



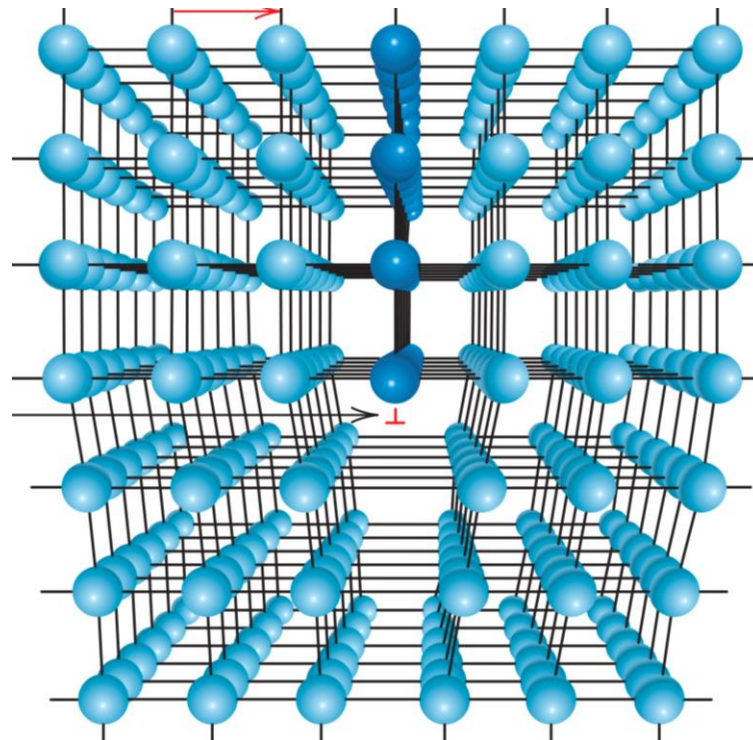
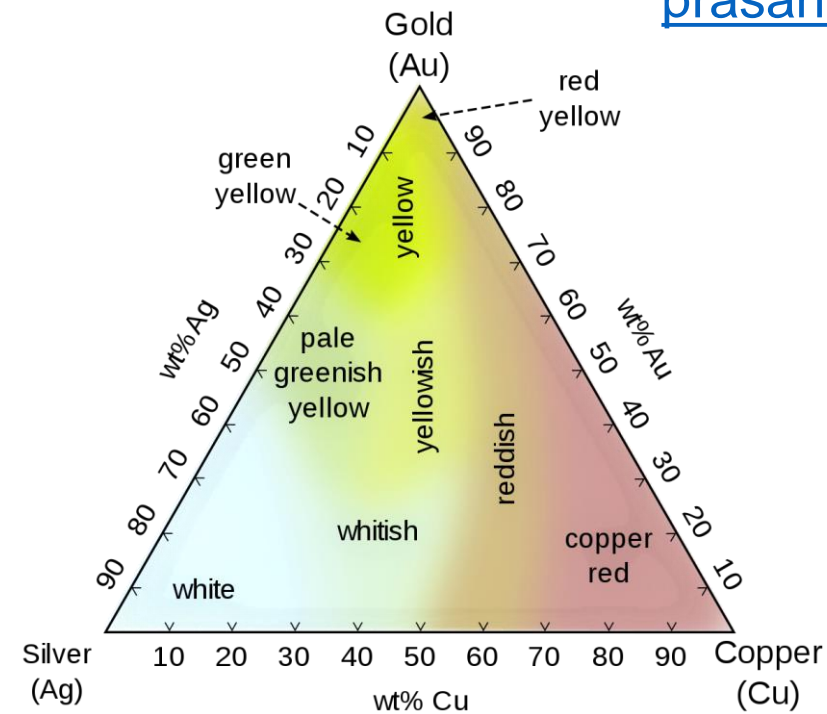
MS31007: Materials Science

Chapter 4: Part II

Solidification & Imperfections in SOLIDS

Instructor: Prasana Kumar Sahoo

prasana@matsc.iitkgp.ac.in



TOKYO 2020 MEDAL COMPOSITIONS



GOLD MEDAL

Mass: 556 grams

Ag SILVER 98.8%

Au GOLD 1.2%



SILVER MEDAL

Mass: 550 grams

Ag SILVER 100%



BRONZE MEDAL

Mass: 450 grams

Cu COPPER 95%

Zn ZINC 5%

This year's medals are the first to be made entirely from recycled metals.

The metals used to make all of the approximately 5,000 medals were extracted from used electronic devices donated across Japan. This amounted to approximately 32 kg of gold, 3,500 kg of silver, and 2,200 kg of bronze extracted from 78,985 tons of donated devices.

	1 MEDAL	812 MEDALS
VALUE OF GOLD MEDAL (6g) <small>IDC minimum requirement</small>	\$548	\$445,130
VALUE OF SOLID GOLD MEDAL (500g)	\$21,674	\$17,599,182



Objectives

- Describe the process of the solidification of metals distinguishing between homogeneous and heterogeneous nucleation.
- Describe the two energies involved in the solidification process of a pure metal, and write the equation for the total free-energy change associated with the transformation of the liquid state to solid nucleus.
- Distinguish between equiaxed and columnar grains and the advantage of the former over the latter.
- Explain, in general terms, why alloys are preferred materials over pure metals for structural applications.
- Distinguish between single crystal and polycrystalline materials
- Classify various types of crystalline imperfections and explain the role of defects on the mechanical and electrical properties of crystalline materials.
- Determine the ASTM grain size number and average grain size diameter and describe the importance of grain size and grain boundary density on the behavior of crystalline materials.
- Learn how and why optical microscopy, SEM, TEM, HRTEM, AFM, and STM techniques are used to understand more about the internal and surface structures of materials at various magnifications.





Imperfections in Solids

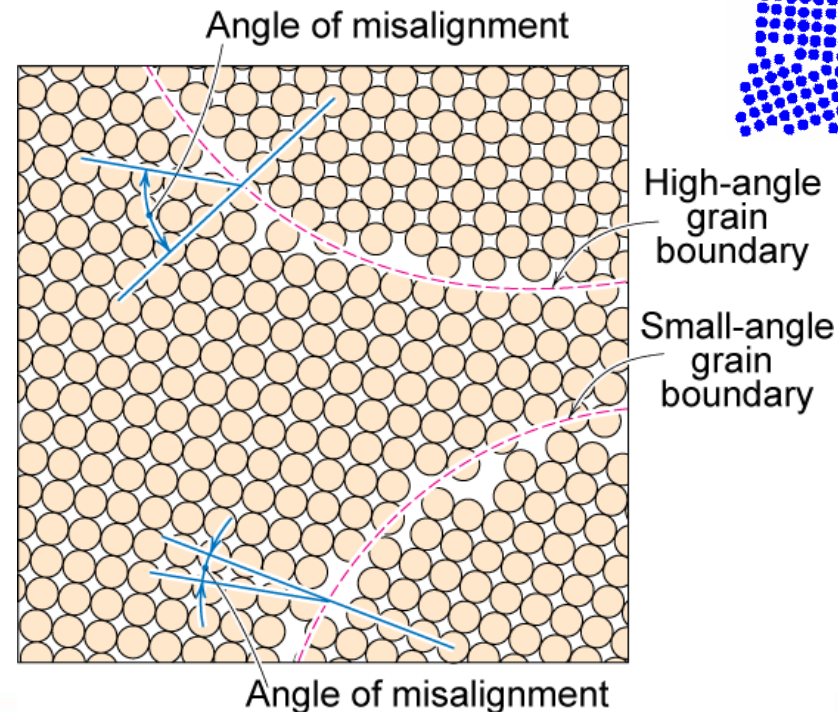
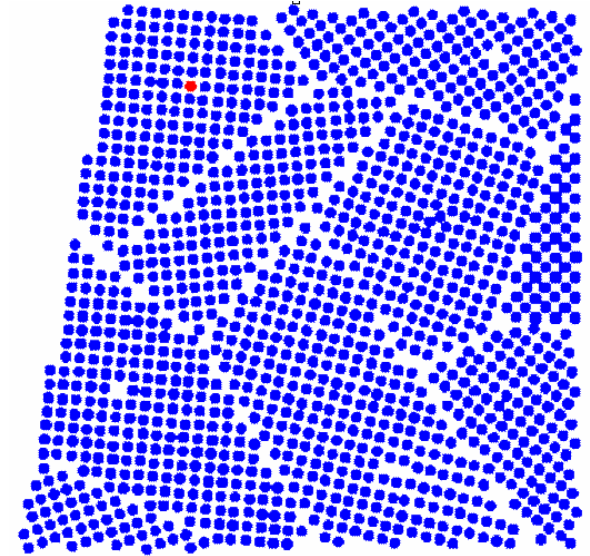
Defects may be classified into four categories depending on their dimension:

- **0D, Point defects** : atoms missing or in irregular places in the lattice
Vacancies, substitutional and interstitial impurities, self-interstitials
- **1D, Linear defects** : **Dislocations** (groups of atoms in irregular positions) e.g. screw and edge dislocations
- **2D, Planar defects**: the interfaces between homogeneous regions of the material
e.g. **Grain boundaries**
(tilt, twist), stacking faults, external surfaces

3D, Bulk or Volume defects

extended defects (pores, cracks)

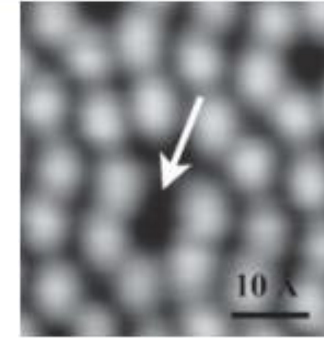
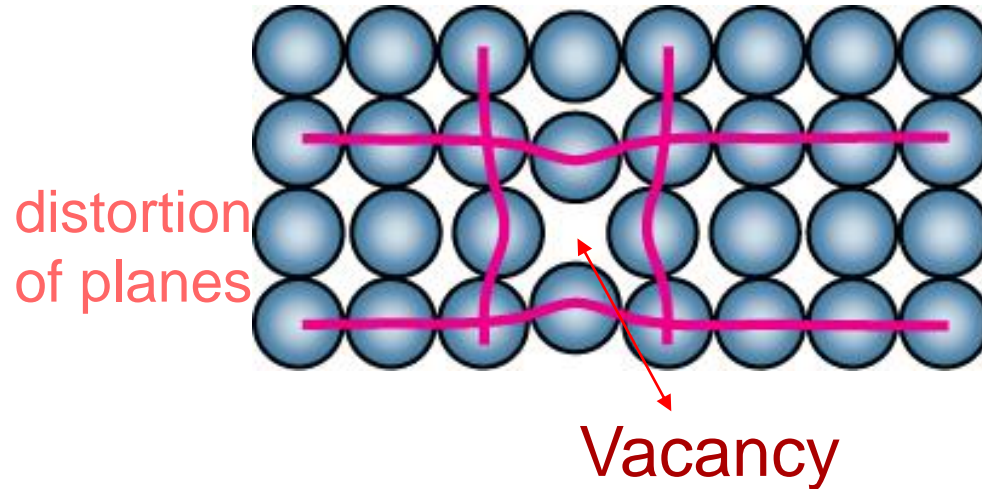
Atomic vibrations



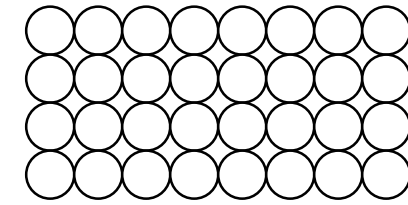


Point Defects: Metals

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

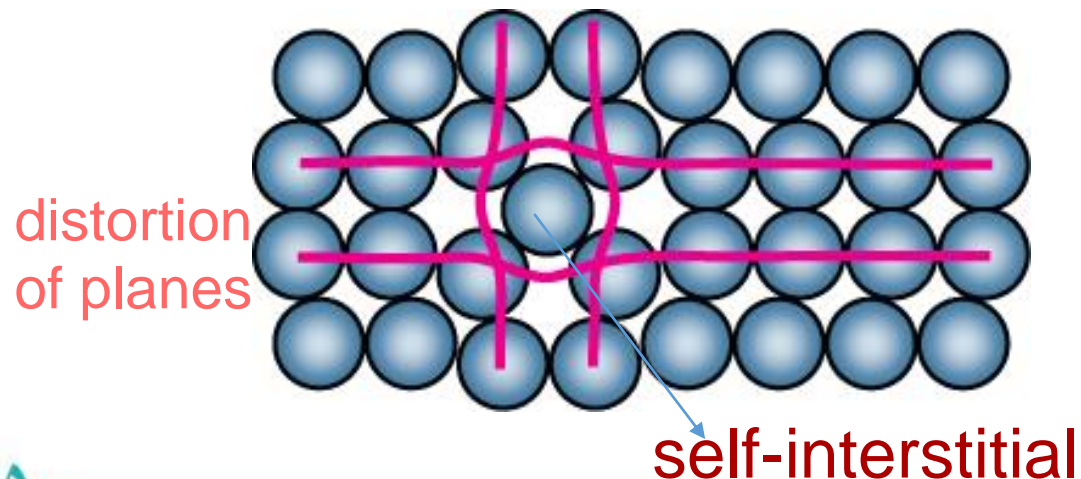


Scanning probe micrograph that shows a vacancy on a (111)-type surface plane for silicon. Approximately 7,000,000 x



Each lattice site
is a potential
vacancy site

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



Equilibrium concentration varies with temperature!

No. of defects $\rightarrow N_v$

No. of potential defect sites. $\rightarrow N$

Activation energy $\rightarrow Q_v$

Boltzmann's constant $\rightarrow k$

Temperature $\rightarrow T$

$$\frac{N_v}{N} = \exp \left(\frac{-Q_v}{kT} \right)$$

(1.38×10^{-23} J/atom-K) (8.62×10^{-5} eV/atom-K)

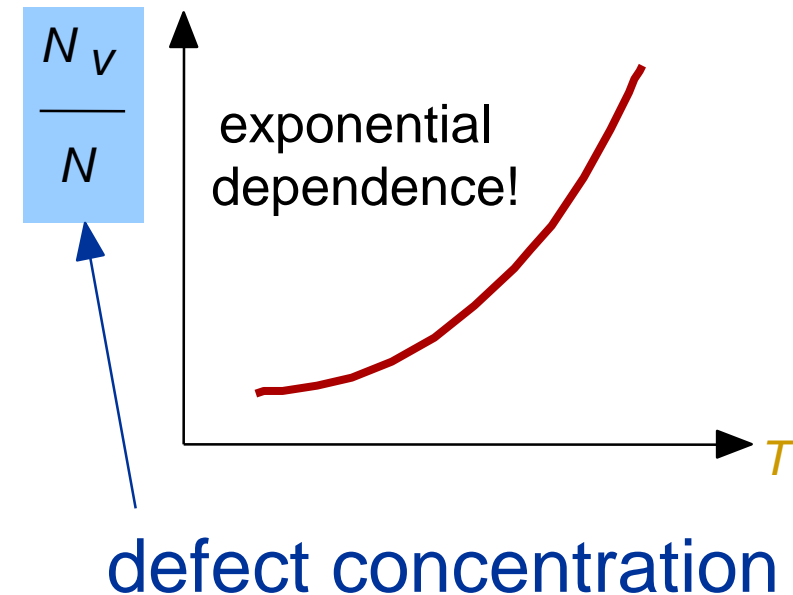


Measuring Activation Energy

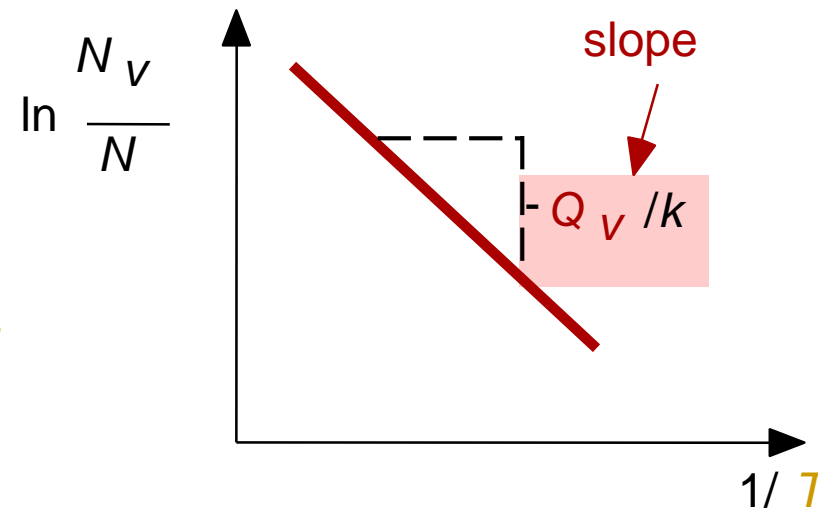
We can get Q_v from an experiment.

$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

- Measure this...



- Replot it...



Find the equilibrium concentration of vacancies in 1 m³ of Cu at 1000°C

- Given:
 $\rho = 8.4 \text{ g/cm}^3$ $A_{\text{Cu}} = 63.5 \text{ g/mol}$
 $Q_v = 0.9 \text{ eV/atom}$ $N_A = 6.02 \times 10^{23} \text{ atoms/mol}$

$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right) = 2.7 \times 10^{-4}$$

For 1 m³

$$N = \rho \times \frac{N_A}{A_{\text{Cu}}} \times 1 \text{ m}^3 = 8.0 \times 10^{28} \text{ sites}$$

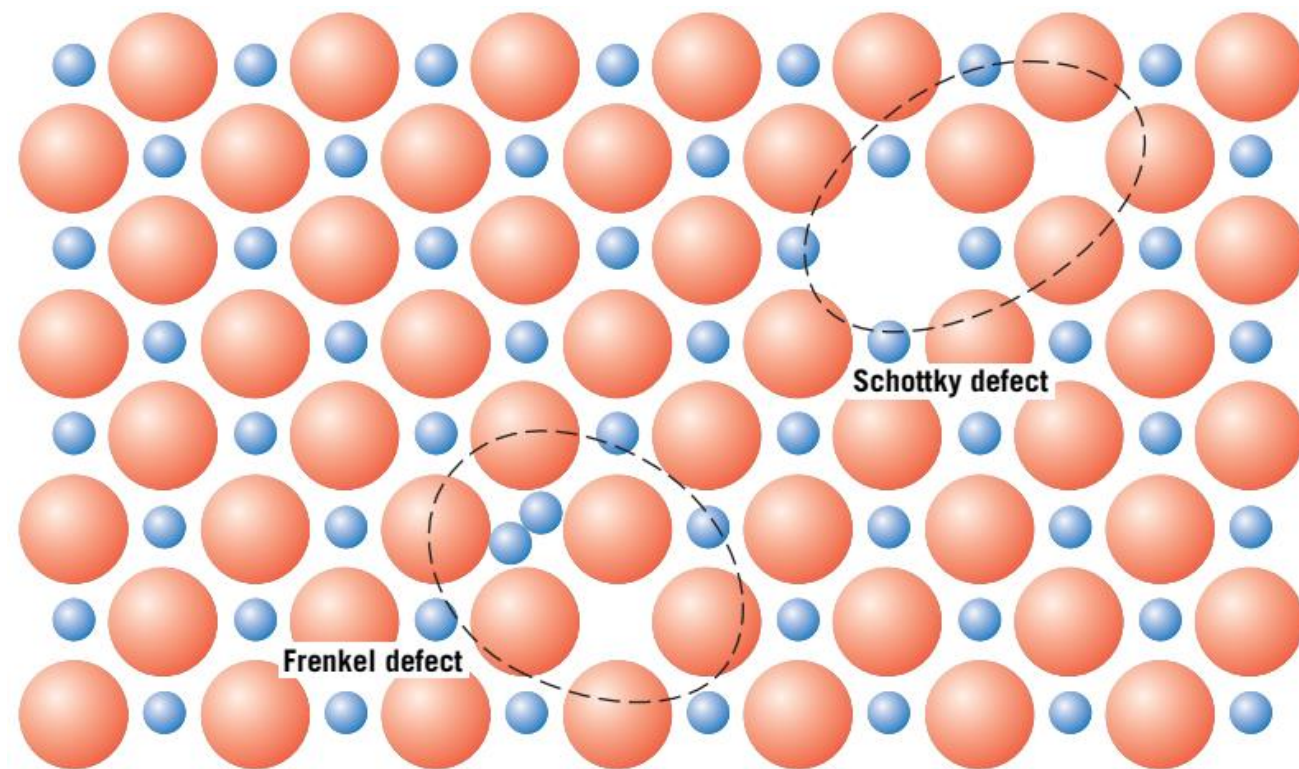
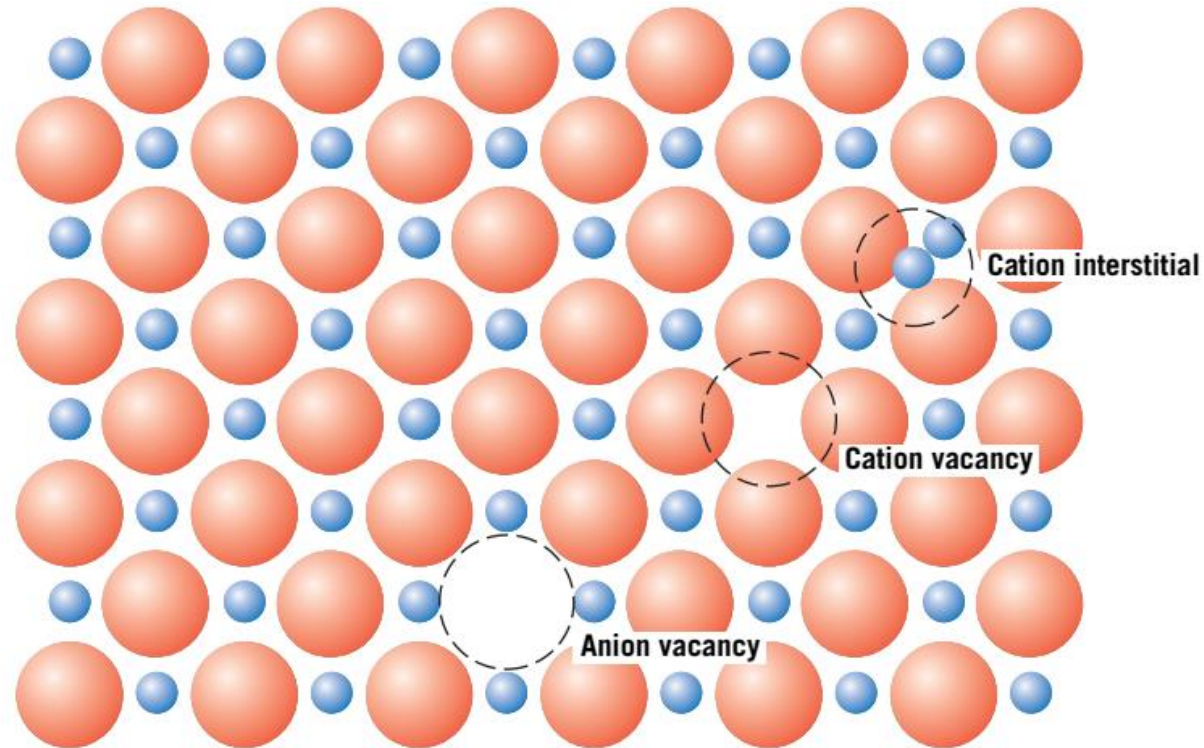
- Answer: $N_v = (2.7 \times 10^{-4})(8.0 \times 10^{28}) \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$



Point Defects in Ceramics

Atoms exist as charged ions - conditions of electroneutrality must be maintained.

Electroneutrality is the state that exists when there are equal numbers of positive and negative charges from the ions.



Frenkel defect: defect involves a cation–vacancy and a cation–interstitial pair

Schottky defect : is a cation vacancy–anion vacancy pair

The ratio of cations to anions is not altered by the formation of either a **Frenkel** or a **Schottky** defect.



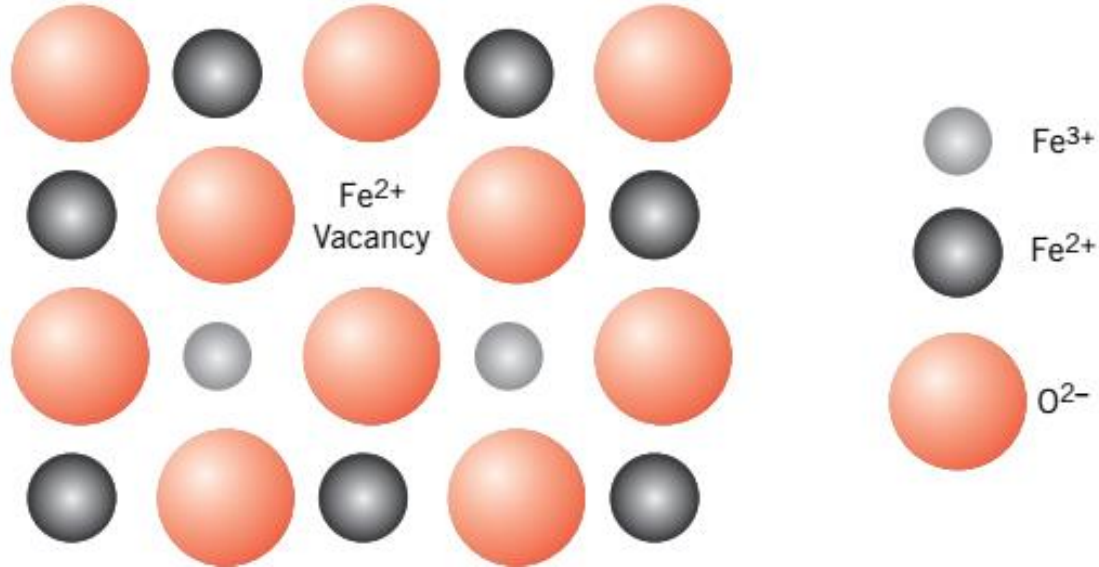


Point Defects in Ceramics

Stoichiometry: state for ionic compounds wherein there is the exact ratio of cations to anions predicted by the chemical formula.

Nonstoichiometric : if there is any deviation from this exact ratio

Iron oxide (wüstite, FeO)



For Frenkel defects, the number of cation–vacancy/cation–interstitial defect pairs (N_{fr})

$$N_{fr} = N \exp\left(-\frac{Q_{fr}}{2kT}\right)$$

For Schottky defects; the equilibrium number (N_s)

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right)$$

Formation Fe^{3+} ion : disrupts electroneutrality
- accomplished by the formation of one Fe^{2+} vacancy for every two Fe^{3+} ions

Charge neutrality is established, but not the stoichiometry





Impurities In Solids : Solid Solutions

Even with sophisticated techniques, it is difficult to refine metals to a purity in excess of 99.9999%. At this level, on the order of 10^{22} - 10^{23} impurity atoms are present in 1 m^3 of material. Most familiar metals are not highly pure; rather, they are **alloys**

- Impurity atoms to a metal results in the formation of a **Solid Solution** and/or a new **second phase**, depending on the **kinds of impurity**, their **concentrations**, and the **temperature** of the alloy

Solvent: element or compound that is present in the greatest amount

Solute: element or compound present in a minor concentration

Solid Solutions: forms when the solute atoms are added to the host material, - the crystal structure is maintained and no new structures are formed.

- compositionally homogeneous
- impurity atoms are randomly and uniformly dispersed
- Impurity point defects are found in solid solutions (**substitutional** and **interstitial**)

Several features of the solute and solvent atoms determine the degree to which the former dissolves in the latter.

These are expressed as four **Hume-Rothery rules** :

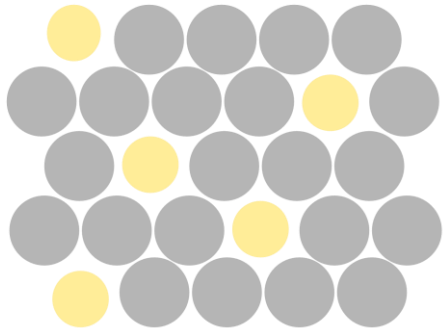
1. **Atomic size factor**. Appreciable quantities of a solute may be accommodated in this type of solid solution only when the **difference in atomic radii** is $< \pm 15\%$. Otherwise the solute atoms create substantial lattice distortions and a new phase forms.
2. **Crystal structure**. For appreciable solid solubility, the crystal structures for metals of both atom types must be the same.
3. **Electronegativity factor**. The more electropositive one element and the more electronegative the other, the greater the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.
4. **Valences**. Other factors being equal, **a metal** has more of a tendency to dissolve another metal of higher valency than to dissolve one of a lower valency.



Solid Solutions

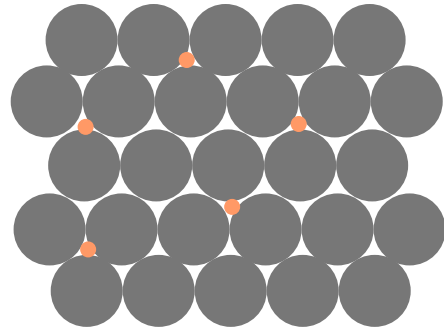
Two outcomes if impurity (B) added to host (A):

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



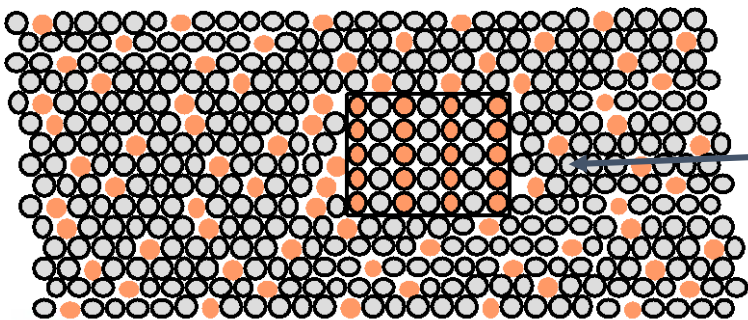
Substitutional solid soln.
(e.g., **Cu** in Ni)

OR



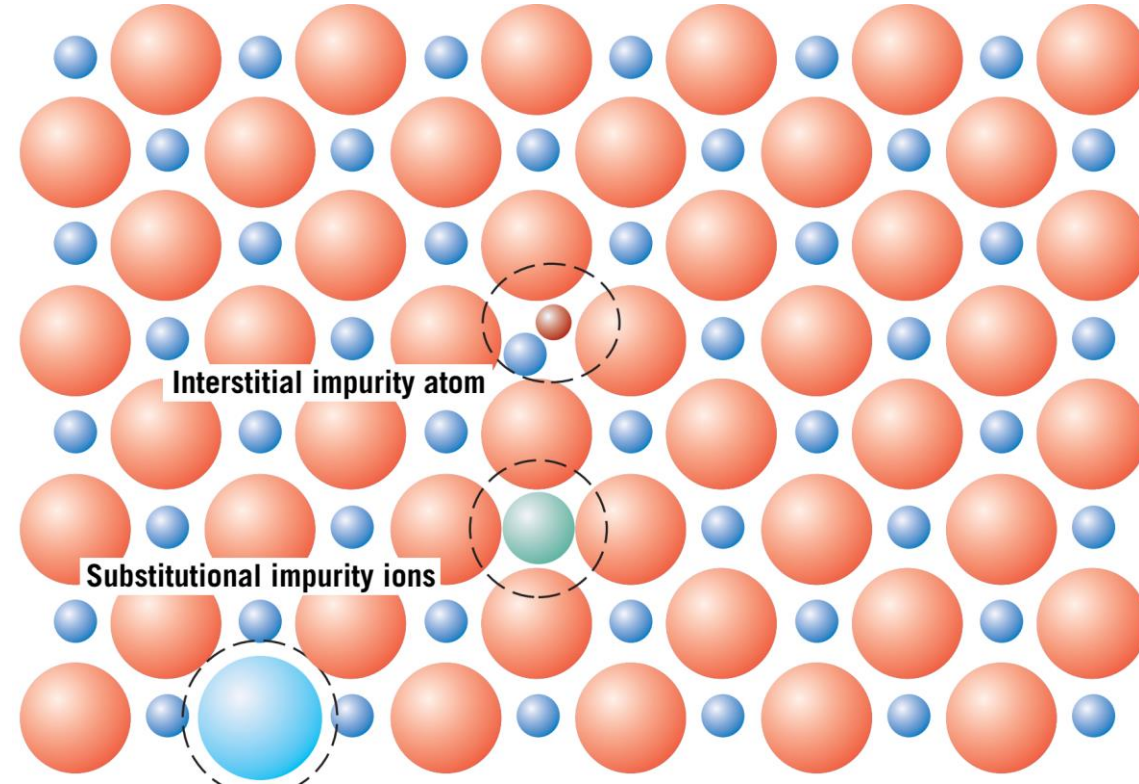
Interstitial solid soln.
(e.g., **C** in Fe)

- 2) 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.

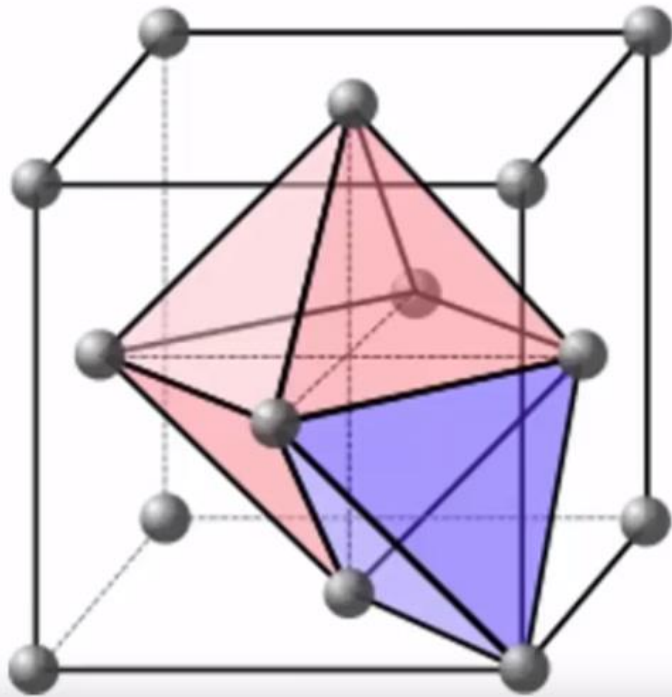
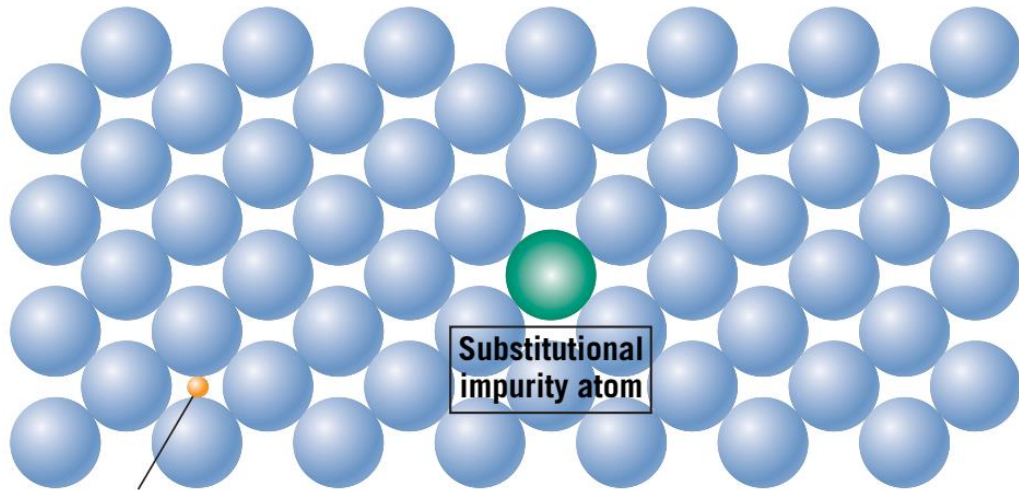
Impurities in Ceramics



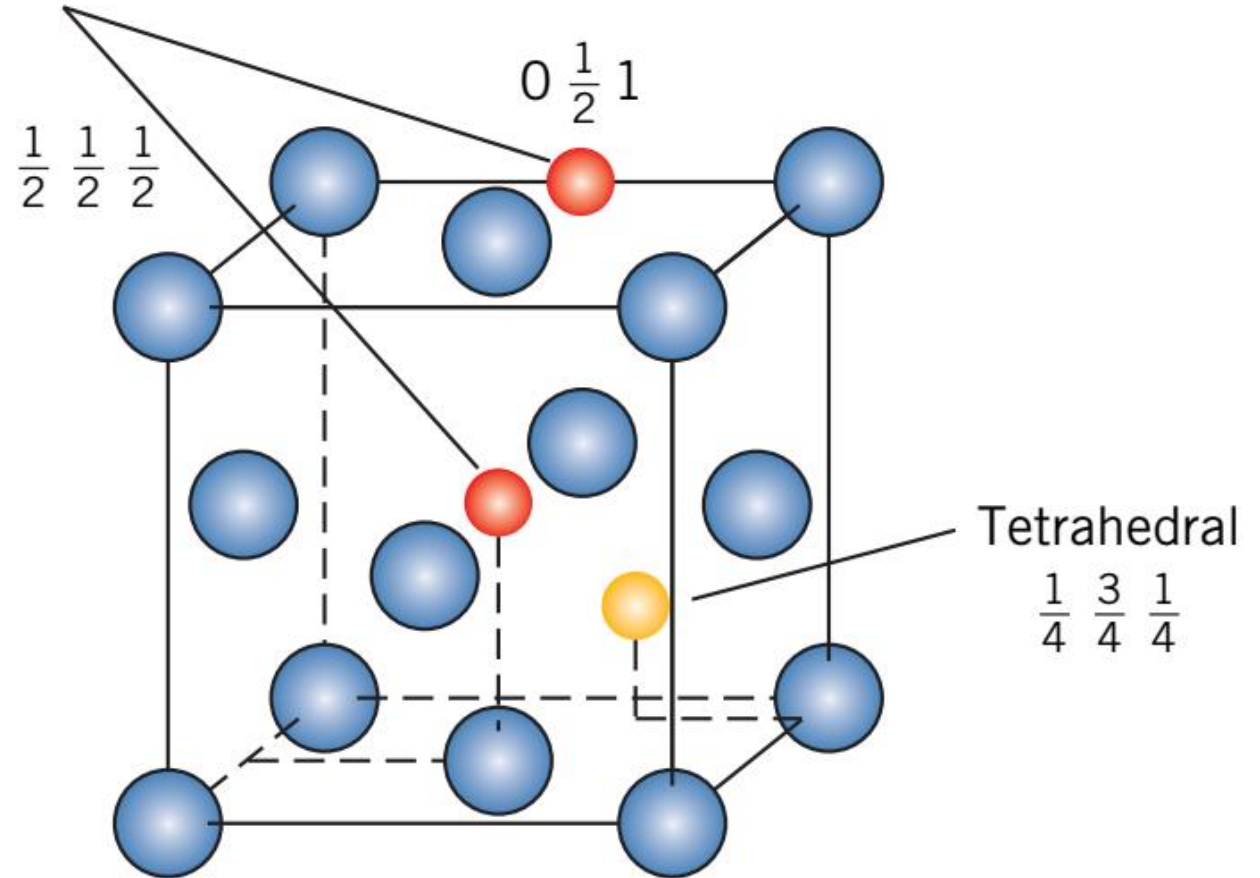
For example, in sodium chloride, impurity Ca^{2+} and O^{2-} ions would most likely substitute for Na^+ and Cl^- ions, respectively.



FCC Interstitial Sites: Octahedral & Tetrahedral



Octahedral

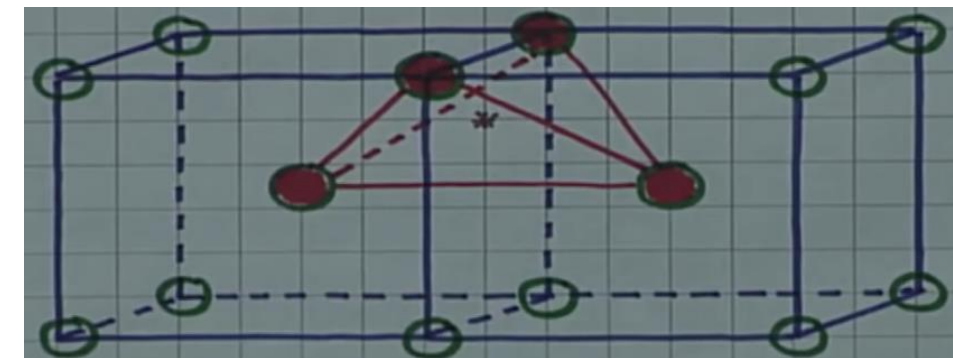
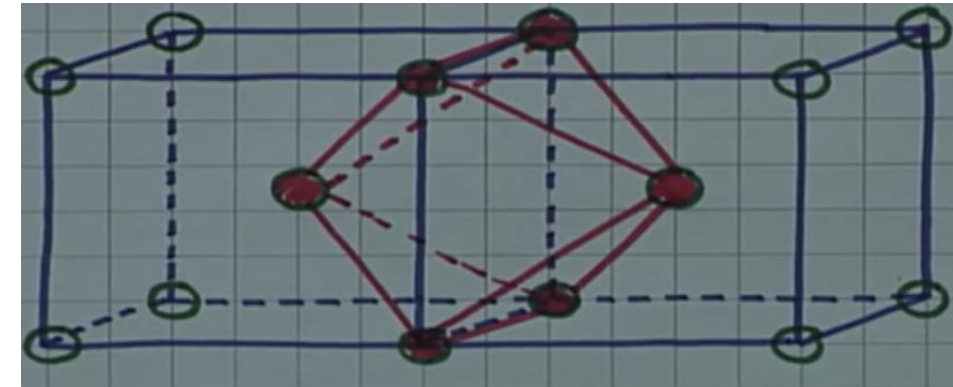
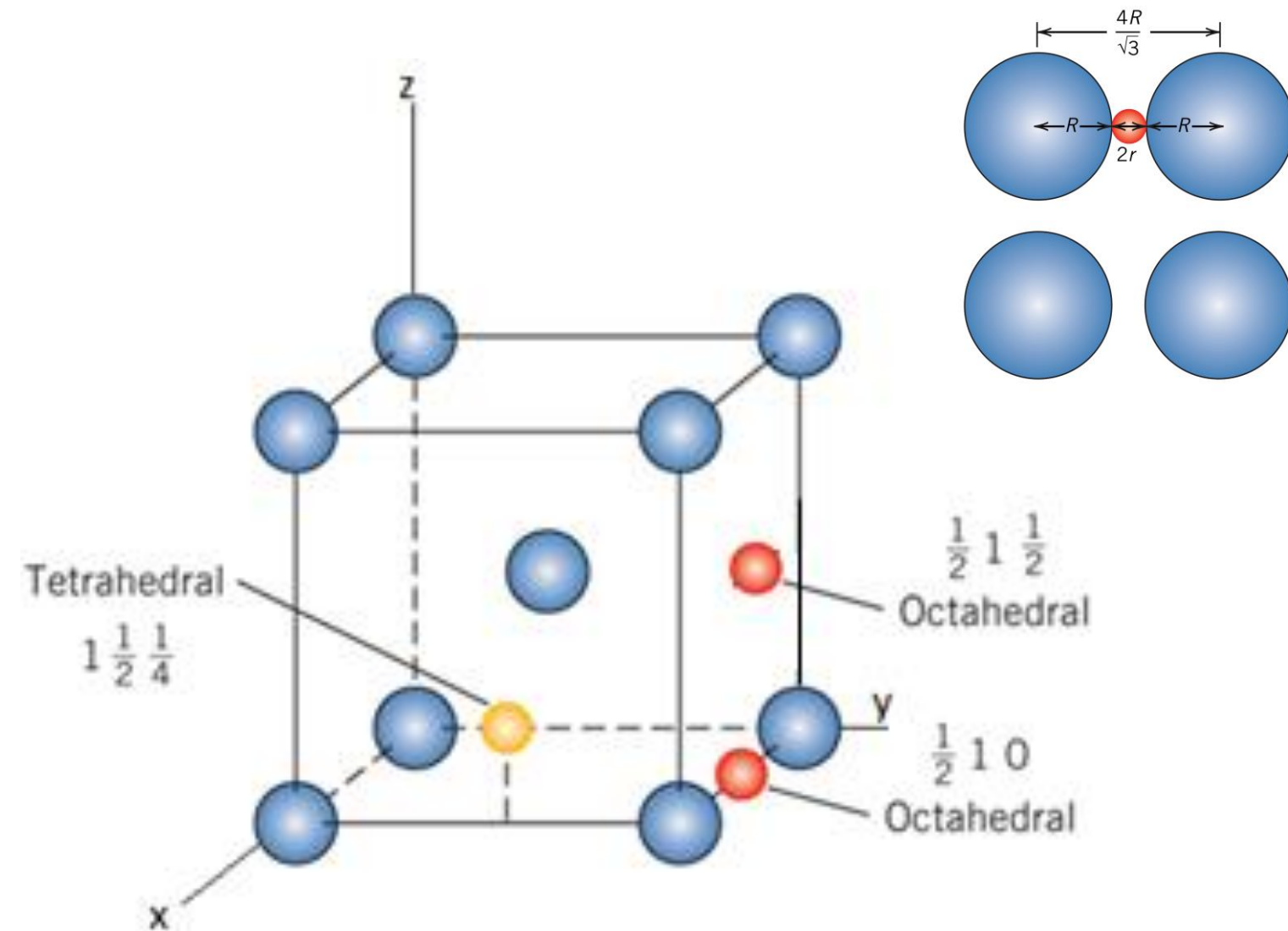


Locations of tetrahedral and octahedral interstitial sites within FCC and unit cells



BCC Interstitial Sites: Octahedral & Tetrahedral

Locations of tetrahedral and octahedral interstitial sites within BCC and unit cells





Solid Solutions

Application of Hume–Rothery rules – Solid Solutions

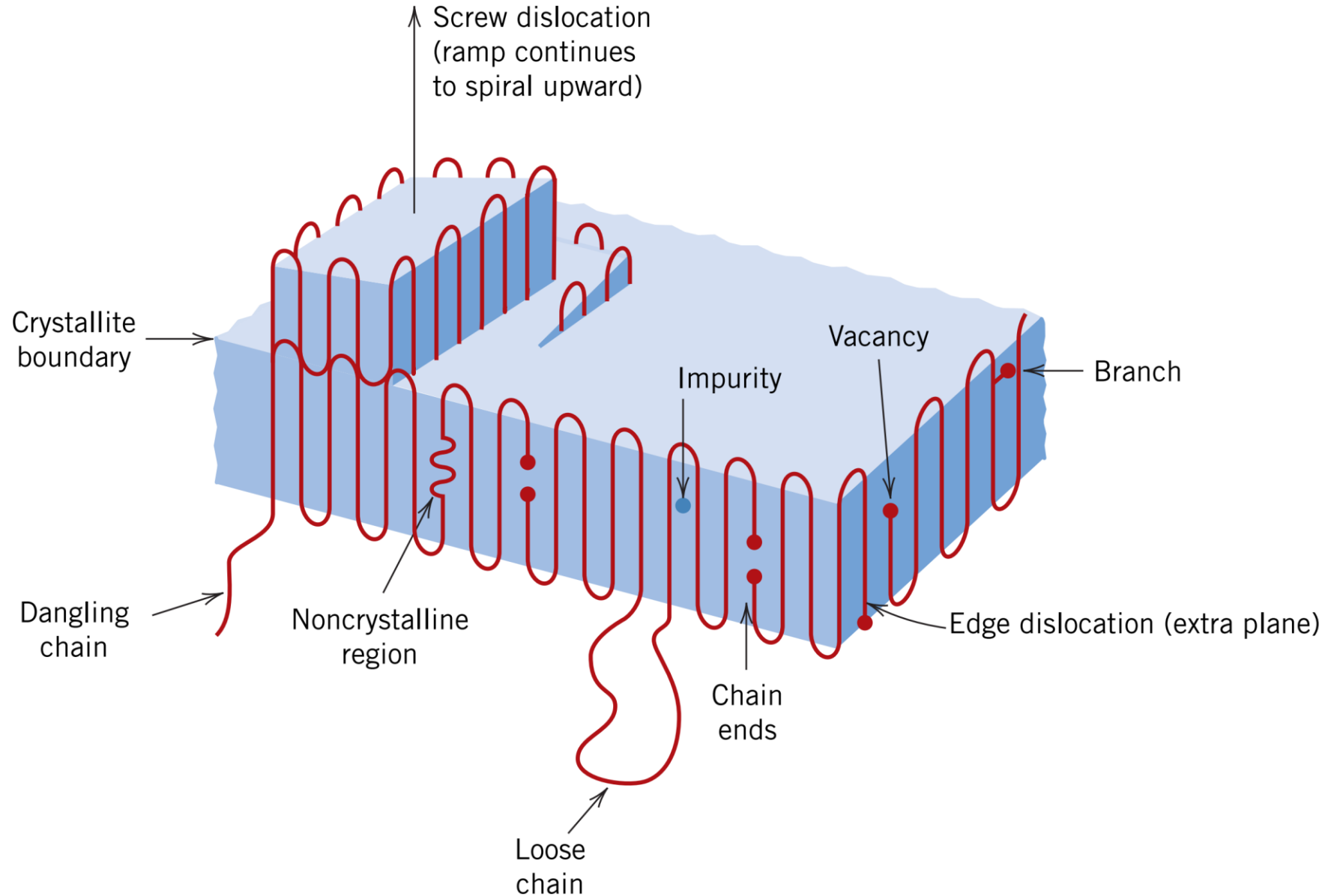
1. Would you predict more Al or Ag to dissolve in Zn?

2. More Zn or Al in Cu?

<i>Element</i>	<i>Atomic Radius (nm)</i>	<i>Crystal Structure</i>	<i>Electro-negativity</i>	<i>Valence</i>
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2



Point Defects In Polymers





Specification of Composition

To express the **composition** (or *concentration*) of an alloy in terms of its constituent elements

- Weight percent (wt%) : the weight of a particular element relative to the total alloy weight.

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

m_1 = mass of component 1

$$C_1 = \frac{m_1}{m_1 + m_2 + m_3 + \dots + m_n} \times 100$$

- Atom percent (at%): is the number of moles of an element in relation to the total moles of the elements in the alloy.

n_{m1} = number of moles of component 1

$$n_{m1} = \frac{m'_1}{A_1}$$

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2} + n_{m3} + \dots + n_{mn}} \times 100$$

m'_1 and A_1 denote the mass (in grams) and atomic weight





Composition Conversions

To convert wt% denoted by C_1 and C_2 , **at%** by C'_1 and C'_2 , and atomic weights as A_1 and A_2

$$C_1 + C_2 = 100$$

$$C'_1 + C'_2 = 100$$

Derivation of Composition-Conversion Equation

Assume that masses are expressed in units of grams and denoted with a prime (e.g., m'_1). Furthermore, the total alloy mass (in grams) M' is

$$M' = m'_1 + m'_2 \quad \& \quad n_{m1} = \frac{m'_1}{A_1}$$

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100 \quad \rightarrow \quad m'_1 = \frac{C_1 M'}{100}$$

$$\begin{aligned} C'_1 &= \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \\ &\downarrow \\ &= \frac{\frac{m'_1}{A_1}}{\frac{m'_1}{A_1} + \frac{m'_2}{A_2}} \times 100 \end{aligned}$$

$$C'_1 = \frac{\frac{C_1 M'}{100 A_1}}{\frac{C_1 M'}{100 A_1} + \frac{C_2 M'}{100 A_2}} \times 100$$

$$C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C'_2 = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100$$

$$C_1 = \frac{C'_1 A_1}{C'_1 A_1 + C'_2 A_2} \times 100$$

$$C_2 = \frac{C'_2 A_2}{C'_1 A_1 + C'_2 A_2} \times 100$$



Composition Conversions

Weight percent to mass of one component per unit volume of material
(i.e., from units of wt% to kg/m³)

density ρ in units of g/cm³; C''_1 and C''_2 in kg/m³

Concentrations in terms C''_1 and C''_2

$$C''_1 = \left(\frac{C_1}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}} \right) \times 10^3$$

$$C''_2 = \left(\frac{C_2}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}} \right) \times 10^3$$

$$\rho_{\text{ave}} = \frac{C'_1 A_1 + C'_2 A_2}{\frac{C'_1 A_1}{\rho_1} + \frac{C'_2 A_2}{\rho_2}}$$

$$\rho_{\text{ave}} = \frac{100}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}}$$

$$A_{\text{ave}} = \frac{100}{\frac{C_1}{A_1} + \frac{C_2}{A_2}}$$

$$A_{\text{ave}} = \frac{C'_1 A_1 + C'_2 A_2}{100}$$



Dislocations—linear Defects

Dislocations:

- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

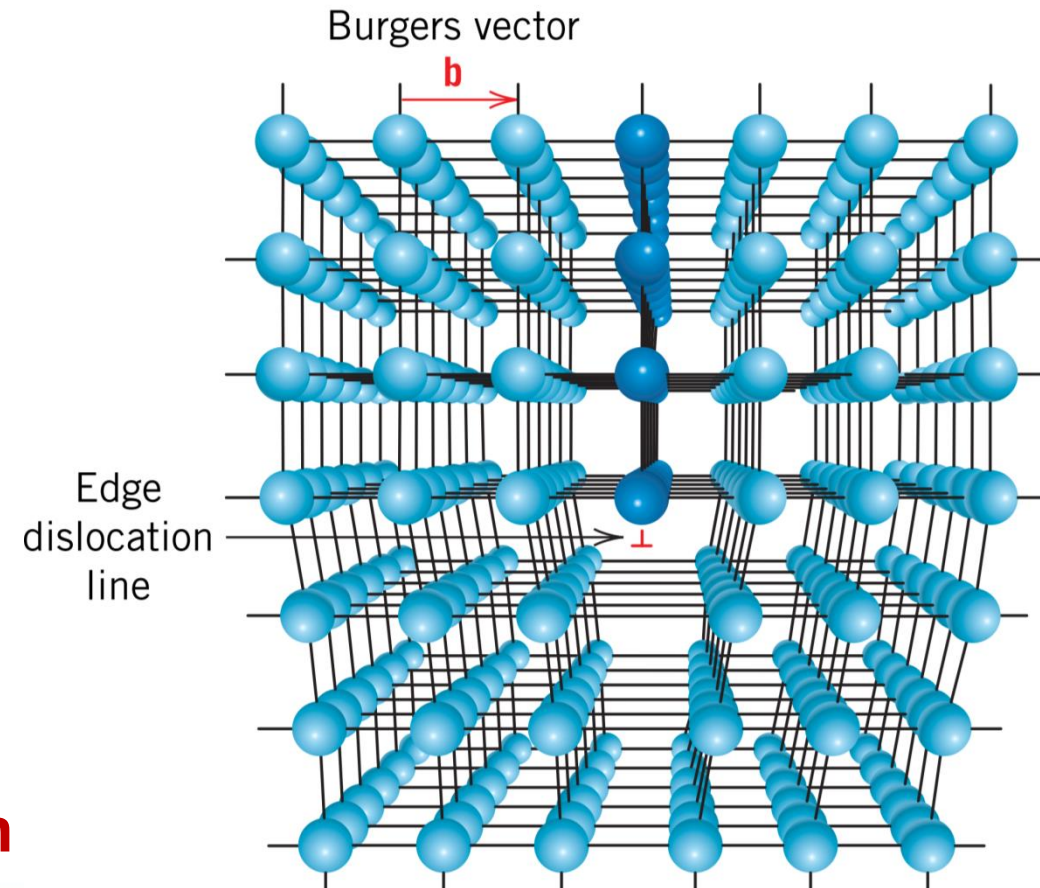
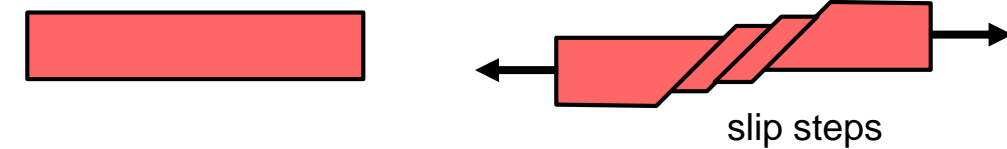
Linear Defects (Dislocations)

- Are one-dimensional defects around which atoms are misaligned
- **Edge dislocation:**
 - extra half-plane of atoms inserted in a crystal structure
 - $\mathbf{b} \perp$ to dislocation line
- **Screw dislocation:**
 - spiral planar ramp resulting from shear deformation
 - $\mathbf{b} \parallel$ to dislocation line

Burger's vector, \mathbf{b} : measure of lattice distortion

Schematic of Zinc (HCP):

- before deformation
- after tensile elongation

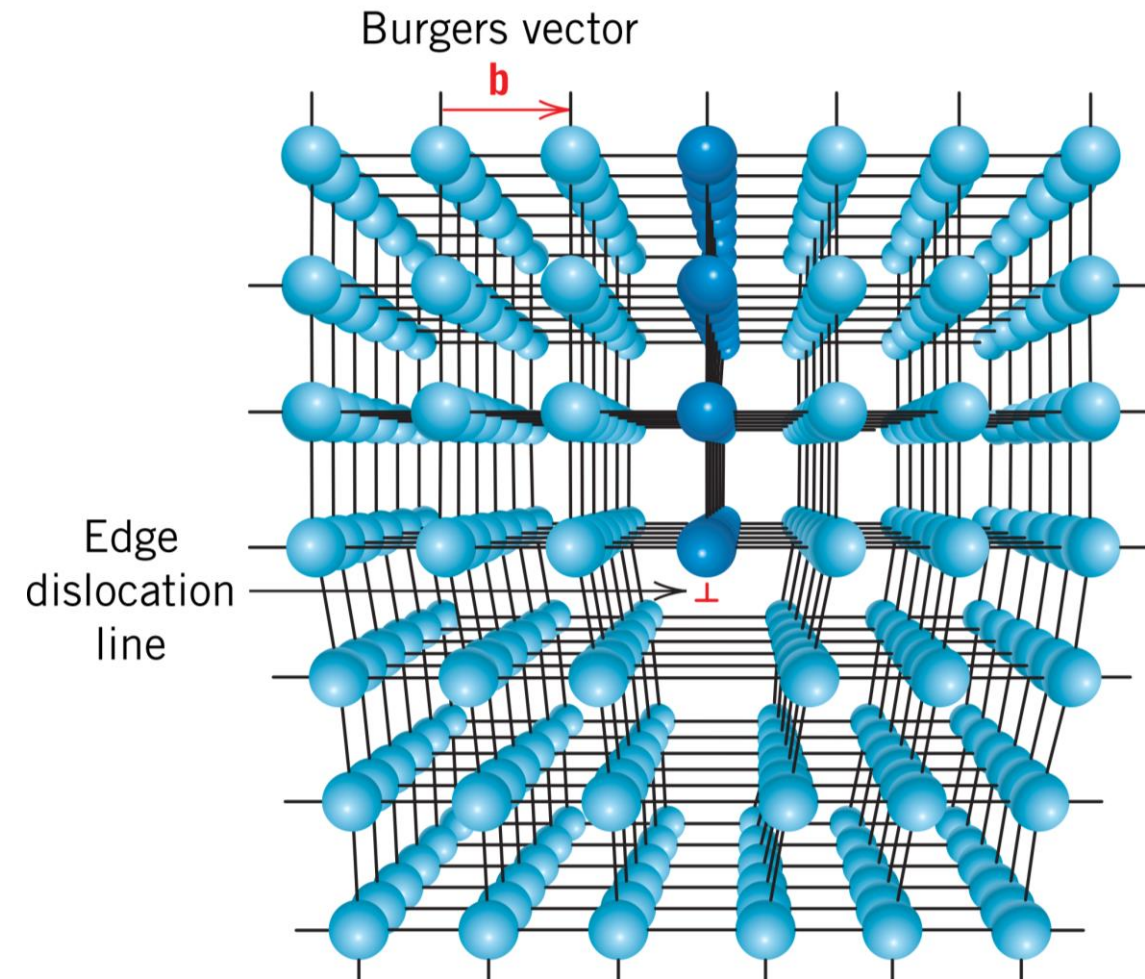
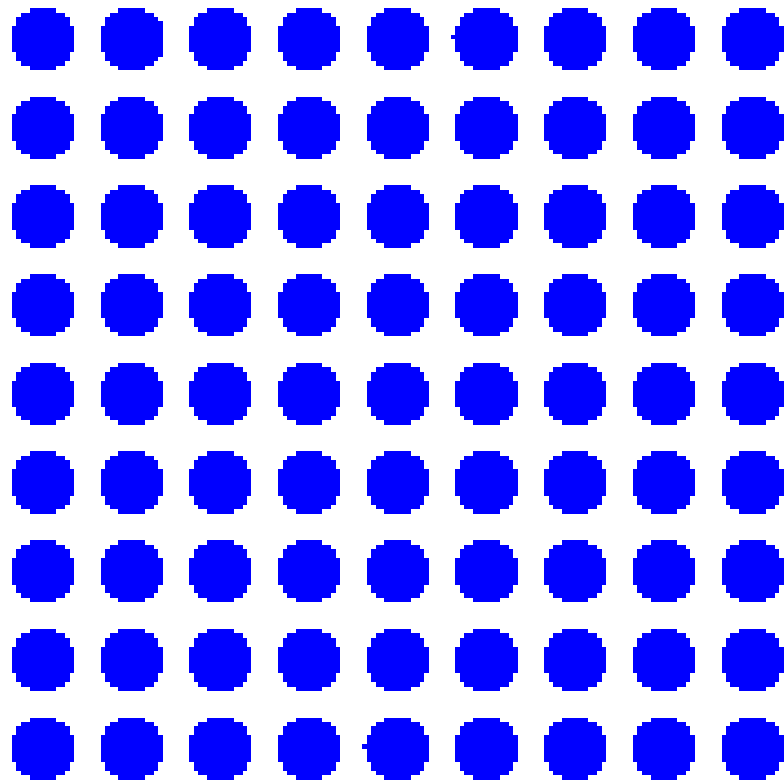




Motion of Edge Dislocation

- 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.

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

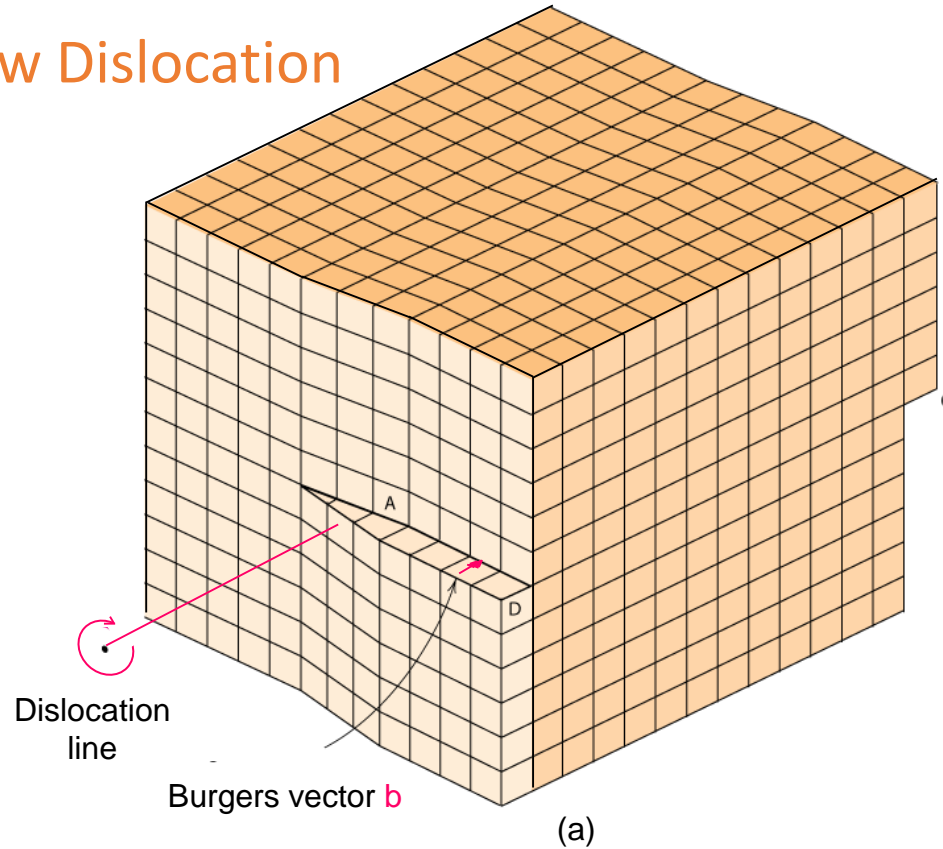




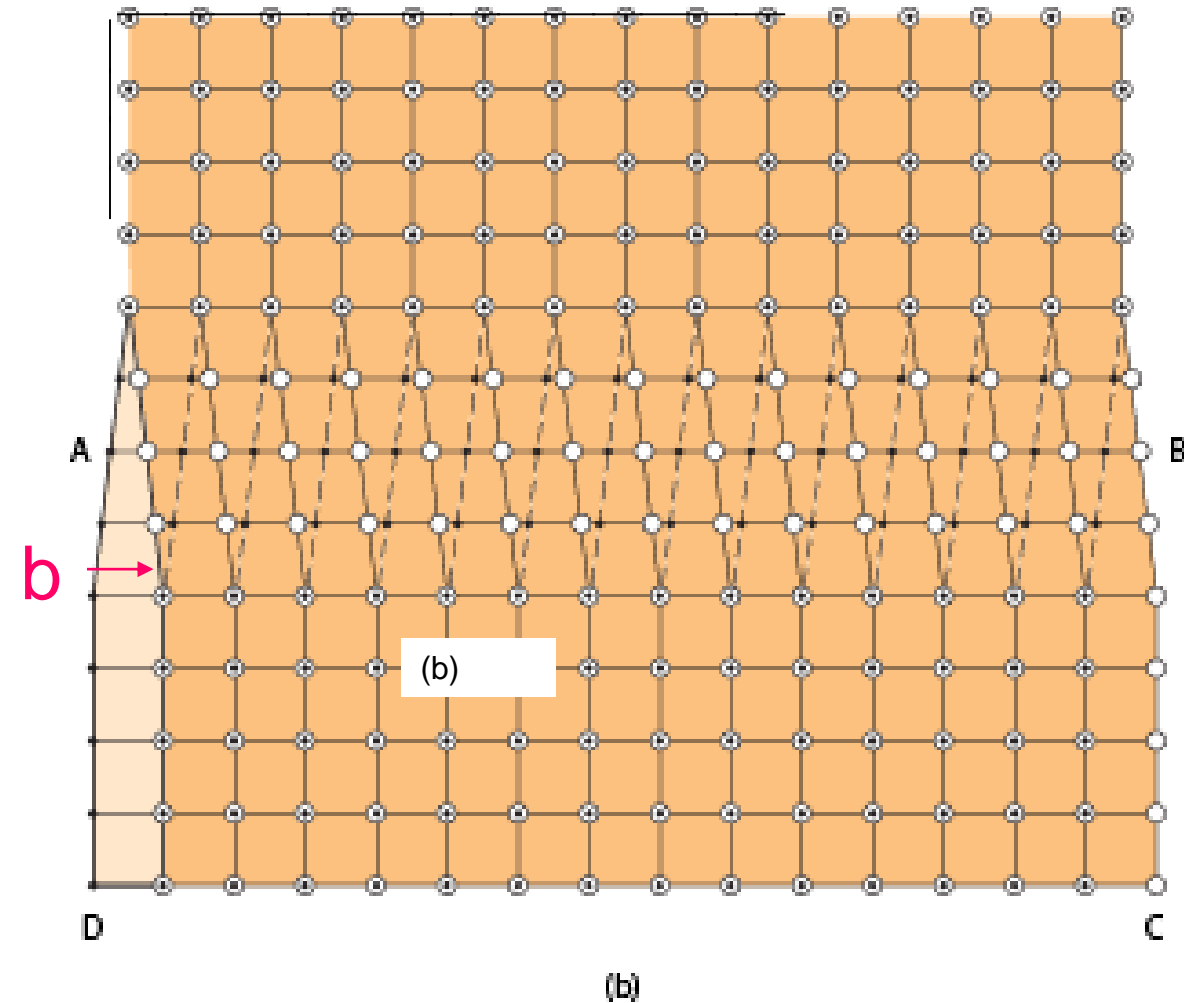
Screw Dislocation

Screw dislocation - formed by a shear stress that is applied to produce the distortion

Screw Dislocation



The atomic distortion associated with a screw dislocation is also linear and along a dislocation line; AB line

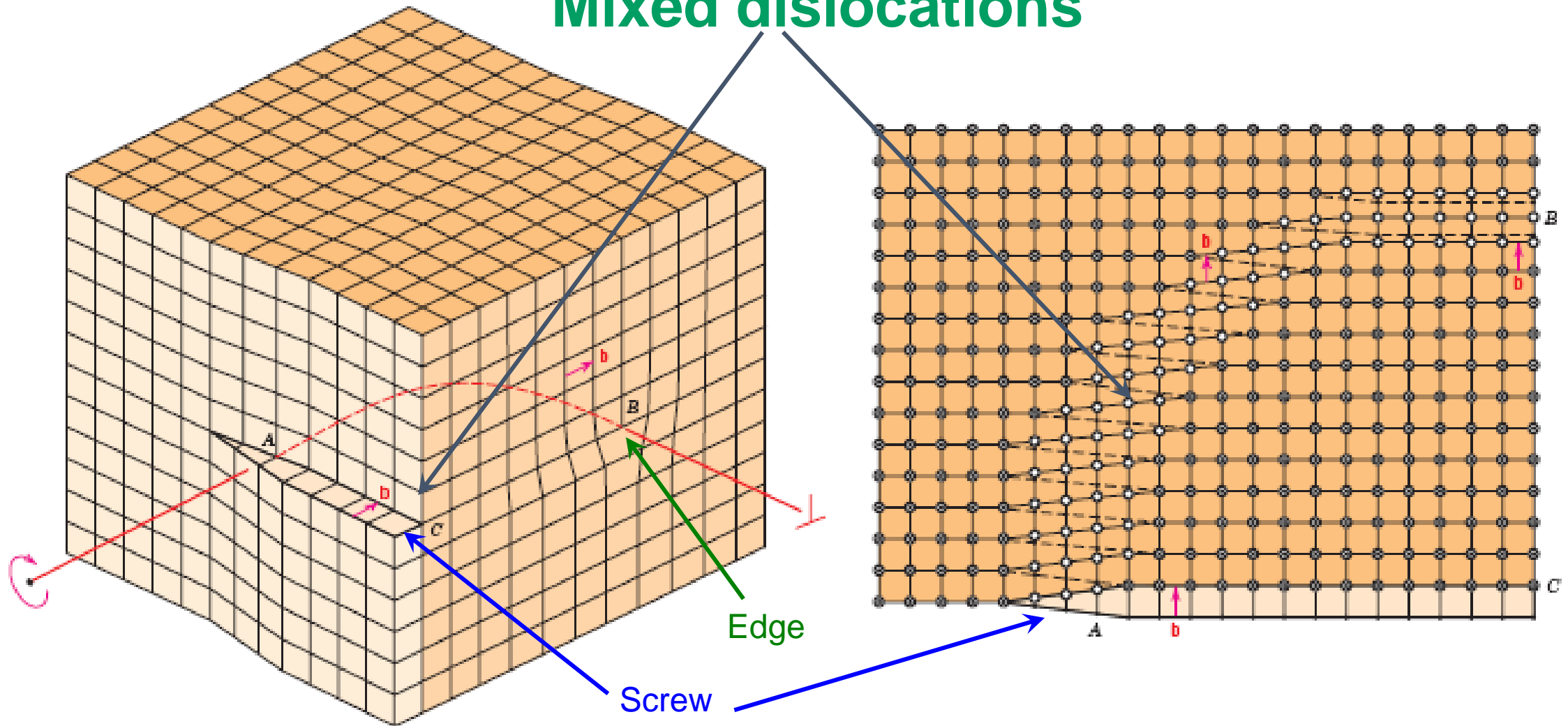




Edge, Screw, and Mixed Dislocations

Most dislocations found in crystalline materials are probably neither pure edge nor pure screw but exhibit components of both types; these are termed

Mixed dislocations

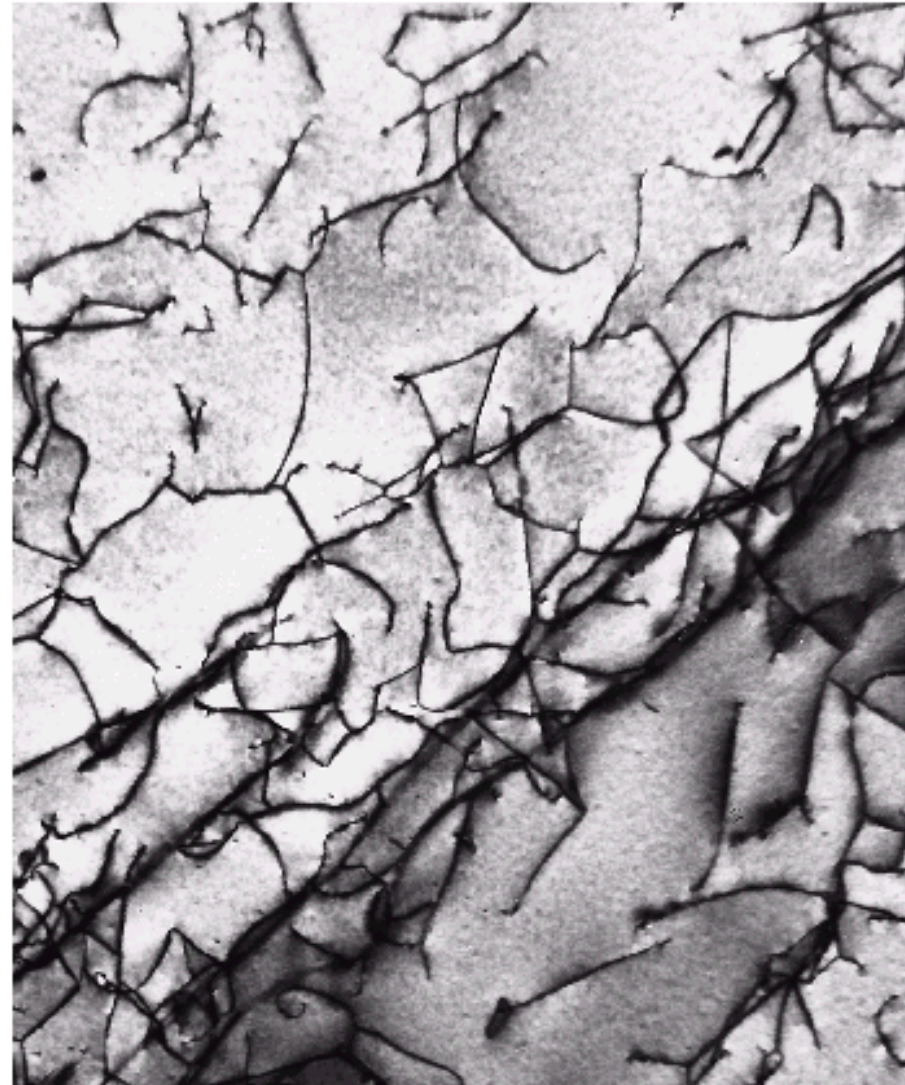




Dislocations—linear Defects

Dislocations are visible in electron micrographs

A transmission electron micrograph of a titanium alloy in which the dark lines are dislocations.
51,450×



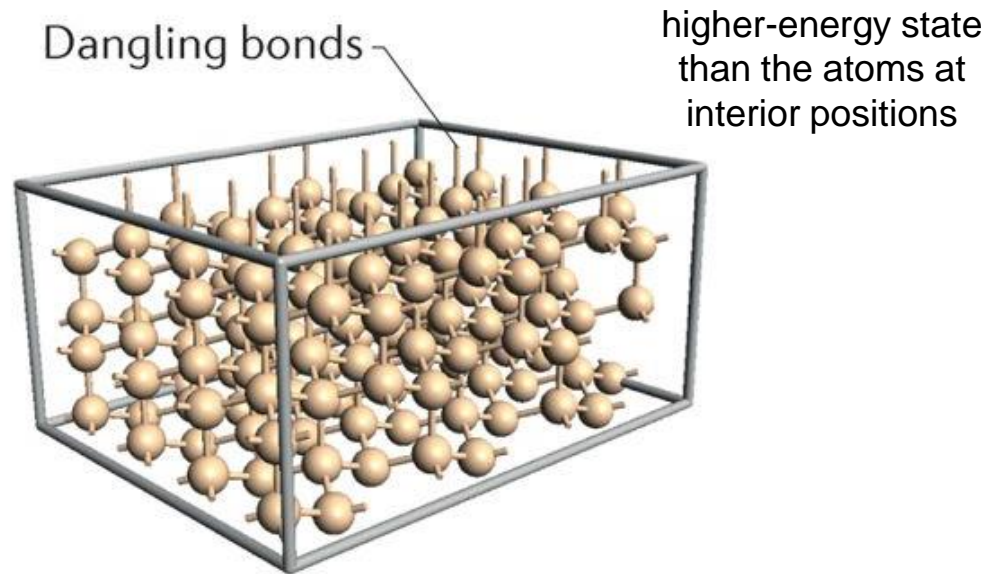


Interfacial Defects

Interfacial defects are boundaries that have two dimensions and normally separate regions of the materials that have different **crystal structures** and/or **crystallographic orientations**.

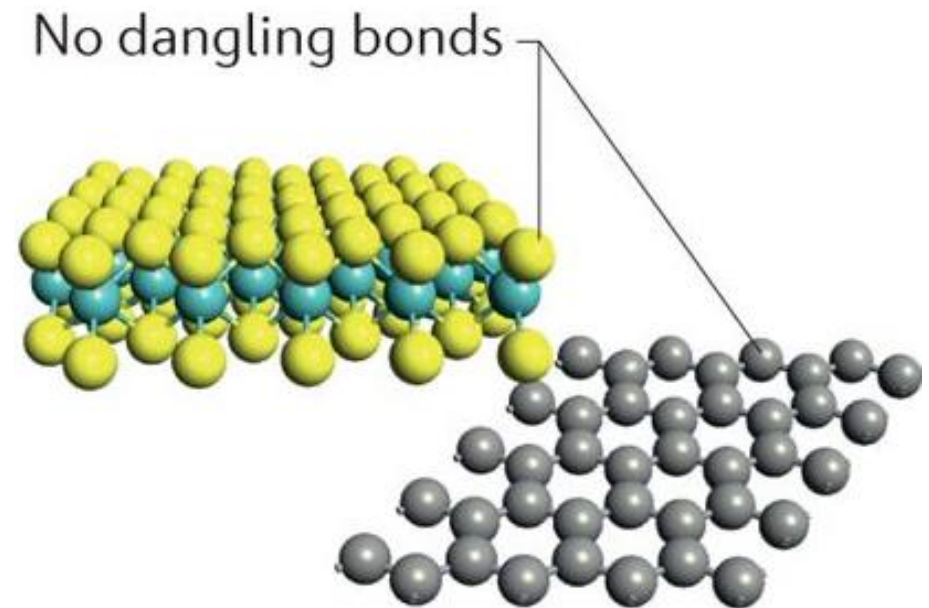
- **external surfaces**, **grain boundaries**, **phase boundaries**, **twin boundaries**, and **stacking faults**.

External surfaces



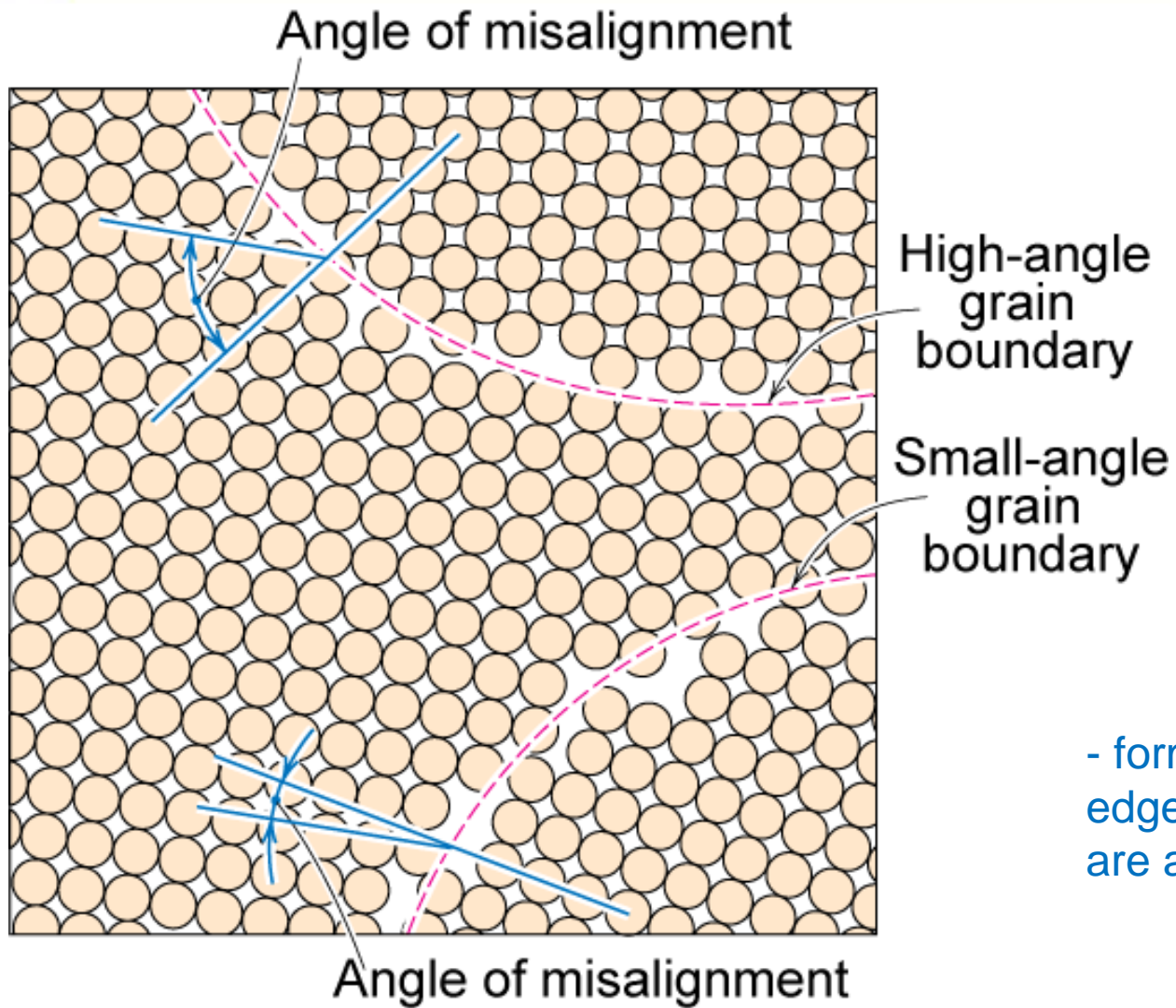
- give rise to a surface energy,
- energy per unit area (J/m^2 or erg/cm^2)

2D materials



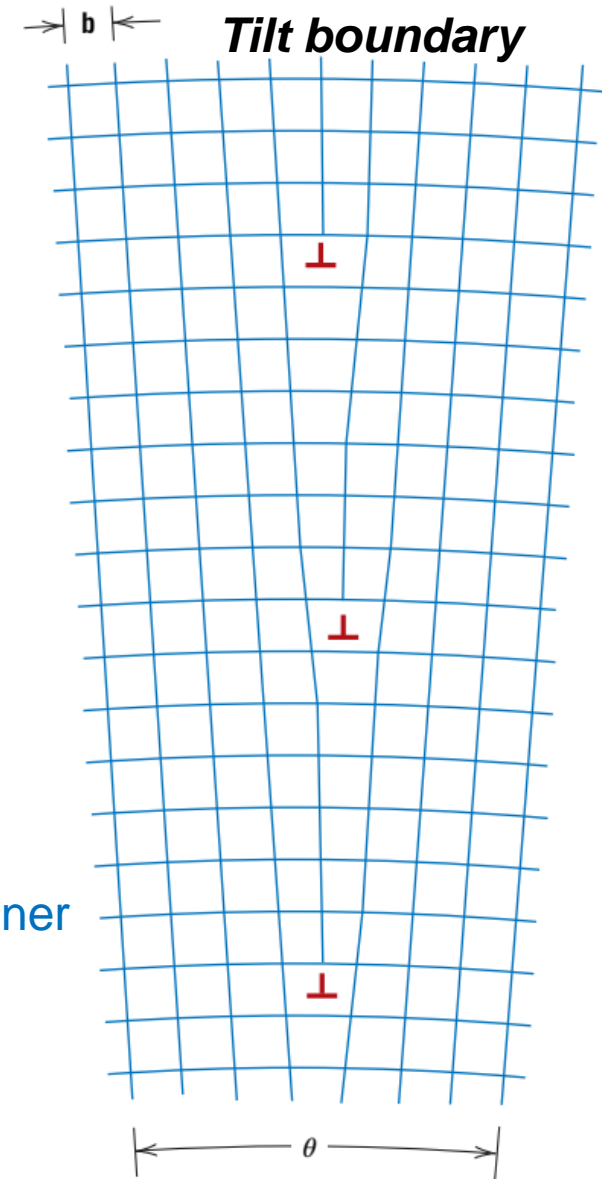


Interfacial Defects : Grain Boundaries



- formed when edge dislocations are aligned in the manner

tilt boundary

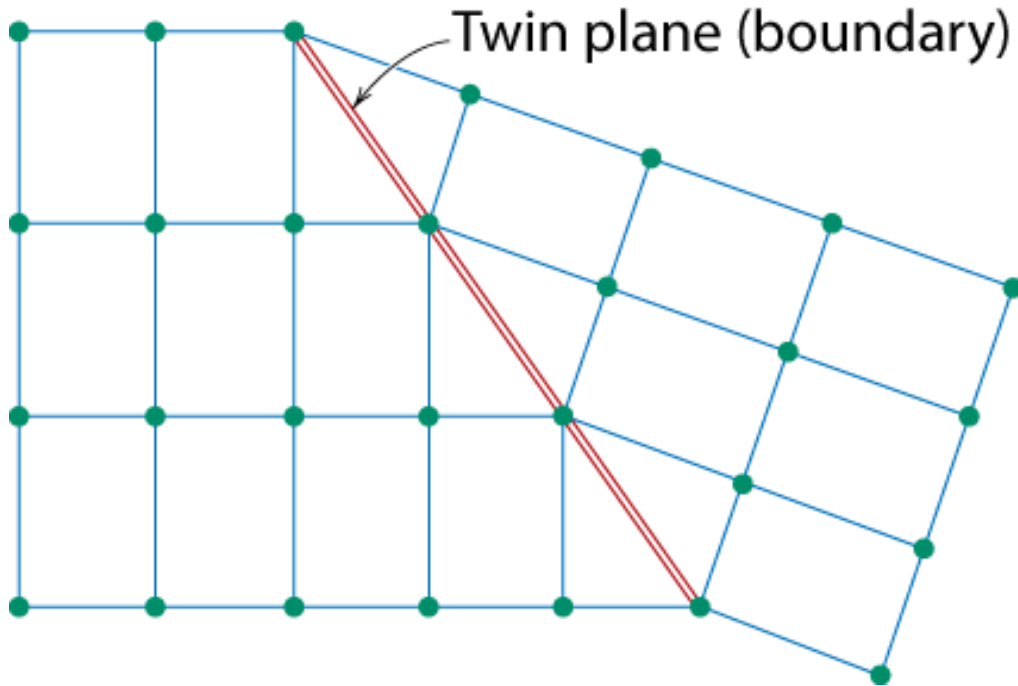




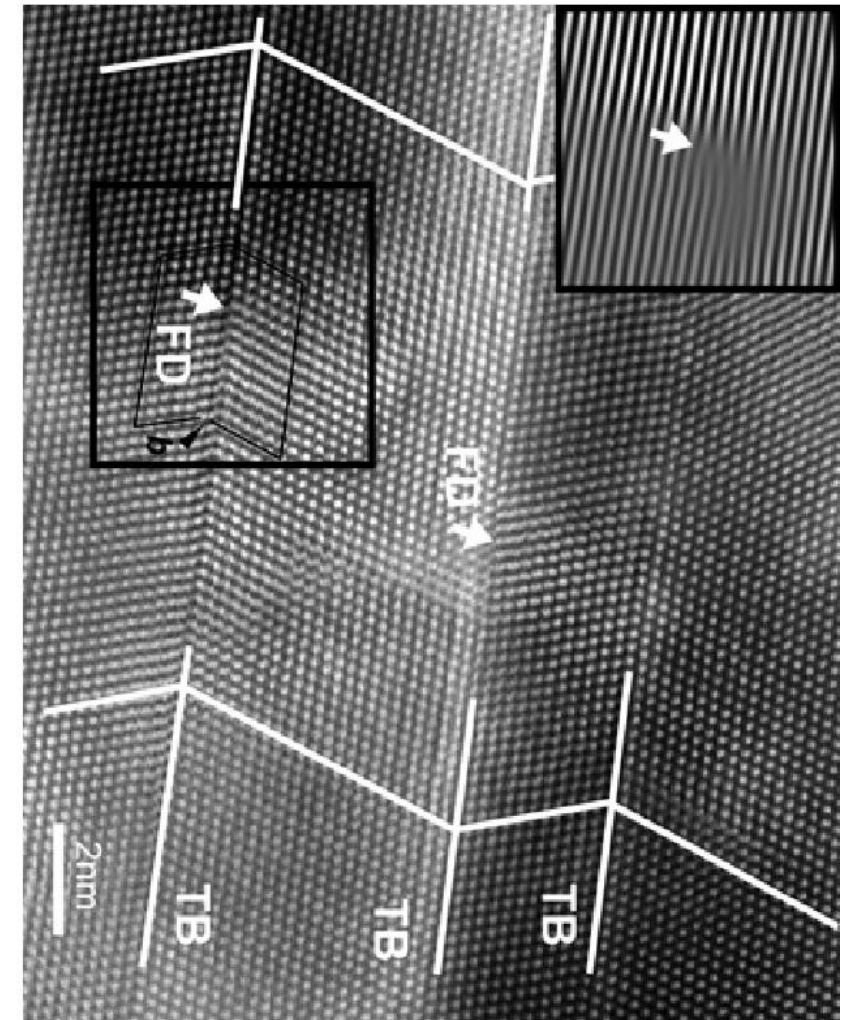
Planar Defects in Solids

One case is a **twin boundary (plane)**

Essentially a reflection of atom positions across the **twin plane**.



- result from atomic displacements that are produced from applied mechanical shear forces (mechanical twins) and also during annealing heat treatments following deformation (annealing twins)



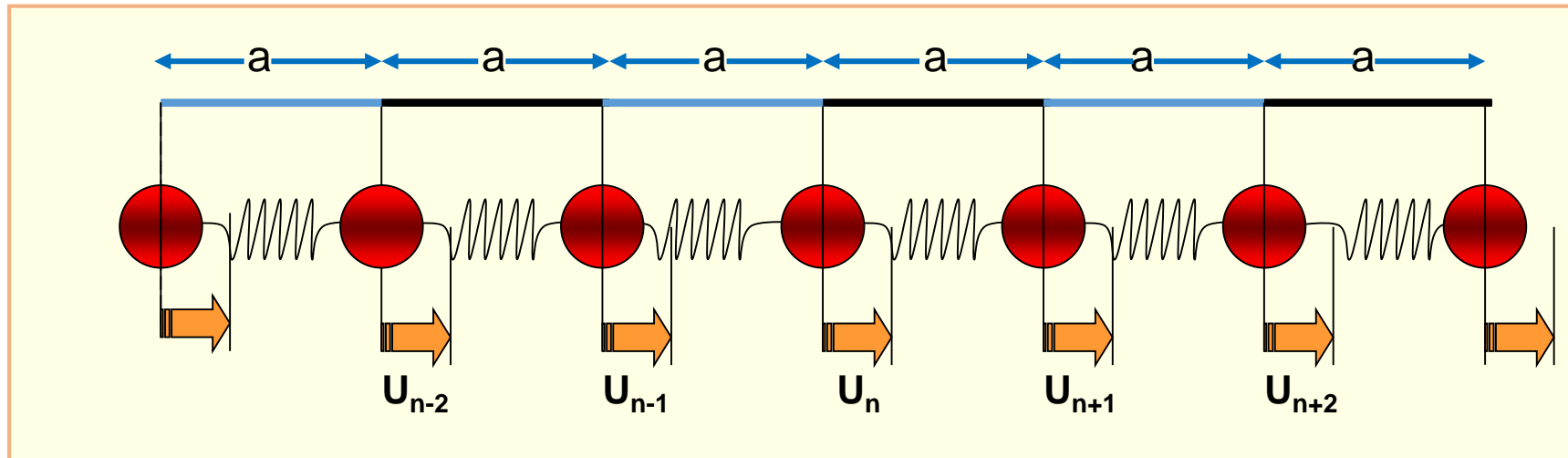
Stacking faults

For FCC metals an error in ABCABC packing sequence Ex: ABCABABC



Monoatomic Chain

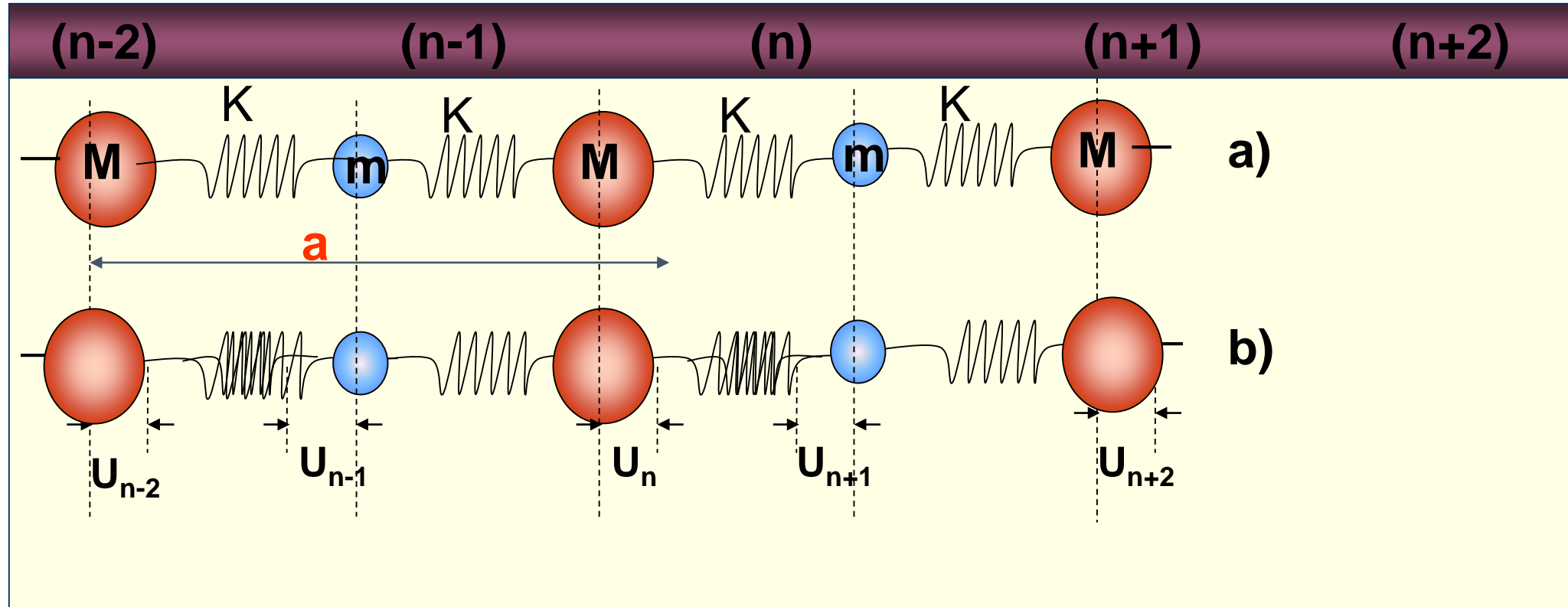
- The simplest crystal is the one dimensional chain of identical atoms.
- Chain consists of a very large number of identical atoms with identical masses.
- Atoms are separated by a distance of “ a ”.
- Atoms move only in a direction parallel to the chain.
- Only nearest neighbours interact (short-range forces).





Chain of two types of atom

- Two different types of atoms of masses M and m are connected by identical springs of spring constant K ;



- This is the simplest possible model of an ionic crystal.
- Since a is the repeat distance, the nearest neighbors separations is $a/2$





Surface Defects

