Point and Line Defects: Defects in crystals

0-dimensional: point defects
- vacancy (missing atom)
- self-interstitial (extra atom, off lattice site)
- impurity, substitutional or interstitial
- antisite defects in ordered alloy
  (e.g., As on Ga site in GaAs)
- conduction electron or hole in semiconductor
- complexes formed from above defects
  (e.g., solute-vacancy pair, color center,
  Frenkel pair, Schottky defect, ...)

2-dimensional: planar defects
- boundary: grain-, twin, interphase
- antiphase boundary
- stacking fault

1-dimensional: line defects
- dislocation, perfect
- dislocation, partial
- boundary dislocation
- disconnection
- loop formed by vacancies or
  self-interstitials
- specialized defect: {311}-Si defects

3-dimensional: volumetric defects
- precipitate
- void
- stacking-fault tetrahedron

Our focus: point and line defects, their interaction, and with other higher dimensional defects

Material properties governed by defects

electronic and transport properties
- resistivity / conductivity
- (ion) diffusion
- photo emission
- transparency / photoadsorption
- superconductivity

mechanical properties
- strength
- ductility
- toughness
- corrosion resistance

structural properties
- crystal growth
- grain size
- recrystallization mechanism
- phase transformations

Defect properties

structural: where are the atoms, relative to the perfect crystal?

tic displacements)

lative to the perfect crystal?

chemical: participation in reactions

, positrons, neutrons)
  - scattering cross-section? cause of contrast in microscopy?

thermodynamic: formation energy/enthalpy/entropy
  - equilibrium (local or global) concentration
  - interaction between defects
  - migration of defects

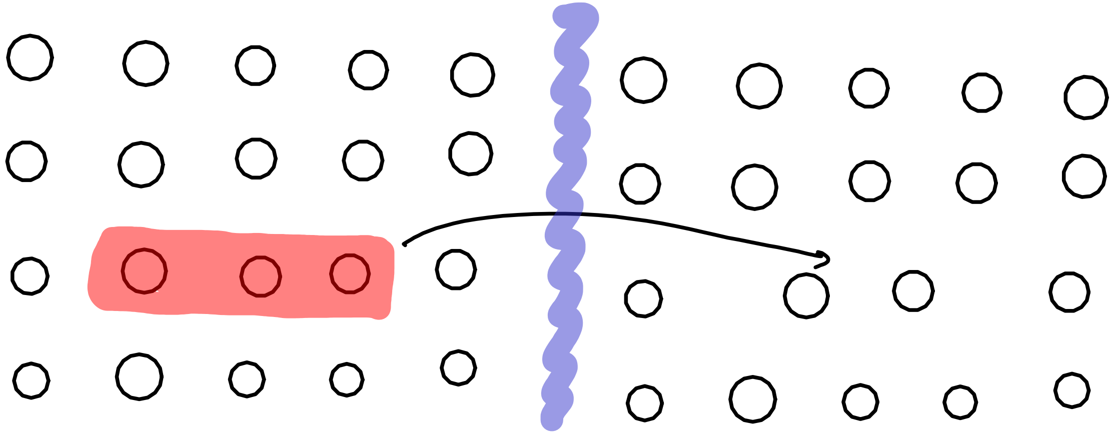
Primary focus: structural, electronic, thermodynamics properties

Example: Point Defect Properties

Start "simple": vacancy = remove atom from crystal

Structure? Remove an atom, yes? Multiple approaches. Take 1 atom out. Replace 2 (neighboring) atoms with 1. Etc...

Anything that goes from N to N-1 atoms is a vacancy



= 1 vacancy.

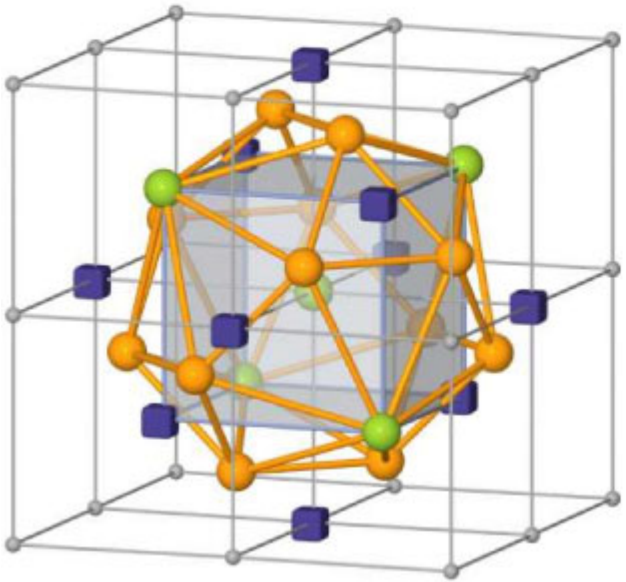
But also note: even in our simple case where we remove one atom, neighboring atoms will "relax" (displace from their ideal position

Suggests we may want a way to unambiguously define the "size" of a point defect to differentiate these structural differences

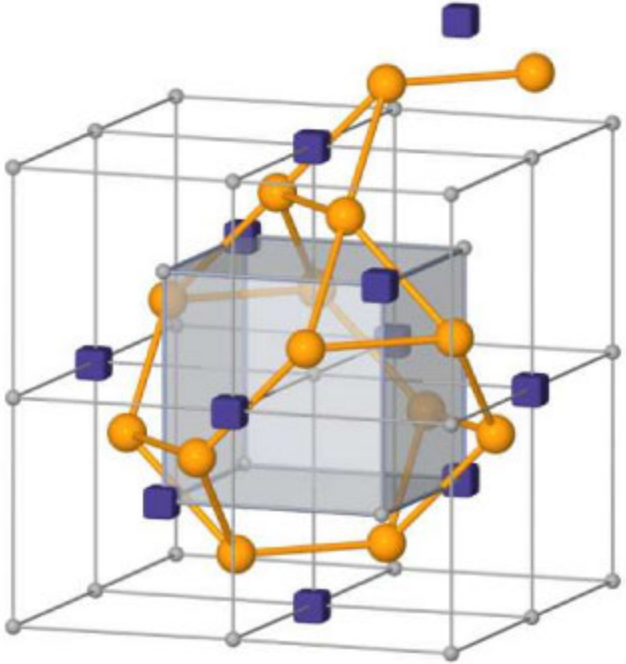
Can also make similar arguments for interstitials. Classic example: crowdion where N+1 atoms in a row replace N atoms.

Unusual defect structures: Iron

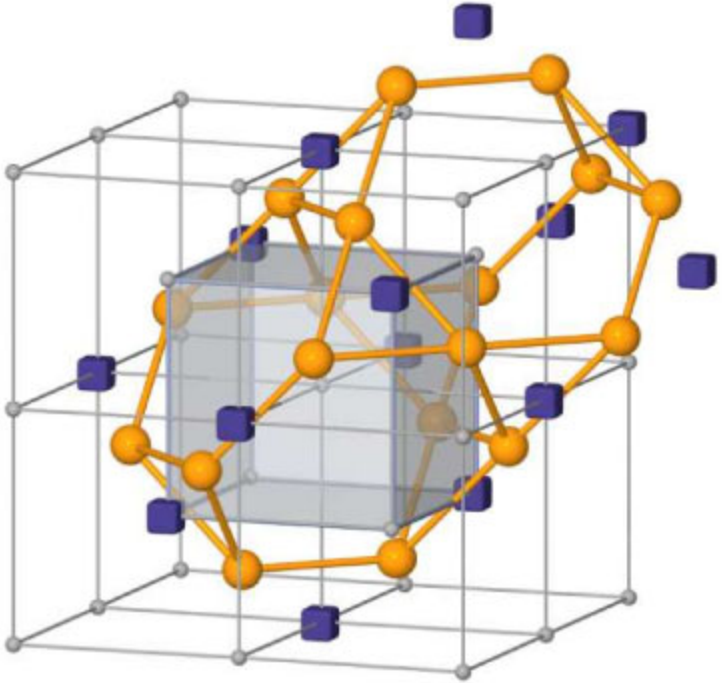
di-interstitial structure = 12 self-interstitials + 10 vacancies



di-interstitial



tri-interstitial



tetra-interstitial

blue squares = vacancies

orange atoms = self-interstitials

MC Marinica et al. Phys. Rev. Lett. 108, 025501 (2012

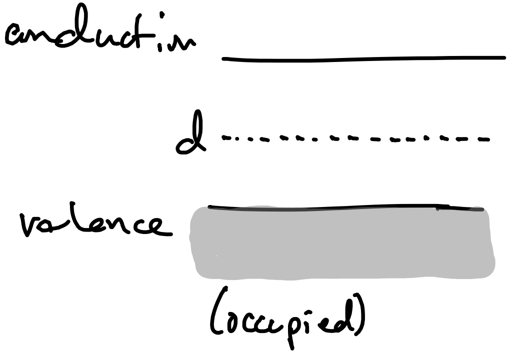
But there are other properties to consider (even for our humble vacancy)!

- electronic: charge? If we make a vacancy in NaCl, say, remove a Na^+ ion, there is a negative (relative) charge left behind.

  → requires compensation of charge <u>somewhere</u>:
  - hole
  - Cl^- vacancy
  - Na^+ interstitial
  - X^+ interstitial

  these are all valid! and correspond to different defect complexes

- electronic: defect levels? In a semiconductor, the charge state of a defect depends on the Fermi level (can correspond to an electronic state in the band gap)



← corresponds to E_F where defect charge state changes

can couple to <u>structure</u> of defect too!

defect with an extra e^- (or a hole) may even break symmetry in a different way.

(techniques like EPR are sensitive to this change)

Thermodynamic properties

- Basic question for point defects: how many are present? Depends on equilibrium vs. non-equilibrium. and local vs. global equilibrium.

Changing conditions change what defines equilibrium (and this can be more than just change in T)

E.g.: vacancies have an equilibrium concentration $c_v^0(T) = e^{-G_v^f/k_BT}$ (Arrhenius form)

So as T ↓, c_v^0 ↓

But that equilibrium value may be smaller than the current concentration — and adjustment requires elimination of vacancies at sinks. If sinks are not available → concentration is locally frozen in place

→ this may drive defect reactions, like two vacancies forming a divacancy

Note also that the conditions for equilibrium can vary spatially, as it depends on more than just T.

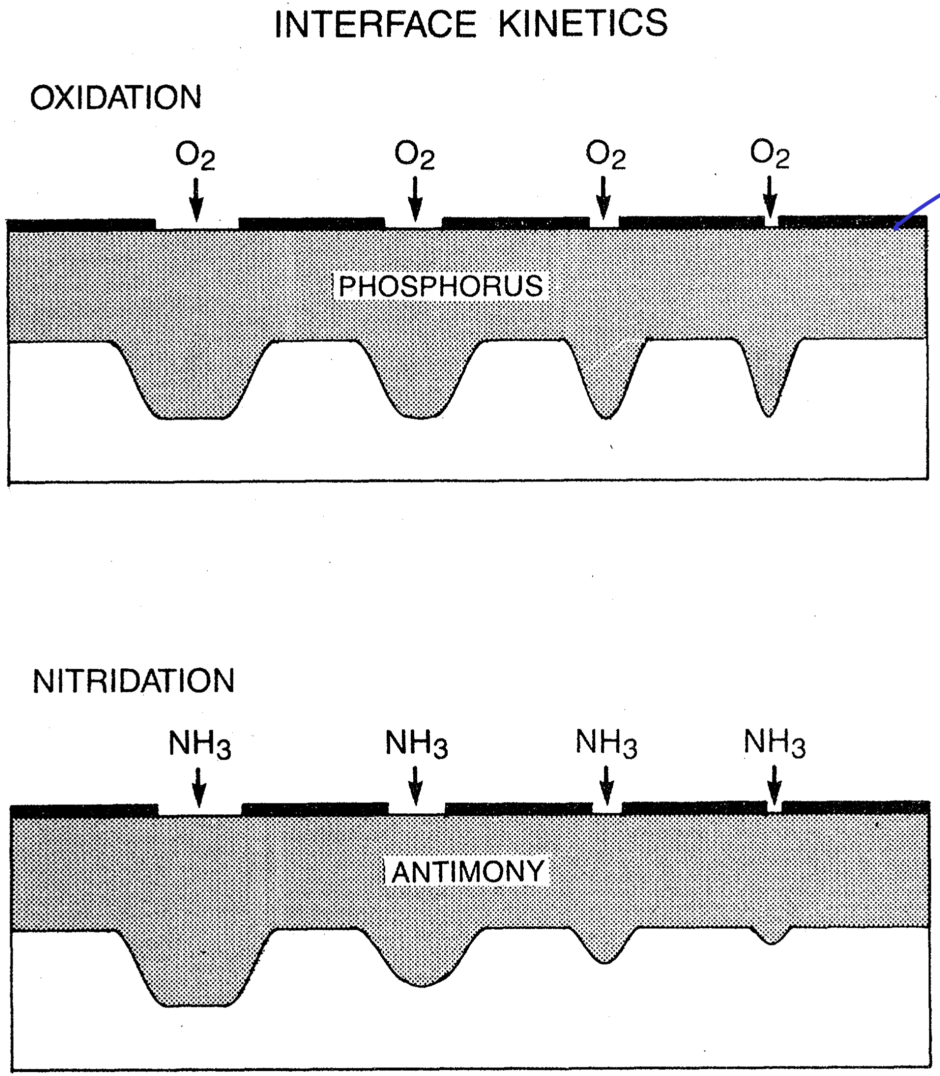
Ex: strain. Equil. vacancy (and self-interstitial) concentration depends on strain, and strain is often spatially heterogeneous (in part, due to defects)

→ we can see this in properties that depend on defect concentration, like <u>diffusion</u>.

Oxide-enhanced diffusion

Injection of self-interstitials and vacancies affects diffusion

free surfaces also act as sources & sinks for vacancies and interstitials, making it easier to produce equil. conditions



$\Delta\mu$ drives diffusion

$\Delta\mu$ drives diffusion

mask layer (makes oxide formation on surface controllable)

PM Fahey et al., Rev. Mod. Phys. 61, 289 (1989)

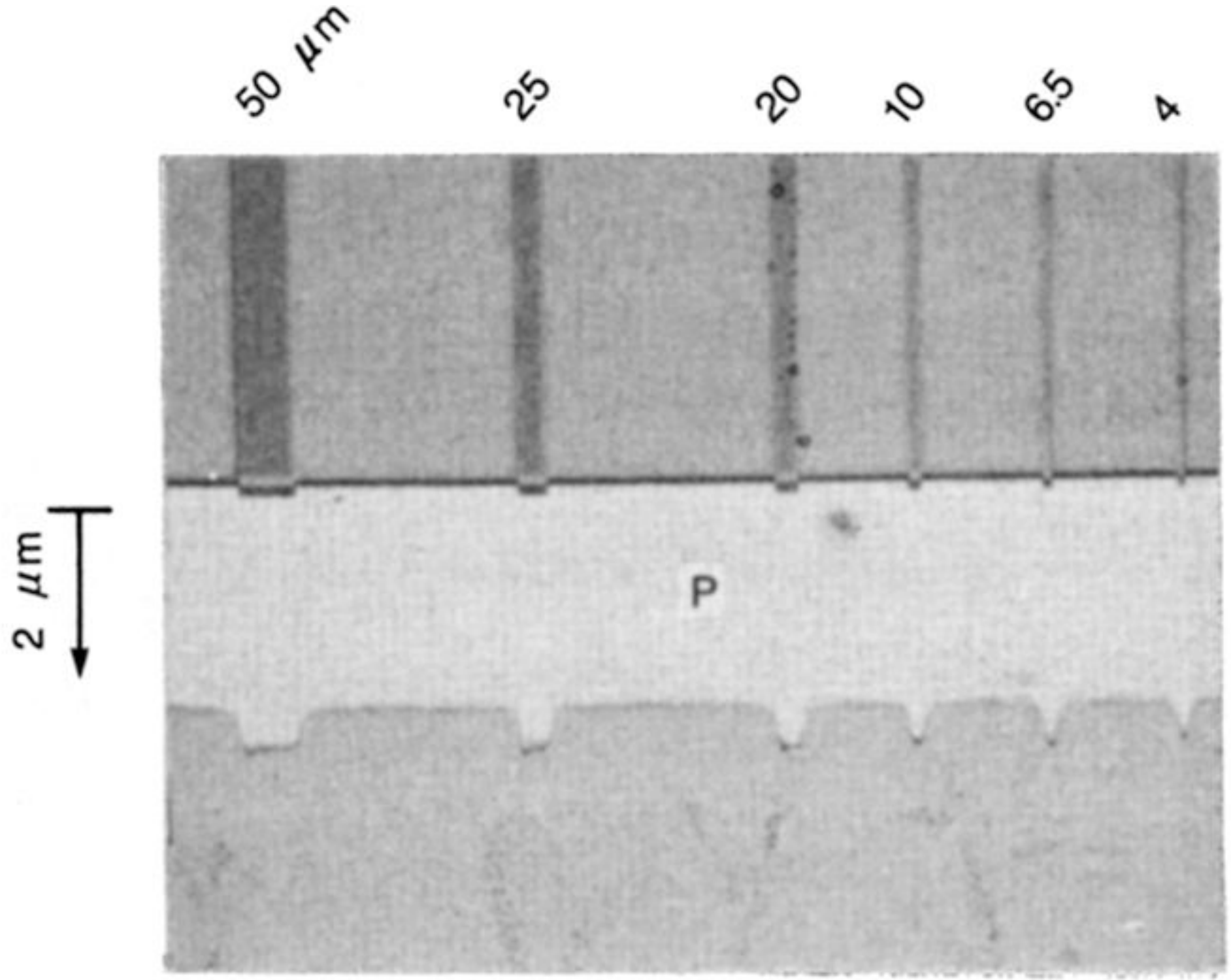
Oxide-enhanced diffusion

Oxide layer injects self-interstitials into bulk

local expansion at the surface due to lattice mismatch between oxide and Si

→ more interstitials below the oxide.

P diffusion occurs via kick-out in Si → dependent on self-interstitial concentration



4h at 1100 C

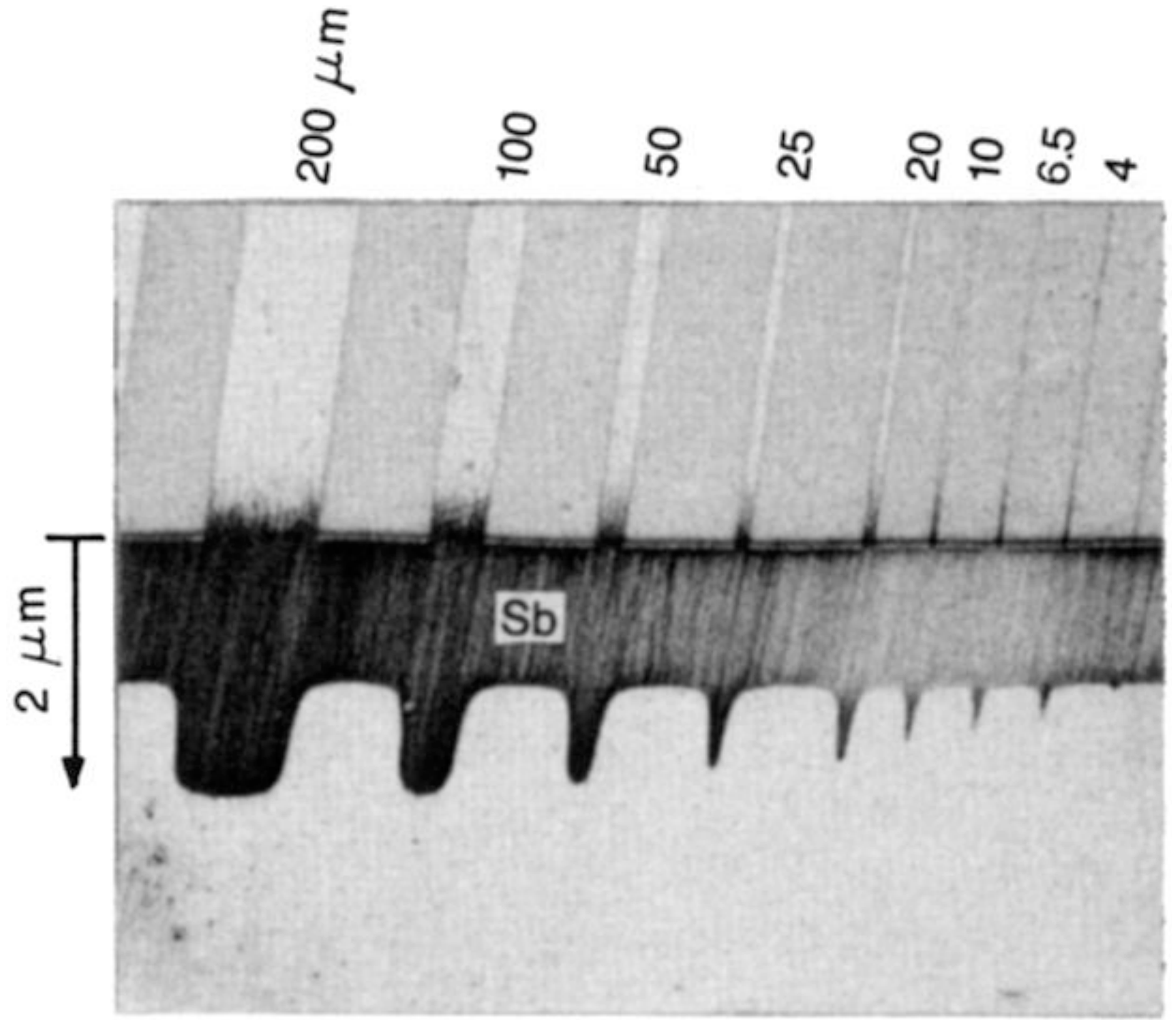
Oxide-enhanced diffusion

Nitride layer injects vacancies into bulk

local compression at the surface due to lattice mismatch between nitride and Si

→ more vacancies below the nitride

Sb diffusion occurs via a vacancy-mediated mechanism → dependent on vacancy concentration



1h at 1100 C

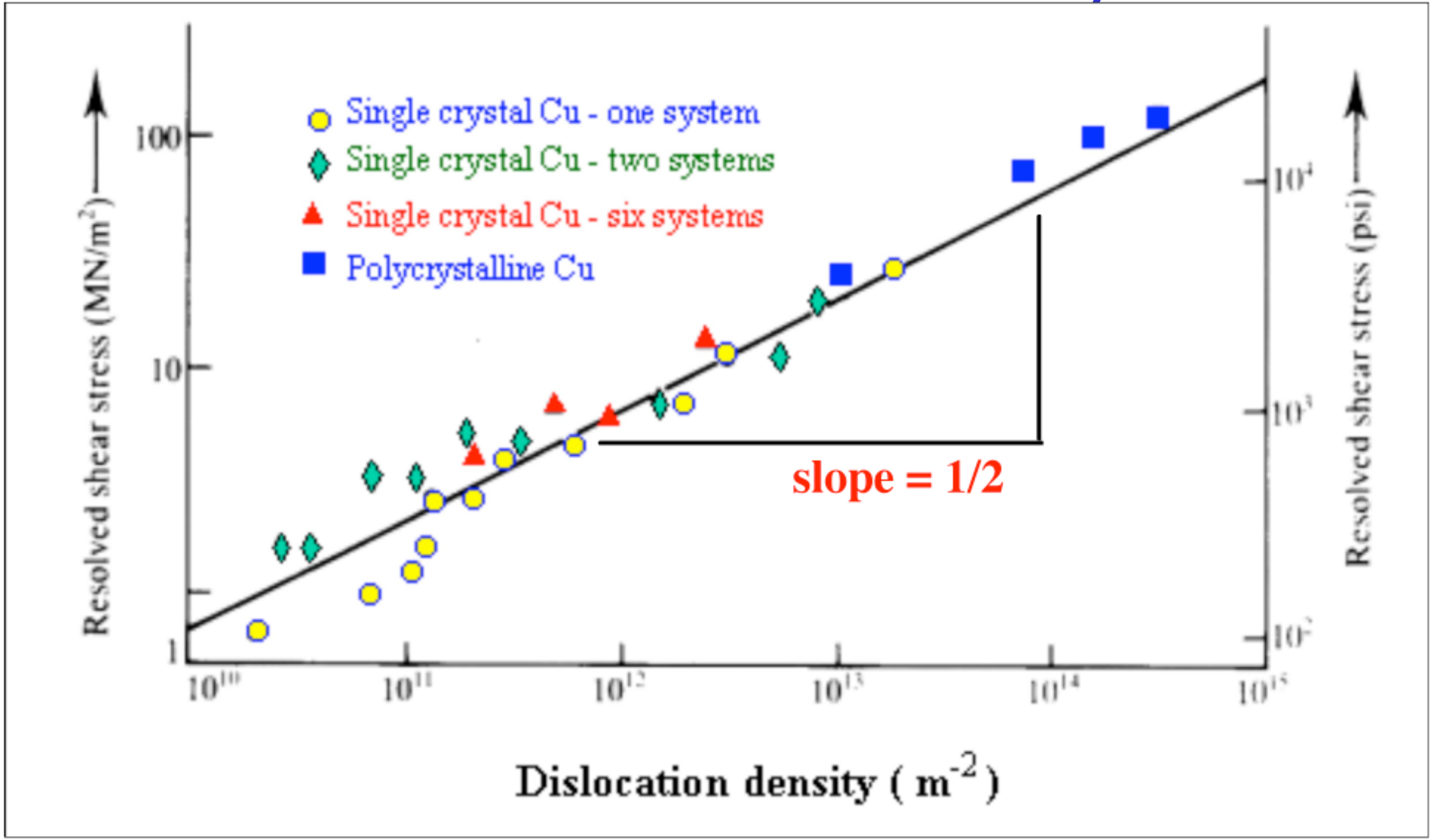
Cu CRSS vs. dislocation density

Plastic deformation in metals primarily through motion of dislocations (⊥)

⊥/⊥ interactions make ⊥ density ↑

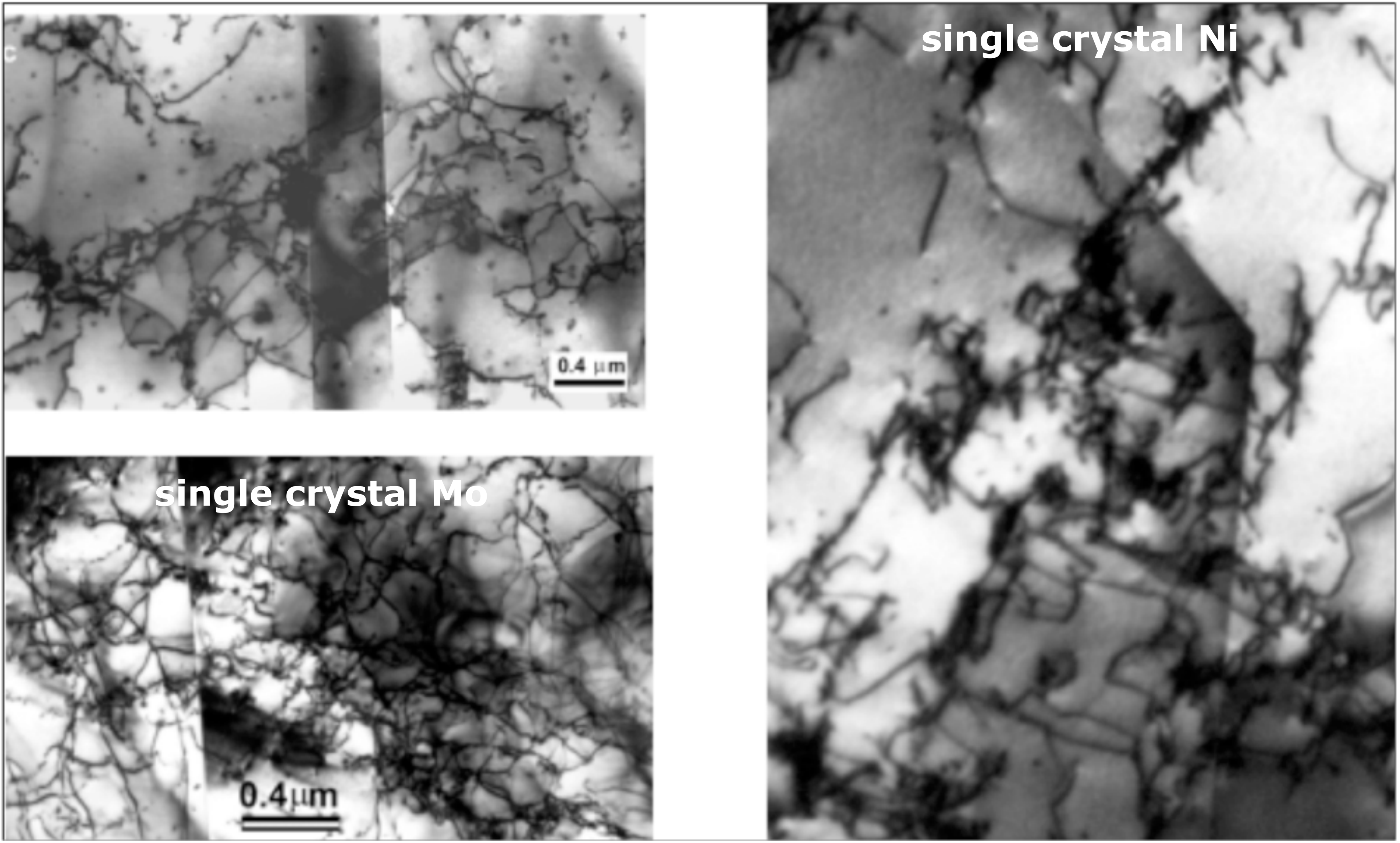
and requires higher stress to move ⊥

= work hardening.

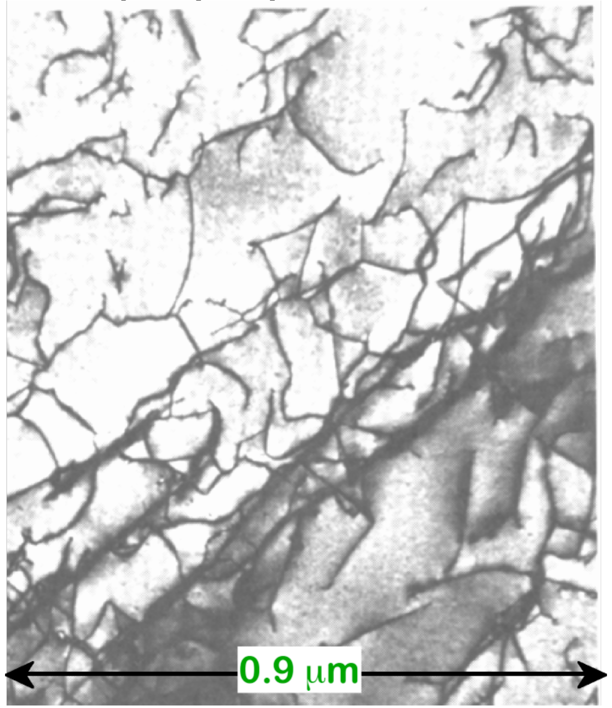


adapted from H Weidersich, J. Metals 16, 425 (1964)

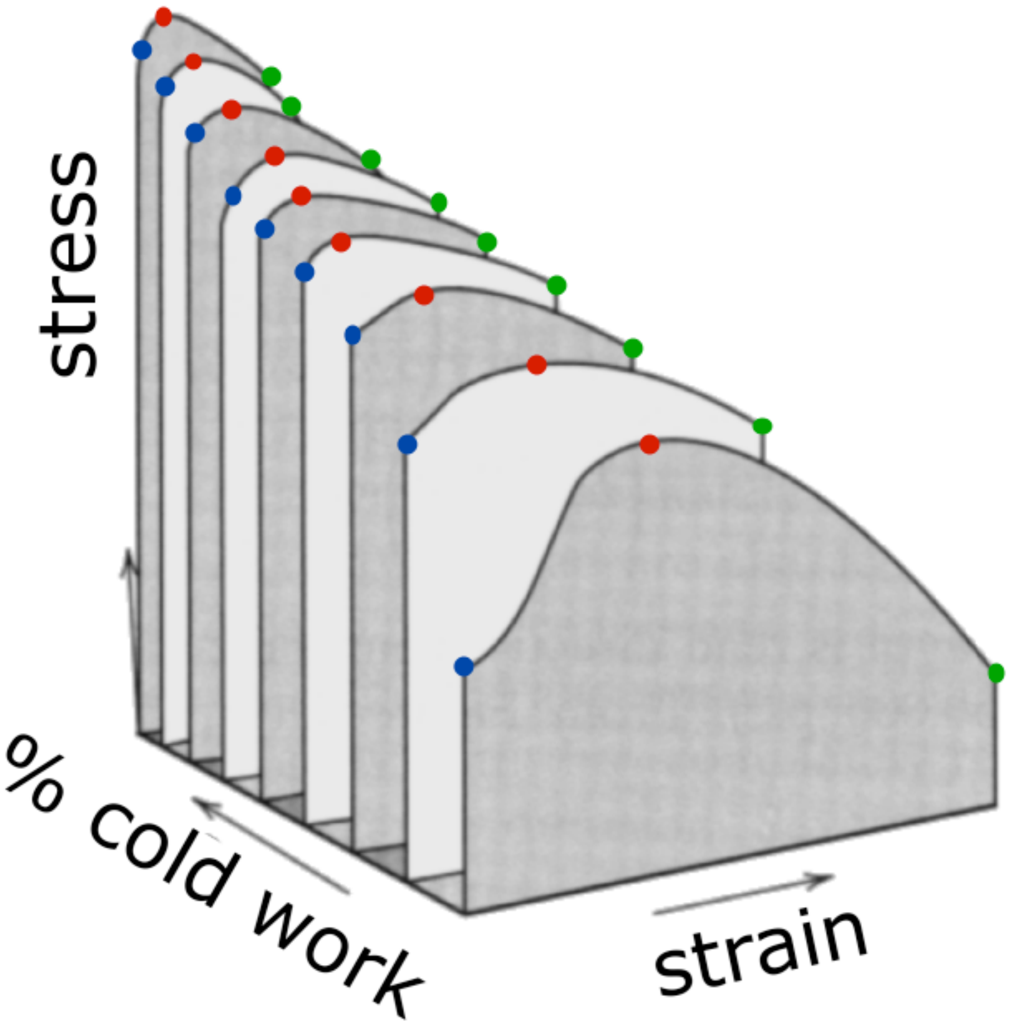
Cold work microstructure



polycrystalline Ti



Effect of repeated cold work



repeated wire-drawing:

raises yield stress

raises tensile stress

lowers ductility

all due to persistent dislocation microstructure