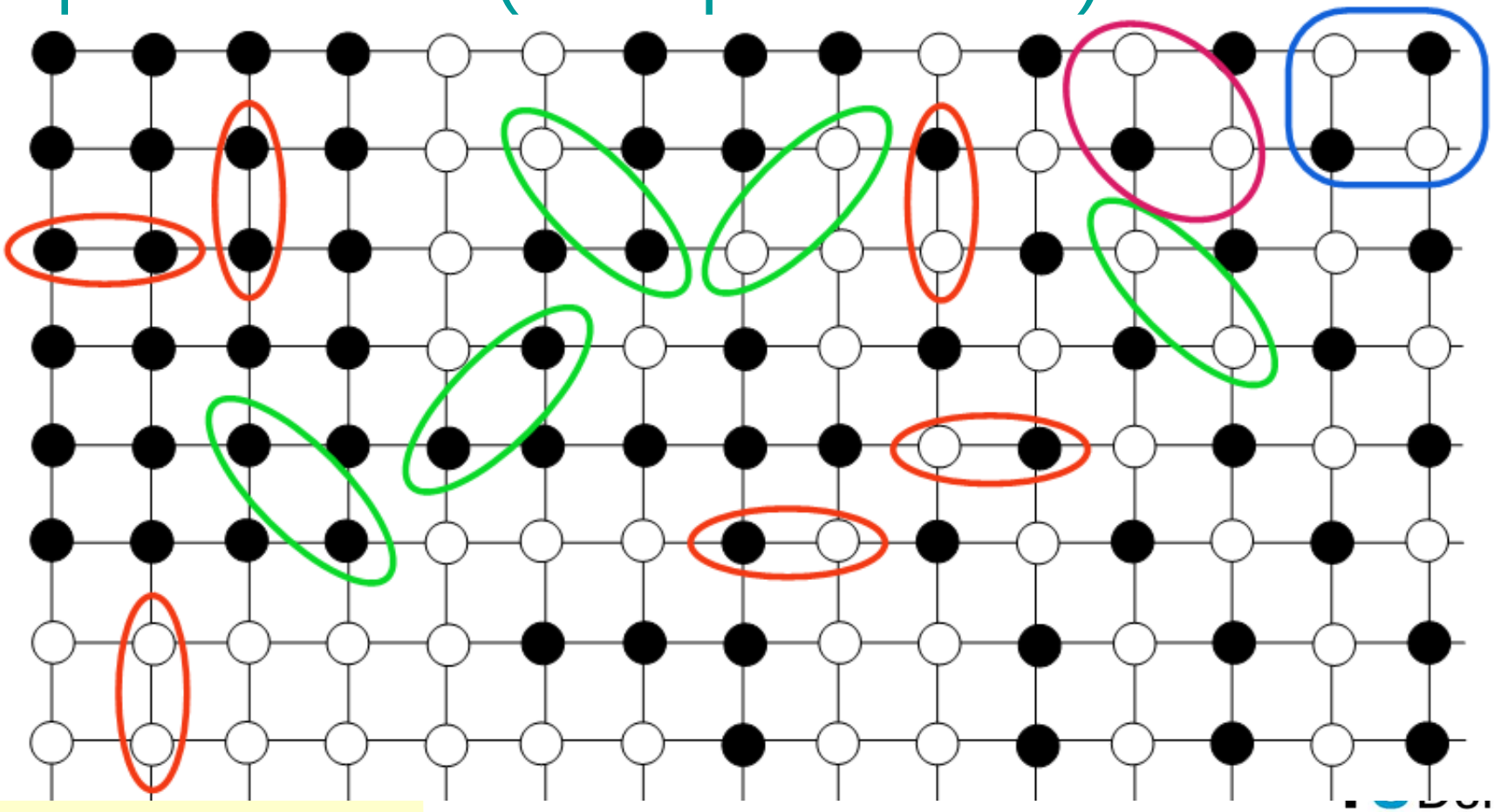
2 C-C bonds sacrificed (in diamond C has 4 C nearest neighbors => 2 C-C bonds per C)

2 H-H bonds lost ($2H_2$ molecules atomized)

$$\Delta H_{form}(CH_4)=4\Delta H(C\text{-}H)-2\Delta H(C\text{-}C)-2\Delta H(H\text{-}H)$$

How it was done: Cluster Expansion (2)

- Cluster expansion method
- specify structure in terms of cluster probabilities: (SRO parameters)



How it was done: Cluster Expansion (3)

Enthalpy, H, in terms of cluster contributions (similar to bond energies in organic chemistry)

$$H = \sum_{\alpha}^{\alpha_{max}} J_{\alpha}\xi_{\alpha},$$

J =effective cluster interaction,

ξ=correlation function

(measure of AA and BB, AB pairs, $<\sigma\ \sigma>$),

s =structure, α = type of cluster

J is used in CVM (Cluster Variation Method)/Monte Carlo to get entropy

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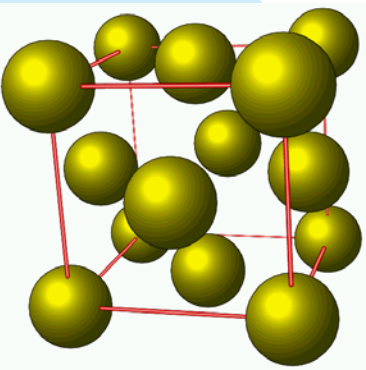
Cluster Expansion (4)



A atom σ=+1; B atom σ=-1

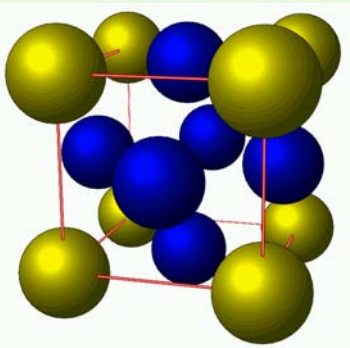
One type of tetrahedron: A_4 ➔

all points are A ➔ $\langle\sigma\rangle = 1$

All nn pairs are AA ➔ $\langle\sigma_i\sigma_j,\rangle = 1$

All nn triangles are AAA ➔ $\langle\sigma\sigma\sigma\rangle = 1$

All tetrahedra AAAA $\langle\sigma\sigma\sigma\sigma\rangle = 1$



All tetrahedra are AB_3 ➔

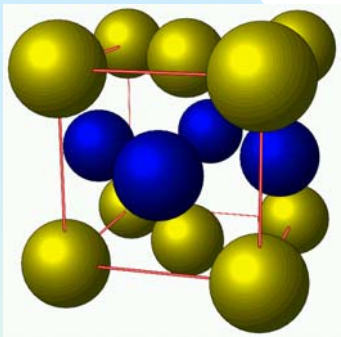
$\langle\sigma\rangle$ = [1*(+1)+3*(-1)]/4=-0.5

$\langle\sigma\sigma\rangle$=[3*(-1*1)+3*(-1*-1)]/6=0

$\langle\sigma\sigma\sigma\rangle$=[3*(-1*-1*1)+1*(-1*-1*-1)]/4=+0.5

$\langle\sigma\sigma\sigma\sigma\rangle$=-1*-1*-1*1=-1

Cluster Expansion (5)



A atom σ=+1; B atom σ=-1

One type of tetrahedron: A_2B_2 ➔

$\langle\sigma\rangle$ = [2*(+1)+2*(-1)]/4=0

$\langle\sigma\sigma\rangle$=[1*(-1*-1)+1*(1*1)+ 4*(-1*1)]/6=-1/3

$\langle\sigma\sigma\sigma\rangle$=[2*(-1*-1*1)+2*(-1*1*1)]/4=0

$\langle\sigma\sigma\sigma\sigma\rangle$=-1*-1*1*1=1

$$E[L1_0] = J_0 + \langle\sigma\rangle_{L10} J_1 + \langle\sigma\sigma\rangle_{L10} J_2 + \langle\sigma\sigma\sigma\rangle_{L10} J_3 + \langle\sigma\sigma\sigma\sigma\rangle_{L10} J_4$$

Matrix-form:

$\mathbf{E} = \xi\ \mathbf{J}$ (**E** and **J** vectors, ξ matrix)

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Cluster Expansion (6)

$E[L1_0] = J_0 + \langle\sigma\rangle_{L10} J_1 + \langle\sigma\sigma\rangle_{L10} J_2 + \langle\sigma\sigma\sigma\rangle_{L10} J_3 + \langle\sigma\sigma\sigma\sigma\rangle_{L10} J_4$

$E[\text{fcc A}] = J_0 + J_1 + J_2 + J_3 + J_4$
$E[\text{A3B}] = J_0 + 1/2\ J_1 + 0\ J_2 - 1/2\ J_3 - J_4$
$E[\text{L10}] = J_0 + 0\ J_1 - 1/3\ J_2 + 0\ J_3 + J_4$
$E[\text{AB3}] = J_0 - 1/2\ J_1 + 0\ J_2 + 1/2\ J_3 - J_4$
$E[\text{fcc B}] = J_0 - J_1 + J_2 - J_3 + J_4$

(Connolly & Williams 1983 PRB)
Matrix-form:
$\mathbf{E} = \xi\ \mathbf{J}$ **(E** and **J** vectors**,** ξ matrix**)**

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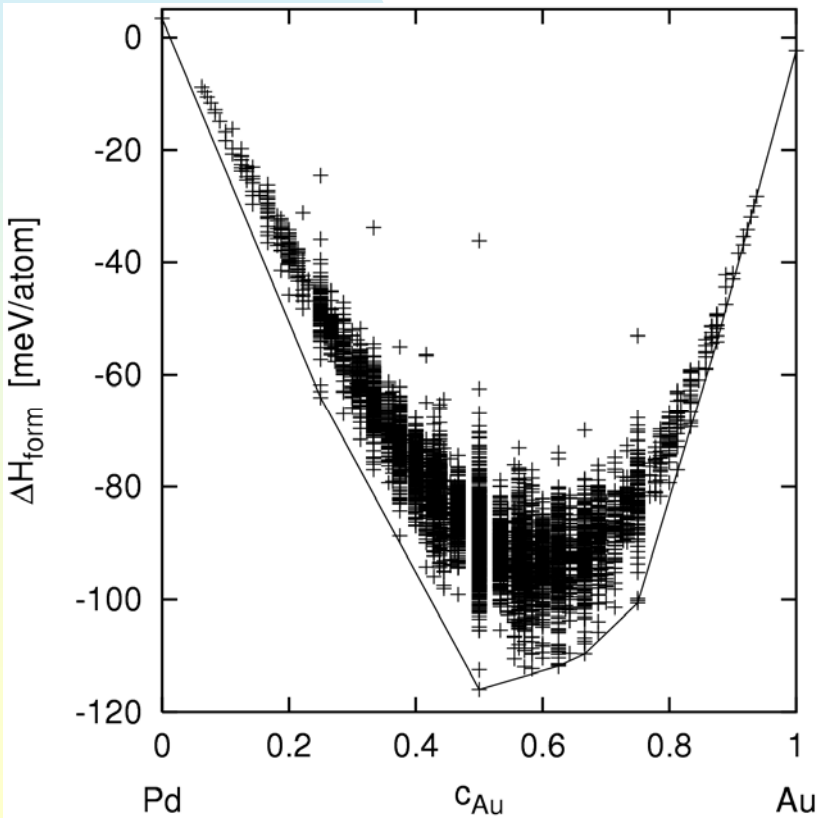
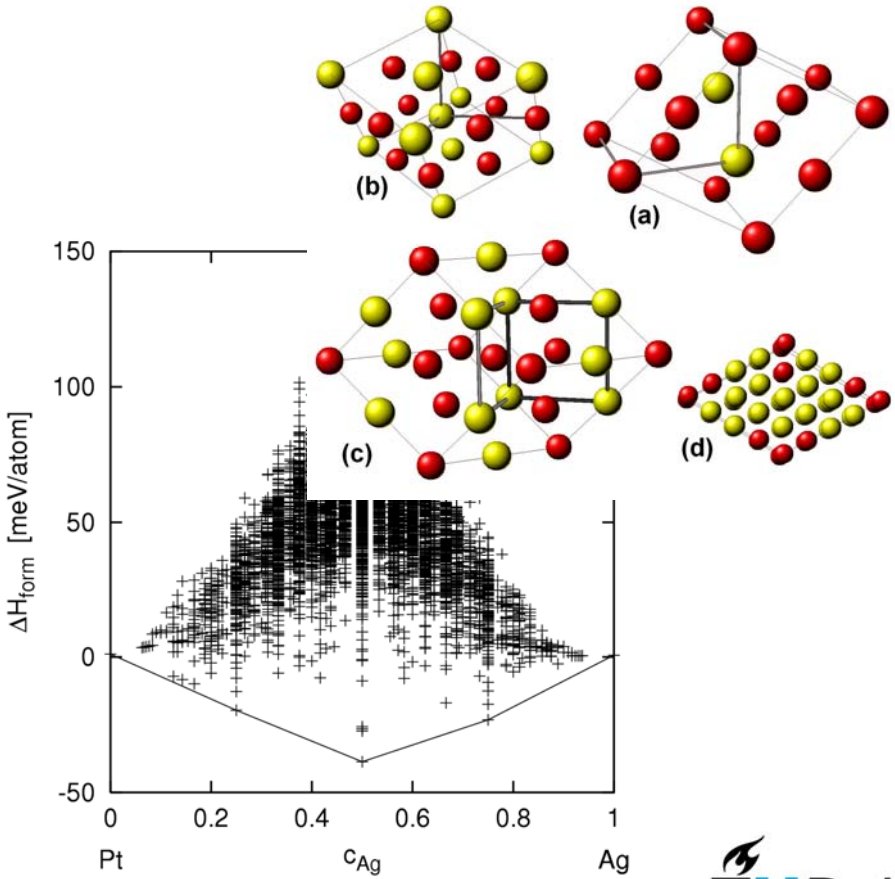
Cluster Expansion: Ground state search

$$H = \sum_{\alpha}^{\alpha_{max}} J_\alpha \xi_\alpha,$$

Simple eqn. allows very quick estimation of stability of any ordered structure ➔ ground state search





prb 73, 174204 (2006)

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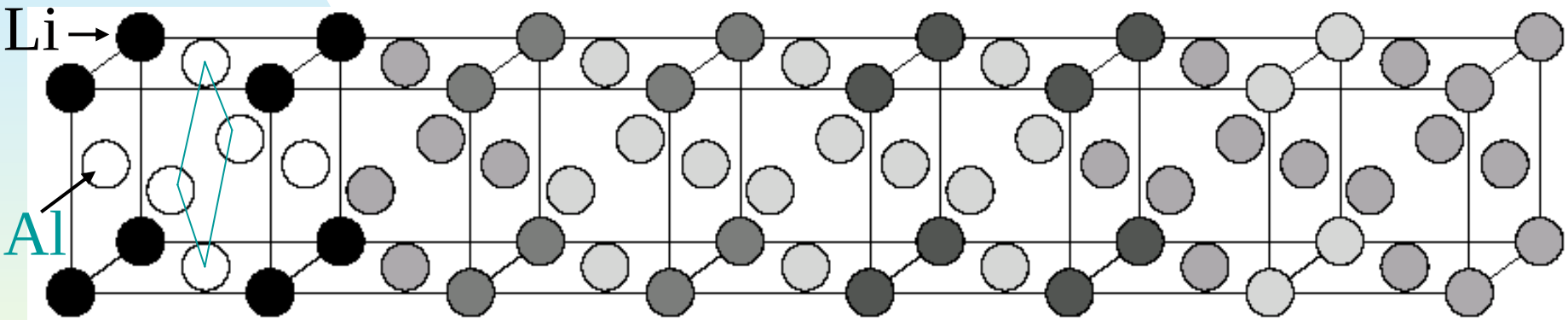
Al_3Li-Al (1)

Cluster expansion gives energy for any configuration, so also for … coherent interphase between matrix and precipitate

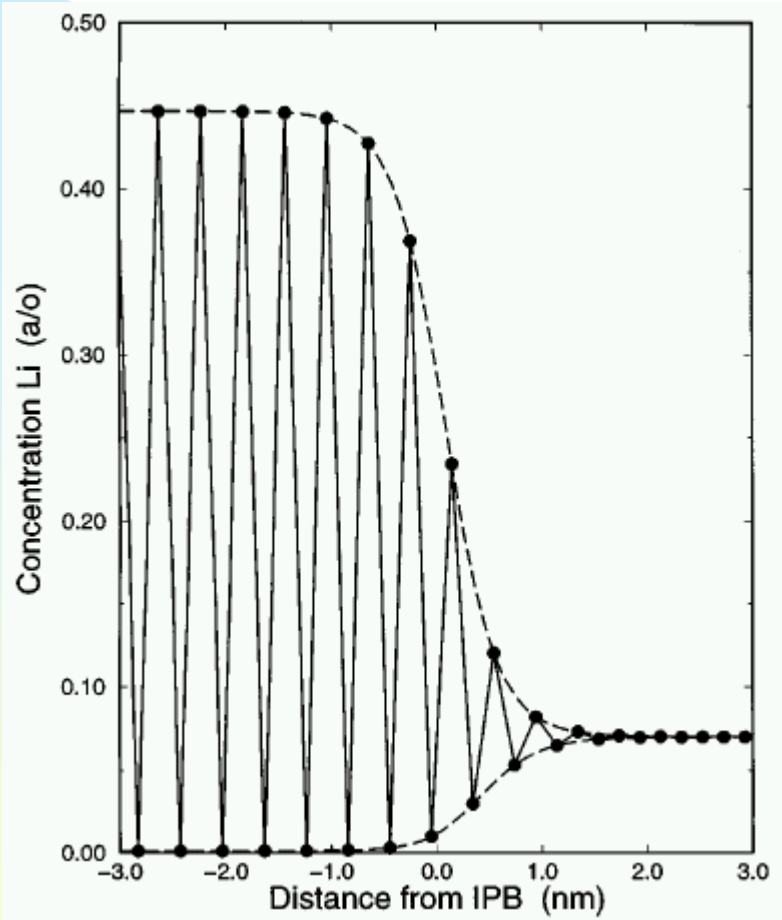


Al_3Li (precipitate)

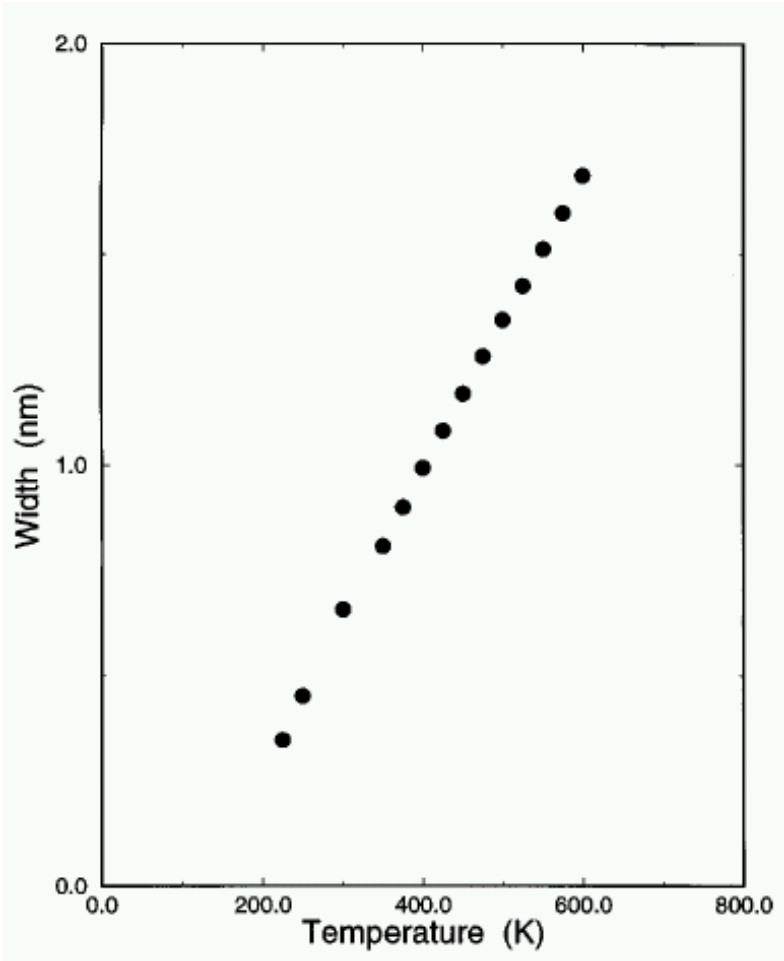
fcc Al (matrix)

Modeling of coherent interphase boundary Between matrix and precipitate (Al=white, Li=black, Al-Li mixture=grey)

coherent interfaces Al_3Li-Al (2)



composition profiles…



interphase boundary width vs temperature

(PRB 54, 10381, 1996)

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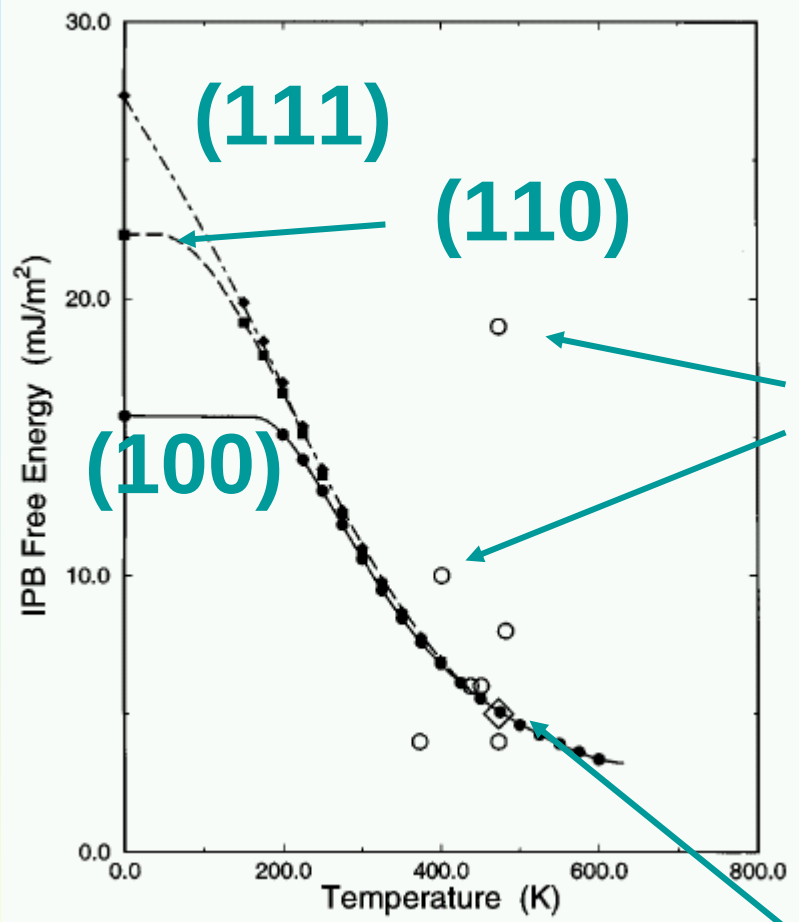
coherent interfaces Al_3Li-Al (3)



Experimental data (SAXS, coarsening rates)

Assessment of all experimental data (Hoyt & Spooner)

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Summarizing Al - Li

1) Can predict phase diagram
2) Can identify origin of phase stability (strength of chemical interactions, importance of atomic size difference – partial molar volume, e.g. minority Li in Al has SAME size as Al)
3) If phase diagram good ➔ can also predict subtle properties such as matrix-precipitate interface energies
4)Thermodynamic modeling is integral part of understanding an alloy

Cluster Expansions

$$H = \sum_{\alpha}^{\alpha_{max}} J_\alpha \xi_\alpha,$$

- **H** (configurational) enthalpy, **α** cluster, **J** ECI effective cluster interaction, **ξ** correlation function

$$\sum_{s} w^s [H^s - \sum_{\alpha=1}^{\alpha_{max}} J_\alpha \xi_\alpha^s]^2 = minimal,$$

- s structure, use singular value decomposition

Go easy on Ising?

can select occupation variable more efficiently…

$$E = \sum_{\alpha} J_{\alpha}^{(\sigma)} \langle \sigma_{\alpha} \rangle, \qquad \langle \sigma_{\alpha} \rangle = \langle \sigma_{i_1}, \sigma_{i_2}, \sigma_{i_3}, \ldots, \sigma_{i_{n_\alpha}} \rangle,$$

σ_i takes the value $1(-1)$ when site i is occupied by an $A(B)$ atom

$\sigma_i = A s_i + B$, where A, B are arbitrary but $A \neq 0$.

$s = 0(1)$ occupied by an A (B) species

$$\langle \sigma_{\alpha} \rangle = \sum_{\beta \subseteq \alpha} A^{n\beta} B^{n\alpha - n\beta} \langle s_{\beta} \rangle,$$

where $\beta \subseteq \alpha$ means that β is a subcluster of α, including the cluster α itself and also including the empty cluster.

$$E = \sum_{\alpha} J_{\alpha}^{(\sigma)} \sum_{\beta \subseteq \alpha} A^{n\beta} B^{n\alpha - n\beta} \langle s_{\beta} \rangle,$$

$$= \sum_{\beta} \left[A^{n\beta} \sum_{\alpha \supseteq \beta} B^{n\alpha - n\beta} J_{\alpha}^{(\sigma)} \right] \langle s_{\beta} \rangle = \sum_{\beta} J_{\beta}^{(s)} \langle s_{\beta} \rangle,$$

where $\alpha \supseteq \beta$ indicates clusters α which have β as subcluster, inclusive.

$$J_{\beta}^{(s)} = A^{n\beta} \sum_{\alpha \supseteq \beta} B^{n\alpha - n\beta} J_{\alpha}^{(\sigma)}$$

prb 71, 212201 (2005)

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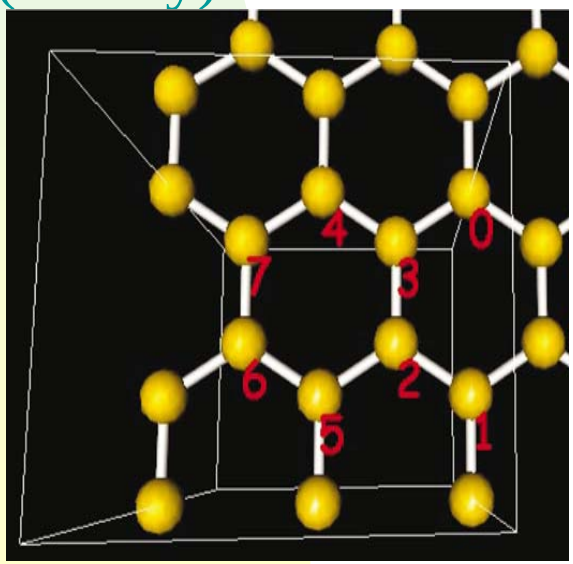
“Bulk” only?

Hydrogenation of graphene via cluster expansions

$$\sigma_i = \begin{cases} (100), & A \text{ atom at site } i \\ (010), & B \text{ atom at site } i \\ (001), & C \text{ atom at site } i. \end{cases}$$

C atom can have H above, H below, or no H bonded to it at all (ternary)



Define occupation variable as a vector, so that we can generalize to arbitrary number of components (much easier than “orthogonal function formalism” by Gratias, Ducastelle, and Sanchez)

$$c^P = \frac{1}{N} \sum_i \sigma_i^P = \langle \sigma^P \rangle,$$

Definition of concentrations and correlations easier also
PRB 68, 085410 (2003)

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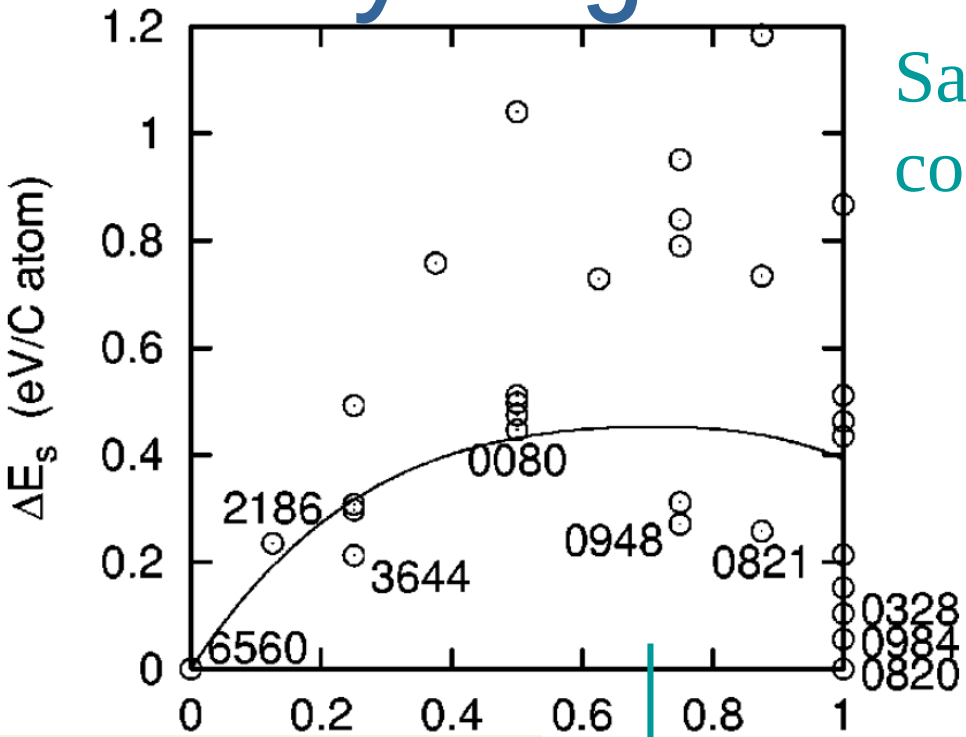
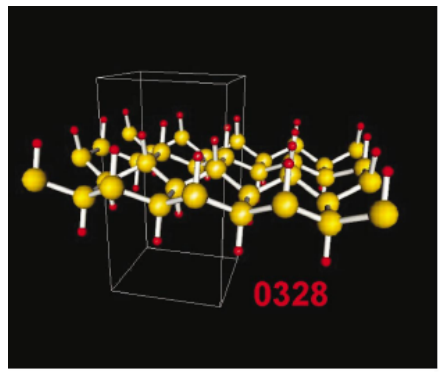
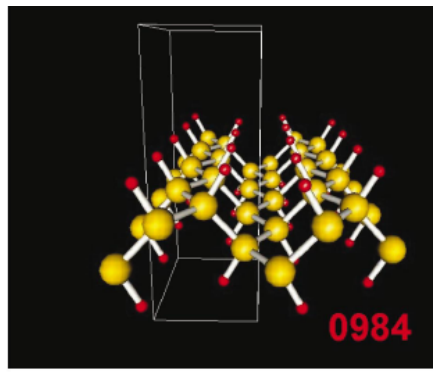
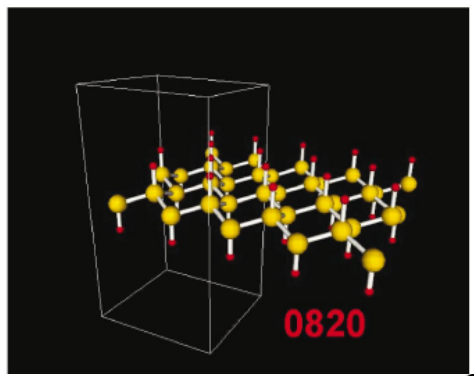
Hydrogenation of Graphene



Sample sufficient number of configurations







Partial coverage not favorable, island formation, minimization of stress

PRB 68, 085410 (2003)

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First-Principles Kinetics

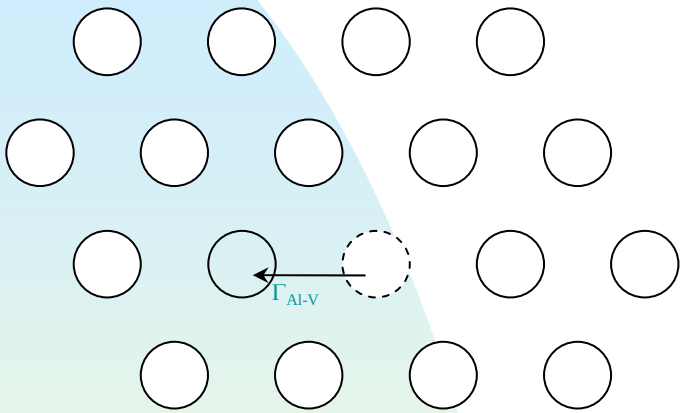
- atoms vibrate,
- sometimes atom makes a jump to a nearby site, by overcoming an activation barrier

geometry, activation energy barriers, temperature determine this process

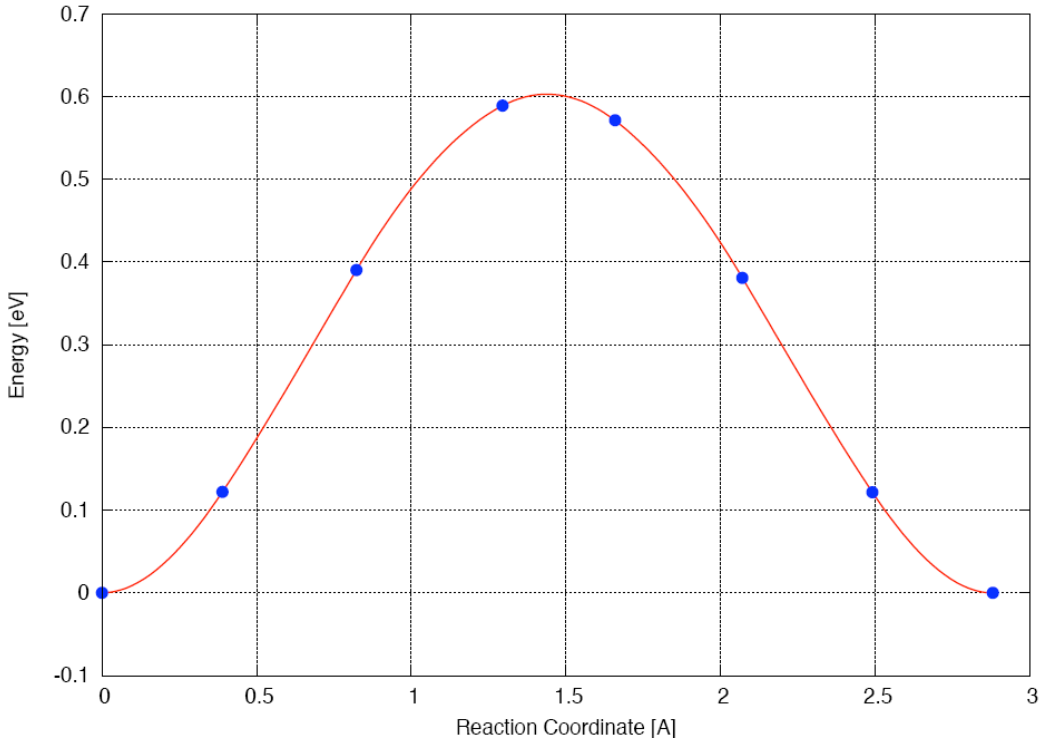
Biggest challenges:

1) finding all types of jumps
2) activation energy barriers for each type of jump

Vacancies and jumps



Jump into a vacancy



Activation energy barrier

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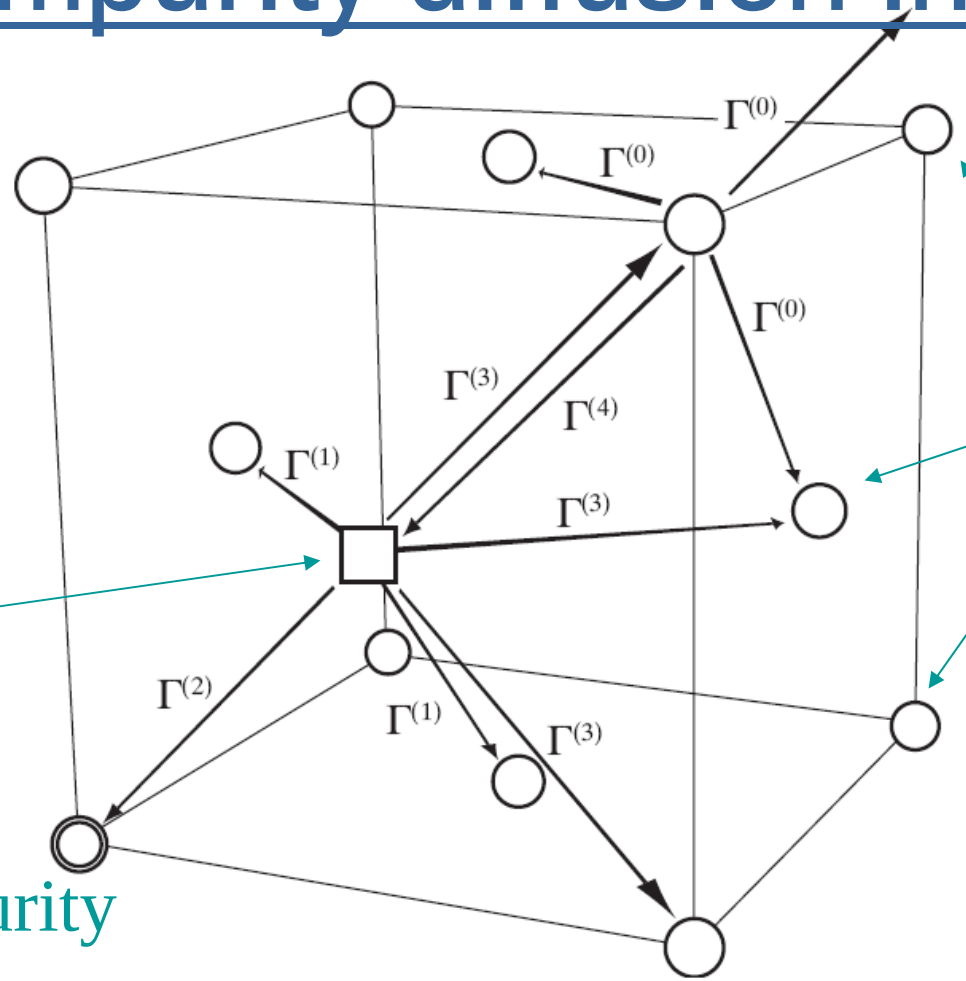
Impurity diffusion in fcc Al



Al atoms

vacancy

impurity

Many possible jumps into the vacancy, some help in giving a net impurity displacement (PRB 2009)

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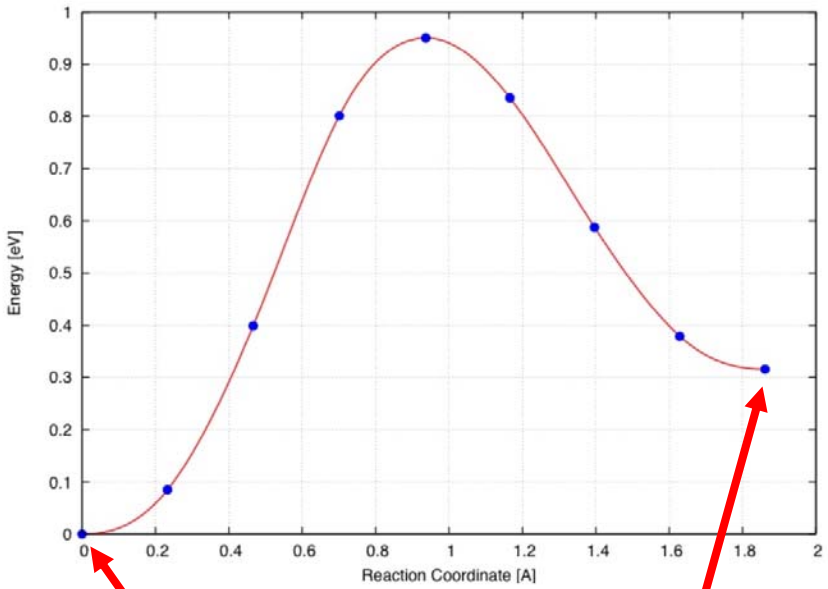
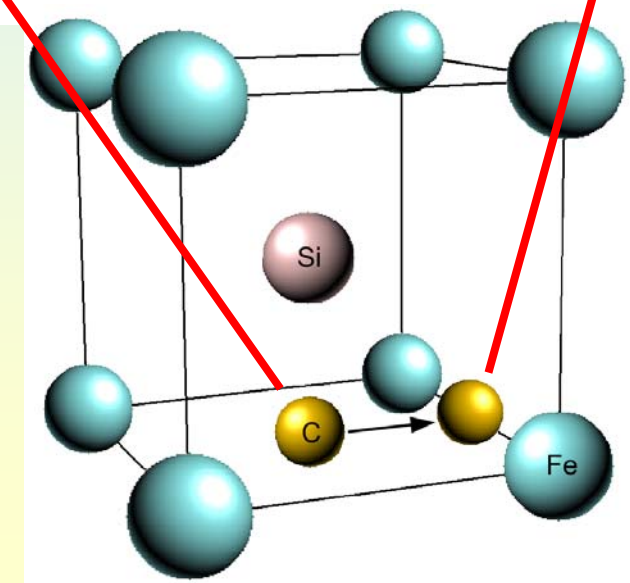
Diffusion in Alloys

Effect of local environment:

When an atom jumps, local configurational order changes…..

Local configurations + diffusion





In presence of Si complications because not all octahedral sites at same energy….

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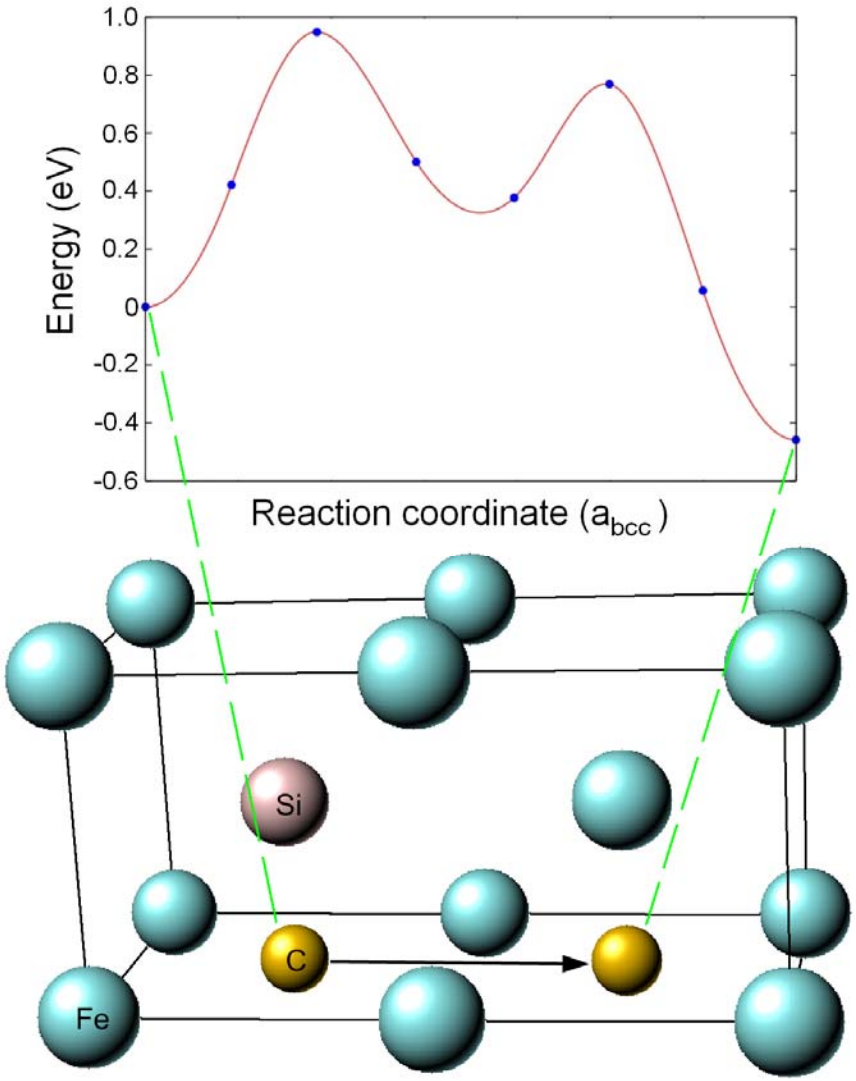
From 1st to 2nd to 3rd neighbor

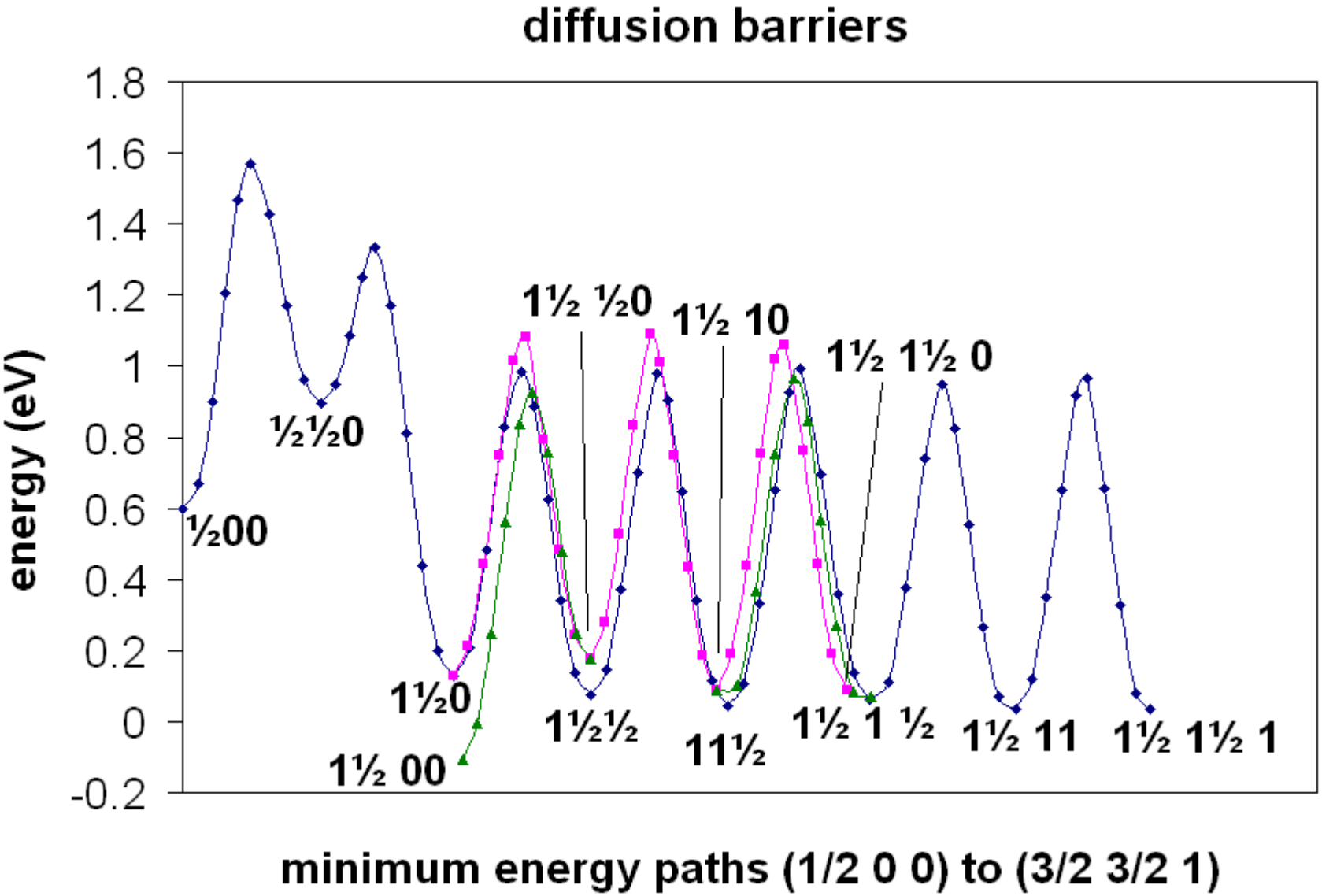


1st neighbor of Si (0.5 0 0) unfavorable,

2nd neighbor (0.5 0.5 0) even less favorable,

3rd neighbor (1 0.5 0) weakly favorable

C around substitutional Si



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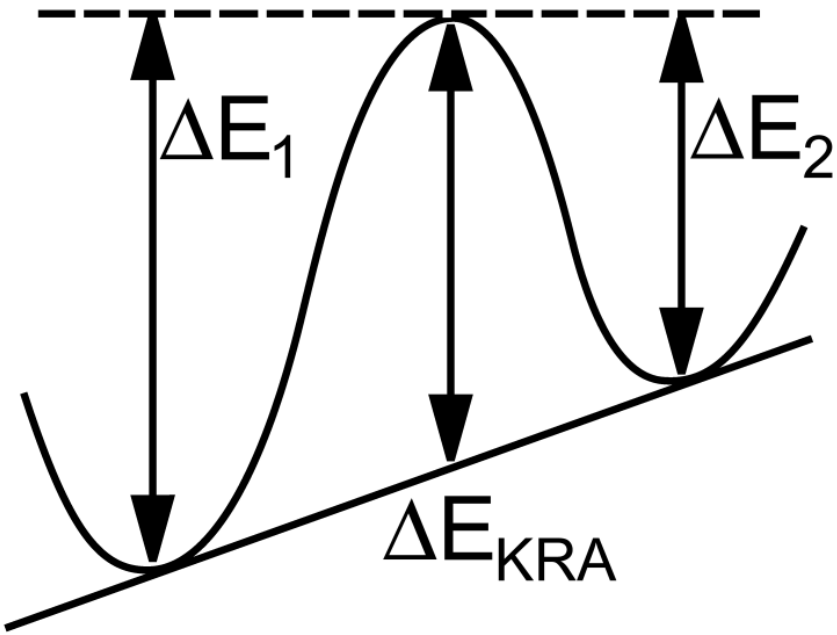
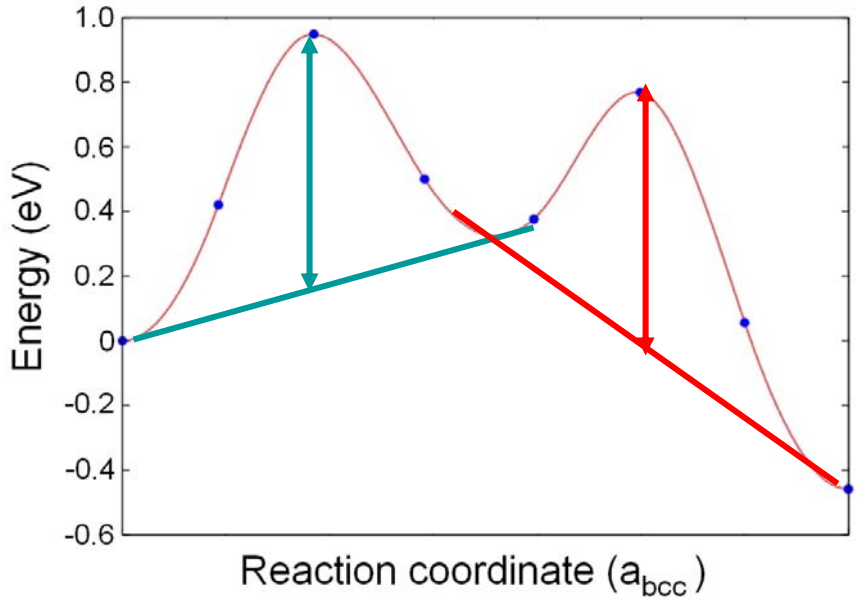
Kinetically Resolved Activation

Minimum energy path with inequivalent end-points: Kinetically Resolved Activation (KRA) barrier:





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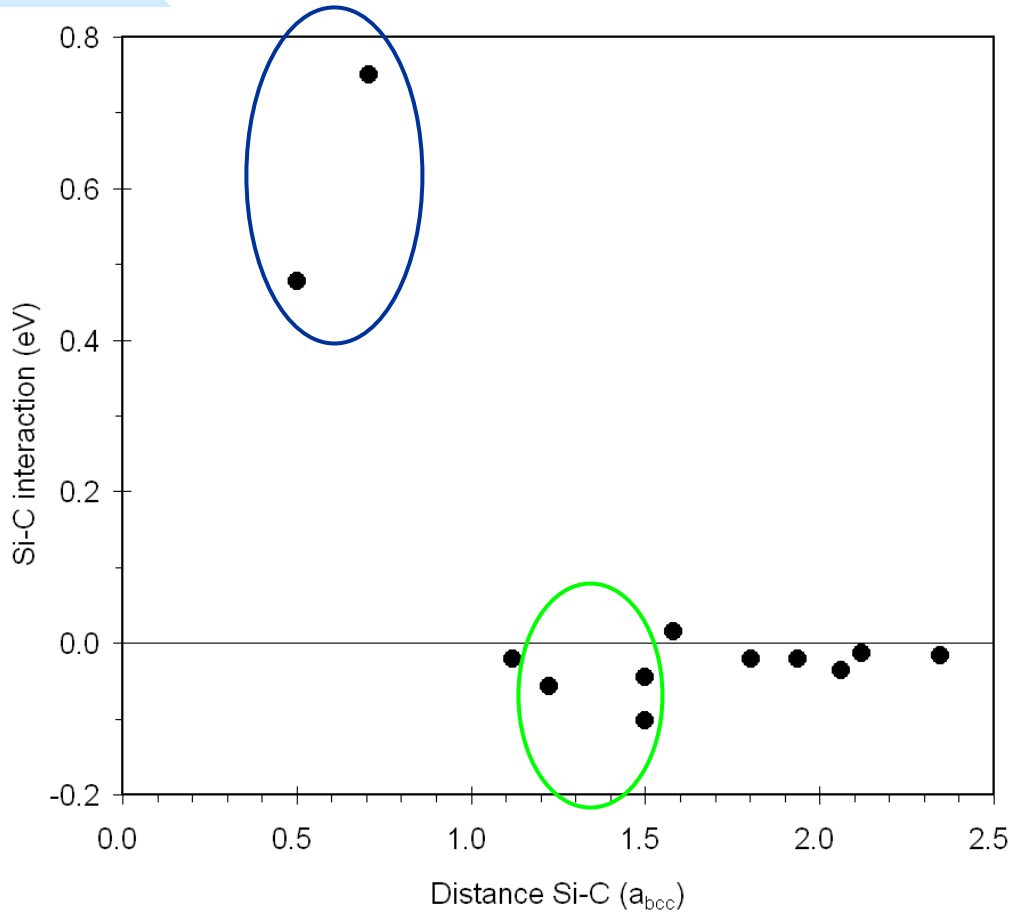
Si-C

Interaction between Si (subst) and C (oct)



1st and 2nd strong repulsion, then weakly attractive, Beyond 1.5 a_{bcc} vanishing

Kinetic Monte Carlo

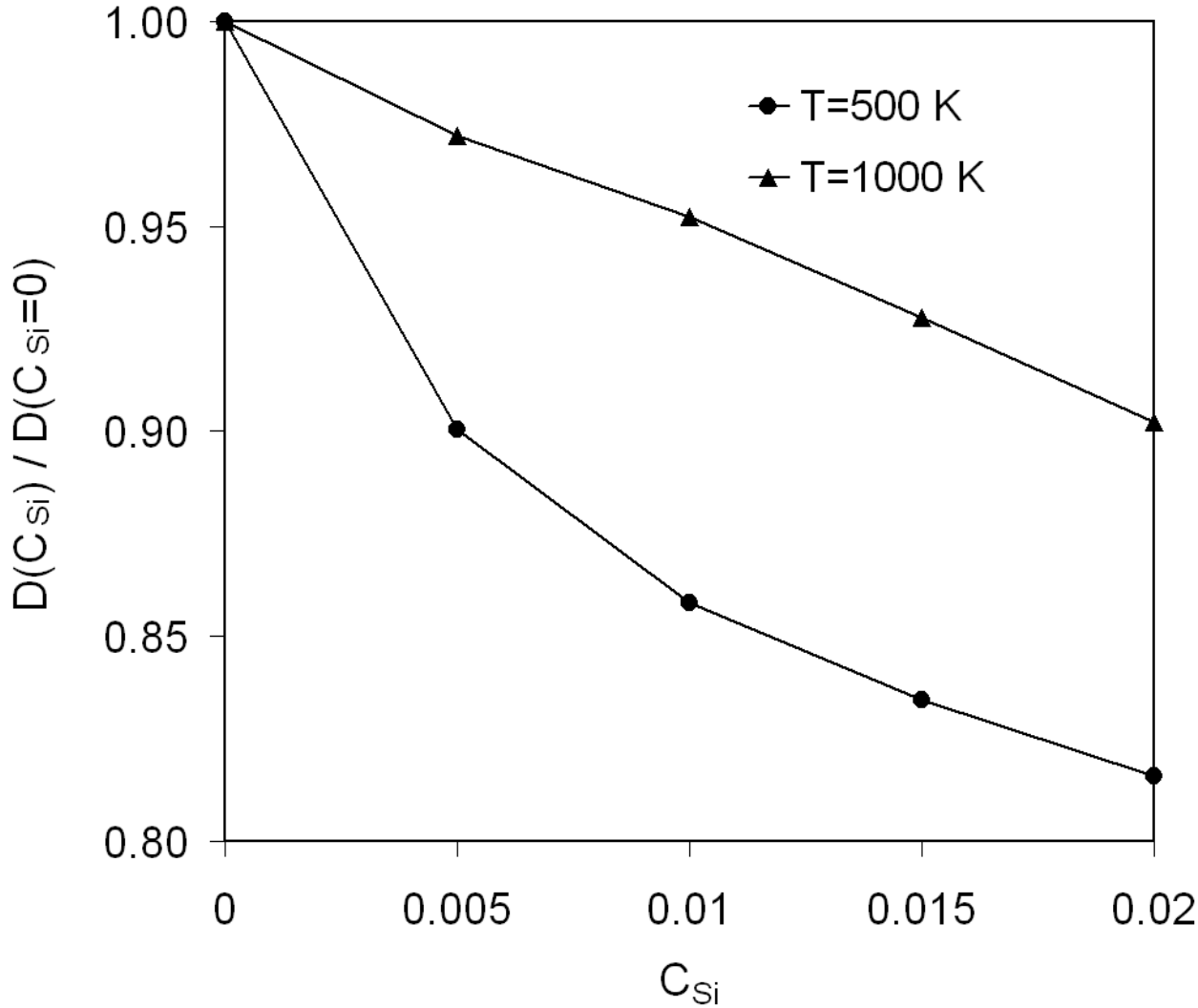
Kinetic Monte Carlo (KMC):

100x100x100 bcc cells, place C in the middle and watch it move…. Without Si, with random distribution of Si

Attempt frequency determines time scale, from Einstein oscillator, from curvature of potential well around equilibrium position, also more accurate model possible which involve coordinated motion of neighbors through transition state theory (Vineyard)

$\langle r^2 \rangle = 6\ D\ t$ (in 3 dimensions)

Effect of Si on Diffusion of C



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Al-Mg-Si

Widely used (car hoods: 0.5% Mg 1% Si)
Automotive applications: (paint) bake hardening vs natural aging
Natural aging during storage causes deterioration in post bake hardening state… desire to understand treatments prior to storage (pre-aging treatment)

Al-Mg-Si interesting stages during precipitation:

SSSS → *clusters* → *initial-β”* → *pre-β”* → *β”* (Mg_5Si_6) → *β’*,U2,U1→ *β* (*Mg_2Si, stable)*

Here fcc superlattices only (early stages, up to and including pre-β”)

Formation enthalpies Al-Mg-Si-Vac

Truly quarternary alloy!
large number of interatomic effective interactions (effective cluster interactions) ➔ many configurations required to get a reliable fit
about 100 small cell ordered structures
+ about 20 Al_{64} supercells, with single and double defects in order to describe dilute solid solution

With M. van Huis, H. Zandbergen, M. Zandbergen

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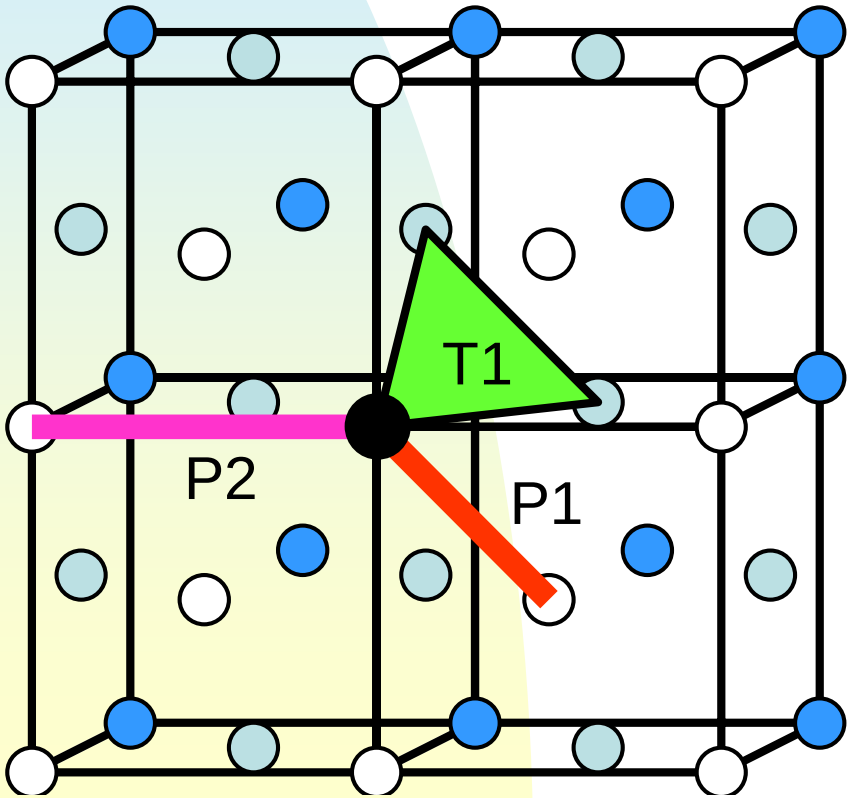
Simple cluster expansion

P1: Nearest neighbor pairs (6 numbers in quarternary)

P2: 2nd neighbor pair (6 numbers in quarternary)

T1: Equilateral triangle formed by nearest neighbors (10 numbers in quartenary)



Phys. Rev. B **71**, 212201 (2005)

Al-Mg-Si: Binding energies of NN dimers (this work), and activation barriers for vacancy-assisted jumps of host and solute atoms

Dimer	Binding energy (eV)	Interaction type
Mg-Mg	0.019	repulsive
Si-Si	-0.003	zero
vac-vac	0.085	repulsive
Mg-Si	-0.031	attractive
Mg-vac	0.016	repulsive
Si-vac	-0.056	attractive

Dimer	Activation barrier ***q*** (eV)	reference
Al-vac	0.55	PRB **79,** 054304 (2009)
Mg-vac	0.39	PRB **79,** 054304 (2009)
Si-vac	0.45	PRB **79,** 054304 (2009)

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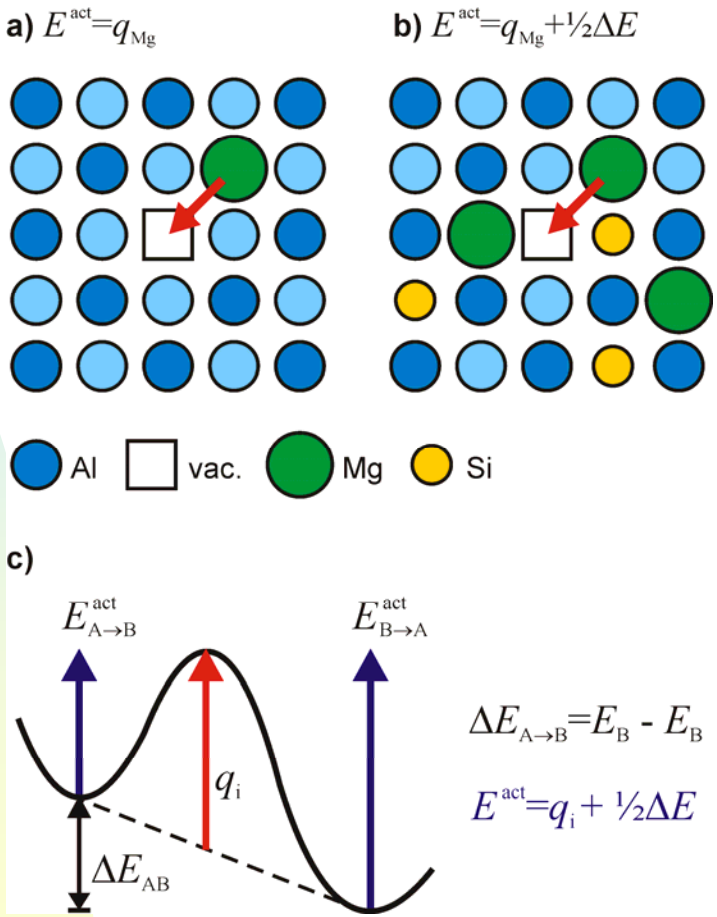
Diffusion in Alloys

Kinetically resolved activation barrier



Phys. Rev. B **81**, 054116 (2010). With Simonovic, Duff, Ande

kMC simulations

	solid solution heat treatment (SSHT)	natural ageing (NA)	pre-ageing (PA)	spike pre-ageing (SPA)	paint bake hardening (PB)
Temp. (° C)	550	20	80	180	180
Annealing time	30 min	1 week	2 hours	2 min	30 min
c_{vac}^{eq} (vacs. per atom)	$6.6 \cdot 10^{-5}$	$2.5 \cdot 10^{-12}$	$2.3 \cdot 10^{-10}$	$2.9 \cdot 10^{-8}$	$2.9 \cdot 10^{-8}$
D_{vac} ($m^2 s^{-1}$)	$3.0 \cdot 10^{-13}$	$5.1 \cdot 10^{-28}$	$3.5 \cdot 10^{-24}$	$4.7 \cdot 10^{-20}$	$4.7 \cdot 10^{-20}$
Nr. of kMC steps	N.A.	$1.9 \cdot 10^{8}$	$9.0 \cdot 10^{7}$	$8.0 \cdot 10^{7}$	$1.0 \cdot 10^{9}$

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Cluster formation (paint bake 180 C, 30 min)

Movie of clustering in Al-Mg-Si was shown

by M. van Huis

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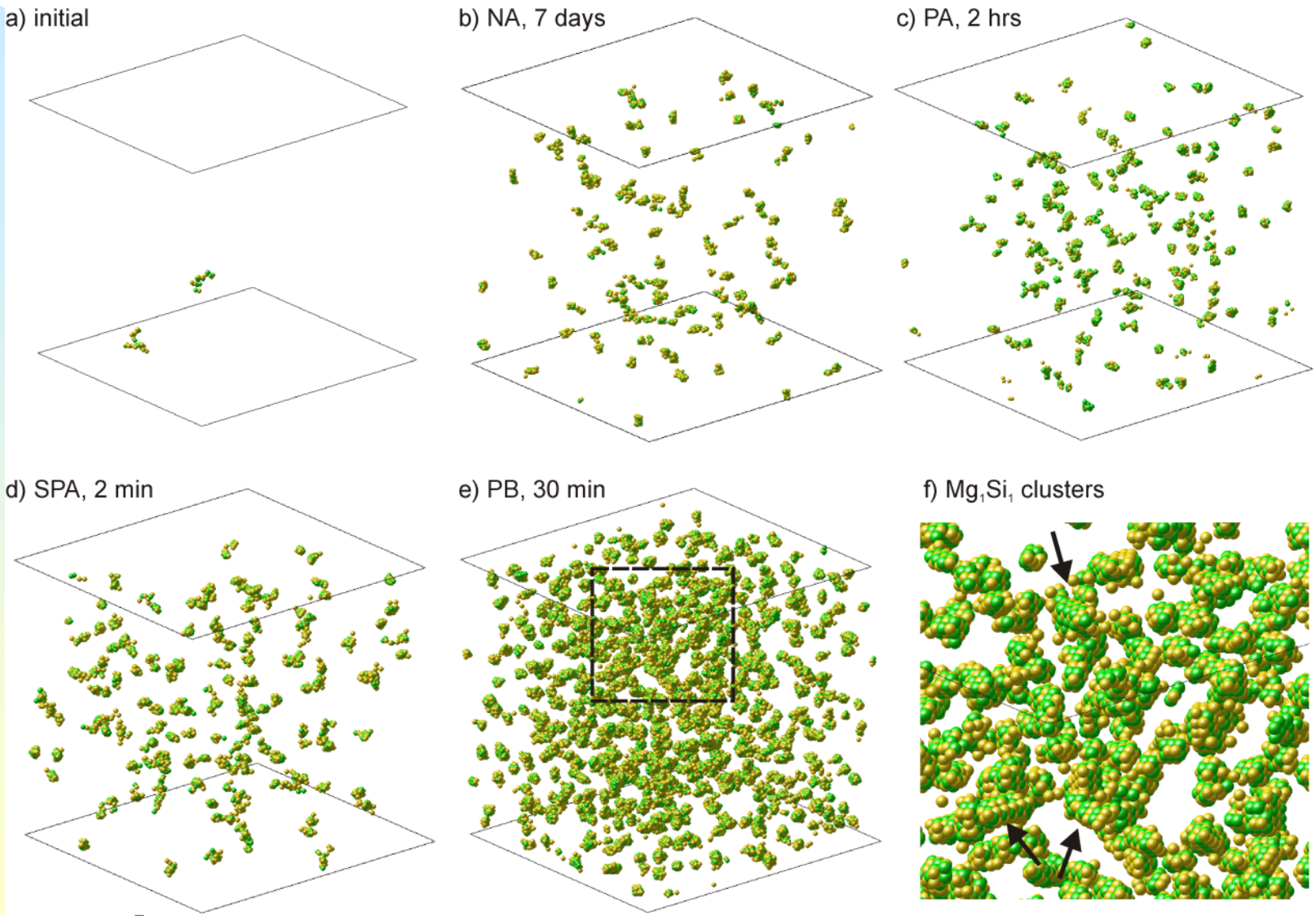
Clusters



Pics by M. van Huis

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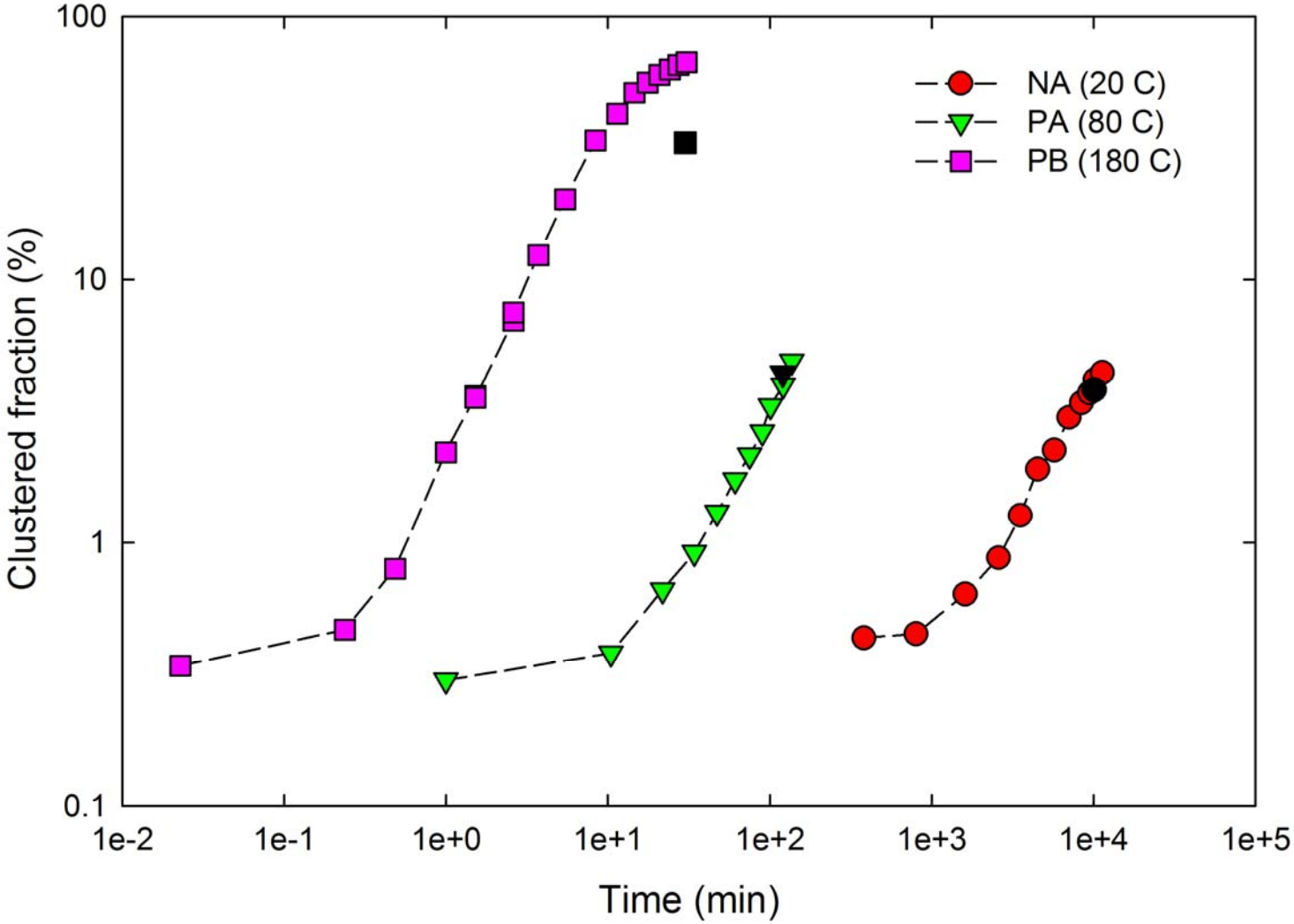
Fraction solute precipitated



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Summary so far

Cluster expansions on fixed lattices involving 4 species: Al Mg Si/Li and vacancies

Can get phase diagram – but not so easy (sometimes vibrational props needed to get correct solubilities)

If phase diagram can also get matrix-precipitate interface properties (ab initio Gibbs isotherm…)

Special tricks in cluster expansion make it feasible to go to very long time scales (occupation number=0 for majority species)

Conclusions

- 1st principles at core of understanding alloys
- Connects thermodynamics, structure, bulk properties
- Properties of interfaces
- Cluster expansions, nuts and bolts
- Diffusion
- Utility of the kinetically resolved activation concept
- Trapping and labyrinthic factors in diffusion
- Kinetic Monte Carlo requires fast cluster expansions
- Cluster expansions for dilute alloys can use a vector representation for σ, in which the majority element can be "eliminated" for speed

Group members

MSc
- Maarten de Jong (now at UC Berkeley)

PhDs
- Darko Simonovic, phase stability in Al-Sc-X alloys
- Chaitanya K. Ande, phase stability of ferrous carbides

Postdocs
- Andrew Duff, modeling of interstitials in Fe (now at MPIE)
- Emre Tasci, data mining for transformation toughening (now at Univ San Sebastian, Spain)
- Tetyana Klymko, ferrous carbonitrides

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