

Chapter 4

Crystal Defects and Noncrystalline Structure–Imperfection

ME 2105 – Dr. Lindeke

**In our pervious Lecture when
discussing Crystals we
ASSUMED PERFECT ORDER**

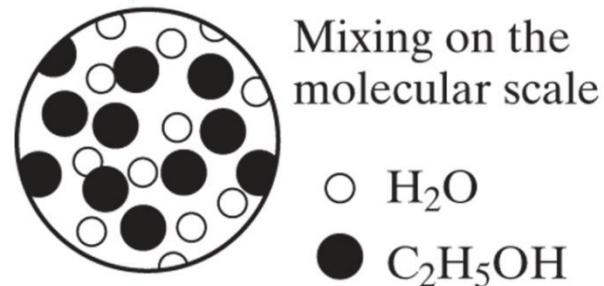
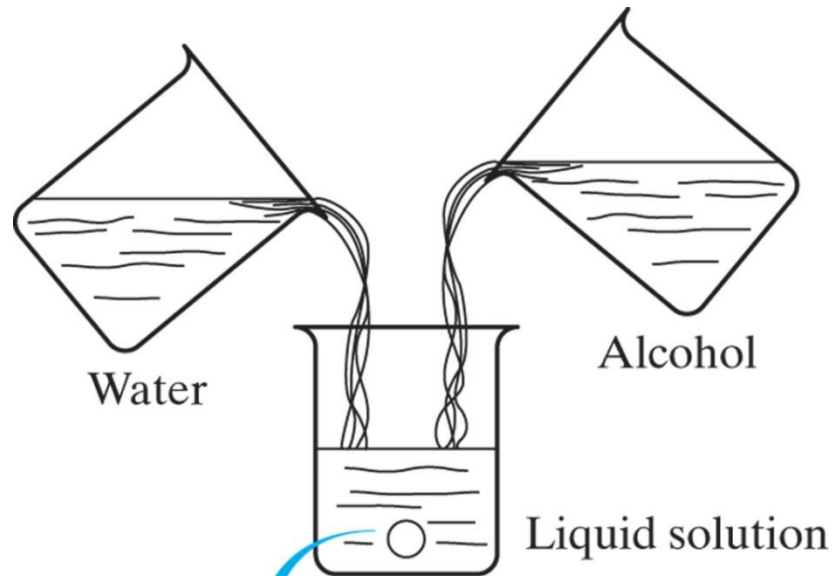
*In real materials we find:
Crystalline Defects or lattice irregularity*

*Most real materials have one or more “errors in perfection”
with dimensions on the order of an atomic diameter to many
lattice sites*

Defects can be classification:

- 1. according to geometry
(point, line or plane)**
- 2. dimensions of the defect**

*Forming a liquid solution of water and alcohol.
Mixing occurs on the molecular scale.*

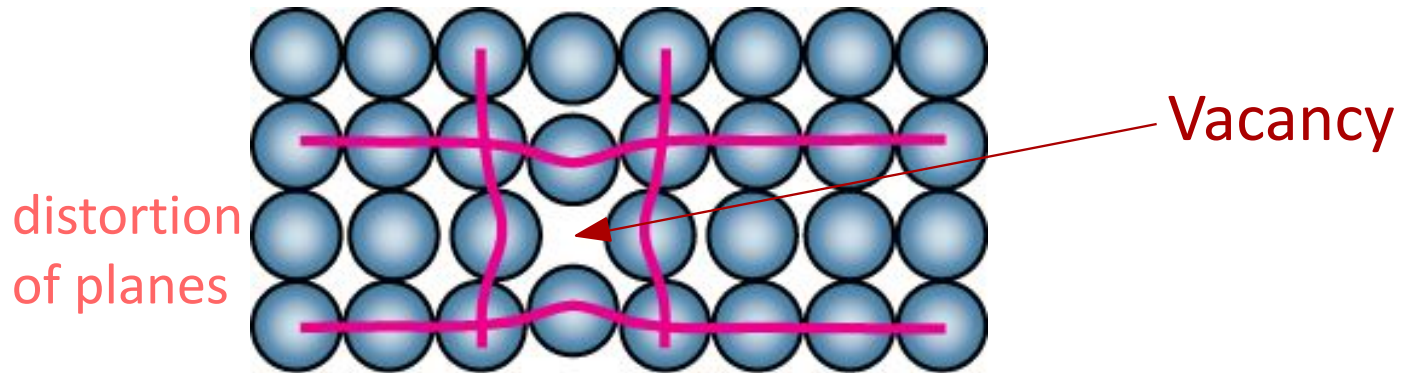


We can define this mixture/solution on a weight or "atomic" basis

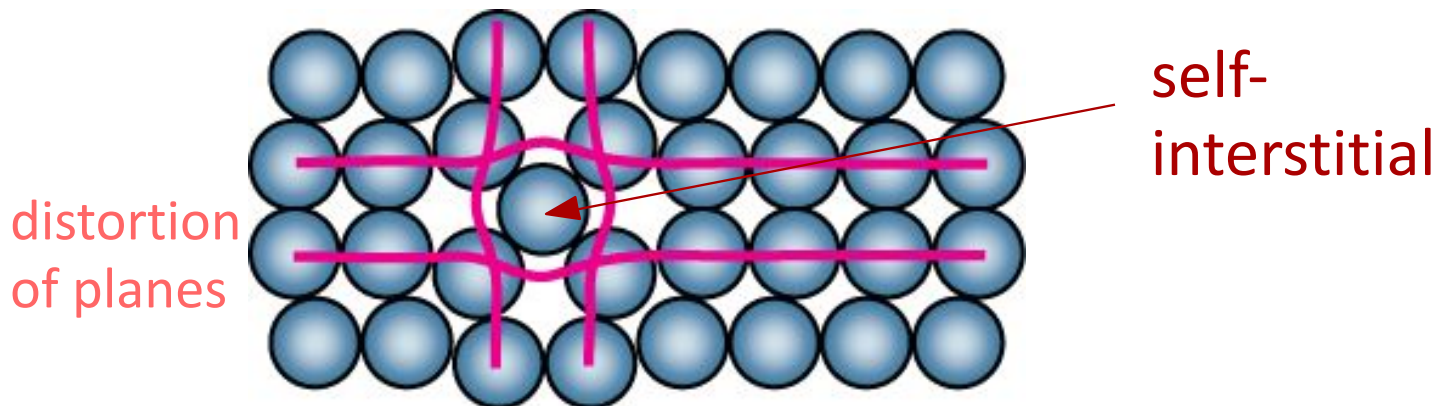
A similar discussion can apply to "mixtures" of metals – called alloys

Point Defects – in the solid state are more predictable

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



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



POINT DEFECTS

- The simplest of the point defect is a vacancy, or vacant lattice site.
- All crystalline solids contain vacancies.
- Principles of thermodynamics is used explain the necessity of the existence of vacancies in crystalline solids.
- The presence of vacancies increases the entropy (randomness) of the crystal.
- The equilibrium number of vacancies for a given quantity of material depends on and increases with temperature as follows: (an Arrhenius model)

Equilibrium no. of vacancies → $N_v = N \exp(-Q_v/kT)$

Total no. of atomic sites → N

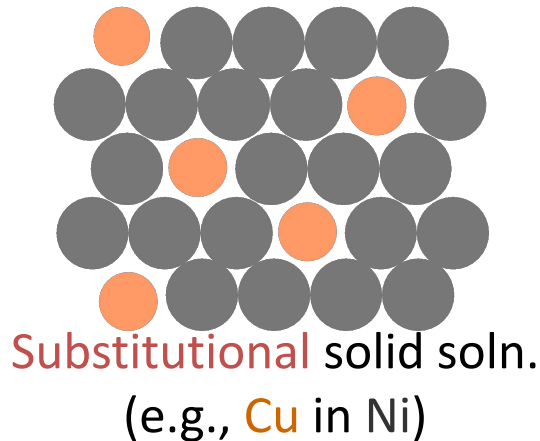
Energy required to form vacancy → Q_v

T = absolute temperature in °Kelvin
 k = gas or Boltzmann's constant

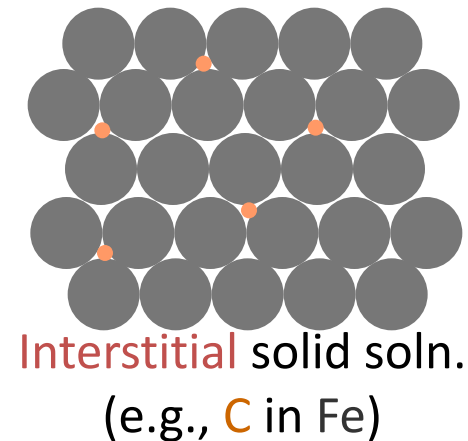
Point Defects in Alloys

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

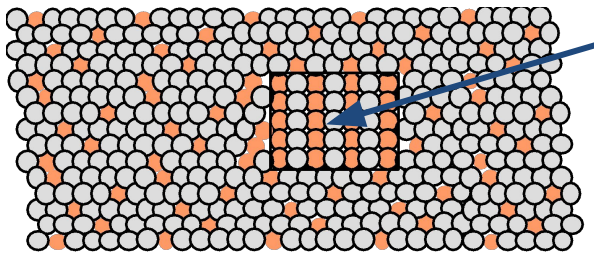
- **Solid solution** of B in A (i.e., random dist. of point defects)



OR

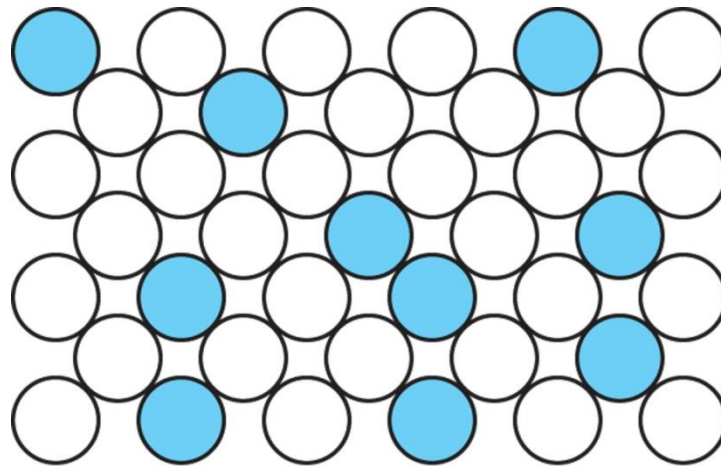


- Solid solution of B in A plus particles of a **new phase** (usually for a larger amount of B)



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

Solid solution of nickel in copper shown along a (100) plane. This is a substitutional solid solution with nickel atoms substituting for copper atoms on fcc atom sites.



Imperfections in Solids

Conditions for substitutional solid solution (S.S.)

- Hume – Rothery rules

- 1. Δr (atomic radius) < 15%
- 2. Proximity in periodic table
 - i.e., similar electronegativities
- 3. Same crystal structure for pure metals
- 4. Valency equality
 - All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency (it provides more electrons to the “cloud”)

Imperfections in Solids

Application of Hume–Rothery rules – Solid Solutions

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

More Al because size is closer and val. is higher – but not too much because of structural differences – FCC in HCP

2. More Zn or Al in Cu?

Surely Zn since size is closer thus causing lower distortion (4% vs 12%)

Element	Atomic Radius (nm)	Crystal Structure	Electro-Valence	
			Structure	negativity
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

Table on p. 106, Callister 7e.

Imperfections in Solids

- **Specification of composition**

- weight percent

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

m_1 = mass of component 1

- atom percent

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

n_{m1} = number of moles of component 1

Wt. % and At. % -- An example

Typically we work with a basis weight (100g or 1 kg) or moles given: alloy by weight -- 60% Cu, 40% Ni

$$n_{Cu} = \frac{600g}{63.55g / m} = 9.44m$$

$$n_{Ni} = \frac{400g}{58.69g / m} = 6.82m$$

$$C'_{Cu} = \frac{9.44}{9.44 + 6.82} \approx .581 \text{ or } 58.1\%$$

$$C'_{Ni} = \frac{6.82}{9.44 + 6.82} \approx .419 \text{ or } 41.9\%$$

Converting Between: (Wt% and At%)

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

Converts from wt%
to At% (A_i is atomic
weight)

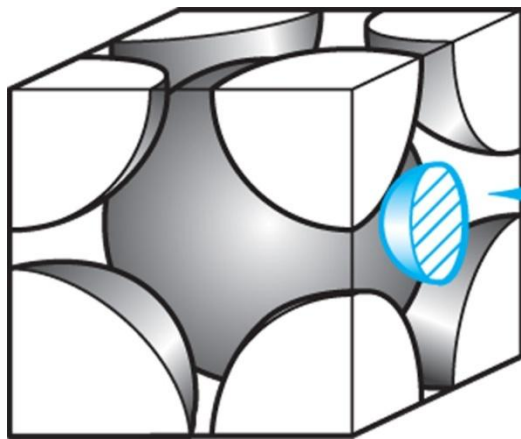
$$C_2' = \frac{C_2 * A_1}{C_1 * A_2 + C_2 * A_1} \times 100$$

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

Converts from at%
to wt% (A_i is atomic
weight)

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

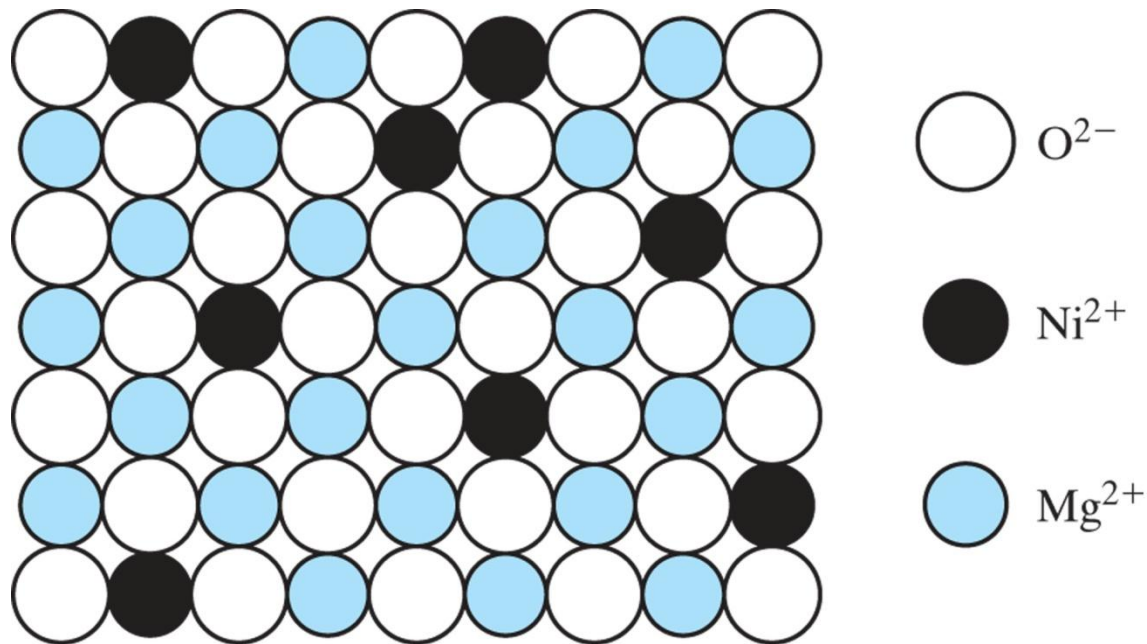
Interstitial solid solution applies to carbon in α -iron. The carbon atom is small enough to fit with some strain in the interstice (or opening) among adjacent Fe atoms in this important steel structure. [This unit-cell structure can be compared with that shown in Figure 3.4b.]



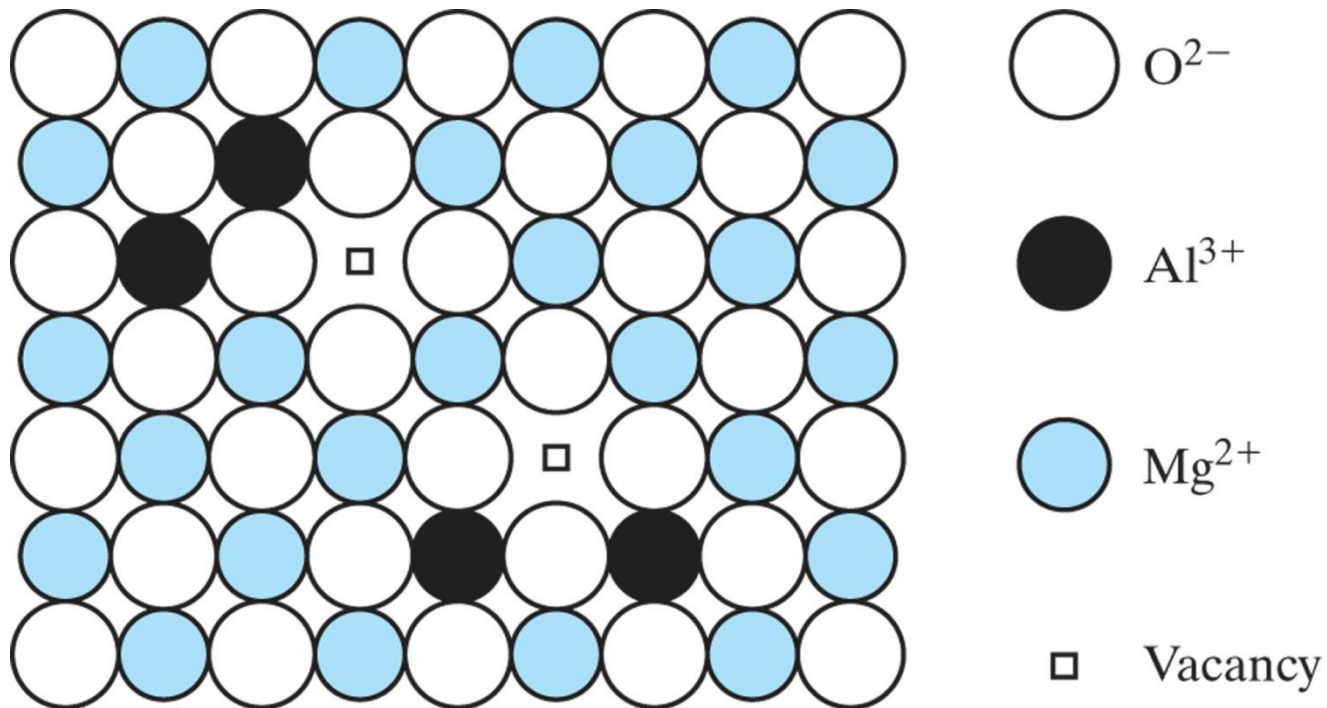
C atom dissolved interstitially at a $\frac{1}{2} 0 \frac{1}{2}$ -type position in the bcc structure of α -Fe

But the interstitial solubility is quite low since the size mismatch of the site to the radius of a carbon atom is only about 1/4

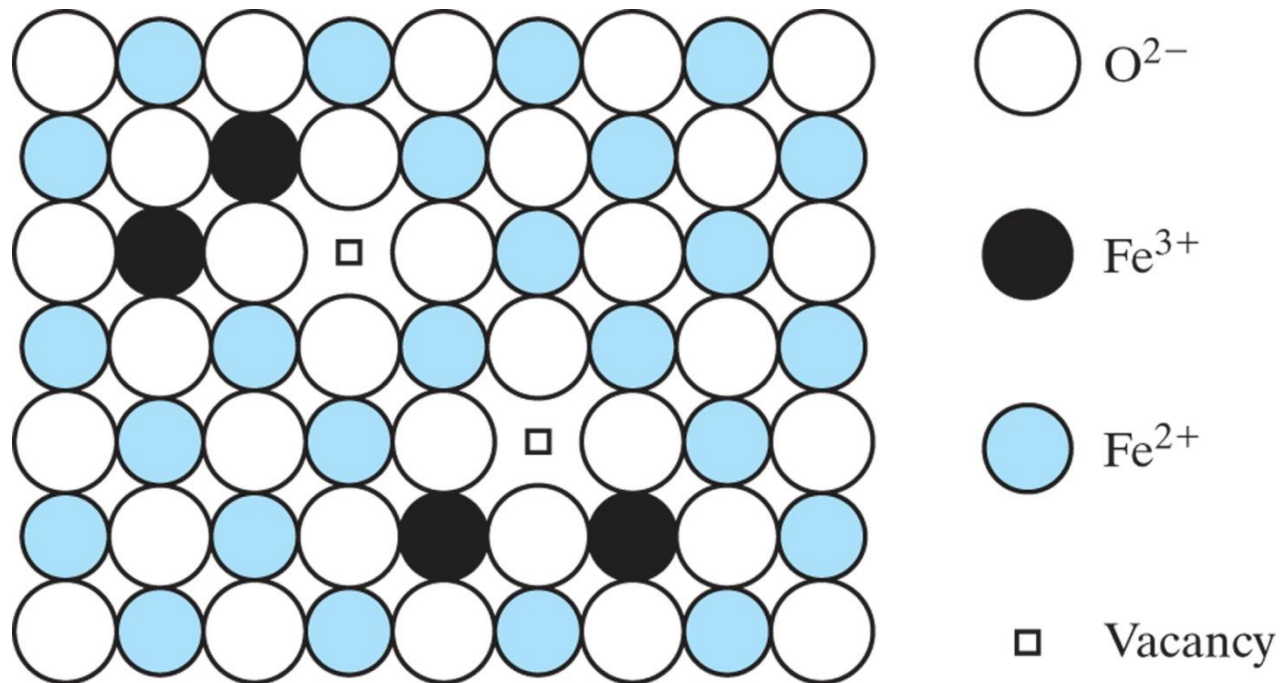
Random, substitution solid solution can occur in Ionic Crystalline materials as well. Here of NiO in MgO. The O^{2-} arrangement is unaffected. The substitution occurs among Ni^{2+} and Mg^{2+} ions.



A substitution solid solution of Al_2O_3 in MgO is not as simple as the case of NiO in MgO . The requirement of charge neutrality in the overall compound permits only two Al^{3+} ions to fill every three Mg^{2+} vacant sites, leaving one Mg^{2+} vacancy.

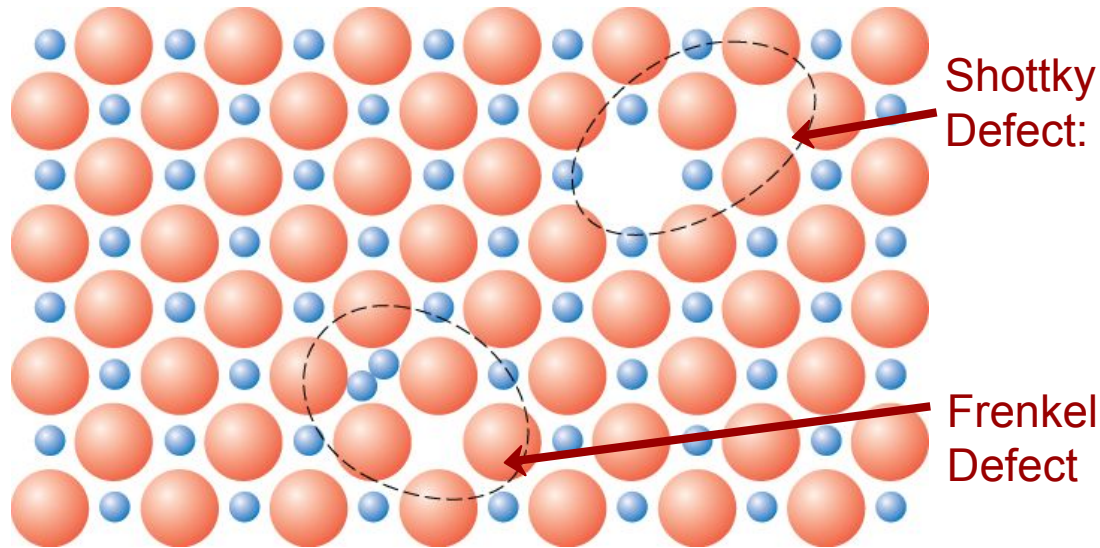


Iron oxide, $Fe_{1-x}O$ with $x \approx 0.05$, is an example of a nonstoichiometric compound. Similar to the case of Figure 4.6, both Fe^{2+} and Fe^{3+} ions occupy the cation sites, with one Fe^{2+} vacancy occurring for every two Fe^{3+} ions present.



Defects in Ceramic Structures

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



from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.

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

Line Defects

Are called Dislocations:

And:

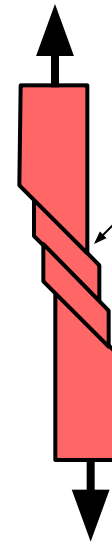
- slip between crystal planes result when dislocations move,
- this motion produces permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



slip steps which are the physical evidence of large numbers of dislocations slipping along the close packed plane $\{0001\}$

Adapted from Fig. 7.8, Callister 7e.

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 (the berger's vector)** is \perp (perpendicular) to dislocation line
- **Screw dislocation:**
 - spiral planar ramp resulting from shear deformation
 - **b** is \parallel (parallel) to dislocation line

Burger's vector, b: is a measure of lattice distortion and is measured as a distance along the close packed directions in the lattice

Edge Dislocation

Edge Dislocation

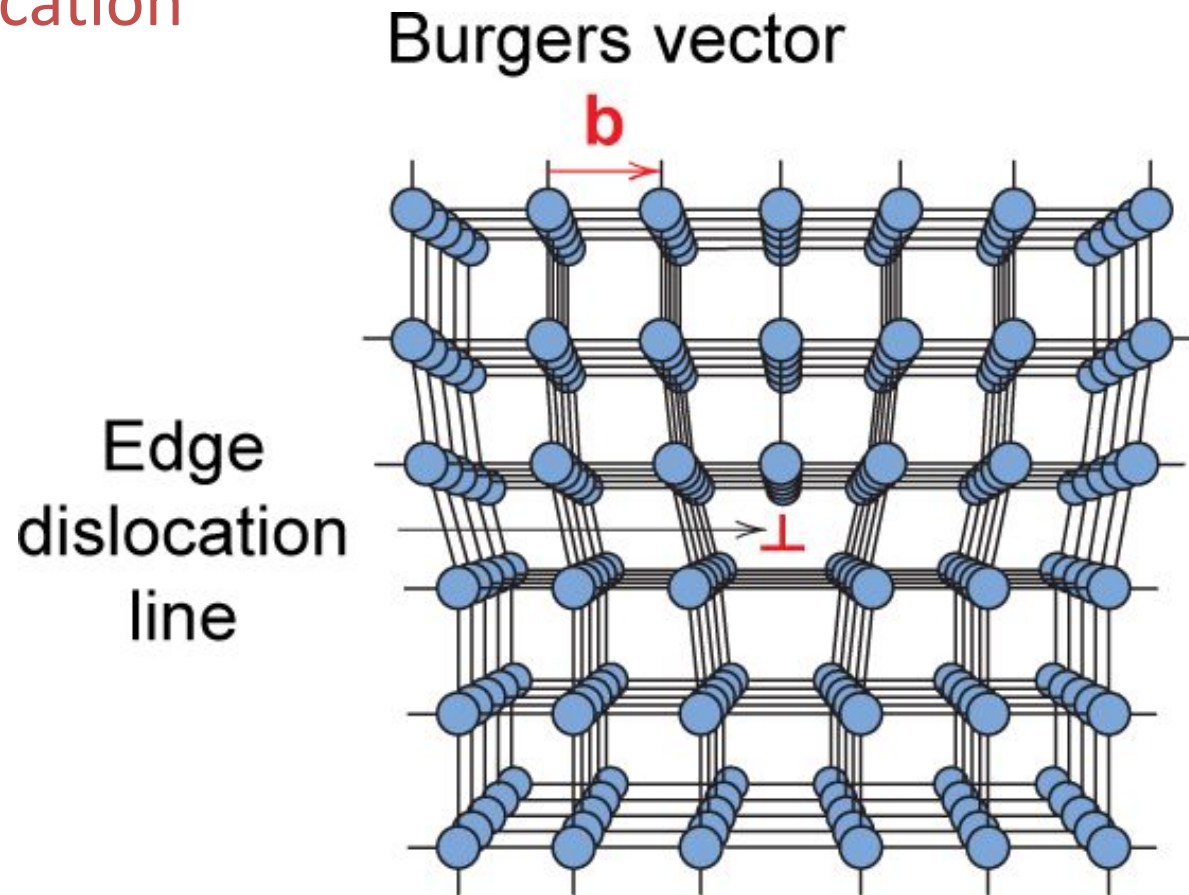
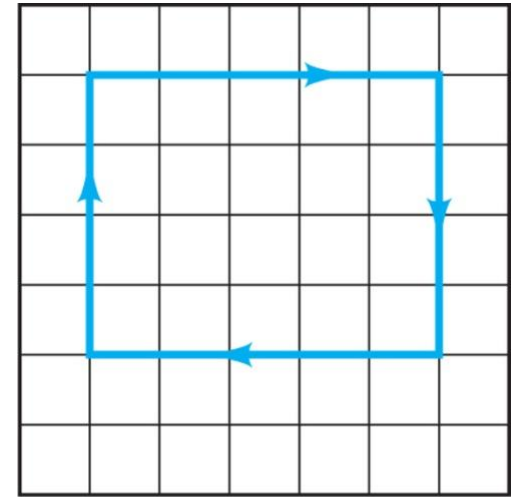
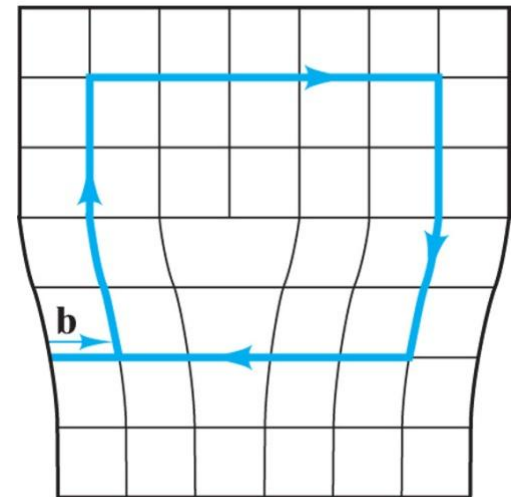


Fig. 4.3, Callister 7e.

Definition of the Burgers vector, \mathbf{b} , relative to an edge dislocation. (a) In the perfect crystal, an $m \times n$ atomic step loop closes at the starting point. (b) In the region of a dislocation, the same loop does not close, and the closure vector (\mathbf{b}) represents the magnitude of the structural defect. For the edge dislocation, the Burgers vector is perpendicular to the dislocation line.

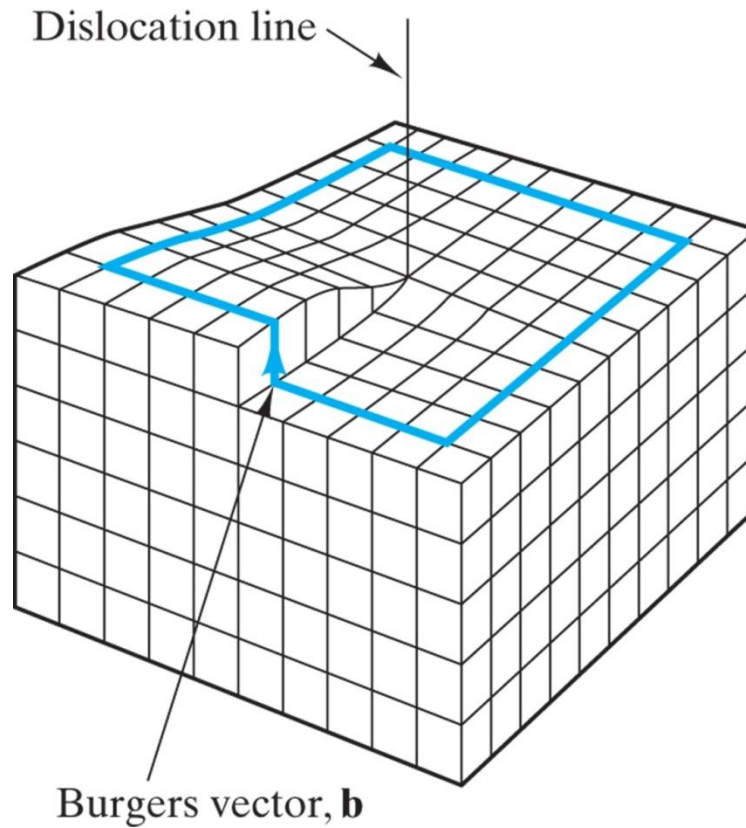


(a)

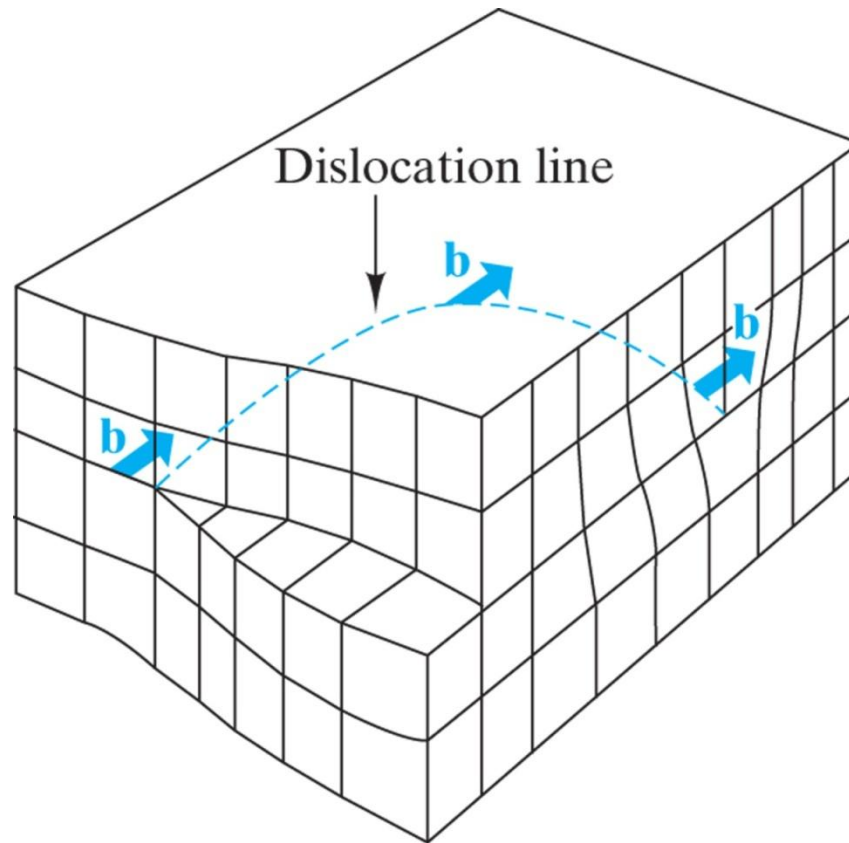


(b)

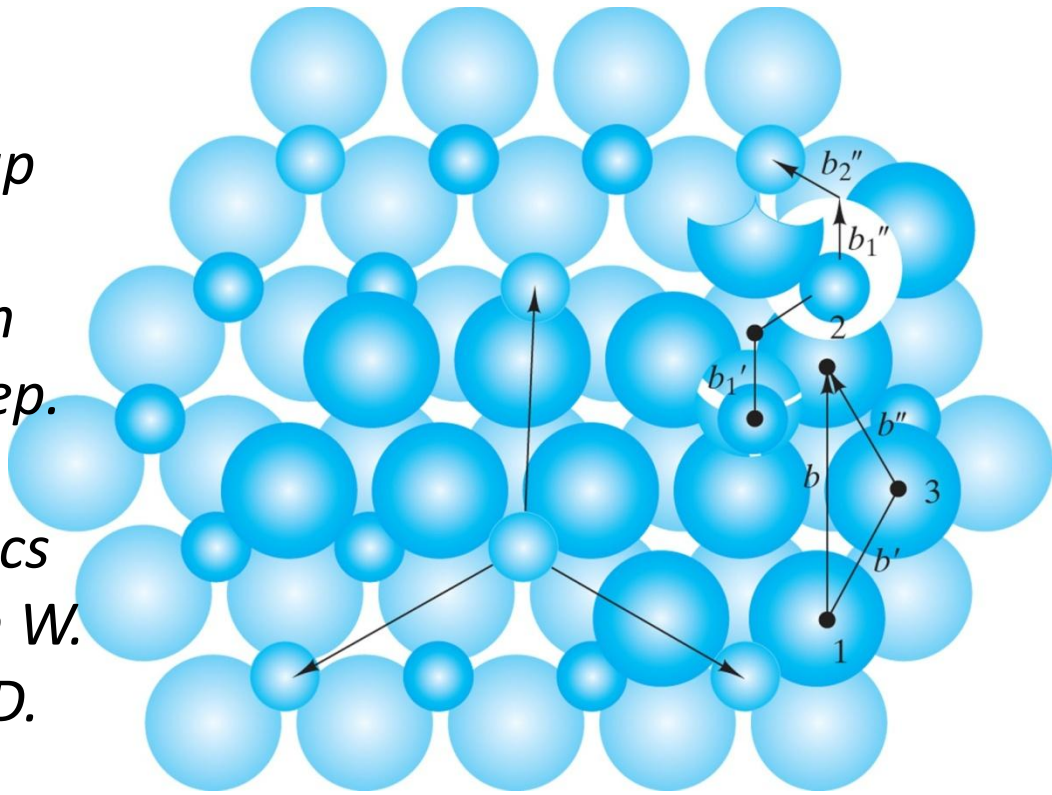
Screw dislocation. The spiral stacking of crystal planes leads to the Burgers vector being parallel to the dislocation line.



Mixed dislocation. This dislocation has both edge and screw character with a single Burgers vector consistent with the pure edge and pure screw regions.



Burgers vector for the aluminum oxide structure. The large repeat distance in this relatively complex structure causes the Burgers vector to be broken up into two (for O^{2-}) or four (for Al^{3+}) partial dislocations, each representing a smaller slip step. This complexity is associated with the brittleness of ceramics compared with metals. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, Introduction to Ceramics, 2nd ed., John Wiley & Sons, Inc., New York, 1976.)



Imperfections in Solids

Dislocations are visible in (T) electron micrographs

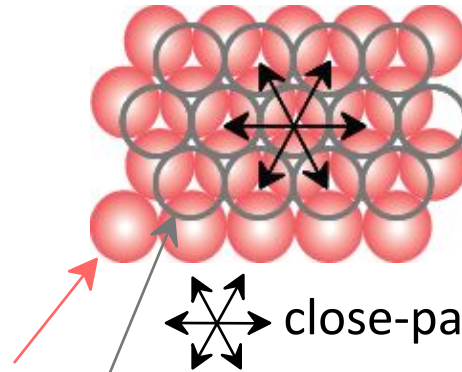


Adapted from Fig. 4.6, *Callister 7e*.

Dislocations & Crystal Structures

- Structure: **close-packed** planes & directions are preferred.

close-packed plane (bottom)

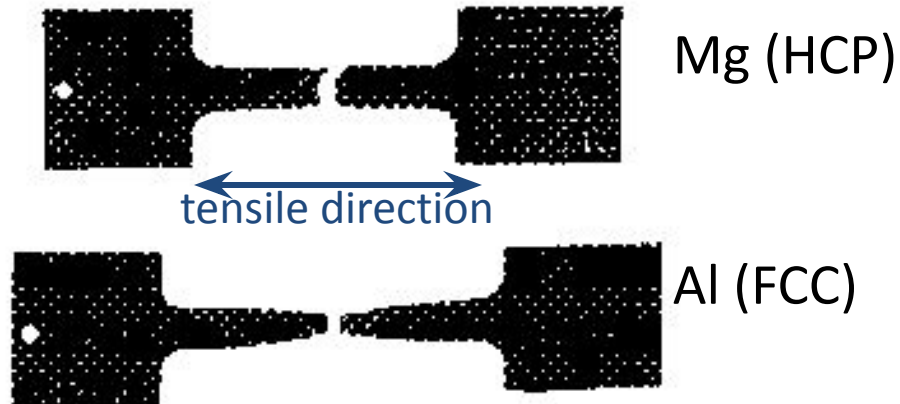


view onto two close-packed planes.

close-packed directions
close-packed plane (top)

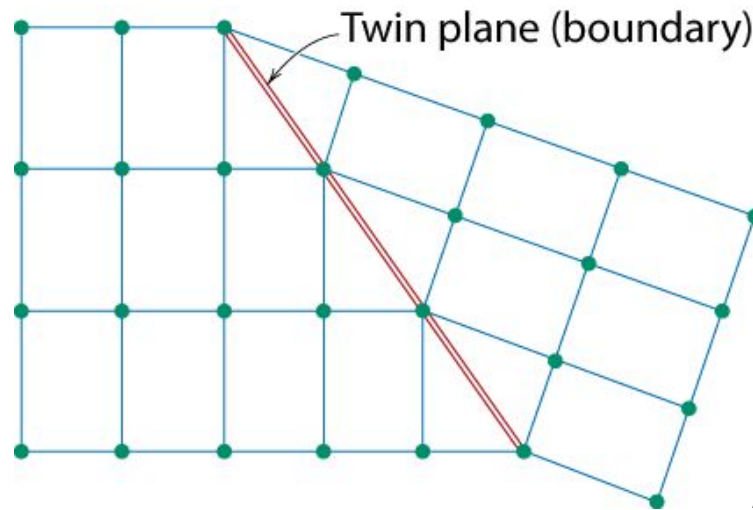
- Comparison among crystal structures:
FCC: many close-packed planes/directions;
HCP: only one plane, 3 directions;
BCC: none “super-close” many “near close”

- Specimens that were tensile tested.



Planar Defects in Solids

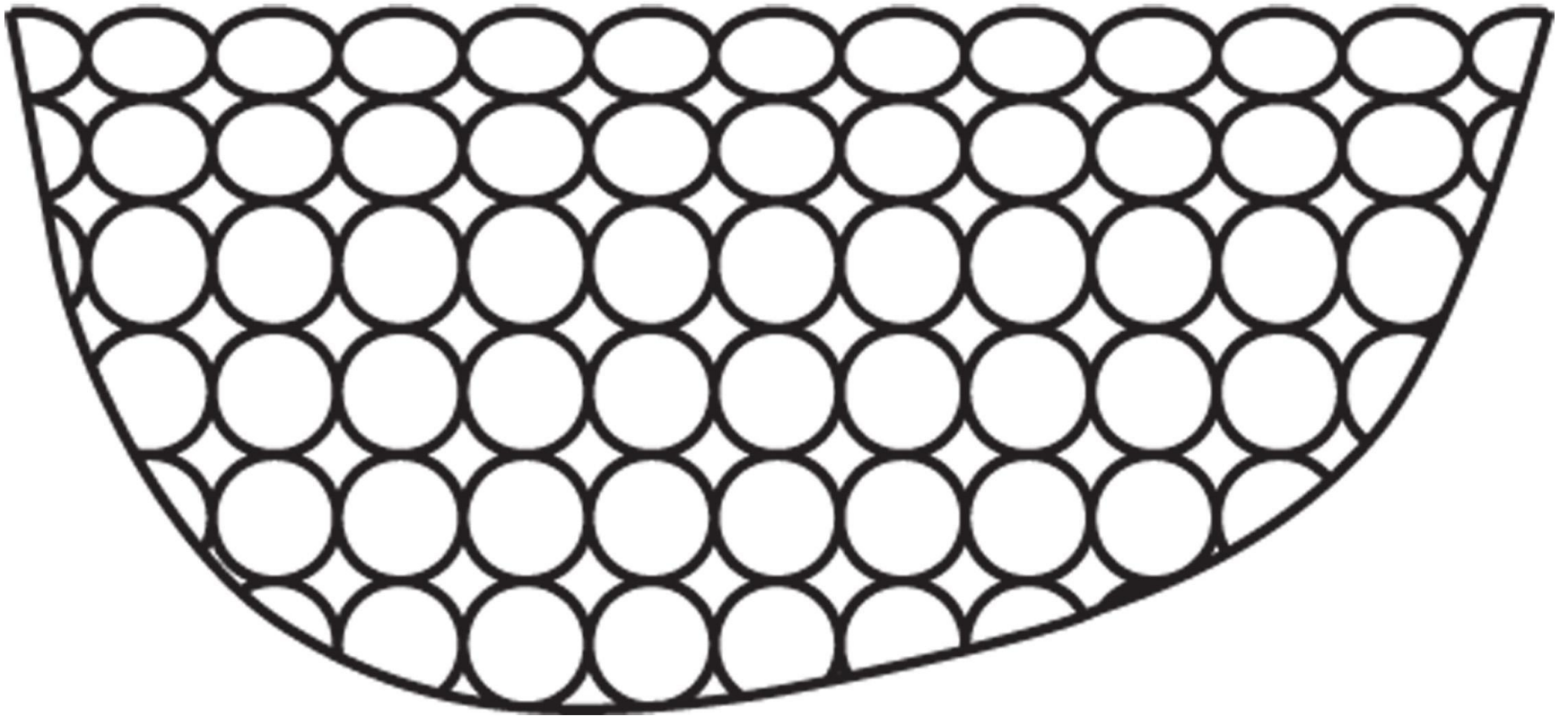
- One case is a **twin boundary (plane)**
 - Essentially a reflection of atom positions across the **twinning plane**.



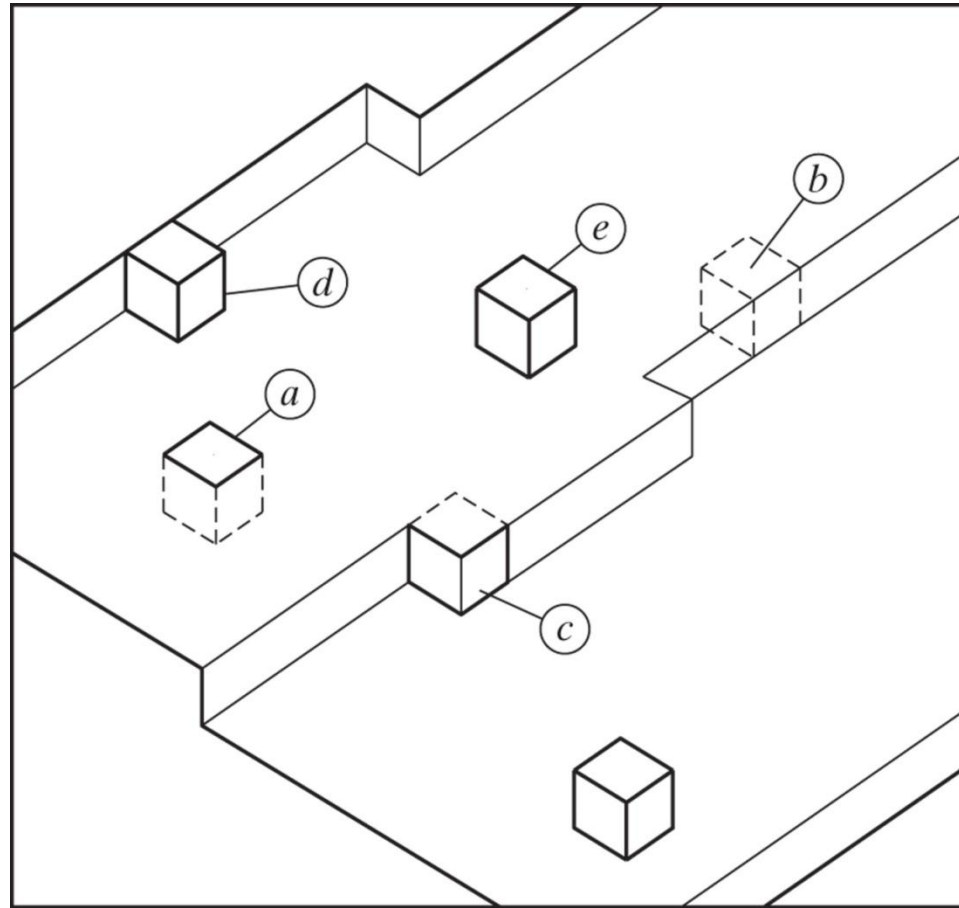
Adapted from Fig. 4.9, *Callister 7e*.

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

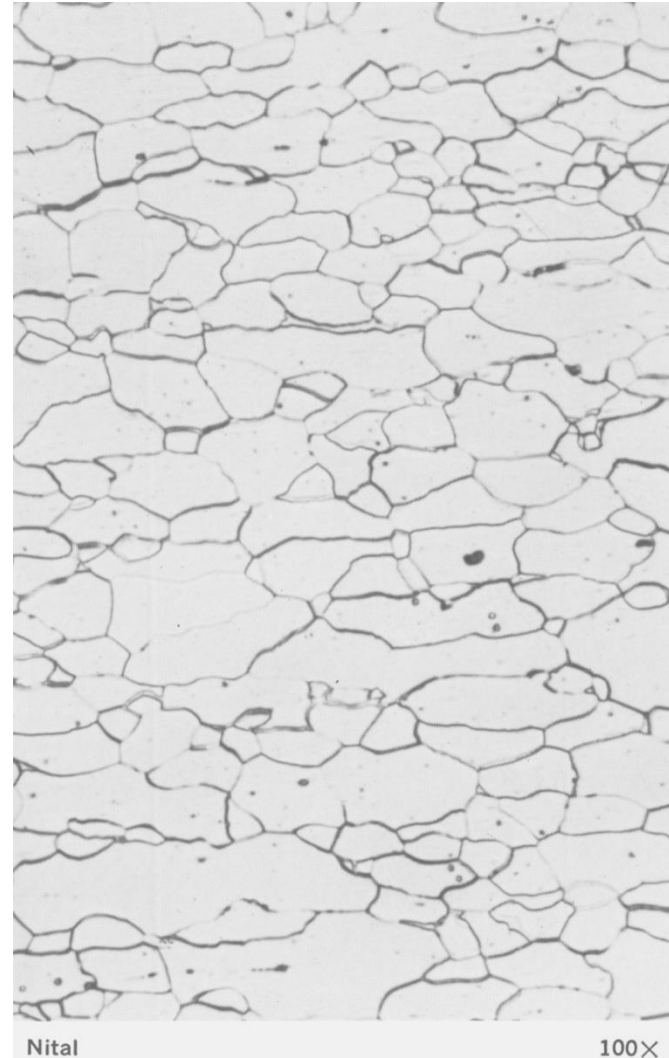
Simple view of the surface of a crystalline material.



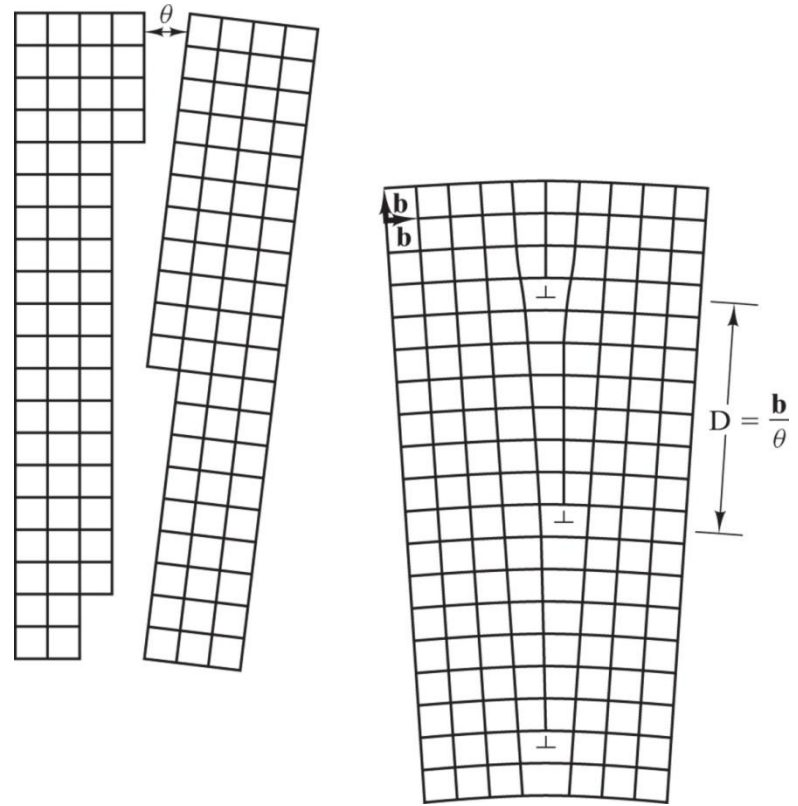
A more detailed model of the elaborate ledgeline structure of the surface of a crystalline material. Each cube represents a single atom. [From J. P. Hirth and G. M. Pound, J. Chem. Phys. 26, 1216 (1957).]



Typical optical micrograph of a grain structure, 100×. The material is a low-carbon steel. The grain boundaries have been lightly etched with a chemical solution so that they reflect light differently from the polished grains, thereby giving a distinctive contrast. (From Metals Handbook, 8th ed., Vol. 7: Atlas of Microstructures of Industrial Alloys, American Society for Metals, Metals Park, OH, 1972.)



Simple grain-boundary structure. This is termed a tilt boundary because it is formed when two adjacent crystalline grains are tilted relative to each other by a few degrees (θ). The resulting structure is equivalent to isolated edge dislocations separated by the distance b/θ , where b is the length of the Burgers vector, \mathbf{b} . (From W. T. Read, Dislocations in Crystals, McGraw-Hill Book Company, New York, 1953. Reprinted with permission of the McGraw-Hill Book Company.)

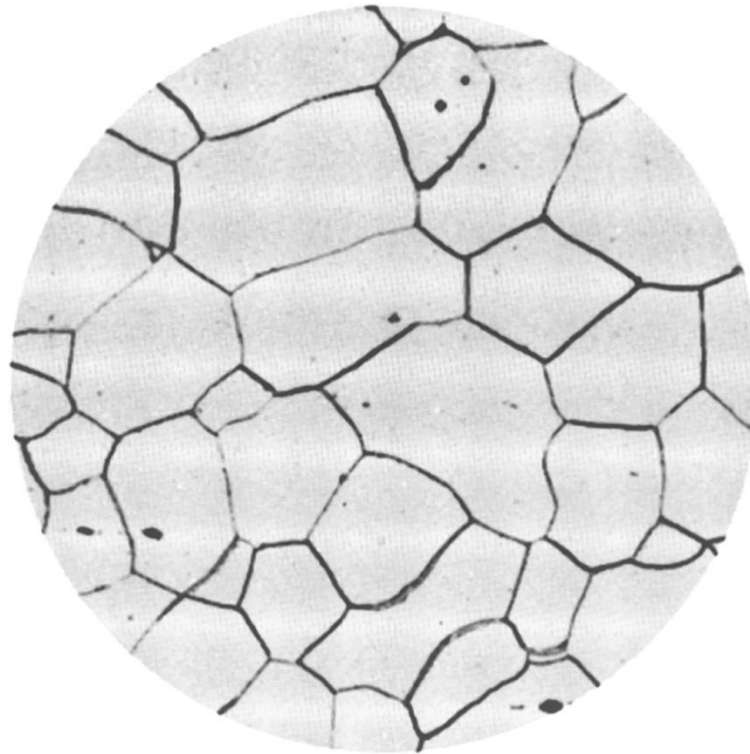


The ledge Growth leads to structures with Grain Boundries The shape and average size or diameter of the grains for some polycrystalline specimens are large enough to observe with the unaided eye. (Macrosopic examination)



FIGURE 4.10 High-purity polycrystalline lead ingot in which the individual grains may be discerned. $0.7\times$. (Reproduced with permission from *Metals Handbook*, Vol. 9, 9th edition, *Metallography and Microstructures*, American Society for Metals, Metals Park, OH, 1985.)

Specimen for the calculation of the grain-size number, G is defined at a magnification of $100\times$. This material is a low-carbon steel similar to that shown in Figure 4.18. (From Metals Handbook, 8th ed., Vol. 7: Atlas of Microstructures of Industrial Alloys, American Society for Metals, Metals Park, OH, 1972.)

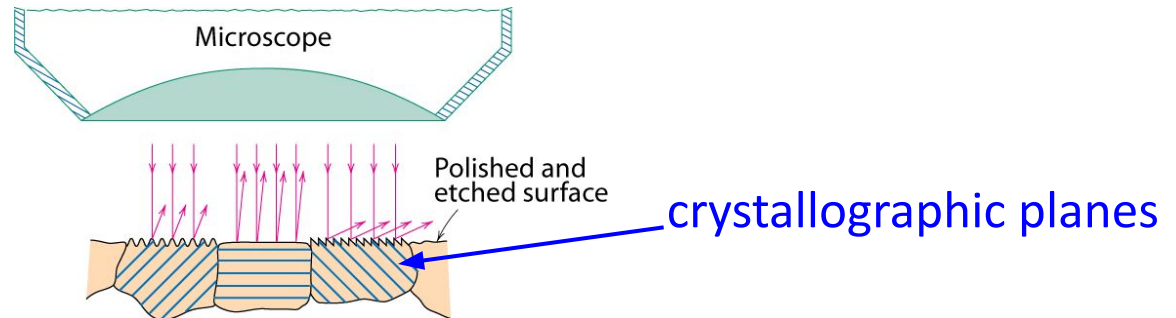


Nital

$100\times$

Optical Microscopy

- Useful up to $\sim 2000\times$ magnification (?).
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation since different Xtal planes have different reactivity.



Courtesy of J.E. Burke, General Electric Co.



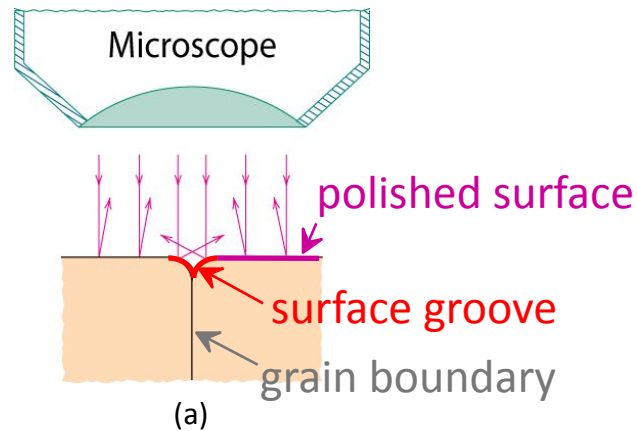
Micrograph of brass (a Cu-Zn alloy)

← 0.75mm →

Optical Microscopy

Since Grain boundaries...

- are planer imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- relate change in crystal orientation across boundary.



(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].)

ASTM grain size number

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

number of grains/in²
at 100x
magnification

ASTM (American Society for testing and Materials)

ASTM has prepared several standard comparison charts, all having different average grain sizes. To each is assigned a number from 1 to 10, which is termed the grain size number; the larger this number, the smaller the grains.

VISUAL CHARTS (@100x) each with a number
Quick and easy – used for steel

$$\text{No. of grains/square inch} \rightarrow N = 2^{G-1}$$

Grain size no. ←

NOTE: The ASTM grain size is related (or relates) a grain area *AT 100x MAGNIFICATION*

Determining Grain Size, using a micrograph taken at 300x

- We count 14 grains in a 1 in² area on the (300x) image
- To report ASTM grain size we needed a measure of N at 100x not 300x
- We need a conversion method!

$$N_M \left(\frac{M}{100} \right)^2 = 2^{G-1}$$

M is mag. of image

N_M is measured grain count at M

now solve for G:

$$\log(N_M) + 2(\log(M) - \log(100)) = (G - 1)\log(2)$$

∴

$$G = \frac{\log(N_m) + 2\log(M) - 4}{\log(2)} + 1$$

$$G = \frac{\log(14) + 2\log(300) - 4}{0.301} + 1 = 7.98 \cong 8$$

For this same material, how many Grains would I expect /in² at 100x? At 50x?

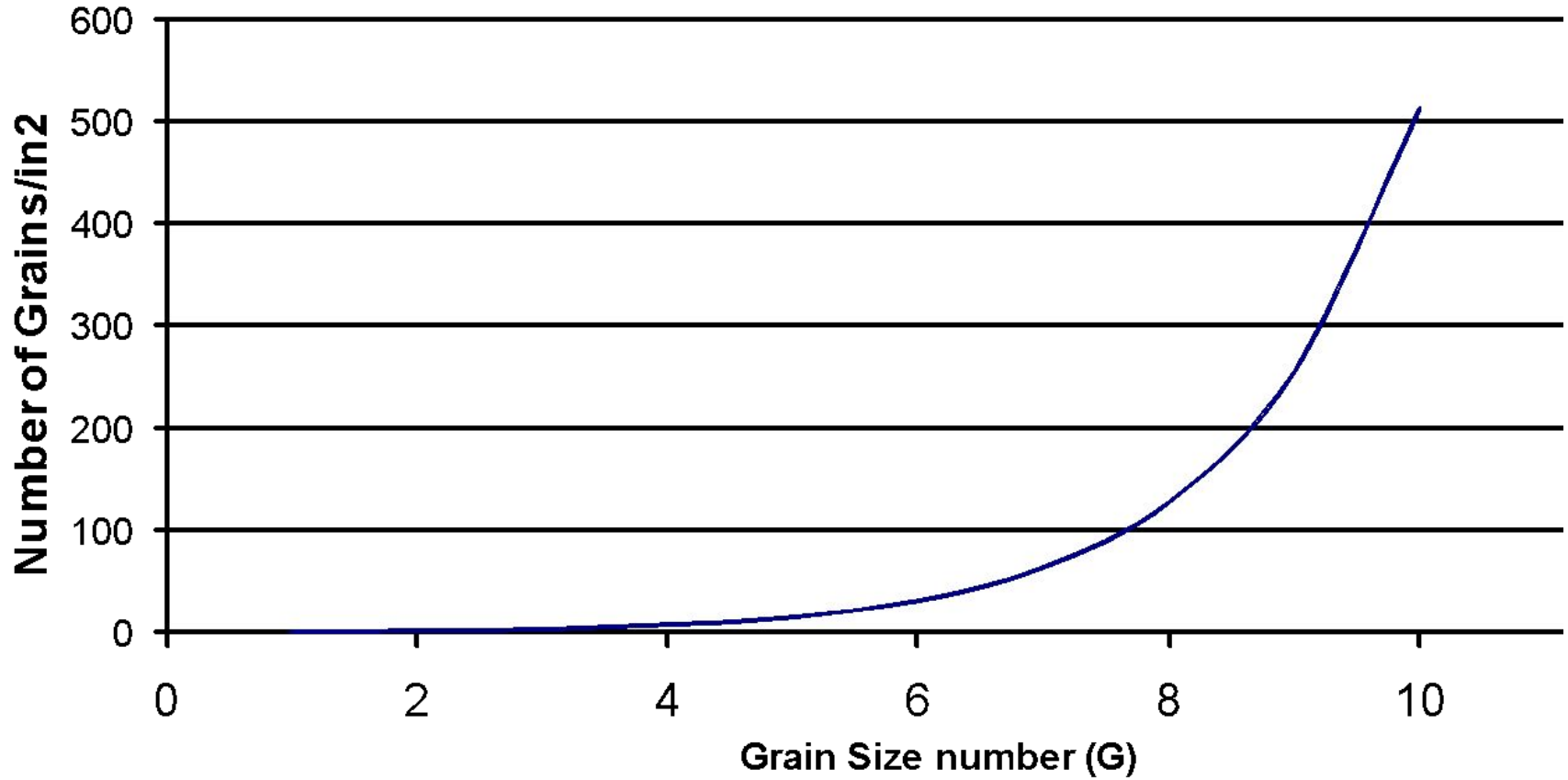
$$N = 2^{G-1} = 2^{8-1} \cong 128 \text{ grains/in}^2 \text{ (at 100x)}$$

Now, how many grain would I expect at 50x?

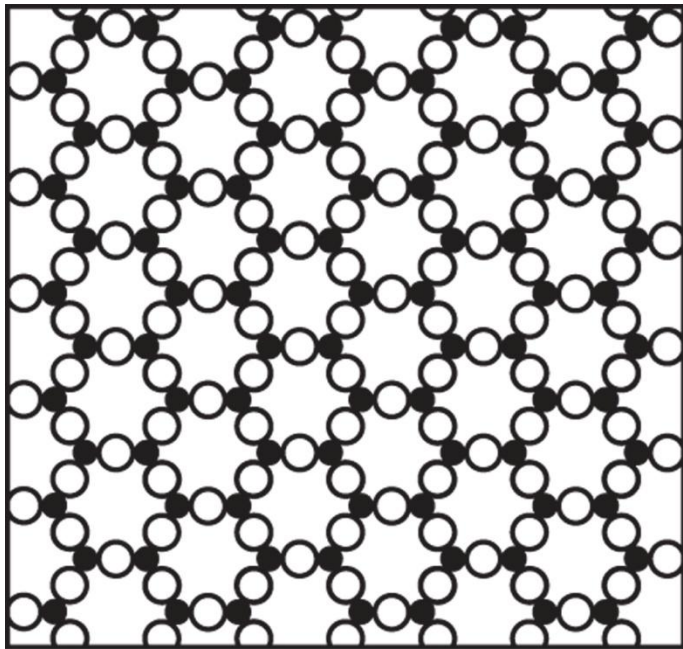
$$N_M = 2^{8-1} * \left(\frac{100}{M}\right)^2 = 128 * \left(\frac{100}{50}\right)^2$$

$$N_M = 128 * 2^2 = 512 \text{ grains/in}^2$$

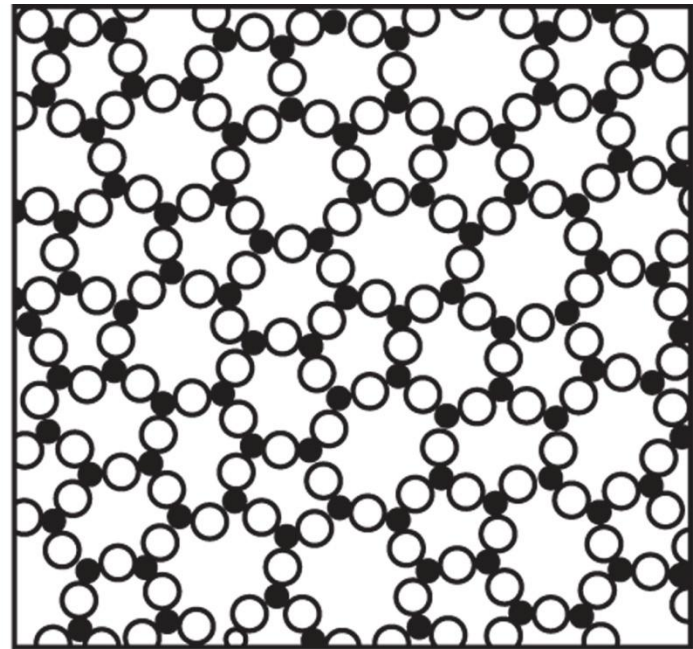
At 100x



Two-dimensional schematics give a comparison of (a) a crystalline oxide and (b) a non-crystalline oxide. The non-crystalline material retains short-range order (the triangularly coordinated building block), but loses long-range order (crystallinity). This illustration was also used to define glass in Chapter 1 (Figure 1.8).

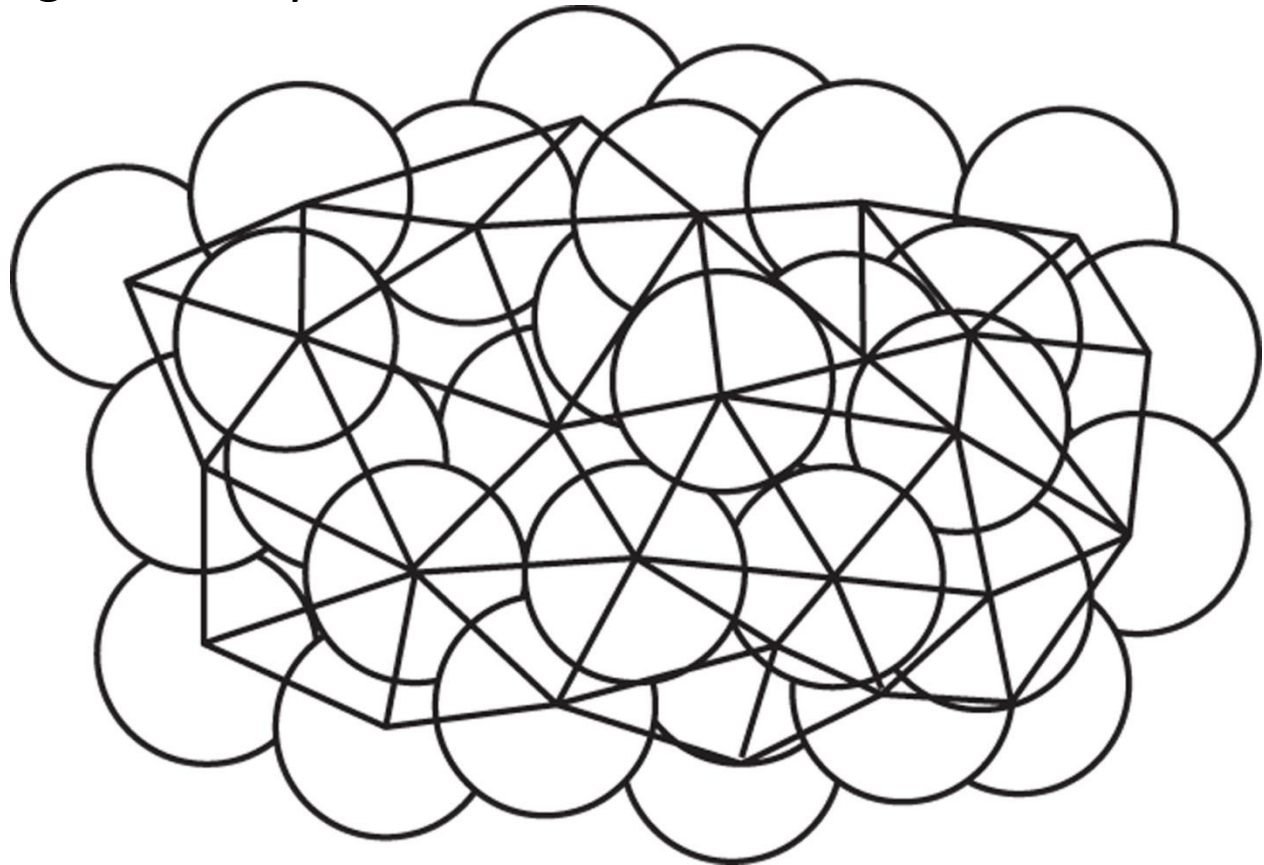


(a)

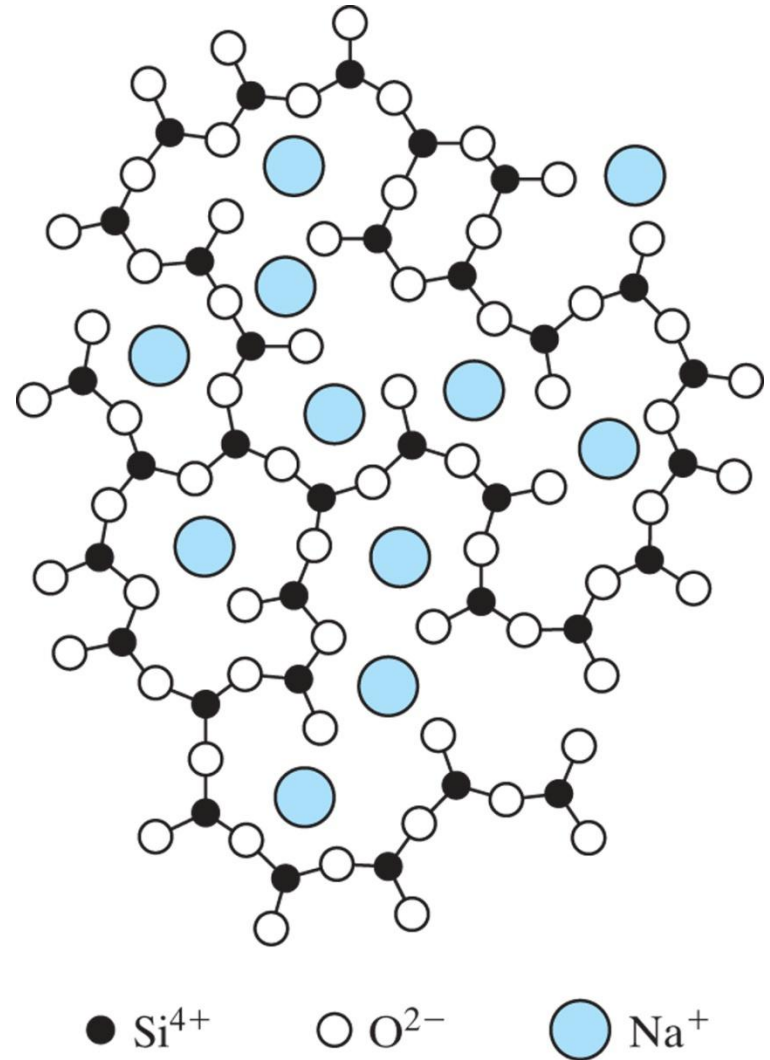


(b)

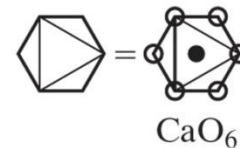
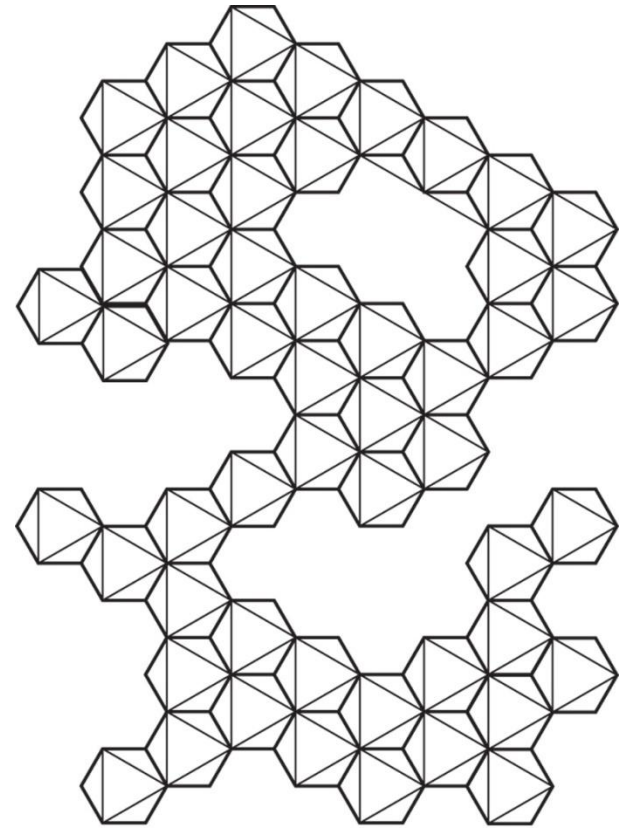
Bernal model of an amorphous metal structure. The irregular stacking of atoms is represented as a connected set of polyhedra. Each polyhedron is produced by drawing lines between the centers of adjacent atoms. Such polyhedra are irregular in shape and the stacking is not repetitive.



A chemical impurity such as Na^+ is a glass modifier, breaking up the random network and leaving nonbridging oxygen ions. [From B. E. Warren, J. Am. Ceram. Soc. 24, 256 (1941).]



Schematic illustration of medium-range ordering in a CaO–SiO₂ glass. Edge-sharing CaO₆ octahedra have been identified by neutron-diffraction experiments. [From P. H. Gaskell et al., Nature 350, 675 (1991).]



Summary

- **Point**, **Line**, **Surface** and **Volumetric** defects exist in solids.
- The number and type of defects can be varied and controlled
 - T controls vacancy conc.
 - amount of plastic deformation controls # of dislocations
 - Weight of charge materials determine concentration of substitutional or interstitial point 'defects'
- 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.
 - Inclusions can be intention for alloy development