# Ab-initio simulations and their application to modelling solute drag during the austenite-to-ferrite transformation

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# Density Functional Theory (DFT)

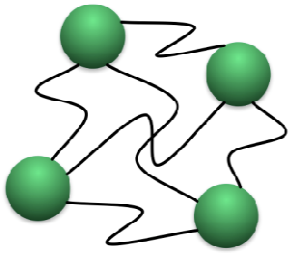
Hohenberg and Khon :

$$\rho(\vec{r}) \xrightarrow{F(\rho(\vec{r}))} E_{Total}$$

Electron density

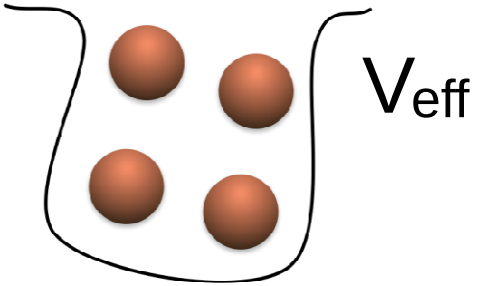
Total energy

Khon and Sham:



Replace interactions with an effective potential

$\rho_{int} = \rho_{nonint}$




Since ρ is the same, the total energy must be the same too.

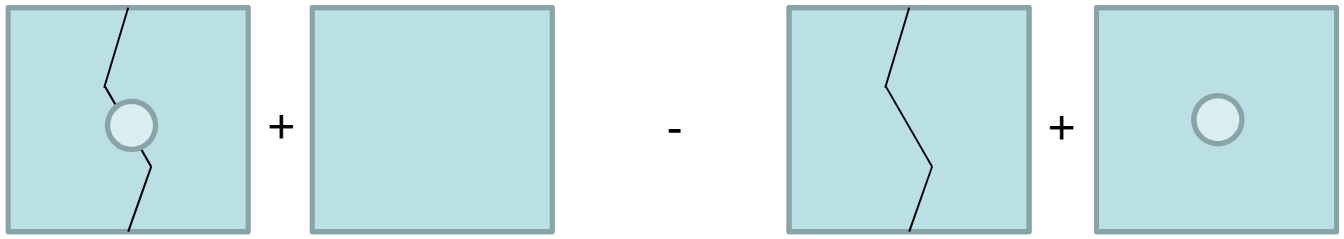
Need to find approximations for $V_{eff}$ using theory of interacting electron gas (LDA, GGA).

**Note: Ground state theory – T = 0 K, can consider ~ 100 atoms**

# DFT Simulations for Interfaces

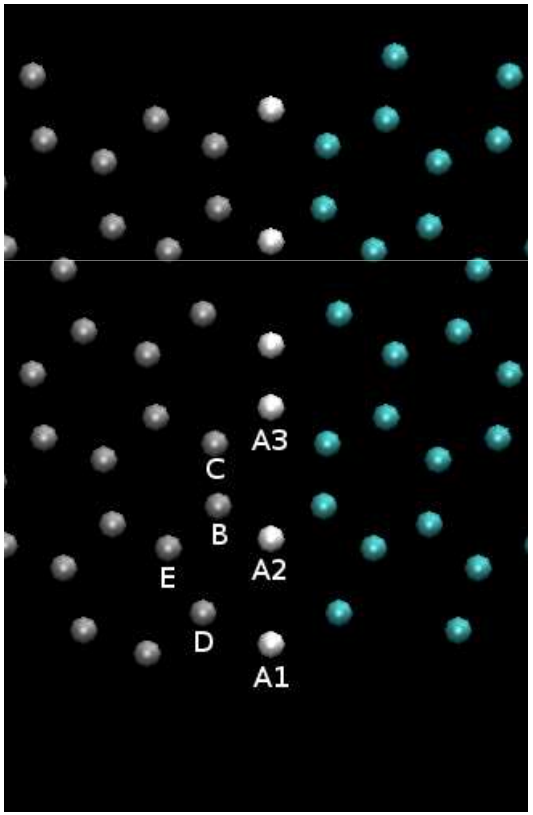
- DFT calculations using the VASP code
- Periodic boundary conditions: Can only consider special boundaries (e.g. low Σ boundaries) with small unit cell
- Solute-grain boundary (GB) binding energies (segregation energy)—cost to move solute from the *i*th GB site to the bulk:

$$E_s = (E_{X+GB} + E_{ref}) - (E_{GB} + E_X)$$



# Σ7 Grain Boundary in Magnesium

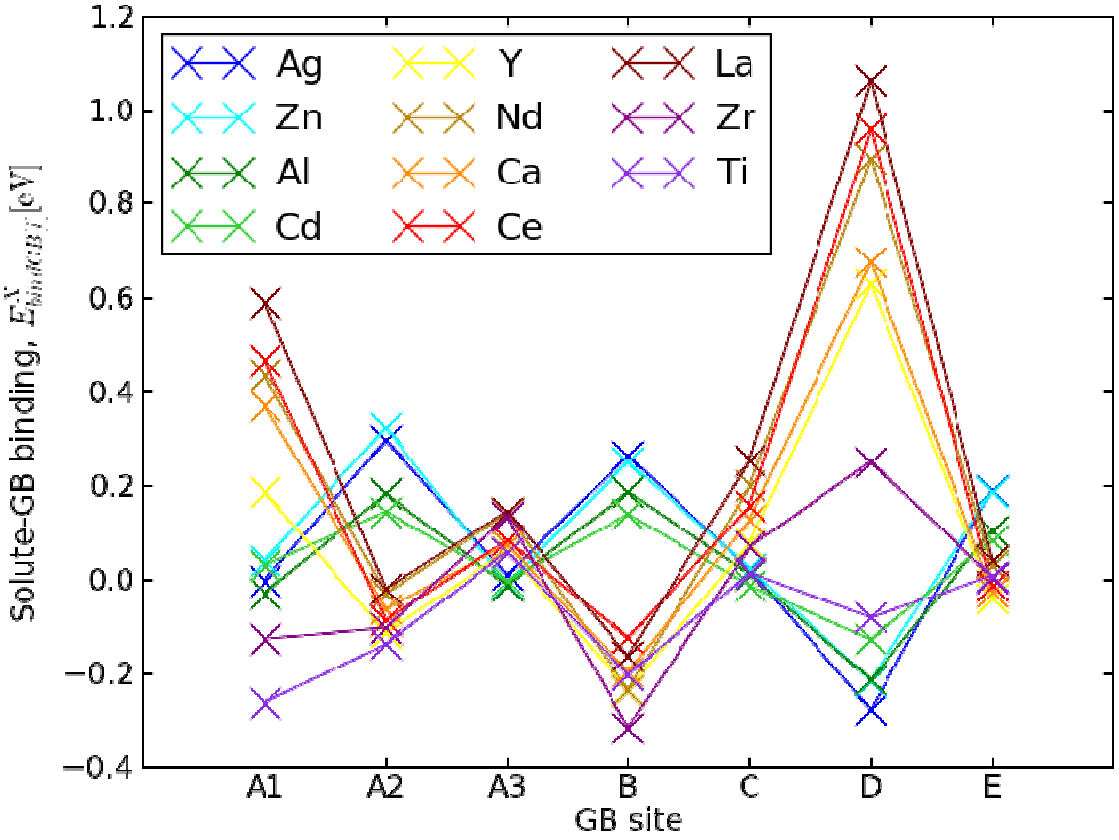
- Σ7 tilt (21.8° on 0001 axis) boundary with two conformations (A- and T-type)
  - Repeats over short enough distance to be used in DFT
  - 232 (184) atom cells used for A-(T-)type boundary

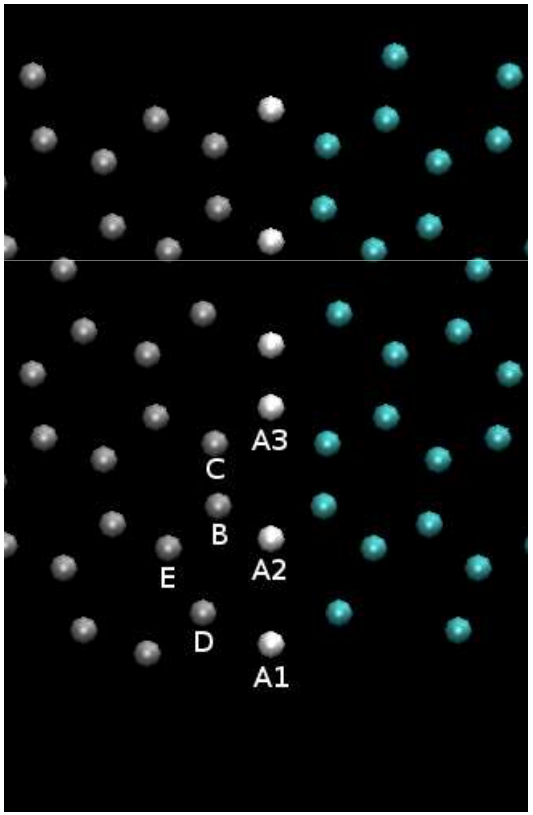



- A-type grain boundary looking down *c*-axis
  - Grain 1 in grey, grain 2 in green, and coincident sites in white
  - Sites labelled by distance from GB plane

# Solute Segregation Energies at Σ7 in Mg

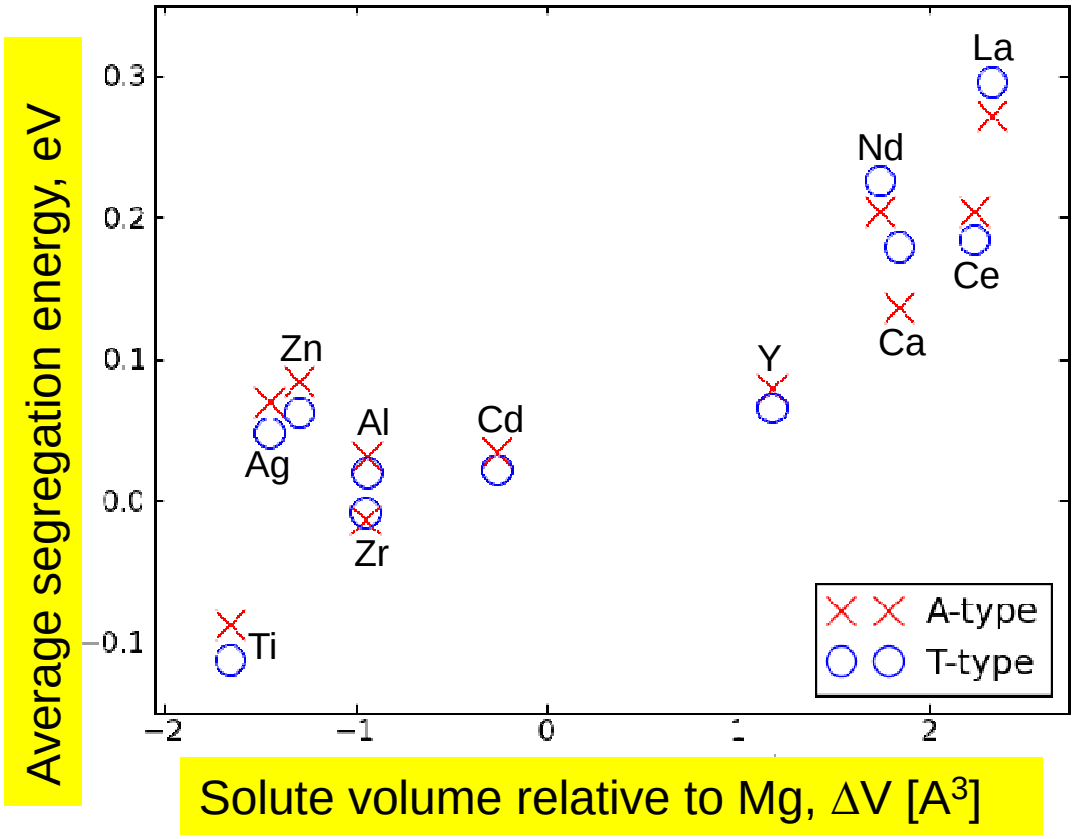
- Three families of behaviour: La-like, Al-like, Zr-like



# Average Segregation Energy at Σ7 in Mg

- A- and T-type boundaries similar
- In general, larger solutes with stronger binding

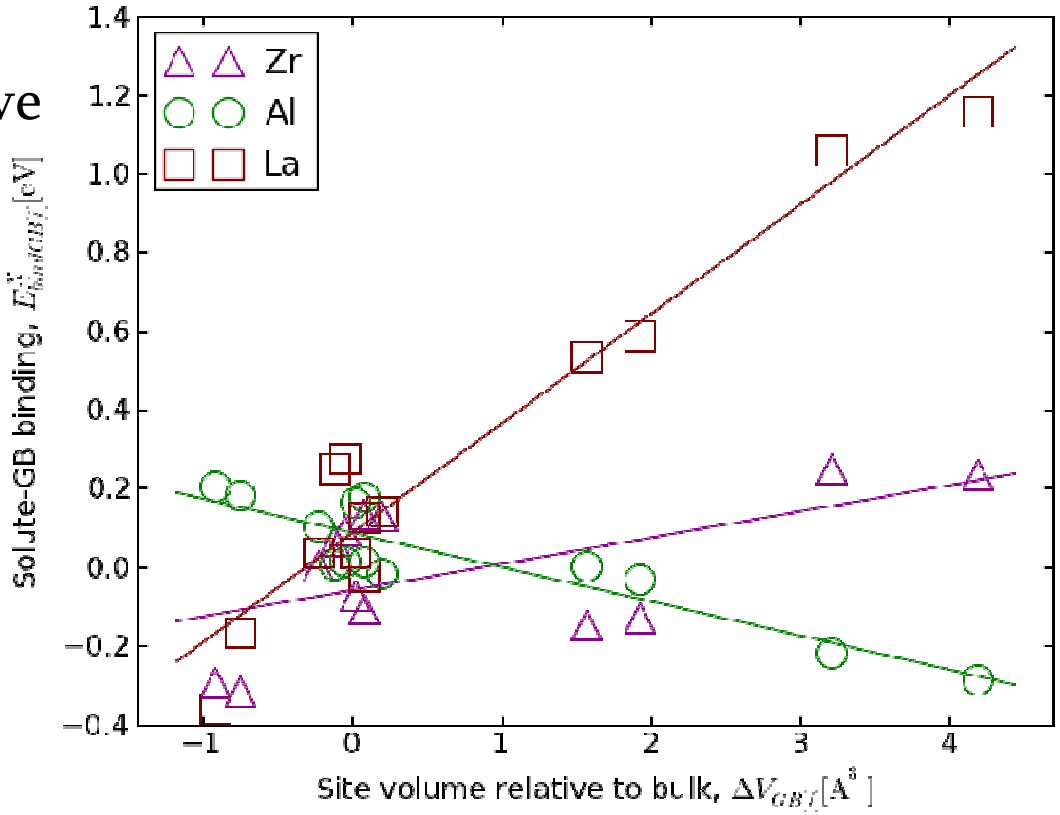


# Elastic Analysis

- GB sites may have different volume compared to bulk sites—what is binding dependence?
- Al, La, and Zr representative of their families.
- Al and La: simple linear model works well

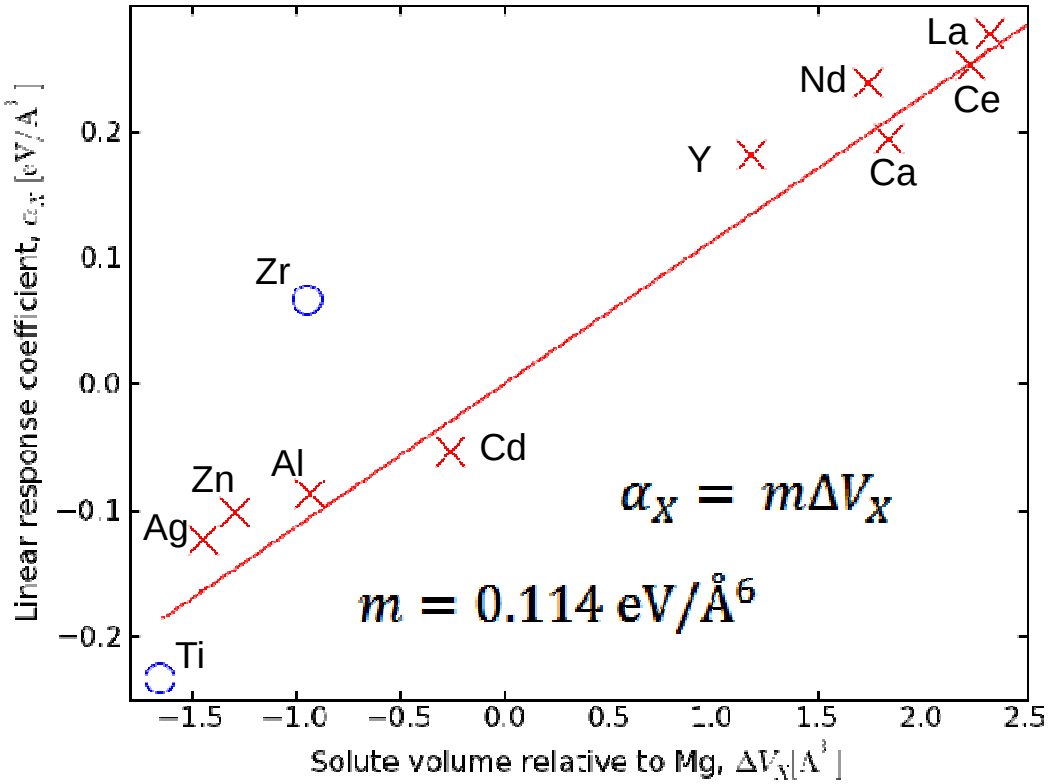
$$E^{X}_{bind\ GB\,[i]} = \alpha_X \Delta V_{GB\,[i]} + b_X$$

- Zr family: poor correlation with excess site volume



# Elastic Analysis

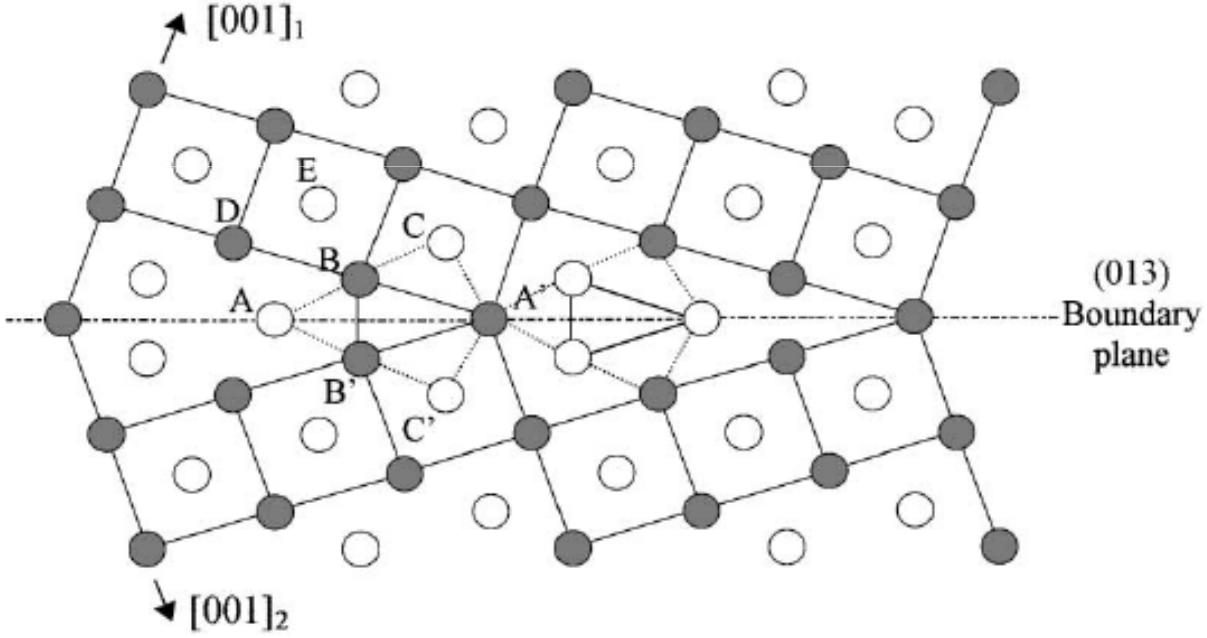
- Linear elastic response as function of solute volume (relative to Mg)



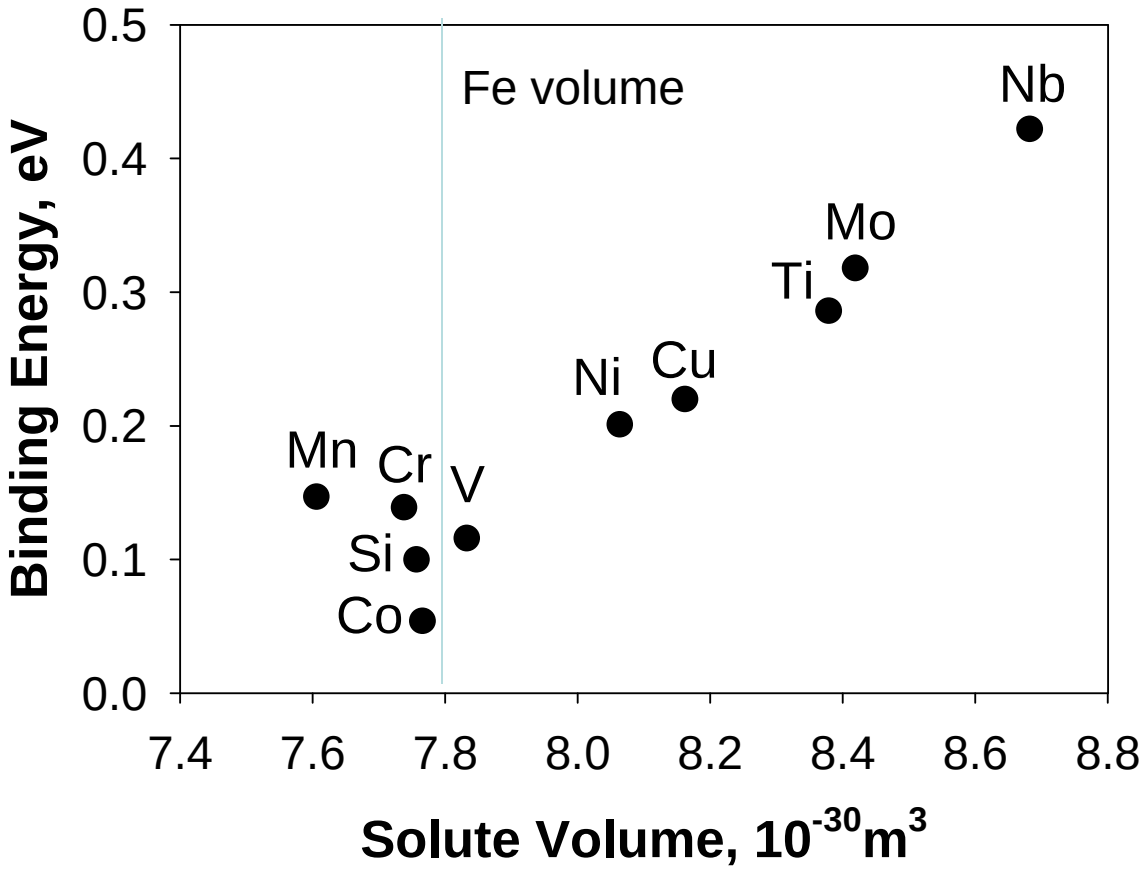

- Most solutes of interest in Mg elastically dominated solutes
- May be able to extend to random boundaries using molecular mechanics

# Σ5 Grain Boundary in BCC-Iron

Σ5 [001] {013} Tilt Grain Boundary in BCC-Fe



# Average Binding Energies at Σ5 in BCC-Fe



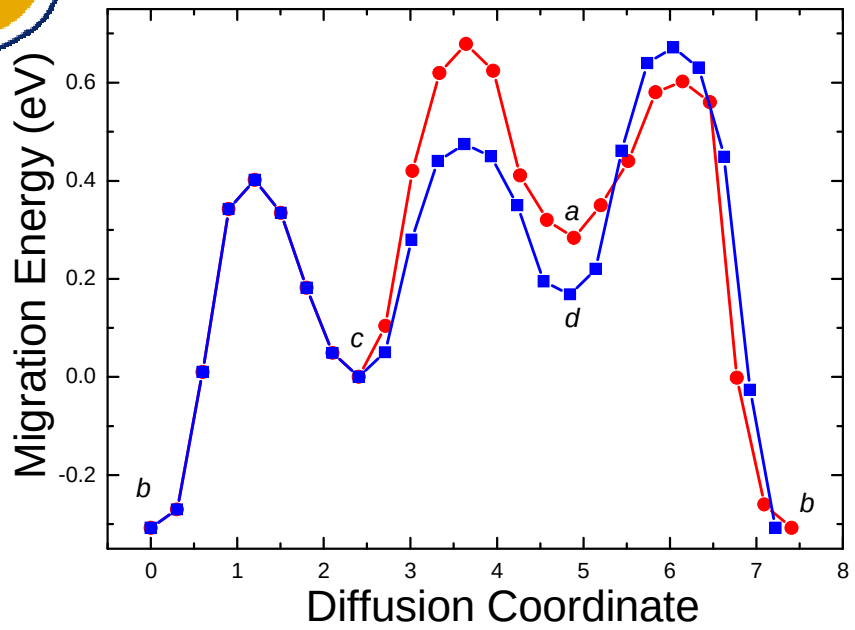

**Nb**
**40 kJ/mol**

**Mo**
**30 kJ/mol**

**Mn**
**15 kJ/mol**

Binding energy increases with size of solute atom
but also magnetic contributions (see e.g. Cr and Mn)
Nb with higher binding energy compared to Mo, Ti, Mn, Si and V
→ strong interaction of Nb with grain boundaries (consistent with recrystallization delay)

# Grain Boundary Diffusion



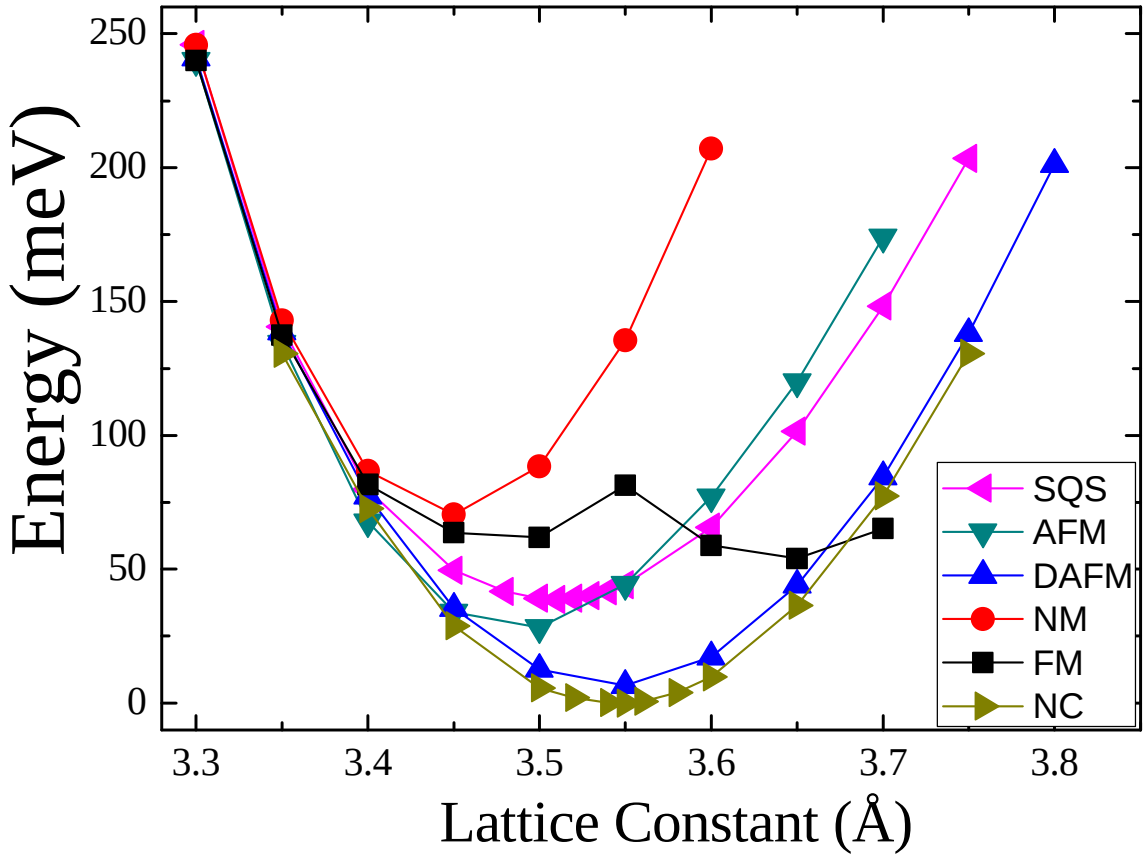

Determine activation energies for individual jumps from DFT

Kinetic Monte Carlo simulation to obtain effective grain boundary diffusivity:
$D_b=D_0\exp(-Q_b/RT)$

| | Fe | V | Mn | Cu | Ti | Nb | Mo |
|---|---|---|---|---|---|---|---|
| $Q_b$ (eV) | 2.24 | 2.05 | 1.97 | 2.11 | 1.92 | 1.88 | 2.09 |
| $Q_{bulk}$ (eV) | 2.84 | 2.6 | 2.37 | 2.49 | 2.35 | 2.21 | 2.53 |
| $Q_b/Q_{bulk}$ | 0.79 | 0.79 | 0.83 | 0.85 | 0.82 | 0.85 | 0.83 |

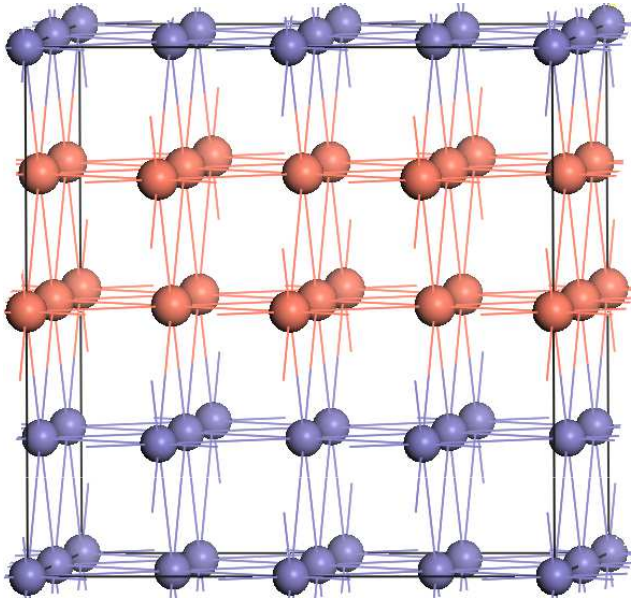
Activation energies at Σ5 boundary
approximately 80-85% of those for bulk diffusion

# Magnetic Configurations for FCC-Fe

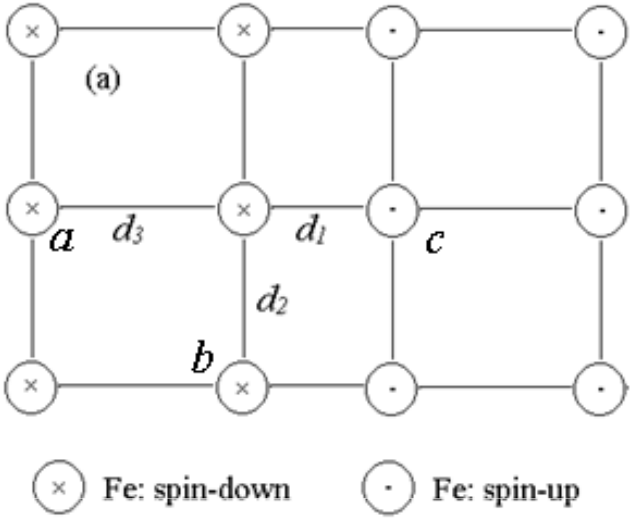



Non-Magnetic (NM), Ferro-Magnetic (FM), Anti-FM (AFM), Special Quasi-random Structure (SQS), DAFM (double-layer AFM), and non-collinear (NC) configurations vs. the lattice constant in fcc Fe.
Note:: 3.56Å lattice constant concluded from experimental studies

# DAFM Structure for FCC-Fe



Schematics of DAFM structure for fcc Fe




For non-relaxed pure bulk lattice:

$d_1 = d_2 = d_3 = 2.51$ Å

For relaxed pure bulk lattice:

$d_1$=2.46 Å, $d_2$=2.51 Å, $d_3$=2.56 Å

## Vacancy formation energy:

DAFM state: 1.72eV

Experiments [1]: 1.70±0.2eV

[1] Kim SM, Buyers WJL. Journal of Physics F-Metal Physics 1978;8:L103

## Activation energy:

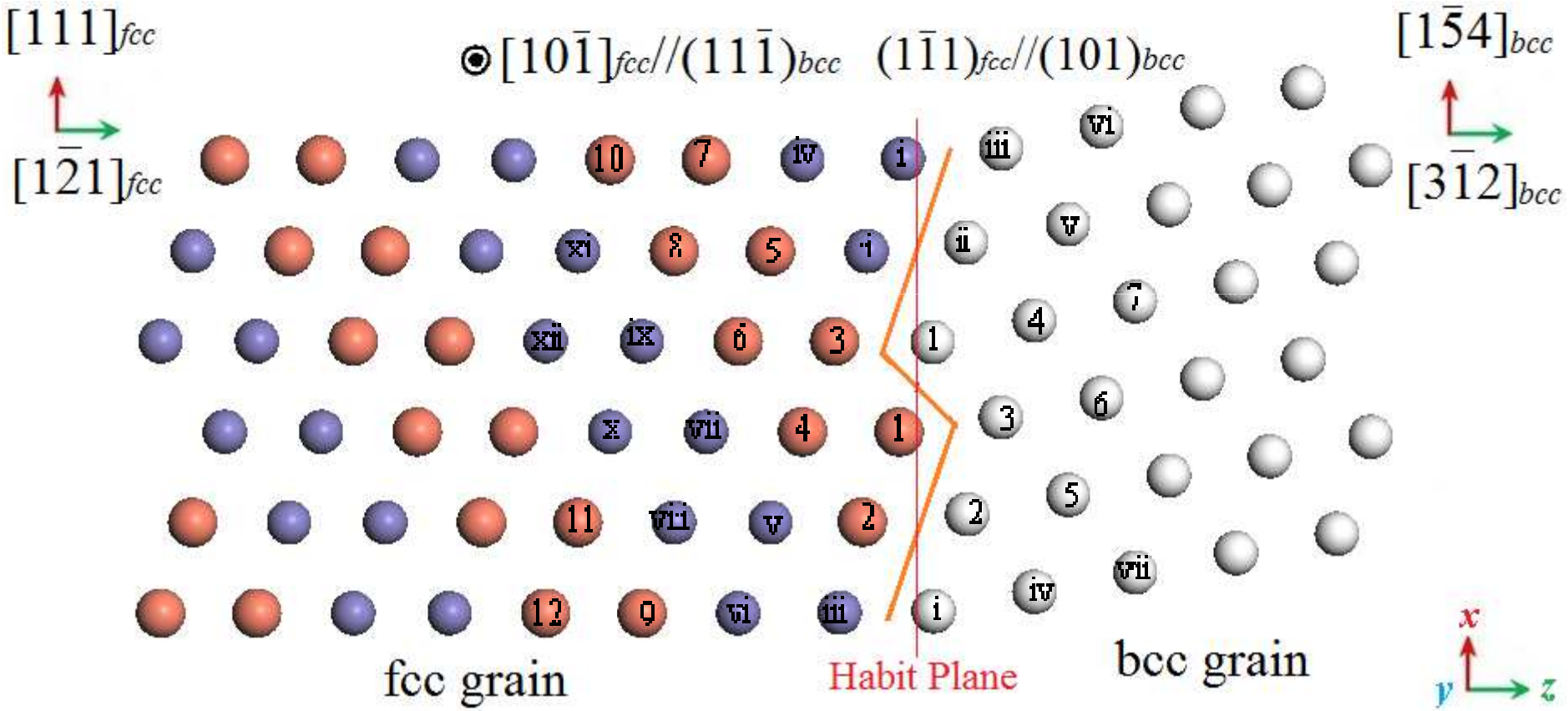
DAFM state: 2.81eV, 2.46eV, 2.65eV at *a*, *b*, *c* positions

Experiments: 2.80~2.94 eV;

Temp. 1223~1473 K

# α–γ (bcc-fcc) Interface (K-S OR)

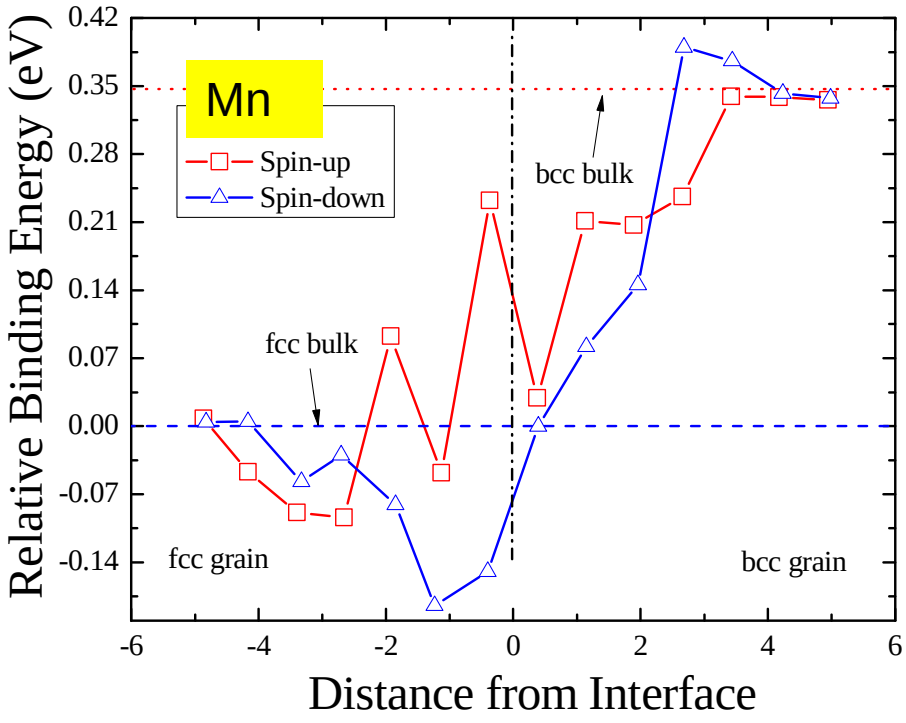
Kurdjumov-Sachs (K–S) OR: $(111)_{fcc} \parallel (101)_{bcc}, [10\bar{1}]_{fcc} \parallel [1\bar{1}1]_{bcc}$

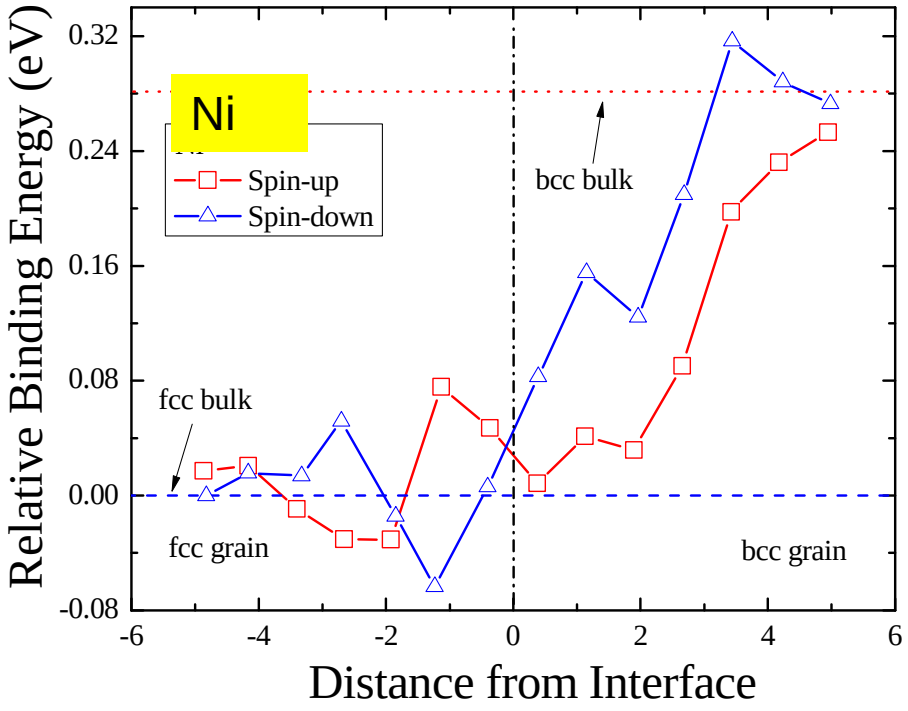


# Relative Binding Energies for Solutes with α– γ Interface

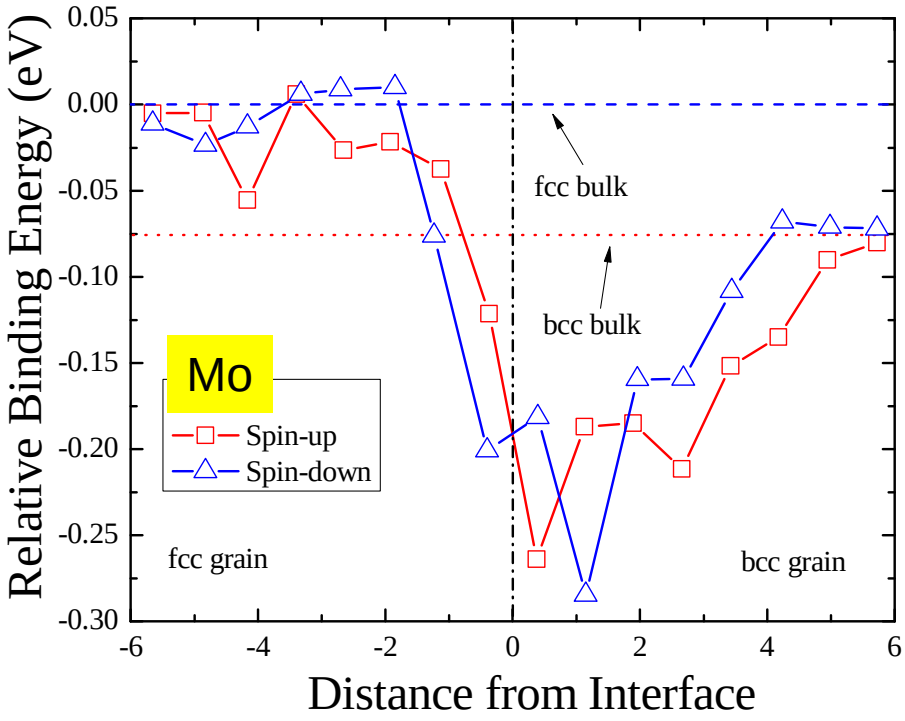
$$E_b = (E_{I+X} - E_I) - (E_{\gamma+X} - E_\gamma)$$

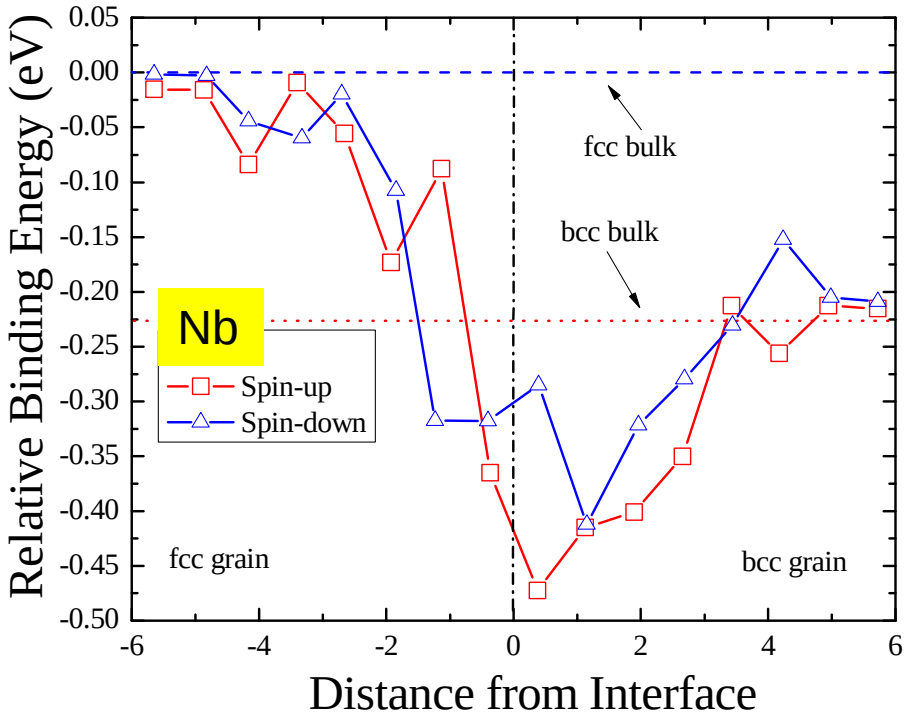
where $E_{I+X}$ and $E_I$ are the total energies of bcc-fcc interface with and without solute.
$E_{\gamma+X}$ and $E_\gamma$ are the total energies of fcc bulk with and without solute.



# Relative Binding Energies for Solutes with α– γ Interface

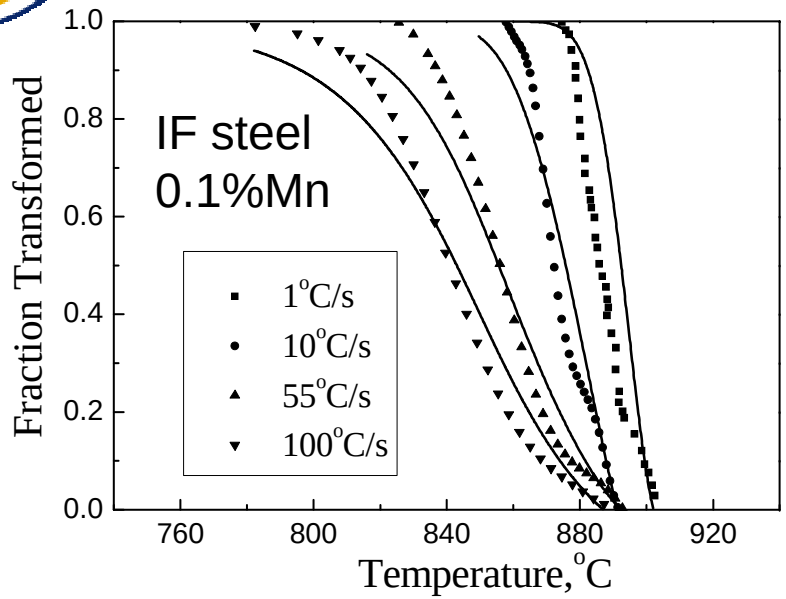


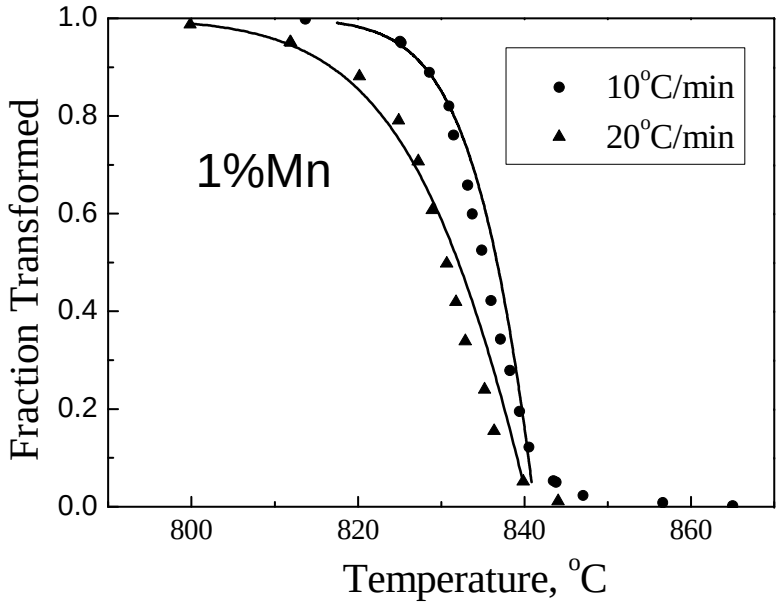



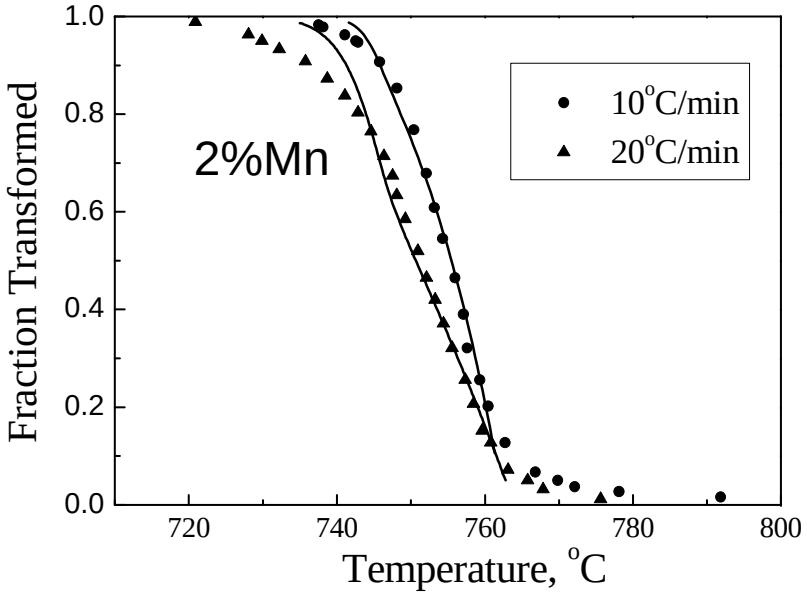

Similar binding energies predicted for Nb, Mo and Mn as at Σ5:

**Nb: 40 kJ/mol**
**Mo: 20-30 kJ/mol**
**Mn: 10-20 kJ/mol**

# CCT in IF Steel and Fe-Mn Alloys




Krielaart & van der Zwaag (1998)

| *Mn* % | $M_0$ (cm mol/Js) | $Q$ (kJ/mol) | $Q_b$ (kJ/mol) | $E_0$ (kJ/mol) |
|---|---|---|---|---|
| 0.1 | | | | **16** |
| 1 | **450** | 140 | **216** | **11** |
| 2 | | | | **6** |

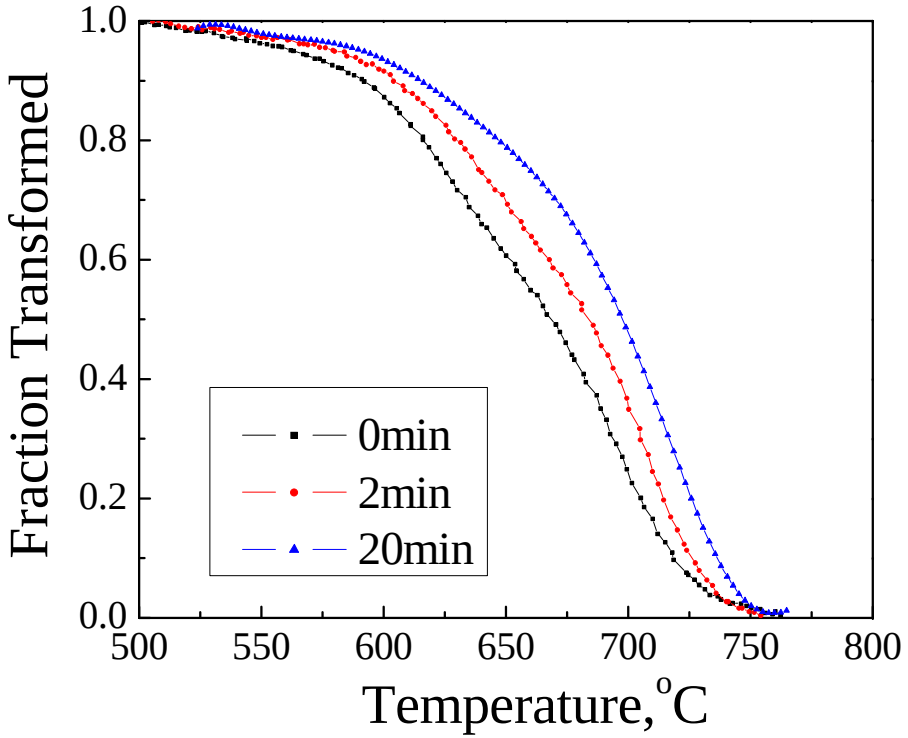
94% of
BCC bulk value

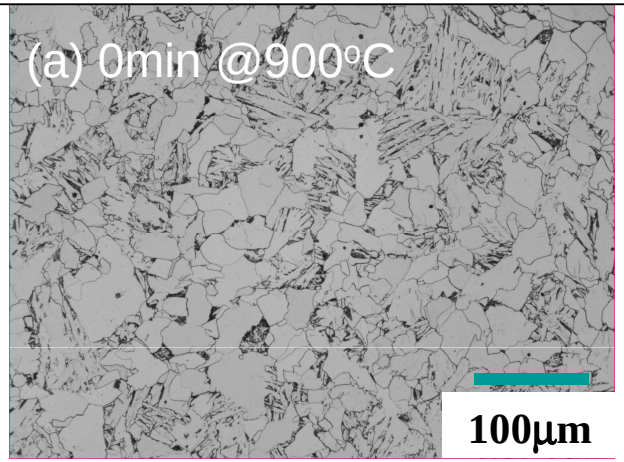
# Effect of Nb on Phase Transformation

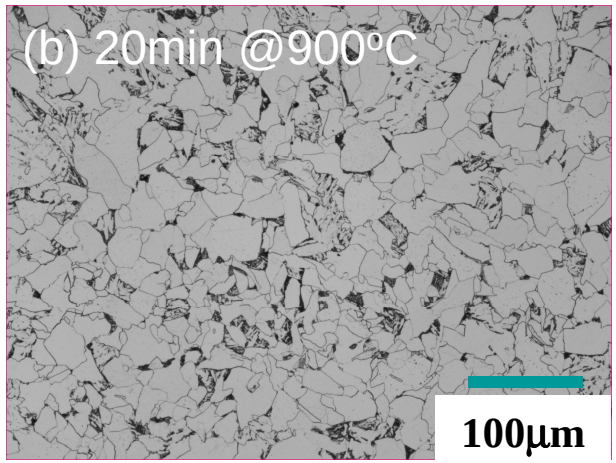
**X65 steel**

| C | Mn | Si | P | S | Al | Nb | N | $A_{e3}$ |
|---|---|---|---|---|---|---|---|---|
| 0.06 | 1.49 | 0.2 | 0.009 | 0.002 | 0.038 | 0.047 | 0.0094 | 839°C |

## Continuous Cooling – 1°C/s



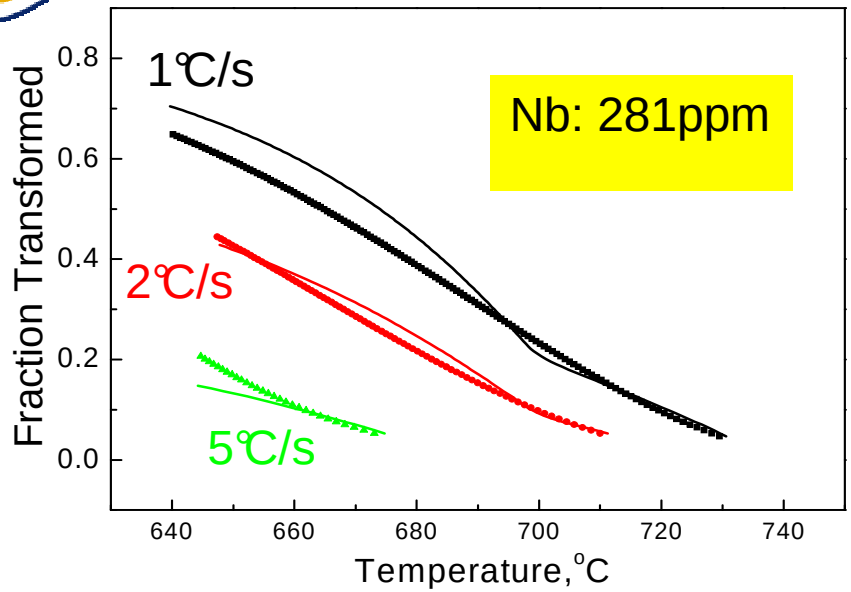



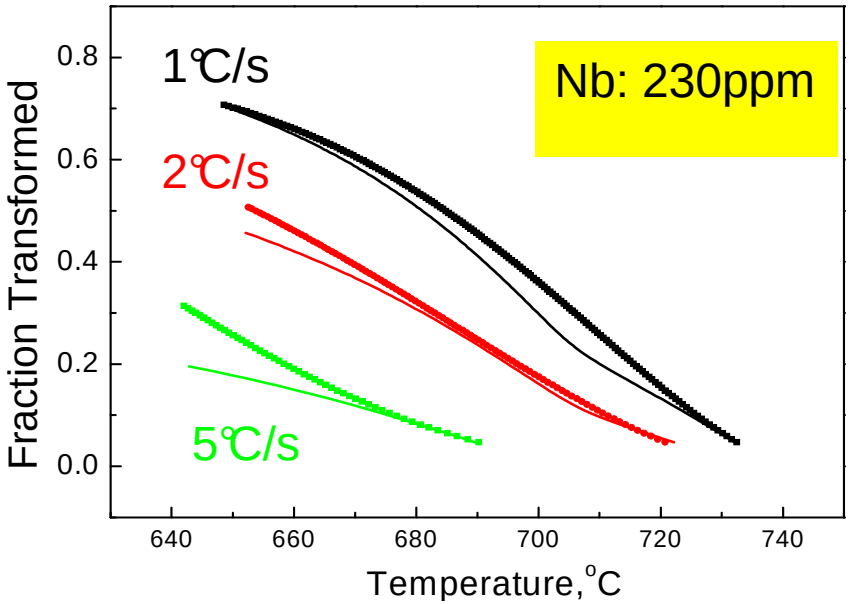



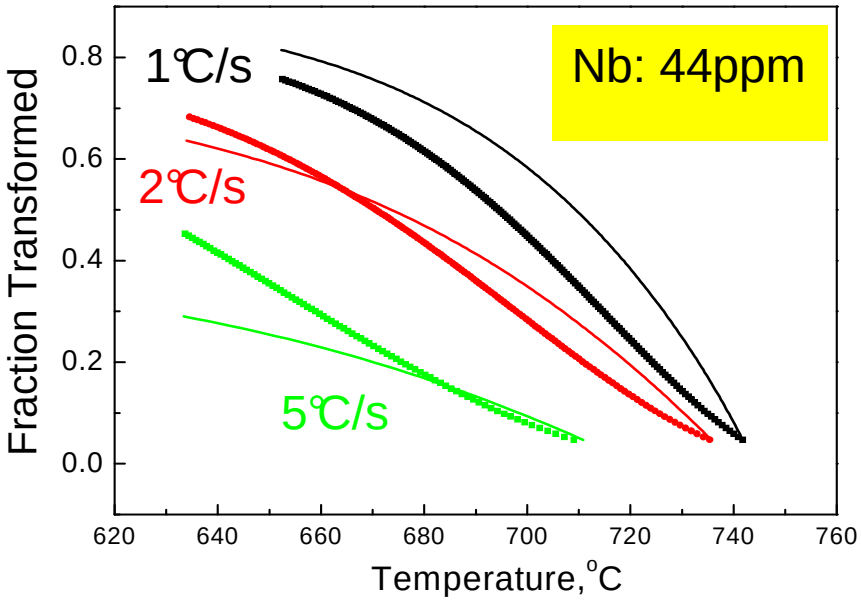

| | 0min | 2min | 20min |
|---|---|---|---|
| $C_{Nb}$(ppm) | 281 | 230 | 44 |

*J.S. Park, Metall. Mater. Trans. A, 2009, 560.*

# Solute Drag based Transformation Model




**Mixed-mode transformation (Fe-C-Nb system)**

**$M_0$ = 2.4 cm mol/Js**

Q = 140 kJ/mol

**$Q_b$ = 245 kJ/mol**

**$E_0$ = 48 kJ/mol**

between FCC & BCC bulk value

# Conclusion & Outlook

- Promise of multi-scale modelling approach to account for effect of solutes on austenite decomposition kinetics
- Reliable trend predictions but still need a limited number of physically well defined fit parameters
- Need to extend current model from binary/ternary systems to more complex steel chemistries, e.g. Nb-Mo interaction
- Challenges: Ab-initio simulation of paramagnetic FCC-Fe and extension to bainite transformation