Computational Chemistry and Materials Modeling

Lecture 11. Defects in solids

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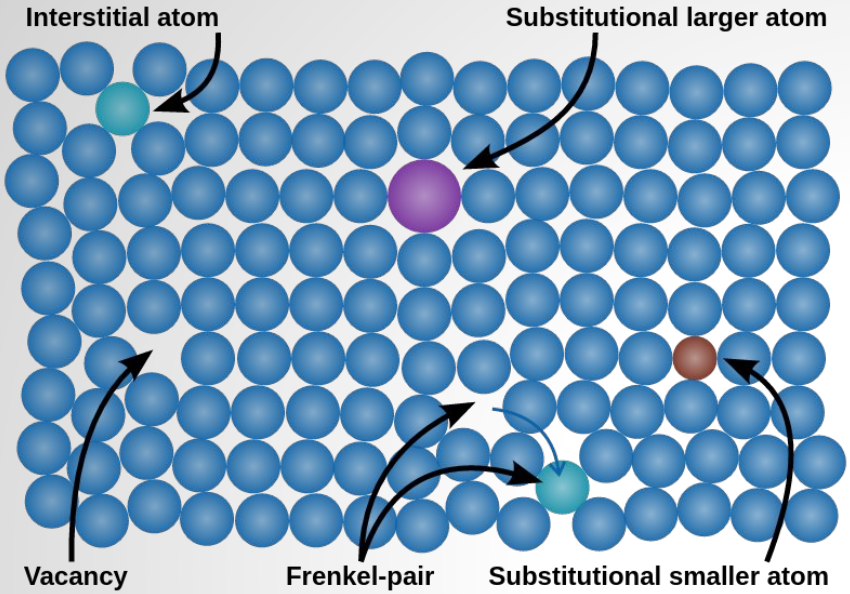
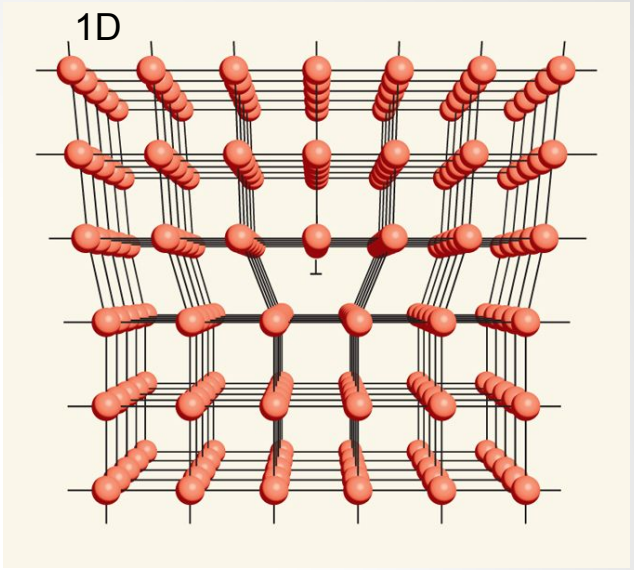
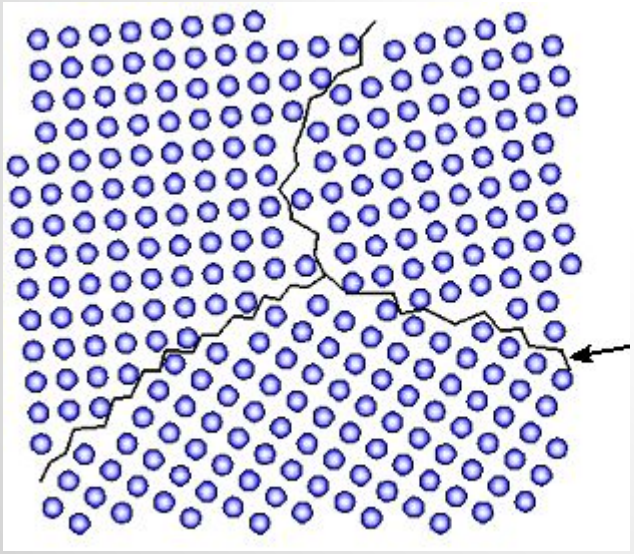
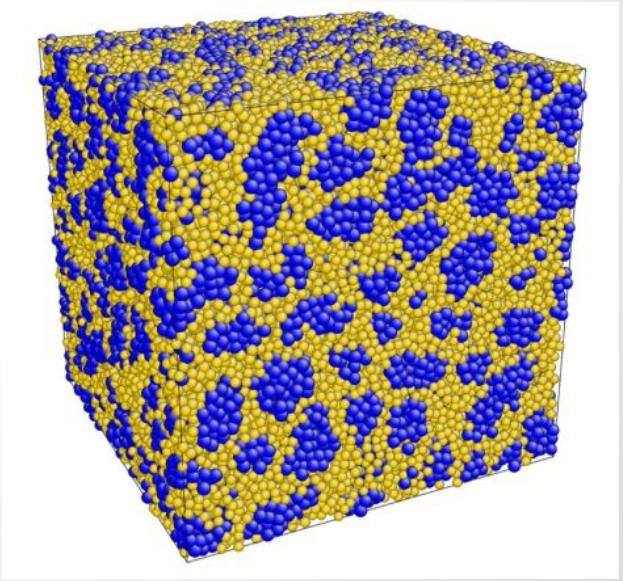
What is a defect in crystal solid?





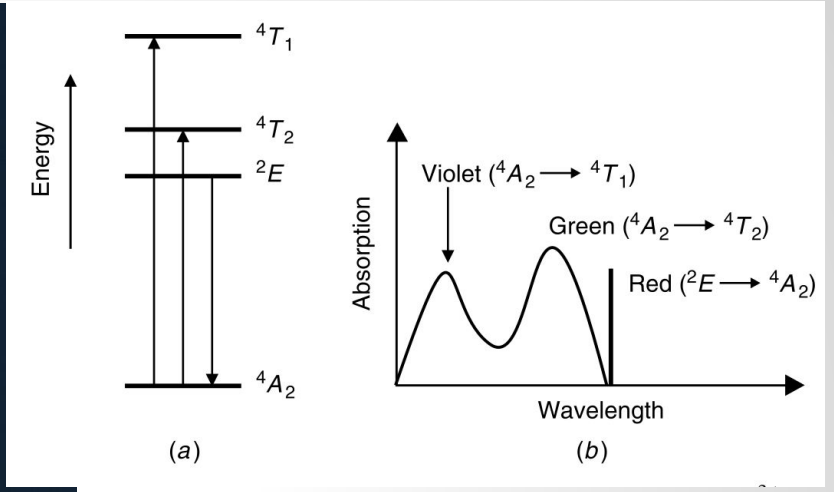




Properties of solids are controlled by defects

- every aspect of the physics and chemistry of solids are influenced by the defects
  - on the one hand the influence can be harmful
  - on the other hand the most advanced modern technologies owe to the defects

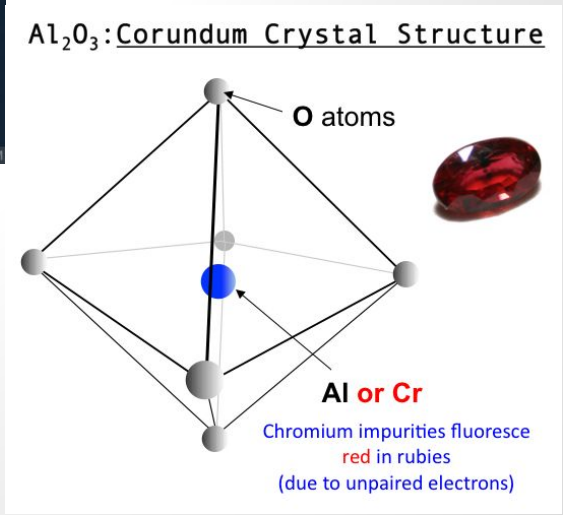
Cr solutes are responsible for red color



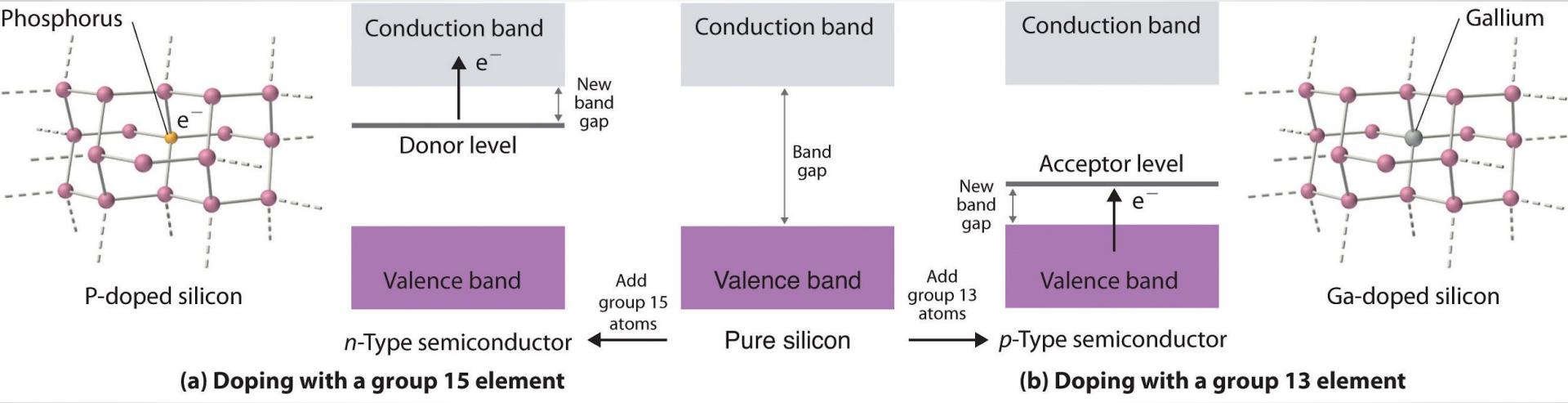
Hanamura, Quantum nonlinear optics
Sridharan - group representations

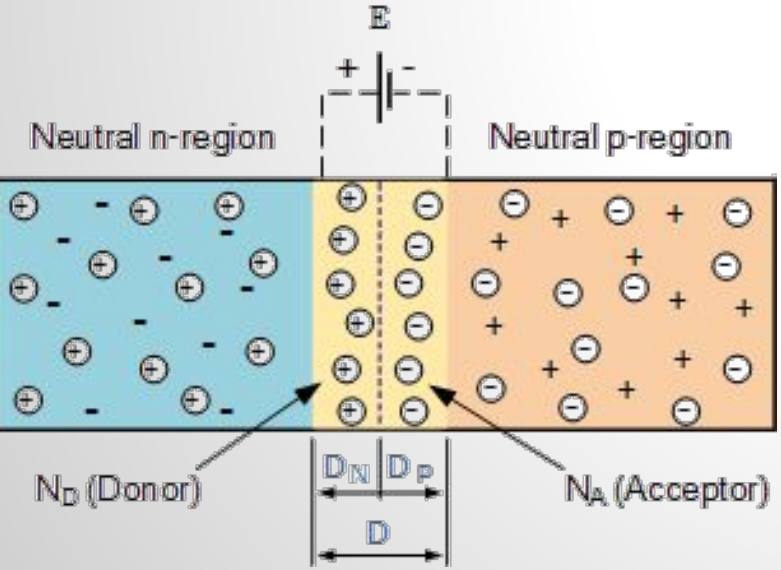
α-Al_2O_3 transparent

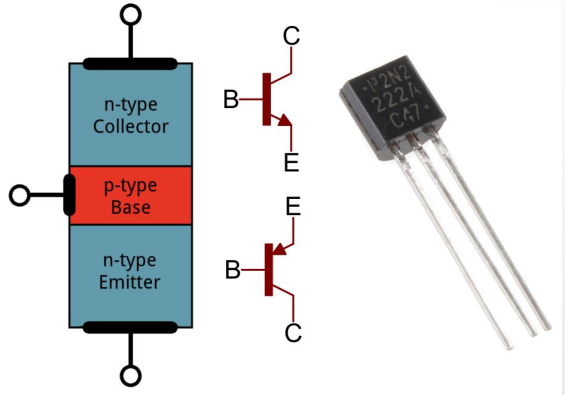
$Cr_{0.005}Al_{0.995}O_3$ red



P and Ga dopants allows semiconductors

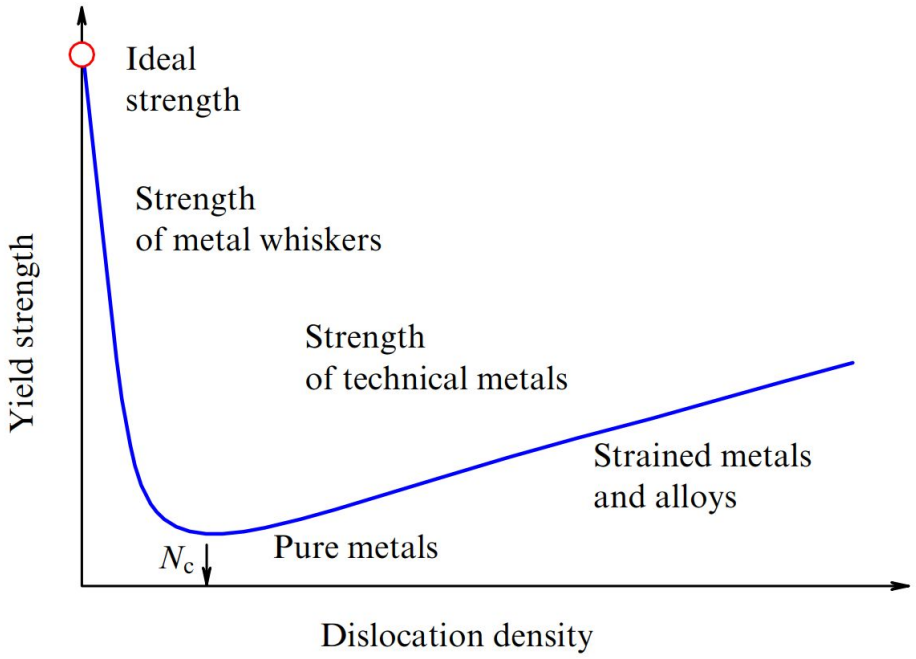


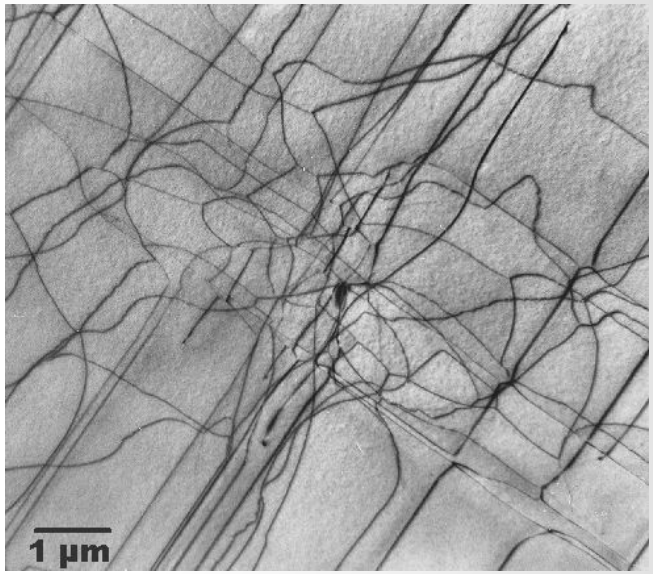




Metal strength depends on dislocation density

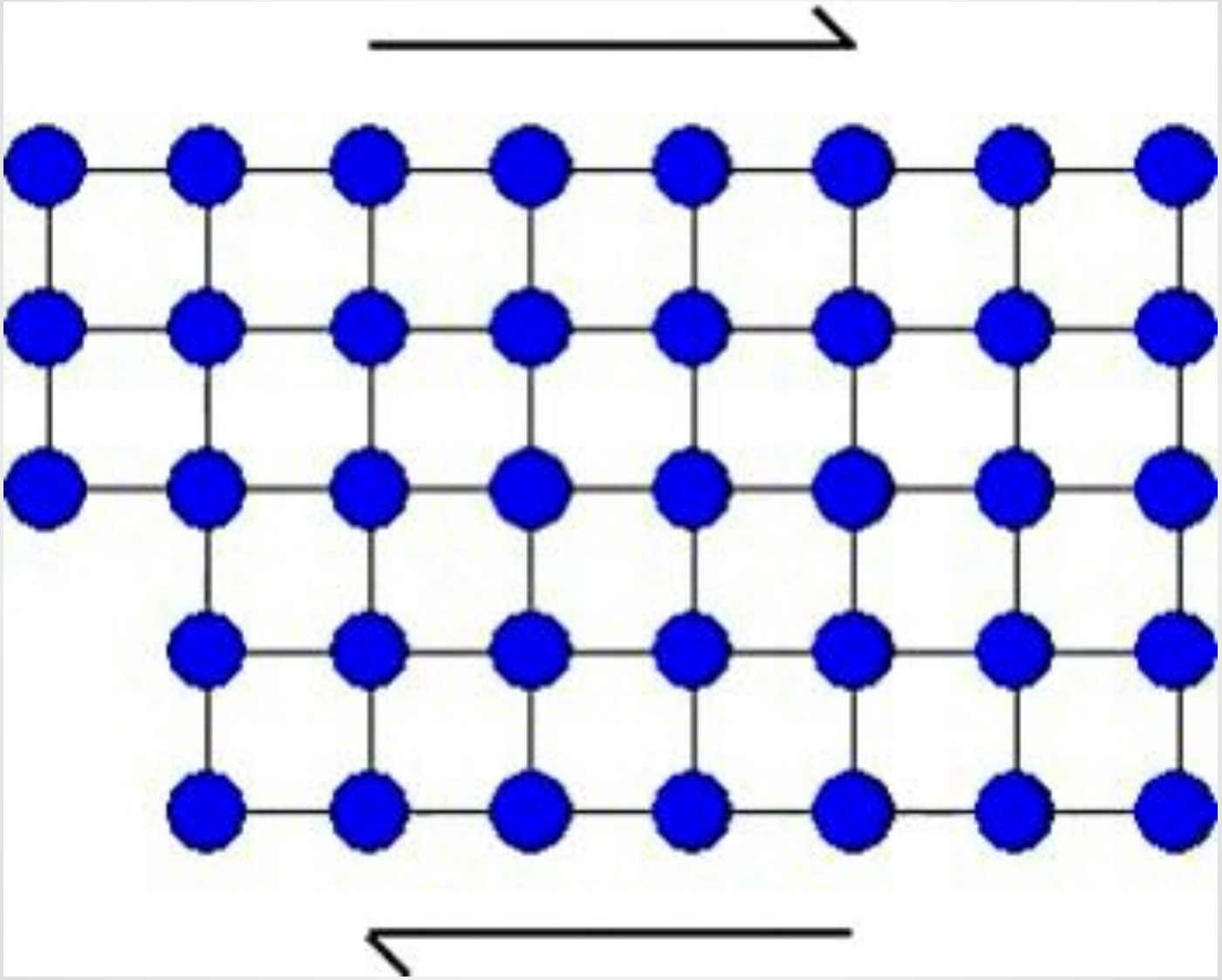
Strength depending on dislocation density





- The whole range of metal alloys - properties are controlled with defects
  - Solid solutions - point defects
  - Mechanical treatment cold-hardening - dislocations
  - Thermal treatment - grain boundary
  - Secondary phases
  - Segregations - embrittlement

Dislocation movement



Strength depends on grain size

Hall petch relationship

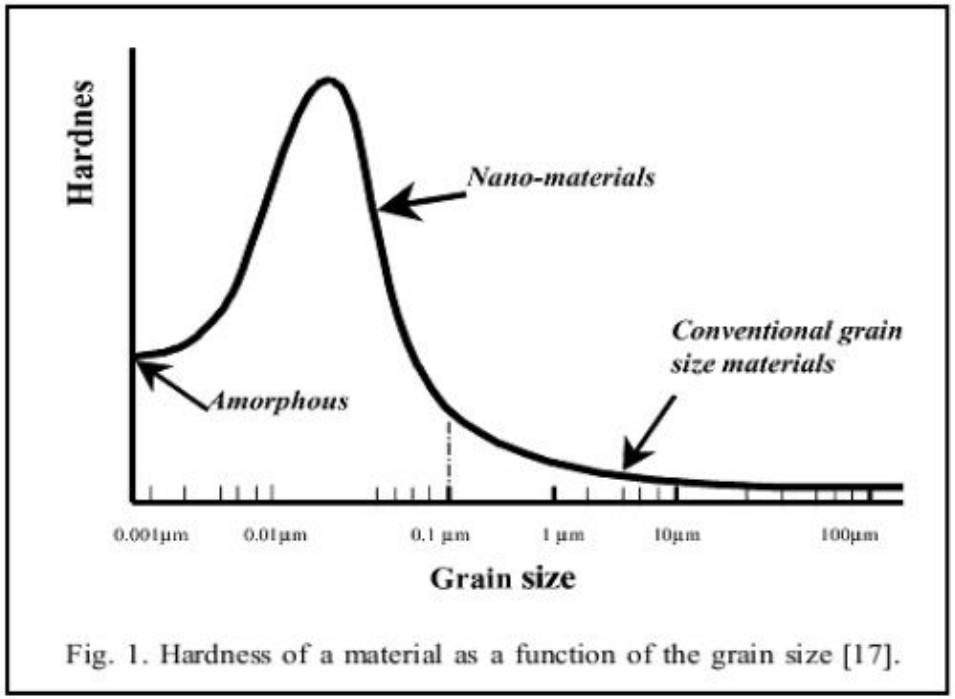
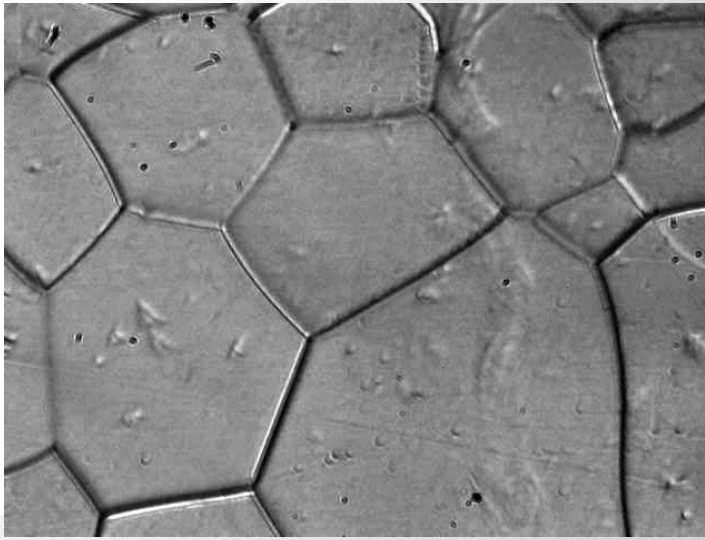


Fig. 1. Hardness of a material as a function of the grain size [17].

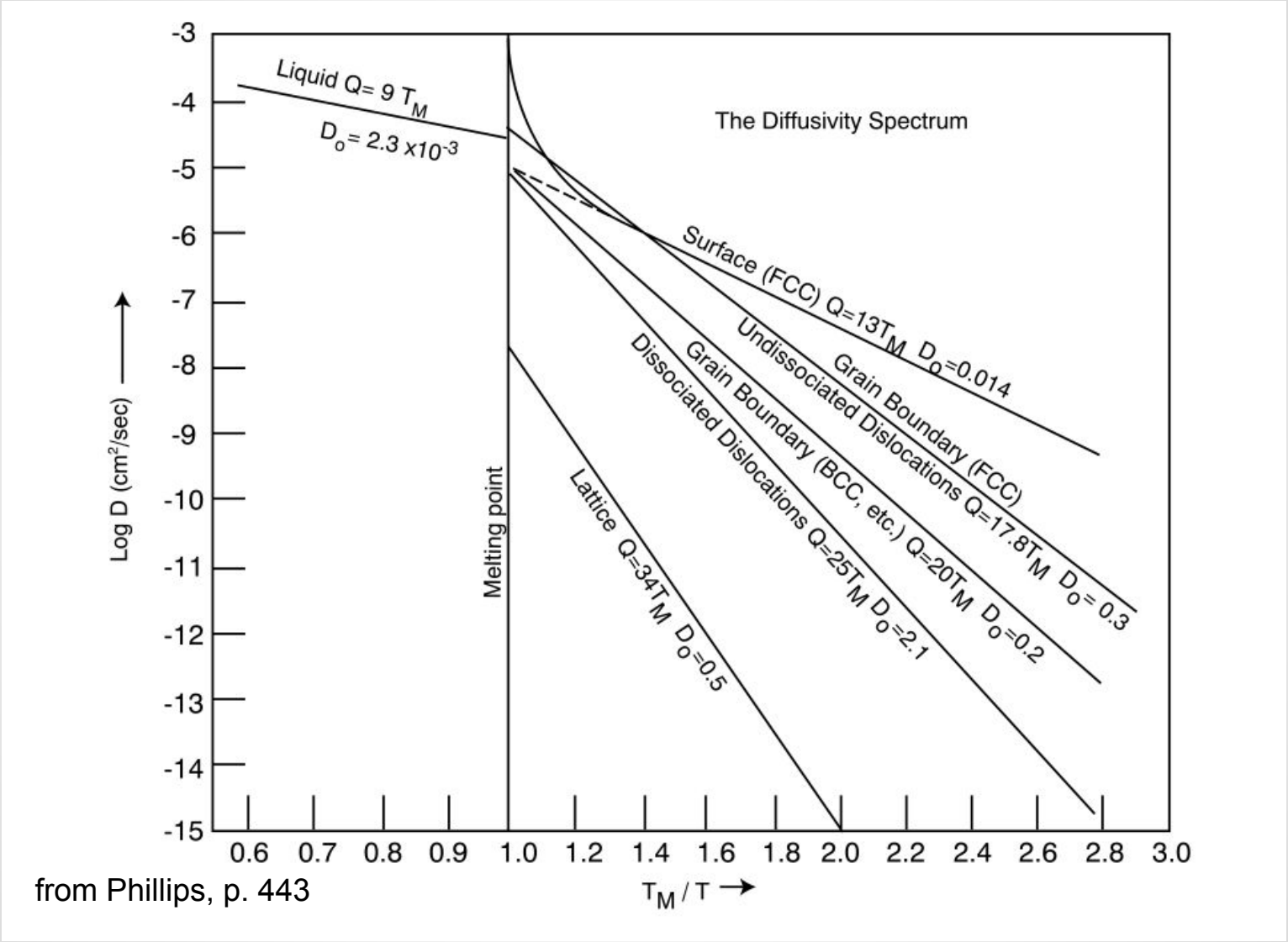
Strength

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

Average grain diameter



Influence of defects on diffusion



from Phillips, p. 443

Studying of defects

- The control of defects is a key for developing new materials

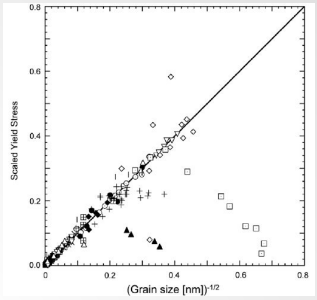
- Experimental study of defects is difficult:
  - usually inside material
  - atomic level
  - fast in time

- Computational modelling of defects!

Scales and Methods

Influence of defects on macroscopic properties

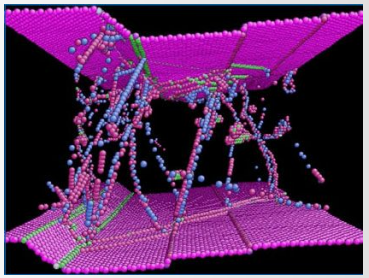
Analytical models



20x20x20 nm
nanoseconds

Evolution of defects in time

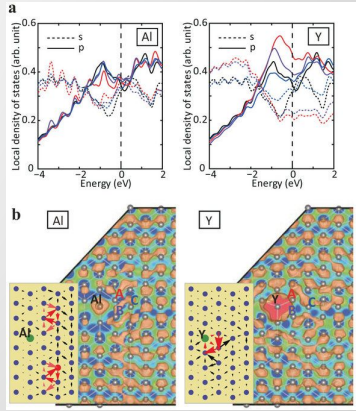
Classical Molecular Dynamics and Monte-Carlo



2x2x2 nm
100-500
atoms

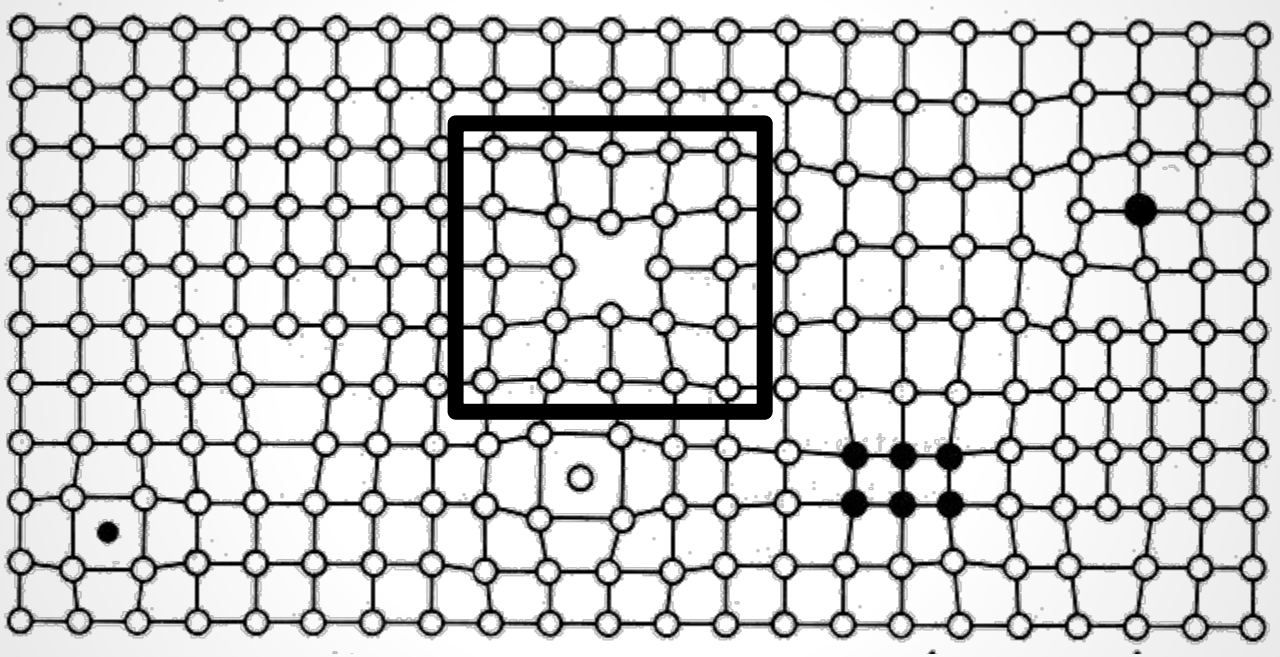
Structure and energies of defects

Quantum mechanics: Density Functional Theory

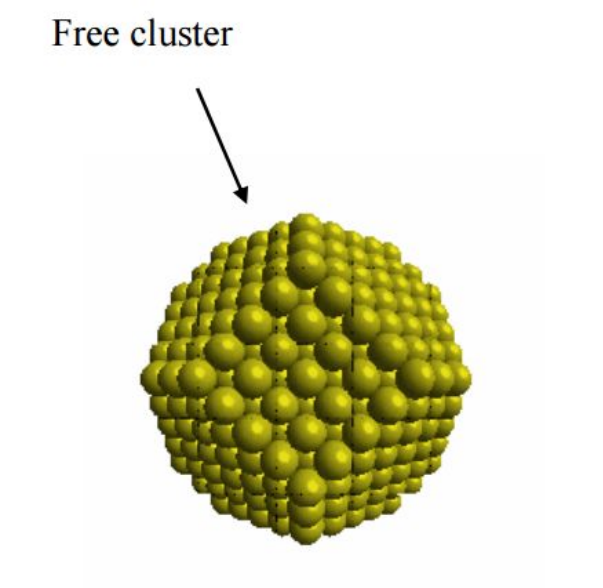


How to model a defect

Cut the region with defect from large crystal



Free boundary conditions



Pros:

- no translation symmetry - amorphous or disordered solids

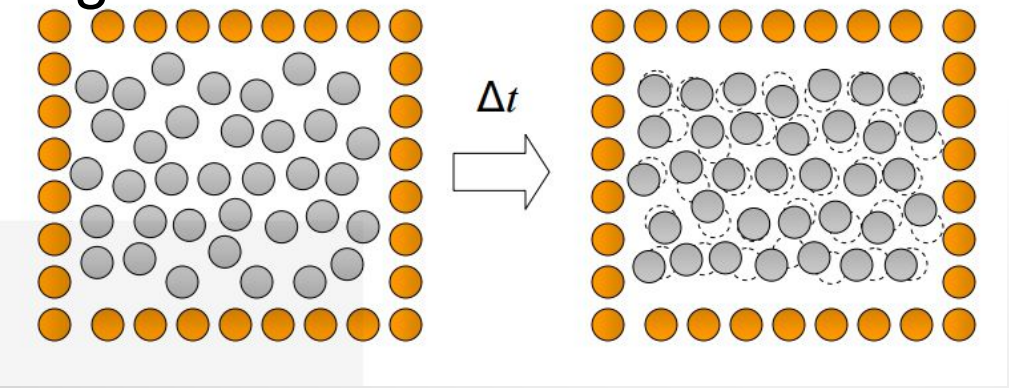
Cons:

- non physical electronic states, levels in the gap, finite size quantum effects
- the surfaces can be terminated with hydrogen atoms or cluster can be embedded into charges

Therefore:

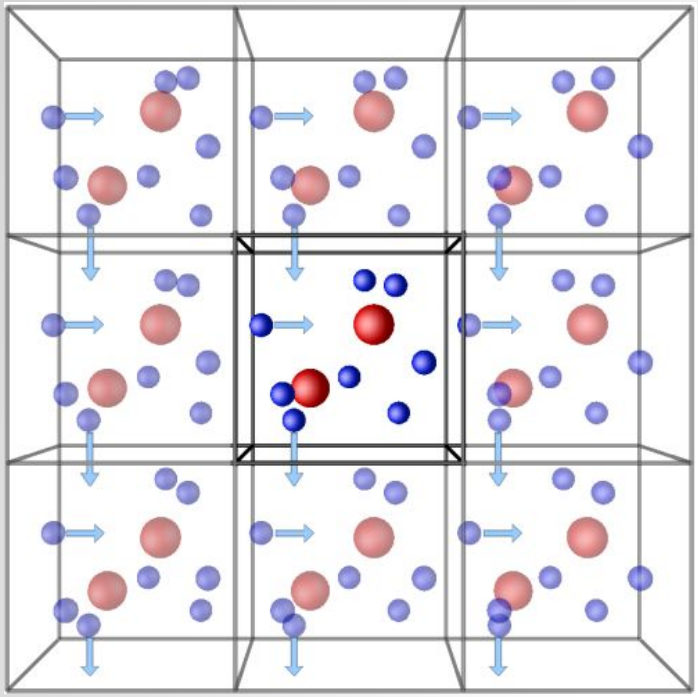
- For molecules and clusters in classical MD simulations

Rigid walls

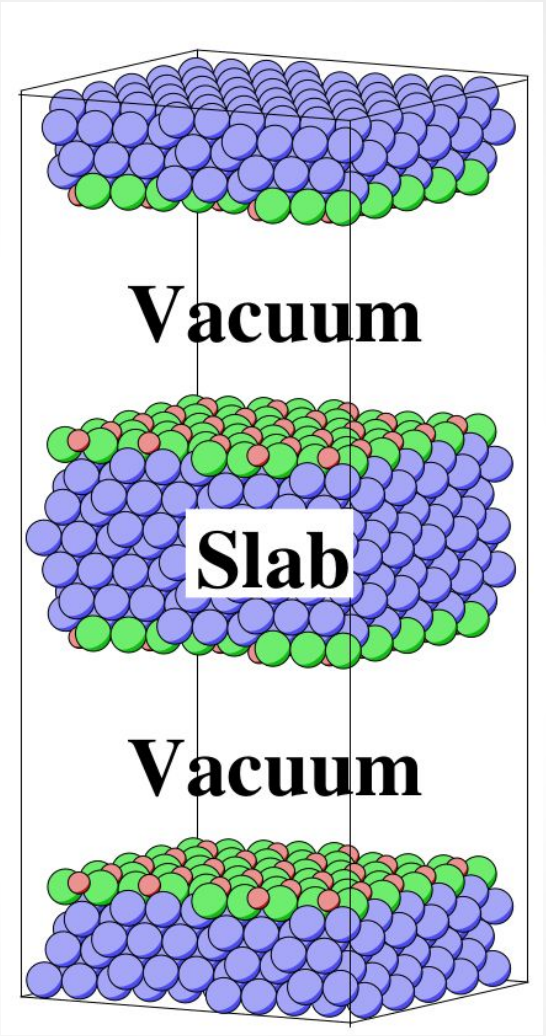


- Usually unphysical, but still better than free surface for classical MD simulations

Periodic boundary conditions - most popular



- classical MD and quantum mechanics
- for MD the size of cell should be larger than 2*Rcut
- the size of defect should be smaller than the size of cell



Limitations:

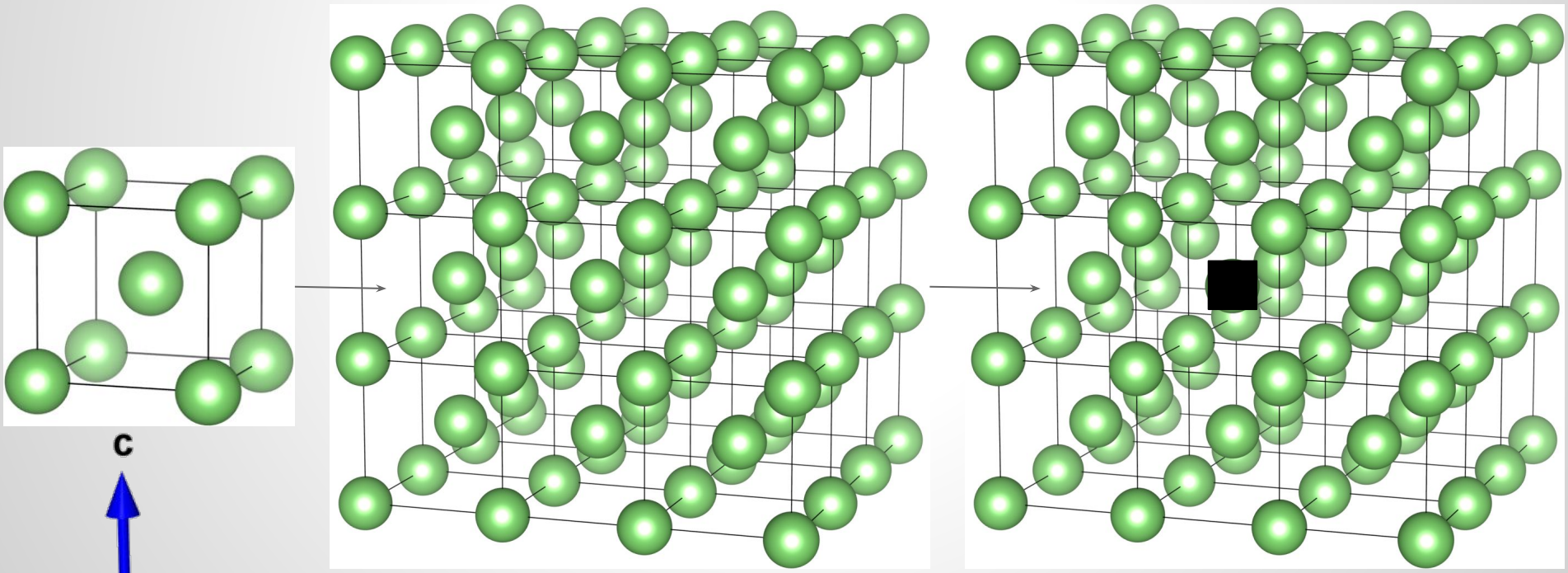
- the net electrostatic charge of the system must be zero
- interaction between defects distorts low-frequency phonon parts
- check size convergence

Mixed boundary conditions are also possible - mostly MD simulations

Point defects: vacancies, solutes

- doping
- diffusion

1. Take initial unit cell and optimize lattice constants
2. Construct large-enough supercell
3. Create defect
4. Optimize atomic positions
5. Optimize supercell sizes (to find formation volume)



Convergence with respect to cell size

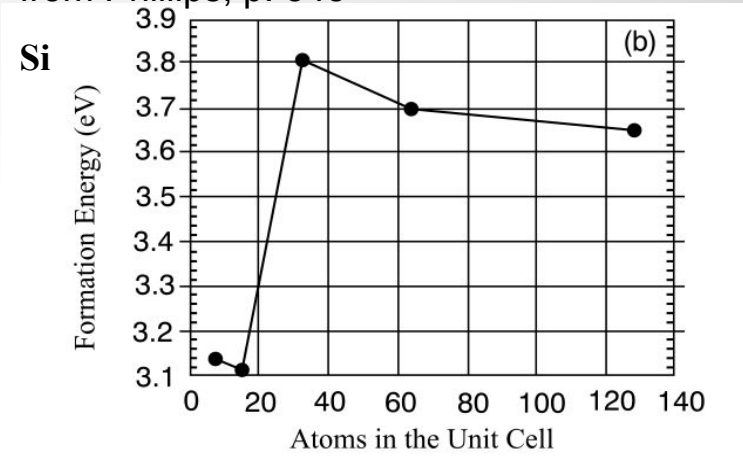
Formation energy of vacancy:

$$E^{f}_{vac} = E(N-1) - (N-1)/N\, E(N),$$

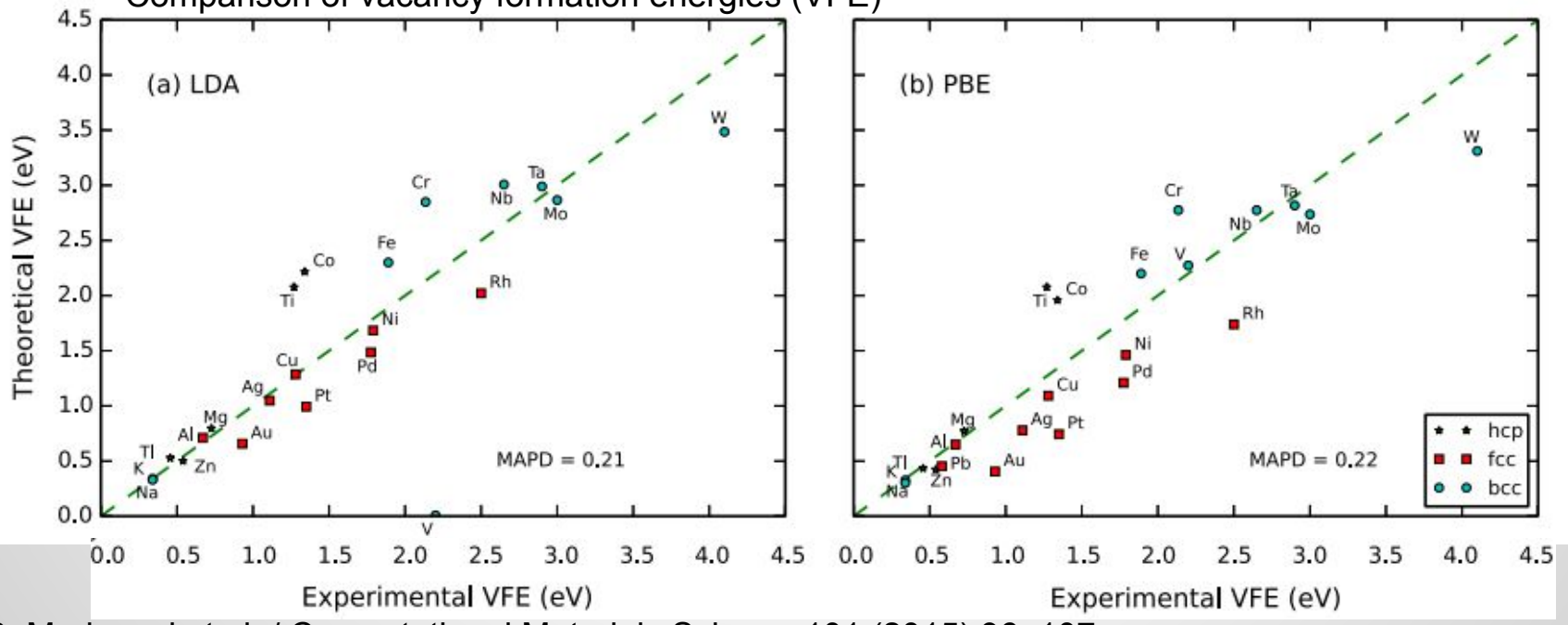
E(N) is total energy of cell with N atoms

For metals the convergence of
50 meV is achieved for 100 atoms cells

from Phillips, p. 345



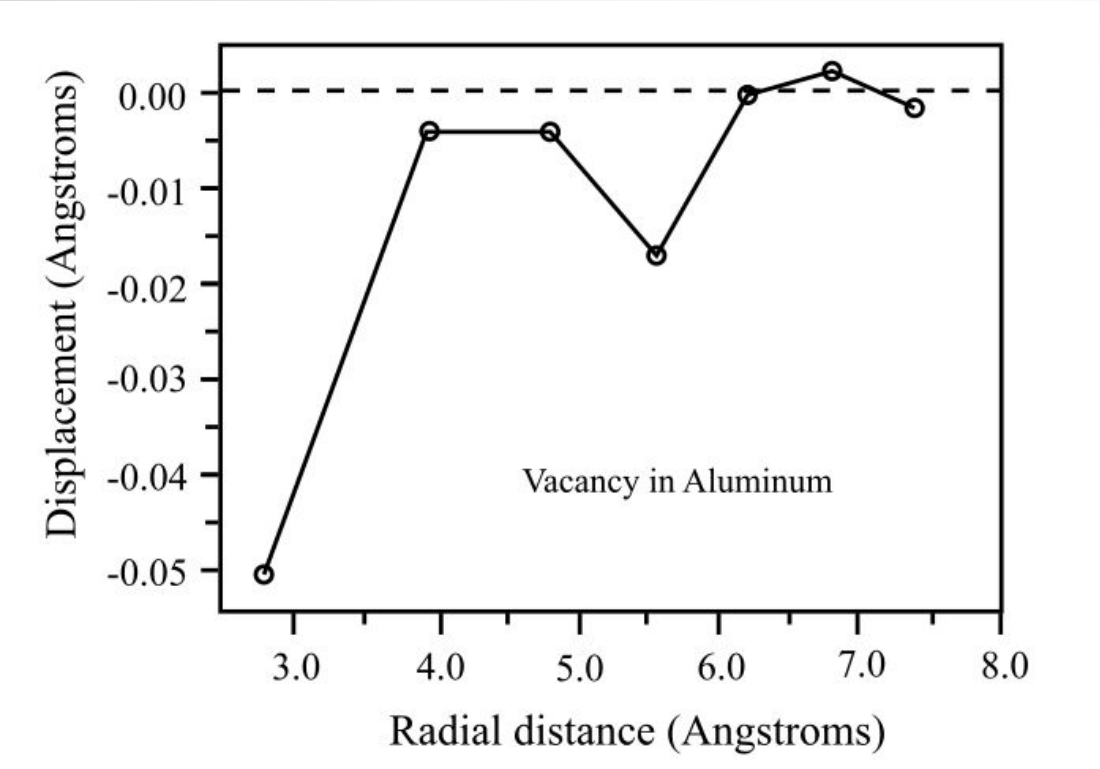
Comparison of vacancy formation energies (VFE)



B. Medasani et al. / Computational Materials Science 101 (2015) 96–107

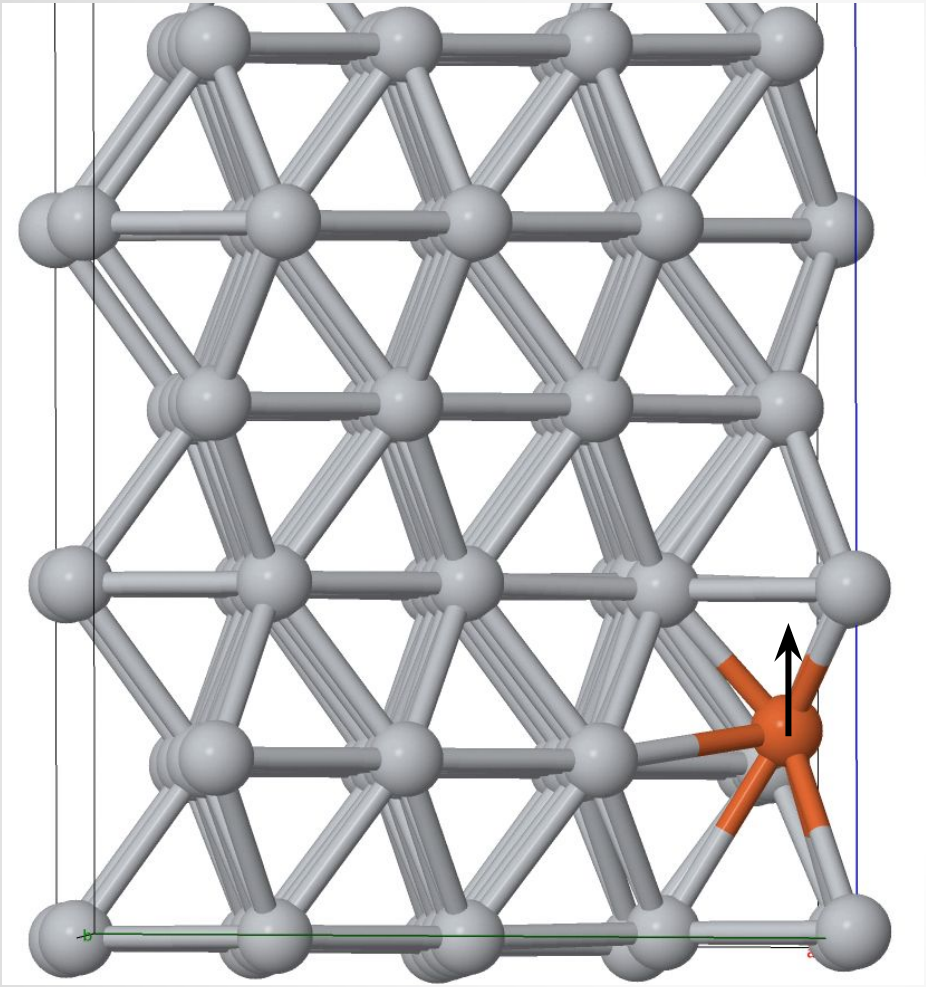
Relaxation of atomic positions

from Phillips, p. 338



- Relaxation of atomic positions around point defect is very important
- Reduce formation energy, especially for interstitials
- The final atomic structure can be different

Substitutional Fe atom in hcp Ti



The iron atom is shifted along *c* by 0.5 Å

D.A. Aksyonov, A.G. Lipnitskii / Computational Materials Science 137 (2017) 266–272

Interaction of point defects

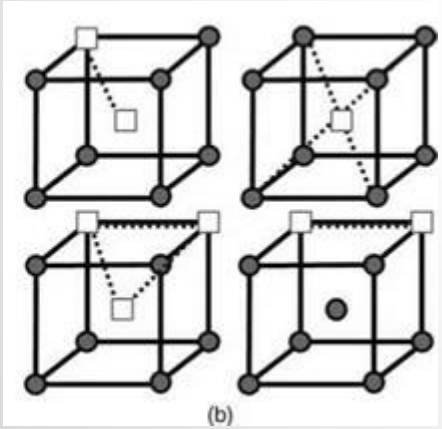
- Real material contains numerous defects
- The properties are determined not only by defects itself but also by their interaction
- The computational study of defects interaction is proved to be very fruitful in explaining materials behaviour

Binding energy of two point defects

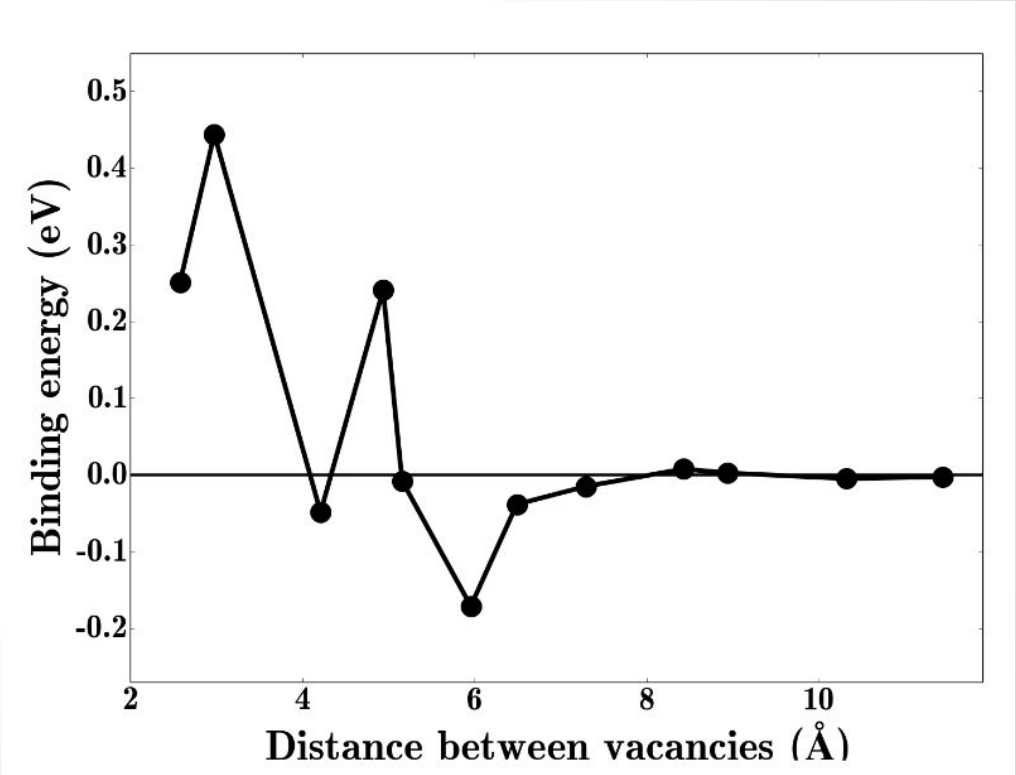
$$E_b = E^f[A] + E^f[B] - E^f[AB].$$

E^f are formation energies of separate and combined point defects

- Vacancies can combine with each other forming divacancies and triple vacancies:



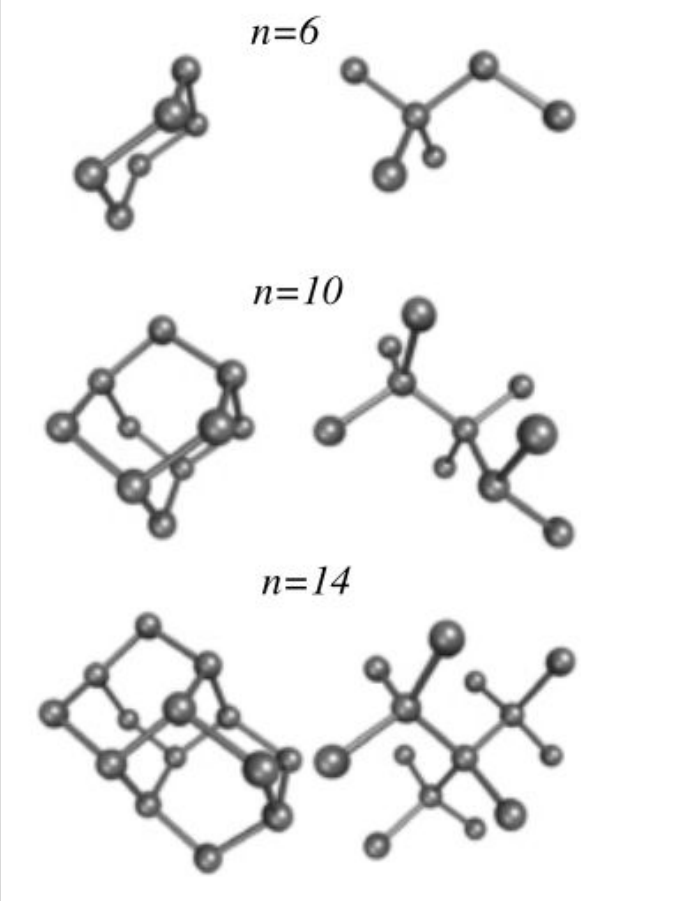
Divacancy binding energy in bcc V:



A.O. Boev et al. / Journal of Nuclear Materials 492 (2017) 14–21

Vacancy clustering, magic numbers

Shape of vacancy clusters in Si:

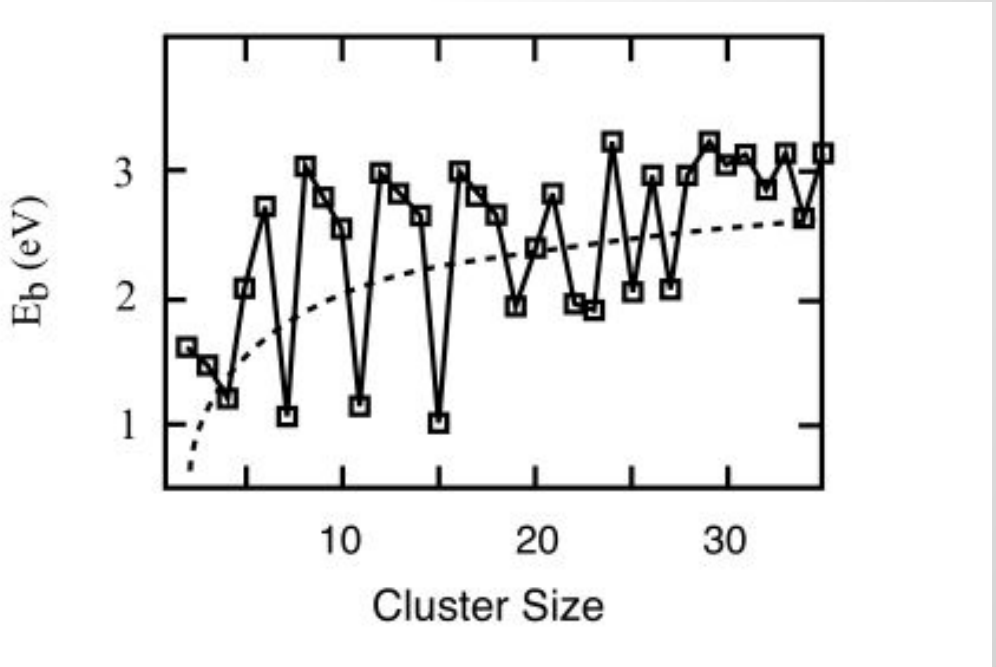


from Phillips, p357

$$\Delta E = n\epsilon^f_{vac} - \epsilon^f_{nvac}.$$

Binding energy of cluster with n vacancies

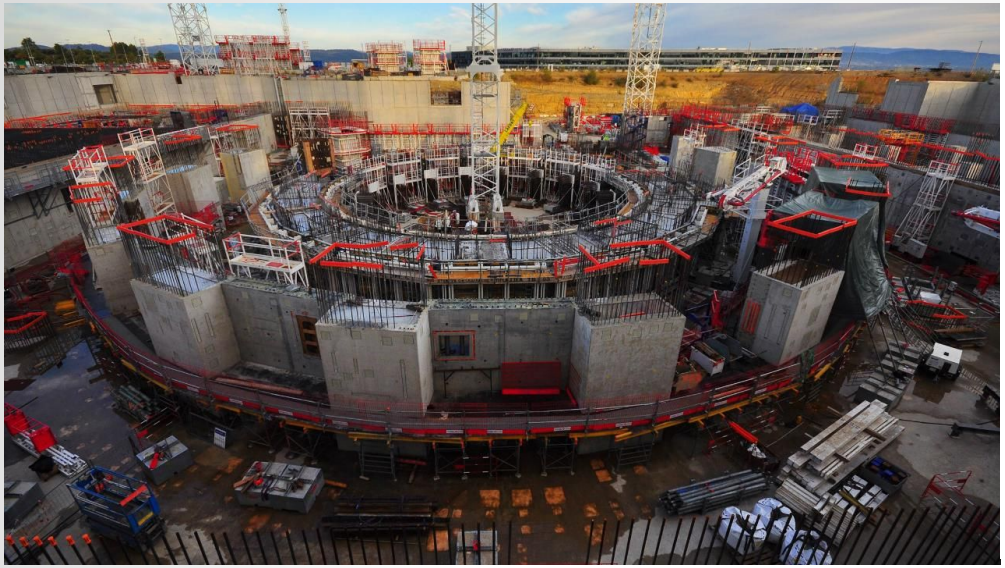
Dependence of binding energy on cluster size in Si

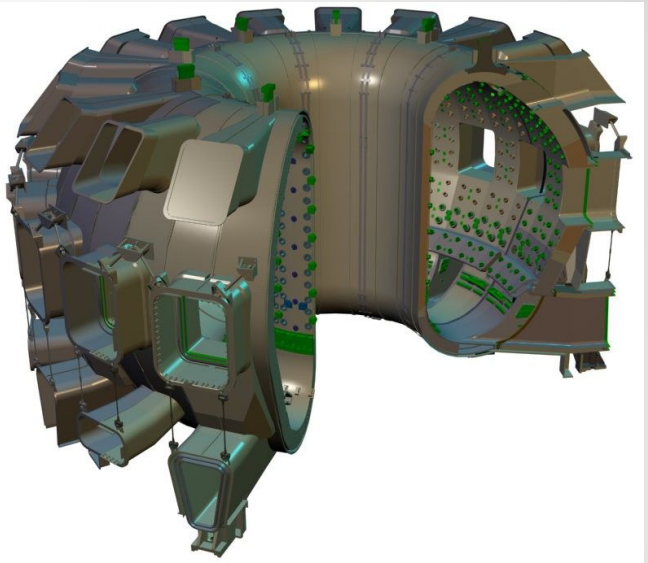


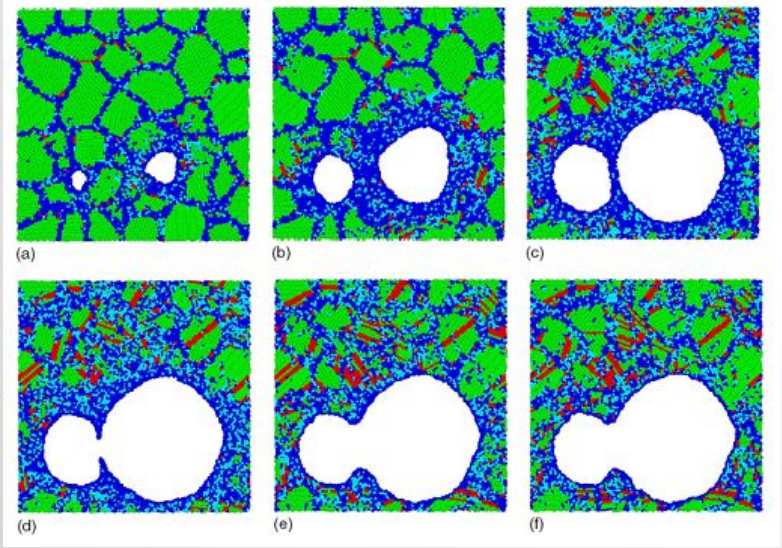
La Magna 1999, PRL 82, 8

Case study: radiation swelling and vacancies

ITER - Thermonuclear reactor



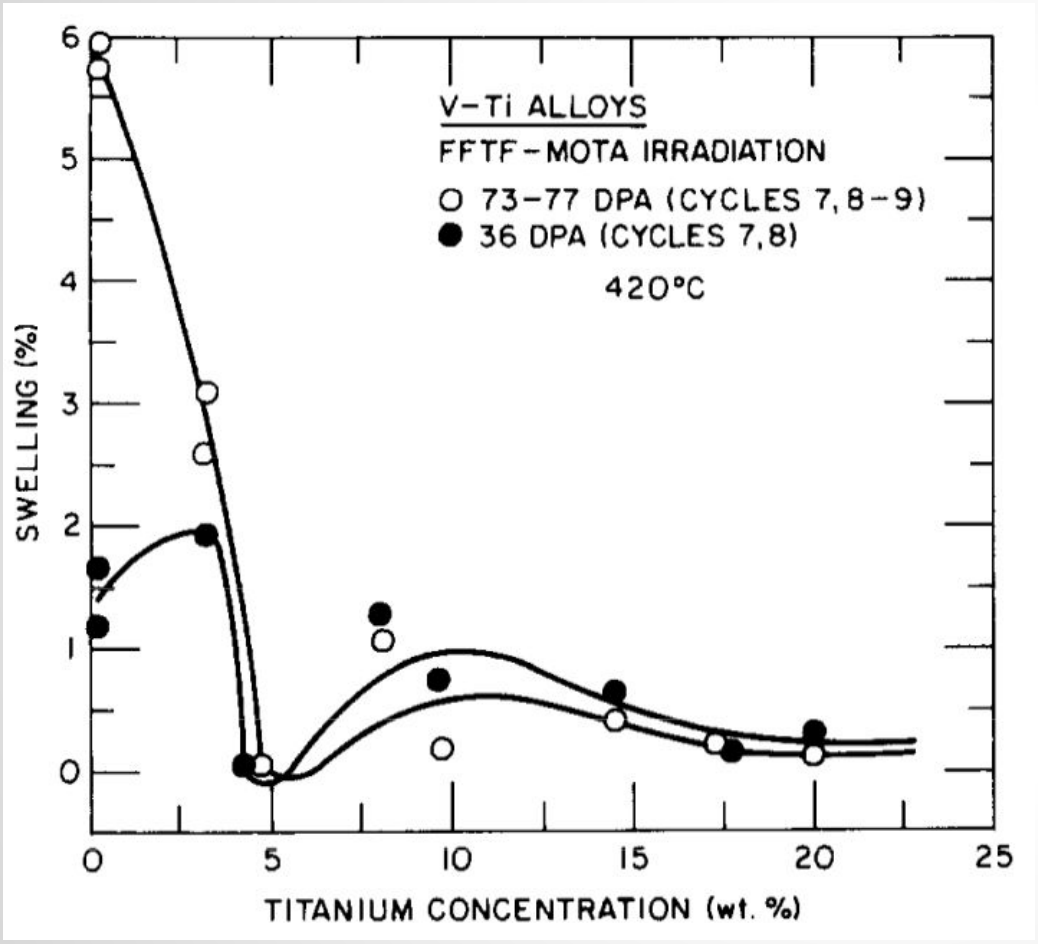




- First wall is irradiated with high intensity neutrons - common alloys degrade due to void swelling very quickly - special low-swelling alloys are developed
- The reason of swelling is agglomeration of vacancies into voids

Vanadium-Titanium alloys

The reduction of radiation swelling due to the addition of Ti to Vanadium:

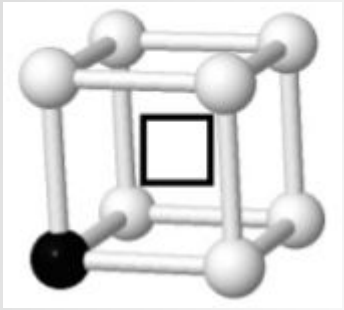


B.A. Loomis et al. / Swelling of neutron-irradiated vanadium alloys

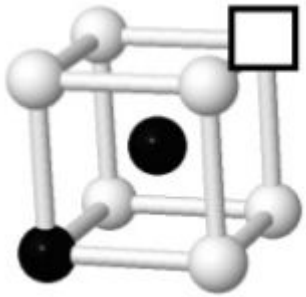
- The mechanism of radiation swelling reduction was unknown until recently

Interaction of titanium with vacancies

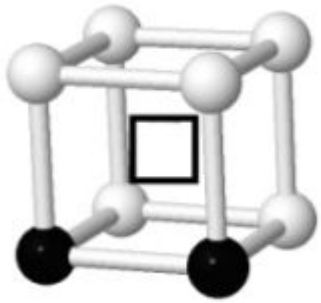
Titanium is forming solid solution in vanadium
Numerous vacancy-titanium defects are formed.



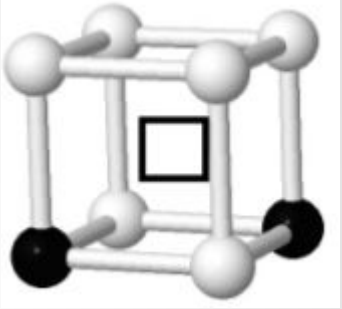
0.6 eV



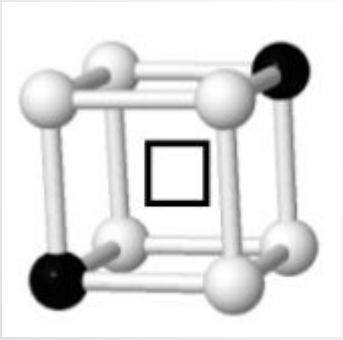
not stable



0.6 eV



0.8 eV



1.2 eV

$$D_V^{eff} = \frac{D_V}{1 + \tau_V \kappa_V C_t}$$

$$\tau_V = \frac{b^2 exp(\frac{(E_V^b + E_V^m)}{kT})}{D_{0V}}$$

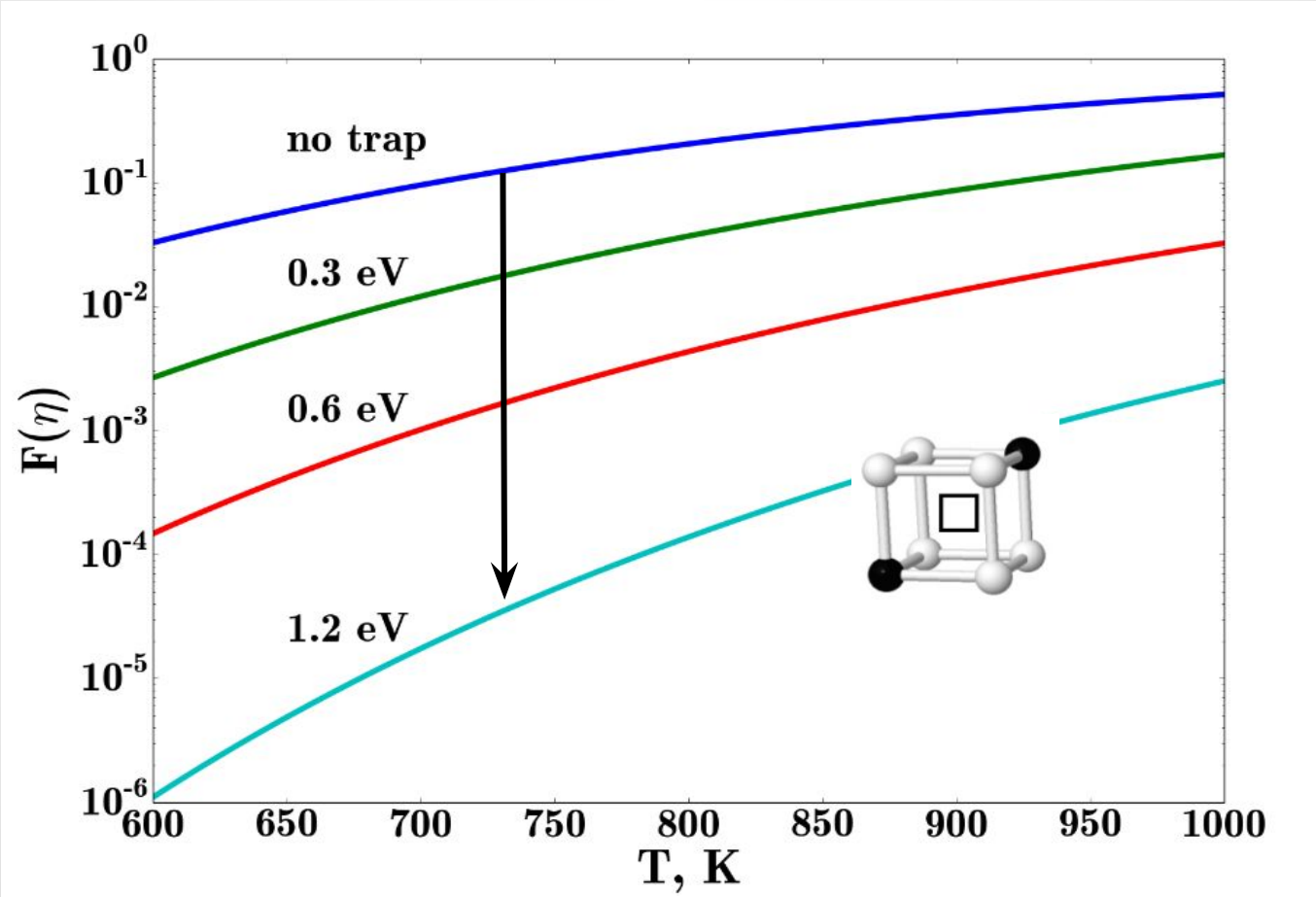
Effective diffusion coefficient,
E^b_V is binding energy
E^m_V is migration energy
C_t is concentration of solute atoms
k_V is capture coefficient
b is Burgers vector

A.O. Boev et al. / Journal of Nuclear Materials 492 (2017) 14–21

Growth rate of void depending of binding

$$G - RC_I C_V - S_V D_V C_V = 0$$
$$G - RC_I C_V - S_I D_I C_I = 0,$$

C are concentrations of vacancies and interstitials, D are diffusion coeficients,
R is recombination rate, S are sink strengths for vacancies are interstitials, G is generate rate of defects



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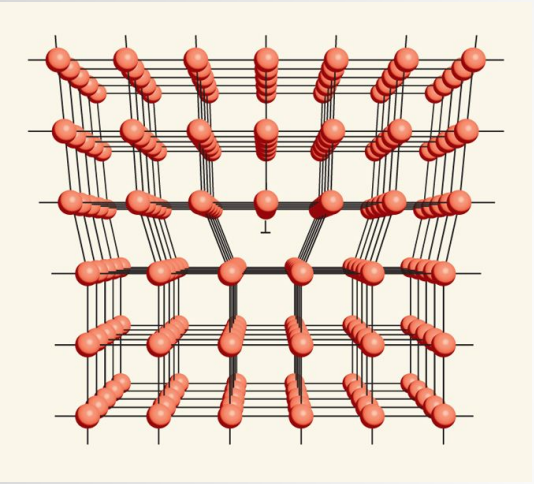
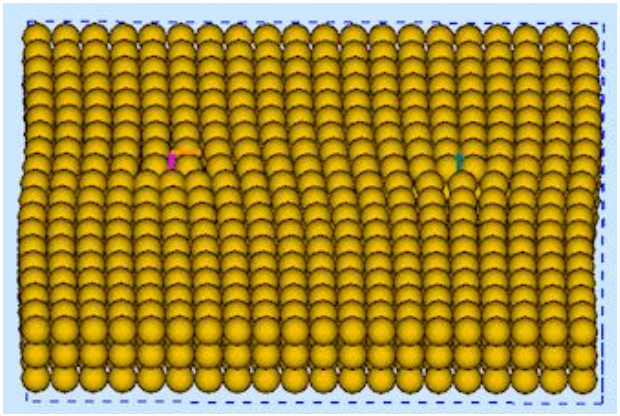
Dislocations - deformation, mechanical properties

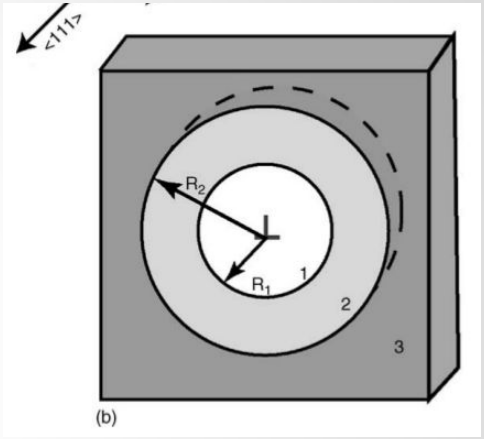
Not compatible with PBC without introducing a large artificial stress field due to broken translation symmetry

Solutions:
Dislocation dipoles - additional interactions, also for fixed boundaries Peierls stress is wrong

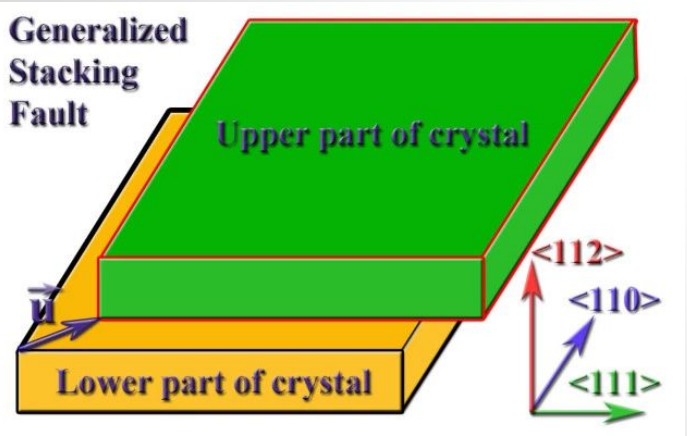
Flexible boundary conditions
(Lattice Green functions)

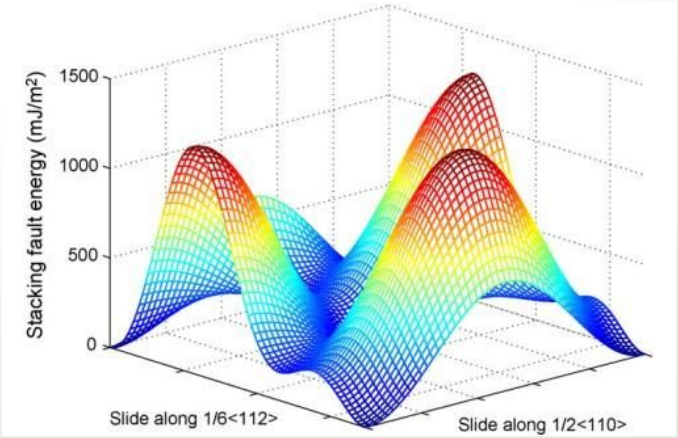






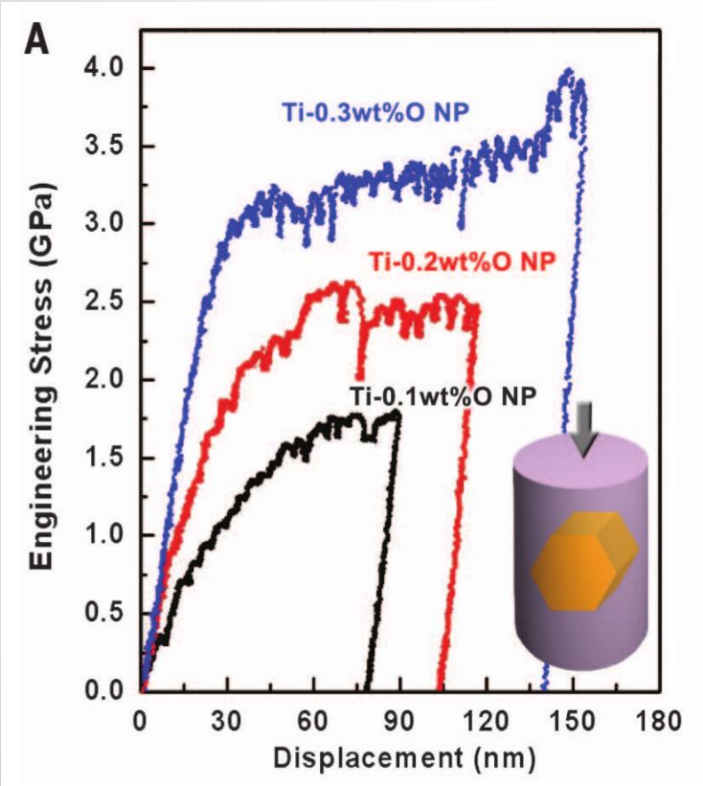
Woodward2005



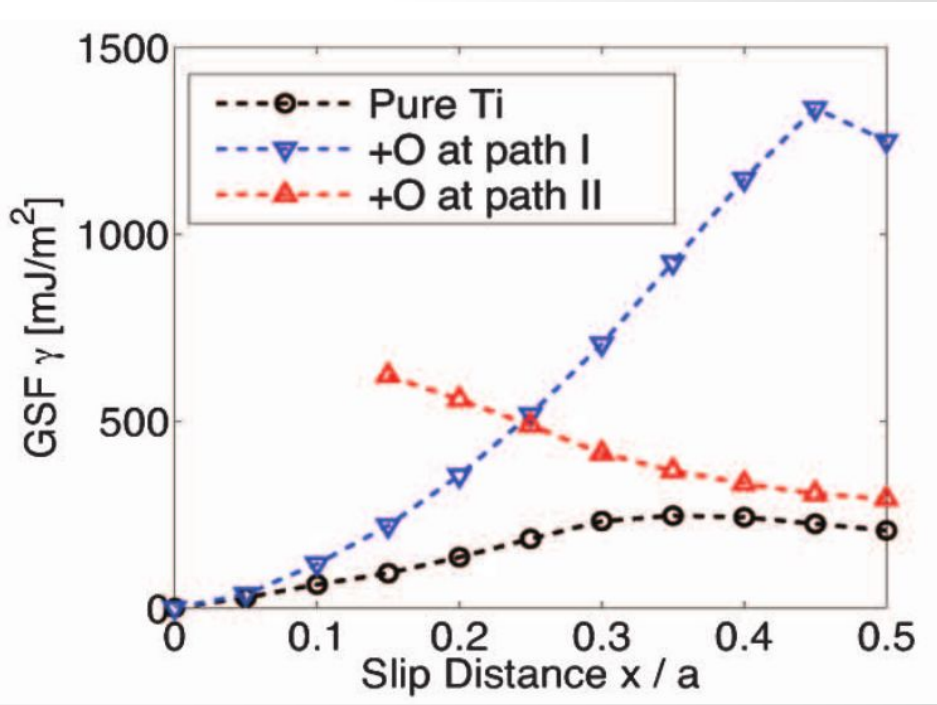


Case study: Influence of oxygen on Ti strength

- oxygen increased Ti strength
- solid solution strengthening is due to elastic interaction with dislocations
- problem - according to elasticity theory screw dislocations does not interact with solute atoms



- in 2015 using DFT it was explained:
- the barrier for oxygen to shuffle (hop) from the original site in path I to the new site in path II varies from between 0.42 to 0.95 eV
- oxygen interstitials combine resulting in a strong pinning effect on screw dislocations



Yu, Qian, et al. "Origin of dramatic oxygen solute strengthening effect in titanium." *Science* 347.6222 (2015): 635-639.

2-D defects: surfaces and interfaces

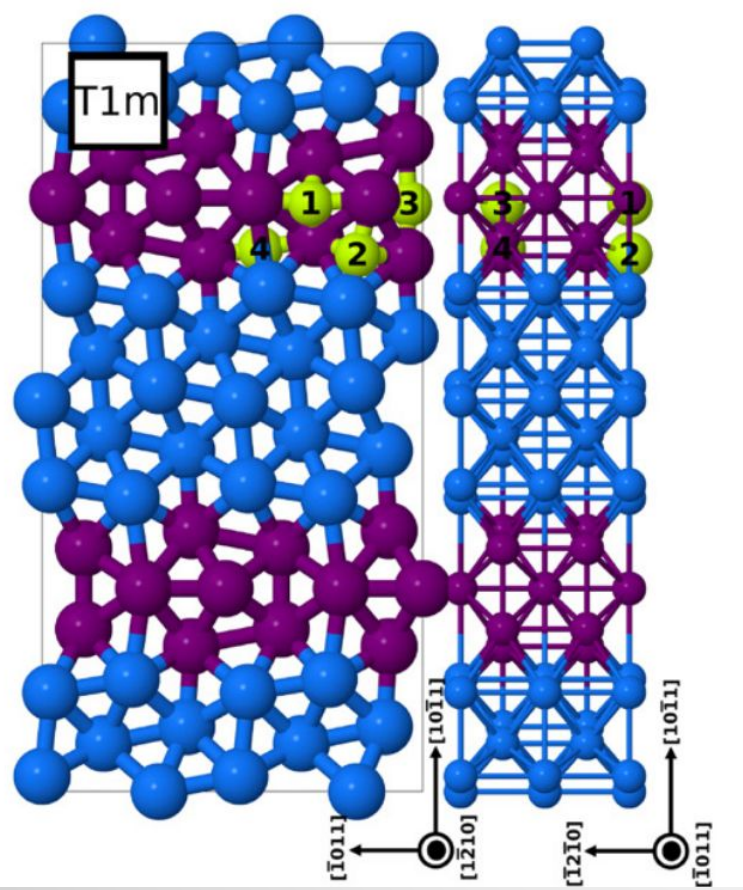
God made solids, but surfaces were the work of the Devil [W. Pauli]

$$\gamma_{GB} = \frac{E_N(GB) - E_N(bulk)}{2A}.$$

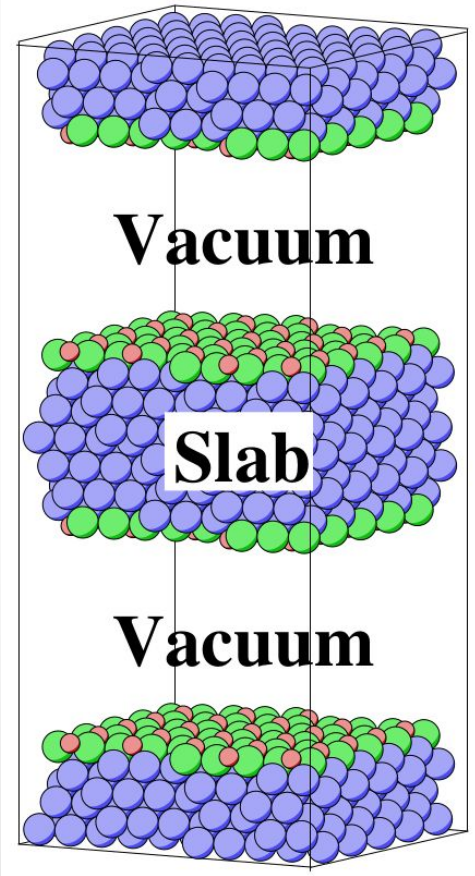
total energies

Area

$$\gamma_{100} = \frac{E_N(surface) - E_N(bulk)}{2A},$$

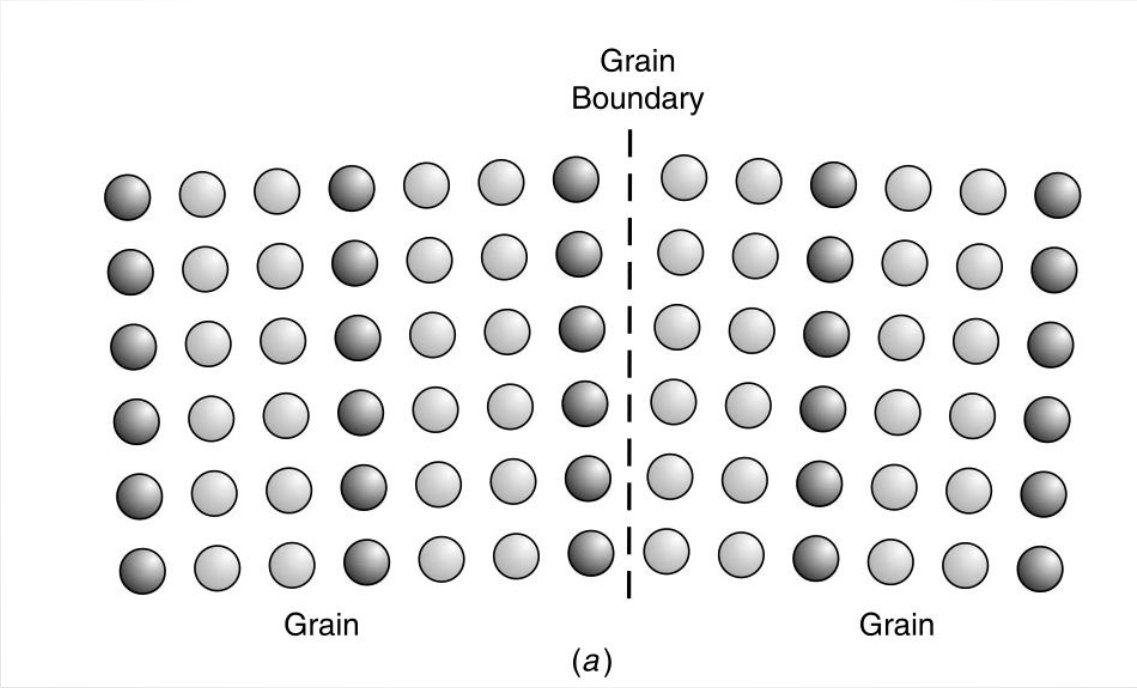


- Formation energy γ is the main characteristics of interfaces [J/m^2]
-
- Typical values lie within **0.5-2.0** J/m^2

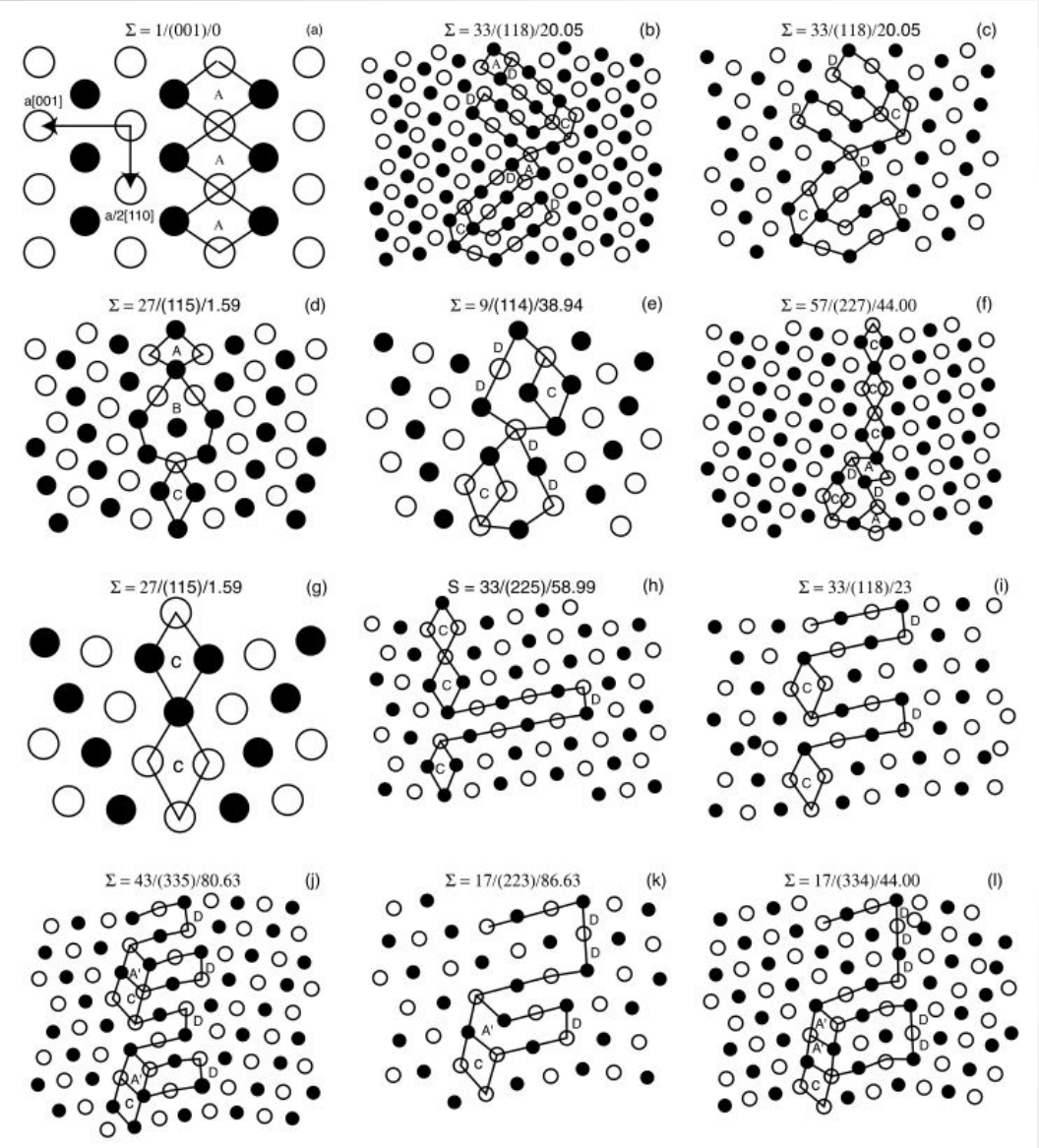


Grain boundaries

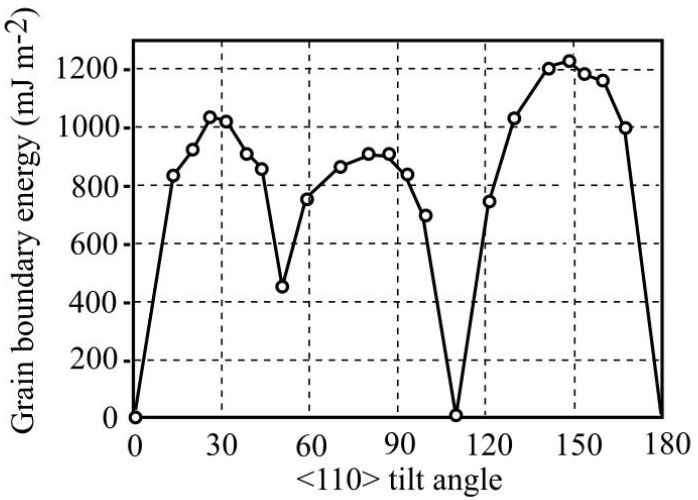
- Interaction with dislocations
- Fracture
- Diffusion
- Segregation



Grain boundaries in Ni



Dependence of energy on tilt energy



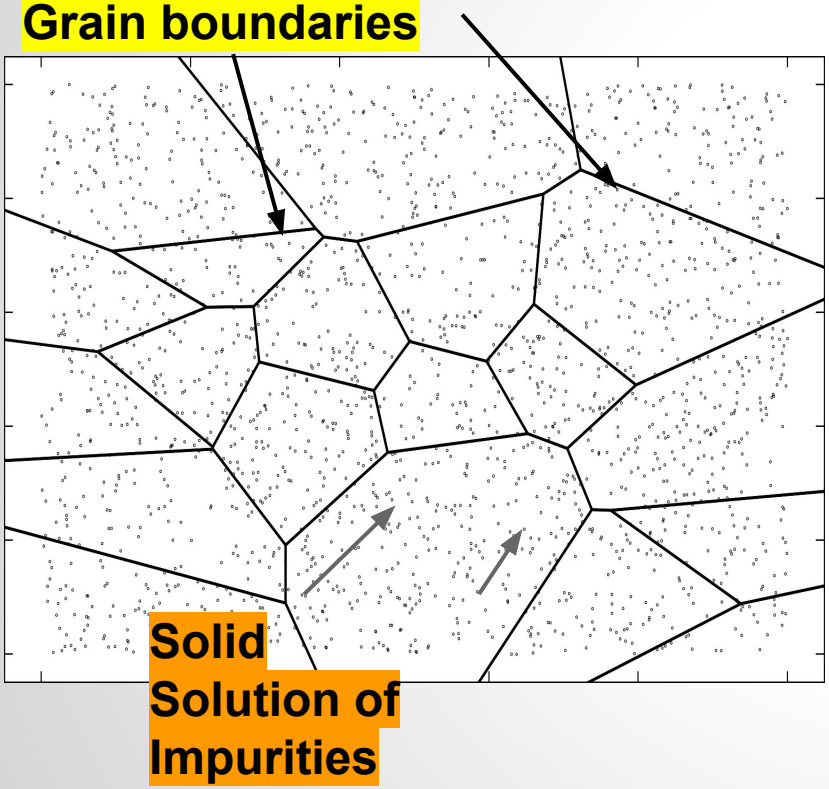
Understanding of structure is important for

- mechanical characteristics
- segregation and fracture
- paths for diffusion

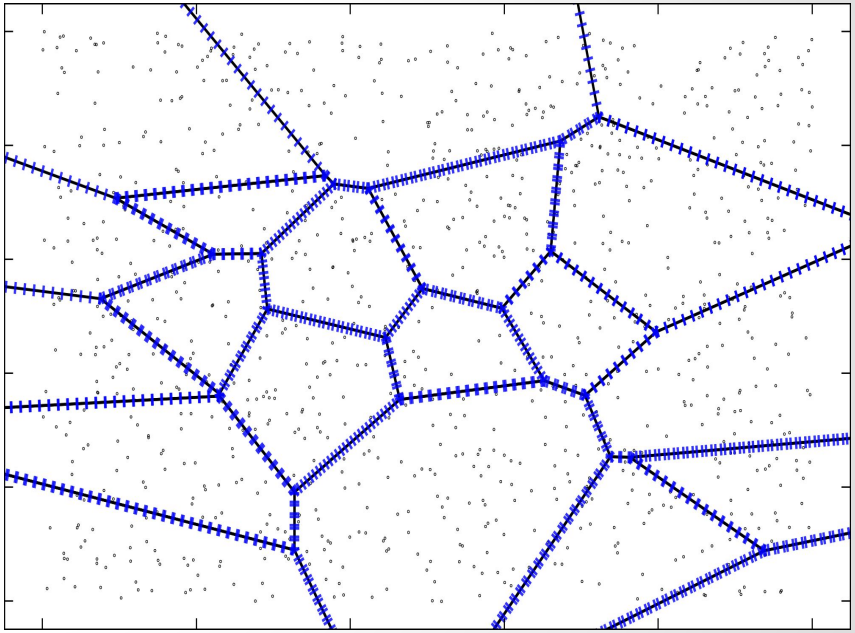
Phillips, p 498

Grain boundary segregation

Clean boundaries and solid solution:

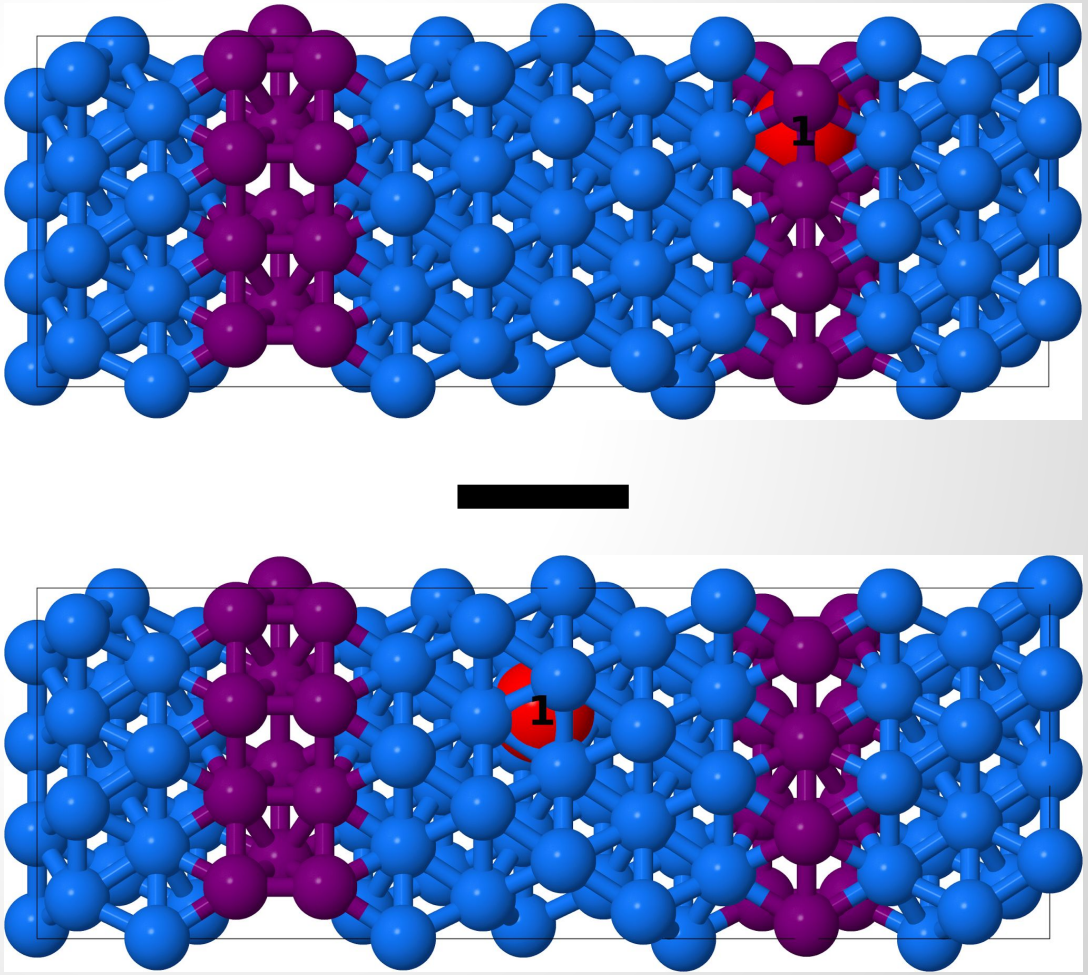


Solid solution and grain boundaries enriched with impurities:



Calculation of segregation energy

$$E_{seg} =$$



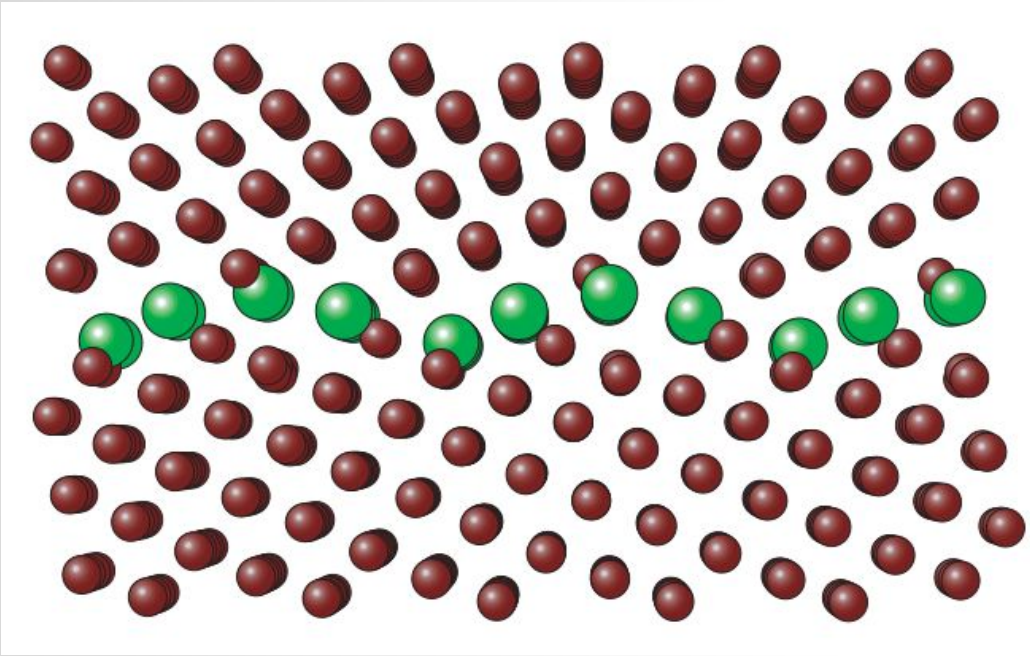
- Negative values mean attractive interaction of impurity with grain boundary

Influence of grain boundary segregation

- Grain boundary cohesion
  - $dE = E_{seg}(GB) - E_{seg}(surface)$ - the strengthening energy
    - $dE > 0$ - cohesion enhancer (C, B in Fe)
    - $dE < 0$ - embrittlers (P, S in Fe)
- Grain boundary stabilization
  - Segregation reduces grain boundary energy improving the thermal stability of material
  - Segregation reduces grain boundary mobility

Case study: embrittlement of Cu with Bi

The copper embrittled just by 0.01 % of bismuth



Schweinfest, R., Paxton, A. T., & Finnis, M. W. (2004) *Nature*, *432*(7020), 1008-1011.

Problem:

- How can minute traces of Bi in Cu cause ductile metal to fail in a brittle manner?
- For one hundred years the problem was not solved!

Three hypotheses:

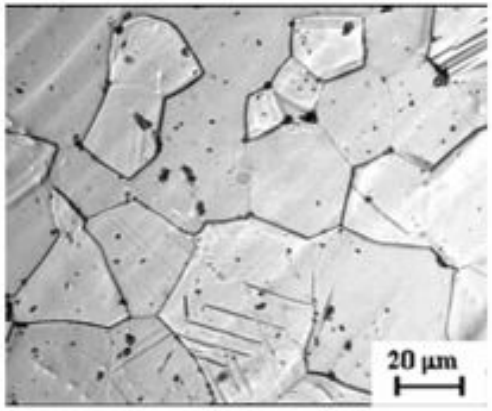
- an electronic effect to strengthening of Cu bonds
- electronic effect or weakening of Cu bonds across the boundary
- simple atomic size effect

DFT showed that this just an atomic size effect

Case study: Stability of Nanostructured metals

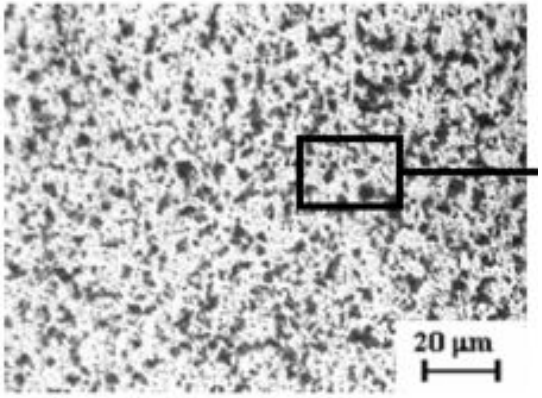
Commercially pure Ti in conventional state
Grain size: 25000 nm

The same material after severe plastic deformation; Grain size: 150 nm



a)

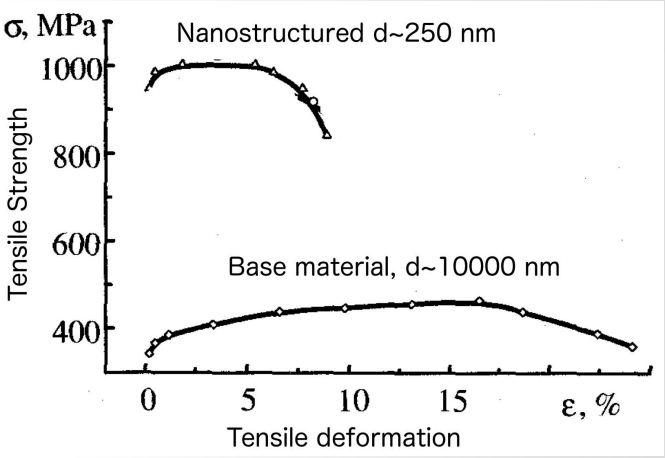
Optical microscopy



b)

Transmission electron microscopy

Increase of strength:



Problem:
At increased temperature the grains are growing and the mechanical characteristics reduces
Solution:
Grain boundary segregation

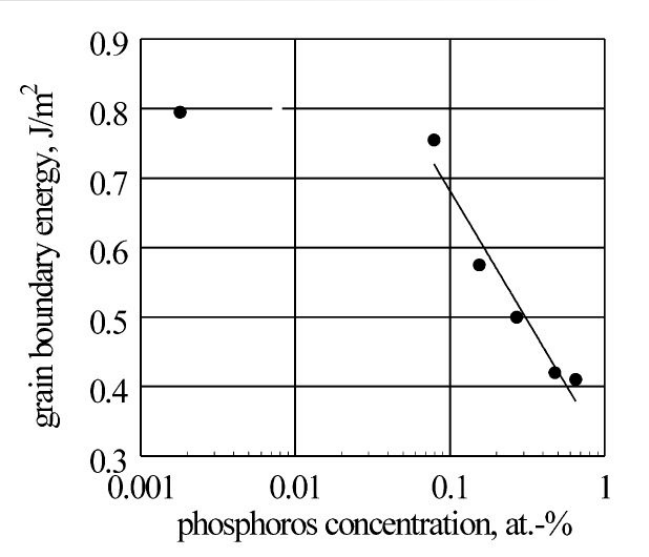
R. Valiev et al., Materials Science Forum, V. 584-586 (2008) pp. 49-54

Stabilization of grain boundary structure

$$\gamma = \gamma_0 + \Gamma E_{seg}$$

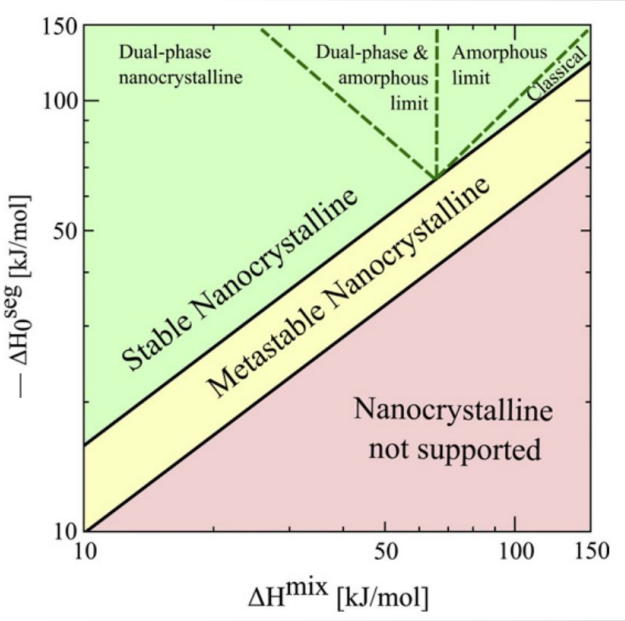
where Γ is excess of impurities at boundary,

example of grain boundary energy is reduced due to P segregation in Fe-P alloys:



Kirchheim2002

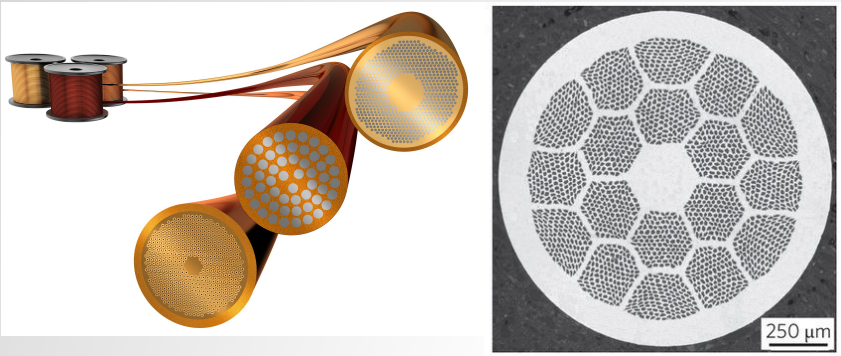
Computational model, which allows to predict stability of nanocrystalline materials based on segregation energy and enthalpy of mixing



Murdoch2013

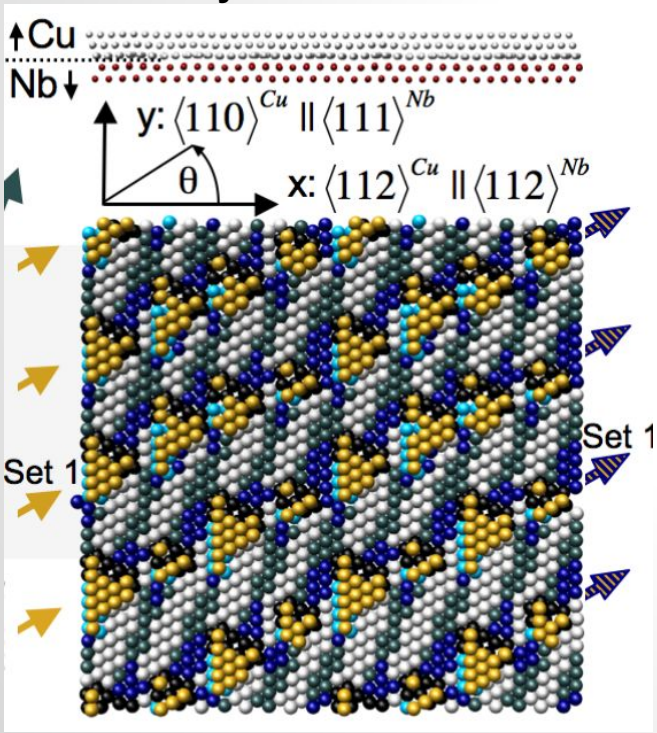
- Computational screening of segregating elements (DFT methods)
- Mechanisms of grain boundary migration (Molecular dynamics methods)

Case study: radiation resistant Cu-Nb nanocomposite

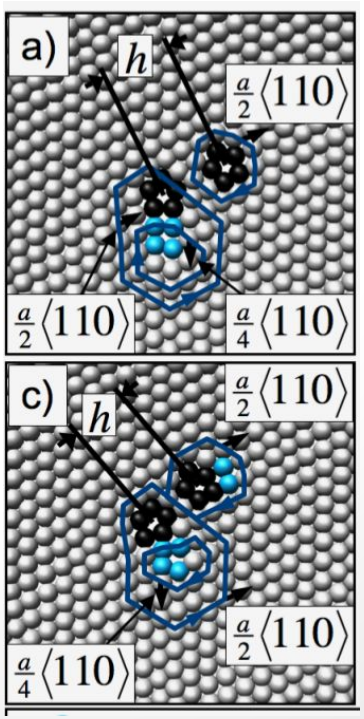


- High-strength superconductive wires
- High strength room temperature low-resistance wires for creating very strong magnetic fields

Molecular dynamics and Monte Carlo study of interface defects:

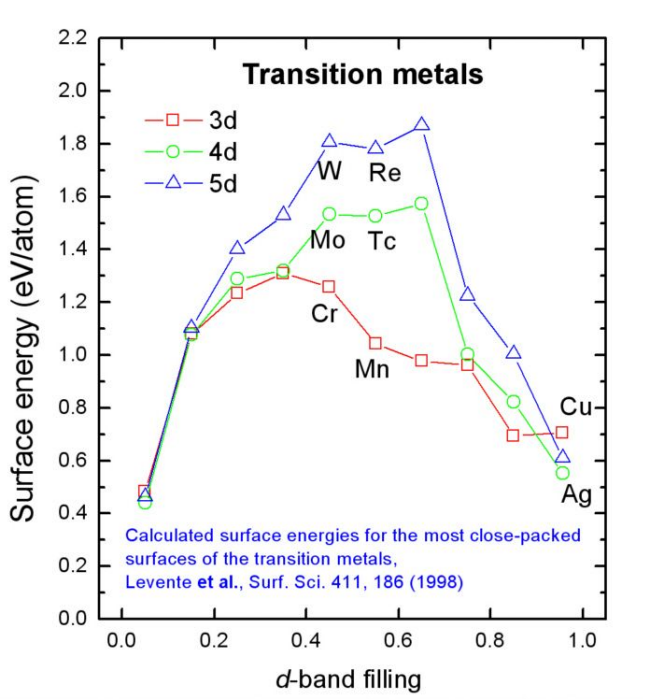


M. Demkowicz, PRL 100, 136102 (2008)



- The interface serves as a sink of point defects
- Vacancies and interstitials produce interfaces dislocations with different signs
- Interfaces dislocations effectively annihilate

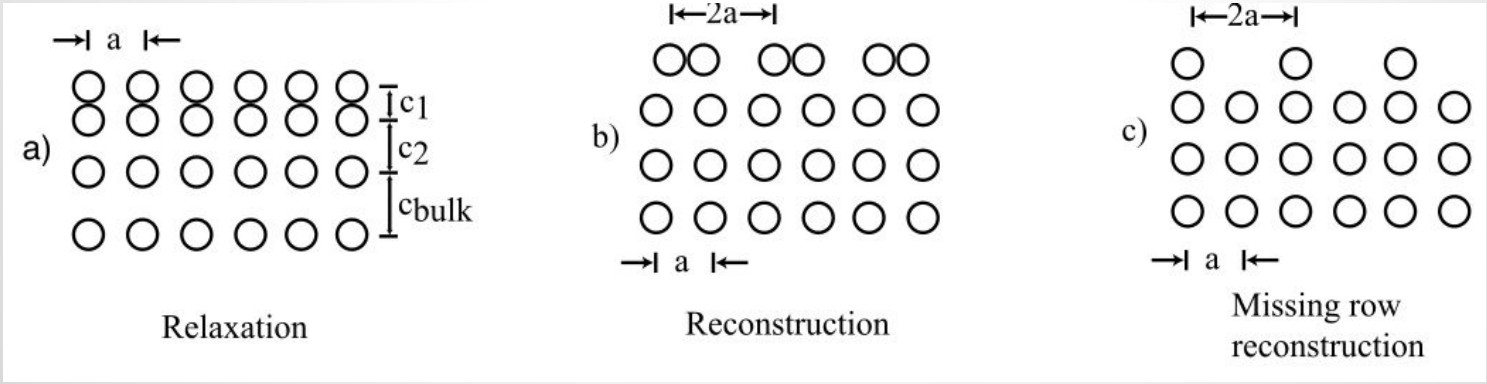
Surfaces



- Catalysis, chemical reactions, crystal growth, corrosion, etc.
- Surface energies is a point of departure for more elaborate analyses involving reconstructions, surface steps and islands.
- Characteristic rise until the d-band is half-filled and then decline as the number of d-electrons is further increased.

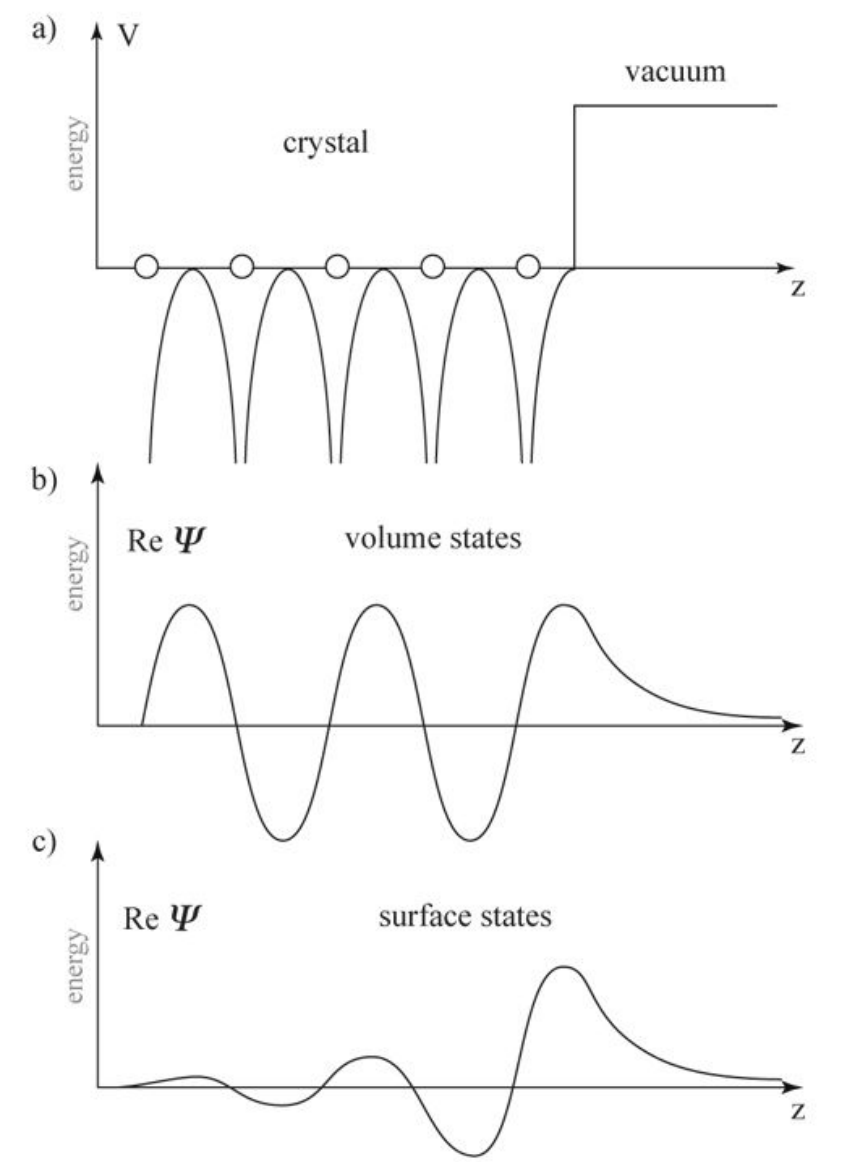
also Phillips, p 452

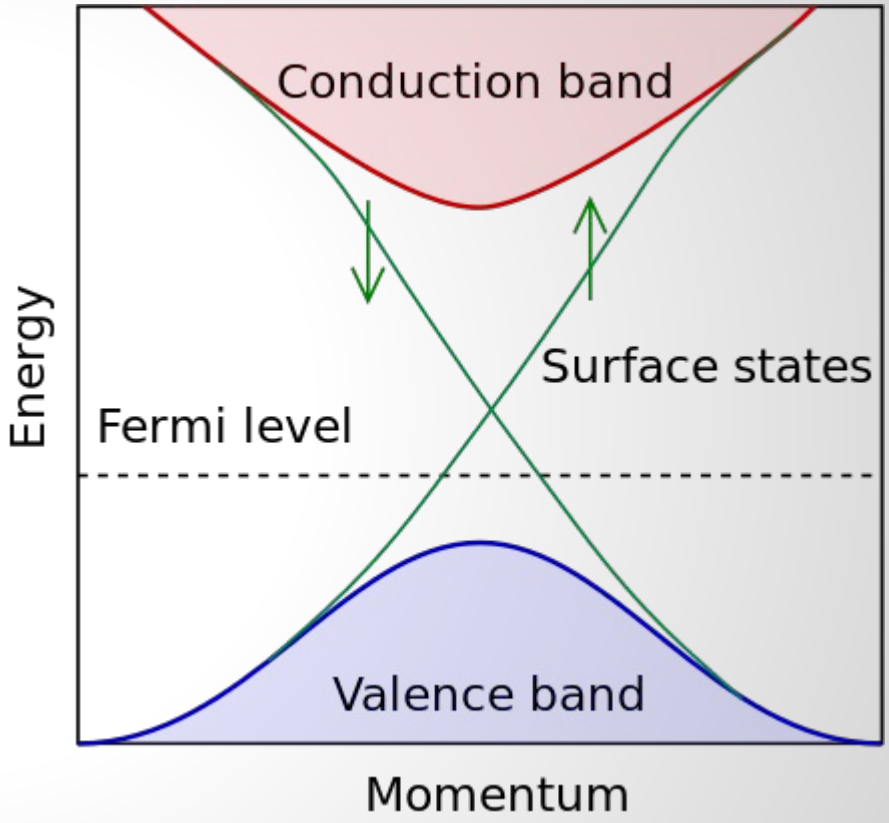
Types of rearrangements at surfaces:



from Phillips, p 454

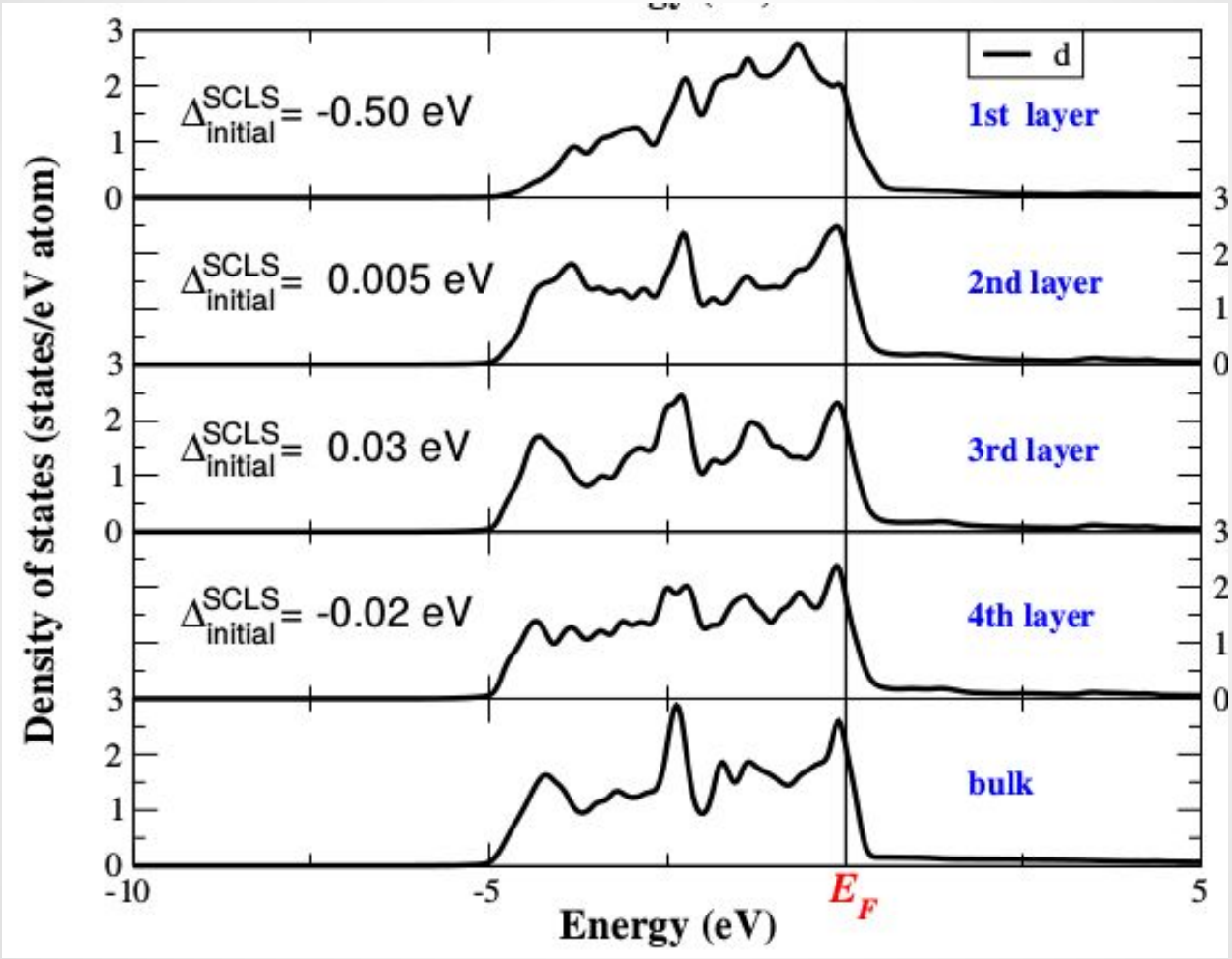
Surface states





Local density of states at surface (LDOS)

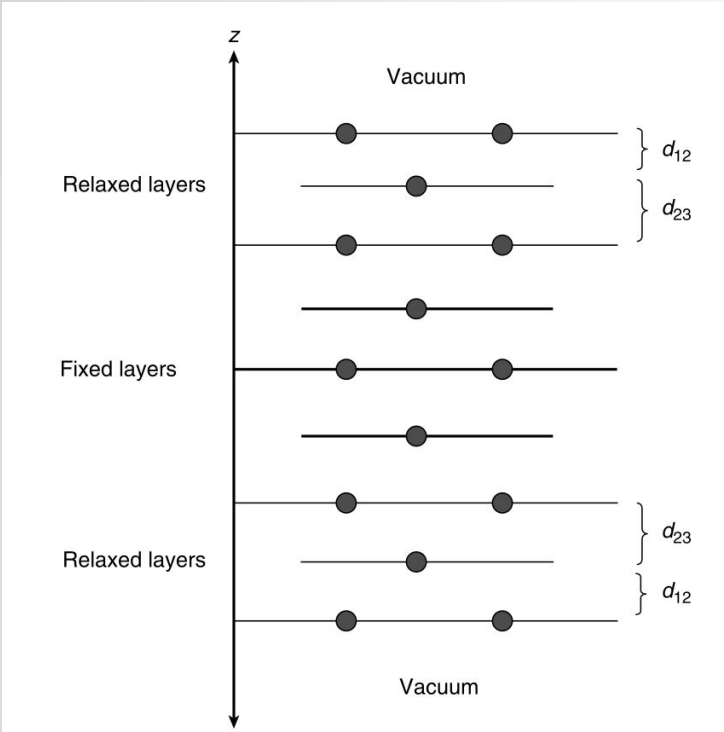
Surface core-level shifts (SCLS) - can be measured experimentally



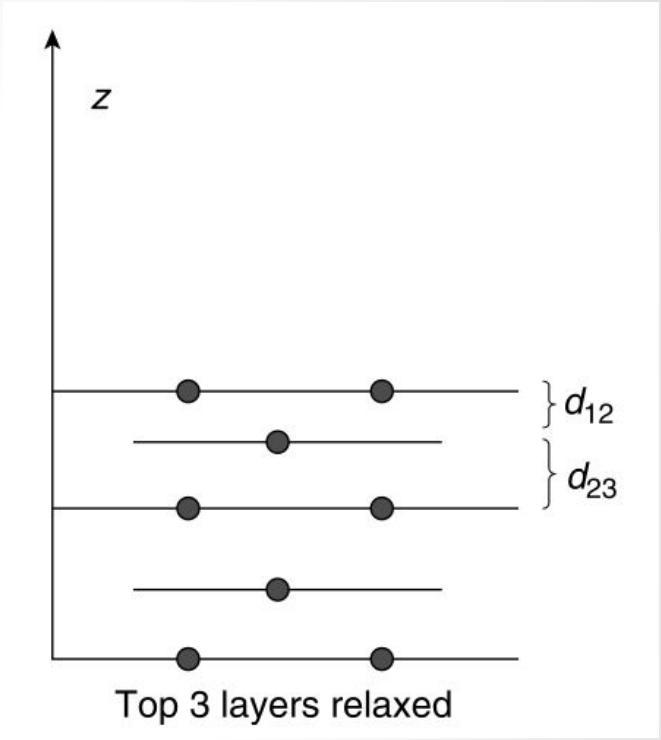
Zhang2008 dissertation

Symmetric and asymmetric slabs

Symmetric



Asymmetric



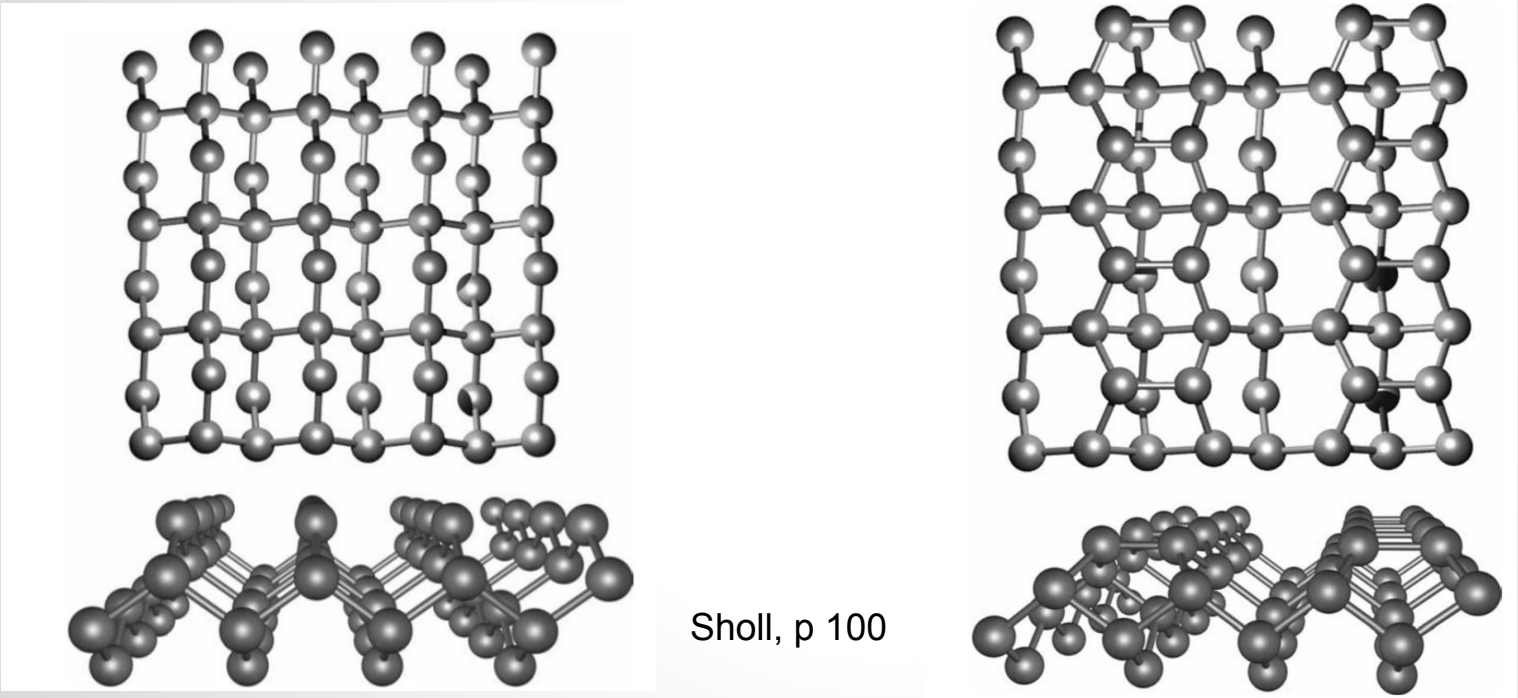
Sholl,

- For asymmetric slab a dipole moment could arise leading to spurious electrostatic interaction
  - use dipole correction of potential in vacuum (**IDIPOL**, **LDIPOL** in VASP)
  - use symmetric slab

Si surface reconstruction

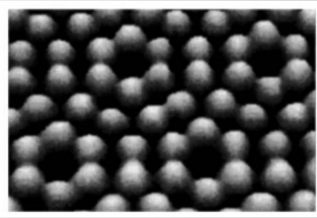
Unreconstructed Si (001)

Dimer reconstructed Si (001) by 0.7 eV/surface atom lower energy!!



Sholl, p 100

Si (111) 7x7



DFT assisted

- Problem!: DFT does not automatically find reconstructed structure, it sticks in local minima
  - Use global energy optimization algorithms: genetic, Monte-Carlo, etc.

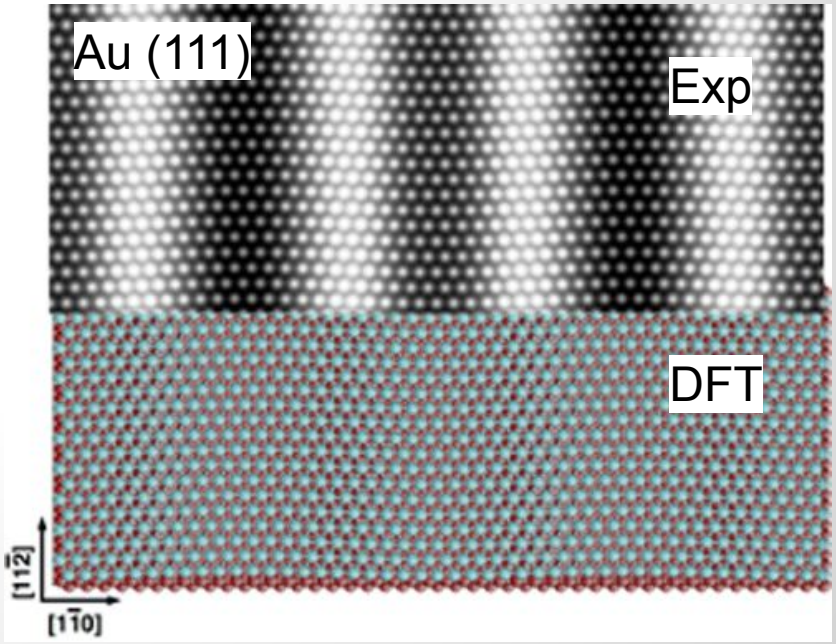
Surface reconstruction

Problem:

- The supercell heavily constraints possible surface reconstructions - large supercells are needed

- Therefore use classical methods
- Still DFT could be used

Torres et al. predicted the structure of (111) surface of gold using DFT in agreement to experiment



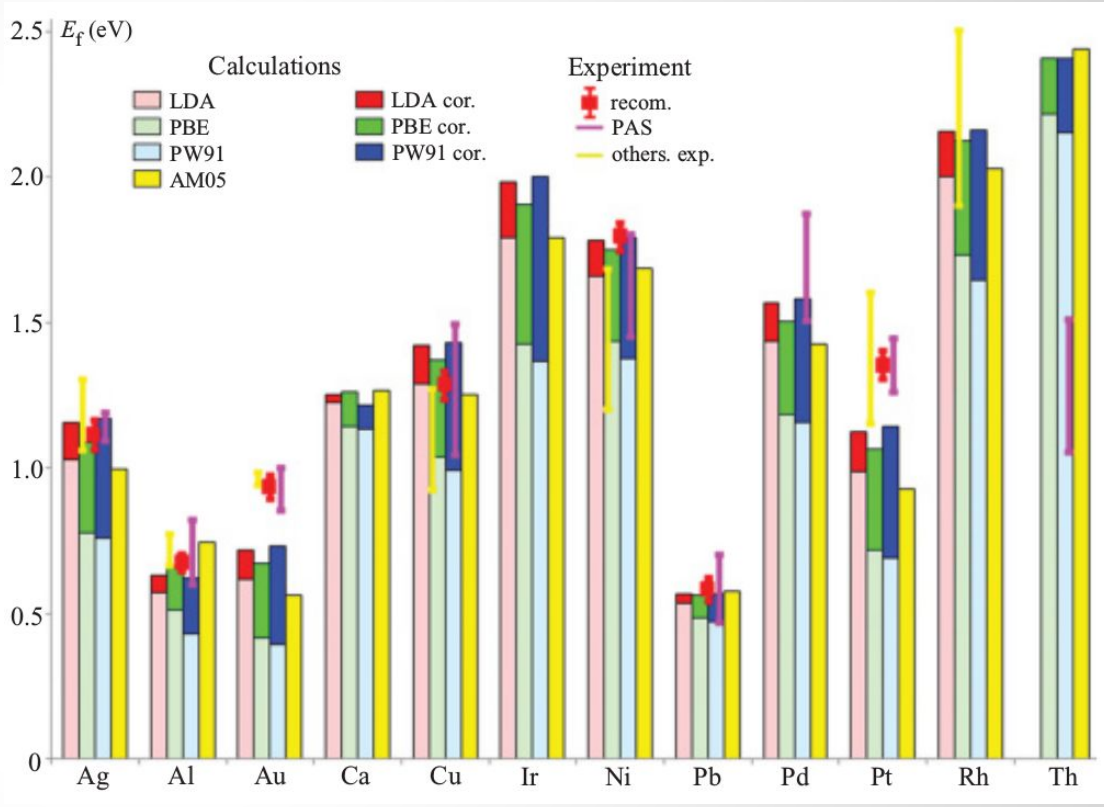
Torres, E, and DiLabio G., *The Journal of Physical Chemistry C* 118.29 (2014): 15624-15629.

Surfaces in DFT!

- **LDA** largely overestimates exchange energy of a free metal surface, but underestimates by approximately the same magnitude the correlation

- **GGA (PBE)** the exchange surface energy is underestimated but the correlation surface energy is only slightly overestimated, resulting in too small vacancy formation energies

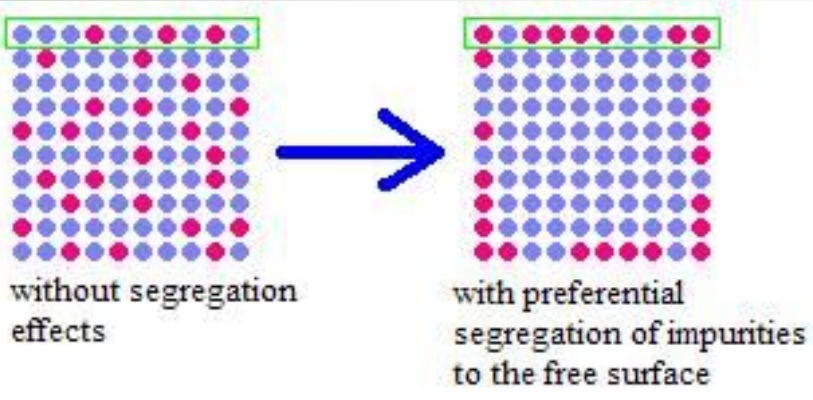
Vacancy could be considered as a defect with surface. Vacancy formation energies:

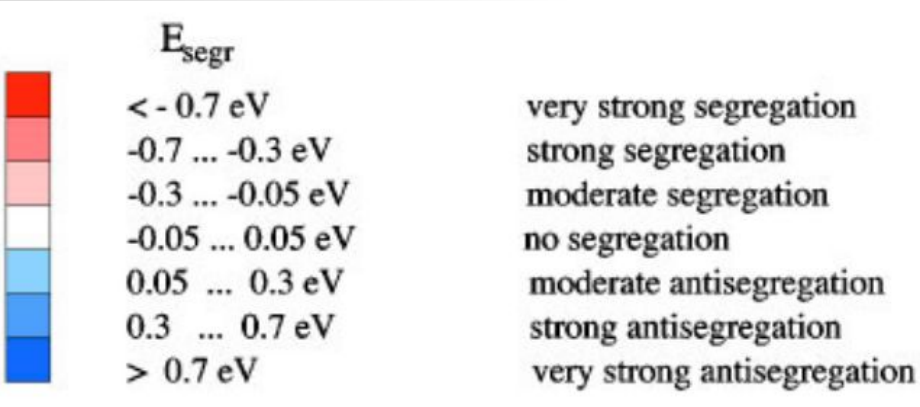


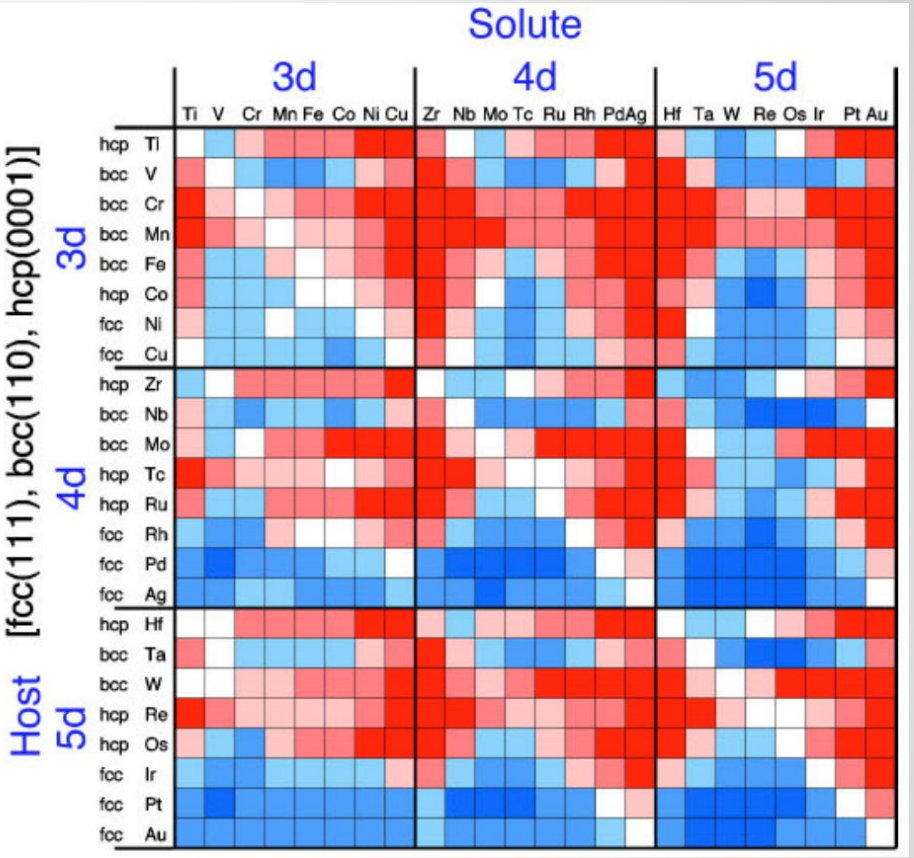
R. Nazarov, PRB 85, 144118, (2012)

Surface Segregation

$$E_{seg} = E(imp\ at\ surface) - E(imp\ in\ bulk)$$







A.V. Ruban, PRB 59, 15995 1999, DFT LDA + CPA + Green function for semi-infinite surface

- The component with lowest surface energy tend to segregate
- Structural contribution to segregation energy

Practical notes

- check convergence of defects formation energy with respect to supercell sizes
- for slab calculations try to use symmetrical cells, otherwise use dipole corrections
- for surfaces check XC functional

Conclusion

Computer modelling allows:

- consider almost all kind of defects in solids
- study interaction of defects
- explain the influence of defects on macroscopic properties of solids

Literature

- ***Reading***

Required: *Sholl (Ch.4), Phillips (7.1, 7.3, 7.5; 8.1-8.4; 9.1-9.4)*

1. **R. Tilley**, Defects in solids, New Jersey, Wiley, 2008
2. **D. Sholl**, Density functional theory
   A Practical Introduction, New Jersey, Wiley, 2009
3. **R. Phillips,** Crystals, defects and microstructure,
   Modelling across scales, Cambridge, 2004

Thank you for your attention!