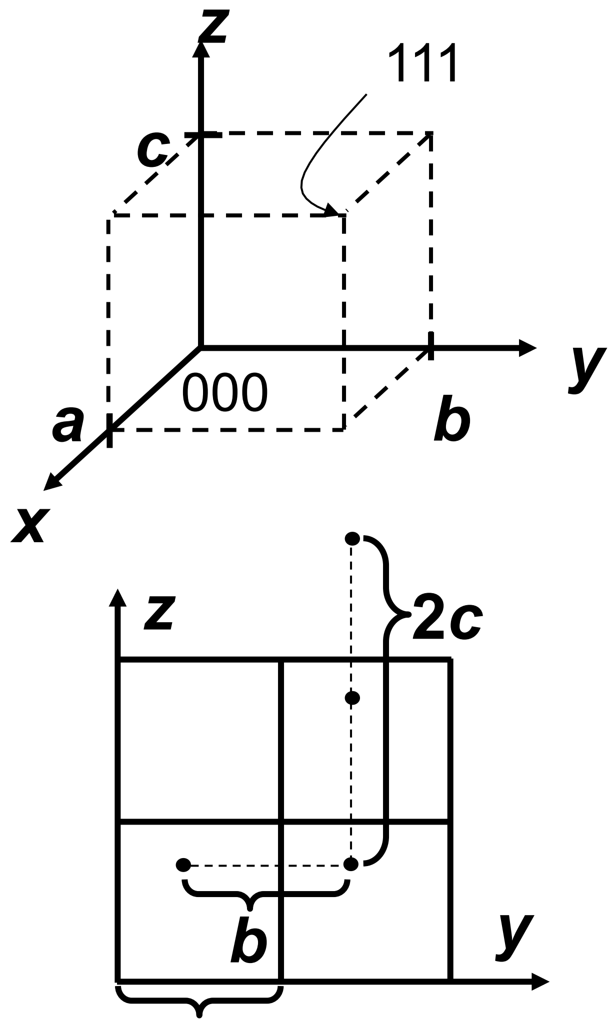
Point coordinates

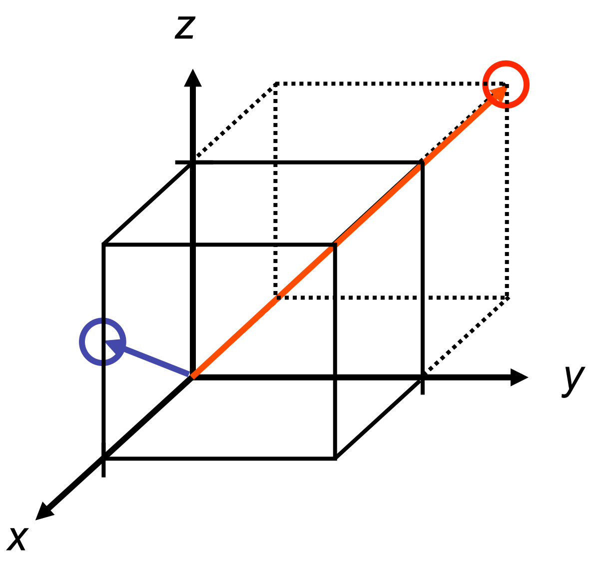


- Point coordinates for unit cell center are

  $a/2$, $b/2$, $c/2$ ½ ½ ½

- Point coordinates for unit cell corner are 111
- Translation: integer multiple of lattice constants → identical position in another unit cell

Directions



Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions *a*, *b*, and *c*
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

[*xyz*]

ex: 1, 0, ½ => 2, 0, 1 => [201]

-1, 1, 1 => $[\bar{1}11]$ where overbar represents a negative index

families of directions <*xyz*>

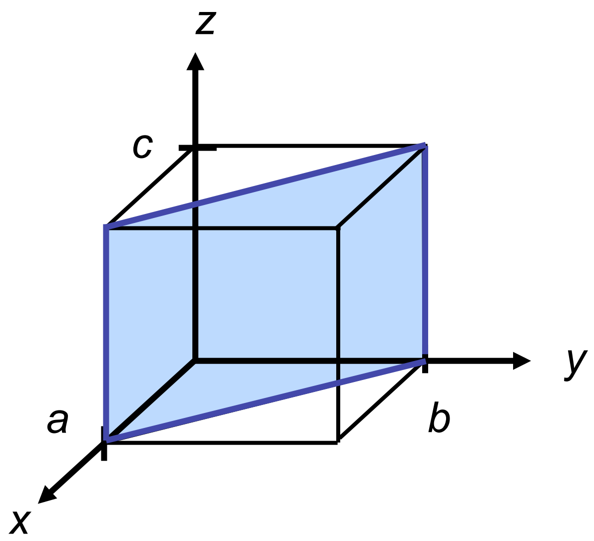
Crystallographic planes

Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.

Algorithm

1. Read off intercepts of plane with axes in terms of *a*, *b*, *c*
2. Take reciprocals of intercepts
3. Reduce to smallest integer values
4. Enclose in parentheses, no commas i.e., (*hkl*)

example		*a*	*b*	*c*
1. Intercepts		1	1	∞
2. Reciprocals		1/1	1/1	1/∞
3. Reduction		1	1	0
4. Miller Indices	(110)			

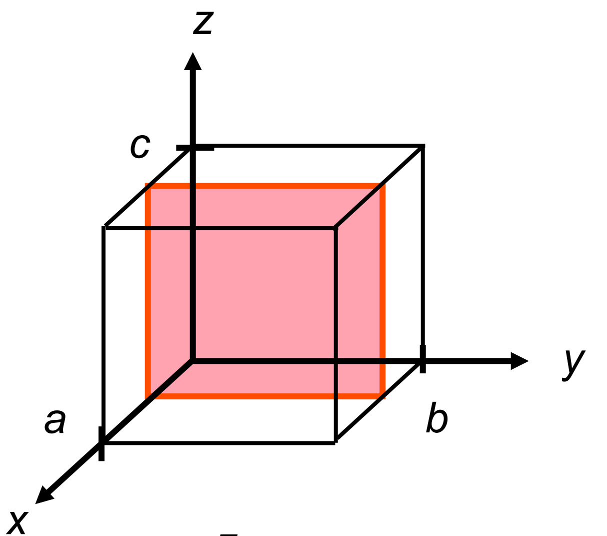


Crystallographic planes

<u>example</u>

	a	b	c
1. Intercepts	1/2	∞	∞
2. Reciprocals	1/½	1/∞	1/∞
	2	0	0
3. Reduction	2	0	0

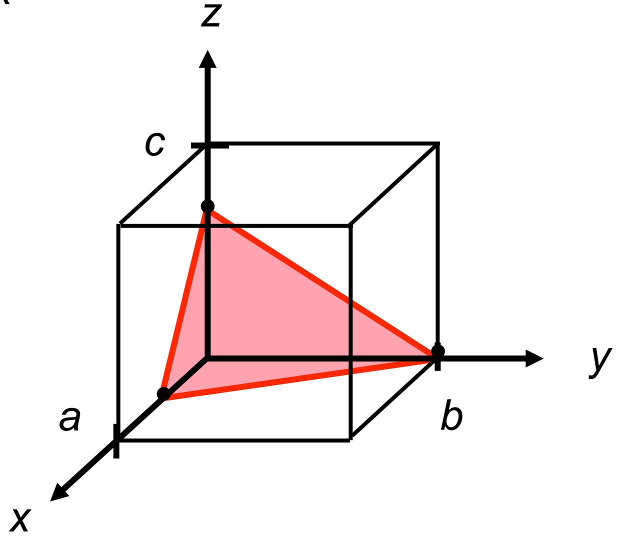
4. Miller Indices (200)



<u>example</u>

	a	b	c
1. Intercepts	1/2	1	3/4
2. Reciprocals	1/½	1/1	1/¾
	2	1	4/3
3. Reduction	6	3	4

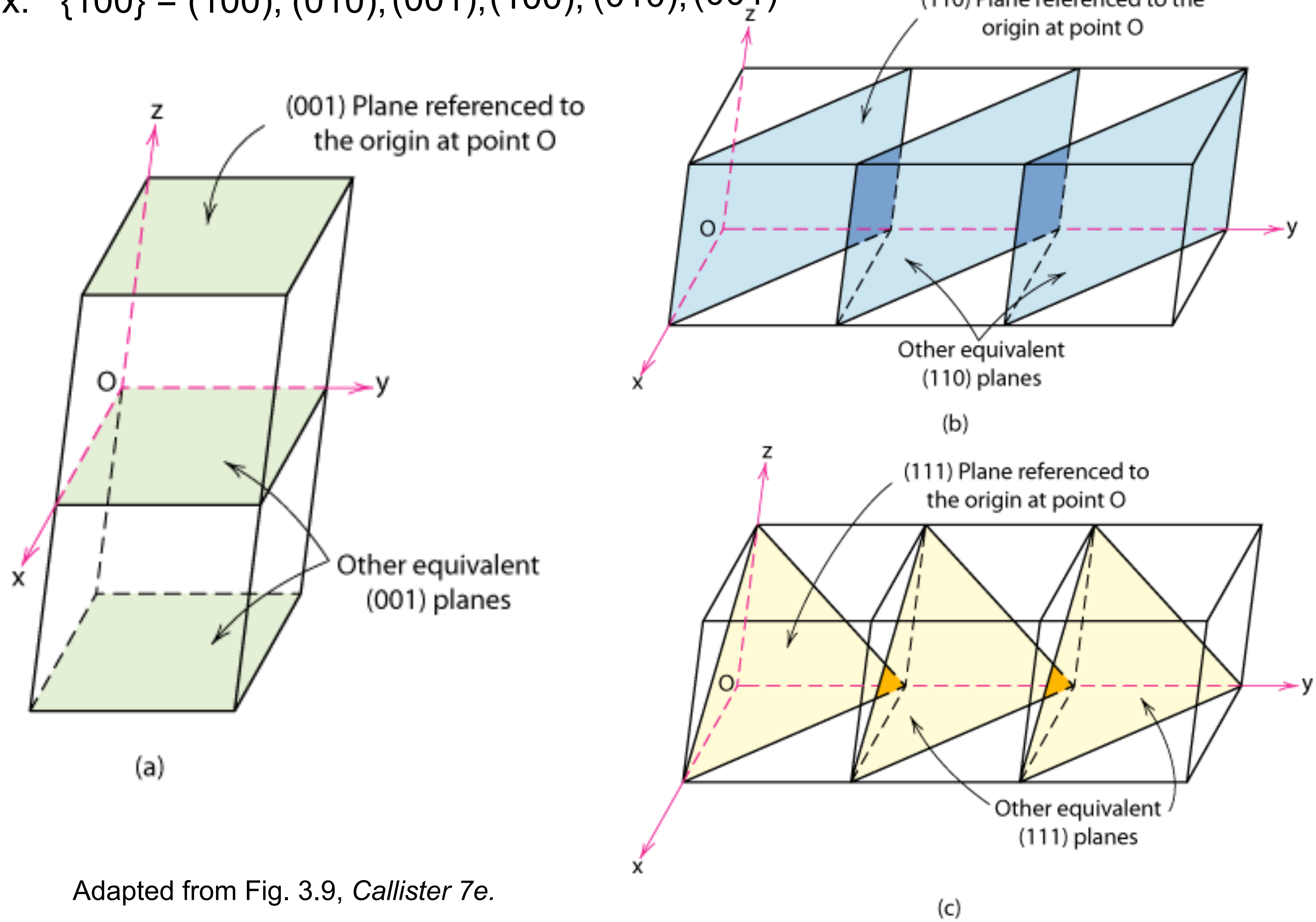
4. Miller Indices (634)



Crystallographic planes

Family of Planes {*hkl*}

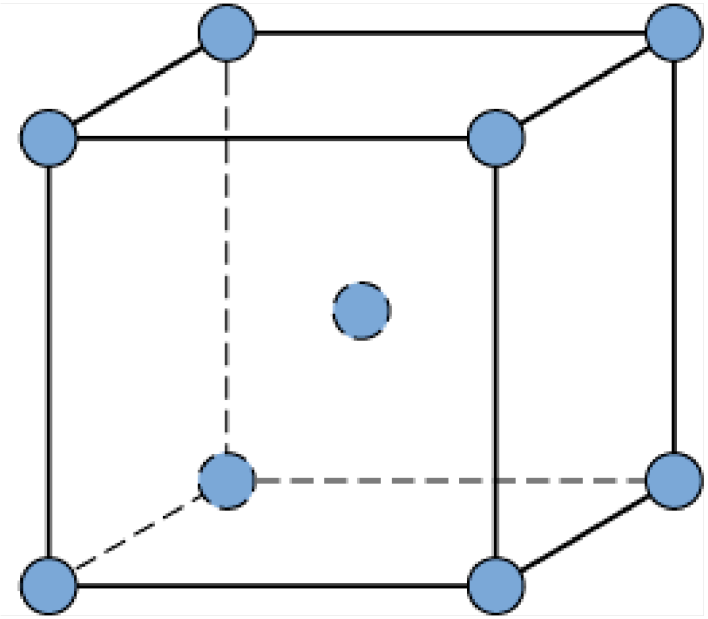
Ex: {100} = (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$



Adapted from Fig. 3.9, *Callister 7e.*

Linear density: BCC

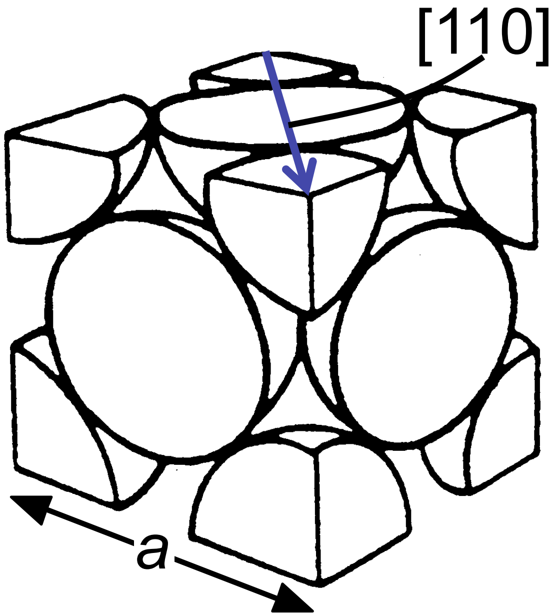
$$\text{Linear Density of Atoms} \equiv \text{LD} = \frac{\text{Number of atoms}}{\text{Unit length of direction vector}}$$



$$[100]\text{: LD} = \frac{1}{a} = \frac{\sqrt{3}}{4R}$$

$$[111]\text{: LD} = \frac{2}{4R} = \frac{1}{2R}$$

Linear density (FCC) and planar densitry



ex: linear density of Al in [110] direction
a = 0.405 nm

\# atoms

length

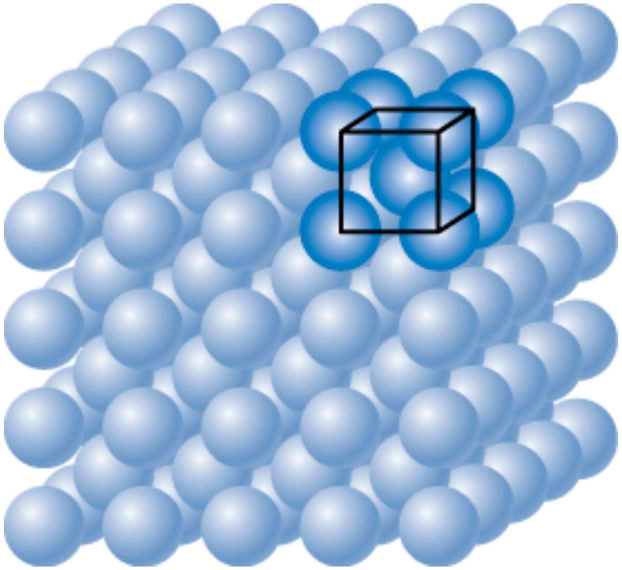
$$\mathrm{LD} = \frac{2}{\sqrt{2}\,a} = 3.5\ \mathrm{nm}^{-1}$$

$$\text{Planar Density of Atoms} \equiv \mathrm{PD} = \frac{\text{Number of atoms}}{\text{Area of plane}}$$

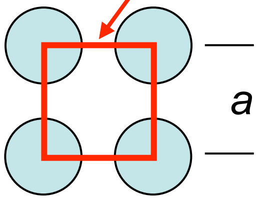
Planar density

- We want to examine the atomic packing of crystallographic planes
- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.
  - a) Draw (100) and (111) crystallographic planes for Fe.
  - b) Calculate the planar density for each of these planes.

  R = 0.1241 nm and Fe has a BCC structure at room temperature



Adapted from Fig. 3.2(c), *Callister 7e.*



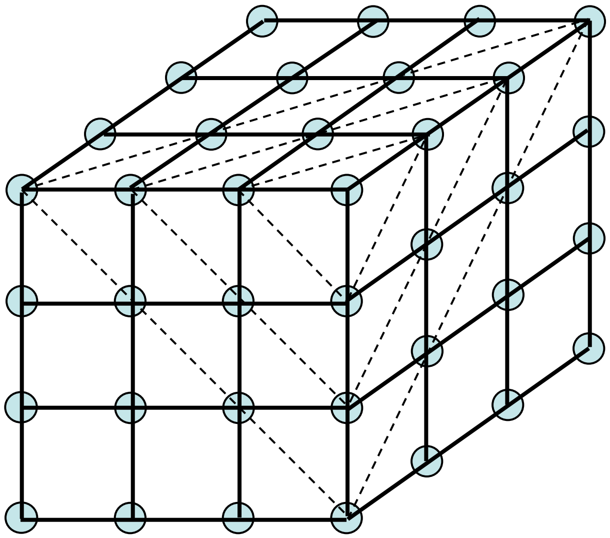
2D repeat unit

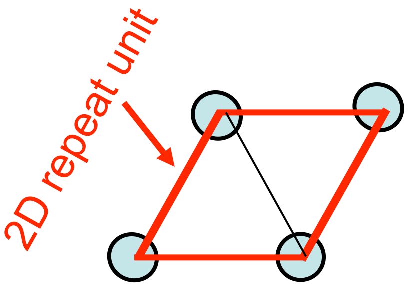
$$a = \frac{4\sqrt{3}}{3}R$$

$$\text{Planar Density} = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}}}{\dfrac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{a^2} = \frac{1}{\left(\dfrac{4\sqrt{3}}{3}R\right)^2}$$

$$= \boxed{1.2 \text{ x } 10^{19}\ \frac{\text{atoms}}{\text{m}^2}}$$

Planar density





$$\text{area} = \sqrt{2}\ ah = \sqrt{3}\ a^2 = \sqrt{3}\left(\frac{4\sqrt{3}}{3}R\right)^2 = \frac{16\sqrt{3}}{3}R^2$$

$$\frac{\text{atoms}}{\text{2D repeat unit}}$$

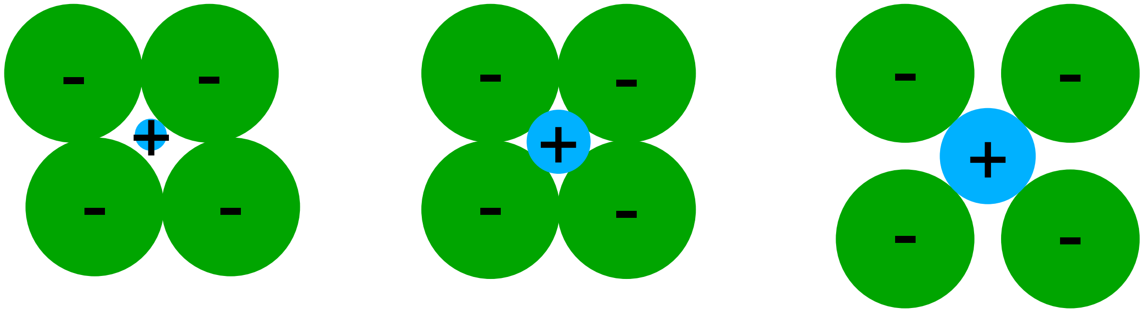
$$\text{Planar Density} = \frac{1}{\frac{16\sqrt{3}}{3}R\ 2} = 7.0\ \frac{\text{atoms}}{\text{nm}^2} = \boxed{0.70 \times 10^{19}\ \frac{\text{atoms}}{\text{m}^2}}$$

$$\frac{\text{area}}{\text{2D repeat unit}}$$

Ceramic crystal structures

- Site selection rules

1. Like charges do not touch
2. Charge balance (stoichiometry)



unstable stable stable

Adapted from Fig. 12.1,
Callister 7e.

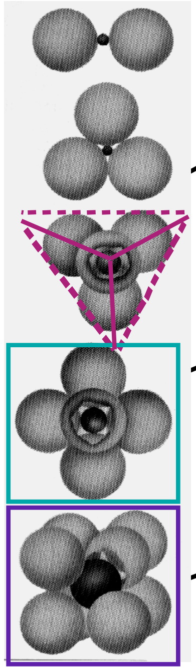
Coordination number and ionic radii

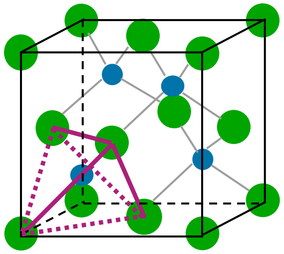
- Coordination # increases with $\dfrac{r_{\text{cation}}}{r_{\text{anion}}}$

Issue: How many anions can you arrange around a cation?

$\dfrac{r_{\text{cation}}}{r_{\text{anion}}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.0	8	cubic

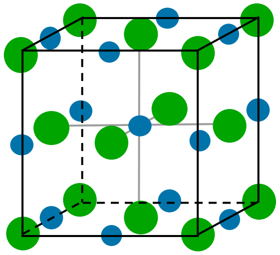
Adapted from Table 12.2, *Callister 7e.*





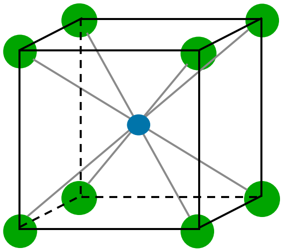
ZnS (zincblende)

Adapted from Fig. 12.4, *Callister 7e.*



NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister 7e.*



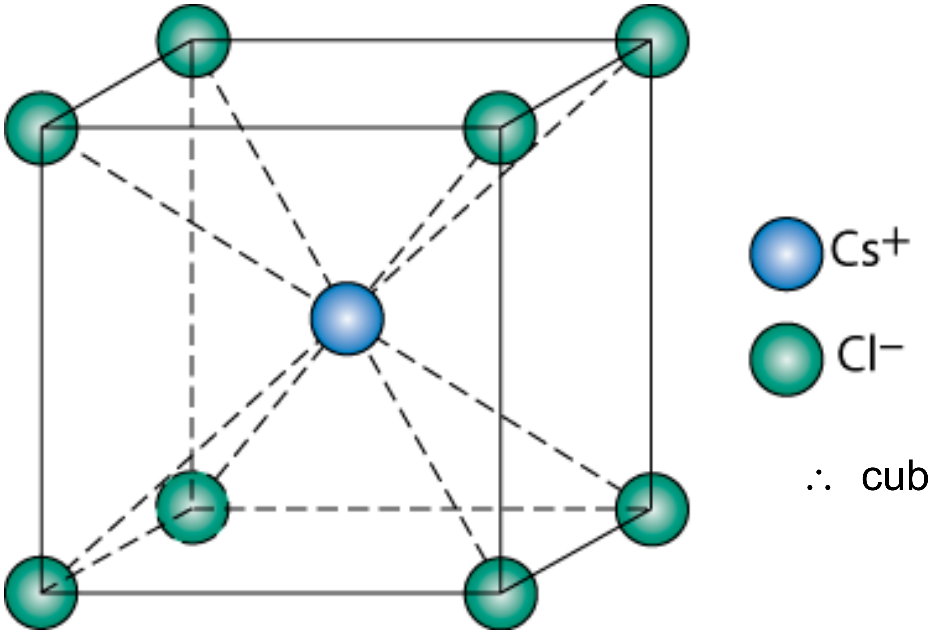
CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister 7e.*

AX crystal structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



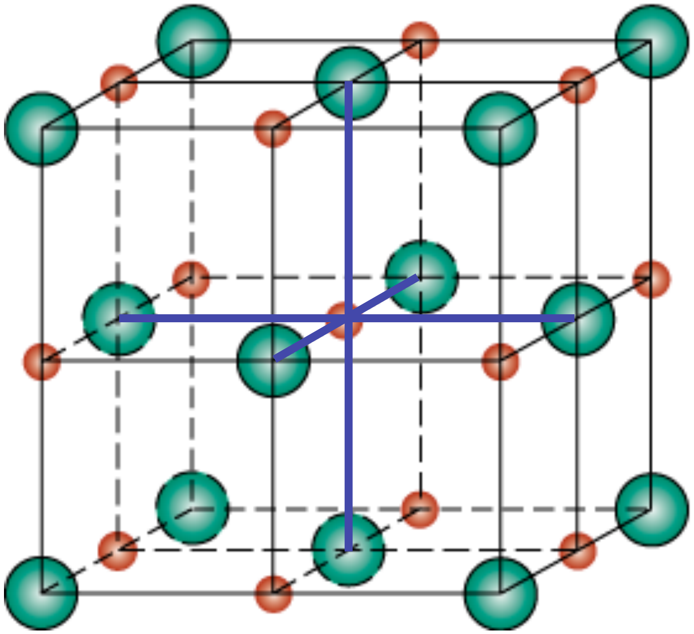
$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

∴ cubic sites preferred

So each Cs^+ has 8 neighboring Cl^-

Adapted from Fig. 12.3, *Callister 7e.*

Rock salt structure (NaCl)



Adapted from Fig. 12.2, *Callister 7e.*

● Na^+ $r_{Na} = 0.102$ nm

● Cl^- $r_{Cl} = 0.181$ nm

$r_{Na}/r_{Cl} = 0.564$

∴ cations prefer O_H sites

Single crystal vs. Polycrystalline structures

Single crystals: Atoms all have the same arrangement throughout.

Polycrystalline: Many crystals put together.

Anisotropic

Isotropic

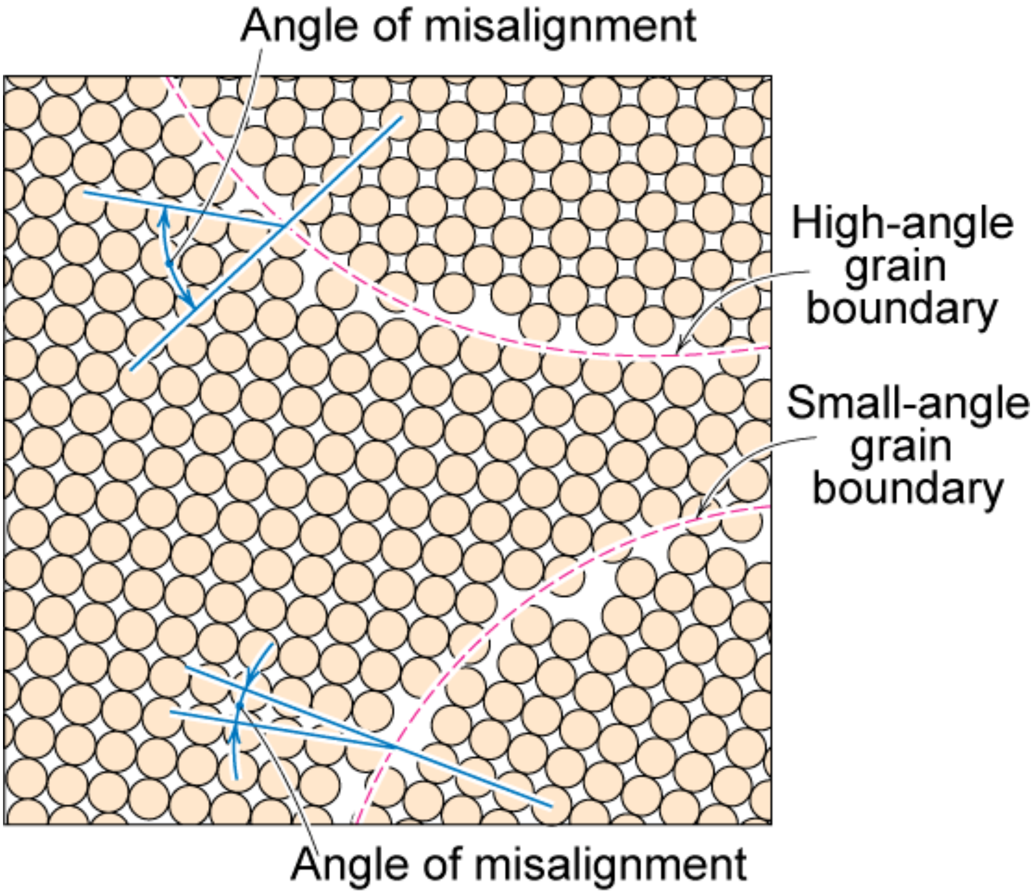
Adapted from Fig. K, color inset pages of *Callister 5e*. (Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented,
  overall component properties are not directional.
- Grain sizes typ. range from 1 nm to 2 cm
  (i.e., from a few to millions of atomic layers).

Polycrystalline structures

Grain Boundaries

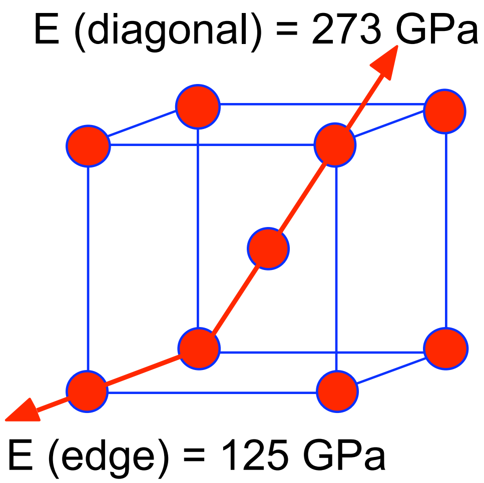
- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
  - high mobility
  - high diffusivity
  - high chemical reactivity



Adapted from Fig. 4.7, *Callister 7e.*

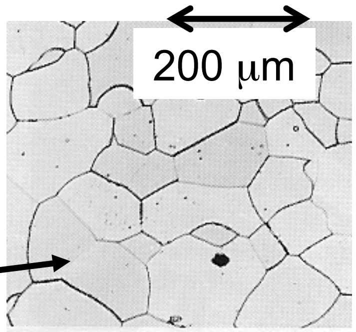
Single crystal vs. Polycrystalline structures

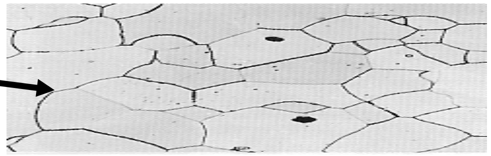
- Single Crystals
  - -Properties vary with direction: anisotropic.
  - -Example: the modulus of elasticity (E) in BCC iron:



Data from Table 3.3, *Callister 7e*.
(Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

- Polycrystals
  - -Properties may/may not vary with direction.
  - -If grains are randomly oriented: isotropic. ($E_{\text{poly iron}}$ = 210 GPa)
  - -If grains are textured, anisotropic.



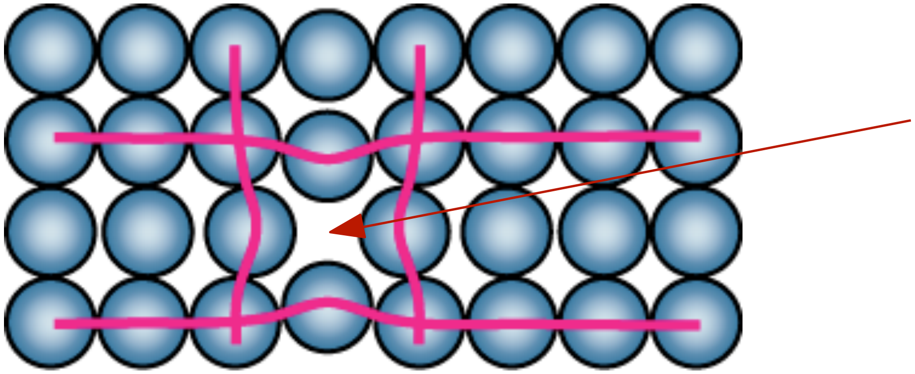


Adapted from Fig. 4.14 (b), *Callister 7e*.
(Fig. 4.14(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

Point defects

- Vacancies:

  -vacant atomic sites in a structure.

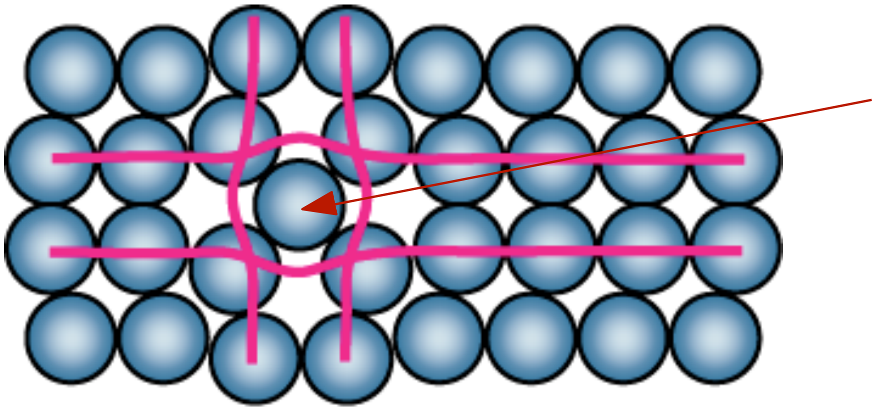


distortion of planes

Vacancy

- Self-Interstitials:

  -"extra" atoms positioned between atomic sites.

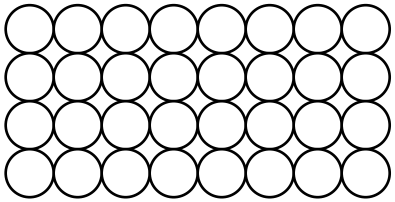


distortion of planes

self-interstitial

Equilibrium concentration of defects

- Equilibrium concentration varies with temperature



Each lattice site is a potential vacancy

No. of defects

Activation energy

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

No. of potential defect sites.

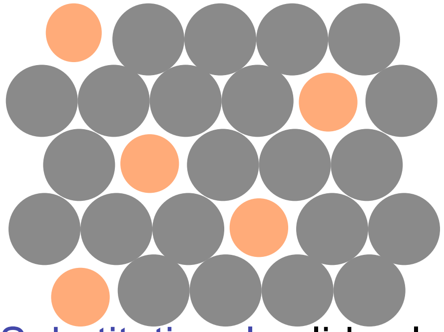
Temperature

Boltzmann's constant

Point defects in alloys

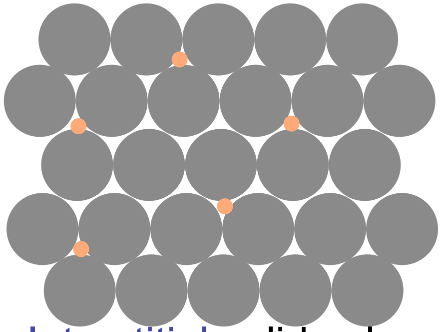
Two outcomes if impurity (B) added to host (A):

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



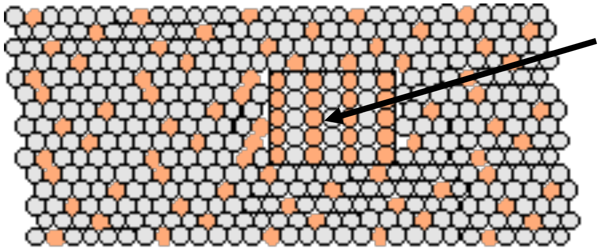
Substitutional solid soln.
(e.g., Cu in Ni)

OR



Interstitial solid soln.
(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.

Imperfections of solids

Conditions for substitutional solid solution (S.S.)

W. Hume – Rothery rule

1. Δr (atomic radius) < 15%
2. Same crystal structure for pure metals
3. Proximity in periodic table

   i.e., similar electronegativities
4. Valency

   All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

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

2. More Zn or Al in Cu?

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-nega-tivity*	*Valence*
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
Ni	0.1246	FCC	1.8	+2
Zn	0.1332	HCP	1.6	+2

Table on p. 106, *Callister 7e.*

Line defects

- Linear Defects (Dislocations)
  - Are one-dimensional defects around which atoms are misaligned
- Edge dislocation:
  - extra half-plane of atoms inserted in a crystal structure
  - **b** ⊥ to dislocation line
- Screw dislocation:
  - spiral planar ramp resulting from shear deformation
  - **b** ∥ to dislocation line

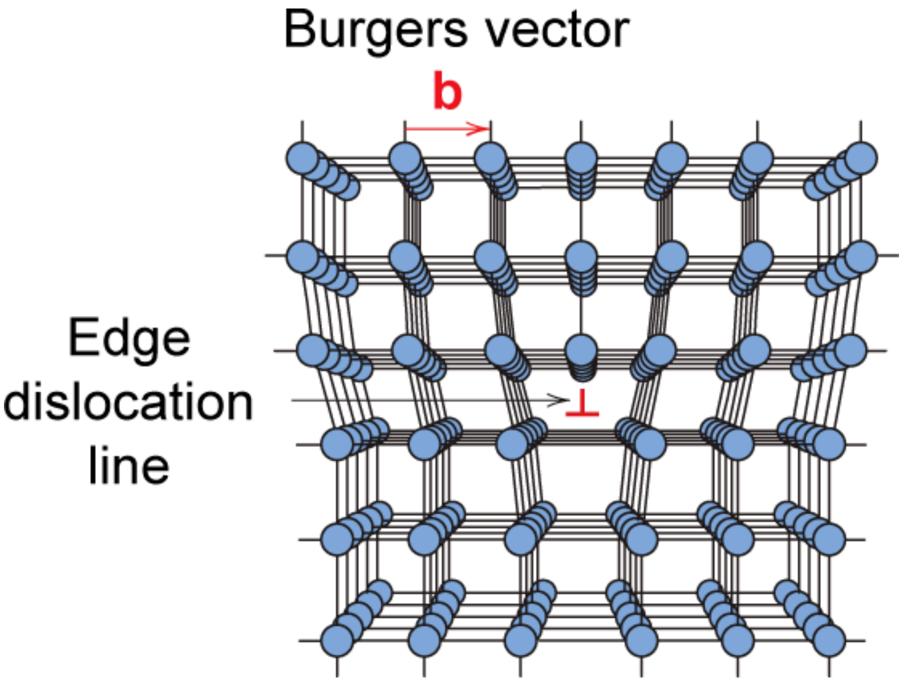
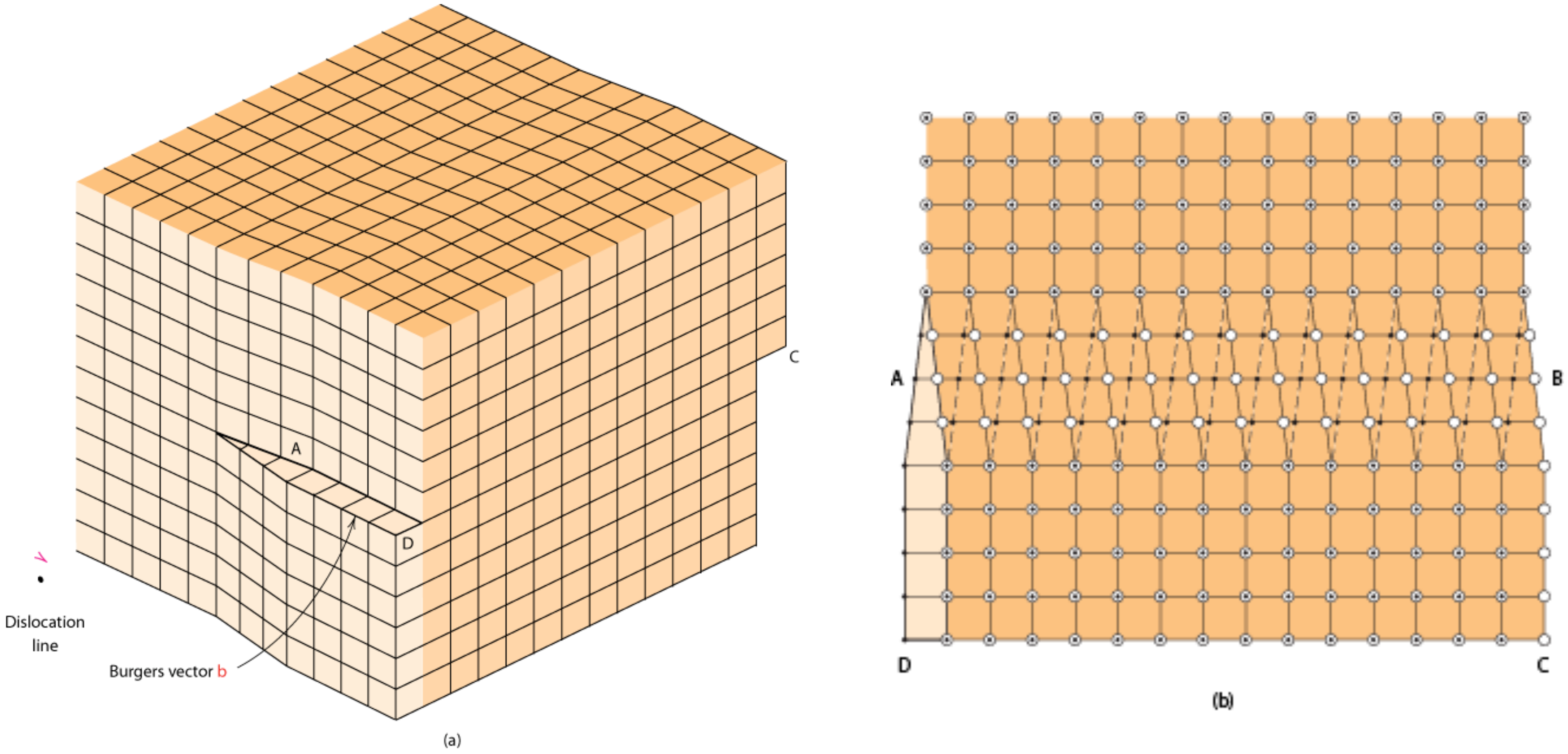


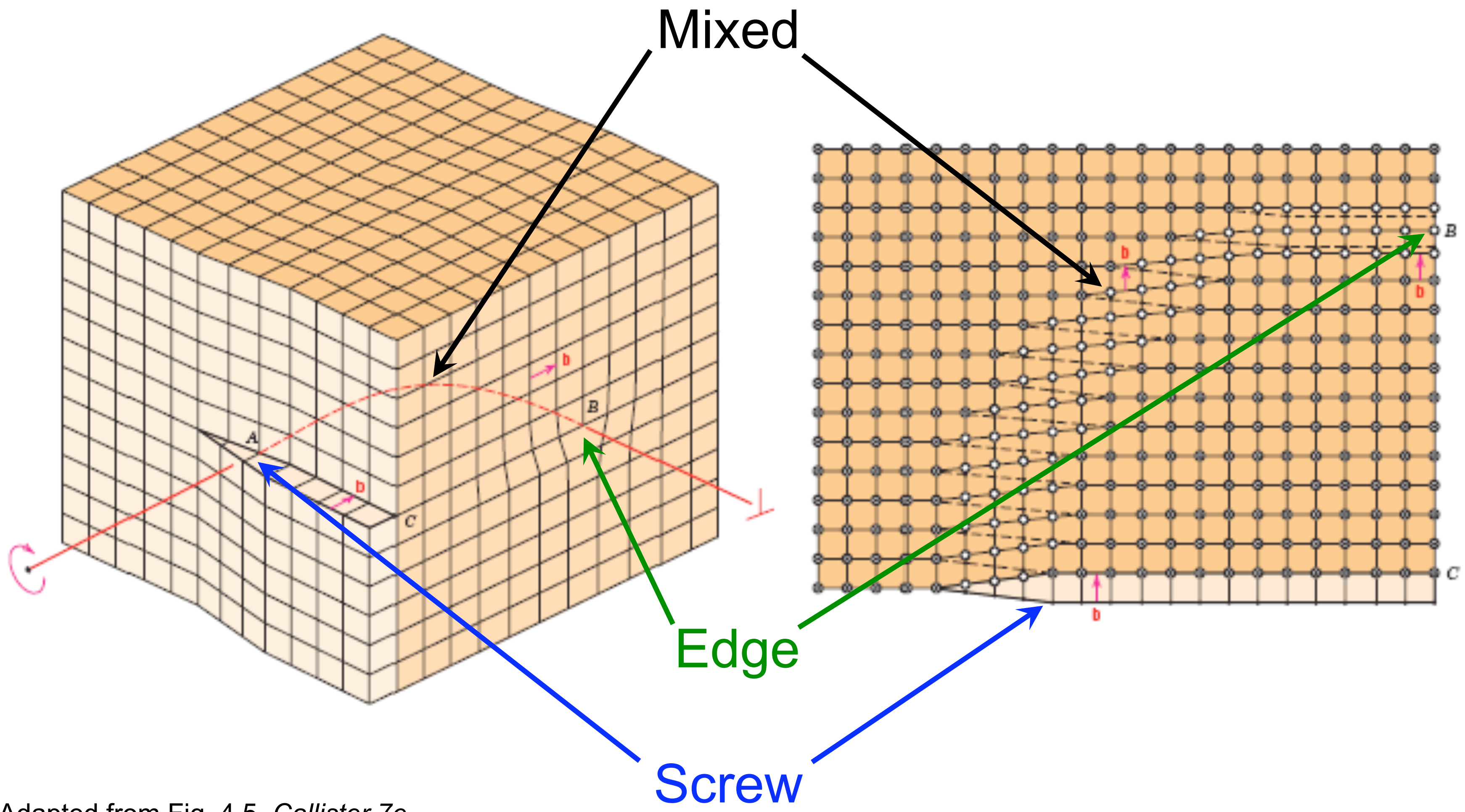
Fig. 4.3, *Callister 7e.*

Screw defects



Adapted from Fig. 4.4, *Callister 7e.*

Mixed defects



Mixed

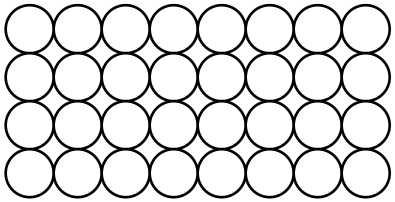
Edge

Screw

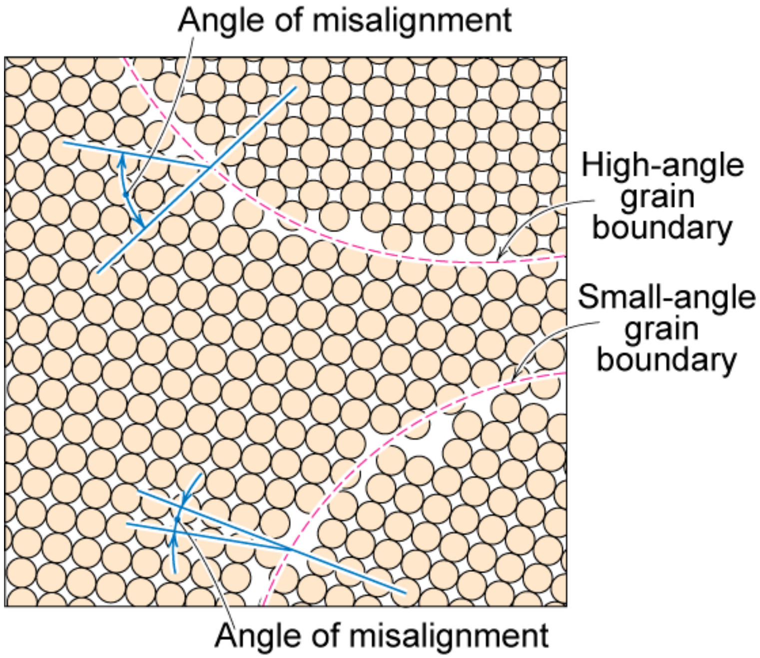
Adapted from Fig. 4.5, *Callister 7e.*

Planar defects

- External defects
  - On the surface
  - Unsatisfied bonds

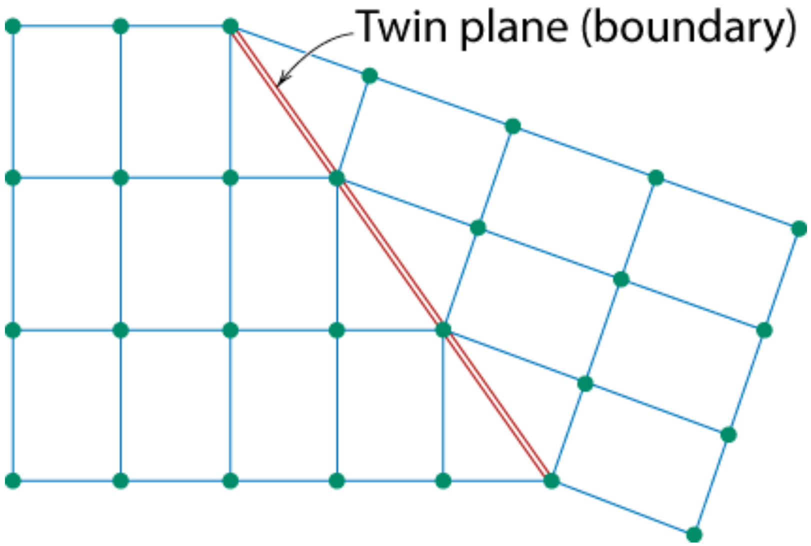


- Internal defects
  - Grain boundaries



Planar defects

- Twin boundary (plane)
  Essentially a reflection of atom positions across the twin plane.



Adapted from Fig. 4.9, *Callister 7e.*

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