IMPERFECTIONS IN SOLIDS

ISSUES TO ADDRESS...

- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
- Are defects undesirable?
- How do point defects in ceramics differ from those in metals?
- In ceramics, how are impurities accommodated in the lattice and how do they affect properties?

TYPES OF IMPERFECTIONS

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

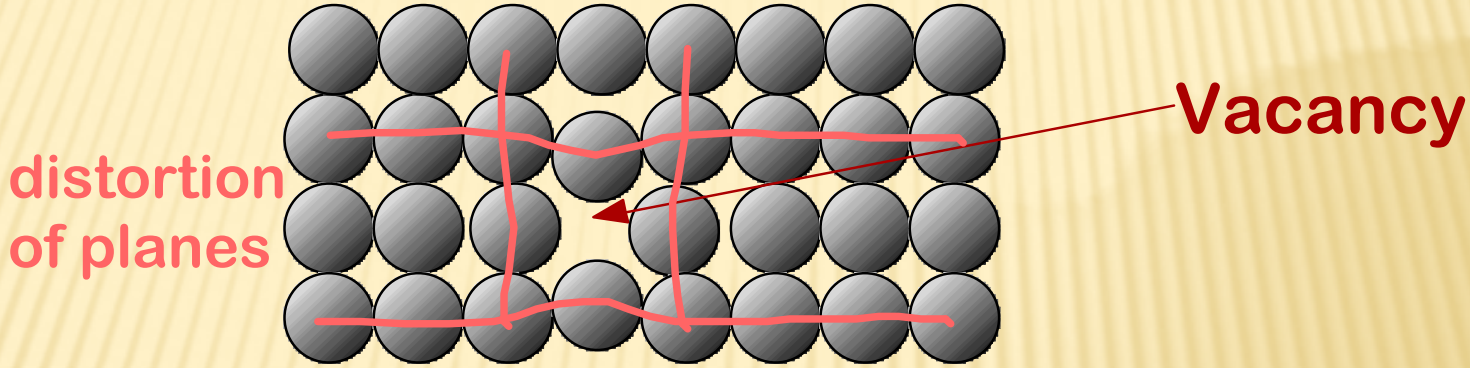
Line defects

- Grain Boundaries

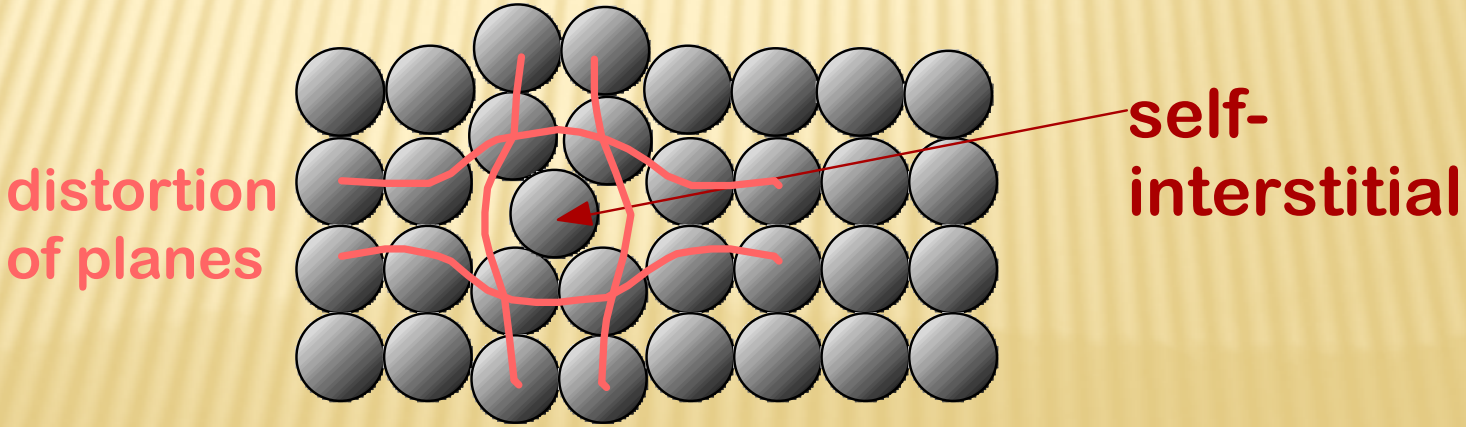
Area defects

POINT DEFECTS

- **Vacancies**:
  -vacant atomic sites in a structure.



- **Self-Interstitials**:
  -"extra" atoms positioned between atomic sites.



EQUIL. CONCENTRATION: POINT DEFECTS

- Equilibrium concentration varies with temperature!

No. of defects

Activation energy

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

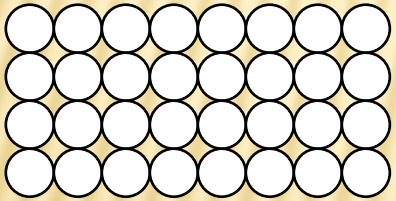
No. of potential defect sites.

Boltzmann's constant

(1.38 x 10^{-23} J/atom K)

(8.62 x 10^{-5} eV/atom K)

Temperature



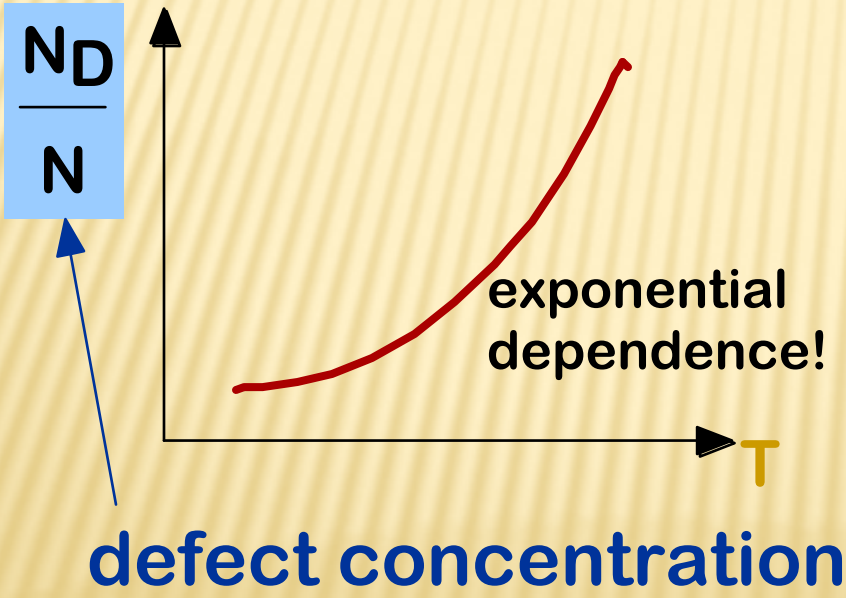
Each lattice site is a potential vacancy site

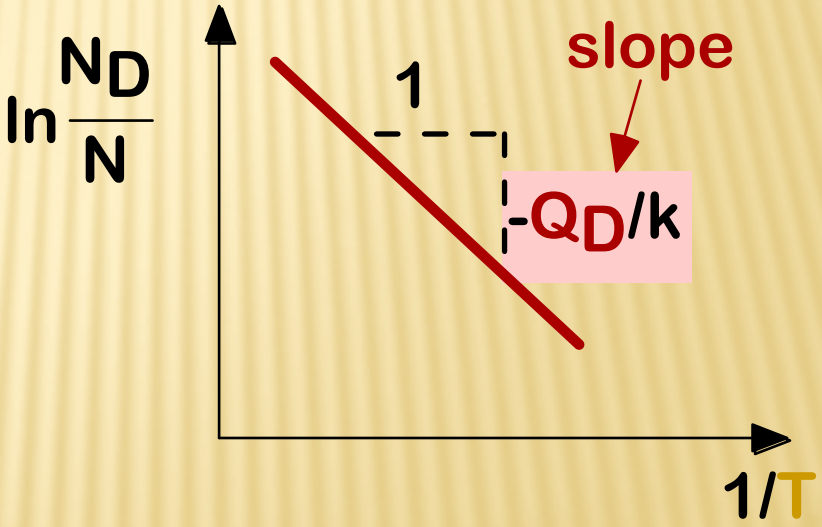
MEASURING ACTIVATION ENERGY

- We can get Q from an experiment.
- Measure this…

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

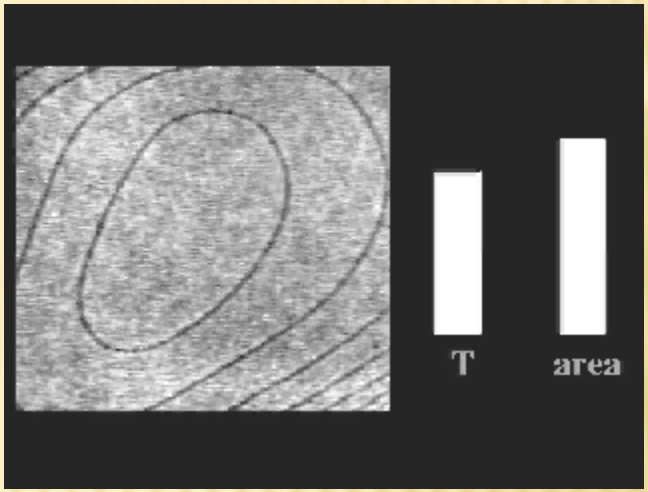
- Replot it…





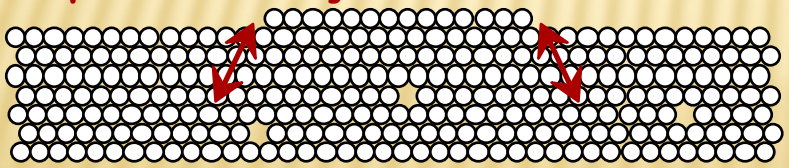
OBSERVING EQUIL. VACANCY CONC.

- Low energy electron microscope view of a (110) surface of NiAl.
- Increasing T causes surface island of atoms to grow.
- Why? The equil. vacancy conc. increases via atom motion from the crystal to the surface, where they join the island.



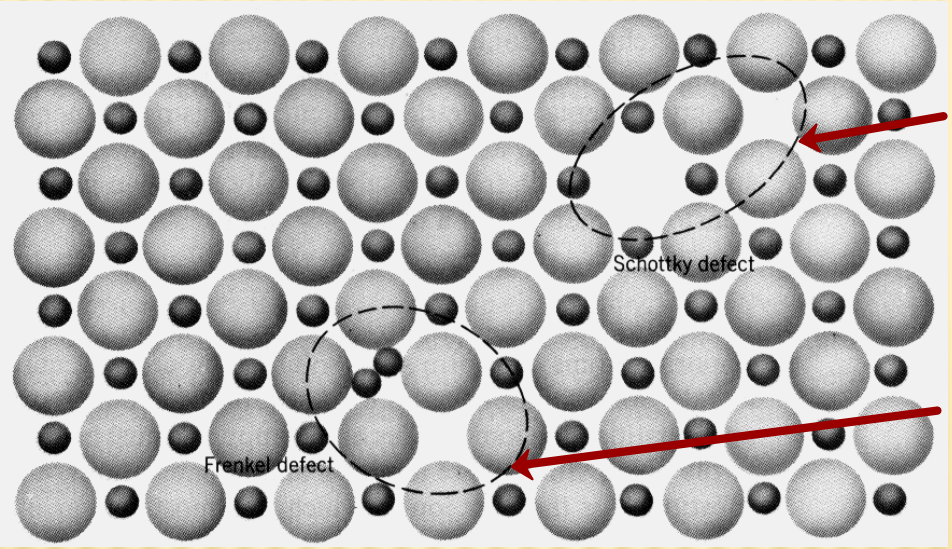
Click on image to animate

Island grows/shrinks to maintain equil. vancancy conc. in the bulk.



DEFECTS IN CERAMIC STRUCTURES

- **Frenkel Defect**
  --a cation is out of place.
- **Shottky Defect**
  --a paired set of cation and anion vacancies.

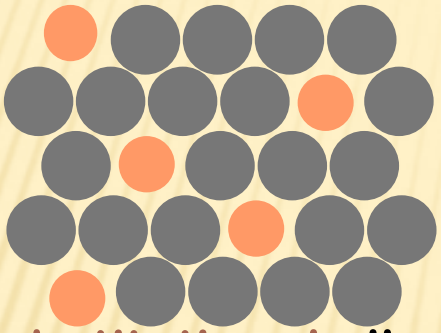


- **Equilibrium concentration of defects** $\sim e^{-Q_D/kT}$

POINT DEFECTS IN ALLOYS

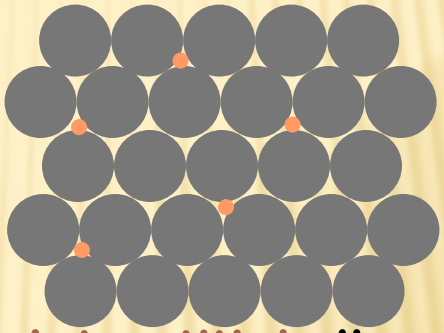
Two outcomes if impurity (B) added to host (A):

- **Solid solution of B in A (i.e., random dist. of point defects)**



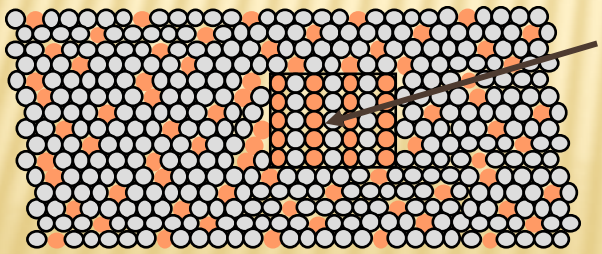
Substitutional alloy
(e.g., Cu in Ni)

OR



Interstitial alloy
(e.g., C in Fe)

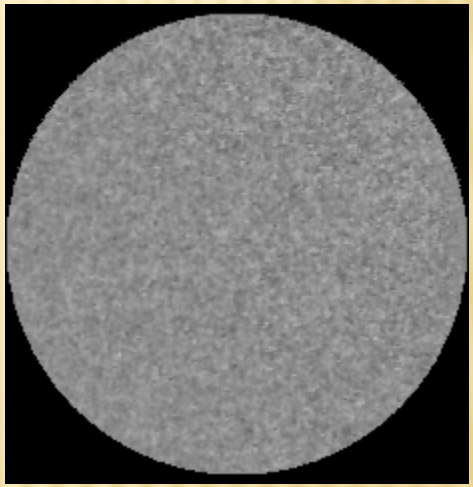
- **Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)**



Second phase particle
--different composition
--often different structure.

ALLOYING A SURFACE

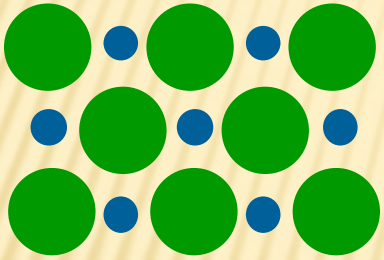
- Low energy electron microscope view of a (111) surface of Cu.
- Sn islands move along the surface and "alloy" the Cu with Sn atoms, to make "bronze".
- The islands continually move into "unalloyed" regions and leave tiny bronze particles in their wake.
- Eventually, the islands disappear.



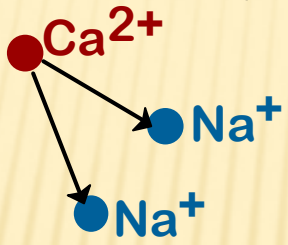
IMPURITIES

- Impurities must also satisfy charge balance
- Ex: NaCl 

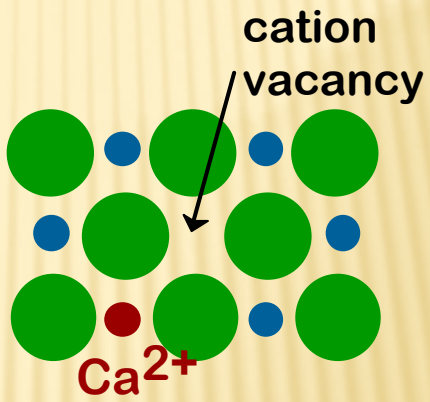
- Substitutional cation impurity



initial geometry

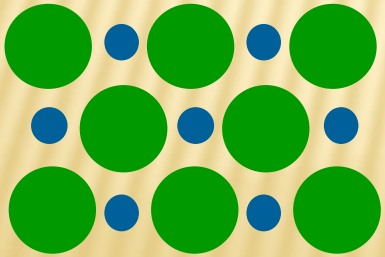


Ca^{2+} impurity

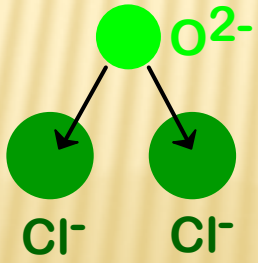


resulting geometry

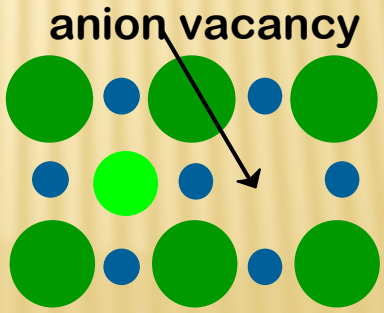
- Substitutional anion impurity



initial geometry



O^{2-} impurity



resulting geometry

COMPOSITION

Definition: Amount of impurity (B) and host (A) in the system.

Two descriptions:

- Weight %

$$C_B = \frac{\text{mass of B}}{\text{total mass}} \times 100$$

- Atom %

$$C'_B = \frac{\text{\# atoms of B}}{\text{total \# atoms}} \times 100$$

- Conversion between wt % and at% in an A-B alloy:

$$C_B = \frac{C'_B A_B}{C'_A A_A + C'_B A_B} \times 100 \qquad C'_B = \frac{C_B/A_B}{C_A/A_A + C_B/A_B}$$

- Basis for conversion:

mass of B = moles of B x A_B ← atomic weight of B

mass of A = moles of A x A_A ← atomic weight of A

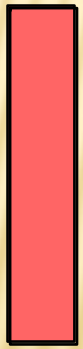
LINE DEFECTS

Dislocations:

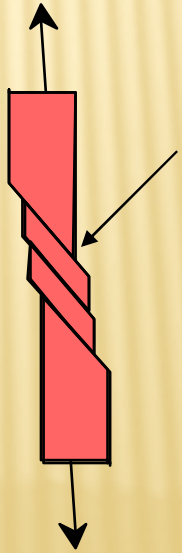
- are line defects,
- cause slip between crystal plane when they move,
- produce permanent (plastic) deformation.

Schematic of a Zinc (HCP):

- before deformation



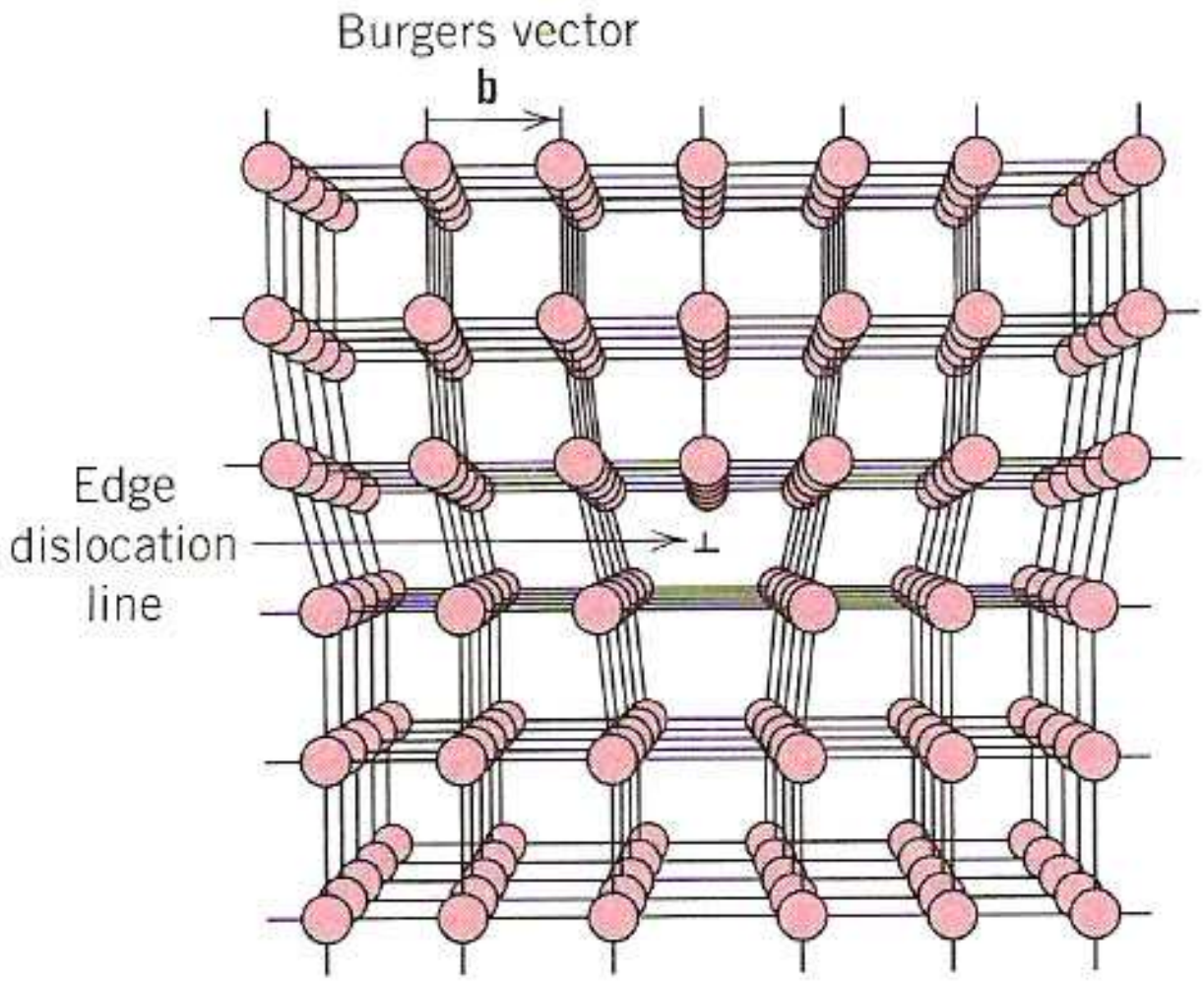
- after tensile elongation



Edge Dislocation

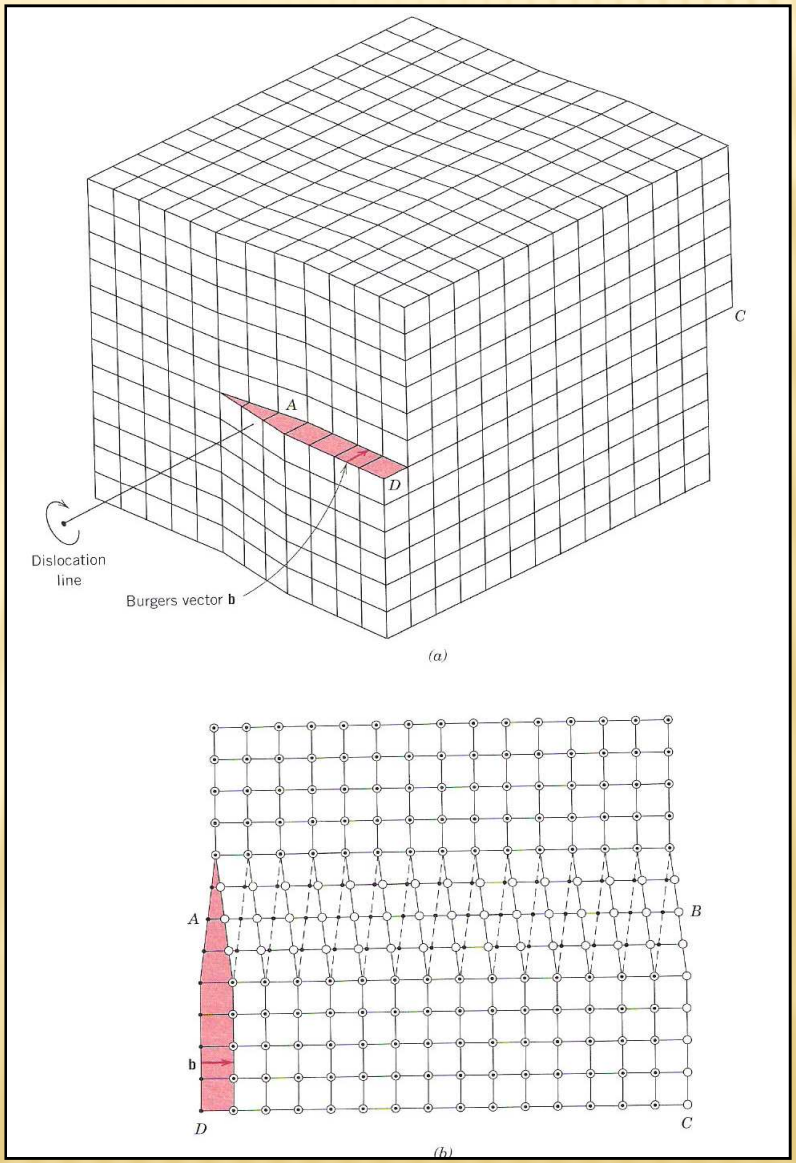
An edge dislocation results from a mismatch in the rows of atoms, as if an extra plane of atoms was inserted.

The burger's vector, **b**, represents how far we would have to move an atom to bring it back into registry. The burgers vector is perpendicular to the dislocation line.



SCREW DISLOCATION

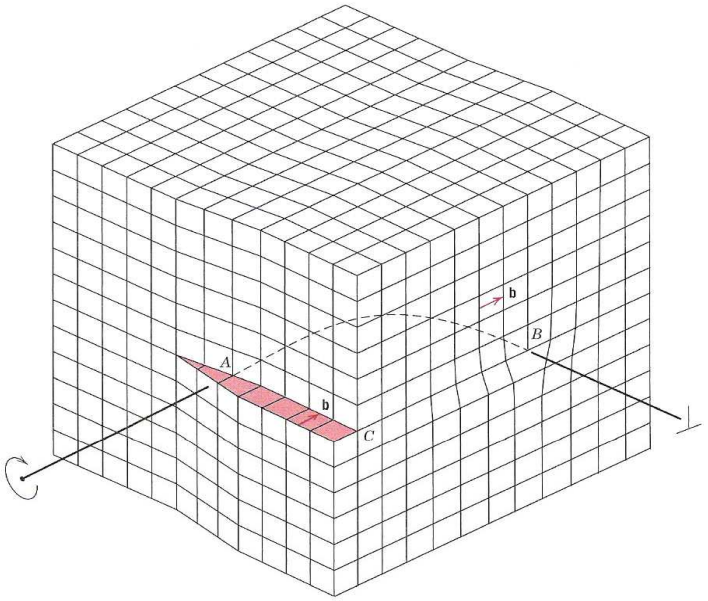
Screw dislocations result from "shearing" in the crystal. The burgers vector, **b**, is parallel to the slip plane

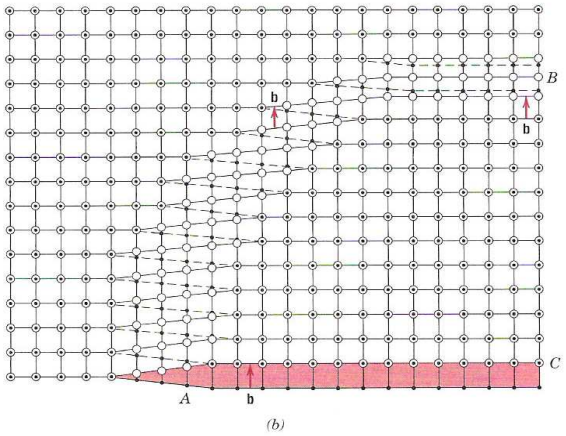


MIXED DISLOCATION

Dislocations virtually never are purely "edge" or "screw" type.

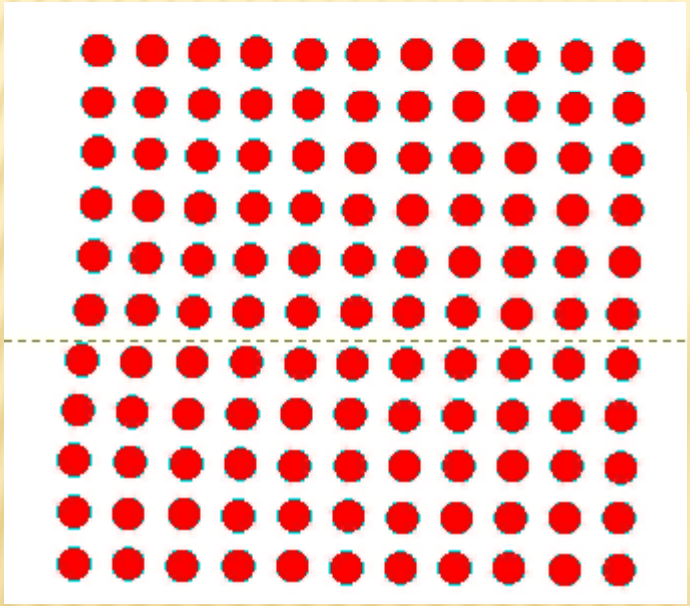
They are usually combinations of the two, or "mixed"





BOND BREAKING AND REMAKING

- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right here).
- Bonds across the slipping planes are broken and remade in succession.



Click on image to animate

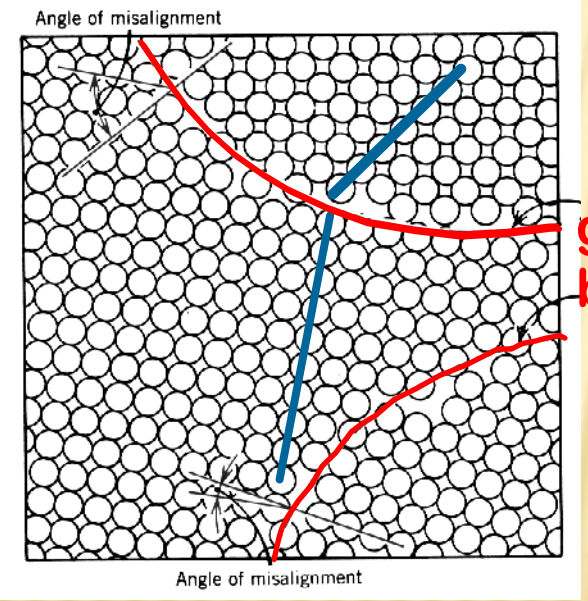
Atomic view of edge dislocation motion from left to right as a crystal is sheared.

AREA DEFECTS: GRAIN BOUNDARIES

Grain boundaries:

- are boundaries between crystals.
- are produced by the solidification process, for example.
- have a change in crystal orientation across them.
- impede dislocation motion.

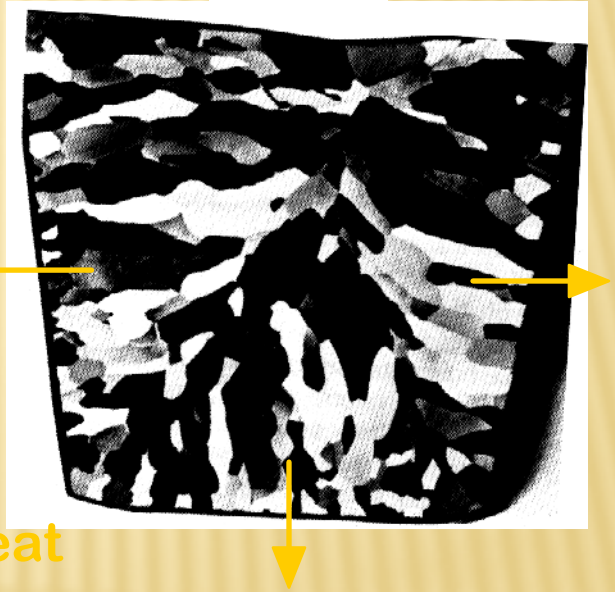
Schematic



grain boundaries

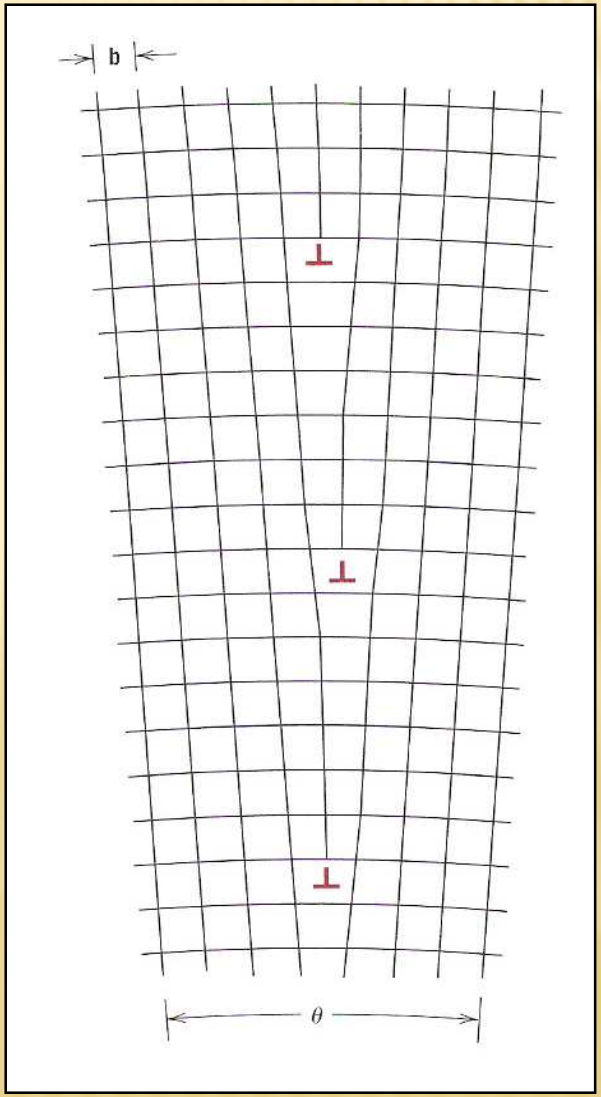
Adapted from Fig. 4.7, *Callister 6e.*

Metal Ingot



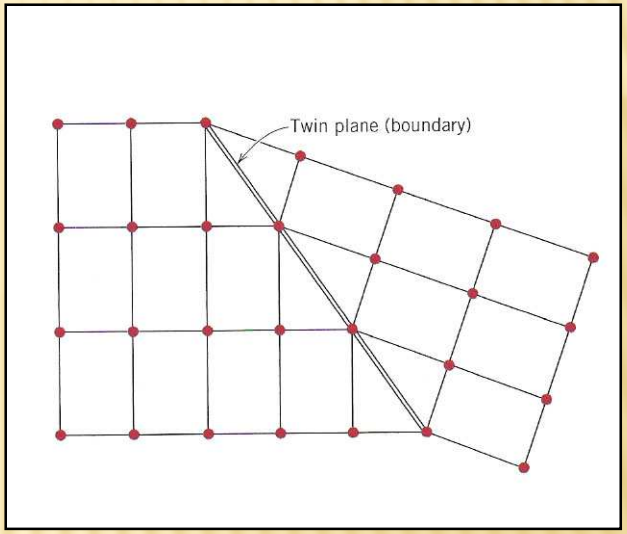
LOW ANGLE GRAIN BOUNDARY

Low angle grain boundaries are made up of equally spaced dislocation to accommodate the mismatch in lattices between two grains

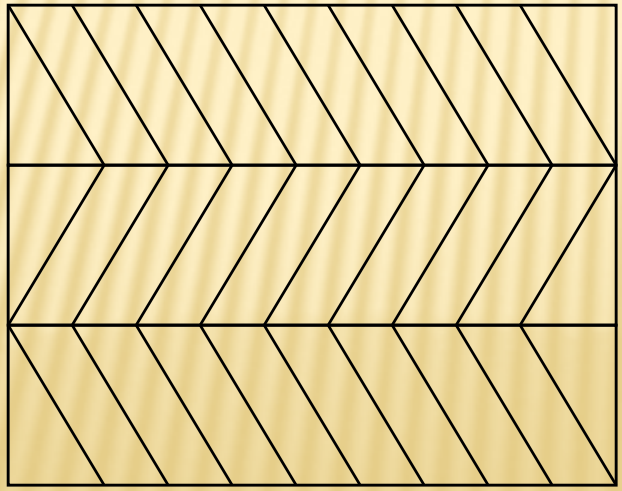


VOLUME DEFECTS - TWINS

Twins occur when atoms jump from one site to a "mirror" site



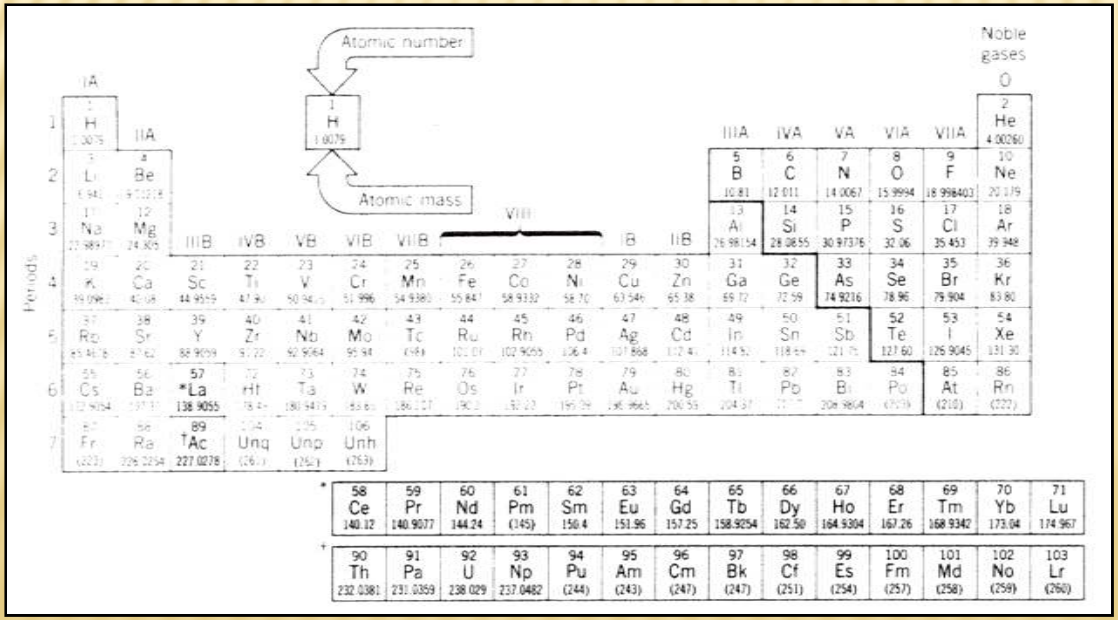
Plane jumps to mirror image



Twins can occur because of thermal treatment (annealing twins) or mechanical deformation

HUME-ROTHERY RULES FOR SUBSTITUTIONAL SOLIDS

1. Atomic sizes agree within 15%
2. Same crystal structure
3. Similar electronegativity
4. Similar valence



Consider Cu and Ni:

r_{Cu}=0.128 nm

r_{Ni}=0.125 nm

Size difference: 2.3%

Both FCC

Cu & Ni electronegativity: 1.9 and 1.8, respectively

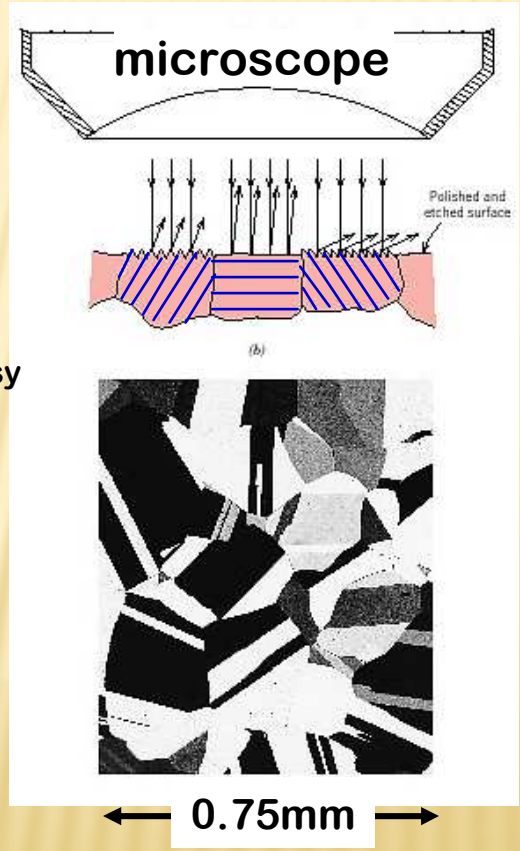
Valence:

Cu: 2

Ni: 2,3

OPTICAL MICROSCOPY (1)

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.



Adapted from Fig. 4.11(b) and (c), *Callister 6e.* (Fig. 4.11(c) is courtesy of J.E. Burke, General Electric Co.

close-packed planes

micrograph of Brass (Cu and Zn)

OPTICAL MICROSCOPY (2)

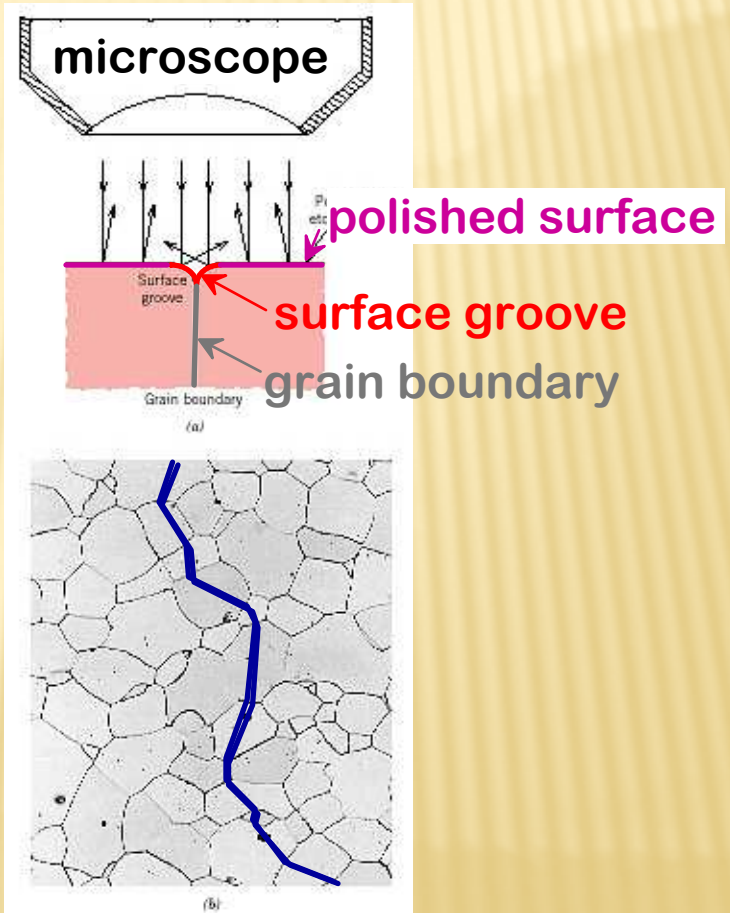
Grain boundaries…

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change direction in a polycrystal.

ASTM grain size number

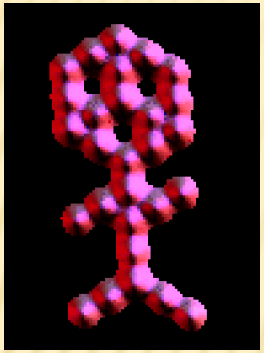
$$N = 2^{n-1}$$

N: no. grains/in^2 at 100x magnification

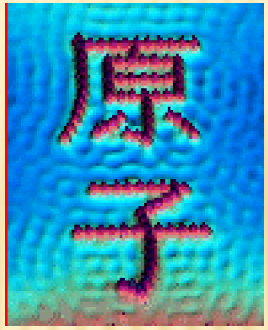


SCANNING TUNNELING MICROSCOPY

- **Atoms can be arranged and imaged!**



Carbon monoxide molecules arranged on a platinum (111) surface.



Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word "atom".

SUMMARY

- Point, Line, and Area defects arise in solids.
- The number and type of defects can be varied and controlled (e.g., T controls vacancy conc.)
- Defects affect material properties (e.g., grain boundaries control crystal slip).
- Defects may be desirable or undesirable (e.g., dislocations may be good or bad, depending on whether plastic deformation is desirable or not.)