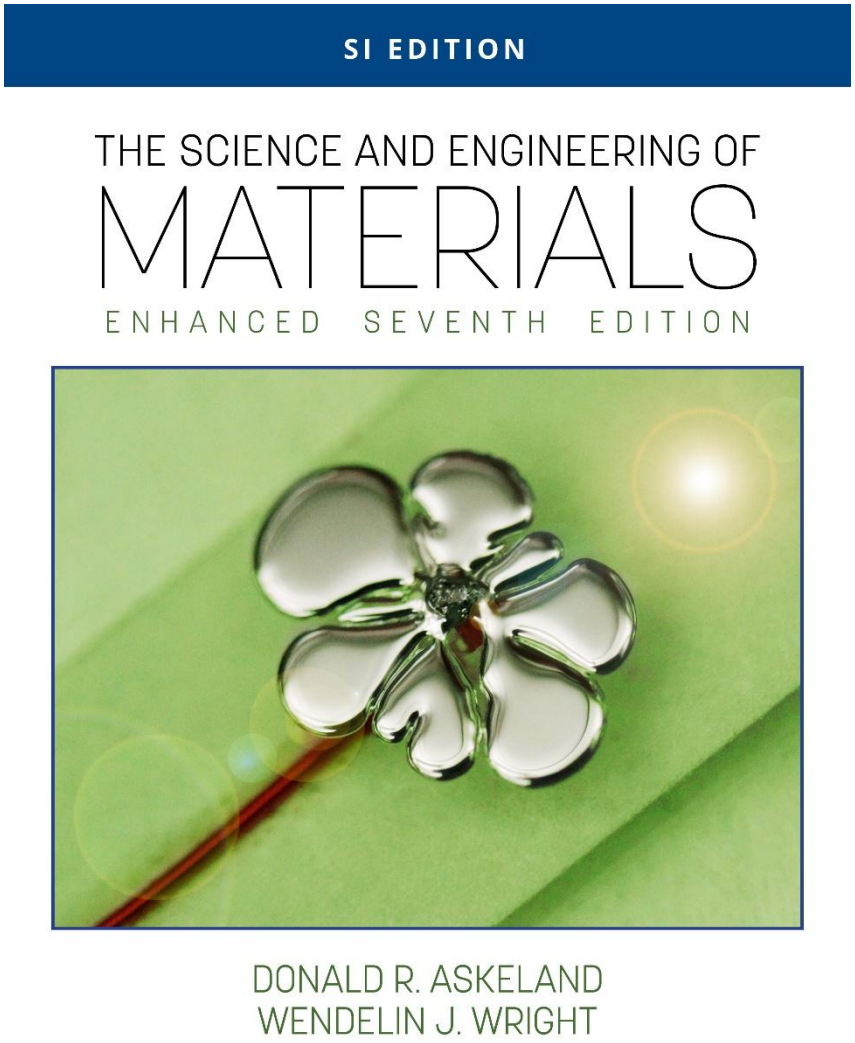


Chapter 3

Atomic and Ionic Arrangements

Chapter Learning Objectives

- Visualize how the atoms are arranged in the face-centered cubic, body-centered cubic, and hexagonal close-packed crystal structures and define the spatial relationships among the atoms in these structures. Given the parameters for a crystal structure other than those listed, visualize the atomic arrangements.
- Calculate properties of crystalline materials based on the crystal structure.
- Identify close-packed planes and directions in a crystal structure.
- Identify and use Miller indices for directions and planes in a crystal coordinate system.

Chapter Outline

Sections

- 3-1 Short- vs. Long-Range Order
- 3-2 Amorphous Materials
- 3-3 Lattice, Basis, Unit Cells & Crystal Structures
- 3-4 Allotropic or Polymorphic Transformations
- 3-5 Points, Directions & Planes in the Unit Cell
- 3-6 Interstitial Sites
- 3-7 Crystal Structures of Ionic Materials
- 3-8 Covalent Structures
- 3-9 Diffraction Techniques for Crystal Structure Analysis

3-1 Short- vs. Long-Range Order

- In different states of matter, we can find various levels of order.

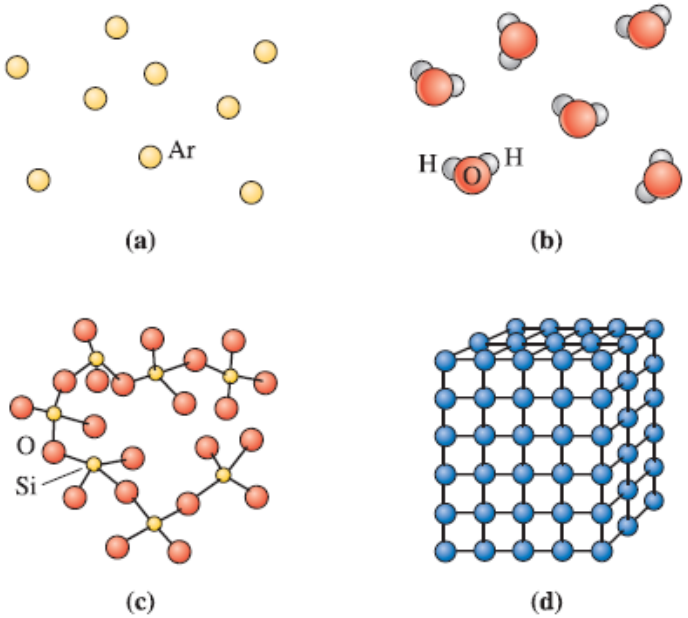


Figure 3-1 Levels of atomic arrangements in materials: (a) Inert monoatomic gases have no regular ordering of atoms. Some materials, including water vapor (b) and silicate glass (c), have short-range order. (d) Metals, alloys, many ceramics, and some polymers have regular ordering of atoms/ions that extends through the material.

3-1 Short- vs. Long-Range Order

- No order: Monoatomic gases

- Short-Range Order (SRO): If order extends only to nearest neighboring particles e.g., in water molecules (hydrogen bonding), polymers, inorganic glasses, etc.
- Long-Range Order (LRO): Materials with a crystal structure fall in the LRO category. Crystalline materials may consist of either:
  - A single crystal
  - Many misaligned crystals, called grains – these materials are called polycrystalline.

3-1 Short- vs. Long-Range Order

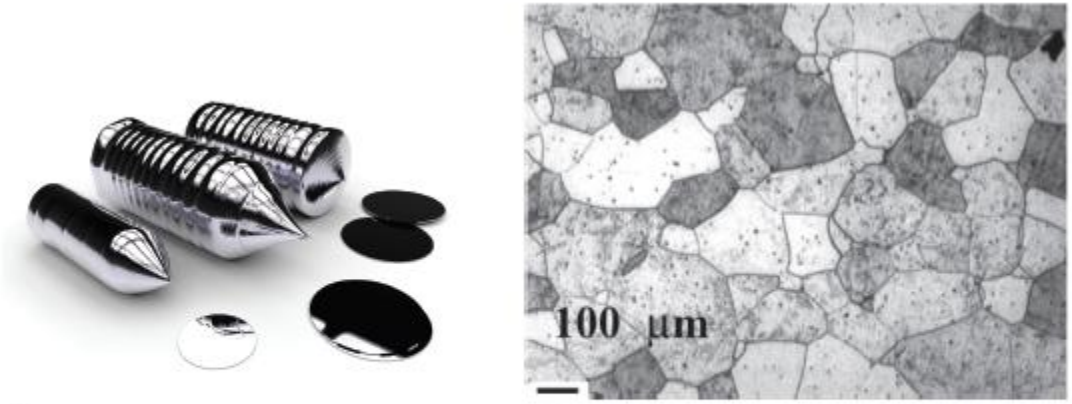


Figure 3-2 (a) Photograph of a silicon single crystal. (*Petr Sobolev/iStock/Thinkstock*) (b) Micrograph of a polycrystalline stainless steel showing grains and grain boundaries. (*Micrograph courtesy of Dr. A.J. Deardo, Dr. M. Hua and Dr. J. Garcia*)

- Many engineering materials are polycrystalline, e.g., steels.

- Liquid crystals have a special type of order. They exhibit different levels of ordering in different states induced by external stimuli.

3-2 Amorphous Materials

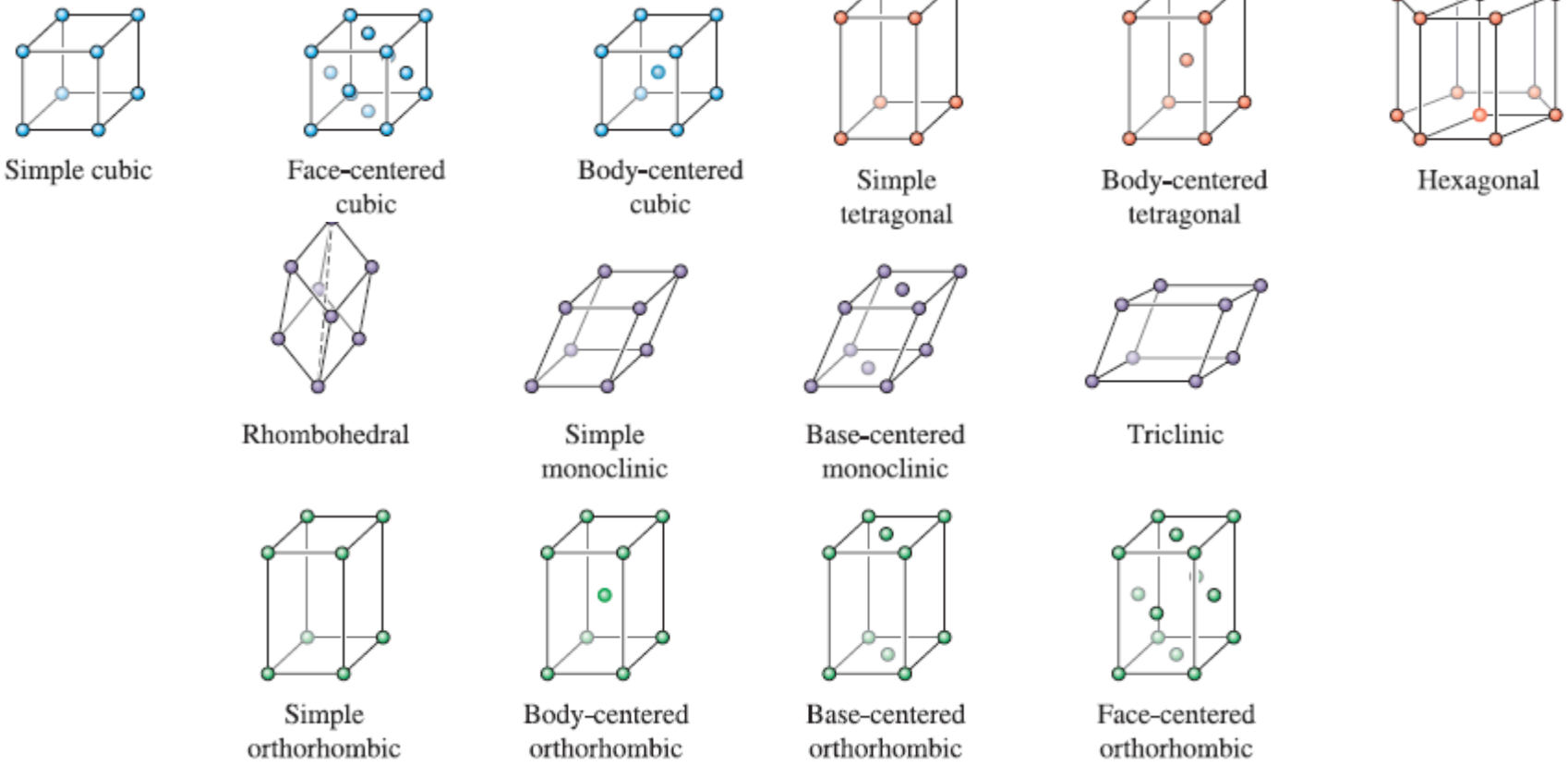
- Any solid exhibiting only SRO of atoms/ions is an amorphous material.
- In general, amorphous materials form when the process kinetics prevent the material from reaching its LRO equilibrium state.
- Glasses typically form in polymer & ceramic systems.
- Metallic glasses, possessing interesting properties, may be formed by rapidly cooling metals/alloys to prevent crystallization.

3-3 Lattice, Basis, Unit Cells & Crystal Structure

- To describe the 3-D spatial arrangement of atoms/ions in a solid, we use the concept of crystal structure, lattice and basis.
- Crystal structure = lattice + basis.
- A lattice is a collection of points arranged in a periodic pattern, such that each lattice point's surroundings are identical.
- A basis is a group of 1 or more atoms arranged in a particular way with respect to each other and associated with each lattice point.

3-3 Lattice, Basis, Unit Cells & Crystal Structure

- There are 14 unique ways to arrange points in 3D space. There are called the Bravais lattices.



3-3 Lattice, Basis, Unit Cells & Crystal Structure

- Although there are 14 Bravais lattices, there can be infinite bases associated with them.

- There are 7 crystal systems associated with the Bravais lattices: cubic, tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic & triclinic.

- A unit cell is a subdivision of the lattice that still captures the overall lattice characteristics.

3-3 Lattice, Basis, Unit Cells & Crystal Structure

- The lattice parameters (axial lengths) and interaxial angles are used to classify unit cells for each of the 7 crystal systems.

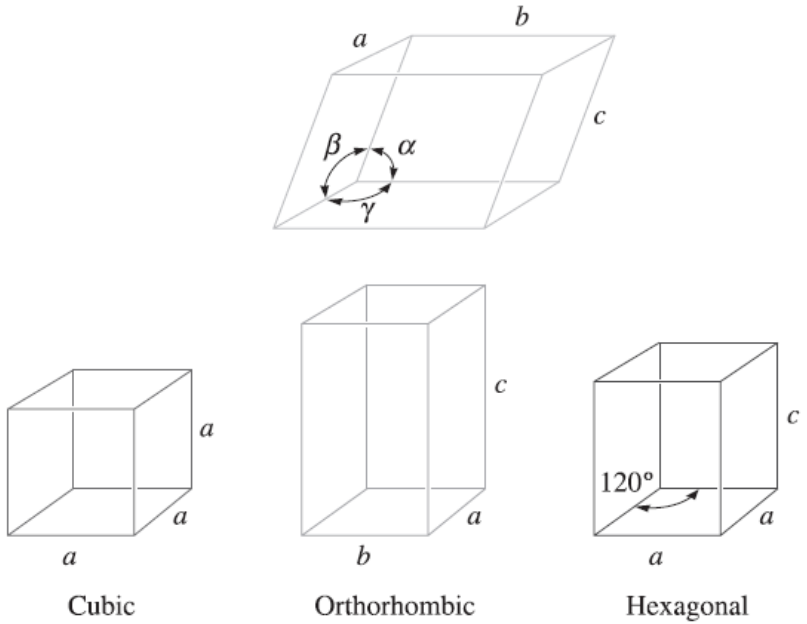


Figure 3-6 Definition of the lattice parameters and their use in cubic, orthorhombic, and hexagonal crystal systems.

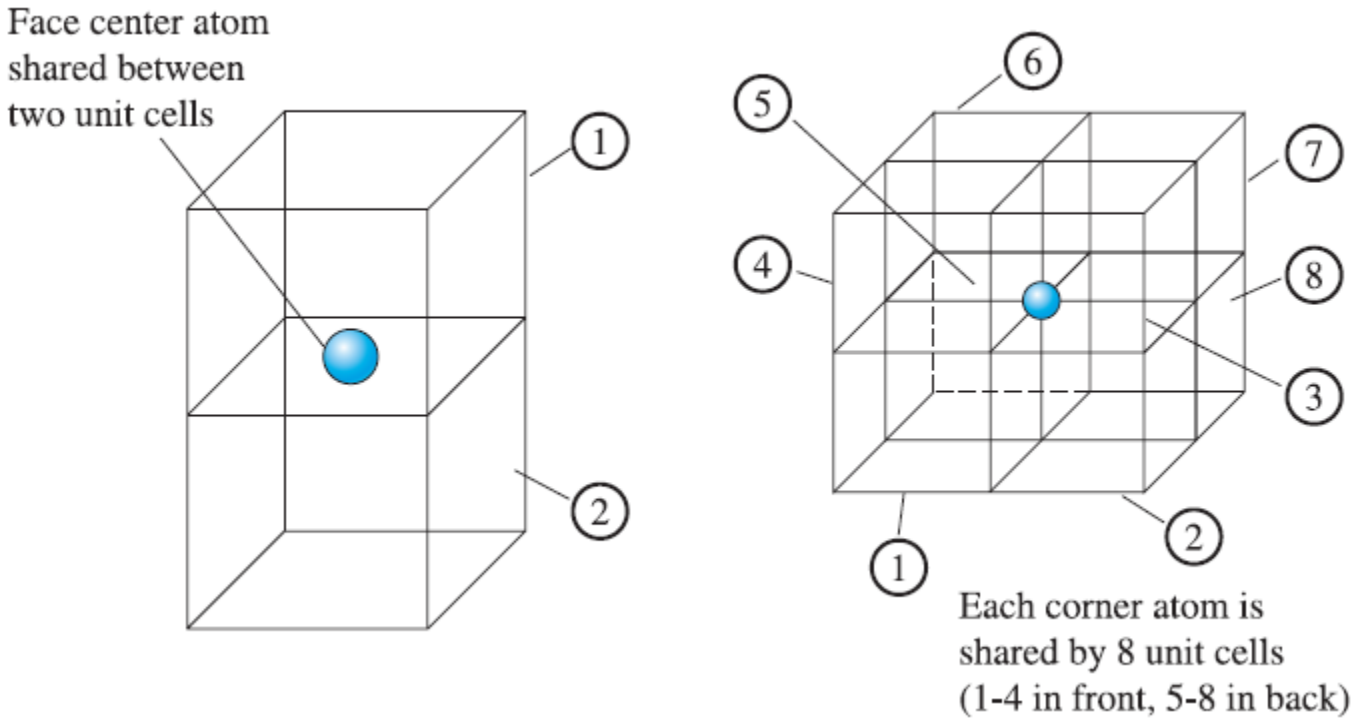
3-3 Lattice, Basis, Unit Cells & Crystal Structure

Table 3-1 Characteristics of the seven crystal systems

Structure	Axes	Angles between Axes	Volume of the Unit Cell
Cubic	$a = b = c$	All angles equal 90°.	a^3
Tetragonal	$a = b \neq c$	All angles equal 90°.	a^2c
Orthorhombic	$a \neq b \neq c$	All angles equal 90°.	abc
Hexagonal	$a = b \neq c$	Two angles equal 90°. The angle between a and b equals 120°.	$0.866a^2c$
Rhombohedral or trigonal	$a = b = c$	All angles are equal and none equals 90°.	$a^3\sqrt{1 - 3\cos^2\alpha + 2\cos^3\alpha}$
Monoclinic	$a \neq b \neq c$	Two angles equal 90°. One angle (β) is not equal to 90°.	$abc \sin\beta$
Triclinic	$a \neq b \neq c$	All angles are different and none equals 90°.	$abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$

3-3 Lattice, Basis, Unit Cells & Crystal Structure

- The number of atoms per unit cell depends on the number of atoms on corners, faces, enclosed, etc.



Determine the number of lattice points per unit cell in the cubic crystal systems. If there is only one atom located at each lattice point, calculate the number of atoms per unit cell.

3-3 Lattice, Basis, Unit Cells & Crystal Structure

- Directions within the unit cell in which the atoms are in continuous contact are called close-packed directions.

- We can define a lattice parameter a_0 which relates the dimensions of the unit cell to the size of the atoms, using close-packed directions.

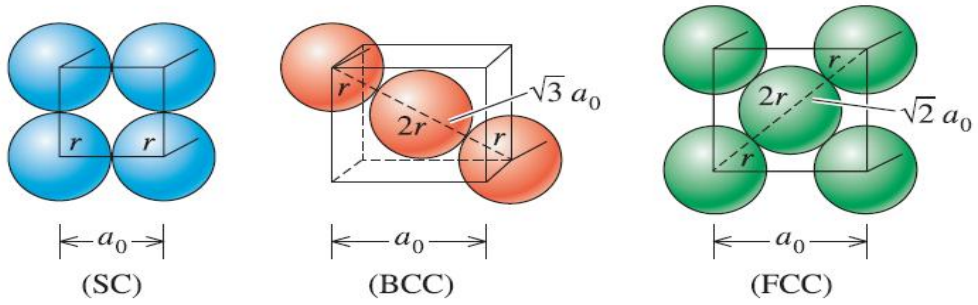


Figure 3-9 The relationships between the atomic radius and the lattice parameter in cubic systems (for Example 3-3).

3-3 Lattice, Basis, Unit Cells & Crystal Structure

- The coordination number is the number of atoms touching a given atom, or the number of its nearest neighbors.

- The packing factor is the fraction of space occupied by atoms (modeled as hard spheres) within the unit cell.

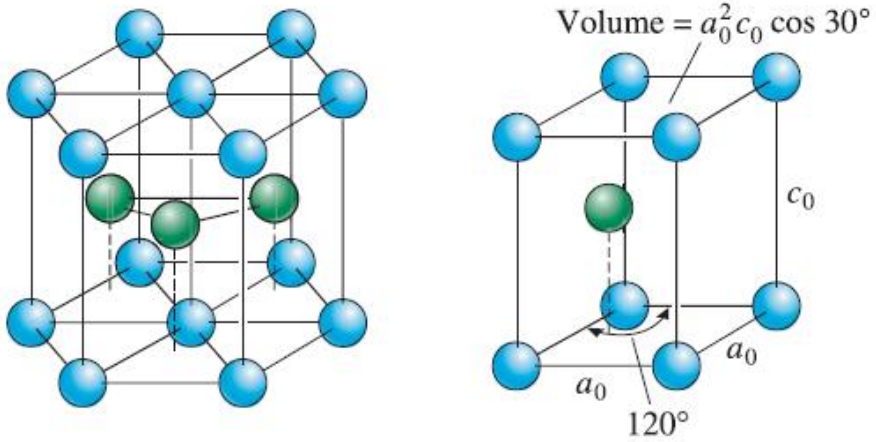
$$\text{Packing factor} = \frac{(\#\ \text{of atoms/cell})(\text{volume of each atom})}{\text{volume of unit cell}}$$

3-3 Lattice, Basis, Unit Cells & Crystal Structure

- The theoretical density of a material may be found via

$$\text{Density } \rho = \frac{(\#\text{ of atoms/cell})(\text{atomic mass})}{(\text{volume of unit cell})(\text{Avogadro number})}$$

- The hexagonal close-packed (HCP) structure:



3-3 Lattice, Basis, Unit Cells & Crystal Structure

Table 3-2 Crystal structure characteristics of some metals at room temperature

Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α-Mo
Body-centered cubic (BCC)	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, W, Mo, Nb, Ta, K, Na, V, Cr
Face-centered cubic (FCC)	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed (HCP)	$a_0 = 2r$ $c_0 \approx 1.633a_0$	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd

3-4 Allotropic/Polymorphic Transformations

- Materials with more than one crystal structure are called allotropic (pure elements) or polymorphic (compounds).

- At room temperature, iron has BCC structure, but at higher temperature it changes to FCC.

- Many ceramic materials, such as silica or zirconia, are polymorphic. The crystal structure changes upon heating, and dopants are used to stabilize the material from the volume change after heating.

3-5 Points, Directions & Planes in the Unit Cell

- We can locate points in the unit cell, e.g., atom positions, by a right-handed coordinate system.

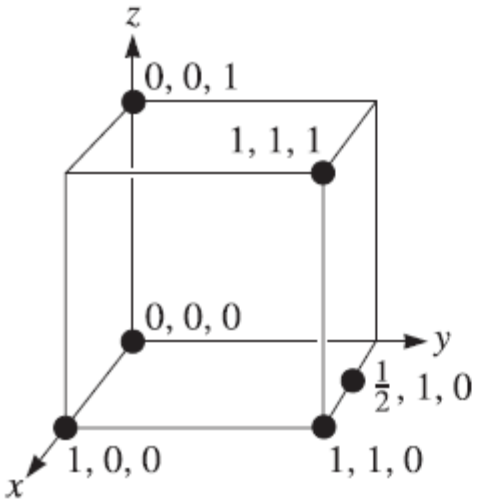


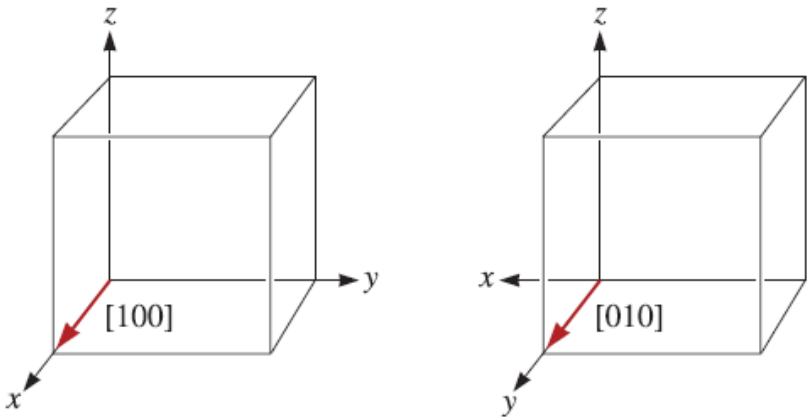
Figure 3-12 Coordinates of selected points in the unit cell. The number refers to the distance from the origin in terms of lattice parameters.

3-5 Points, Directions & Planes in the Unit Cell

- Certain important directions in the unit cell are represented by Miller indices. To determine Miller indices for a direction:
  - Identify 2 points in that direction
  - Subtract the coordinates of the "tail" point from the "head" point.
  - Clear any fractions to lowest possible integers
  - Enclose the numbers in square brackets [], and replace any negative signs with a bar over the number.

3-5 Points, Directions & Planes in the Unit Cell

- Several points should be noted about Miller Indices:
  - A direction and its negative are not equal, e.g, $[100]$ is not equal to $[\bar{1}00]$
  - A direction and its multiple are identical
  - Certain groups of directions are equivalent



$$\langle 110 \rangle = \begin{cases} [110]\ [\bar{1}\bar{1}0] \\ [101]\ [\bar{1}0\bar{1}] \\ [011]\ [0\bar{1}\bar{1}] \\ [1\bar{1}0]\ [\bar{1}10] \\ [10\bar{1}]\ [\bar{1}01] \\ [01\bar{1}]\ [0\bar{1}1] \end{cases}$$

Figure 3-14 Equivalency of crystallographic directions of a form in cubic systems.

3-5 Points, Directions & Planes in the Unit Cell

- Repeat distance (distance between lattice points along the direction) is another way to classify directions.

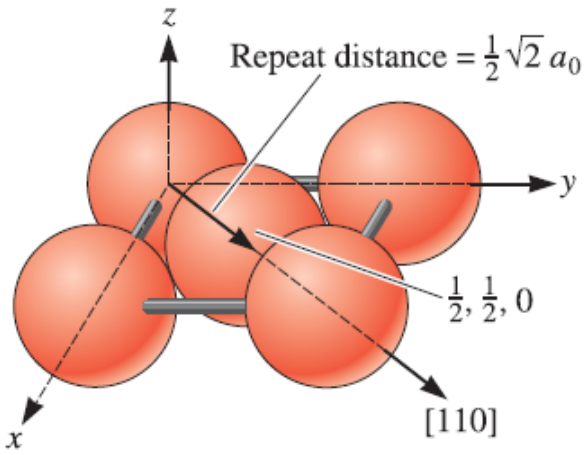


Figure 3-15 Determining the repeat distance, linear density, and packing fraction for a [110] direction in FCC copper.

- Linear density is the reciprocal of repeat distance

- $\text{Packing fraction} = (\text{linear density})(2r)$

3-5 Points, Directions & Planes in the Unit Cell

- Certain planes of atom (e.g., close-packed planes) are also significant. Miller indices can be used to identify these planes as follows:
  - Identify the x,y,z intercepts of the plane in terms of lattice parameters. If the plane passes through the origin, the origin must be moved to an adjacent unit cell.
  - Take reciprocal of the intercepts.
  - Clear fractions but do not reduce to lowest integers.
  - Enclose resulting numbers in parentheses (), and use an overbar for negative numbers.

3-5 Points, Directions & Planes in the Unit Cell

- Some things to keep in mind when using Miller indices for planes:
  - Unlike directions, planes and their negatives are identical.
  - Unlike directions, planes and their multiples are not identical.
  - In each unit cell, planes of a family represent groups of equivalent planes, denoted by {}.
  - In cubic systems, a direction is perpendicular to a plane if both have the same indices.

3-5 Points, Directions & Planes in the Unit Cell

- A special set of Miller-Bravais indices has been devised for hexagonal unit cells.

- We can use either a 3-axis or a 4-axis system for the HCP cells.

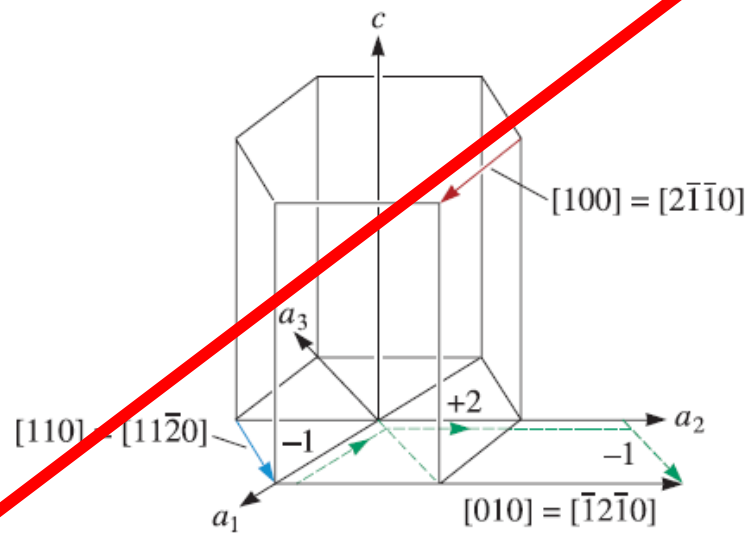


Figure 3-20 Typical directions in the HCP unit cell, using both three- and four-axis systems. The dashed lines show that the [$\bar{1}$2$\bar{1}$0] direction is equivalent to a [010] direction.

3-5 Points, Directions & Planes in the Unit Cell

- The interaction of close-packed directions and planes is important for the mechanical behavior of materials.

- The Miller indices for close-packed directions and planes in various crystal systems are

Table 3-5 Close-packed directions and planes

Structure	Directions	Planes
SC	⟨100⟩	None
BCC	⟨111⟩	None
FCC	⟨110⟩	{111}
HCP*	[100], [010], [110]	(001), (002)

**In the four-axis notation, the close-packed directions and planes are <11$\bar{2}$0> and (0001).*

3-5 Points, Directions & Planes in the Unit Cell

- Unit cells can also be considered as being composed of a stacking of close-packed planes

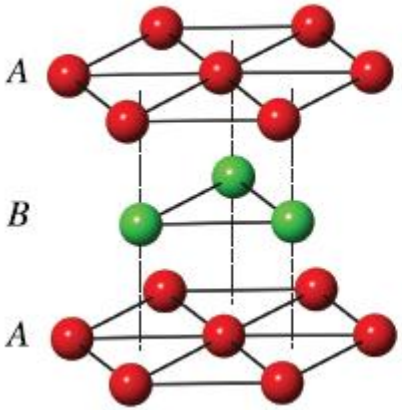
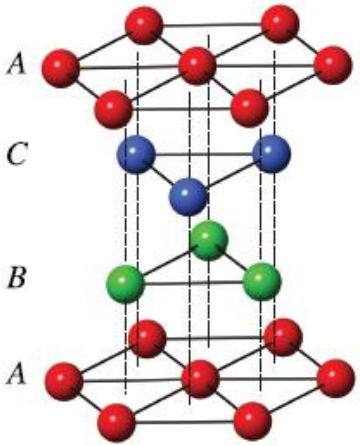


Figure 3-21 The *ABABAB* stacking sequence of close-packed planes produces the HCP structure.



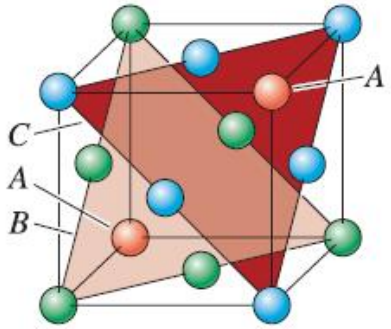


Figure 3-22 The *ABCABCABC* stacking sequence of close-packed planes produces the FCC structure.

3-5 Points, Directions & Planes in the Unit Cell

- Material properties can vary with direction. If this is the case, the material is crystallographically anisotropic.

- If a material's properties are identical in all directions, the material is called isotropic.

- Many polycrystalline materials are effectively isotropic, because the random orientation of grains cancels out the anisotropy of individual grains.

3-5 Points, Directions & Planes in the Unit Cell

- The interplanar distance between 2 adjacent parallel planes with the same Miller Indices can be found for *cubic* materials via

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

3-6 Interstitial Sites

- In all crystal structures, there are interstitial sites between atoms where smaller atoms may be placed.

- There are different kinds of interstitial sites, such as cubic, tetrahedral and octahedral

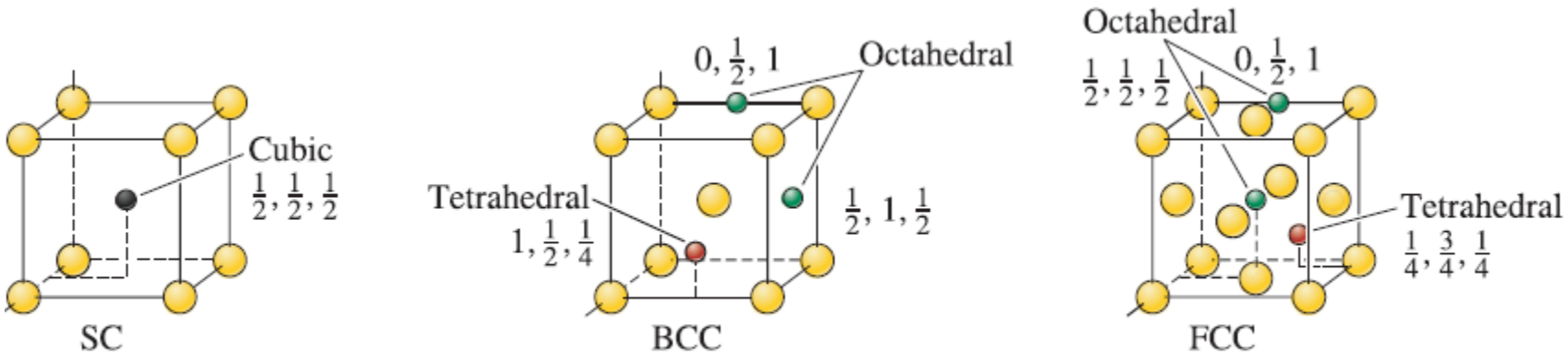
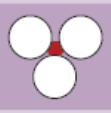
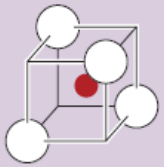
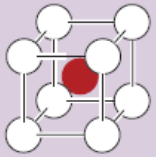


Figure 3-23 The location of the interstitial sites in cubic unit cells. Only representative sites are shown.

3-6 Interstitial Sites

- Depending on the relative size of the interstitial atom, it prefers to occupy different types of sites based on their coordination number.

Table 3-6 The coordination number and the radius ratio. The atoms/ions are drawn less than full for clarity

Coordination Number	Location of Interstitial	Radius Ratio	Representation
2	Linear	0–0.155	
3	Center of triangle	0.155–0.225	
4	Center of tetrahedron	0.225–0.414	
6	Center of octahedron	0.414–0.732	
8	Center of cube	0.732–1.000	

3-7 Crystal Structure of Ionic Materials

- To consider the crystal structure of ionically bonded materials, we need to consider the following factors:
  - Ionic Radii: Anions (larger) occupy the lattice positions, while cations (smaller) occupy interstitial sites. Ionic radii are not fixed and may vary between different crystal structures for the same ion
  - Electrical Neutrality: The overall material has to be neutral, so the coordination numbers of the anions and cations need to be related to their valence
  - Anion Polyhedra: As a rule, coordination polyhedra (formed by anion close-packing) share corners, as opposed to faces/corners, to reduce electrostatic repulsion between cations

3-7 Crystal Structure of Ionic Materials

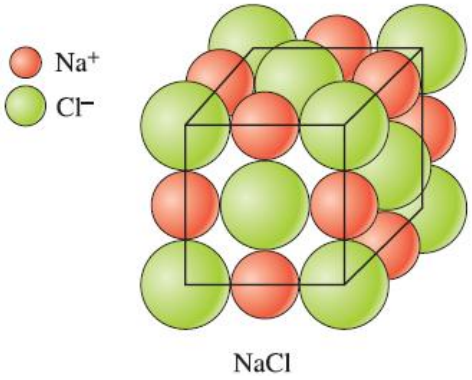


Figure 3-24 The sodium chloride structure, an FCC unit cell with two ions (Na^+ and Cl^-) per lattice point. *Note*: ion sizes not to scale.

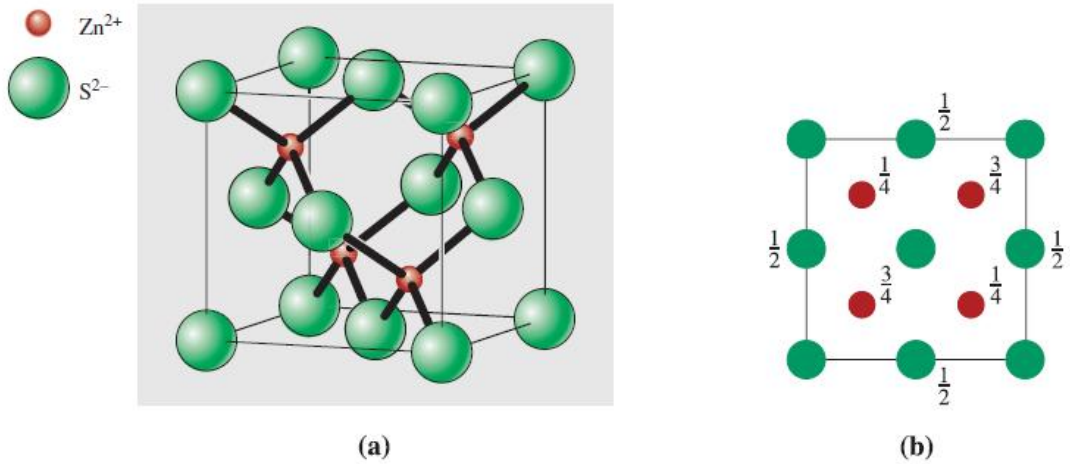
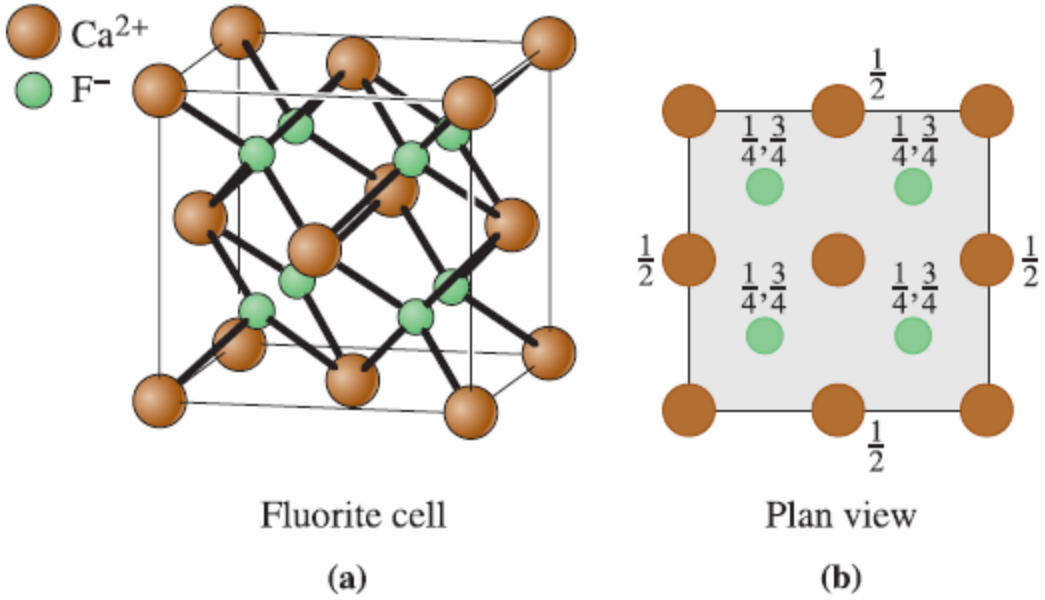


Figure 3-25 (a) The zincblende unit cell, (b) plan view. The fractions indicate the positions of the atoms out of the page relative to the height of the unit cell.

3-7 Crystal Structure of Ionic Materials



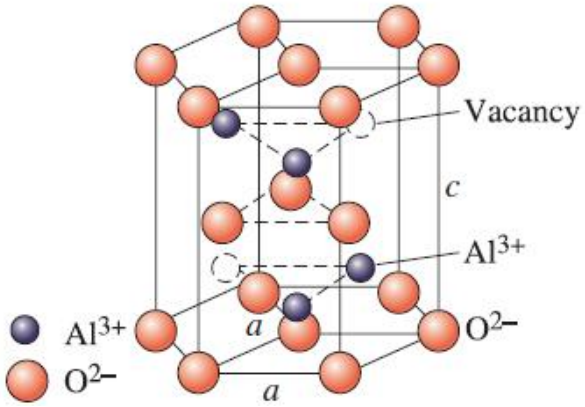


Figure 3-27 Corundum structure of alpha-alumina (α-Al_2O_3).

3-8 Covalent Structures

- Covalent crystalline structures are frequently complicated due to the directionality of the covalent bonds.

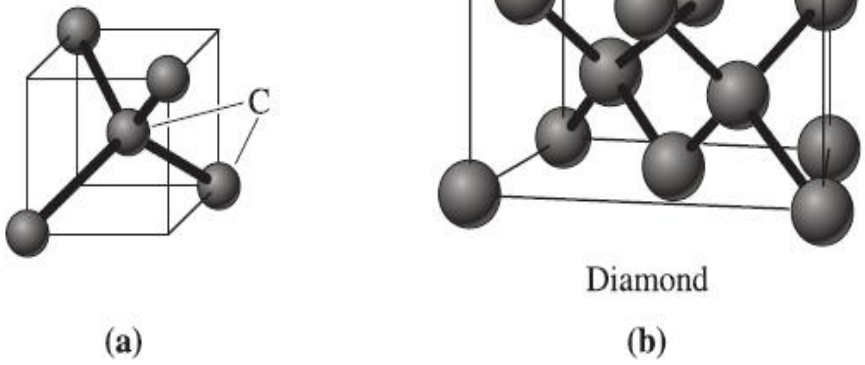


Figure 3-30 (a) Tetrahedron and (b) the diamond cubic (DC) unit cell. This open structure is produced because of the requirements of covalent bonding.

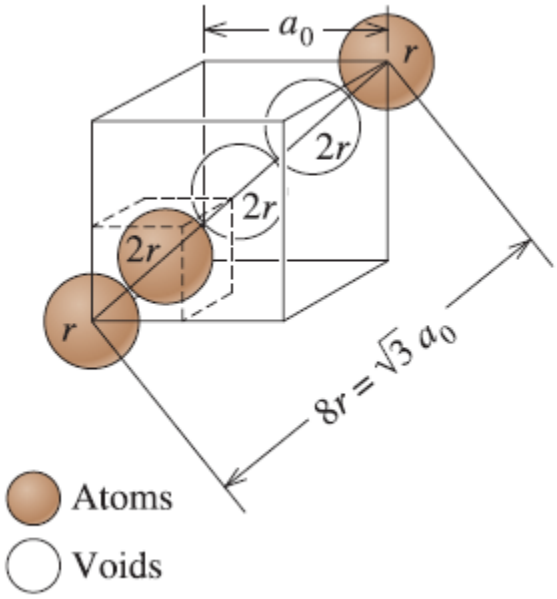


Figure 3-31 Determining the relationship between the lattice parameter and atomic radius in a diamond cubic cell (for Example 3-17).

3-8 Covalent Structures

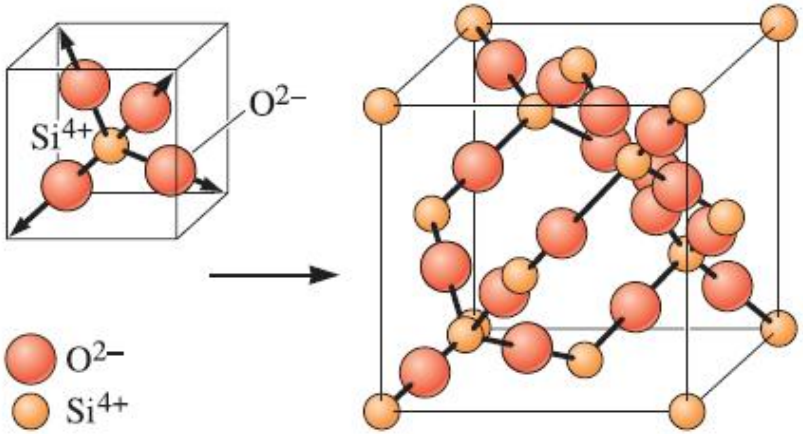


Figure 3-32 The silicon-oxygen tetrahedron and the resultant β-cristobalite form of silica.

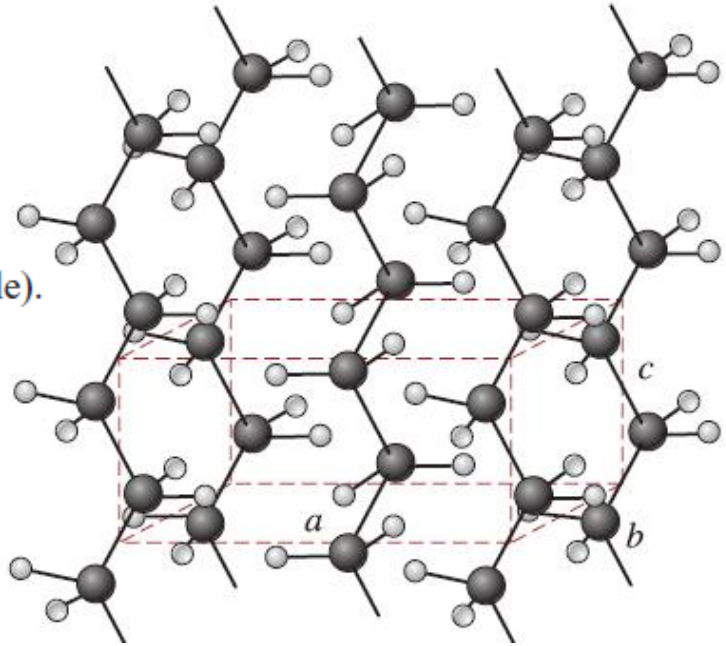


Figure 3-33 The unit cell of crystalline polyethylene (not to scale).

3-9 Diffraction Techniques

- A material's crystal structure can be found by a technique called X-ray diffraction (XRD).

- X-ray diffraction gives knowledge of the various crystallographic planes in a powdered sample. Knowledge of the planes present can then be used to infer the crystal structure of the material.

- X-ray diffraction is based on Bragg's Law

$$\sin\theta = \frac{\lambda}{2d_{hkl}}$$

3-9 Diffraction Techniques

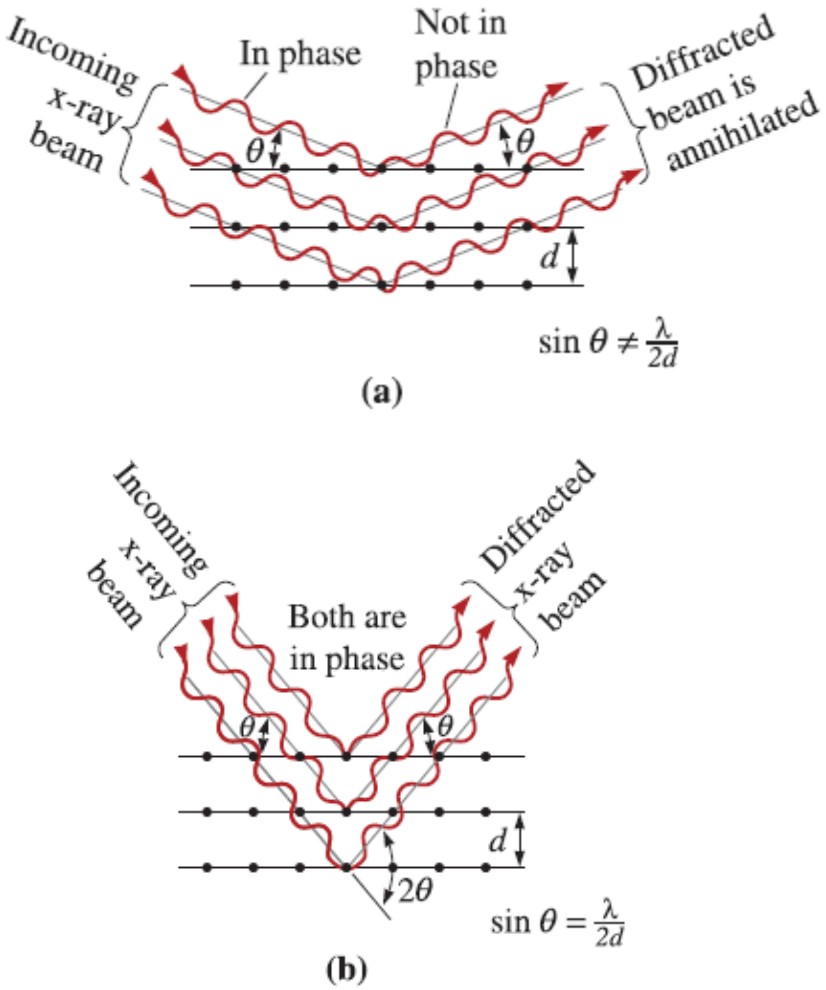
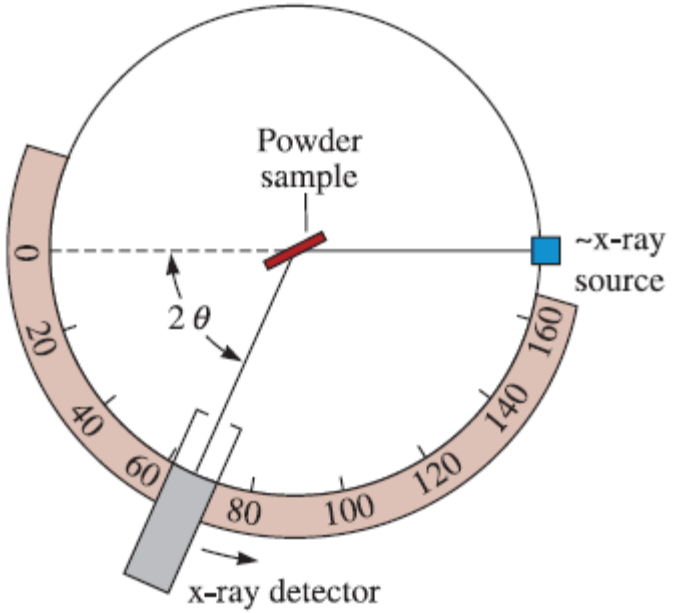
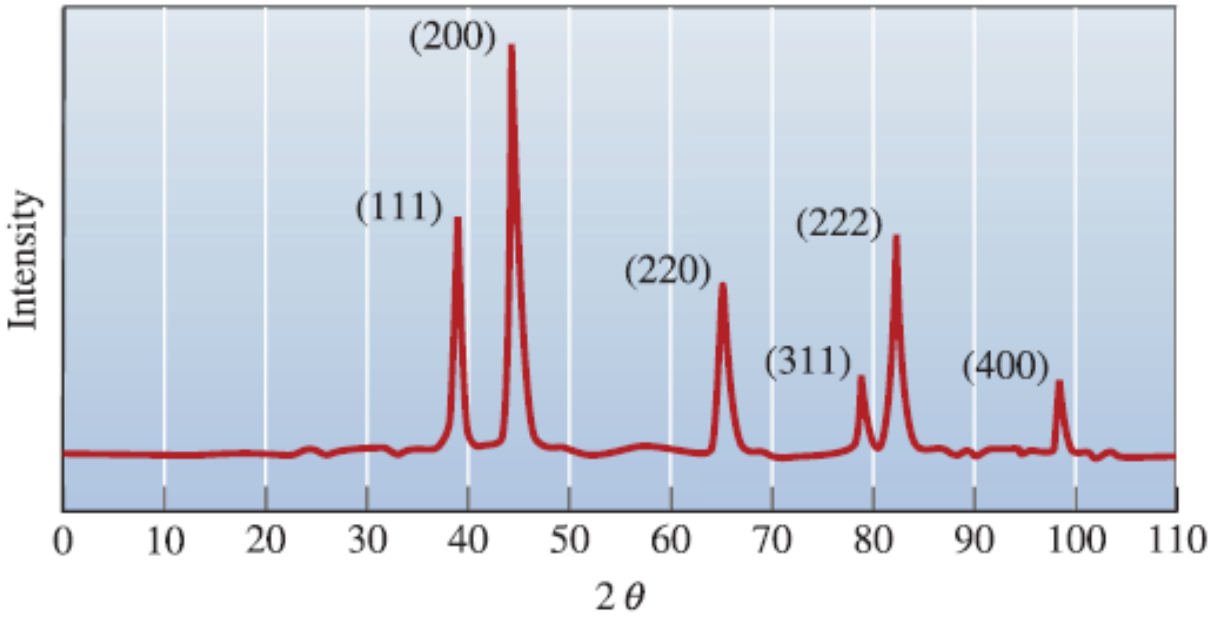


Figure 3-34 (a) Destructive and (b) reinforcing interactions between x-rays and the crystalline material. Reinforcement occurs at angles that satisfy Bragg's law.



3-9 Diffraction Techniques



- XRD samples can be imaged in a short time (30-60 minutes) and the data analysis is quite straightforward for a trained technician.

3-9 Diffraction Techniques

- Transmission electron microscopy (TEM) is a technique which uses high-energy electrons to image the microstructure of a material.

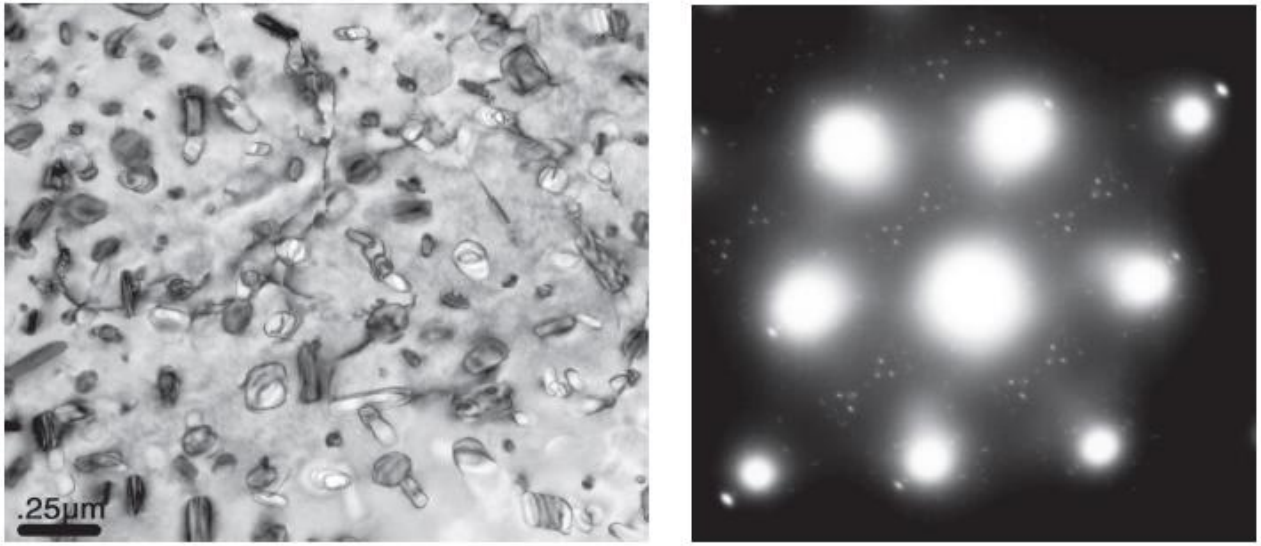


Figure 3-36 A TEM micrograph of an aluminum alloy (Al-7055). The diffraction pattern at the right shows large bright spots that represent diffraction from the aluminum matrix grains. The smaller spots originate from the nanoscale crystals of another compound that is present in the aluminum alloy. (*Courtesy of Dr. Jörg M.K. Wiezorek, University of Pittsburgh.*)

3-9 Diffraction Techniques

- TEM's advantages are the high spatial resolution and the ability to image the microstructure at fine scales. It is a widely used tool in research of micro- and nano-technologies.

- Disadvantages of TEM include:
  - Time-consuming preparation of samples
  - Considerable expertise/time required for data analysis
  - Only a small volume of the sample is examined
  - The equipment is expensive and requires great care to use

Summary

- Atoms/ions can be arranged in solid materials with either a short- or long-range order.
- Amorphous materials (e.g., silicate/metallic glasses, polymers, etc.) only have short-range order.
- Amorphous materials form when the kinetics of the formation process prohibit atoms/ions from assuming equilibrium positions. They often offer novel properties.

Summary

- Crystalline materials (e.g., metals & ceramics) exhibit both short- & long-range order. The crystal structure describes the long-range periodicity.

- Atomic/Ionic arrangements of crystalline materials are described by 7 crystal systems, including 14 Bravais lattices. E.g., cubic, FCC, BCC, hexagonal.

- A lattice is a collection of points organized in a unique manner. A crystal structure is defined by a lattice and a basis.

Summary

- There are only 14 Bravais lattices, but 100s of crystal structures.
- A unit cell is a subdivision (conventionally the smallest subdivision) of the crystal structure that still describes the lattice.
- Crystal structures are characterized by the lattice parameters of the unit cell. Other characteristics include: the coordination number, the packing factor & number of atoms/ions per unit cell.

Summary

- Allotropic & polymorphic materials have more than one possible crystal structure. Material properties can strongly depend on the allotrope/polymorph.
- For metals with FCC & HCP crystal structures, the atoms are arranged in a manner that occupies the greatest possible fraction of space.
- The closest-packing achieved in FCC & HCP structures is due to stacking different sequences of close-packed planes of atoms.

Summary

- The greatest achievable packing fraction of uniform size spheres is 0.74, independent of sphere radius.
- Points, directions & planes within crystal structures can be formally identified by assigning coordinates and Miller indices.
- Anisotropic materials are those which have different properties along different directions/planes within a crystal.

Summary

- Isotropic crystals have uniform properties along all directions/planes. Anisotropy may be masked in a polycrystalline material due to random grain orientation.

- Interstitial sites (holes between atoms/ions in a crystal structure) may be filled by other atoms/ions.

- Crystal structures of ceramic materials can be understood by considering interstitial site occupation.

Summary

- Atoms/ions located in interstitial sites play important roles in: material strengthening, influencing material physical properties, and controlling material processing.

- Crystal structures of many ionic materials form by anion packing. Cations fit into coordination polyhedra formed by anions. Coordination polyhedral typically share corners.

- The conditions of charge neutrality and stoichiometry must also be met for ionic materials.

Summary

- Crystal structures of covalently bonded materials tend to be open. E.g., diamond cubic (Si, Ge).
- XRD (X-Ray Diffraction) and electron diffraction are used to determine crystal structures in crystalline materials.
- TEM (Transmission Electron Microscopy) can be used for imaging microstructural features of materials at smaller length scales.